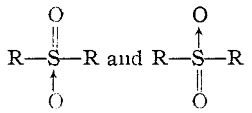
Summary

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



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

The chemically reactive sulfoxide would then be written

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

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.

BETHLEHEM, PENNSYLVANIA RECEIVED MARCH 9, 1950

[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

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

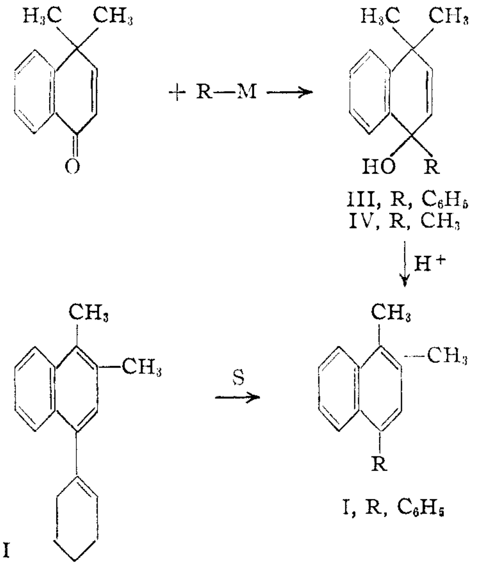
BY NORMAN H. CROMWELL, HAROLD H. EBY[1] AND DAVID B. CAPPS[2]

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]



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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[1] Eastman Kodak Co. Research Fellow, 1947–1948; Ph.D. Thesis 1948, University of Nebraska.

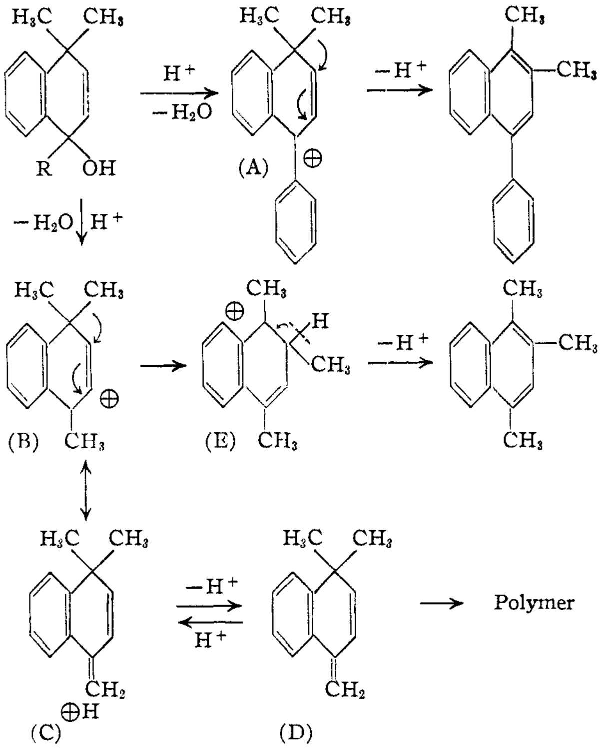
[2] M.S. Thesis 1950, University of Nebraska.

[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).

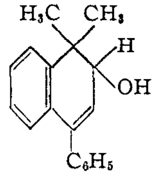
[6] Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 479.



No-bond resonance in the carbonium ion as indicated by (B) ⟷ (C), facilitates the loss of the proton to form the seminaphthalene (D). In contrast with the semibenzenes, this compound (D) is more readily polymerized than rearranged to 1,3,4-trimethylnaphthalene, *via* (C) ⟷ (B) → (E). In only a few cases was it found that the semibenzenes gave polymers under these conditions.[5]

The ultraviolet absorption spectra of the carbinols III, IV and triphenylcarbinol are contrasted with those of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene and 4,4-dimethyltetralone; see Fig. 1. The differences in the molar extinction coefficients of the maxima for the three carbinols near 260–270 mμ may be associated with the polarities of the carbon–hydroxyl bonds and the relative abilies of these compounds to form carbonium ions.

ADDED IN PROOF.—It now seems more probable to the senior author that compound(III) is not actually a tertiary carbinol as implied above, but instead is a secondary carbinol, 1-phenyl-4,4-dimethyl-3,4-dihydronaphthalenol-3. As shown in Fig. 1 the strong band (ε, 7500) at λ, 272mμ for carbinol(III) indicates its structure contains the chromophoric arrangement $(C_6H_5)_2C{=}CH{-}\overset{|}{\underset{|}{C}}{-}$, resonance being dampened somewhat by a steric inhibition associated with the cyclic arrangement of the structure



Ramart-Lucas and Amagat, *Bull. soc. chim.*, **51**, 108 (1932), have reported the spectrum of 1,1-diphenylpropene (λ, 270–273mμ, log ε, 4.38). The primary product of the phenyl lithium reaction, 1-phenyl-4,4-dimethyl-1,4-dihydronaphthalenol-1, appears to have undergone an anionotropic rearrangement to the thermodynamically more stable 1-phenyl-4,4-dimethyl-3,4-dihydronaphthalenol-3, wherein the aliphatic double bond is then conjugated with both phenyl groups.

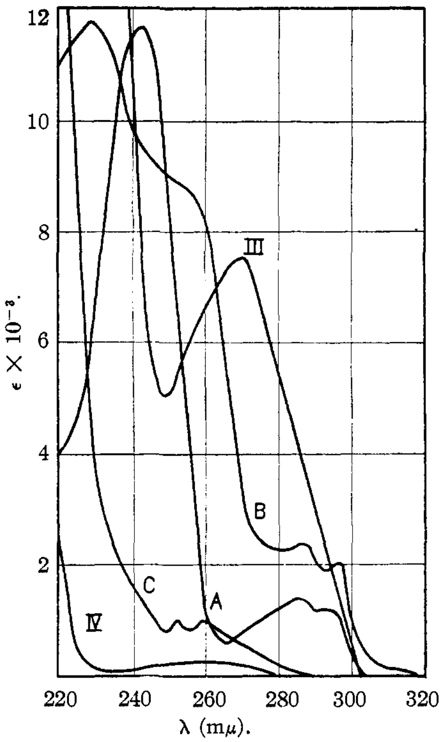


Fig. 1.—Ultraviolet absorption spectra of carbinols III and IV: triphenylcarbinol, C; 4,4-dimethyltetralone, A; and 4,4-dimethyl-1-keto-1,4-dihydronaphthalene, B.

Experimental[7]

Reaction of 4,4-Dimethyl-1-keto-1,4-dihydronaphthalene with Phenylmagnesium Bromide.—To a phenylmagnesium bromide solution prepared from 2.82 g. (0.116 mole) of magnesium and 18.2 g. (0.116 mole) of bromobenzene was added 5.0 g. (0.029 mole) of the unsaturated ketone.[4] The reaction mixture was refluxed for one hour and decomposed with iced ammonium chloride. The oily product could not be induced to crystallize. Vacuum distillation gave 1.1 g. of biphenyl and 5.5 g. of a thick, colorless oil, I, b.p. 160–165° (1 mm.); m.p. 75–76° (recrystallized from 95% alcohol).

Anal. Calcd. for $C_{18}H_{16}$: mol. wt., 232; C, 93.06; H, 6.94. Found: mol. wt., 236; C, 92.83; H, 7.16.

1,2-Dimethyl-4-(1′-cyclohexenyl)-naphthalene (II).—This hydrocarbon was synthesized in a yield of 51% by a method similar to that used by Weiss and Woidich[8] for the preparation of α-(1′-cyclohexenyl)-naphthalene. Although 3,4-dimethyl-1-naphthylmagnesium bromide has been reported[9] we found it necessary to employ the entrainment technique using an equivalent amount of ethyl bromide. The cyclohexanone (4.45 g., 0.045 mole) was added to the mixed Grignard solution prepared from 5.2 g. (0.022 mole) of 1-bromo-3,4-dimethylnaphthalene, 2.40 g. (0.022 mole) of ethyl bromide and 1.10 g. (0.044 mole) of magnesium. The desired product distilled at 165–175° (1 mm.), and formed colorless plates from alcohol, m.p. 81–82°.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.24; H, 8.75.

1,2-Dimethyl-4-phenylnaphthalene (I).—One gram of II on heating with 0.28 g. of sulfur at 260° for 28 minutes gave a 35% yield of the pure product; b.p. 160–168° (1 mm.);

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[7] Some of the micro analyses for carbon and hydrogen are by the Clark Microanalytical Laboratories, Urbana, Illinois, arranged for through the courtesy of the Smith, Kline and French Laboratories, Philadelphia, Pennsylvania.

[8] Weiss and Woidich, *Monatsh.*, **46**, 453 (1925).

[9] Hewett, *J. Chem. Soc.*, 293 (1940).

m.p. 74–74.5° (recrystallized from 95% alcohol). When mixed with I, obtained as described above, no depression of m.p. was observed.

1-Phenyl-4,4-dimethyl-3,4-dihydronaphthalenol-3 (III).—To an ether solution of phenyllithium prepared from 0.92 g. (0.132 mole) of lithium pellets and 9.4 g. (0.06 mole) of bromobenzene was added 5.17 g. (0.03 mole) of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene. After refluxing for 45 minutes the reaction mixture was decomposed with iced ammonium chloride. The product was crystallized from aqueous alcohol to give a 40% yield of colorless crystals, m.p. 96–97°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.60; H, 7.08.

Dehydration–Rearrangement of III.—A 0.10-g. sample of III was allowed to stand at room temperature for 4.5 hours in 2.0 ml. of glacial acetic acid containing a drop of concd. sulfuric acid. The reaction mixture was poured into 20 ml. of cold water to precipitate 0.088 g. of a product identical with 4-phenyl-1,2-dimethylnaphthalene (I).

1,4,4-Trimethyl-1,4-dihydronaphthalenol-1 (IV).—A 10.0-g. (0.058-mole) sample of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene was added to an ether solution containing about four molar equivalents of methylmagnesium iodide. The reaction mixture was refluxed for 90 minutes and decomposed with iced ammonium chloride. The product was crystallized from petroleum ether to give 8.6 g. (78.8% yield) of colorless crystals, m.p. 83–85°.

Anal. Calcd. for $C_{13}H_{16}O$: mol. wt., 188; C, 82.93; H, 8.57. Found: mol. wt., 183; C, 82.71; H, 8.66.

This carbinol IV decolorized an ethanol solution of potassium permanganate and a carbon tetrachloride solution of bromine. On standing, the solid carbinol changed to an oil which could not be induced to crystallize. When carefully compared with IV this oil decolorized the bromine solution more rapidly. Attempted vacuum distillation of IV produced water in the Dry Ice cooled receiver, leaving a hard brittle mass in the distilling flask. No trace of 1,3,4-trimethylnaphthalene was observed.

Dehydration and Rearrangement of IV.—A 1.11-g. sample of IV was allowed to stand at room temperature for 4 hours in 15 ml. of glacial acetic acid containing one drop of concd. sulfuric acid. The reaction mixture was poured into cold water to give a semi-solid precipitate. This was taken up in ether and washed several times with dilute sodium hydroxide (nothing was base soluble). Evaporation of the ether solution gave a thick oil of which only a small portion was soluble in methanol. The methanol extract was treated with a methanol solution of picric acid to give a small amount of bright, orange, long needles, m.p. 145–148°; mixed with an authentic sample of the picrate of 1,3,4-trimethylnaphthalene, m.p. 146–148°.[9] The majority (98%) of the product from the dehydration was a thick, alcohol insoluble oil which was not investigated further.

Absorption Spectra.—Measurements were made with heptane solutions using a Beckman model D.U. quartz spectrophotometer over the range of 220–400 mμ. See Fig. 1 for the curves.

Summary

1. A new rearrangement of a retropinicol type and related to the dienol–semibenzene–benzene changes investigated by v. Auwers[5] has been studied with 1-methyl- and 1-phenyl-4,4-dimethyl-1,4-dihydronaphthalenol-1. In the latter case a good yield of the 1,3,4-trisubstituted naphthalene resulted, while in the former the major course of the reaction was a polymerization. These changes are acid catalyzed.

LINCOLN, NEBRASKA RECEIVED JULY 20, 1950

[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Endocyclic α,β-Unsaturated Ketones. II.[1] Reactions of 8-Bromoperinaphthenone-7 with Amines

BY NORMAN H. CROMWELL, DAVID B. CAPPS AND S. EDWARD PALMER

It was the main objective of the present work to investigate the reactions of an endocyclic α-bromo-α,β-unsaturated carbonyl system with amines to discover whether or not the stereochemical restrictions imposed by such an arrangement greatly affect the course of such reactions. 8-Bromoperinaphthenone-7 has been found to react with the amines, morpholine and piperidine to produce both 8-amino- and 9-aminoperinaphthenone-7 derivatives. The 8-amino products were also obtained from 8,9-epoxyperinaphthanone-7. A comparison of their ultraviolet-visible absorption spectra, and their acid hydrolysis products serve to distinguish and identify the members of these two new classes of α-amino and β-amino-α,β-unsaturated ketones. The infrared spectra of the two series of compounds are reported from 1100–3400 $cm.^{-1}$ and found to be somewhat similar. With a primary amine, cyclohexylamine, 8-bromoperinaphthenone-7 gives a single racemic ethylene imine ketone. Stereoisomerism at nitrogen was not observed. The ethylene imine ketone readily reacts with acid to produce the isomeric 8-aminoperinaphthenone-7. It may be concluded that it is not a necessary requirement that the initial addition to the 1,4-unsaturated system involve a proton transfer from nitrogen to oxygen *via* a quasi six-membered ring. The results indicate however, that the opportunity for such a proton transfer, which is available in the open chain series, is a facilitating factor.

Extensive studies of the reactions of open chain α-bromo-α,β-unsaturated ketones with amines have been reported.[2] No careful study of the reactions of amines with an endocyclic system of this type has been reported previously in the chemical literature.[3] One of the most readily available starting materials for such studies is 8-bromoperinaphthenone-7. This compound is the nearest possible cyclic analog to α-bromobenzalacetophenone, with which many of the previous studies have been made. In contrast to this latter substance[2] 8-bromoperinaphthenone fails to react even at room temperature with one or two molar equivalents of morpholine, piperidine or cyclohexylamine in ether or ethanol solution. In all cases a large excess of the amine was required for the reaction to take place even in the absence of solvent. In the present studies it was not possible to isolate the probable intermediate α-bromo-β-aminoketone,[2] 8-bromo-9-aminoperinaphthanone-7, (A).

At room temperature 8-bromoperinaphthenone-7 reacted with an excess of morpholine and piperidine to give mainly the 9-morpholino and 9-piperidinoperinaphthenone-7, III and IV, respectively.

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[1] For the first paper in this series see Cromwell, Eby and Capps, THIS JOURNAL, **72**, 1224 (1950).

[2] See for example, Cromwell, *Chem. Revs.*, **38**, 83 (1946).

[3] In a U. S. Patent No. 2,174,751, Oct. 1939, *Chem. Abstracts*, **34**, 1194 (1940), assigned to General Aniline Works, Inc., New York, Koeberle, Rohland and Steigerwald reported the preparation of 8-aminoperinaphthenone-7 compounds from 8-halo-perinaphthenone-7. The conditions used were different from those employed in the present work and the purity and identity of the products were not rigorously established in the publications.