PHOTHOCHEMICAL STUDIES
ON
2-HYDROXY-and 2-METHOXY
1,4-NAPHTHOQUINONE

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Solomon Libsu

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SCHOOL OF GRADUATE STUDIES

PHOTOCHEMICAL STUDIES ON 2-HYDROXY- AND 2-METHOXY-1,4-NAPHTHOQUINONE

by

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DEDICATION

TO MY PARENTS, BROTHERS, AND SISTERS.

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ABSTRACT

Photochemical Studies on 2-Hydroxy - and 2-Methoxy-1,4-naphthoquinone

by

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Research Advisor: Dr. Berhanu Abegaz

Photolysis of a dilute chloroform solution of 2-hydroxy 1,4-naphthoquinone with diffuse day light yielded 2-chloro-3-hydroxy-1,4-naphthoquinone (SB) and an unidentified compound (SA). Compound SB was characterized by spectroscopic methods. Its photoformation from the materials used in the present study is unprecedented.

The photochemical reaction of 2-hydroxy-1,4-naphthoquinone is carbon tetrachloride failed to yield to compound SB. On the other hand, the room temperature reaction of thionyl chloride or phosgene with the hydroxy quinone afforded a compound which, by comparative TLC, was identified as compound SB. The significance of these results is discussed.

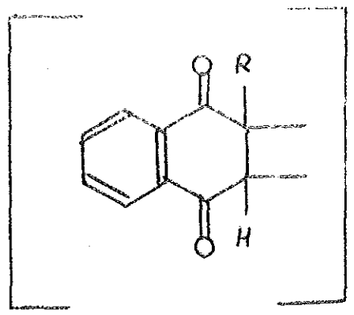
Photolysis of a dilute chloroform solution of 2-methoxy-1,4-naphthoquinone also gave a major reaction product (SC) which has not been fully elucidated.

1. INTRODUCTION

It has long been recognized that many novel and synthetically useful transformations including elimination, cycloaddition, rearrangement, oxidation, reduction, substitution, and elimination may be subsequent upon absorption of ultraviolet (200-400nm) and visible (400-750nm) light by organic molecules. 1,4-Quinones, which form one of the earlies classes of organic compounds to be photostructed, have been known to undergo light-induced reactions for over a century.

The history of photo-chemistry of 1,4-naphthoquinone systems goes back to 1874 during which time appeared a report on the formation of a photopolymer of 2-phenyl-1,4-naphthoquinone, which regenerates the monomer when heated.[1] Though Kughelmer and Henkel[2] latter on described it as a photodimer, it remained for Shonberg and coworkers[3] to assign the cyclobutane ring structure 1 (R=Ph) to it in 1951. The analogous structure 1 (R=H) was assigned three years earlier by these same workers to the photodimer of α-naphthoquinone[4] by analogy with Kaufmann-Vittis's[5] assignment of structure 1 (R=Me) to the photoproduct of 2-methyl-1,4-naphthoquinone obtained similarly. These structures have now been confirmed by spectral as well as chemical evidence.[6,7]

Not unexpectedly, photochemical work carried out on the 1,4-benzoquinone series not only shared a more or less identical beginning with that of its 1,4-naphthoquinone counterpart, but also followed the same general trend. Thus, eventhough thymoquinone had been known to dimerize in sunlight as long ago back as 1885,[8,9] it took more than seventy years to elucidate its structure as the cyclobutane dimer 2.



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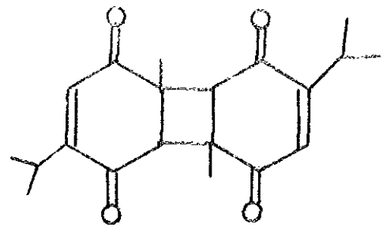
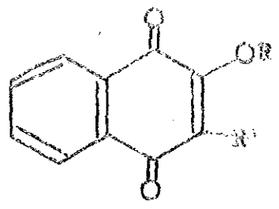
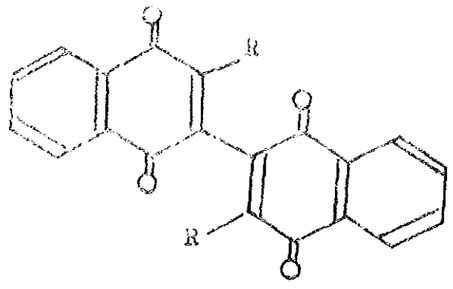


1 2

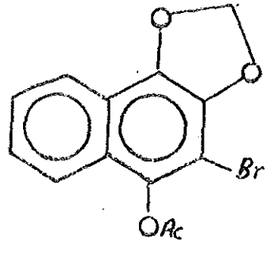
The study of photochemical behavior of 1,4-quinones is still a ubiquitous area of research interest. The photo-investigations carried out on this class of compounds are wide-ranging: dimerizations and/or cyclo-additions; isomerizations; hydrogen atom abstraction reactions; etc. together with postulated mechanisms (*vide infra*) are only few of the numerous publications that come out yearly on the subject. However, the literature reveals relatively few reports on similar work carried out on 2-hydroxy-1,4-naphthoquinone 3 and its methy ether 4, whose photolysis in chloroform is the subject of this thesis. Indeed, only two reports[12,13] have appeared in the chemical literature on the photochemical behavior of the hydroxy quinone 3, both of which deal with its phototransformation in water to yield the diol 5 as well as dimer 6 (*syn*-DP) while a 1968 report[14] disclosed successful thermal alkylations at the 3-position of this quinone.





2: R = R' = H
4: R = Me, R' = H
5: R = H, R' = OH

2



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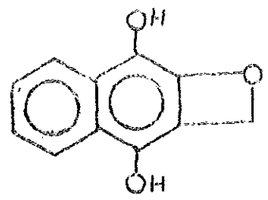
The photochemistry of the methoxy quinone 4, on the other hand, has been dealt with to a greater extent than its hydroxy analogue 3. Photolysis of 2-methoxy-1,4-naphthoquinone has recently been shown to give the cyclobutane photodimer 1[15,16](R=OMe). Moreover, cyclobutane and tetrahydropyran adduct formation with olefins,[17,18] nucleophilic substitution reaction at C-3,[12,19] demethylation and dimerization of the demethylated product to yield compound 6(R=OH)[1] constitute the photoprocesses recorded for quinone 4. Interestingly there is no report on photoinduced cyclization of the methoxy group either onto the nearby carbonyl oxygen in a manner similar to the photoformation of the methylenedioxy compound 7,[20] or onto C-3 to yield 2H-naphth[2,3-b]oxet-3,8-dio[7] 8. The literature reports

summarized above constitute the current state of knowledge on the photo-chemical behavior of quinones 3 and 4.



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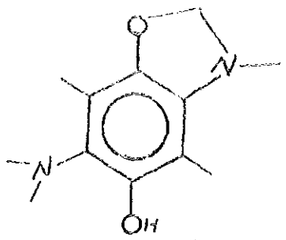

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Eventhough a number of workers have been dealing with light-induced reactions of 1,4-naphthoquinones in a variety of solvents in the presence or absence of other substrates, similar work done in chloroform is scanty; a fact which justifies the present study. An example[21] of the case in point, however, exists in the 1,4-benzoquinone series whereby 2,5-bisdimethylamino-3,6-dimethyl-1,4-benzoquinone photocyclizes in chloroform (as well as other solvents) to give the benzoxazoline 9.

The work described in the present report is the first example of photoreactions of quinones 3 and 4 carried out in chloroform, and as such represents the first instance of photochlorination of the hydroxy quinone at the 3-position. Photoformation of the 3- chloro-derivative of quinone 3, discussed shortly, is preceded by only one report that appeared a decade ago.[22]

1,4-quinones are known to photoadd hydrogen to give quinols following irradiation in alcohols.[45,47,62] Several derivatives of 1,4-benzoquinone have been reported to undergo side-chain

alkoxylation when irradiated in methanol or ethanol.[62] The formation of acetyl quinol has been reported from the photoreaction of 1,4-naphthoquinone and acetaldehyde.[50] Analogous photoinvestigations of 1,4-quinones inchloroform are rare in the chemical literature. Particularly, there is no documented work on the photochemical behavior of 1,4-naphthoquinone or its derativ in chloroform. The study undertaken presently was thus believed to throw some light on the reaction consequent upon exposure of chloroform solutions of 1,4-naphthoquinones to sunlight.

The structures and nubering systems used for 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-phenanthraquinone are shown below by structures (a) through (d), respectively, in Fig 1.

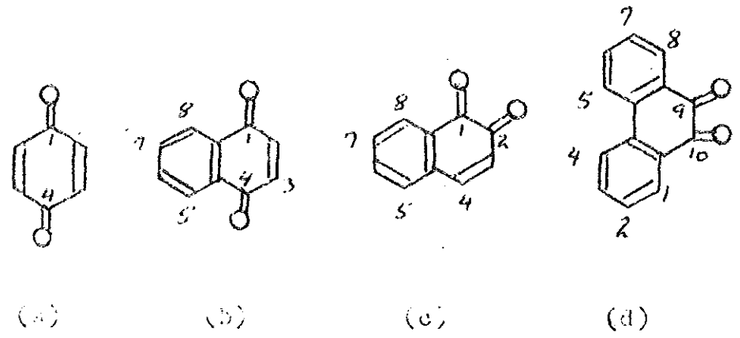


Fig.1. Structures and numbering systems of some quinones: (a) 1,4-benzoquinone (b) 1,4-naphthoquinone, (c) 1,2-naphthoquinone, (d) 9,10-phenanthraquinone.

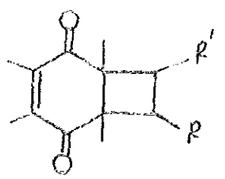
II. BACKGROUND (LITERATURE REVIEW)

1. Light-Induced Reactions of Quinones

1.1 Photocycloadditions

During the past several years, many para-benzoquinones have been shown to undergo photodimerization reaction to yield cyclobutane adducts of type 1.[23-25] Analogous photodimers 1 have been reported for variously substituted 1,4-naphthoquinones.[3-7,15,16,26-28] Sunlight irradiation[28,29] of the cyclobutane photodimers 1 (R=H,Me,Ph,Cl,Br) yielded the corresponding 2,2'-bi(1,4-naphthoquinonyl) derivatives 6 (same R). Compounds of type 6 (R=Me,OH) have also been obtained from the photolyses of the corresponding monomeric quinones.[7,12,13]

Photocycloadditions of olefins and dienes to the carbonyl group of para-benzoquinones were shown to lead to spiro-oxetans[30] and spiro-pyrans,[31] respectively. Olefins are also known to photoreact with the C=C double bond of these quinones to yield mono-and bis-cyclobutane adducts, 10 and 11, respectively.[32] Similar photoaddition reactions with 1,4-naphthoquinone derivatives have been reported to afford both oxetanol-and cyclobutane-ring compounds.[18,33-35] Tetrahydropyran ring compounds like 12 have been isolated from photoadditions of 2-alkoxy-1,4-naphthoquinones with olefins.[17,36,37]



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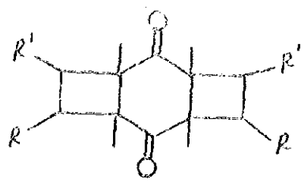

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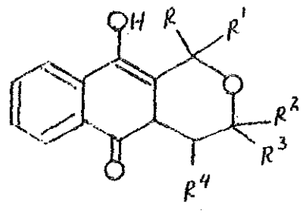

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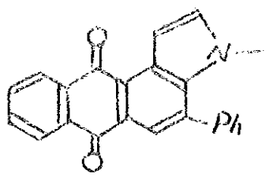
The photoadducts 13 through 15 have been described to arise from the reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with the unsaturated compounds 16 through 18, respectively.[38,40] The sulfur-analogue of compound 13, shown by structure 19, was obtained for the first time photochemically from the reaction of the same qui with 1-phenyl-1-(2-thienyl) ethylene.[41] B,B-Dimethyldihydrofurano-1,4-naphthoquinone 20, which is similar to compound 14, was reportec in 1950 by Ettlinger[42] as one of the products isolated following exposure of a solution of 2-hydroxy-3-isobutyl-1,4-naphthoquinone to sunlight.



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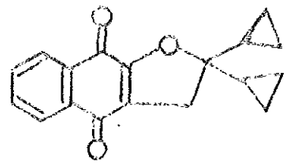

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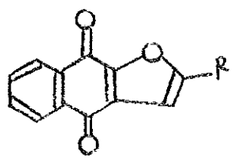

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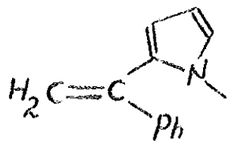

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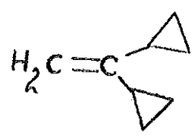

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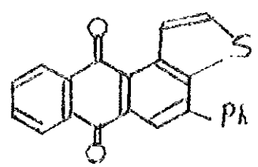

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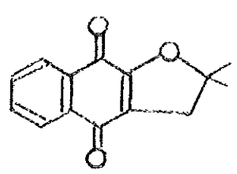

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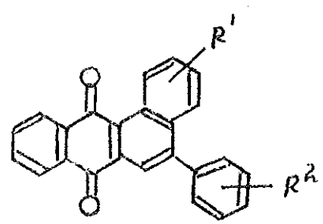

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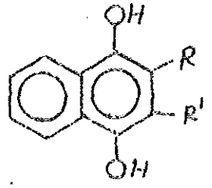
Several other polycyclic quinones like 21 have been shown to arise from similar photochemical reaction of 2-halogenated 1,4-naphthoquinones with 1,1-diarylethylenes in a variety of solvents like benzene, ethanol, ethylacetate, and chloroform.[18,43,44] The photochemical access to benz-[a]anthracene-7,12-dione derivatives like 21 offers a convenient route to the corresponding aromatic hydrocarbons via reduction.

Photocycloaddition reactions have also been shown to take place between olefins and phenanthraquinone, leading to the formation of 1,4-dioxins.[45]

1.2. Photochemical Hydrogen Abstraction Reactions.

1.2.1. Intermolecular

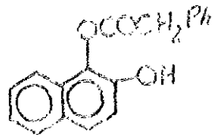
A number of examples of light-induced reactions of 1,4-quinones with substrates carrying abstractable hydrogen atoms are available.[46] The quinone-aldehyde system is one of the most widely studied of quinone photochemistry.[47] It has been demonstrated through these studies that irradiations of para-benzoquinones in the presence of acetaldehyde yielded mainly the acetyl quinols[48,49] while the use of aromatic aldehydes afforded the quinol monoesters exclusively or together with small amounts of the aroyl quinols.[49] 1,4-Naphthoquinone and its 2-methylderivative behaved similarly giving the ring-acylated quinols 22 and 23, respectively, following photolysis in the presence of acetaldehyde.[50] This regioselectivity,



22: R=H;R^1= CH_3CO

23: R=CH_3 R^1= CH_3CO

also noted from the product distribution in the photochemical reactions 1,2-naphthoquinone or its derivatives with aliphatic and aromatic aldehydes,[48,51] has been discussed in terms of the polarity of the acyl or aroyl radicals as well as substituent groups on the quinone ring.[52,53] An extension of these studies to mono-and diphenyl acetaldehyde revealed that a mixture of the photoadducts 24 through 26 were obtained from the reaction of 1,2-naphthoquinone with phenyl acetaldehyde while the diol 27 was the only product isolated when diphenyl acetaldehyde was employed as the substrate.[54]



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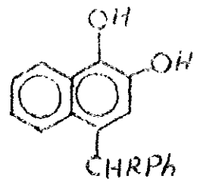
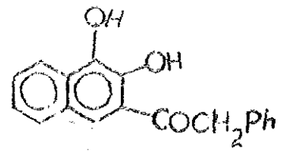


26: R=H

27: R=Ph



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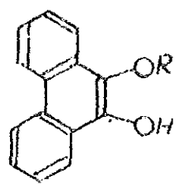
Phenanthraquinone also behaves analogously giving 1,4-addition products 28 when photoreacted with aldehydes,[55] ethers,[56] and esters.[57] Adducts of type 28 and 29 have been reported for the corresponding reaction with toluenes.[58]



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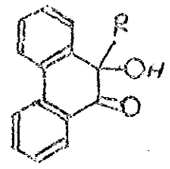

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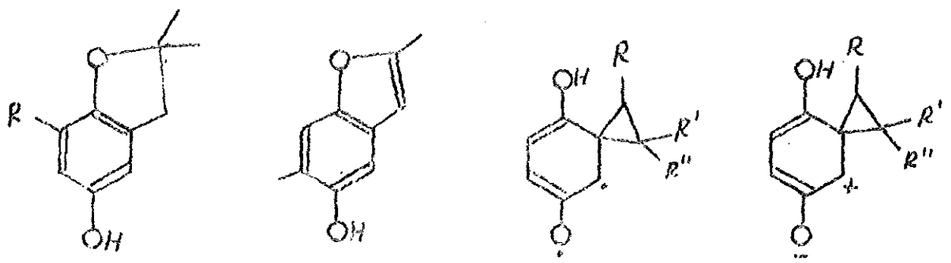
1.2.2. Intramolecular

Formation of cyclobutanols by intramolecular hydrogen abstraction reactions that proceed through six-membered transition states is a well-studied photochemical reaction of aliphatic ketones carrying a γ-hydrogen atom.[59] Similar reactions of 1,4-quinones bearing side-chains that contain fairly easily abstractable hydrogen atoms are known to lead to photocyclized products.

Irradiation of t-butyl-or 2,6-di-t-butyl-1,4-benzoquinone in neutral media as well as acetic acid yielded the dihydro-benzofurans 30 and 31, respectively.[60] Thymoquinone also behaves similarly in methanol giving the benzofuran 32 as one of the photoproducts.[61] A spirocyclopropyl of type 33 or its ionic form 34 has been postulated as an intermediate to account for these results.[62] But-3'-enyl-1,4-benzoquinone gives a low yield of 1,4-

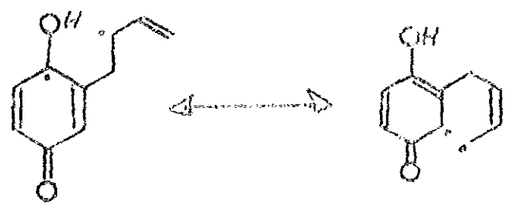


32 33 34

30: R=H

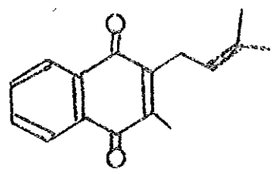
31: R=t-Bu

dihydro-5,8-dihydroxynaphthalene, which is believed to arise by intramolecular abstraction of the 2'-hydrogen of the side-chain via a favorable six-membered transition state followed by electron-pairing in the biradical 35 thus formed.[63]



35

While reports on similar photoprocesses of 1,4-benzoquinones have also been recorded elsewhere,[64] analogous work done in the 1,4-naphthoquinone series is rare. However, irradiation of an ethanolic solution of the isoprenoid naphthoquinone 36 has been shown to afford the chromenol 37.[65]



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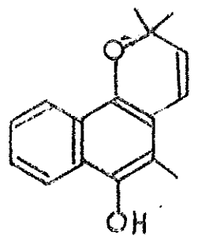

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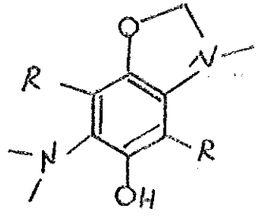
1,4-quinones carrying side-chains that contain a hetero-atom(oxygen or nitrogen) also behave in a manner similar to those that carry only hydrocarbon side-chains. Various benzoxazolines of type 38 or 39 are obtained from irradiations of diaminated derivatives of 3,6-disubstituted-1,4-benzoquinones.[21,66]



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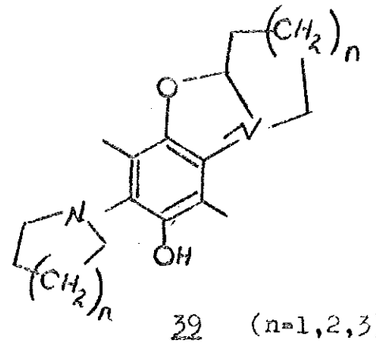
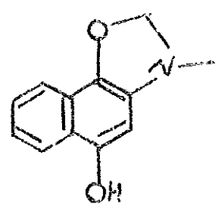


39 (n=1,2,3)

2,5-Dimethoxy-3,6-dimethyl-1,4-benzoquinone, however, failed to give the dioxole analogue of the benzoxazoline 38($R=CH_3$)[21,67]

2-Dimethylamino-1,4-naphthoquinone like-wise yielded the photoisomerized product 40.[68] Photolyses of acetic anhydride

solutions of 2-isopropoxy-1,4-naphthoquinone or 2-bromo-3-methoxy-1,4-naphthoquinone offered the corresponding methylenedioxy compounds 41 and 42, respectively, together with the photo-Fries rearrangement product 43 in the former case.[16,20] Intermediacy of the diradical 44 that undergoes electron-transfer to the nucleus to yield a dipole 45 was postulated to lead to photoproduct 42 by direct ring-closure.[20]



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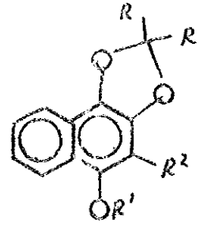
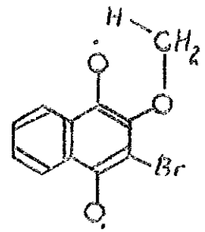


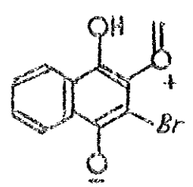
41: R=CH_3;R'=CH_3CO;R^2=H

42: R=H;R'=CH_3CO;R^2=Br

43: R=CH_3;R'=H;R^2=CH_3CO



44



45

From these results, it has been inferred that a six-membered transition state is essential for the intramolecular photo-induced hydrogen abstraction reactions discussed thus far.[62]

1.3. Photosubstitution

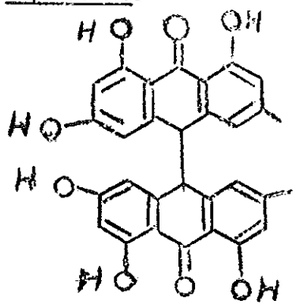
Photochemically induced nucleophilic substitution reactions of α-naphthoquinone systems are known to take place on both the benzenoid[69,70] and quinonoid rings.[19] The reaction of 5-methoxy-1,4-naphthoquinone with methylamine resulted in photoproducts due to substitution of the methoxy and the hydrogen at position-8 by the substrate[70] while the corresponding reaction with the

2-methoxy isomer proceeded with high regiospecificity leading to replacement of hydrogen at position-3 by the amine.[19] 2,3-Dichloro-1,4-naphthoquinone behaves analogously when photoreacted with thiophen[71] or furan[72] derivatives giving products in which one of the halogens has been replaced by the substrate.

The hydroxy function has also been introduced into the quinoid ring of 1,4-naphthoquinone nucleus photochemically. Irradiation of buffer solutions of 1,4-naphthoquinone and its 2-methyl derivative in the absence of air afforded the corresponding monohydroxylated compounds.[73] The photolyses of 2-hydroxy-,[12] 2-methoxy-[12] and 2-amino-1,4-naphthoquinone[74] in water resulted in replacement of hydrogen at position-3 by the hydroxy group. A 1979 report[22] mentioned the formation of 2-chloro-3-hydroxy-1,4-naphthoquinone as one of several minor photoproducts following irradiation of 2,3-dichloro-1,4-naphthoquinone in a mixture of benzene and 2-propanol. A survey of the literature revealed no other documented work on the photoformation of this compound.

III. Statement of The Research Problem

The work described herein was initiated by the observation that emodin bianthrone, 46, which was absent in the original crude extract of the fruits of Rhamnus prinoides, was isolated as an experimental artefact following purification on silica gel column chromatography using chloroform/ethyl acetate as the eluent. That compound 46 so obtained is indeed not a genuine natural plant metabolite was amply verified by the fact that it was not isolated when the crude extract was chromatographed on a column of acetylated polyamide.(75) This provoked the suspicion that light, the adsorbent (silica gel) or both might have been involved in the formation of compound 46 from its monomer 47 which was also obtained from R.prinoides(75)



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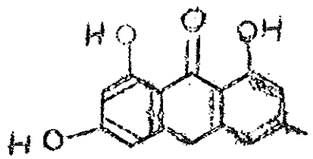
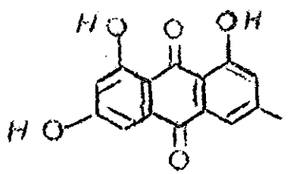


47

The literature reveals that certain compounds are unstable when adsorbed on inorganic supports. 7-Methyljuglone undergoes transformations in the dark leading to oxygenation and dimerization products when adsorbed on silica gel.(76) A recent report by Mazur and Aronovitch(77) disclosed the formation of benzophenone following exposure of 1,1-diphenylethylene adsorbed on chromatographic grade silica gel

to air and laboratory light. Whereas the transformation of 7-methyljuglone adsorbed on silica gel is non-photochemical,[76] the oxidation of 1,1-diphenylethylene didnot occur in the dark.[77] Exposure of a chloroform solution of compound 47 adsorbed on silica gel to laboratory light in this laboratory has also been noted[78] to yield the dimer 46.

In view of these and other results,[79,80] preliminary work was undertaken with the objective of finding out which of the variables (light or silica gel) was responsible for the transformation of compound 47 to 46. The more rigorous task of isolation and characterization of compound 46 (in those cases where its formation was detected by TLC) was hampered by scarcity of the starting material, 47, Nevertheless, the results derived from the preliminary experiments carried out indicate that the conversion of compound 47 adsorbed on chromatographic grade silica gel to its dimer 46 occurred in the dark while the corresponding light reactions also showed a slight sign of formation of compound 46 (TLC) which, however, was seen to vanish with the passage of time to give the oxidation product emodin (48) as the only reaction product detectable by TLC.



48

The work was further extended to include simple 1,4-naphthoquinone derivatives which, as seen from the preceding literature review, are known to undergo a variety of light-induced reactions. The photostudies carried out on dilute(10^{-3} M) chloroform solutions of 2-hydroxy-and-2-methoxy-1,4-naphthoquinone form the major part of the present work.

The choice of these compounds was based primarily on the availability of the methoxyquinone which is quantitatively convertible to the hydroxy compound upon basic hydrolysis.

The summary of literature reports presented earlier on photochemical work carried out on these two simple naphthoquinones shows that the hydroxy derivative has recieved the least attention. The appearance of only two essentially similar reports[12,13] over a span of more than fourty years on the photolysis of this quinone, coupled with the non-existence of photochemical work done on chloroform solutions of either this quinone or its methyl ether prompted an undertaking of the present study. The results of the foregoing photoinvestigation are described hereunder.

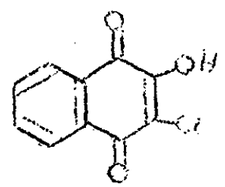
IV. RESULTS AND DISCUSSIONS

1. Photo-experiments on 2-Hydroxy-1,4-naphthoquinone

The one week-long photoreaction of a dilute chloroform solution of the title quinone (1.15×10^{-3} M) under an atmosphere of nitrogen led to the isolation of two major photoproducts, labelled SA and SB, in a combined yield of greater than 90% . Other few minor ones were also noted (TLC) to have been formed in trace quantities. Compound SB has a lower R_f value than its coproduct, SA-(0.125 and 0.25, respectively; PhH/EtOAc/HOAc, 70/30/1). No sign of formation of either of these two compounds was detected by TLC in the corresponding dark reaction from which the starting material was quantitatively recovered. The non-appearance of compounds SA and SB in the latter experiment demonstrates that these substances are indeed genuine photoproducts. A discussion of the identification of these compounds is the subject of this section.

1.1. Compound SB

Compound SB, m.p. 217-219°, is an orange crystalline compound obtained in about 65% yield ('Based on the starting material consumed). It is soluble in polar solvents like methanol or dimethyl-sulfoxide as well as dilute alkaline medium. On the basis of these properties and its spectral data, photoproduct SB has been established to be 2-chloro-3-hydroxy-1,4-naphthoquinone whose structure is shown below.



SB

1.1.1. Infrared Spectrum

The infrared spectrum of photoproduct SB, reproduced in Fig.2, showed a broad OH absorption band in the 3500 cm^{-1} region together with carbonyl stretching frequency appearing at 1680 cm^{-1}. Aside from the characteristic aromatic C=C skeletal vibration and O-H deformation banus appearing in the 1500-1600 and 1400 cm^{-1}, respectively, the absorption frequency at 740 cm^{-1} is particularly significant as it is indicative of an ortho-disubstituted benzene ring. This latter absorption band suggests that the aromatic ring of the parent quinone is unaffected by the phototransformation leading to compound SB and, therefore, is intact in photoproduct SB.

1.1.2. ^{1}H NMR spectrum

The 400 MHZ ^{1}H NMR spectrum of this compound, run in hexadeuterodimethyl sulfoxide, displayed four distinct sets of multiplets appropriate to the various benzenoid protons of compound SB. The most down field pair of multiplets appearing at δ 7:92 and 7.89 ppm are attributable to the two peri- protons while those singnals at δ 7.79 and 7.57 ppm are ascribable to the hydrogens at C-6 and C-7. These proton signals occurred in the same intensity ratio as that required by the formulated structure of compound SB. Moreover, this pattern of resonance lines, coupled with the absorption band at 740 cm^{-1} in its infrared spectrum, conclusively demonstrate that the benzenoid ring of the parent compound is intact in photproduct SB. The complete and partially expanded ^{1}H NMR spectra of this compound are displayed in Figs. 3 and 4, respectively.

Comparison with the corresponding spectrum of the parent quinone (DMSO-d_6), depicted in Fig.5, shows that the signal due to the hydrogen at C-3 of the latter compound has vanished in the spectrum of the photoproduct showing that C-3 is the site of attack in the course of the photochemical transformation to compound SB.

1.1.3. Mass Spectrum

A low resolution mass spectrum showed the molecular ion peak of compound SB at m/z 208 which is 35 mass units higher than the molecular weight of the parent compound minus one hydrogen atom. Furthermore, the appearance of an ion peak at m/z 210 with a relative intensity of one-third that of the parent peak is indicative of incorporation of a chlorine atom in the photoproduct. The inclusion of the halogen is further verified by the characteristic 3:1 relative intensity ratio of the ion peaks at 180 and 182 which arise by loss of carbonmonoxide from the parent ion. A molecular formula of $C_{10}H_5ClO_3$, suggested for the molecularion species, nicely accommodates the foregoing. Other significant peaks displayed in the mass spectrum include those at m/z 173 and 145 corresponding to successive losses of chlorine and carbonmonoxide from the molecular ion peak. The base peak appeared at m/z 105, due to the benzoyl cation. This peak is characteristic of the spectra of naphthoquinones containing aC-2 or C-3 hydroxy substituent.[81]

The fragmentation pattern of this compound bears out a similarity to that reported for 2-chloro-3-hydroxy-1,4-naphthoquinone by Cameron and coworkers.[81] A comparison of our mass spectral datumof compound SB with that of the literature for

2-chloro-3-hydroxy-1,4-naphthoquinone is shown in Table I.

It had already been inferred (Vide Supra) that the aromatic ring of the starting material is intact in compound SB where-as the hydrogen at position -3 must have been photosubstituted. The mass spectrum of the photoproduct undoubtedly indicates that the species replacing the said hydrogen must be chlorine.

TABLE I. Comparison of the mass spectrum of 2-chloro-3-hydroxy-1,4-naphthoquinone[81] with that of compound SB.

Compound											
2-chloro-3-hydroxy-1,4-naphthoquinone	m/z	76	77	104	105	145	173	180	182	208 (M.)	210
	Rel.Int. (%)	21	13	16	17	24	30	41	19	100	40
SB	m/z	76	77	104	105	145	173	180	182	208 (M.)	210
	Rel.Int. (%)	50	44	18	100	10	18	26	8	34	12

1.1.4. ^{13}C NMR Spectrum

The ^{13}C NMR spectrum (MEOH-d_4) of the compound under discussion showed a total of nine carbon signals whose chemical shift values in δ ppm appeared at 179.8(C-1,C-4); 168.6(C-3); 135.7(C-6); 134.9(C-2) 133.0(C-7); 131.3(C-4a); 129.4(C-8a); 127.6(C-8); and 126.7(C-5).

The absence of reports on the ^{13}C NMR spectrum of 2-chloro-3-hydroxy-1,4-naphthoquinone precluded us from making a direct comparison with our datum for compound SB. Nevertheless, attempt is made to substantiate the coincidence of the resonance lines for C-1 and C-4 on the basis of known substituent effects.

An oxygen substituent at C-3 of 1,4-naphthoquinone exerts a shielding effect of 4.7 and 28.6ppm on, respectively, C-4 and C-2; deshields the site of attachment by 21.9 ppm but has no significant effect on the resonance line of C-1. Similarly, introducing chlorine at C-3 of 1,4-naphthquinone deshields the site of substitution by 77 ppm while C-1, C-2 and C-4 are shielded by 2.3, 2.7, and 7.0 ppm respectively.(82,83,84) In the light of thse results, it is evident that the extent of shielding induced on C-4 of compound SB by both the hydroxy and chlorine substituents is comparable to the same effect the latter substituent exerts on C-1, Thus, the most down field line of absorption in the ^{13}C NMR spectrum of photoproduct SB is reasonably attributed to both C-1 and C-4. This assignment is further corroborated by its nearly two-fold intensity compared to the resonance lines of the remaining quaternary carbon atoms.

1.1.5. Visible Absorption Spectrum

The visible absorption spectrum of compound SB, Fig.6, $\lambda_{max}^{(MeOH)}$= 474nm($E=1315 M^{-1}cm^{-1}$), is in accordance with its identification as 2-chloro-3-hydroxy-1,4-naphthoquinone. The electronic spectrum of 2-hydroxy-1,4-naphthoquinone consists of, among others, a weak quinonoid electrontransfer band at 380nm(E=750) which is sensitive to

Fig. 2, IR spectrum of compound SB

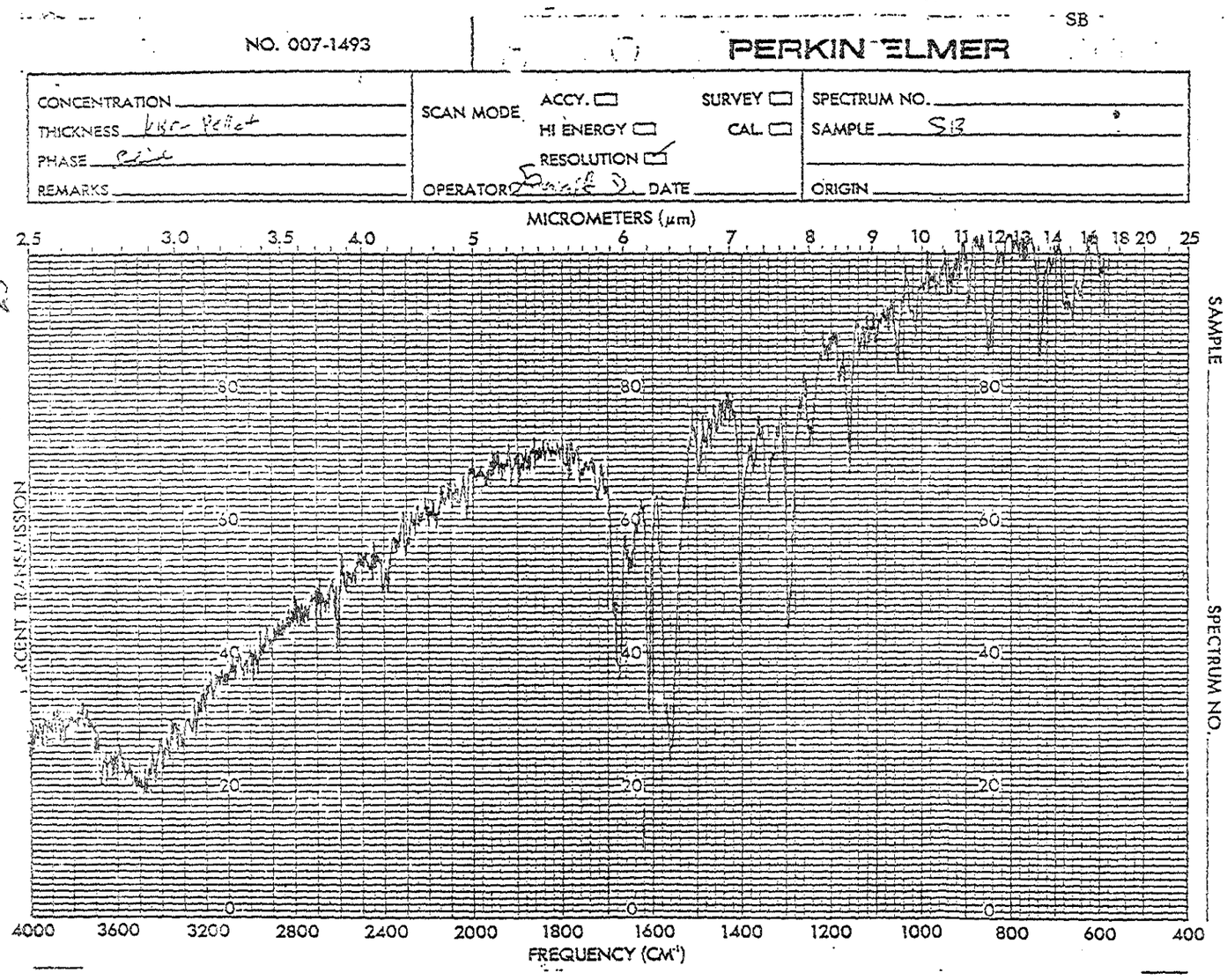
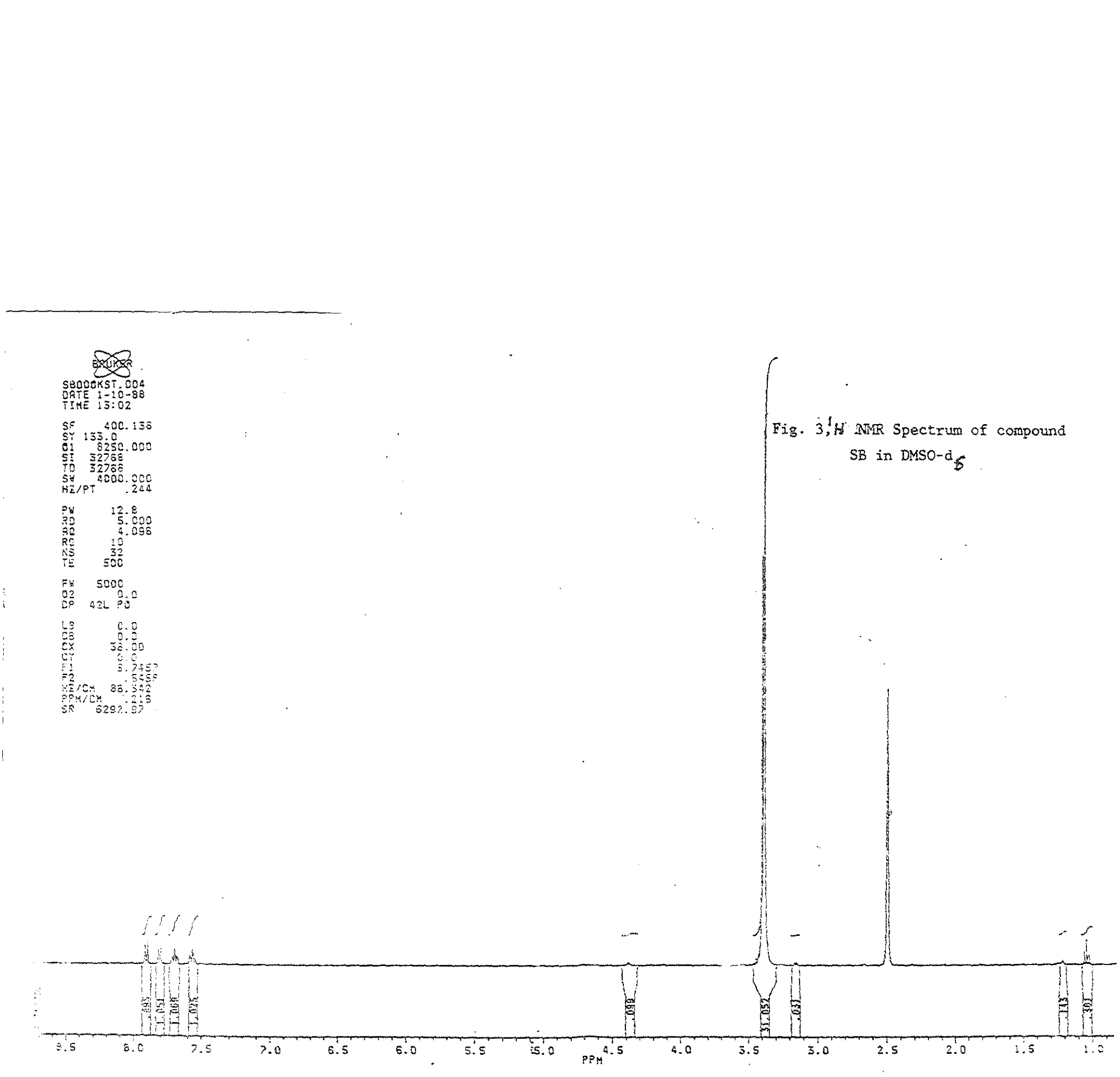


Fig. 3, ^1H NMR Spectrum of compound SB in DMSO-d_6



Fig, 4. Partial, expanded ^1H-NMR spectrum of compound SB

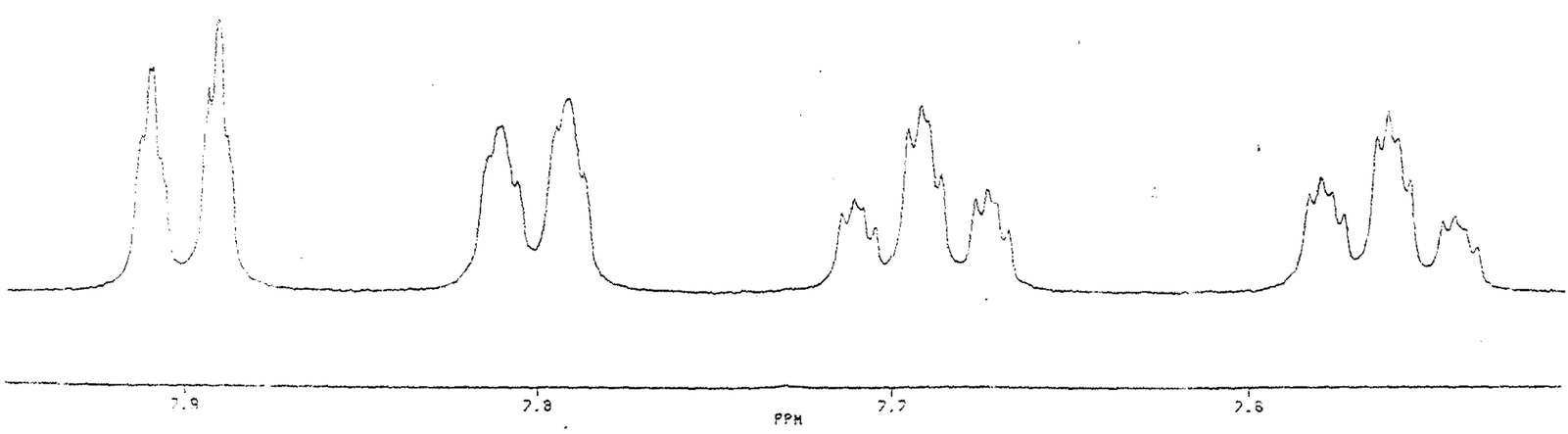


Fig. 5. The NMR spectrum of 2-hydroxy-
4-methoxyacetophenone in DMSO-d_6.

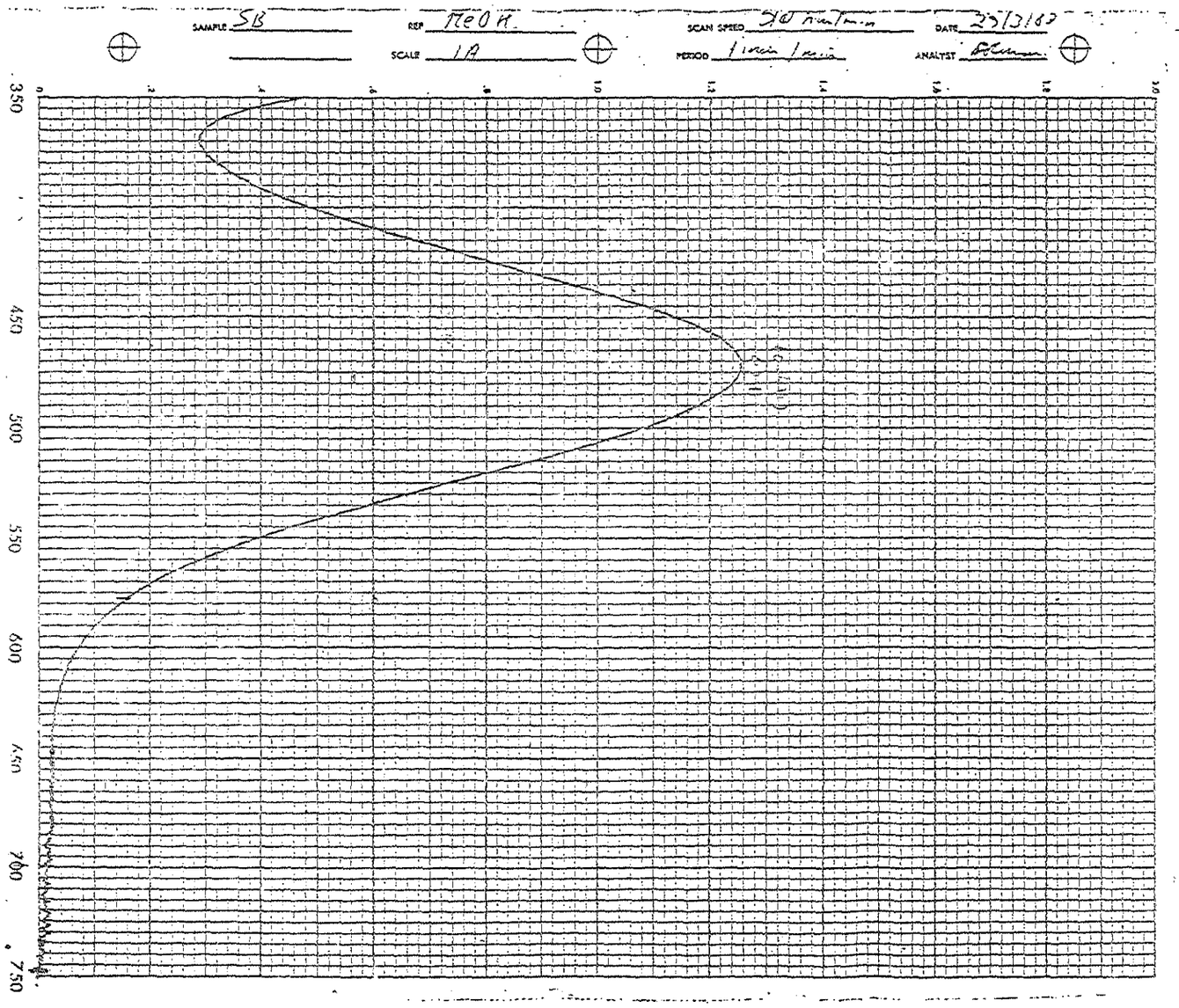


Fig. 6, Visible absorption spectrum of SB in MeOH

substitution at the free quinonoid ring carbon atom.(85) Furthermore, introducing an electron-withdrawing substituent at either the 3-,5-, or 8- position of 1,4-naphthoquinone bearing an electron-donating group at the 2-position is known to shift the visible band bathochromically.(86) Attachment of the halogen at either of the alternative benzenoid [illegible] positions (C-5 or C-8) of compound SB is ruled out on the ground that the resulting isomeric structures would be inconsistent with the rest of the data generated for it.

Though the foregoing is convincingly in agreement with the proposed structure of the compound, confirmatory evidence was obtained from the ensuing discussion of spectral data produced for its acetate, designated as SB-AC.

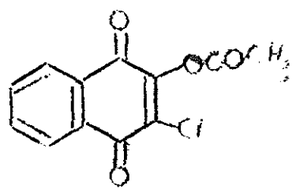
1.2. Compound SB-AC

The low solubility of compound SB in common organic solvents had been a major problem in generating neat spectral data. Its acetylation with acetic anhydride/pyridine at room temperature was therefore undertaken with the view of getting more simplified spectral data.

TLC(silica plates) monitoring of the progress of the acetylation reaction revealed only one major spot which slowly acquired a reddish brown color a short while after the chromatogram had been developed. The same situation was noted when neutral alumina plate was used as the adsorbent. It was evident that SB-Ac underwent adsorbent-induced transformation to yield some product which was identified by comparative TLC as the parent compound, SB. This was achieved as follows: Developing the chromatogram immediately after application

of a solution of Sb-Ac showed only one spot (R_f= 0.5, benzene). There was no sign of material sticking to the base line, with a time lapse of 10 or 30 min. between sample application and development of the chromatogram, however, progressively larger amounts of the reddish-brown material was observed at the base line. Comparative TLC using compound Sb as the reference indicated that the transformation product of compound Sb-Ac on TLC had an identical R_f value (Benzene/Ethylacetate/ acetic acid, 70/30/1) with its parent compound, Sb. Though no statement of reason was given, chromatographic purification of 2-chloro-3-acetoxy-1,4-naphthoquinone, with which compound Sb-Ac has been identified, was achieved using acid-washed alumina as the adsorbent.(87) The conversion of compound Sb-Ac to Sb was also noted during the work-up procedure.

Purification of the acetylation reaction mixture on a micro-column using benzene as the eluent yielded a yellow compound, m.p. 129-131°C, which was exceedingly soluble in common organic solvents. Its spectral data discussed below are in precise agreement with its characterization as 2-chloro-3-acetoxy-1,4-naphthoquinone.



Sb-Ac

1.2.1. Infrared Spectrum

The infrared spectrum of this compound, reproduced in Fig.7, indicates no sign of O-H stretching frequency. The appearance of absorption bands at 2950, 2900(CH_3); 1800(acetoxy carbonyl); and 800 cm^{-1}(C-O-C) (all of which are non-existent in the corresponding spectrum of compound SB(Fig.2.)coupled with its enhanced solubility relative to its parent compound SB-Ac is indeed an acetate.

1.2.2. ^1H NMR Spectrum

The 300 MHz ^1H NMR spectrum ($CDCl_3$) of compound SB-Ac exhibited two closely placed multiplets at 6.16 and 8.13 ppm which are attributable to the peri-protons at C-5 and C-8. The signals due to hydrogens at C-6 and C-7 coincided to give a multiplet at δ 7.77ppm. The resonance line of the acetyl protons appeared as a singlet at δ 2.43ppm. These signals occurred in the same intensity ratio of 1:1:2:3 as required by the structure formulated for compound SB-Ac. The complete and partial, expanded ^1H NMR spectra of this compound are shown in Figs. 8 and 9, respectively.

1.2.3. Mass Spectrum

A high resolution mass spectrum of compound SB-Ac (Fig.10) indicated amolecular weight of 250,0023 corresponding to a molecular formula of $C_{12}H_7O_4Cl$. The base peak occurred at m/z 43 which is believed to be due to the acylium cation. Other significant peaks recorded in the high mass region appeared at m/z 215(loss of chlorine), 208(loss of ketene), 180(loss of ketene and carbon

monoxide), and 175 (loss of ketene and chlorine). Each of the four peaks at m/z 250, 208, 180 and 123 is accompanied by an (M+2) peak whose relative intensity if one-third of the lower ion peak in each case.

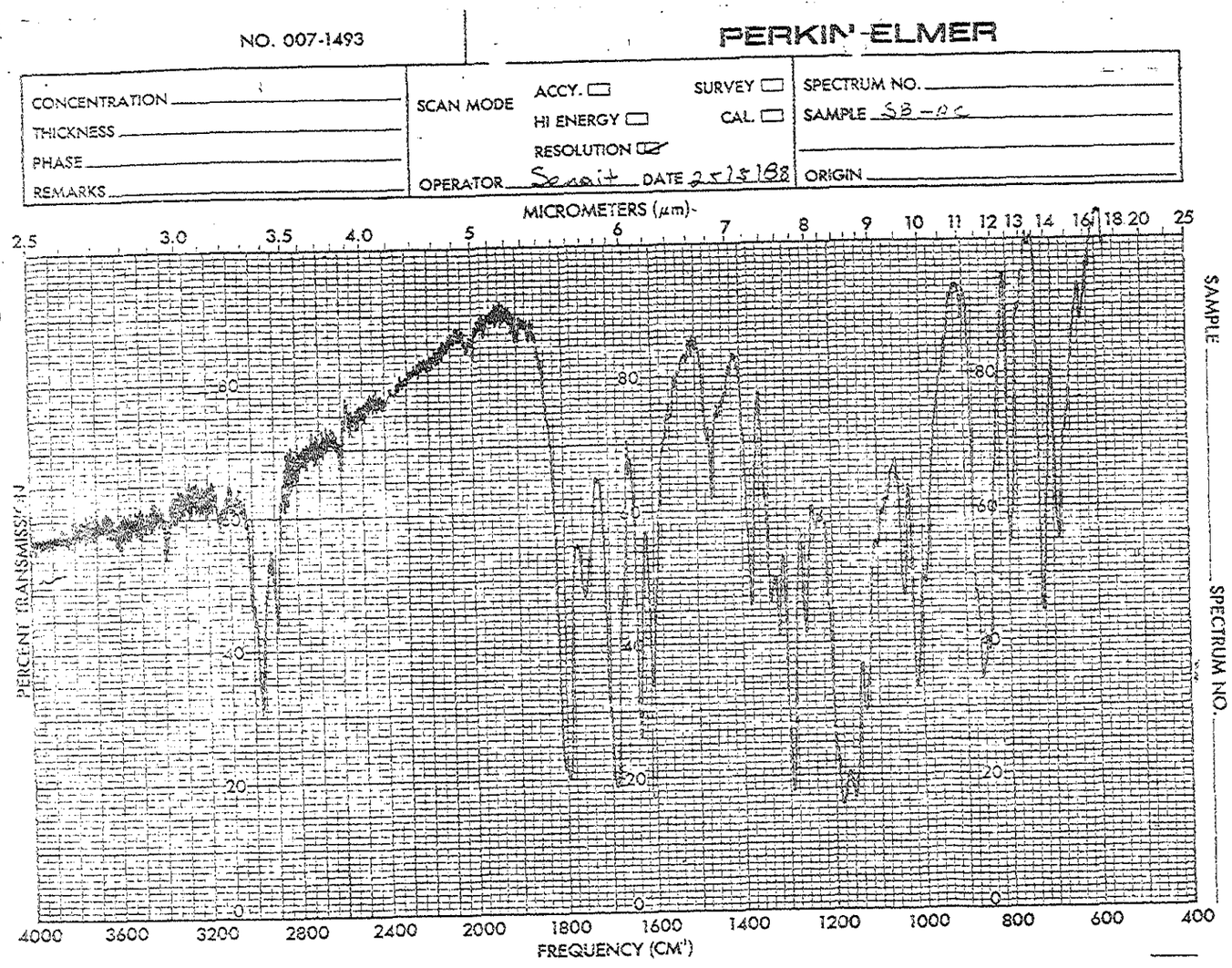
The spectral data discussed thus far clearly justify the characterization of compounds 5B-Ac and 5B as, respectively, 2-chloro-3-acetoxy- and 2-chloro-3-hydroxy-1,4-naphthoquinone.

1.3 Identification of The Most Probable Chlorinating Agent

Having established the structure of photoproduct 5B, it was natural to search for the most probable chemical species that has served as a donor of chloride atoms. It is evident that the quinone must have interacted with one or more reactive species produced from the solvent during the photolysis. Distilled chloroform, which is the solvent used in the present photochemical work, has been known to undergo oxidative breakdown to give chlorine, hydrochloric acid, phosgene, carbon dioxide, and water[88,91] following prolonged exposure to sunlight. While the involvement of each of the first two of these reactive species in the observed photochlorination of the hydroxy quinone at the 3-position may not be ruled out, the evidence presented below favores phosgene to be the dominant source of chlorine atoms.

Treatment of 2-hydroxy-1,4-naphthoquinone in benzene with thionyl chloride at room temperature indicated formation of a compound that exhibited similar chromatographic behavior with photoproduct 5B. Many nonphotochemical chlorinations effected using thionyl

Fig. 7 IR Spectrum of compound SB-Ac



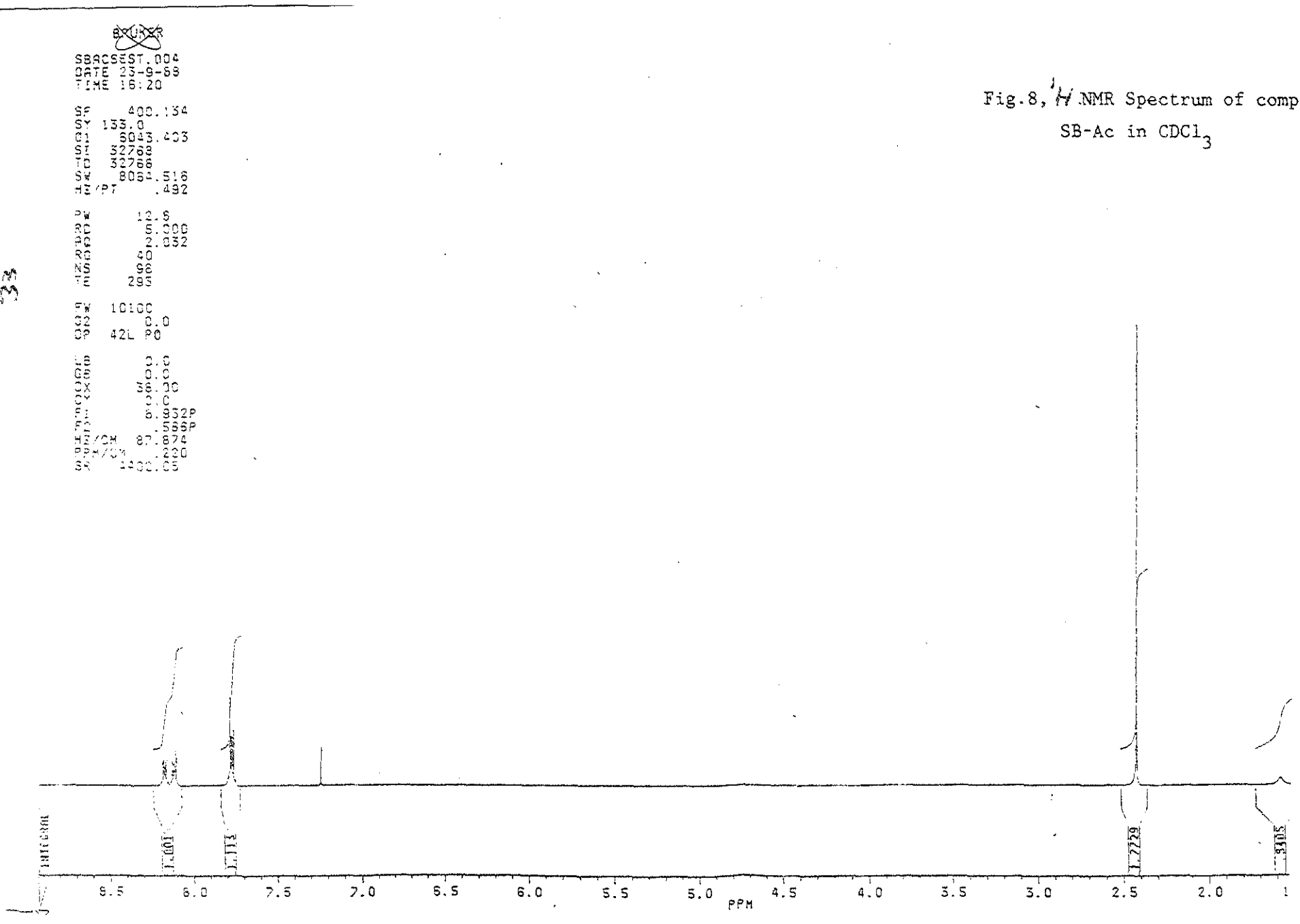


Fig.8, ^1H NMR Spectrum of comp SB-Ac in $CDCl_3$

Fig.9, Partial expanded ^1H NMR Spectrum of compound SB-Ac

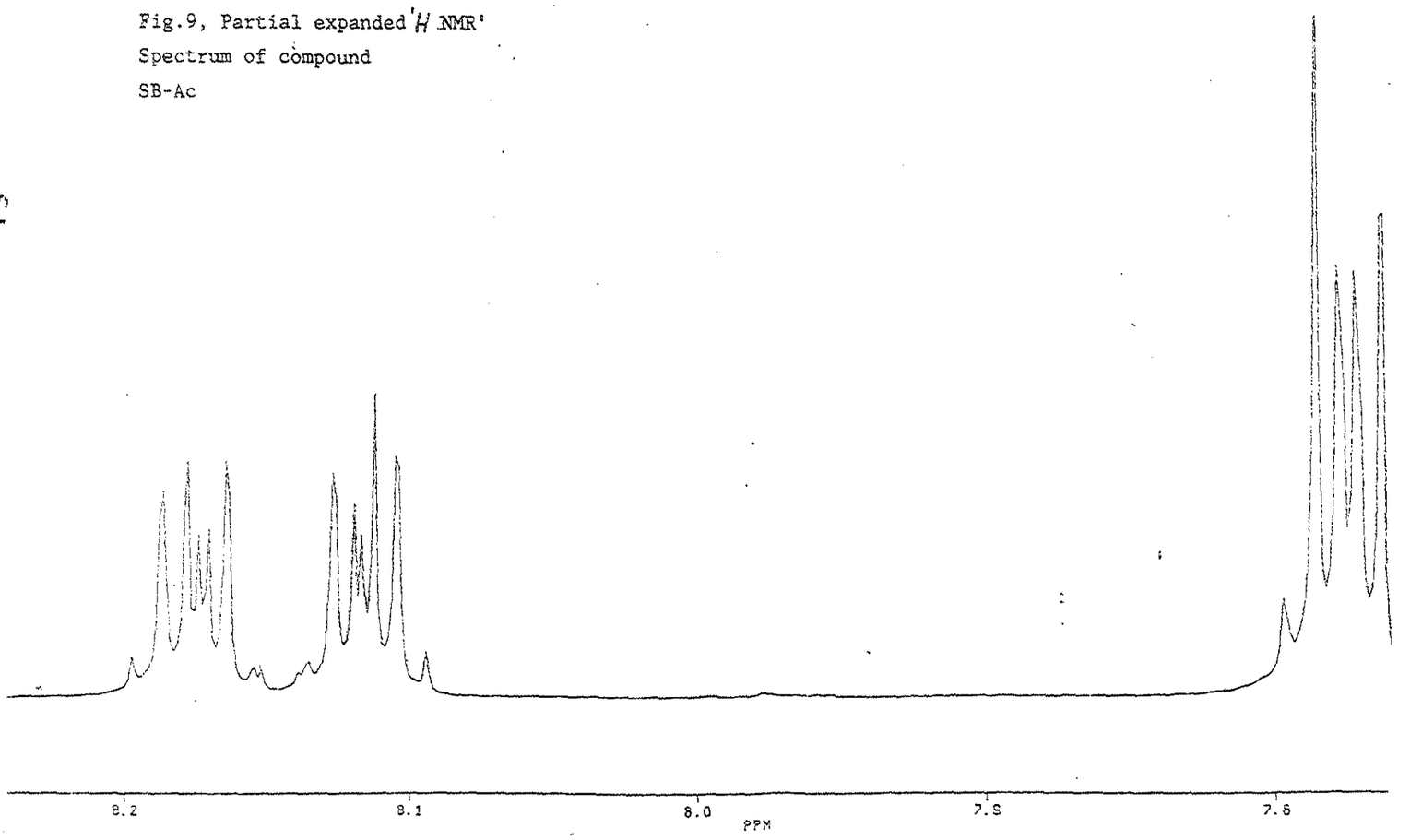
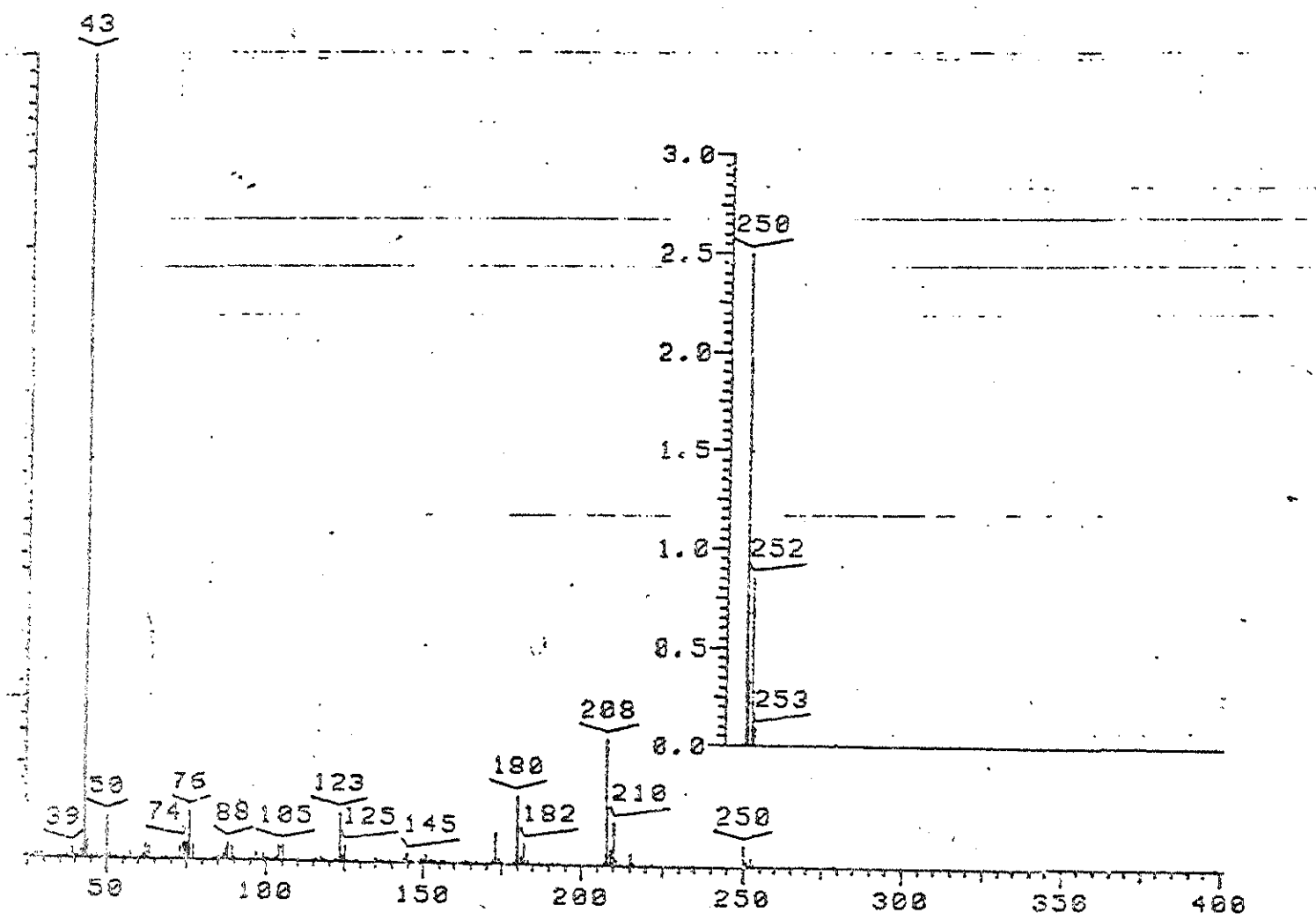


Fig. 10, MS of compound SB-Ac



chloride have also been realized with phosgene. However, we are not aware of whether or not photochlorinations achieved by either of these reagents could also be obtained by the other. Nevertheless, the obvious structural similarity between chlorylchloride and phosgene, coupled with the formation of a compound similar to photoproduct 5b from the reaction between the former ragent and the quinone, lends itself to suggest that phosgene, whose primary photochemical process is generally accepted to be the efficient splitting into chlorine atoms,[89] is the most probable donor of chlorine atoms for the photochlorination of the quinone. This is corroborated by a second piece of evidence discussed below.

Exposure of the same concentration (as that used for photolysis in chloroform) of the quinone in carbon tetrachloride, flushed with nitrogen for the same period of time, to diffuse daylight was found to leave a large amount of unreacted starting material. This is in contrast to the photolysis in chloroform in which virtually all the substrate was consumed. Besides, formation of a compound analogous to photoproduct 5B is hardly discernible by TLC in this photo-experiment as opposed to irradiation of the quinone in chloroform which yielded compound 5B as the major product.(65%). That compound 5B is barely detectable by TLC in the photoreaction involving carbon tetrachloride illustrates that phosgene, which is not expected to be formed from this solvent under the conditions of the photoexperiment, is the dominant, if not the sole, donor of chlorine atoms for the photochlorination of the hydroxyquinone in chloroform. A more direct evidence for the foregoing was derived from the chromatographic detection of a substance similar to compound 5B following treatment of a toluene solution of the hydroxy quinone with

phosgene which was produced by the thermal reaction of carbon tetrachloride and concentrated sulfuric acid[108]

The formation of this toxic gas (phosgene) from chloroform has been demonstrated by both in vivo [90] as well as in Vitro[91] experiments.

1.4 Compound SA

Compound SA, thermally stable upto 300°C, is the second major photoproduct (25-30% yield) obtained from the photolysis of 2-hydroxy-1,4-naphthoquinone in chloroform. Its red color changes to yellow when treated with trace of acid. Addition of base doesn't restore the color. It is soluble in polar solvents like DMSO. The behavior of the compound in alkaline solution is in contrast to that in acidic medium in that it dissolves in the former without loss of color. The dissolutionof thephotoproduct in a sodium bicarbonate solution was not accompanied by any noticeable gas evolution.

The visible absorption spectrum of compound SA showed λ_{max}(meOH) at 451nm. Its infrared spectrum, depicted in Fig.11, displayed an absorption band due to O-H stretching frequency at 3450 cm^{-1}. The solubility of the compound in dilute alkaline medium, together with a consideration of its origin suggest that the hydroxy group is most likely phenolic. The stretching frequency at 1690 cm^{-1} is indicative of carbonyl functionality. The 400 MHZ ^1H NMR spectrum (DMSO-d_6), shown in Figs. 12 and 13, consisted of two closely placed . . . doublets at 7.8-7.65; two sets of triplets centered at 7.57-7.62 and 7.52-7.6ppm together with a singlet at 5.47ppm. These signals occurred in the intensity ratio of 2:1:1:1. Comparison with the ^1H NMR spectrum

of the parent compound (Fig.5) reveals absence of the signal due to the hydrogen at position-3 of the latter compound and appearance of a new absorption line at 5.47 ppm. The pattern of proton signals shown in the spectrum of this compound, in conjunction with the absorption band at 730cm^{-1} in the infrared spectrum strongly indicate that the aromatic ring of the starting material is intact in this photoproduct. The 100.4 MHz ^{13}C NMR spectrum (DMSO-d_6) of photoproduct SA, reproduced in Fig.14, contains a total of ten carbon signals appearing at 188.06, 181.25, 171.35 135.47, 133.89, 131.27, 130.60,125.22, 125.01, and 106.89 ppm. It is intriguing to note that whereas the ^{1}H NMR spectrum of this compound (Fig.12) indicates absence of the hydrogen at C-3 of the starting material, the ^{13}C NMR spectrum (Fig.14) on the other hand, cintains a strong signal at 106.89ppm, suggesting that C-3 of the parent compound undergoes little or no change. The resonance line at 188.06 is too downfield to be attributable to C-4 of the starting material. For example, the carbonyl carbons C-1 and C-4 of 2-methoxy-1,4-naphthoquinone resonate at respectively, 180.0 and 184.7ppm while C-3 absorbs at 109.3ppm.(84) It is therefore apparent that the phototransformation of the hydroxy quinone to compound SA must have entailed deshielding of C-4 of the former compound while leaving C-1 and C-3 relatively unaffected.

The mass spectrum of the compound under consideration (Fig 15) showed a weak molecular ion peak at m/z 330 which is 18 mass units lower than the molecular weight of a dimer of the parent quinone. The most intense peaks occurred at m/z 174 and 105 both of which also appear as the most prominent ion peaks in the spectrum of 2-hydroxy-1,4-naphthoquinone.(81) This situation lends itself to suggest that

photoproduct SA undergoes fission in the mass spectrometer most preferrably to yield radical cation of the parent quinone. The complete absence of an m/z 120 ion in the mass spectrum indicates that the hydroxy group of compound SA is not attached to the benzenoid ring/(81) It is likely from the foregoing discussion that the carbonyl group (C-4) of 2-hydroxy-1,4-naphthoquinone must have beeen affected by the photoprocess.

Compound SA was acetylated (Ac_2O/py., room temperature) with the objective of generating data for its acetate so as to enhance characterization of the photoproduct. Addition of acetic anhydride to compound SA resulted in color change from red to yellow in no time. The yellow color was maintained throughout the acetylation period. Work-up followed by purification on a microcolumn using chromatographic grade silica gel as the adsorbent and benzene as the eluent yielded a yellow compound as the major product, which is here after referred to as SA-Ac. Its ^{1}H NMR spectrum ($CDCl_3$), reproduced in Fig.16, showed a pair of multiplets at 8-1.2 and 7.7-7.8ppm together with singlets at 6.75 and 2.38ppm. These signals occurred in the intensity ratio of 2:2:1:3. A close scrutiny discloses that the ^{1}H NMR spectrum of compound SA-Ac is quite similar, if not identical, with that of 2-acetoxy-1,4-naphthoquinone (Fig.17). The similarity of these two spectra suggests that compound SA is unstable under the conditions of the acetylation reactions. It is tempting to claim that the photoproduct is transformed to the parent quinone upon treatment with the acetylating agent. It is also note-worthy that compound SA fragments in the mass spectrometer to yield the parent quinone radical cation as the most intense peak.

Despite the considerable amount of data accumulated, a positive identification of photoproduct SA has not been achieved.

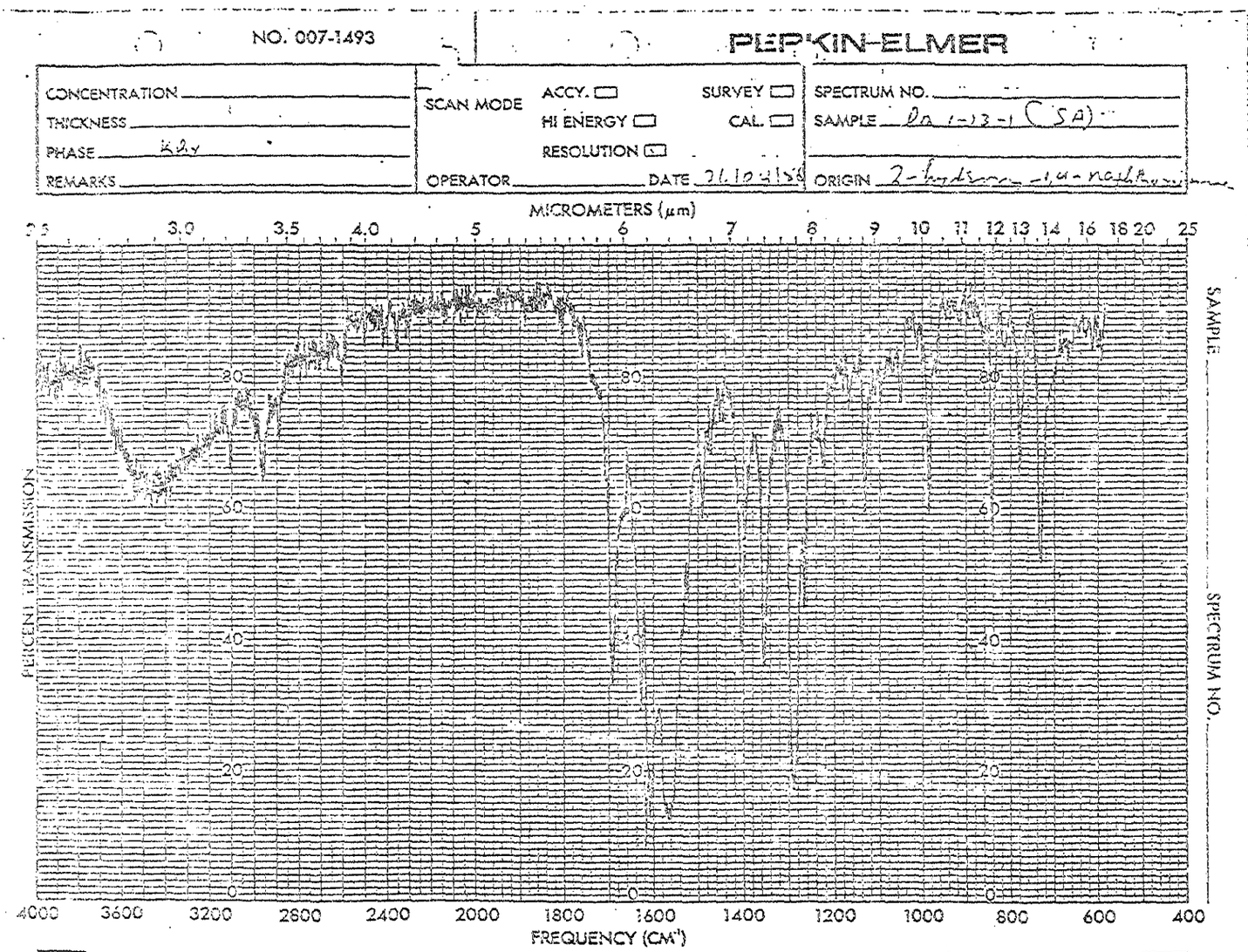


Fig. 11, IR spectrum of compound 5A

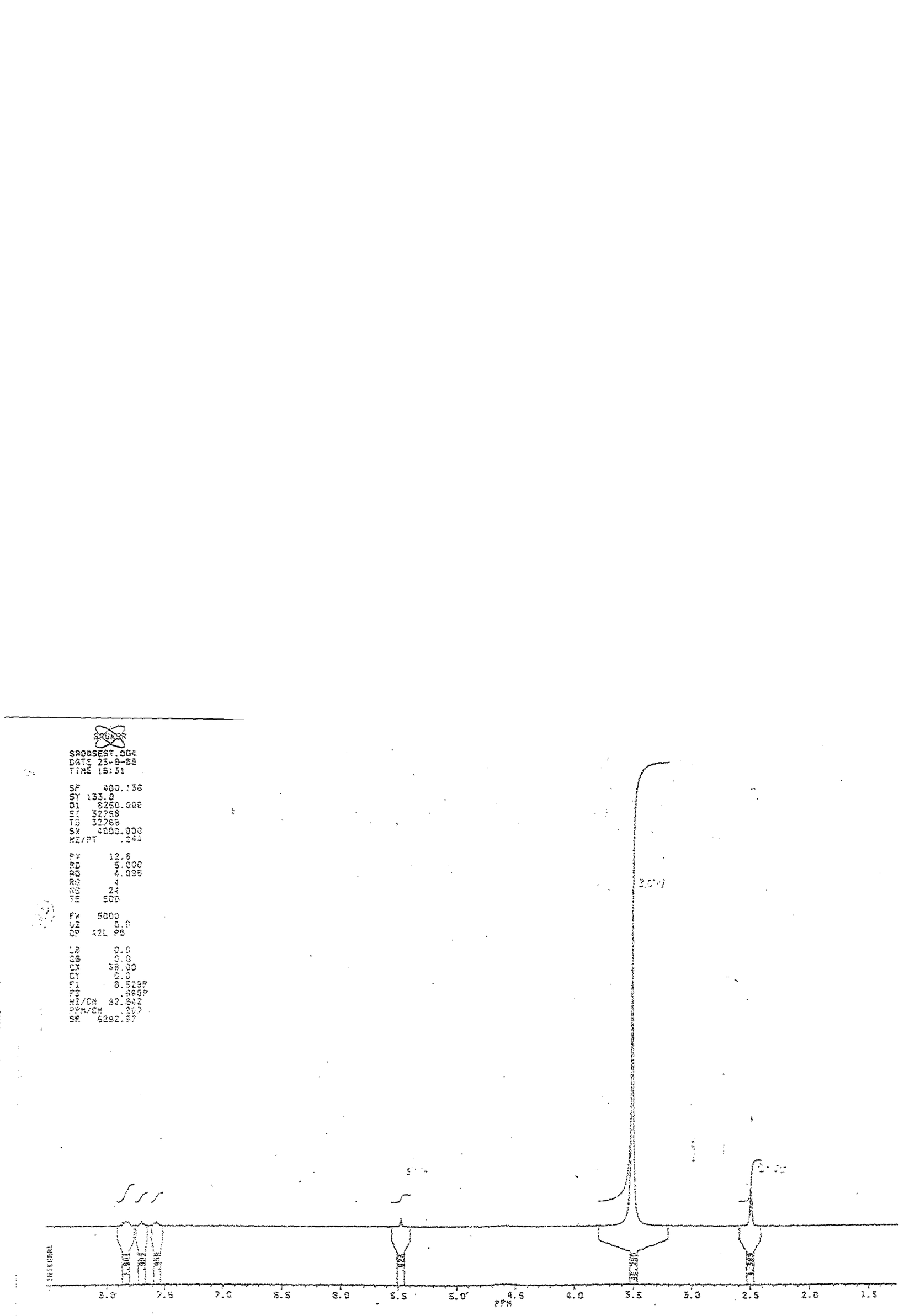


Fig. 12, ^{1}HNMR Spectrum of compound SA in DMSO-d_6

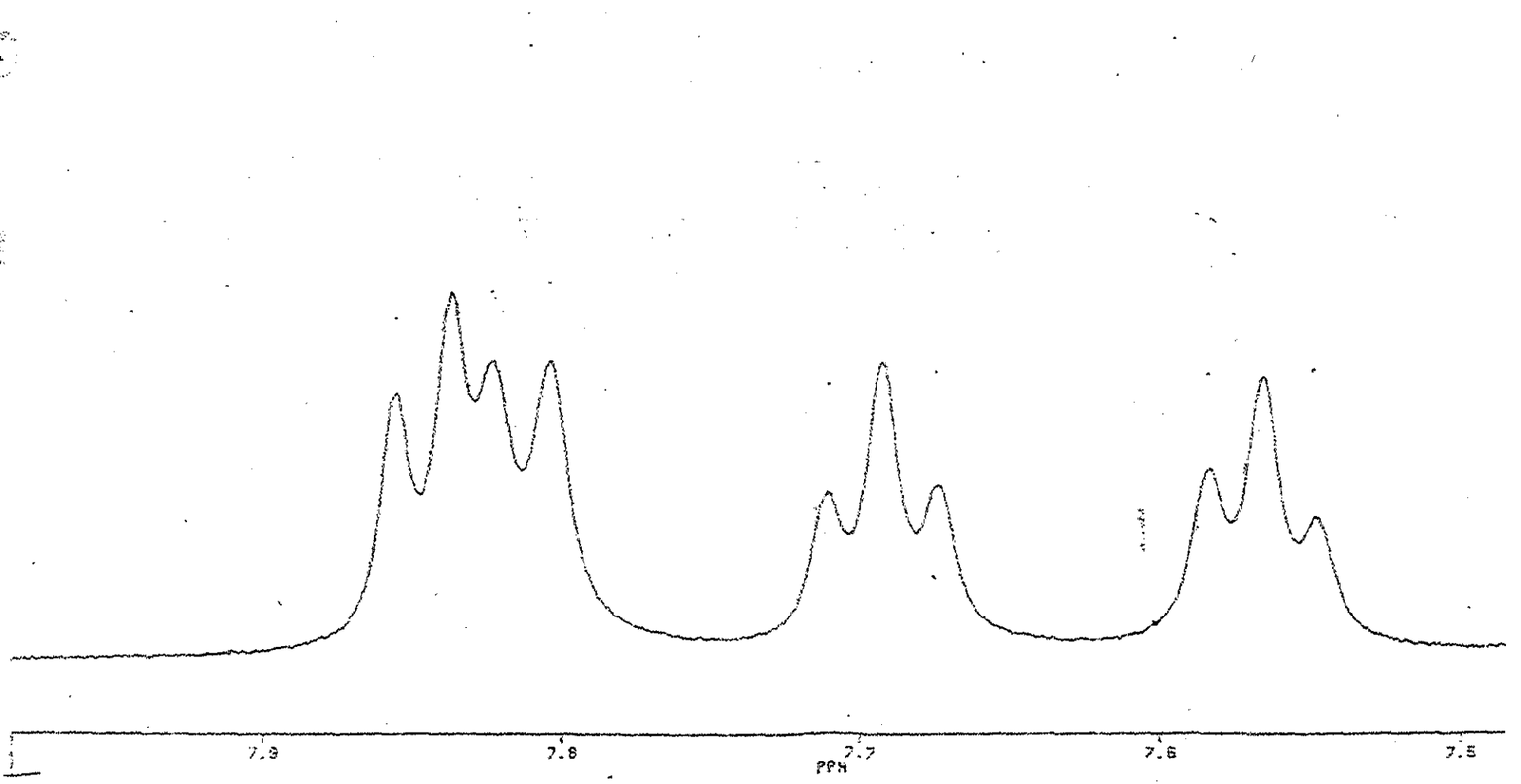


Fig. 13, Partial, expanded ^{1}H NMR Spectrum of compound 5A

Fig. 14, ^{13}C NMR Spectrum of compound 5A in DMSO-d_6

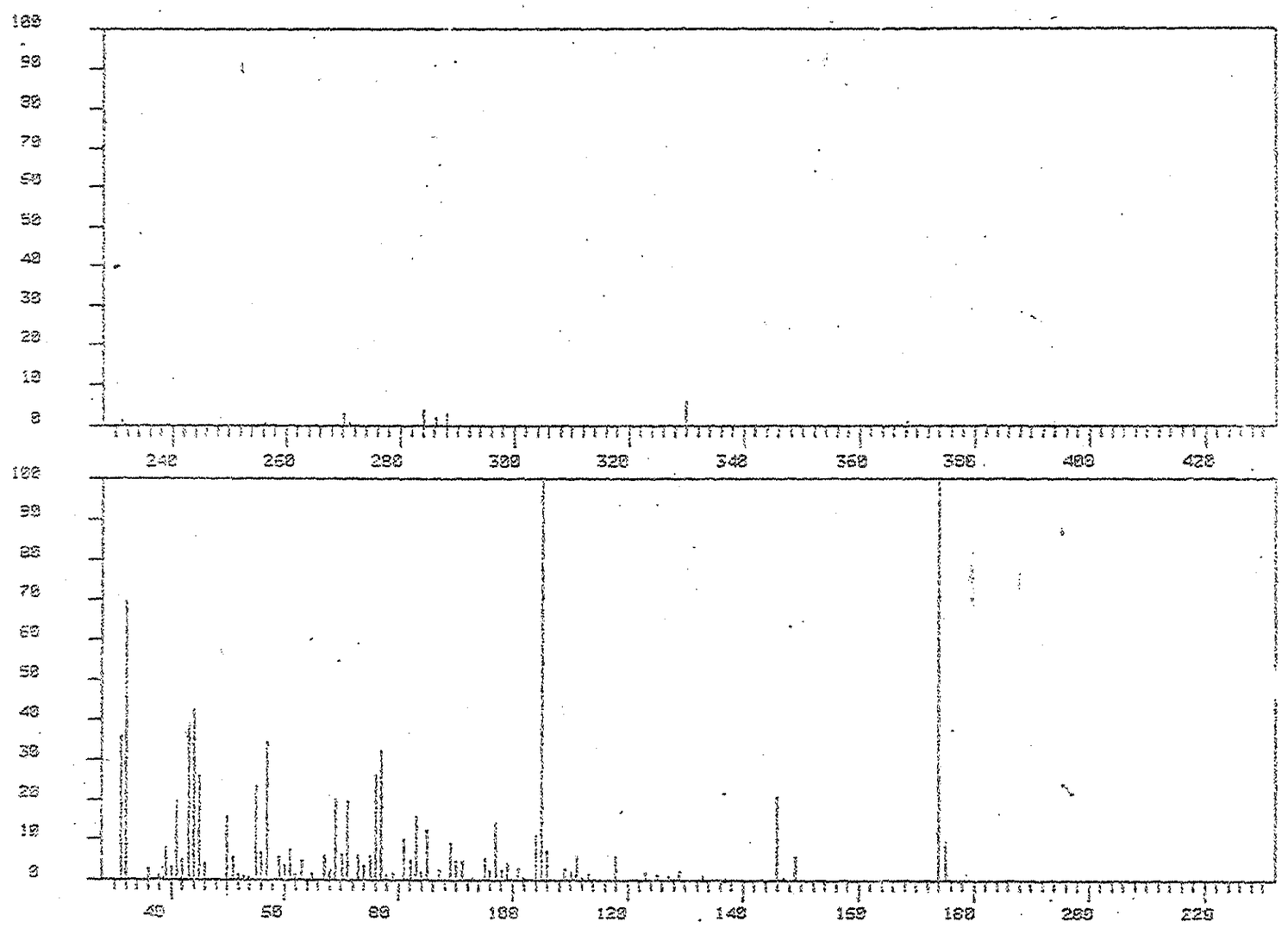


Fig. 15, MS of compound 5A

Fig. 16. ^{1}H-NMR Spectrum of compound SA-4c in $CDCl_3$

1 H-NMR Spectrum of 2-acetoxy-1,4-naphthoquinone in $CDCl_3$

2. Photoexperiment with 2-Methoxy -1,4-naphthoquinone

The reaction consequent upon exposure of a chloroform solution of the title quinone (10^{-3}M) in a pyrex flask flushed with nitrogen, to diffuse daylight during 1.5hrs. resulted in a rapid change of the original faint yellow color of the solution to red. Purification by PTLC led to the isolation of a red compound labeled SC, as the major photo product (about 30% yield based on the starting material consumed) together with several other minor ones. About 23% of unreacted starting material was recovered at the end of the reaction. The corresponding dark reaction was seen to leave the quinone unaffected.

2.1. Compound SC

Compound SC, which decomposes at around 140°C, is red in color and is much more polar than the parent quinone. It dissolves in polar solvents like DMSO as well as dilute alkaline medium. The compound changes its color to yellow when treated with trace of acid. Addition of base to the acidified substance doesn't restore the color. On the other hand, the compound dissolves in alkaline solution without loss of color. These observations demonstrate that photoproduct SC is acidlabile.

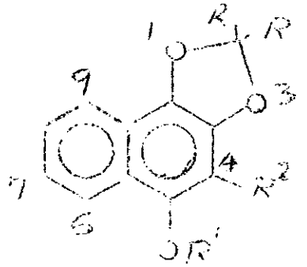
The spectral data of this compound, discussed below, have not enabled an assignment of structure which is compatible with all the available data.

2.1.1. ^{1}H NMR Spectrum

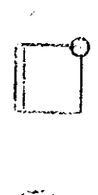
Comparison of the ^{1}H NMR spectrum (DMSO-d_6) of compound 5C with that of the starting material ($CDCl_3$), both of which have been reproduced in Figs. 18 and 19 respectively, shows that the signals of both the methoxyl (δ3.9ppm) & 3-H (δ6.15PPm) of the latter compound have vanished in the spectrum of the photoproduct. Moreover, the reasonance lines of the aromatic protons of compound 5C are shifted upfield by 0.3PPm relative to those in the methoxy compound, whose spectrum had also been obtained in DMSO-d_6. The proton signals displayed by the photoproduct occur at δ7.6-7.9(m) and 5.4(s) ppm in the intensity ratio of nearly 6:1.

The candidacy of the methylene dioxy compound 49 as a possible structure for the compound under discussion in ruled out on the ground that neither the methylene protons nor the hydrogen at C-4 are observed in the ^{1}H NMR spectrum of the photoproduct. Besides whereas photolysis of 2-bromo-3-methoxy-1,4-naphthoquinone in AC_2O has been noted[20] to afford compound 49(R=H,R^1=AC,R^2=Br) the

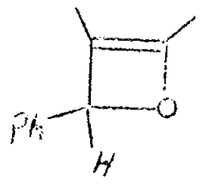
analogous reaction of the halogen free methoxy quinone failed to yield the corresponding 49($R=R^2=H, R^1=Ac$). Photolysis of 2,5-dimethoxy-3,6-dimethyl-1,4-benzoquinone has also been reported [21,67] not to afford the expected methylenedioxy compound as opposed to the corresponding reaction of the 2,5-diaminated derivative which readily yields the benzoxazoline.



49



50



51

A second structure speculated for photoproduct SC was that represented by structure 8 which might be envisaged as arising from photocyclization of the methoxy side chain onto C-3 of the parent quinone. The absorption positions of the methylene and methine protons of oxetens 50 and 51, reported [93,94] to occur at δ5.27 and 5.81ppm, respectively, together with the suggestion [92] that hydrogens α - to oxygen in oxetanes appear at δ 4.0-5.0 ppm, tend to suggest that the multiplet at δ 7.6 - 7.9 and the singlet at δ5.4ppm in the ^{1}HNMR spectrum of photoproduct SC may be attributed to the benzenoid and methylene protons, respectively, of the speculated structure 8 . However, the observed integrated ratio (6:1) deviates

from that expected (2:1) for structure 8.

2.1.2. ^{13}C NMR Spectrum

A DEPT ^{13}CNMR spectrum (DMSO-d_6) of compound SC displayed a total of eleven carbon signals, six of which are due to quaternary carbon atoms. The resonance lines of these carbons appeared at δ167.80, 143.04, 137.78, 136.29, 131,77, and 128.88 ppm. Four of the remaining five signals are due to CH carbons whose absorption lines are centered at δ135.52, 132.59, 127.64, and 127.29 ppm. A CH_2 unit is indicated by the signal at δ128.02ppm.

The C-3 signal of the starting material, expected at 109.3ppm[84], is not observed in the spectrum of photoproduct SC and therefore must have shifted downfield. Likewise the two carbonyl carbon signals which have been reported[84] to resonate at 180.0 and 184.7ppm, are absent in the spectrum of compound SC suggesting that their absorption lines have shifted upfield. On the other hand, the chemical shift values of the benzenoid carbons C-5 through C-8 of the parent quinone, which absorb[84] at δ126.1, 134.3, 133.3, and 126.6ppm, respectively, are affected only slightly by the photo-transformation relative to the quinonoid carbons

C-1 to C-4. This is supported by the chemical shift values (see above) of the four CH carbons of photoproduct SC. A similar inferrence is derived when one compares the absorption positions of the ring junction carbon atoms C-4a and C-8a of the starting material which resonate[84] at δ132.0 and 131.1ppm, respectively, with those signals appearing at δ131.77 and 128.88ppm in the spectrum of photoproduct SC.

It is therefore clear that the quinonoid portion of the parent compound must have been affected by the photoprocess leading to compound SC while the benzenoid ring remains intact.

2.1.3. Mass Spectrum

A high resolution mass spectrum of compound SC, reproduced in Fig. 20, showed the parent peak at 188.048 (rel.Int., 9) corresponding to a molecular formula of $C_{11}H_8O_3$. This composition shows that photoproduct SC is an isomer of the starting material.

The weak ion peak at m/z 204(rel,Int.,3%) in the mass spectrum is neglected as it requires incorporation of an oxygen atom into the starting material, which is difficult to substantiate considering the conditions of irradiation.

Comparison of the ion peaks common in the high mass region of the spectra of both starting material[81] and compound SC, depicted in Table II, reveals a high variation in the relative intensities of these ion peaks. Furthermore, the peaks at m/z 174,149,147,146 and 106, which are abundant in the spectrum of photoproduct SC, are completely absent in the corresponding spectrum of the parent quinone,[81]. These features, coupled with the absence of the methoxy signal in the ^{1}HNMR spectrum of compound SC, rule out the likelihood that those ion peaks common to both the spectra (Table II) could be due to fragments of the starting material, which might be suspected to be a contaminant of compound SC.

The composition $C_{10}H_6O_3$ indicated in the mass spectrum (Fig. 20) for the base peak at m/z 174 shows that the preferred mode of cleavage of photoproduct SC in the mass spectrometer leads to the formation of 2-hydroxy -1,4- naphthoquinone radical cation. This claim is strengthened by the characteristic decomposition products[81] of this species.

Table II. Comparison of the high mass region ion peaks common to the spectra of 2-methoxy-1,4-naphthoquinone[81] and photoproduct SC

Compound									
$^{+}$NaOMe	M/z	89	102	104	105	158	159	173	188($M.^{+}$)
	rel. int. (%)	46	38	10	6	36	20	39	100
SC	m/z	89	102	104	105	158	159	173	188($M^{\cdot +}$)
	rel. int. (%)	15	5	4	96	5	4	4	9

+ NaOMe 2-methoxy-1,4-naphthoquinone.

2.1.4. Infrared and Visible Absorption Spectra

The infrared spectrum of compound SC showed absorption bands at 3450(O-H) and 1560cm^{-1}, both of which are absent in the corresponding spectrum of the parent quinone. On the other hand, the band at 1460cm^{-1}, which is clearly seen in the ir spectrum of the parent quinone and which is attributed to the C-H deformation vibration of the methoxy side chain, has completely vanished in the spectrum of the photoproduct. This demonstrates that the methoxy group of the parent compound must have been

involved in the photochemical reaction. The presence of an ortho-disubstituted benzene ring is indicated by the absorption frequency at 730 cm^{-1} which suggests that the aromatic ring of the methoxy quinone is intact in photoproduct SC. As was noted earlier the NMR spectra of compound SC also lead to the same inferrences. The visible absorption spectrum of compound SC exhibited λ_{max} (abs. EtOH) at 448nm.

2.1.5. Attempted Acetylation of Compound SC

Acetylation of photoproduct SC with AC_2O/Py. at room temperature was undertaken with the view of getting spectral data for the resulting acetate so as to enhance the characterization of the compound. Compound SC experienced an immediate color change from red to yellow when dissolved in the acetylating agent. The yellow color was maintained throughout the acetylation period. Work-up of the reaction mixture followed by purification on a microcolumn silica gel chromatography using benzene as the elvent afforded a yellow compound which behaved similarly in every aspect on TLC with 2 acetoxy 1,4 naphthoquinone. Besides, the ^{1}HNMR spectrum ($CDCl_3$, Fig. 21) of this compound, designated as SC-AC, displayed signals at δ8.1(m), 7.75(m) 5.75(S) and 2.38(s) in the intensity ratio 2:2:1:3. Comparison

of this spectrum with that of 2-acetoxy-1,4-naphthoquinone ($CDCl_3$, Fig. 17) which is the same as literature values,[107] discloses no distinction between the two. It is thus seen that the acetylation of compound SC did not yield the expected acetate. The similarity of these two spectra also makes structure speculated for compound SC doubtful.

In summary, the spectral data generated for photoproduct SC have not led to an identification of a structure which would best represent it.

3. Summary of Results

The synthesis and characterization of 2-chloro-3-hydroxy-1,4-naphthoquinone by photolysis of a dilute chloroform solution of 2-hydroxy-1,4-naphthoquinone has been described in the predeeding pages. It has also been noted that work documented on photoprocess leading to the formation of this compound from the materials used in the present study is non-existent. The literature discloses only one report[22] on the photoformation of this compound as one of several minor photoproducts from 2,3-dichloro-1,4-naphthoquinone.

2-Chloro-3-hydroxy-1,4-naphthoquinone, first reported[95] in 1887, is known to have tumorcidal[96] as well as

PMR Spectrum of 2-methoxy-1,4-naphthoquinone in $CDCl_3$

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PROG410L.0011.00
 2/20/09   9: 7

NO. PEAKS:  350
BASE/REF DIF:  29130./  9730.
TIC:  159937.
MASS RANGE:  30.0034 -  742.9934
RETN TIME/DISC:  31:/ 222/  1/  7%

  C   C13 H   O   DEV  MASS MASS  %PTS  %INT
 16   1      9

 11   0   8   4   1.7  294.0449   22    3.84
 11   3   6   3   0.3  193.0482   25    8.60
  9   1   6   2  -1.5  175.6332   44   12.49
 10   0   6   3  -0.8  174.0317   27  100.00
  9   1   5   2   4.9
 10   0   5   3   0.2  173.0241   33    4.01
  9   1   4   3   4.7

LIMIT OF DATA
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DB-50 MASS INTENSITY REPORT: 9410L.11 (TIC=159937, BBX=97/80)

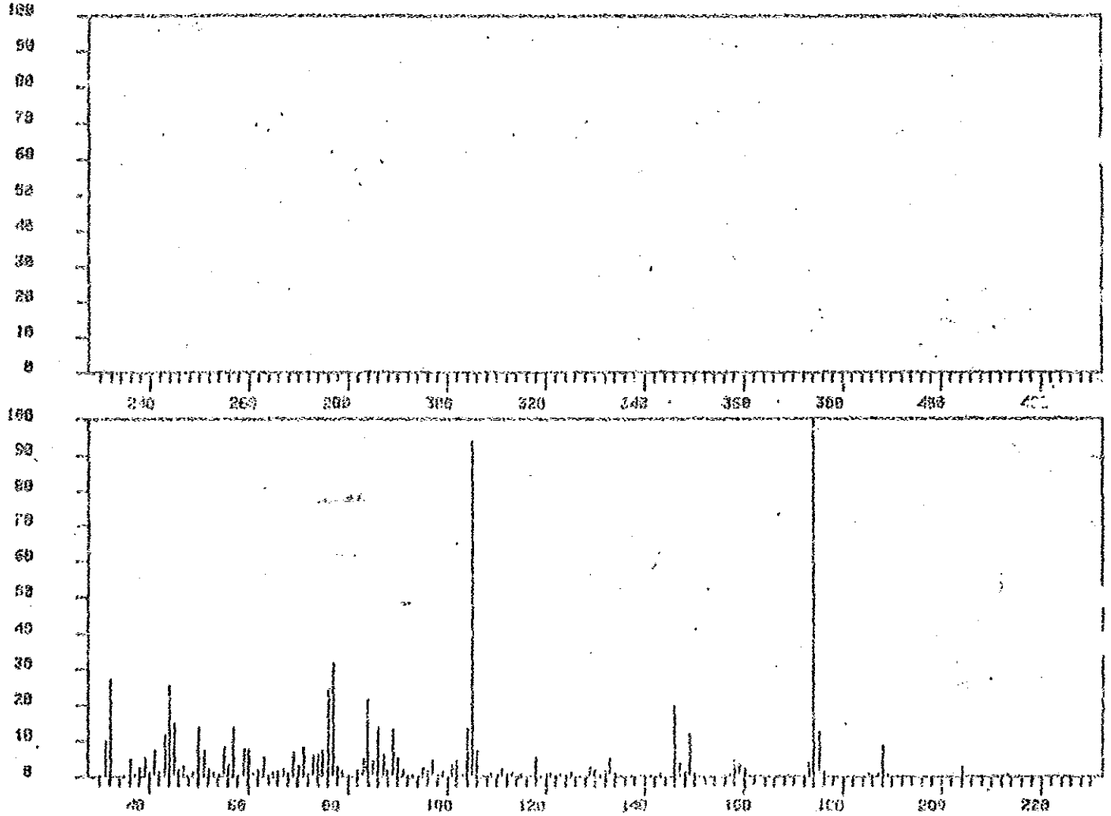

Fig. 21. ^{1}H NMR Spectrum of compound SC-4c in $CDCl_3$

fungicidal[97] prpperty. Besides, it inhibits the growth of some kinds of bacteria[98-100] while its copper salt is reported to be a disinfect[101]

While several preparative methods have been developed for the synthesis of this compound, some of them involve very stringent conditions like refluxing[102], or the use concentrated hydrochloric acid at higher temperatures[103] whereas others suffer from the drawback of low yield.[104]

The photochemical route to 2-chloro-3-hydroxy-1,4-naphthoquinone discussed in the present work, despite the relatively long time it required, is simple and affords the compound in an acceptable synthetic yield. Analysis of the spectral data (IR,NMR,MS,visible absorption spectrum) of this photoproduct and those of its acetate accorded with its identification. The melting point of this compound and its mass spectrum are in reasonable agreement with literature data.[81,102]

Compound 5A, which is the second major photoproduct of the photolysis of the hydroxy quinone, has not been fully characterized.

Though an unambibuous identification of compound 5C, which is the major reaction product obtained from irradiation of 2-methoxy-1,4-naphthoquinone in chloroform,

has not been achieved, its spectral data (IR,MS,NMR) strongly indicate that the aromatic ring of the starting material is intact in the photoproduct. It is also evident from these data that the quinoid portion of the parent quinone is involved in the photochemical transformation leading to compound SC.

V. Experimental

1. General

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Unless stated otherwise, NMR spectra were recorded using a Jeol FX90QFT Nuclear Magnetic Resonance Spectrometer. Spin multiplicity is denoted by s(singlet), d(doublet), t(triplet), and m(multiplet), Visible absorption spectra were measured on a Beckmann Model 24 instrument. IR spectra were measured as KBr pellets on aPerkin-Elmer 727B spectrophotometer. 400MHz NMR and all the mass spectra were recorded at Ruhr-Universitaet Bochum and the Institute of Organic Chemistry and Biochemistry of the University of Bonn(FRG).

Analytical thin layer chromatography were run on a 0.25mm thick layer of silica gel GF_{254} (Merck). Adsorbent used for column chromatography was silica gel 60(Merck).

2. Sources of Compounds Studied

2.1. Emodin anthrone

This compound was obtained following the procedure published in the literature.[75]

2.2. 2-Methoxy-1,4-naphthoquinone

An impure sample of the title quinone, prepared earlier in this laboratory,[105] was purified by recrystallization

ethanol which yielded pale yellow needles of the compound. Mp 183-184°C (lit.[106] Mp 183.5°C). IR ν_{max}^{KBr} cm^{-1}: 1695, 1660, 1620, 1580, 1460, ^{1}H NMR($COCl_3$): δ8.17(m,H-5,H-8), 7.73 (m,H-6,H-7), 6.15(S,3-H), 3.9(S,OMe).

2.3. 2-Hydroxy-1,4-naphthoquinone

This compound was obtained in pure form by basic hydrolysis of its methyl ether according to a published procedure: 2 Methoxy-1,4-naphthoquinone (3g, 0.016mol) was dissolved in aqueous 0.5M NaOH (40ml) solution and the mixture was heated to the boiling point for about 10min. followed, immediately, by filtering the resulting deep red solution under vacuum. The filtrate was acidified while still hot by adding 6N HCl (4ml) slowly, and with continuous stirring. The resulting yellow suspension of hydroxy naphthoquinone was cooled to 0°C and allowed to stand for 2hrs. The compound was collected by suction filtration, washed with cold water, dried overnight in a dessicator, and finally to constant weight at 60-80°C to give bright yellow, granular 2-hydroxy-1,4-naphthoquinone. MP. 189-191°C dec (lit.[106] MP 188-189°C(dec.)). IR ν_{max}^{KBr} Cm^{-1}: 3200, 1690, 1680, 1580. ^{1}H.NMR(DM50-d_6): δ8.1-7.8(m,H-5,H-6,H-7, H-8), 6.2 (S 3-H)

3. Irradiations and Purification of Photoproducts

3.1. Emodin Anthrone

5 mg of the compound in 10ml of each of distilled acetone, ethylacetate, methanol, and chloroform/methanol (1:1) was placed into four separate test tubes (pyrex) each containing 0.15g of chromatographic grade silica gel (silica gel 60 Merck). These were exposed to day laboratory light while another set of solutions of the same substrate, prepared in the same way, was placed in the dark.

The dark reactions were found to yield the dimer within a day as evidenced by comparative TLC (PhMe/EtOAc/HOAc, 80/15/5) using an authentic specimen of emodin bianthrone[75] as the reference. The dimer formed in the corresponding light reactions was, however, short-lived. Its intensity diminished progressively with the passage of time (TLC). The major reaction product in these cases was the photooxidized product, emodin 48.

3.2. 2-Methoxy-1,4-naphthoquinone

In a preliminary experiment, 10mg of the quinone was dissolved in 50 ml of distilled chloroform. The solution was placed in a 50ml pyrex flask, purged with nitrogen for about 15min. amd exposed to diffuse sunlight reaching the flask through the laboratory window glass. TLC

monitoring of the progress of the photoreaction indicated appearance of reaction products after about 40 min. from the onset of the reaction, after which time the reaction mixture rapidly developed a red color with concomittant formation of, among others, one major reaction product which is designated as SC(R_f0.33, PhH/EtOAc/HOAc,70/30/1). The reaction mixture was worked-up after 1.5hrs. of irradiation which led to recovery of 23% of unreacted starting material.

The photolysis was carried out on a preparative scale as described above by dissolving 100mg of the quinone in 500ml of distilled chloroform. Following concentration under reduced pressure, purification by preparative TLC (PhH/EtOAc/HOAc,70/30/1) led to the isolation of a red compound, labeled SC (third band), as the major photoproduct (30% yield). Mp 140°C/dec.) IR ν_{max}^{KBr} cm^{-1}: 3450,1690,1670,1600,1580,740. ^1H NMR (DMSO-d_6): δ7.7(m), 5.4(s),MS m/z (rel.int.%): 188.0482 (8.6,M^+, Calc. for $C_{11}H_8O_3$ 188.1824), 174(100), 173(4), 160(3), 159(4) 158(5), 149(10), 146(20), 105(93). ^{13}C NMR (DMSO-d_6): δ167.80, 143.04, 137.78, 136.29, 135.52, 132.59, 131.77, 128 128.88, 128.02, 127.64, 127.29. Vis λ_{max} (abs. EtOH)nm: 448.

3.3. 2-Hydroxy-1,4-naphthoquinone

3.3.1. Photolysis in Chloroform

The preliminary photoexperiment was carried out as described in section 3.2. TLC monitoring of the progress of the photolysis showed appearance of photoproducts only after about 8hrs. of irradiation while leaving a substantial amount of unreacted starting material. A similar situation was noted following photolysis for three consecutive days. TLC analysis of the reaction mixture after seven days of irradiation revealed the appearance of two major photoproducts whose formation was also noted during the earlier hours of the photolysis. A purification method was developed for the isolation of the major photoproduct prior to carrying out the photoreaction on a preparative scale as described in section 3.2.

For large scale photolysis, 100mg of the quinone in 500 ml of distilled chloroform was placed in a 500ml pyrex flask. The solution was purged with nitrogen for about 20min. and exposed to day laboratory light for seven days as described in section 3.2. Solvent removal under reduced pressure and subsequent purification by preparative TLC (PhH/EtOAc/HOAc,70/30/1; or CH_2Cl_2/EtOAc/HOAc, 80/20/1) afforded photoproducts S$_4$ and S8 in a combined yield of greater than 90%. The latter product

has been identified as 2-chloro-3-hydroxy-1,4-naphtho-quinone. MP 217-219°C(lit.[102] MP 215°C IR ν_{max}^{KBr} cm^{-1}: 3500,1680,1600,1560,1400,1300,840,740. ^1H NMR (DMSO-d_6): δ7.92(m,H-5),7.82(m,H-8),7.72(m,H-6),7.57(m,H-7) MS m/z (rel.int.%): 210(12), 208(34,M^+), 182(8), 180(26), 173(18), 145(10), 105(100), 104(18), 77(44), 76(50). ^{13}C NMR(MeOH-d_4): δ179.8, 168.6, 135.7, 134.9, 133.0, 131.3, 129.4, 127.6, 126.7. Vis. λ_{max} (MeOH)nm:474.

Compound 5A:MP>300°C. IR ν_{max}^{KBr} cm^{-1}: 3450,1690,1635, 1600,1560,1480,1400,1360,1290,1140,980,840,780,740 ^1H NMR(DMSO-d_6) δ7.85(d,J=7.12Hz), 7.81(d,J=7.12Hz), 7.69(t,J=7.12Hz), 7.57 (t,J=7.12Hz). MS m/z (rel.int.%) 330(7,M^+). ^{13}C NMR(DMSO-d_6):δ188.08, 181.25, 171.75, 135.47,133.89,131.27,130.60,125.22,125.01,106.89. Vis. λ_{max}(MeOH)nm:451.

3.3.2. Photolysis in Carbon tetrachloride

A solution of 10mg of 2-hydroxy-1,4-naphthoquinone is 50 ml carbon tetrachloride (BDH) was placed in a 50 ml pyrex flask, flushed with nitrogen for about 15min. and exposed to day laboratory light as described in section 3.2. for one week. ILC examination of the reaction mixture at the end of the reaction time showed a large amount of unreacted starting material. The formation of compound similar to photoproduct B was hardly detectable by TLC.

4. Reaction with Thionyl Chloride

(i) Into a solution of 10 mg of 2-hydroxy-1,4-naphthoquinone in 20ml benzene was added 5 ml of thionyl chloride. The reaction was allowed to proceed at room temperature in a hood with continuous stirring. The formation of a compound that exhibited similar chromatographic behavior with that of compound S 3 was noted within 2hrs. of reaction time (TLC examination).

(ii) A mixture of 10 mg of 2-methoxy-1,4-naphthoquinone, 20ml benzene and 5 ml of thionyl chloride was placed in a round-bottom flask equipped with a reflux condenser to which was attached a drying-tube. The mixture was heated gently (40-50°C) over a water-bath for about 8 hrs. in a hood. Purification by silica gel column chromatography (silica gel 60 Merck) using benzene as the eluent afforded 5.6 mg of a yellow compound which is less polar than the methoxyquinone (TLC). This reaction product is similar neither to photoproduct S. nor S.

5. Generation of Phosgene

This gas was generated according to a procedure published in the literature.[108]

6. Acetylations

Into a dry 25 ml flask containing 15 mg of

Compound S3

or Compound SA

or Compound SC

or 2-hydroxy-1,4-naphthoquinone

was added 5 ml of AC_2O and a few drops of dry pyridine. Compounds SA and SC underwent a rapid color change from red to yellow when dissolved in the acetylating agent.

The acetylation reaction was carried out for 4 hrs. at room temperature with continuous stirring. The reaction mixture was then poured into a clean beaker containing ice-cold water. Subsequent extraction with CH_2Cl_2 or $CHCl_3$ followed by purification on column chromatography (silica gel 60 Merck) using benzene as the eluent yielded compounds S3-A6 (8.6mg), SA-Ac (9.3mg), SC-Ac(10,mg), and 2-acetoxy-1,4-naphthoquinone (12mg).

Compound S3-Ac is a yellow crystalline acetate which was identified as 2-chloro-3-acetoxy-1,4-naphthoquinone. Mp 129-131^{o}C (lit.,[87] Mp142.5^{o}C). IR ν_{max}^{KBr} cm^{-1}: 2950, 2900, 1800, 1690, 1640, 1460, 860, 800, 720, 690. ^1H NMR ($CDCl_3$): δ8.18(m,H-5), 8.13(m,H-8), 7.77(m,H-6, H-7), 2.43 (s,CH_3CO) MS m/z (rel.int.%) : 252(0.85), 250(2.5,M^+), 215(1), 210(6), 208(20), 182(4), 180(10), 43(100).

Compound SA-Ac: ^{1}H NMR ($CDCl_3$): δ8.1(m), 7.7(m), 6.75(s), 2.37(s).

Compound 5C-Ac: ^{1}H NMR ($CDCl_3$): δ8.1(m), 7.7(m), 6.75(s), 2.38(s).

2-Acetoxy 1,4 naphthoquinone: ^{1}H NMR($CDCl_3$): δ8.1 (m,H-5,H-8), 7.7(m H-6,H-7), 6.75(5,3-H), 2.38(5,CH_3CO).

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DECLARATION

I,the undersigned,declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

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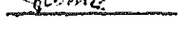
Signature: 

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