[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

The Chemistry of Derivatives of 2-Benzaltetralone. III. Reaction of 2-Bromo-4,4-dimethyltetralones with Amines. Endocyclic Eliminations

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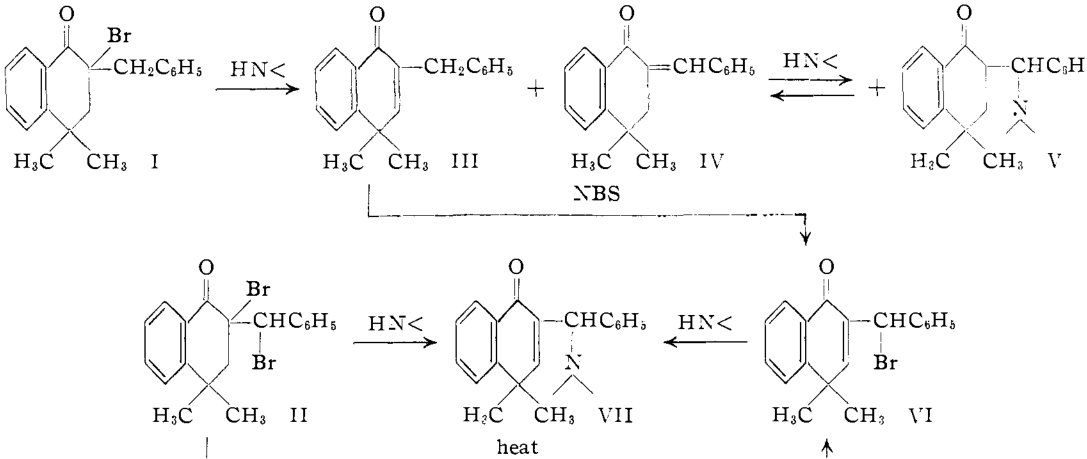
Dehydrobromination of 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) and 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (II) can be effected by amines at room temperature, the products being mainly the endocyclic α,β-unsaturated ketones III and VII, respectively. 2-(α-Bromobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VI) obtained by allylic bromination of III or by loss of hydrogen bromide from II reacts instantaneously with piperidine or morpholine yielding VII. These results are discussed in connection with the new mechanism of dehydrobromination of 2-halo-1-tetralones by amines, previously postulated.[2]

The interesting and facile conversion of 2-bromo-2-benzyl-1-tetralones with amines at room temperature to 2-benzyl-1-naphthols[2] has prompted us to investigate the behavior of the analogous 4-*gem*-dimethyl substituted compounds. In the reaction of the latter with amines the isolation of intermediates should be possible because aromatization of the expected α,β-unsaturated endocyclic ketone under mild basic conditions is not expected.

Allylic side chain bromination of III with N-bromosuccinimide afforded 2-(α-bromobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VI) in 83% yield. The same compound resulted in a 44% yield from the thermal dehydrobromination of II. Decomposition of an α,β-dibromoketone often results in a debromination.[4] One analogous example has been reported where hydrogen bromide was evolved upon heating 2-bromo-2-(α-bromobenzyl)-6-methyl-4-thiocoumarone.[5] The allylic bromide VI reacted rapidly with alcoholic silver nitrate and with warm methanol. With piperidine or morpholine in benzene solution the corresponding amine hydrobromide salts were precipitated very rapidly and 80% yields of the aminoketones VII were obtained. These aminoketones VII also resulted in lower yields together with the debromination product IV from the interaction of the dibromoketone II and a large excess of the same amines. When 2-[α-(N-piperidino)-benzyl]-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VIIa) was allowed to stand in acetic anhydride and in the presence of sulfuric acid for 2.5 days, no dienone–phenol rearrangement took place. Evidently in acidic medium the amino nitrogen competes successfully with the keto oxygen for a proton. Opportunity for hydrogen bonding and the presence of a positive charge on nitrogen appears to suppress further attack by a proton at oxygen which would be expected to lead to rearrangement.



The action of various amines upon 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) in a heterogeneous phase as well as in a solvent resulted in elimination of hydrogen bromide and formation of α,β-unsaturated ketones. The main product was 2 - benzyl - 4,4 - dimethyl - 1 - keto - 1,4 - dihydronaphthalene (III), separated by fractional crystallization from the second elimination product, 2-benzal-4,4-dimethyl-1-tetralone (IV). The latter was identified in a mixed product of III and IV by comparison of m.p. and the ultraviolet spectrum of this mixture with the m.p. and spectrum of a synthetic mixture of III and IV. From the interaction of I with morpholine a third product was isolated in 1% yield and identified as 2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (V), the previously prepared addition product of morpholine and IV.[3]

The isolation of the endocyclic α,β-unsaturated ketones III and VII from the reactions of amines

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[2] A. Hassner, N. H. Cromwell and S. J. Davis, THIS JOURNAL, **79**, 230 (1957).

[3] A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958).

[4] W. S. Johnson, *ibid.*, **65**, 1317 (1943).

[5] F. Krollpfeiffer, H. Schultz, E. Schlumbohm and E. Sommermeyer, *Ber.*, **58**, 1674 (1925).

with the α-bromoketones I and II, respectively, is in accord with the previously proposed course for the related reactions with the analogous tetralone derivatives.[2] The probable intermediate VI, in the reaction of II with amines, was shown to be too reactive for isolation in the presence of bases.

A series of quantitative product studies was designed to give information concerning the relative reactivities of the various cyclic α-haloketones with amines. The bromoketone I reacted with secondary amines only slightly slower than its 4-unsubstituted analog,[2] but at least four times faster than 2-bromo-4,4-dimethyl-1-tetralone (VIII). Similarly, γ-picoline effected dehydrobromination of I readily but gave only a 10% yield of its hydrobromide salt upon interaction with VIII under analogous conditions. 2,2-Dibromo-4,4-dimethyl-1-tetralone (IX), prepared by the further bromination of VIII, reacted with morpholine much faster than VIII to produce the known 2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (XII).[6] Bromoketone I reacted at least ten times as fast with morpholine as it did with N-methylmorpholine, as measured by the rate of formation of the hydrobromide salts.

The α-bromoketone I reacted sluggishly with potassium acetate in boiling alcohol giving a 39% yield of the endocyclic unsaturated ketone III. This α-bromoketone I released iodine rapidly from potassium iodide in acetone and reacted readily with warm alcoholic silver nitrate.[7]

The bromoketone II reacted less than one-half as fast as bromoketone I in benzene solution with piperidine as measured by the rate of production of piperidine hydrobromide. The rate of reaction of II with piperidine was found to be at least five times as fast as the reaction with morpholine in benzene solution.

The α-bromoketones I and II, as well as their 4-unsubstituted analogs, have been shown by analysis of their ultraviolet and infrared spectra to possess essentially axial oriented halogen, while the bromoketone VIII has a halogen atom of predominantly equatorial character.[3] Thus it is to be expected that the bromoketones I, II (and IX which also has an axial bromine) will dehydrobrominate more rapidly than VIII since a *trans* diaxial loss of hydrogen and bromine is possible with these first three materials. Moreover, the endocyclic α,β-unsaturated ketones III and VII, respectively, are to be expected from I and II rather than the exocyclic α,β-unsaturated ketones, since their elimination transition states will be favored. These considerations have been shown to apply for bimolecular 1,2-eliminations of the E2 type,[8] but might also be expected to apply in an (S$_N$–E) polar transition state of the type postulated previously[2] and shown in more detail in Fig. 1. They are also expected to apply for 1,2-eliminations of the E1 type[8] (*e.g.*, silver-catalyzed reaction).

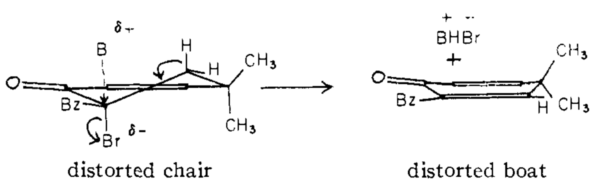

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Fig. 1.—Endocyclic elimination of axial bromine and axial hydrogen in α-bromoketones.

In a forthcoming paper in this series[7] it will be shown that 2-bromo-2-benzylindanone, which has the β-hydrogens in the five-membered ring eclipsed with the α-bromine and α-benzyl groups, reacts slowly (relative to I) with silver nitrate to produce mainly the exocyclic α,β-unsaturated ketone, 2-benzalindanone. It is also interesting to observe that these results fit the empirical generalization of Brown[9] which states that reactions proceed in such a manner as to favor the formation of an exo double bond in the 5-ring systems and to avoid the formation of the exo double bond in related 6-ring systems.

In the bromoketones I, II and IX an unhindered approach of the amine to the α-carbon atom holding the axial halogen is to be expected. Collapse of these transition states[10] leads wholly to elimination products and no trace of a substitution product has been found for the reactions of I.

The conjugation of the benzene ring with the exo double bond and the increased acidity of the benzyl hydrogen might have been expected to favor the production of the benzaltetralone IV from I if the mechanism of this elimination were E2. Although steric crowding at the benzyl carbon could be a factor with the amine-catalyzed eliminations, it can hardly be responsible for the endocyclic orientation of the elimination process under the other conditions which have been found applicable.[7]

The extent of the sensitivity of the rate of dehydrobromination of bromoketones I and II to the steric demands of the amines leads us to suggest that these amine reactions are not E2 eliminations. This point probably will be settled by the isotope effect studies now being carried out. It is hoped that the kinetically controlled studies now under way will allow us to distinguish between the postulated intermediate shown in Fig. 1 and other possibilities, such as the related alternative one involving attack by the amine nitrogen on the carbonyl carbon atom followed by a neighboring assist by oxygen to release a bromide ion; see Fig. 2.

Amine substitution products of 2-bromo-tetralones or cyclohexanones have been reported,[11] but

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[6] N. H. Cromwell, H. H. Eby and D. B. Capps, THIS JOURNAL, **73**, 1230 (1951).

[7] In a forthcoming paper it will be shown that 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone produces the endocyclic α,β-unsaturated ketone III on treatment with silver nitrate or potassium hydroxide, or on boiling with an aqueous solution of dioxane. Thus this interesting α-halo-ketone possesses a labile bromine capable of easy ionization. Most probably the silver-catalyzed reaction is an E1 type elimination.

[8] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

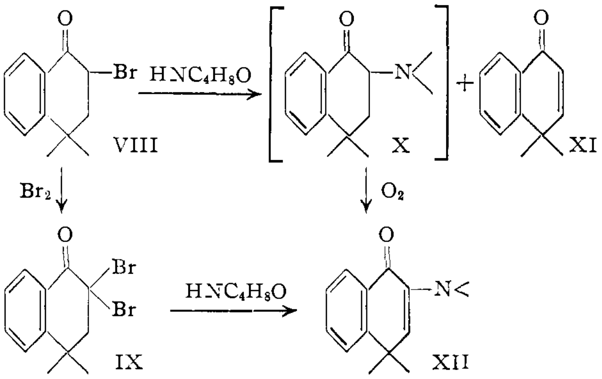
[9] H. C. Brown, J. H. Brewster and H. Schecter, THIS JOURNAL, **76**, 469 (1954); H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

[10] S. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956), refer to the formation of an actual pentavalent carbon intermediate from the nucleophilic attack of halide ion on *trans* 4-*t*-butyl-cyclohexyl *p*-toluenesulfonate, which resembles the S$_N$2 transition state and which decomposes to give both the elimination product and a substitution product. In our case we prefer to use the term "transition state" at this time since there is no evidence for the existence of a discrete intermediate as implied in the simple diagram of Fig. 1.

[11] S. Wawzonek and J. Kozikowski, THIS JOURNAL, **76**, 1641 (1954); M. Mousseron, J. Jullien and Y. Jolchine, *Bull. soc. chim.*

more often dehydrobromination takes place.[12,13]

Earlier an anomalous formation of α-amino-α,β-unsaturated ketones XII from the α-bromoketone VIII had been observed.[6] Preliminary experiments now indicate that a substitution product X, formed along with the dehydrobromination product XI in the reaction of VIII with morpholine, dehydrogenates in the presence of oxygen[14] with excess amine serving as the oxygen carrier. This was clearly shown by uptake of oxygen from the air in a gasometer; in a nitrogen atmosphere no such gas uptake was observed. The presence of X also is indicated by the infrared spectrum of the reaction product of VIII with morpholine in benzene under nitrogen. The reaction of saturated cyclic α-aminoketones with oxygen is being investigated in detail.



Acknowledgment.—This investigation was supported in part by a grant from the National Science Foundation, NSF-G1091.

Experimental[15]

Reaction of 2-Bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) with Amines.—The synthesis of 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (III) from I with cyclohexylamine has been reported.[3] In the following the relative reactivity of I with various organic bases in heterogeneous phase or in a solvent is described.

A mixture of 1.0 g. of α-bromoketone I and one to three molar equiv. of an amine, or a benzene solution of these reagents, was allowed to stand under conditions specified below. Isopropyl ether was added and the insoluble amine hydrobromide salt removed by filtration, washed well with ether and weighed. The combined ether filtrate and washings were washed with water, then extracted with 5% hydrochloric acid, dried and evaporated. Fractions of solid were collected and washed with methanol. Most of the solids were found to be pure III, the last fractions of solid were mixtures of III and IV or of III, IV and unreacted I.

The acid extract was made alkaline with sodium carbonate in the cold with stirring. The precipitated amino compounds V were collected by filtration, washed well with water, dried and weighed. Because of the low yields (1–3%) of these compounds, none of them was characterized, except for the morpholino derivative, 2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (V), m.p. 150–152°, which was identical with the compound previously[3] found upon addition of morpholine to IV.

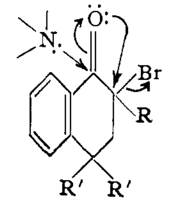


Fig. 2.

Evidence for the presence of the exocyclic unsaturated ketone IV was obtained from melting point behavior and spectra of products which were isolated from the reaction mixture. These solid mixed products had the same melting range (88–105°) and identical absorption in the ultraviolet as did known mixtures of the unsaturated ketones III and IV. One such product as obtained in the reaction of I with piperidine analyzed as expected for a mixture of the two isomers III and IV, and was estimated from spectra to consist of 14% III and 86% IV.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.85; H, 7.12.

Further recrystallization of the product mixture gave pure III, but pure IV could not be isolated in most cases due to the presence of unreacted starting material I. The yield of IV in the reactions below was estimated from absorption data to be less than 10%. The reactions were carried out at room temperature (25°) unless marked differently. Higher temperature favored a faster reaction.

The following data for the reaction of I with amines describes in consecutive order amine employed, molar equivalents of amine (m.e.), solvent used, reaction time in hours, % yields of amine hydrobromide (a measure of the extent of reaction) and % yields of pure endocyclic unsaturated ketone III isolated: (1) morpholine, 3.1 m.e., slurry, 24 hr., 88%, 56%; (2) piperidine, 2.05 m.e., ethanol, 2 hr. boiling, not isolated, 49%; (3) piperidine, 2.15 m.e., benzene, 72 hr., 100%, 52%; (4) piperidine, 2.09 m.e., benzene, 50 hr., 91%, 44%; (5) piperidine, 2.1 m.e., benzene, 0.3 hr. boiling, 87%, 26%; (6) cyclohexylamine, 1.07 m.e., benzene, 108 hr., 34%, not isolated; (7) cyclohexylamine, 2.08 m.e., benzene, 108 hr., 67%, not isolated; (8) cyclohexylamine, 3.45 m.e., slurry, 20 hr., 100%, 72%; (9) γ-picoline, 7.4 m.e., γ-picoline, 48 hr., 93%, 60%; (10) N-methylmorpholine, 6.9 m.e., N-methylmorpholine, 84 hr., 23% (70% of I recovered).

In an experiment analogous to (9) above, but using 2-bromo-4,4-dimethyl-1-tetralone (VIII) instead of I, only 10% of γ-picoline hydrobromide was secured.

Preliminary qualitative kinetic measurements on the reaction of I with piperidine (2 molar equiv.) and of VIII with piperidine (3 molar equiv.), in isopropyl ether at 35°, at 0.2 molar concentration, showed the rate of reaction of I to be at least four times as fast as that of VIII. The formation of Br^-, a measure of the extent of reaction, was followed by silver nitrate titration and potassium thiocyanate back-titration in the presence of ferric salt indicator.

Reaction of I with Potassium Acetate.—A 0.5-g. sample of bromoketone I was heated for 5.5 hours under reflux with 13 ml. of ethanol containing 0.143 g. of anhydrous potassium acetate. The solvent was removed by evaporation and the residue shaken with water and ether. Evaporation of the ether layer gave 0.3 g. of white bromine-containing solid, m.p. 85–106°. Its infrared spectrum showed the presence of bromoketone I (1690 cm.$^{-1}$) and endocyclic unsaturated ketone III (1663, 1650 cm.$^{-1}$). Recrystallization from petroleum ether (60–70°) afforded 0.15 g. of III, identified by its m.p. and infrared spectrum.

2-(α-Bromobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VI). a. By Allylic Bromination of III.—A mixture of 0.5 g. (0.0019 mole) of unsaturated ketone III, 0.35 g. (0.00196 mole) of N-bromosuccinimide and 2.0 ml. of carbon tetrachloride was heated on the steam-bath for 35 min. During the last 20 min. the mixture was irradiated with ultraviolet light. Succinimide was removed by filtra-

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France, **19**, 757 (1952); A. Burger and W. B. Bennet, THIS JOURNAL, **72**, 5415 (1950).

[12] E. C. Horning and R. U. Schock, *ibid.*, **70**, 2941 (1948); for examples in the steroid field, see V. R. Mattox and E. C. Kendall, *ibid.*, **70**, 882 (1948).

[13] However, F. Ramirez and A. F. Kirby, *ibid.*, **74**, 4331 (1952), reported that 2-bromo-1-tetralone upon standing with 2,4-dinitrophenylhydrazine forms the hydrazone without the usual elimination of hydrogen bromide.

[14] Similar air oxidations have been observed, *e.g.*, E. C. Kornfeld, E. J. Fornefeld, G. B. Kline, M. J. Mann, D. E. Morrison, R. G. Jones and R. B. Woodward, *ibid.*, **78**, 3094 (1956).

[15] Melting points were read on a calibrated thermometer. Ultraviolet absorption spectra determinations were made with 10^{-4} molar methanol solutions and infrared spectra were determined with CCl_4 solutions.

tion. Evaporation of carbon tetrachloride gave 0.54 g. of crude VI. After purification from isopropyl ether it melted 116.5–117.5°, and was identical with the bromoketone VI obtained by dehydrobromination of II.

b. **By Thermal Dehydrobromination** of II.—Two grams of 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (II) was heated with stirring and under a stream of nitrogen at about 145° in an oil-bath. It was essential to raise the temperature of the oil-bath very slowly from 140 and 145°, so that the melting and decomposition of II took place gradually and slowly. The gas initially evolved was mainly bromine as indicated by a potassium iodide–starch paper test. Later only hydrogen bromide was given off. The gas evolution and total heating lasted 15–20 min. Isopropyl ether was added to the cooled mixture and the red solution was treated with charcoal. Evaporation *in vacuo* gave an orange colored solid which when washed well with isopropyl ether and petroleum ether left 0.7 g. (44% yield) of white solid, m.p. 115–116°. Pure 2-(α-bromobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VI), obtained from isopropyl ether–petroleum ether, melted at 117–118°; λ_{max} 251, 297 (inflection) mμ (ε 12,100, 2,900); $\gamma_{C=O}$ 1665 cm.$^{-1}$, $\gamma_{C=C}$ 1650 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{17}OBr$: C, 66.86; H, 5.02. Found: C, 66.67; H, 5.46.

The bromine atom in VI is very reactive. Silver nitrate gives instantly a precipitate of silver bromide with an alcoholic solution of VI. When the bromoketone VI was heated with methanol the solution was found to be strongly acidic against *p*H paper and upon evaporation only a yellow gum resulted, that did not crystallize.

2-(α-Aminobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalenes (VII). Reaction of VI with Amines. a. With Piperidine.—To a solution of 0.3 g. (0.00081 mole) of α-bromoketone VI in 1.0 ml. of benzene was added 0.16 g. (0.00188 mole) of piperidine. Instantly a precipitate appeared. After 14 hr. isopropyl ether was added and a 95% yield of piperidine hydrobromide was removed by filtration. The ether solution was washed with water and extracted with dilute hydrochloric acid. Neutralization of the acid layer with sodium carbonate gave 0.25 g. (83%) of white solid, m.p. 102–103°. Purified from dilute hydrochloric acid and then by recrystallization from ethanol–water it melted at 104.5–105°. A mixed melting point with 2-[α-(N-piperidino)-benzyl]-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VIIa), prepared from II with piperidine, showed no depression.

b. **With Morpholine.**—In a manner analogous to the one described above, **2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VIIb)** was prepared from 0.53 g. of VI and 2.13 molar equiv. of morpholine. The reaction time was 48 hr. The yield was 81%. Ketone VIIb was very soluble in organic solvents from which it came out as an oil. It was therefore purified by neutralizing its hydrochloric acid solution with sodium carbonate, m.p. 57–59°; λ_{max} 255, 298 (inflection) mμ (ε 10,000, 3,200); $\gamma_{C=O}$ 1657, $\gamma_{C=C}$ 1645(shoulder) cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{25}O_2N$: C, 79.50; H, 7.25. Found: C, 79.48; H, 7.83.

2-(α-Aminobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalenes (VII). Interaction of II with Amines.—The general procedure consisted in allowing 1.0 g. of 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (II)[3] and three to six molar equivalents of amine to stand in 3.0 ml. of benzene at room temperature for several days. Isopropyl ether was added and the insoluble hydrobromide salt by-product isolated by filtration. The filtrate was washed with water, extracted with 5% hydrochloric acid, dried and evaporated to give several fractions of solid. Much of this solid was starting material; the last fractions were mixtures of II and debromination product IV. The acid-soluble portion was neutralized with sodium carbonate and the precipitated amino compound VII was recrystallized from ethanol–water. **2-[α-(N-Piperidino)-benzyl]-4,4-dimethyl-1-keto-1,4-dihydronaphthalene** (VIIa) thus obtained melted at 104.5–105° and was identical with VIIa prepared from VI and piperidine; λ_{max} 255, 298 (inflection) mμ (ε 10,000, 3,000); $\gamma_{C=O}$ 1658, $\gamma_{C=C}$ 1645 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{27}ON$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.46; H, 8.08; N, 4.20.

In one reaction of II with piperidine, 2-benzal-4,4-dimethyl-1-tetralone (IV), resulting from a debromination of II, was isolated in a 7% yield and its identity verified by melting and mixed melting point experiments. In other runs IV was found contaminated with larger amounts of unreacted II and its presence was deduced from ultraviolet absorption curves of the impure products. In the absence of solvent and with an excess of amine, II reacted much faster, and the yields of crude VII were higher than in benzene solution. The following results were obtained: 1. With 3.2 molar equivalents of piperidine for 2.5 days, 52% of the expected piperidine hydrobromide salt, 11% of VIIa and 33% of unreacted II were isolated. 2. With 3.08 molar equivalents of piperidine for 8.5 days, 76% of amine hydrobromide salt, 31% of VIIa and 12% of II were obtained. The unsaturated ketone IV was estimated to have been formed in 20% yield. 3. With 6.1 molar equivalents of piperidine for 10.5 days, in the absence of benzene, 94% of hydrobromide salt and 30% of VIIa were found. 4. With 13 molar equivalents of piperidine for 2 days, in the absence of benzene, 95% of hydrobromide salt and 42% of VIIa were obtained. 5. With 3.15 molar equivalents of morpholine for 6 days, 16% of morpholine hydrobromide salt, 10% of VIIb and 65% of II were isolated. **The morpholinoketone VIIb** did not melt sharply and gave gummy products upon attempted recrystallizations, as was observed with VIIb obtained from the bromoketone VI and morpholine.

Both VIIa and VIIb gave hydrochloride salts that were sticky, white solids and not readily purified for analysis.

Unlike the α-bromoketone I, the dibromoketone II was not readily dehydrobrominated by γ-picoline. After 6 days interaction in benzene solution a 10% yield of γ-picoline hydrobromide salt and 65% of unreacted II was isolated. Similarly, heating of II with 1.02 molar equiv. of potassium acetate in ethanol for 5 hr. resulted in a recovery of 85% of the starting material.

Attempts to Rearrange VIIa.—The rearrangement of 0.25 g. of dieneone VIIa with sulfuric acid in acetic anhydride, as described[3] for III, did not take place. Unaltered VIIa was recovered in 80% yield, upon neutralization of the acid solution with concd. ammonium hydroxide. When the reaction time was prolonged to 7.5 days and 0.25 g. of sulfuric acid was used, an unsharp-melting solid was isolated. Purification from methanol and petroleum ether enabled the recovery of 10% of the starting aminoketone VIIa. A gray colored material also was obtained, 0.015 g., m.p. 120–130°. Its ultraviolet absorption spectrum suggested the presence of a naphthol derivative. No further characterization was made.

Reaction of 2-Bromo-4,4-dimethyl-1-tetralone (VIII) with Morpholine. Under Air.—A mixture of 0.01 mole of VIII and three molar equivalents of morpholine was allowed to stand under air at 28–32° in a gasometer. Within two days the gas volume had decreased by 12 ml. (out of 60 ml. air present at the start). Heating the mixture for 45 min. at 60° and further standing did not cause any additional change in gas volume. If, however, fresh air was allowed to enter the apparatus, a further volume decrease by 8 ml. was observed within 8 days. The total uptake was approx. 20 ml. (0.0008 mole of oxygen). Isopropyl ether was added and the theoretical amount of salt by-product removed by filtration. The filtrate was washed well with water, extracted with 5% hydrochloric acid, and the acid layer neutralized in the cold with sodium carbonate to give 0.8 g. of white solid, m.p. 100–115°; λ_{max} 248, 290 mμ (ε 10,500, 2100); at 320 mμ, ε 500. The light absorption of a methanol solution of this substance did not change to any extent when air was blown in for 12 hours. The ultraviolet absorption spectrum of the pure unsaturated aminoketone, 2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene[6] (XII), in methanol was found to be: λ_{max} 256, 297 mμ (ε 10,100, 3100); at 320 mμ, ε 1600. After repeated recrystallization of the above product from methanol–water, some pure unsaturated aminoketone XII was isolated.

From the acid-washed ether solution, upon water washing and drying, 0.65 g. (38%) of endocyclic unsaturated ketone XI was isolated.

Under Nitrogen.—The above experiment was repeated using a nitrogen atmosphere, obtained by slightly evacuating the system four times and allowing nitrogen to enter the apparatus. Standing of the reaction mixture for 3.5 days caused a volume change of approximately 2 ml. (probably due to small amounts of air present in the system and in the morpholine). When air was allowed to enter the system, 12 ml. of gas was adsorbed within 1.5 days. The yields of amine salt, unsaturated ketone and aminoketone mixture were similar as reported above. For control purposes 3.0 g. of morpholine was allowed to stand in the described apparatus under air, but no change in gas volume was observed within 6 days.

In Boiling Benzene.—Bromoketone VIII (0.0095 mole) and 0.03 mole of morpholine were dissolved in 15 ml. of benzene, the air swept out with nitrogen and the solution heated under reflux for 24 hours. The work-up as above gave 73% of amine hydrobromide salt and 1.05 g. (43%) of a white solid, m.p. 94–96°. Mixed with XII it melted at 108–122°. Recrystallization from petroleum ether or from methanol–water gave a white solid, m.p. 97–98°. Infrared analysis in CCl_4 showed it to be still a mixture of saturated and unsaturated aminoketones: $\gamma_{\text{satd ketone C=O}}$, 1690 cm.$^{-1}$ (rel. abs. 98%); $\gamma_{\text{unsatd ketone C=O}}$, 1662 cm.$^{-1}$ (82%), $\gamma_{\text{C=C}}$ 1620 cm.$^{-1}$ (42%).

Standing of a solution of 0.3 g. of this mixed aminoketone product in 1.5 ml. of morpholine in a gasometer under air for 1.5 days caused an 11-ml. decrease in gas volume. A white solid, m.p. 115–116°, was isolated. Mixed with unsaturated aminoketone XII it melted at 118–124°.

Attempts to hydrogenate 2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (XII) in ethanol in the presence of platinum at 50° were unsuccessful. Only unreacted starting material and lower melting impure fractions were isolated.

2,2-Dibromo-4,4-dimethyl-1-tetralone (IX).—To 1.26 g. of VIII in 3 ml. of chloroform was added a solution of 1.0 g. (1.25 molar equiv.) of bromine in the same solvent at room temperature. Initially it was necessary to apply heat to cause decoloration of the solution, then the rest of the bromine was added. Upon evaporation of the solvent, the solid residue was triturated with petroleum ether–benzene, then with dilute solutions of sodium bisulfite, sodium bicarbonate and water. The solid was dried (1.3 g.) and recrystallized from methanol, m.p. 102–103°. The absorption spectra[3] revealed the presence of an axial and an equatorial bromine.

Anal. Calcd. for $C_{12}H_{12}OBr_2$: C, 43.45; H, 3.65. Found: C, 43.80; H, 3.51.

When 0.3 g. of the dibromoketone IX was allowed to stand with 0.3 g. of morpholine in 0.5 ml. of benzene, 0.15 g. of amine salt was isolated. The acid-soluble portion gave a white solid (0.05 g.), m.p. 124–125°, the melting point and infrared spectrum of which was identical with that of the known **2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (XII)**.[6] Some impure starting material was also isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY]

Steric Strains in Methylnaphthalenes

BY J. PACKER, J. VAUGHAN AND E. WONG

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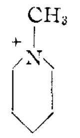
Rates of reaction in nitrobenzene solution of methyl iodide with pyridine, quinoline, isoquinoline, 2-methylquinoline and 8-methylquinoline have been followed over the temperature range 10–50°, using a precise conductimetric method. Relative heats of activation have been taken as quantitative measures of steric strains present in the activated complexes of these reactions. From these results, an estimate is made of the steric strains existing in the homomorphic structures 1-methylnaphthalene, 1,2-dimethylnaphthalene and 1,8-dimethylnaphthalene. Strains associated with these structures are found to be greater than those of comparable alkylbenzenes and the differences are attributed to the rigidity of a fused ring system as compared with an alkyl group.

In naphthalene derivatives, some measure of the magnitude of steric strains associated with the *peri*-CH group in its interaction with functional groups in the 1-position is of primary interest in any attempt to compare reactivities of 1- and 2-derivatives. Any such strain will be enhanced by further substitution in the 2- or 8-position. In the work now reported, estimates of the steric strains in simple examples of such systems were obtained. The method employed was based directly on the "strained homomorph" concept of Brown.[1] Following Brown, values of steric strain obtained by studying the Menschutkin reaction involving quinoline derivatives should also be measures of the strains existing in naphthalene compounds of similar geometry.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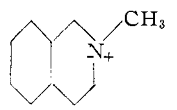
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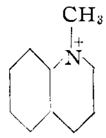
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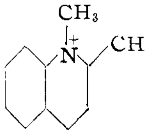
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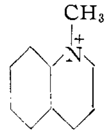
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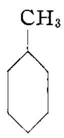
The rates of reaction in nitrobenzene of methyl iodide with quinoline, isoquinoline, 2-methylquinoline, 8-methylquinoline and pyridine were measured at four temperatures over the range 10–50°. The strain in the activated complex of the Menschutkin reaction has been estimated[2] to be *ca.* two-thirds of the strain in the final product and thus the activation energies connected with the formation of the ions should lead to measures of the steric strains associated with the corresponding hydrocarbons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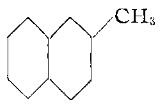
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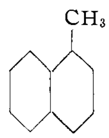
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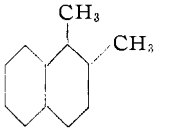
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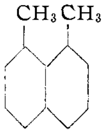
X

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[1] H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

[2] H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).