to which was added 6 ml. of acetyl chloride. A vigorous reaction ensued. After the reaction subsided, the mixture was heated 10 minutes on a steam-bath and the excess acetyl chloride evaporated. The residual light yellow oil was recrystallized once from ethanol to yield 1.5 g. (84%) of material melting at 86–87.5°; no depression on admixture with a sample of VIII prepared by rearrangement of the phenanthrol V.

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[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

The Chemistry of Derivatives of 2-Benzaltetralone. I. A Novel Rearrangement Leading to 2-Substituted-1-naphthols*

BY ALFRED HASSNER,[1a] NORMAN H. CROMWELL[1b] AND STANLEY J. DAVIS[1c]

RECEIVED JUNE 4, 1956

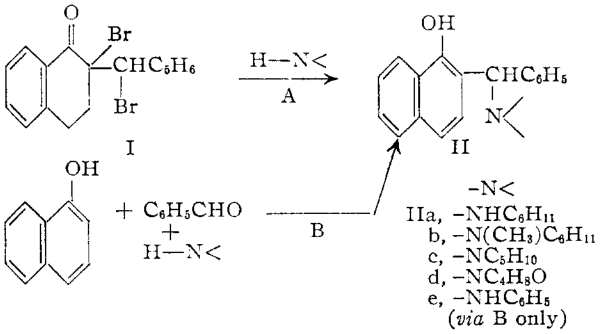
In the presence of an excess of a primary or secondary amine (cyclohexylamine, piperidine, morpholine, N-methylcyclohexylamine), 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) reacted to give good yields of the corresponding 2-(α-aminobenzyl)-1-naphthols (II). The structures of the naphthols were established by synthesis *via* Mannich condensation. In a similar manner, 2-bromo-2-benzyl-1-tetralone was dehydrobrominated and rearranged in the cold to yield 2-benzyl-1-naphthol. These results are discussed.

In five- and six-membered alicyclic systems with aliphatic side chains, the introduction of an olefinic bond can lead to exo- or endocyclic unsaturated compounds.[2] The condensation of cyclic ketones with aldehydes under basic conditions in general seems to yield the exocyclic unsaturated ketone.[3]

We have investigated the chemical and physical properties of 2-benzal-1-tetralone obtained through a base-catalyzed condensation of 1-tetralone with benzaldehyde.[4] That the olefinic double bond in this compound is exo to the ring is shown by its ultraviolet spectrum (λ_{max} 305mμ (ε 17,200)[5]; thus the cinnamoyl band characteristic of chalcone-type ketones is present) and by its stability with acids and bases.

It was found that 2-benzal-1-tetralone, when allowed to stand in acetic anhydride in the presence of sulfuric or hydrobromic acid, did not rearrange to give 2-benzyl-1-naphthol. Under such conditions, dienone–phenol rearrangements readily take place.[6] In this case, no facile route for such a change is available. It is quite possible that a cyclic ketone containing both an endocyclic and an exocyclic double bond represents a stable arrangement, as was recently suggested by Mayer.[7] Oxidation of 2-benzal-1-tetralone with alkaline hydrogen peroxide produced a spiro epoxyketone. The chemistry of such compounds is under investigation in this Laboratory.

Addition of bromine to 2-benzal-1-tetralone gave 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) in 77% yield. The reaction of open chain α,β-dibromo ketones with primary and secondary amines has been fully discussed in a review article.[8] Recent investigations[9] substantiate the view that dehydrobromination to an α-bromo-α,β-unsaturated ketone, as the first step, is followed by a 1,4-addition of the amine. The resulting α-bromo-β-aminoketones react further to yield either α,β-diaminoketones, α- or β-amino-α,β-unsaturated ketones or, when a primary amine is employed, ethylenimine ketones. It was therefore of interest to examine the behavior of the cyclic α,β-dibromo carbonyl compound I where no α-H was available for an analogous elimination of hydrogen bromide. When allowed to stand at room temperature with a tenfold excess of morpholine, piperidine, N-methylcyclohexylamine or cyclohexylamine, the dibromide I reacted within a day, depositing a quantitative amount of the starting amine hydrobromide. Examination of the products (II) showed them to be nearly colorless solids, insoluble in water, 5% sodium hydroxide or 5% hydrochloric acid, giving a red coloration with aqueous ferric chloride in ethanol. They gave hydrochlorides with dry hydrogen chloride



-N<
IIa, $-NHC_6H_{11}$
b, $-N(CH_3)C_6H_{11}$
c, $-NC_5H_{10}$
d, $-NC_4H_8O$
e, $-NHC_6H_5$
(*via* B only)

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[2] For discussion of the ring strains involved, preferential formation of an endocyclic double bond in six-membered rings and further references, see H. C. Brown, J. H. Brewster and H. Schechter, THIS JOURNAL, **76**, 467 (1954).

[3] (a) R. H. Siddiqui and Salah-ud-Din, *J. Indian Chem. Soc.*, **17**, 148 (1940); (b) R. Cornubert and co-workers, *Bull. soc. chim.*, [5] **5**, 513, 521, 534, 1490 (1938); (c) R. Baltzly, E. Lorz, P. B. Russell and F. M. Smith, THIS JOURNAL, **77**, 625 (1955); (d) H. W. Wanzlick and W. Menz, *Ber.*, **87**, 475 (1954).

[4] (a) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 637 (1940); (b) J. van Alphen and J. Drost, *Rec. trav. chim.*, **69**, 1080 (1950).

[5] We have found a similar band for 2-benzalindanone with the λ_{max} displaced to 318 mμ (ε, 22,400), as expected for the less strained five membered ring ketone containing an exo double bond.

[6] See, for instance, E. N. Marvell and J. L. Stephenson, THIS JOURNAL, **77**, 5178 (1955).

[7] R. Mayer, *Angew. Chem.*, **67**, 522 (1955).

[8] N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946), and references cited therein.

[9] N. H. Cromwell and co-workers, THIS JOURNAL, **71**, 708 (1949); *J. Org. Chem.*, **14**, 411 (1949); and unpublished results.

gas in ether and exhibited absorption of ultraviolet light typical of naphthalene derivatives. Their elemental analysis was consistent with that expected for the corresponding 2-(α-aminobenzyl)-1-naphthols. The final proof of structure was furnished through a synthesis of these materials from 1-naphthol, benzaldehyde and the corresponding amines.

These 2-(α-aminobenzyl)-1-naphthols (II), as well as 2-benzyl-1-naphthol exhibited characteristic electronic absorption spectra with maxima at about 214 mμ (ε 32,000); 238 mμ (ε 40,000); 300, 313, 327 mμ (ε 3000–5000); and characteristic infrared bands in CCl_4 solution near 3400–3100 cm.$^{-1}$, (sh.), 2800–2900 cm.$^{-1}$ (sh.), 1630 cm.$^{-1}$, 1310 cm.$^{-1}$ 1120 cm.$^{-1}$, 875 cm.$^{-1}$.

The reaction of benzaldehyde and primary amines with 1- and 2-naphthols was first described by Betti[10] in 1900. The structure of the products was assigned on the basis of their reaction with excess benzaldehyde to yield naphthoxazines. Since then, many other workers have employed this Mannich type condensation with different aldehydes and amines.[11] The fact that the products from the condensation of 1-naphthol, benzaldehyde and amines are identical with the ones obtained in the reaction of the dibromide I with the corresponding amines represents not only a structural proof of the latter but also eliminates the possibility[11a,c] that the former products might be 4-substituted-1-naphthols.

Discussion of Mechanism.—A series of studies designed to throw light on the mechanism of the complex reaction of amines with the dibromoketone I and related α-halotetralones was undertaken. The results from the preliminary studies discussed here and those to be presented in detail in a following article[12] clearly indicate that the 2-(α-aminobenzyl)-1-naphthols are produced from the dibromoketone I by the series of changes outlined below, the first of which is a dehydrohalogenation of unusual form.[13]

The fact that successful reaction of the dibromoketone I with primary and secondary amines required a large excess of the amine is consistent with the formation of a transition state of the SN2 type as indicated by (T). α-Haloketones are expected to be mainly attacked by amines at the carbon atom holding the halogen. It was found that tertiary amines with greater space requirements than morpholine or piperidine, such as N-methylmorpholine and triethylamine, failed to dehydrobrominate the dibromoketone I. Qualitatively measured through the amount of amine hydrobromide by-product obtained, the rate of reaction of N-methylcyclohexylamine with the dibromoketone I was found to be only one-tenth as fast as that of the less sterically hindered piperidine or cyclohexylamine. These are characteristics of an SN2 type reaction rather than of an E2 change. The possibility of an SN2 substitution of the side chain bromine atom in the dibromoketone I as a first step followed by a neighboring group assist from the amino group to release the α-bromine on the cyclohexanone ring was eliminated from consideration as it should have led to an ethylenimine ketone[8,9] when cyclohexylamine was used. Neither amines nor N-bromomorpholine[14] could be made to add to 2-benzal-1-tetralone. The reaction of aniline with the dibromoketone I to give IIe could not be effected.

Collapse of the transition state T in the presence of excess amine involving the formation of the endocyclic ketone[12] K, rather than a substitution product,[13] can probably be attributed to steric-electric factors.[2] The endocyclic ketone K could then either rearrange to the naphthol Y or, more likely,[12] react with excess amine to produce X. Intermediates X or Y would then be expected to produce the final product II. Rearrangement of either K or X to a naphthol is to be expected in the presence of the required excess base, since active allyl hydrogen is available in the 4-position of the oxygenated ring and resonance greatly favors the naphthol structure.

Examples of amine substitutions with 2-halo tetralones and cyclohexanones have been reported in the literature,[15] although no definite structural proof of the amino products has been presented. When tertiary amines and heat are used, dehydrobromination occurs.[16] Thus, 2-bromo-6-methyltetralone, when heated with diethylaniline, produced 6-methylnaphthol,[17] while 2-bromocyclohexanone lost hydrogen bromide on standing alone or in the presence of aniline.[18]

Kendall[19] used 2,4-dinitrophenylhydrazine to eliminate hydrogen bromide from 3-keto-4-bromo steroids. Under identical conditions as employed in the present investigation, Cromwell and coworkers[20] dehydrobrominated 2-bromo-4,4-dimethyltetralone and also reported the anomalous formation of 2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene in this reaction, the mechanism of which is now under investigation in this Laboratory. It is obvious that in all these reactions an

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(10) M. Betti, *Gazz. chim. ital.*, **30II**, 306 (1900); **31II**, 196, 209 (1901).

(11) *Cf.* (a) K. Auwers and A. Dombrowski, *Ann.*, **344**, 282 (1906); (b) W. R. Brode and J. B. Littman, THIS JOURNAL, **53**, 1532 (1931); (c) W. T. Caldwell and T. R. Thompson, *ibid.*, **61**, 2354 (1939); (d) R. L. Shriner, G. F. Grillot and W. O. Teeters, *ibid.*, **68**, 946 (1946); (e) W. J. Burke, M. J. Kolbezen and C. W. Stephens, *ibid.*, **74**, 3601 (1952); and (f) A. Neri, *Gazz. chim. ital.*, **61**, 819 (1931).

(12) In a forthcoming paper by N. H. Cromwell and A. Hassner, it will be shown that the related dibromoketone, 2-bromo-2-(α-bromobenzyl)-4,4-dimethyltetralone reacts with morpholine or piperidine to give 2-(α-aminobenzyl)-4,4-dimethyl-1-keto-1,4-dihydronaphthalenes which are also obtained from the intermediate 2-(α-bromobenzyl)-4,4-dimethylketo-1,4-dihydronaphthalene obtained by the dehydro-halogenation of the dibromoketone.

(13) Since this paper was submitted, S. Winstein, *et al.*, THIS JOURNAL, **78**, 2915 (1956), have made a preliminary report on a reaction with related characteristics which shows second-order kinetics and which they describe as a merged bimolecular substitution and elimination.

(14) P. L. Southwick and W. L. Walsh, *ibid.*, **77**, 405 (1955).

(15) K. Fries and A. Kuester, *Ann.*, **470**, 20 (1924); O. Wallach, *ibid.*, **414**, 271 (1918); **437**, 148 (1924); S. Wawzonek and J. Kozikowski, THIS JOURNAL, **76**, 1641 (1954); G. Scheuing and B. Walach, *C. A.*, **39**, 5042 (1945).

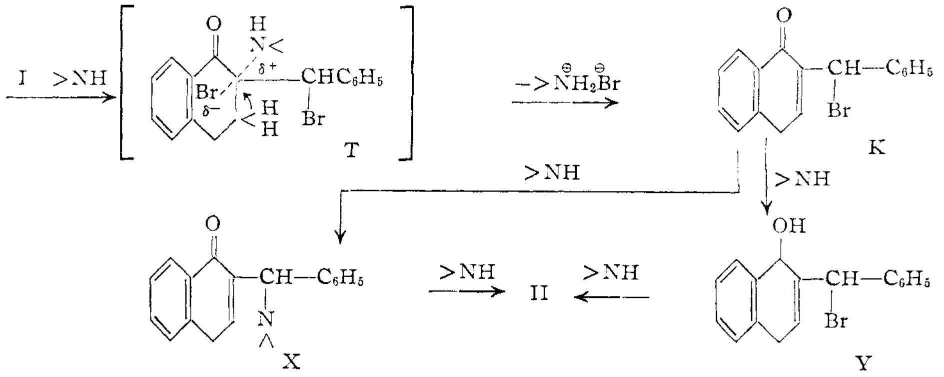
(16) R. T. Arnold, J. S. Buckley and J. Richter, *ibid.*, **69**, 2324 (1947); E. A. Coulson, *J. Chem. Soc.*, 1309 (1938); F. Krollpfeiffer, *Ber.*, **68**, 1169 (1935).

(17) L. F. Fieser and J. T. Dunn, THIS JOURNAL, **58**, 575 (1936).

(18) A. Koetz, *Ann.*, **358**, 183 (1907).

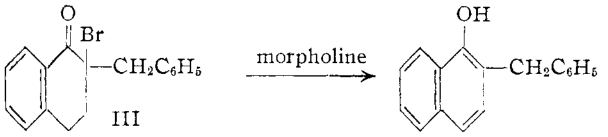
(19) V. R. Mattox and E. C. Kendall, THIS JOURNAL, **70**, 882 (1948); see also W. W. Rinne and co-workers, *ibid.*, **72**, 5759 (1950).

(20) N. H. Cromwell, H. H. Eby and D. B. Capps, *ibid.*, **73**, 1230 (1951).



unusual elimination[21] of hydrogen bromide takes place.[13]

2-Benzal-1-tetralone was hydrogenated in the presence of platinum to 2-benzyl-1-tetralone which, upon bromination, gave 2-bromo-2-benzyl-1-tetralone (III). The latter gave, upon standing for 0.5 hr. with excess morpholine, a 60% yield of 2-benzyl-1-naphthol, also prepared for comparison by the Claisen method.[22] In analogy with the dibromoketone I, 2-bromo-2-benzyltetralone (III)



could be largely recovered unchanged from an attempted reaction with N-methylmorpholine. The mechanism of this elimination–rearrangement must be analogous to that postulated above for the dibromide I. We are currently continuing the investigation of related systems, including comparative rate studies of such unusual eliminations.

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

Experimental[23]

2-Benzal-1-tetralone.[4]—The unsaturated ketone was obtained pure in 88% yield from 1-tetralone, benzaldehyde and 4% ethanolic potassium hydroxide; m.p. 107°; ultraviolet spectrum, λ_{max} 227, 276 (inflection), and 305 mμ (ϵ 11,700, 12,000 and 17,200); infrared bands, γ_{max} in CCl_4, 1666, 1645 (shoulder) cm.$^{-1}$, in Nujol 1657, 1635, 1605, 1590 cm.$^{-1}$. The phenyl group is probably *trans* to the carbonyl grouping.

Alkaline epoxidation[24] with 30% hydrogen peroxide in methanol gave the spiroepoxide **2-benzaltetralone oxide**; yield 93%; recrystallized from methanol, m.p. 77–77.5°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.37; H, 5.42; ultraviolet spectrum, λ_{max} 258, and 295 mμ (ϵ 15,400, and 2,700); infrared bands, γ_{max} in CCl_4 1690, 1603 cm.$^{-1}$, in Nujol 1686, 1603 cm.$^{-1}$. The phenyl group is probably *trans* to the carbonyl grouping.

Attempted Rearrangements of 2-Benzal-1-tetralone.—A solution of 1 g. of 2-benzal-1-tetralone in the specified solvent mixture was allowed to stand at room temperature for several hours or days and then poured into ice-water. The resulting solid, after recrystallization from ethanol, was found to be unchanged 2-benzal-1-tetralone (65–85% recovery of recrystallized material) through melting and mixed melting point experiments. (a) In 20 g. of 28% hydrogen bromide in glacial acetic acid and 8 ml. of acetic anhydride, after 17 hr., 85% of 2-benzal-1-tetralone was recovered. (b) In 26 g. of glacial acetic acid, 16 ml. of acetic anhydride and 1.7 g. of sulfuric acid, after 17 hr., 85% of the ketone was recovered. (c) In 15 ml. of acetic anhydride and in the presence of 12 drops concd. sulfuric acid,[6] after 6 days, 65% of 2-benzal-1-tetralone and a small amount of a red, gummy, unidentified material resulted. (d) In 12 ml. of 10% sodium methoxide in methanol, after 5 hr. of heating under reflux, 85% of the unsaturated ketone was recovered.

Although amines add to 2-benzalcyclohexanone,[3c] attempts to add morpholine or piperidine to 2-benzal-1-tetralone by heating on a steam-bath for 10–45 minutes, followed by standing at room temperature for one day, or by heating under reflux in ethanol, resulted in recovery of the unsaturated ketone in 80–90% yield.

2-Bromo-2-(α-bromobenzyl)-1-tetralone (I).—Bromine, 4.2 ml. (0.083 mole), in 10 ml. of carbon tetrachloride was added to a stirred solution of 18.4 g. (0.08 mole) of 2-benzal-1-tetralone in 150 ml. of carbon tetrachloride at room temperature. The addition took 1 hr., and the solid was collected by filtration (77%), m.p. 149–150° dec. Recrystallization from petroleum ether, b.p. 90–100°, and then ethanol raised the melting point to 153–154° dec.; ultraviolet spectrum, λ_{max} 263 and 297 (sh.) mμ (ϵ 13,100 and 2,700); infrared C=O band in CCl_4, 1686 cm.$^{-1}$, in Nujol 1673 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}OBr_2$: C, 51.81; H, 3.58; Br, 40.55. Found: C, 52.04; H, 3.52; Br, 40.72.

Evaporation of the filtrate and rubbing of the residue with acetone afforded in a single case only a small amount of a solid, melting at 109–109.5°, which analyzed for I and converted into I upon standing. The infrared spectrum was nearly identical with that of I, with $\gamma_{C=O}$ in CCl_4 at 1683 cm.$^{-1}$. In another run, using the technique described above, it was possible to isolate another form of I, melting at 118–119° and giving identical products with morpholine and cyclohexylamine as did I; ultraviolet spectrum, λ_{max} 258 and 290 mμ (shoulder), (ϵ 17,000 and 5,700).

Anal. Calcd. for $C_{17}H_{14}OBr_2$: C, 51.81; H, 3.58. Found: C, 51.81; H, 3.52.

2-(α-Aminobenzyl)-1-naphthols (II). Reaction of (I) with Excess Amines. General Procedure.—Best results were obtained when a mixture of 2 g. of dibromoketone I and 10 equivalents of the corresponding liquid amine were allowed to stand at room temperature under nitrogen for 8–24 hr., after which period isopropyl ether was added and the hydrobromide salt by-product removed by filtration. The ether filtrate was washed with dilute hydrochloric acid, next with water and evaporated to give the aminobenzyl naphthol. Sometimes the ether was first removed *in vacuo*, then the liquid residue poured into cold water and the precipitated product collected. The products II were purified by recrystallization from ethanol or from petroleum ether, b.p. 60–70°. Further recrystallizations for the purpose of raising the melting point were not necessary and only re-

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[21] Apparently the collapse of the S$_N$2 type transition state in this case involves either the loss of HBr and the amine to produce the unsaturated ketone or the loss of HBr followed by air oxidation to produce the α-amino-α,β-unsaturated ketone, ref. 12 and 20.

[22] L. Claisen, *Ann.*, **442**, 242 (1925).

[23] Melting points were read on a calibrated thermometer. Ultraviolet spectra were determined in methanol solution (0.0001–0.00007 *M*) with a Cary recording spectrophotometer, model 11 MS. A Perkin–Elmer, model 21, recording instrument was used for the determination of the infrared spectra.

[24] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

sulted in a considerable lowering of the yield. These products were insoluble in water, dilute base or acid, and gave a red coloration with aqueous ferric chloride in ethanol and a blue coloration with ethereal ferric chloride in benzene or ether. Upon standing in air they darkened in color. Their ethanol solutions were colored yellow. The hydrochlorides were formed readily by passing hydrogen chloride gas into a cooled ether or benzene solution of II. They did not give the ferric chloride color test. Their melting points were unsharp and varied with temperature of immersion into the bath.

2-[α-(N-Cyclohexylamino)-benzyl]-1-naphthol (IIa).—This product was obtained in 80% yield along with a quantitative yield of the hydrobromide salt by-product. The reaction time was 8 hr.; the melting point was 98–100° recrystallized from petroleum ether, b.p. 60–70°. This aminobenzylnaphthol gave tars when heated in ethanol in the presence of air. The m.p. and spectra were identical with those of 2-[α-(N-cyclohexylamino)-benzyl]-1-naphthol, synthesized *via* the Mannich condensation from 1-naphthol.

Anal. Calcd. for $C_{23}H_{25}ON$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.29; H, 7.65; N, 3.89.

2-[α-(N-Methyl-N-cyclohexylamino)-benzyl]-1-naphthol (IIb).—The reaction time was 6 days; the yield, 91%. Recrystallization from petroleum ether, after treatment with Nuchar, brought the melting point to 140–141°. The infrared spectrum and m.p. coincided with those of an authentic sample prepared from 1-naphthol.

Anal. Calcd. for $C_{24}H_{27}ON$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.69; H, 8.13; N, 3.92.

2-(α-Piperidinobenzyl)-1-naphthol (IIc).—The crude product, m.p. 100–102°, was obtained in quantitative yields after 8 hr. of standing. The pure product melted at 108–109° (lit.[11b] m.p. 110°). It was identical with IIc synthesized from 1-naphthol.

Anal. Calcd. for $C_{22}H_{23}ON$: C, 83.24; H, 7.27; N, 4.41. Found: C, 83.08; H, 7.16; N, 4.11.

2-(α-Morpholinobenzyl)-1-naphthol (IId).—The reaction time was 20 hr. Purification of nearly quantitative amounts of the morpholino compound, m.p. 130–133°, from ethanol and finally from petroleum ether gave white crystals, m.p. 139°, identical with the compound obtained from the Mannich condensation.

Anal. Calcd. for $C_{21}H_{22}O_2N$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.32; H, 6.83; N, 4.44.

The hydrochloride of IId melted at 158–159°, placed into bath at 130° and the temperature raised at 3°/min.

Anal. Calcd. for $C_{21}H_{22}O_2NCl$: C, 70.87; H, 6.24. Found: C, 70.71; H, 6.71.

In a comparative study, 1 g. of 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) was allowed to stand for 1 hr. at 25° with a tenfold excess of the corresponding amine. ether was added and the insoluble amine hydrobromide was dried and weighed. Piperidine gave a quantitative yield of its hydrobromide. Cyclohexylamine gave a 95% yield. With N-methylcyclohexylamine only a 10% yield of its salt was obtained. Aniline, after heating for 20 minutes to 50° and subsequent standing for 2.5 days, gave only 4% of its hydrobromide salt.

2-(α-Aminobenzyl)-1-naphthols (II). Condensation of 1-Naphthol with Benzaldehyde and Amines.—The general procedure consisted in dissolving 0.02 mole of sublimed 1-naphthol in two-thirds of its weight of absolute ethanol, adding a mixture of one molar equivalent each of benzaldehyde and the corresponding amine, and allowing the reaction mixture to stand under nitrogen in the dark for one to four days. It was best to seed the mixture in order to obtain a crystalline solid. Otherwise, the glue-like product was scratched in the presence of a little petroleum ether with alternate cooling in a Dry Ice-bath and the mixture allowed to warm to room temperature. The solids were washed with ethanol, then recrystallized from the same solvent, or preferably from petroleum ether, b.p. 60–70°. They were identical with the products obtained in the reaction of 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) with the corresponding amines.

Naphthol IIa.—After standing for one day at 25° and overnight in the ice-box, 38% of pure product, m.p. 99–100°, was obtained; ultraviolet spectrum, λ_{max} 214, 220, 239, 300, 313 and 329 mμ (ϵ 31,000, 32,000, 38,000, 4,800, 4,700 and 3,200); infrared bands, γ_{max} in CCl_4: 3300-3100 (sh.), 3060, 2920, 2850, 2800–2600 (sh.), 1950 (weak), 1632, 1395, 1307, 1120, 1090, 875, 695, 671 cm.$^{-1}$; in Nujol: 3280, 1627 (weak), 1314, 1088, 877, 803, 740 cm.$^{-1}$.

Naphthol IIb.—The reaction time was only 6 hr.; yield 36%, m.p. 139.5–141°; ultraviolet spectrum, λ_{max} 214, 220, 238, 297, 312 and 326 mμ (ϵ 28,200, 31,500, 37,200, 4,700, 3,600 and 2,900); infrared bands, γ_{max} in CCl_4: 3400–3100 (sh.), 3060, 2920, 2850, 2800–2600 (sh.), 1945, 1635, 1392, 1307, 1158, 1127, 1085, 875, 692, 671 cm.$^{-1}$.

Naphthol IIc.—After four days standing and recrystallization from ethanol, a 50% yield of IIc, m.p. 109–110°, was obtained. Similar yields resulted when the reagents were heated for 15 minutes on a steam-bath and then allowed to stand for 2 hr. A sample of IIc, less purified, and melting at 101–103°, analyzed correctly; ultraviolet spectrum, λ_{max} 213, 219, 238, 298, 312 and 326 mμ (ϵ 32,000, 33,000, 39,000, 4,000, 3800 and 3300); infrared bands, γ_{max} in CCl_4: 3400–3100 (sh.), 3050, 2920, 2850, 2800–2600 (sh.), 1945, 1630, 1393, 1310, 1158–1150 (doublet), 1110, 1087, 871, 693, 671 cm.$^{-1}$.

Naphthol IId.—After 20 hr. at room temperature and 1.5 days in the cold, a 75% yield of white crystals, m.p. 131–133°, was obtained. Repeated recrystallization from ethanol and petroleum ether raised the melting point to 139–140°; ultraviolet spectrum, λ_{max} 214, 220, 240, 300, 313 and 328 mμ(ϵ 31,500, 30,500, 37,900, 4,550, 4100 and 3,500); infrared bands, γ_{max} in CCl_4: 3400–3100, 3060, 2960, 2840, 2800–2600 (sh.), 1953, 1635, 1394, 1309, 1122, 875 cm.$^{-1}$; in Nujol: 1630 (weak), 1312, 1120, 1087, 875, 805, 747, 695, 671 cm.$^{-1}$.

Naphthol IIe.—After one day, nearly white crystals (yield 85%) were collected. Upon standing and recrystallization from ethanol or benzene–petroleum ether, yellow crystals, m.p. 138.5–139.5° (lit.[8,9f] 141°), were obtained; ultraviolet spectrum, λ_{max} 213, 220, 242, 285, 297 (sh.) 311 and 326 mμ (ϵ 30,000, 35,000, 39,700, 10,400, 9,100, 6,700 and 5,700).

Attempted Dehydrobromination of I. (a) With Excess N-Methylmorpholine.—A mixture of 2 g. of 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) and 7 g. of amine was allowed to stand for 2 days. Only insignificant amounts of hydrobromide salt were isolated upon addition of ether and 70% of I was recovered unchanged.

When heat was applied, even in benzene solution, 30–50% of the theoretical amount of amine hydrobromide salt by-product was obtained, but no definite product other than impure starting material could be isolated.

(b) **With Other Tertiary Amines.**—Heating of I under reflux with collidine gave only tars. Standing with triethylamine resulted in the recovery of starting material. From the reaction with γ-picoline at room temperature for 3.5 days, 15% of 2-benzal-1-tetralone and largely low-melting polymeric material was isolated.

(c) **With Potassium Acetate.**—When the dibromoketone I was heated under reflux for 6 hours with an equivalent amount of potassium acetate in ethanol, 67% of it was recovered unchanged. No other product could be isolated.

(d) **With Cyclohexylamine.**—Heating of 1 g. of 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) with three molar equivalents of cyclohexylamine for 4 hr. in benzene or acetone produced 30–50% of crude 2-benzal-1-tetralone, which upon purification was characterized by its m.p. and infrared spectrum.

2-Benzyl-1-tetralone.—A solution of 4 g. of 2-benzal-1-tetralone in 150 ml. of abs. ethanol at 55° was shaken for 20 minutes in the presence of 0.25 g. of PtO_2 under 44 lb./in.^{2} pressure of hydrogen. Evaporation to dryness followed by washing with petroleum ether (b.p. 30–40°) left 3.6 g. (90%) of colorless solid, m.p. 51–53°; recrystallized from petroleum ether, m.p. 53–54° (lit.[25] 54°); ultraviolet spectrum, λ_{max} 247 and 292 (broad) mμ (ϵ 12,600 and 1,700); infrared C—O band in CCl_4: 1686 cm.$^{-1}$.

2-Bromo-2-benzyl-1-tetralone (III).—Bromine, 4.2 g. (0.0262 mole) in 5 ml. of chloroform was added slowly to 6.2 g. (0.0262 mole) of 2-benzyl-1-tetralone in 20 ml. of chloroform, initially at room temperature, then under cooling. After 3 more hours, the solution was evaporated and the residue washed with petroleum ether to yield 92% of a white solid, m.p. 82–82.5°.

Anal. Calcd. for $C_{17}H_{15}OBr$: C, 64.77; H, 4.80. Found:

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(25) H. Leuchs, *Ber.*, **61B**, 144, (1928); W. Borsche, P. Hofmann and H. Kuehn, *Ann.*, **554**, 23 (1943).

C, 64.39; H, 4.92; ultraviolet spectrum, λ_{max} 259, 295 (broad) mμ (ϵ 11,800, 1,980); infrared C=O band in CCl_4: 1689 cm.$^{-1}$.

2-Benzyl-1-naphthol. a. From (III) with Morpholine.—One gram of 2-bromo-2-benzyl-1-tetralone (III) was allowed to stand with three equivalents of morpholine for 10 minutes, then heated for 2 minutes on a steam-bath. Isopropyl ether was added and a 96% yield of the hydrogen bromide salt was collected by filtration. Upon evaporation of the washed filtrate, treatment with charcoal and recrystallization from petroleum ether, a 60% yield of a colorless solid, m.p. 73–74°, was obtained. This compound was identical in m.p. and ultraviolet spectrum with 2-benzyl-1-naphthol secured by the Claisen[22] reaction. Poorer yields and the formation of polymeric substances were obtained when the reaction time was prolonged to 1.5 days.

b. By Reaction of 1-Naphthol with Sodium and Benzyl Chloride.—The reaction was carried out in toluene as described by Claisen.[22] Repeated purification from petroleum ether gave white crystals of 2-benzyl-1-naphthol, m.p. 74–74.5° (lit.[22] 73.5–74°). This compound gradually produced a red coloration with the formation of a golden glimmering precipitate when treated with aq. ferric chloride in ethanol solution; ultraviolet spectrum, λ_{max} 214, 220, 236, 270, 290–300, 310 and 326 mμ (ϵ 31,400, 33,000, 40,000, 3,000, 4,400, 3,150 and 2,300); infrared bands, γ_{max} in CCl_4: 3520, 3040, 2900, 1945, 1632, 1395, 1142, 1080, 915, 890, 690, 662 cm.$^{-1}$.

Attempted Reaction of III with N-Methylmorpholine.—When N-methylmorpholine was substituted for morpholine in the reaction with III as described above, only a 10% yield of its hydrobromide salt was isolated. Most of the α-bromo ketone III was recovered (80%), and only traces of an impure solid showing a positive ferric chloride test were formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Stereospecific Ring Formation by Means of Mercuric Salts

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Allyl ether has been condensed with aqueous mercuric acetate under various conditions of time, acidity and temperature to give, after the appropriate sequence of reactions, mixtures of *cis*- and *trans*-2,6-bis-(iodomethyl)-*p*-dioxane. Although the *cis* isomer was not formed exclusively when mercuric acetate was used, it was found that the proportions and yields of that isomer could be markedly increased by higher reaction temperature, higher acid concentration, and by longer elapsed time before workup. The maximum *cis/trans* ratio was sixteen to one. A reaction mechanism involving mercurinium (or carbonium) ions and equilibration is proposed to explain the observed results.

Introduction

Cyclization of allyl ether with aqueous mercuric acetate to form a substituted dioxane was first reported by Nesmeyanov and Lutsenko.[1] The product, after precipitation of the adduct as the halide followed by replacement of the halomercuri group with iodine, yielded 2,6-bis-(iodomethyl)-*p*-dioxane. This was shown to be the *cis* form by Summerbell and Stephens.[2] The latter workers always obtained some of the *trans* form which, although it was difficult to separate in a pure state, could hardly have been missed by Nesmeyanov and Lutsenko if their preparation had contained similar amounts.

A closely related reaction is the one discovered by Sand and Biilmann[3] who condensed allyl alcohol with mercuric nitrate, precipitated the halide, and treated the halide with iodine to obtain only the *trans* form of 2,5-bis-(iodomethyl)-*p*-dioxane.[4] This preparation has been repeated a number of times in our laboratory, and under the specified conditions the *cis* form had never been observed, and the yields of the *trans* form were invariably very high.

The most obvious difference between this reaction which is stereospecific and the closely related preceding one which yields a mixture of *cis* and *trans* isomers is the use of mercuric nitrate, the salt of a strong acid, in place of mercuric acetate, the salt of a weak acid. Since acid is generated in the mercuration of olefins, there can be obtained either a high or low hydrogen ion concentration during the reaction by the proper choice of a mercuric salt. In view of the current interest in ring closure methods that are, or can be made, stereospecific it seemed worthwhile to investigate the effect of acid concentration and other conditions on the stereospecificity of this reaction.

Discussion

The Stereochemistry of the Reaction.—In the present work allyl ether has been condensed with aqueous mercuric acetate under various conditions of time, acidity and temperature. Conditions were found which gave, after the appropriate sequence of reactions, good yields of *cis*-2,6-bis-(iodomethyl)-*p*-dioxane (I) almost uncontaminated with the *trans* isomer II. Although the *cis* isomer was never formed exclusively when mercuric acetate was used, it was found that proportions and yields of that isomer could be markedly increased by higher reaction temperature, higher acid concentration and by longer elapsed time before workup. The results have been summarized in Table I[5] and the effect of time on the yield and isomer ratio is shown in Fig. 1.

A Proposed Reaction Mechanism.—An acceptable mechanism must explain several facts: (a)

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(1) A. N. Nesmeyanov and I. F. Lutsenko, *Bull. acad. sci. (U.S.S.R.) Classe Sci. chim.*, 296 (1943).

(2) R. K. Summerbell and J. R. Stephens, THIS JOURNAL, **76**, 731 (1954).

(3) J. Sand, *Ber.*, **34**, 1394 (1901); E. Biilmann, *ibid.*, **33**, 1644 (1900).

(4) R. K. Summerbell and J. R. Stephens, THIS JOURNAL, **76**, 6401 (1954); **77**, 6080 (1955).

(5) The referee has suggested the possibility that ". . . fractionation of isomers may occur in the conversion of the acetoxymercuric compounds to the iodides." The iodides are quite insoluble and excess iodide was always used. Some years ago, J. R. Stephens attempted a fractionation of the more soluble corresponding chlorides by partial precipitation, but with no success. As to the next step, the time of reaction with the excess of iodine had been found in preliminary experiments to give the maximum yield, and we believe that this reaction goes to virtual completion. Some small amount of fractionation during crystallization of the final product would be unavoidable by our procedure.