Both 4.2 g. of the compound and 5 g. of anhydrous potassium acetate were dissolved in methanol, and a solution of 5.6 g. of **semicarbazide hydrochloride** in water was added. From the clear solution, shiny leaflets began to crystallize immediately: from dioxane, m.p. 221° (dec.); yield 7 g.

Dehydration of 3,5-Dimethyl-1-hexyn-3-ol.—At a temperature of 300°, 167.5 g. of 3,5-dimethyl-1-hexyn-3-ol (b.p. 145°) was passed over 150 cc. of the active carbon diammonium phosphate catalyst in the course of one hundred and sixty-five minutes. The water layer (16 cc.) was separated and the organic layer dried and fractionated. The unsaturated hydrocarbon formed boiled at 100–110° (760 mm.); yield 40.5 g. (40%). Forty-six and one-half grams of starting material was recovered (28%), and 10 g. of a higher-boiling fraction (85–90° (5 mm.)) was obtained which has not been investigated further. The same applies to the considerable distillation residue.

The reaction product showed d^{20}_{4} 0.7519 and n^{20}_{D} 1.4274; (*MR*, found, 36.87; theory, 36.69 (without exaltation)); its analysis gave slightly too low carbon values, perhaps due to autoxidation. *Anal.* Found: C, 87.9, 87.6; H, 11.6, 11.4. Calcd. for C_8H_{12}: C, 88.9; H, 11.1. Whether the dehydration involved the methyl or the isobutyl group (or both), remains to be determined.

Summary

In the vapor phase dehydration of dimethylethynylcarbinol, the expected dehydration product isopropenylacetylene (II) is accompanied by two isomerization products: methyl isopropenyl ketone (III) and β,β-dimethylacrolein (IV).

The differences between liquid and vapor phase dehydration are emphasized and the reaction mechanism is discussed.

REHOVOTH, ISRAEL RECEIVED JULY 28, 1949

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Studies in the Sulfone Series. VIII. Infrared Absorption Spectra and Structure of Some Substituted Diphenyl Sulfones and Sulfoxides

BY E. D. AMSTUTZ, I. M. HUNSBERGER[1] AND J. J. CHESSICK

It has recently been pointed out[2] that an interesting parallelism exists between aldehydes, C-nitroso compounds and sulfoxides on the one hand and acids (or esters), C-nitro compounds and sulfones on the other. In every case the substances in the lower oxidized state exhibit a chemical reactivity which is either lacking or greatly repressed in those in the higher oxidized condition. While no claim is made for the originality of this observation since it doubtless has been noticed by many others, it did suggest the possibility of an interesting solution to the vexing problem of the extreme stability of sulfones. This stability, which is usually taken for granted by chemical investigators, is so extraordinary that we believe it to be a characteristic of the system which is of prime importance. It would appear that since resonance is important in the stabilization of the carboxyl (and carbalkoxyl) and nitro groups it might be responsible likewise for the characteristic inertness of the sulfone structure.

The above parallelism likewise suggested a means of experimentally subjecting the concept to proof. It seemed necessary at the outset to demonstrate a difference between the oxygen to sulfur bond in sulfones and that in sulfoxides. This we have done by demonstrating that the sulfone and sulfoxide oxygen atoms differ considerably in basicity (proton binding power). Secondly, we were interested in determining whether these differences paralleled the known differences between aldehyde-type carbonyl oxygens and ester-type carbonyl oxygens.

It has previously been shown by several investigators that an aldehyde group situated ortho to a phenolic hydroxyl group forms a very strong H-bonded structure. The strong chelation is shown clearly by a shifting to a longer wave length of the characteristic fundamental band of the hydroxyl group in the infrared region of the spectrum. The peculiarly different carbonyl oxygen of the carbomethoxyl group forms a less strongly chelated system with the result that the hydroxyl shift is not as pronounced. A further important difference to be noted is that in salicylaldehyde the hydroxyl band is more diffuse and the maximum cannot be picked out with any degree of certainty (see Table II).

By extrapolating the above considerations it would seem probable that H-bonds of greater strength than that in salicylaldehyde would either give a more diffuse hydroxyl band or none at all in the region of the fundamental. As will be mentioned later this appears to be the case with *o*-hydroxydiphenyl sulfoxide and 1-nitroso-2-naphthol.

Because the infrared spectrum affords a picture of the molecule in its ground state[3] and because the measurements are precise and capable of registering small differences it seemed that the infrared examination of the strength of chelation in *o*-hydroxydiphenyl sulfones and sulfoxides by way of the OH shift might well afford the type of information desired. The present paper reports on the results obtained with a representative series of such compounds.

Experimental

Preparation of Materials.—The hydroxy and methoxy sulfones used in this work were prepared by a standard procedure which involved the synthesis of the nitrodiphenyl sulfide from thiophenol and a nitrochlorobenzene, oxidation of the sulfide to the sulfone and then replacement of the nitro group by hydroxyl by way of reduction, diazotization and hydrolysis. Since the method has been used before

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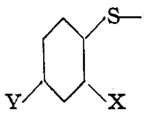
(1) Department of Chemistry, Antioch College, Yellow Springs, Ohio.

(2) Amstutz, Chessick and Hunsberger, *Science*, **111**, 305 (1950).

(3) Recent studies by Fehnel and Carmack, THIS JOURNAL, **71**, 231 (1949); *ibid.*, **72**, 1292 (1950); Fehnel, *ibid.*, **71**, 1063 (1949); Koch, *J. Chem. Soc.*, 408 (1949); and Mathieson and Roberston, *ibid.*, 724 (1949), have dealt with the absorption of highly energized molecules (ultraviolet spectra). There is reason to believe (see Koch, *et al.*, *ibid.*, 2442 (1949)) that the conjugation revealed in the energized state by ultraviolet spectra is not characteristic of the ground state.

the detailed directions for each step will not be given. Rather, the pertinent data are collected in the tables.

TABLE I



X	Y	M. p., °C.	M. p. reported, °C.	Yield, %	Analyses, % Calcd.	Analyses, % Found
			Diphenyl sulfides			
NO$_2$	H	76	77[4]	76.5		
H	NO$_2$	54–55	55[5]	78.8		
NO$_2$	OCH$_3$	Oil[a]	......			
OCH$_3$	NO$_2$	88.2–89.2	......	79	12.27	12.21 (S)
NH$_2$	H	Oil	Oil[4]	84		
H	NH$_2$	94	95[6]	85		
OH	H	Oil	Oil[7]	50.6		
H	OH	Oil	Oil[8]	52		
			Diphenyl sulfoxides			
OH	H	164–165[b]		54	14.67[c]	14.45 (S)
H	OH	143–144		51.5	14.67	14.54 (S)
			Diphenyl sulfones			
NO$_2$	H	146–148	147.5[9]	82.5		
H	NO$_2$	142–143	143[9]	86		
NO$_2$	OCH$_3$	104.2–105.5		86	10.93	10.86 (S)
				(on basis of the anisole) 2 steps		
OCH$_3$	NO$_2$	174–176		88	10.93	10.98 (S)
NH$_2$	H	118–120	122[9]	75		
H	NH$_2$	175–176	176[9]	95		
NH$_2$	OCH$_3$	126.5–128		95	5.32	5.26 (N)
OCH$_3$	NH$_2$	130–131		92	5.32	5.16 (N)
OH	H	96–98	82[10]	47		
OCH$_3$	H	141–142			12.91	12.57 13.13 (S)
H	OH	135–136.2	136–137[11]	60		
H	OCH$_3$	90–90.6	90–91		12.91	12.93 (S)
OH	OCH$_3$	114–115.4			12.13	11.83 (S)
OCH$_3$	OH	167–170			12.13	11.90 (S)
OCH$_3$	OCH$_3$	119–119.5			11.52	11.36 (S)

[a] This oil was converted directly to the sulfone without purification. [b] By oxidation of the sulfide in acetone with H$_2$O$_2$. See Gazdar and Smiles, *J. Chem. Soc.*, **93**, 1834 (1908), for general procedures. [c] Calcd. for C$_{12}$H$_{10}$O$_2$S: C, 66.01; H, 4.62. Found: C, 66.00; H, 4.73.

The 1-nitro-2-naphthol was prepared from 1-nitro-2-naphthylamine by the method described in "Organic Syntheses," Coll. Vol. II, p. 451. It melted at 101–103°. The 1-nitroso-2-naphthol was prepared according to the method outlined in "Organic Syntheses," Coll. Vol. I, p. 413. The yellow air-dried material was vacuum dried to the familiar dark-brown crystals. Vacuum sublimation, twice repeated, afforded pure material which, when finely divided appeared yellow but possessed a bright orange color in large crystals; m.p. 106–109°. Apparently the dark color of previous preparations is due to impurity and not the presence or absence of water since the crude dark material on sublimation always afforded a black residue and the pure material did not.

Discussion

It is of interest and value to the present discussion now to attempt to dissect the chelation process and to state several of the more important factors which contribute to the strength of the sort of H-bond involved in this discussion.[12] Since the strength of a given H-bond varies directly with the acid character of the OH-hydrogen, one important factor will be: (a) The extent of electron drift from the OH-oxygen through the ring to the ortho group (a proton-freeing effect—Effect A). This implies a corollary requirement (met in all present cases, and therefore not further discussed) that the substituted carbons be joined by a polarizable or conducting bond (the double bond). A rough idea of these relative drifts in the case of salicylaldehyde and methyl salicylate can be obtained by a comparison of the strengths of the lower vinylogous acids, formic acid, (HO—C=O—H) and methyl bicarbonate, (HO—C=O—OCH$_3$).[13] It is apparent that the phenolic acidity of the salicyladehyde should be greater than that of methyl salicylate and, other things being equal, the H-bond should be stronger in the case of the aldehyde.

(b) A second important consideration will be the effective basicity of the carbonyl oxygen towards the phenolic proton (Effect B). It has been shown by Gordy[14] that the oxygen of the aldehyde carbonyl is more basic and therefore capable of forming stronger H-bonds than the oxygen of the ester type carbonyl group. This is a second factor strengthening the H-bond of salicylaldehyde over and above that of the ester. Stated in another way the carbonyl oxygen of a resonating system such as an ester group is a poorer proton acceptor than that of an aldehyde system which does not exhibit this type of resonance.[15]

The case of the nitro- and nitrosophenols is interesting and instructive. It has long been known that *o*-nitrophenol differs from its *m*- and *p*-isomers in many of its physical properties and this has been satisfactorily related to the fact that it is chelated and not associated. That an intramolecular H-bond is present is also demonstrated by the absence of hydroxyl absorption (harmonic) in the near infrared.[16] The hydroxyl group *fundamental* appears[17] however at 3300 cm.$^{-1}$ indicating a H-bridge of strength approximating that in *o*-hydroxydiphenyl sulfone (see Table II). We have now found that the fundamental band of hydroxyl

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(4) Mauthner, *Ber.*, **39**, 3597 (1906).

(5) Kehrmann and Bauer, *ibid.*, **29**, 2364 (1896).

(6) Hinsberg, *ibid.*, **36**, 114 (1903).

(7) Bourgeois and Huber, *Rec. trav. chim.*, **31**, 31 (1912).

(8) Bourgeois and Huber, *ibid.*, reported a solid melting at 25°.

(9) Ullman and Pasdermadjian, *Ber.*, **34**, 1154 (1901).

(10) Ullman and Pasdermadjian, ref. 9, reported a m.p. of 82°. Our samples before drying in a pistol over P$_2$O$_5$, frequently exhibited melting points in this vicinity.

(11) Hilbert and Johnson, THIS JOURNAL, **51**, 1531 (1929).

(12) For a general discussion of hydrogen bonding see Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., pp. 22–28.

(13) We realize that the validity of this comparison is based upon the assumption that, in the unknown compound methyl bicarbonate, replacement by methyl of one of the acid hydrogens of carbonic acid does not greatly increase the acidity of the remaining hydrogen. Daniels, "Outline of Physical Chemistry," John Wiley and Sons, Inc., New York, 1948, p. 487, lists the ionization constant of formic acid in water at 25° as 2.1 × 10^{-4}, while (the first H of) carbonic acid is 4.54 × 10^{-7}. The basic assumption involved here seems to us to be eminently reasonable.

(14) Gordy, *J. Chem. Phys.*, **7**, 93 (1939); Gordy and Stanford, *ibid.*, **8**, 170 (1940).

(15) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 75, states that "the two structures R$_2$C=O and R$_2$C$^+$—O$^-$ contribute almost equally to the normal state of the molecule containing this bond." This is what Koch, *et al.*,[20] refer to as ionic-covalent resonance. What we are here referring to is the familiar fact that *additional* resonance stabilization is achieved in molecules containing another basic substituent (such as OH, OR, NH$_2$, etc.) in place of R in R$_2$CO above.

(16) Hilbert, Wolf, Hendricks and Liddel, THIS JOURNAL, **58**, 548 (1936).

(17) Gordy, *J. Chem. Phys.*, **7**, 167 (1939).

absorption is lacking for 1-nitroso-2-naphthol.[18,19] This appears to be conclusive evidence that there is no free OH group whatever in the molecule, which indicates that the molecule exists exclusively in the condition of a completely chelated system of considerable stability. On the other hand, 1-nitro-2-naphthol exhibits a definite although weak band at approximately 3250 cm.$^{-1}$. Both the extent of the displacement and the relative weakness of the band indicate stronger chelation than is present in the *o*-nitrophenol but considerably weaker than in 1-nitroso-2-naphthol. We find this case to be of special interest because it illustrates the importance of Effect B, which was not obvious in the salicylaldehyde–methyl salicylate comparison. Thus, from a comparison of the relative strengths of the lower vinylogous acids (HONO and $HONO_2$) it is apparent that the electron drift through the ring in the *o*-nitrophenol should be greater than in the nitrosophenol. The fact that the H-bond in the nitronaphthol is *weaker* than in the nitrosonaphthol must be due to the fact that the oxygen of a resonating nitro group is a weaker basic center than the oxygen of the nitroso group. (The same conclusion is indicated in the weaker basic strength of the nitrate ion as compared to the nitrite ion.)

The situation in *o*-hydroxydiphenyl sulfone and *o*-hydroxydiphenyl sulfoxide seems to parallel closely the case of the nitro and nitroso compounds. Both of these (sulfur) phenols have been shown to be monomeric[2] and therefore chelated. The extent of the hydroxyl shift in the sulfone (see Table II) indicates a H-bond of considerable strength—approximately that of *o*-nitrophenol. The absence of hydroxyl absorption in the 3000–3600 cm.$^{-1}$ range for the sulfoxide may be interpreted only as evidence of a hydrogen bond of considerably greater strength than that of the sulfone. Because of the greater acidity of $C_6H_5SO_2OH$ as compared to C_6H_5SOOH (the lower vinylogous acids) it appears that the electron drift through the ring in the *o*-hydroxy sulfone should exceed that in the *o*-hydroxy sulfoxide. The fact that the sulfone H-bond is actually weaker than the sulfoxide must then indicate that the oxygen–sulfur bond in the sulfones is significantly different than the corresponding linkage in sulfoxides. It can also be stated that the sulfone oxygen is a weaker base than the sulfoxide oxygen.[20]

It is interesting to note, in connection with the above arguments, that, in the case of the hydroxydiphenyl sulfones the addition of a methoxyl group ortho or para to the sulfone function has a definite effect on the strength of the hydrogen-bond (and therefore, on the extent of the hydroxyl displacement). Thus the addition of a methoxyl group on the 4-position of 2-hydroxydiphenyl sulfone brings about a definite although small displacement towards longer wave lengths. Also, the addition of a methoxyl group on the 2-position of 4-hydroxydiphenyl sulfone causes a somewhat larger displacement in the same direction. The explanation is to be found in the basic character of the methoxyl group and the acidic character of the sulfone group, mesomeric interaction between them allowing the sulfone oxygens to become more electronegative or basic, thus permitting the establishment of stronger H-bonds both of the intramolecular and intermolecular variety.

In the light of several recent publications it is possible to interpret with more assurance the absorption bands ascribed to the sulfone function. Schreiber[21] and Barnard, Fabian and Koch[20] have recently examined the spectra of a number of sulfones and conclude that a band located at about 1150 cm.$^{-1}$ is characteristic of the grouping. It will be observed in Table II that in those cases where H-bonding cannot exist the absorption band lies close to 1150 cm.$^{-1}$. Where the $-SO_2-$ function is involved in H-bonding there is a definite shift of the band to lower frequency. It has been suggested in a preceding paragraph that one of the most important factors determining the strength of a H-bond is the effective basicity of the oxygen (in sulfone, sulfoxides, nitro, etc., groups). The magnitude of the displacements of the sulfone band in several of the disubstituted sulfones exceeds those of the monosubstituted (compare I with V, also II with VI, Table II). As has been mentioned, a likely explanation of the increased displacement is that mesomeric interaction of the methoxyl group increases the basicity of the sulfone oxygens toward both intra- and intermolecular H-bonding. The position of the band in the spectrum of 2,4-dimethoxydiphenyl sulfone (Table II) seems to confirm this conclusion.

Koch and his co-workers[20] established for the sulfoxide function a band at 1035 cm.$^{-1}$ (solid diphenyl sulfoxide). Ortho hydroxydiphenyl sulfoxide exhibited weak maxima at 1034 cm.$^{-1}$. It appears to be possible that the stronger H-bonding of the sulfoxide group is responsible for the very considerable displacement observed (to 994 cm.$^{-1}$).

Conclusion

It seems quite probable, on the basis of the spectral data presented, that in sulfoxides the bond between sulfur and oxygen has considerable double bond character. This is consistent with the thermal data of Phillips, Hunter and Sutton[22] and the spectral data of Koch. At the same time, on the basis of a similarity between sulfoxides, aldehydes and C-nitroso compounds one cannot rule out possible minor contributions from a semi-ionic structure, $\overset{\oplus}{\text{—S}}\text{—}\overset{\ominus}{\text{O}}$.

The spectral data may be interpreted as showing that the oxygens of the sulfone structure are considerably less basic than the oxygens of the sulfoxide. This difference is exactly what would be ex-

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[18] We chose the nitroso- and nitronaphthols for examination because of their ready availability in pure form and their chemical stability. Since we are comparing only the naphthalene compounds with each other we believe the general conclusions given are valid.

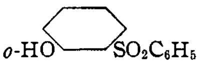
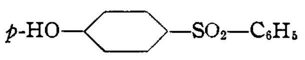
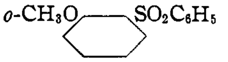
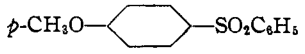
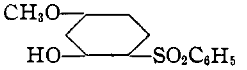
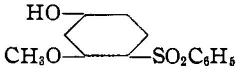
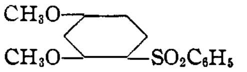
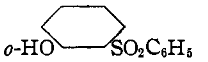
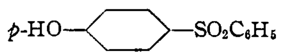
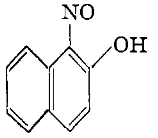
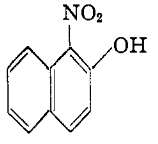
[19] The situation with respect to resonance within the nitroso group is probably quite similar to that in the aldehyde or ketone carbonyl (see footnote 15). We are referring here to the well-known fact that the nitro group, by virtue of its basic extra oxygen atom, is capable of a resonance stabilization denied to the nitroso group.

[20] Barnard, Fabian and Koch, *J. Chem. Soc.*, 2442 (1949), regard the –SO-bond in sulfoxides as essentially a covalent double bond and have likewise found that the oxygen of sulfoxides is capable of forming stronger H-bonds than the oxygen of sulfones. Remick (ref. 12), p. 168, has summarized all except the most recent literature.

[21] Schreiber, *Anal. Chem.*, **21**, 1168 (1949).

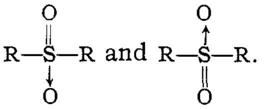
[22] Phillips, Hunter and Sutton, *J. Chem. Soc.*, 158 (1945).

TABLE II

Structural formula	OH band cm.$^{-1}$	Interpretation	SO_2 band cm.$^{-1}$	Interpretation	Solvent	Concn.
	3292[a] 3363[b]	Intramol. H-bond Intramol. H-bond	1138[a] 1145[b]	Bonded –SO_2– Bonded –SO_2–	CCl_4 Nujol	Satd.
	3590 3383 3417	Non-bonded OH Intermol. H-bond Intermol. H-bond	1151 1154	Non-bonded SO_2 Non-bonded SO_2	CH_2Cl_2 Nujol	Satd.
	•		1151	Non-bonded -SO_2-	Nujol	
			1150	Non-bonded -SO_2-	Nujol	
	3290	Intramol. H-bond	1130	Bonded -SO_2-	CCl_4	
	3600[e] 3332	Free OH Intermol. H-bond	1148 1133	Free (?) SO_2 Intermol. (?) SO_2 bond	CH_2Cl_2	Satd.
			1146	Non-bonded SO_2	Nujol	
	..[c]		SO band[d] at 994		Nujol	
	3600	Very weak band due to[c] free OH			CH_2Cl_2	Satd.
	OH Band		CO Band			
	3087–3160[a] 3060–3180[b]		1670[a] 1670[b]		Satd. CCl_4 0.02 M CCl_4	
	3200 3195		1679 1683		Satd. CCl_4 0.02 M CCl_4	
	[f]					
	3240[g]	Intramol. H-bond				

[a] Figures on the left side of any column were obtained at the General Aniline and Film Corporation, Easton, Pennsylvania. The spectrometer was made by the Perkin-Elmer Corporation and was equipped with a General Motors amplifier and recorder. A fluorite prism was used in determining the hydroxyl band positions and a rock-salt prism for the sulfone absorption. [b] The figures at the right side of any column were obtained at the Department of Chemistry, University of Illinois, on a Perkin-Elmer spectrometer equipped with rock-salt optics. [c] Rapidly increasing absorption from about 3250 cm.$^{-1}$ to about 2900 cm.$^{-1}$, with small aromatic C–H band at 3039 cm.$^{-1}$. No evidence of an OH band. [d] The assignment of this strong band at 994 cm.$^{-1}$ to sulfoxide is not certain but it appears to be the 1035 cm.$^{-1}$ band reported by Koch. Strong chelation to an ortho-hydroxyl would be expected to cause a shift in the position of the band of about the extent noted. [e] The extreme weakness of the band at 3600 cm.$^{-1}$ indicates fairly complete association. No other band was noticed. [f] The nitro and nitroso naphthols were examined in the Baird instrument of S. P. Sadtler, Philadelphia. The attempted resolution of the aromatic-OH band of the nitrosonaphthol was done at the General Aniline and Film Laboratory in Easton. A saturated solution in CS_2 or CCl_4 which gave general absorption bands of adequate strength (50–10% transmission) failed to show any trace of hydroxyl band. Even when a saturated solution in CCl_4 and cell thickness of 50 mils was used no OH band could be detected. [g] The OH band here was not strong but was nevertheless unmistakable. Both its position and intensity indicate strong H-bonding.

pected if the sulfone group were a perfectly symmetrical resultant of the resonance contributions of



$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\downarrow}}{S}}-R$ and $R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\|}}{S}}-R$. A major advantage in the resonance hybrid of the above forms is that it becomes possible to explain the chemical stability of the sulfones which is in marked contrast to the chemical reactivity of the sulfoxides. It is interesting to recall in this connection that Toussaint,[23] as a result of a careful analysis of the X-ray diffraction pattern of bis-(4-bromophenyl) sulfone, likewise proposed the resonating decet structure for the sulfone function.

Acknowledgment.—The authors express their warm thanks to Miss Elizabeth Petersen of the Department of Chemistry, University of Illinois, and to Dr. S. Gross of the Physics Department, General Aniline and Film Corporation, Easton, Pennsylvania, for the data shown in Table II. The authors appreciate the kindness of Mr. Phillip Sadtler in obtaining the spectra of the nitro- and nitrosonaphthols. We also are glad to acknowledge the many helpful discussions which we had with Dr. Gross.

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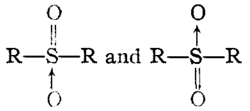
[23] Toussaint, *Bull. soc. chim. Belg.*, **54**, 319 (1945).

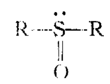
Summary

The greater chemical stability of the sulfone group as compared to the sulfoxide group suggested the possibility of resonance between the equivalent structures



$$R-\underset{\underset{O}{\uparrow}}{\overset{\overset{O}{\|}}{S}}-R \text{ and } R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\uparrow}}{S}}-R$$

The chemically reactive sulfoxide would then be written



$$R-\underset{\underset{O}{\|}}{\overset{\cdot\cdot}{S}}-R$$

The extent of the interaction of an ortho-hydroxyl and the sulfone group is much less than between an ortho-hydroxyl and a sulfoxide group, as measured by the displacement of the fundamental absorption band of the OH group in the infrared region of the spectrum. It is shown that this is consistent with the postulated electronic structures and with the spectral and chemical properties of other similar structures.

Infrared absorption spectra reveal that the chelate ring in 1-nitro-2-naphthol is weaker than that in 1-nitroso-2-naphthol. This is shown to be consistent with the relative reactivities and spectral characteristics of the sulfone–sulfoxide pair and the aldehyde–ester pair.

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[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Endocyclic α,β-Unsaturated Ketones. I. Dehydration–Rearrangement of 1,4-Dihydronaphthalene-1-ols to Naphthalenes

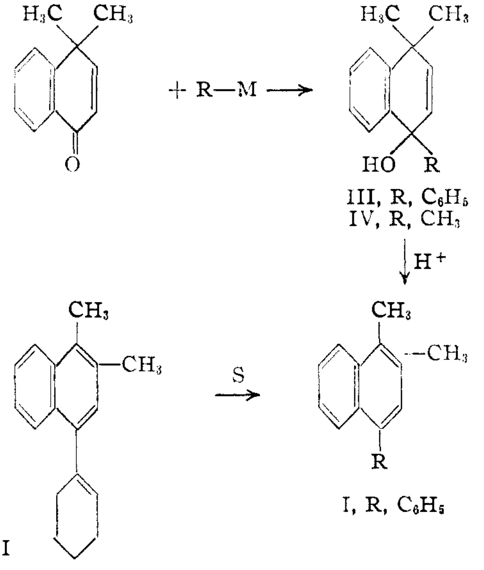
BY NORMAN H. CROMWELL, HAROLD H. EBY[1] AND DAVID B. CAPPS[2]

The chemistry of endocyclic α,β-unsaturated ketones has not been as extensively investigated as that of the related open chain compounds. It seems especially important to study the steric restrictions which the endocyclic α,β-unsaturated carbonyl system imposes upon the so-called 1,4-additions. The two following papers in this series deal with the reactions of such systems with amines.[3]

The present article reports the study of an endocyclic α,β-unsaturated ketone, 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (4,4-dimethyl-4H-naphthalenone-1), the synthesis of which was reported in an interesting paper by Arnold and co-workers.[4]

Phenylmagnesium bromide, phenyl lithium and methylmagnesium iodide give mainly, if not exclusively, 1,2-addition to the carbonyl group of this ketone. It was not possible to isolate the primary product, the tertiary carbinol, III, from the phenylmagnesium bromide reaction. Distillation of the crude product gave the dehydrated–rearranged product, 1,2-dimethyl-4-phenylnaphthalene (I). The structure of this new hydrocarbon was established by an unambiguous synthesis *via* 1,2-dimethyl-4-(1′-cyclohexenyl)-naphthalene (II).

The phenyl lithium reaction produced the carbinol, III, in good yield. This compound readily underwent an acid-catalyzed dehydration–rearrangement to produce the hydrocarbon, 1,2-dimethyl-4-phenylnaphthalene (I). This conversion is closely related to the so-called dienol–semibenzene–benzene changes studied extensively by v. Auwers and co-workers.[5]



III, R, C_6H_5
IV, R, CH_3

II

I, R, C_6H_5

The reactions studied by v. Auwers and the present ones are acid catalyzed and are related to the retropinacol rearrangements. Thus a Whitmore type mechanism may be written to explain these changes.[6]

It was found from a study of the behavior of 1,4,4-trimethyl-1,4-dihydronaphthalenol-1, IV, with heat or in acid solution that the dehydration of a 1,4-dihydronaphthalenol-1 cannot always be expected to give a good yield of the naphthalene. When there is present in the 1-position an alkyl group which can lose a proton to form the seminaphthalene the major product may be a polymer because of the presence of the very reactive diene–styrene type structure, D. Studies with other alkyl groups present in the 1-position should be made and are contemplated.

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[2] M.S. Thesis 1950, University of Nebraska.

[3] For a review of analogous studies with the open chain systems see Cromwell, *Chem. Revs.*, **38**, 83 (1946).

[4] Arnold, Buckley and Richter, THIS JOURNAL, **69**, 2322 (1947). They gave an excellent synthesis for this ketone and showed that it readily undergoes an acid-catalyzed dienone–pinacol rearrangement.

[5] (a) v. Auwers and Muller, *Ber.*, **44**, 1595 (1911); (b) v. Auwers and Ziegler, *Ann.*, **425**, 217 (1921).

[6] Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 479.