[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

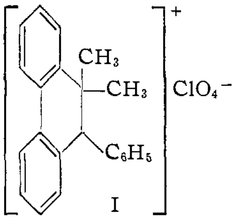
# The Synthesis and Rearrangement of 9,10-Dihydro-10,10-dimethyl-9-phenylphenanthrylium Cation

BY R. L. SHRINER AND LOTHAR GEIPEL[1]

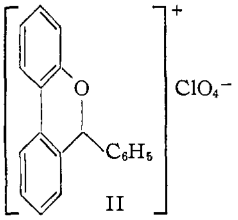
RECEIVED AUGUST 6, 1956

Treatment of 9,10-dihydro-10,10-dimethyl-9-phenyl-9-phenanthrol did not yield a stable isolatable perchlorate salt, but instead the cation rearranged to give 9,10-dihydro-9-methyl-10-methylene-9-phenylphenanthrene. The structure of the phenanthrol was established by oxidation to 2-acetyl-2′-benzoylbiphenyl which in turn was converted to 2′-benzoylbiphenyl-2-carboxylic acid. Independent syntheses of this latter compound were accomplished by treatment of diphenic anhydride with phenylmagnesium bromide and by oxidation of 9-phenylphenanthrene. Oxidation of 9,10-dihydro-9-methyl-10-methylene-9-phenylphenanthrene gave 10-methyl-10-phenyl-9(10H)-phenanthrone. This was independently synthesized by treating 9,10-phenanthrenequinone with phenylmagnesium bromide to give 10-hydroxy-10-phenyl-9(10H)-phenanthrone followed by reaction with methylmagnesium iodide. Treatment with acid caused rearrangement to 10-methyl-10-phenyl-9(10H)-phenanthrone.

The synthesis of 9,10-dihydro-10,10-dimethyl-9-phenylphenanthrylium perchlorate (I) was studied in order to compare its properties with those of 6-phenyl-6-dibenzopyrylium perchlorate (II).



I



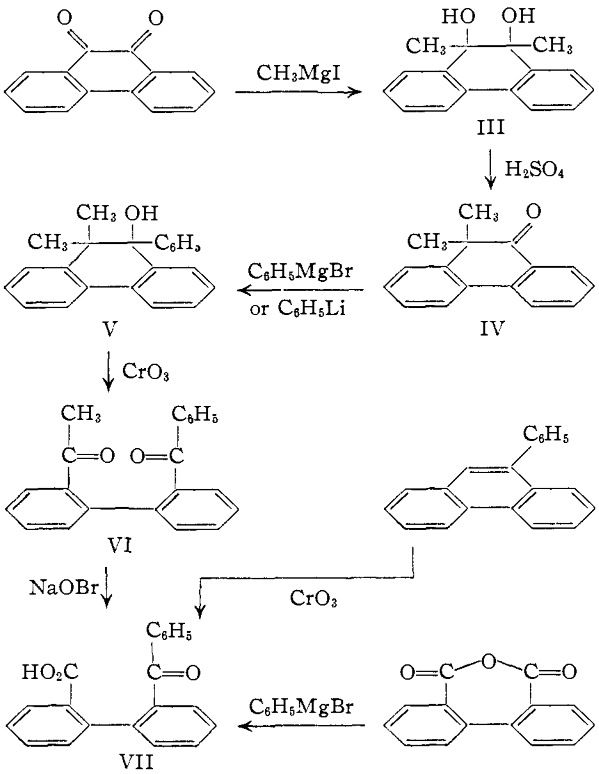
II

The isocyclic structure (I) possesses fewer bond structures contributing to the resonance hybrid of the cation than the heterocyclic structure (II). No salts of the type represented by formula I have been prepared previously.

The synthetic route involved treatment of phenanthraquinone with an excess of methylmagnesium iodide to produce the pinacol III which rearranged under the influence of sulfuric acid to yield the ketone IV as has been previously reported,[2a,b] (see Chart I). This ketone (IV) failed to form an oxime or 2,4-dinitrophenylhydrazone, but its infrared spectrum did show strong carbonyl absorption. Treatment of IV with either phenylmagnesium bromide or phenyllithium gave an oil which was purified by distillation at low pressure. It was a glass whose analysis corresponded to that of 9,10-dihydro-10,10-dimethyl-9-phenyl-9-phenanthrol (V). To show that addition of the organometallic reagent to the phenanthrone involved addition to the carbonyl group (and not 1,4-addition involving the ring), V was oxidized with chromic acid to 2-acetyl-2′-benzoylbiphenyl (VI). Treatment of VI with sodium hypobromite gave 2′-benzoylbiphenyl-2-carboxylic acid (VII) which was independently synthesized by the reaction of phenylmagnesium bromide with diphenic anhydride and by the oxidation of 9-phenylphenanthrene.

When the phenanthrol V was treated with perchloric acid, the expected salt (I) was not obtained, but rather 9,10-dihydro-9-methyl-10-methylene-9-phenylphenanthrene (VIII) was isolated (see Chart II). Compound VIII was also formed when the phenanthrol V was treated with acetyl chloride.

CHART I



The formation of a compound with the structure shown by VIII was mentioned by Bradsher, Rapaport and Anderson[3] in their work on cyclodehydration reactions of certain oxirane derivatives. The product VIII has been shown to be identical with the compound reported by the above workers by mixed melting point. This was also the case with the hydrogenation product, 9,10-dihydro-9,10-dimethyl-9-phenylphenanthrene (IX). To establish the structure of VIII, it was oxidized with chromic acid to 10-methyl-10-phenyl-9(10H)-phenanthrone (X). This compound, like IV, failed to give a test with 2,4-dinitrophenylhydrazine, but its infrared spectrum showed strong carbonyl absorption. When X was reduced with zinc dust and sodium

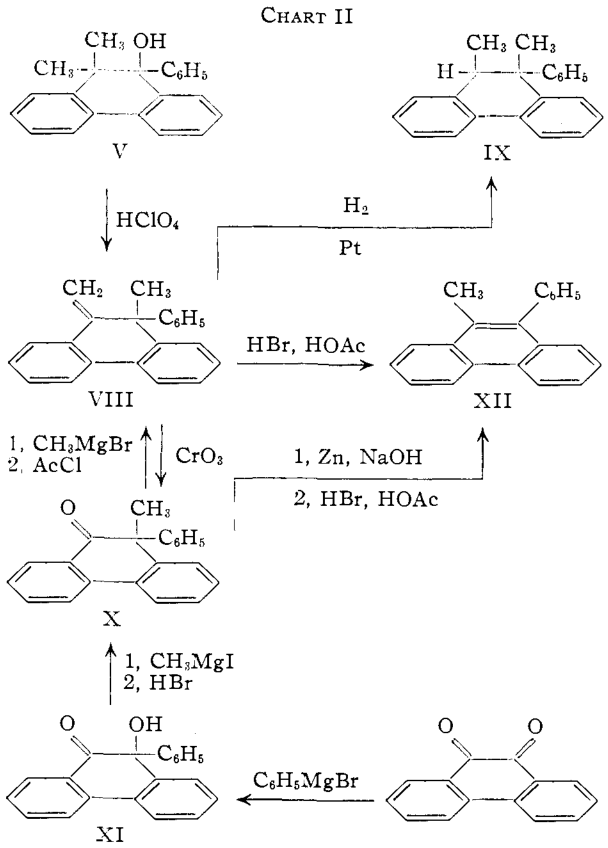
---

[1] From the Ph.D. Thesis of Lothar Geipel, State University of Iowa; Ethyl Corporation Fellow, 1955–1956.

[2] (a) T. Zincke and W. Tropp, *Ann.*, **362**, 242 (1908); (b) H. Meerwein, *Ann.*, **396**, 249 (1913).

[3] C. K. Bradsher, L. Rapaport and P. Anderson, THIS JOURNAL, **68**, 2153 (1946).

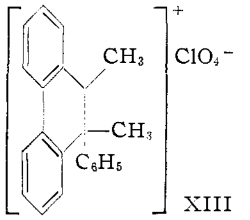
CHART II



hydroxide and the crude product subsequently treated with acid, 9-methyl-10-phenylphenanthrene (XII) was produced. This type of rearrangement has been reported previously for 9,10-dihydro-9-phenanthrols[4] and for certain phenanthrones[5] when subjected to reduction and treatment with acid.

An independent synthesis of X was accomplished as follows: 9,10-phenanthrenequinone was allowed to react with phenylmagnesium bromide to give a low yield (9%) of 10-hydroxy-10-phenyl-9(10H)-phenanthrone (XI). Reaction of XI with methylmagnesium iodide followed by treatment with acid yielded the desired phenanthrone X in 67.5% yield. When the phenanthrone X was treated with methylmagnesium iodide and the crude intermediate carbinol treated with acetyl chloride, the methylene compound (VIII) was formed in 84% yield. These syntheses establish the structure of the rearrangement product as 9,10-dihydro-9-methyl-10-methylene-9-phenylphenanthrene (VIII).

No stable isolatable perchlorate salt of structure I could be obtained although the reaction of perchloric acid with the phenanthrol V was studied in solvents at low temperatures. Evidently this cation I rearranged very rapidly to form the cation XIII which then lost a proton to form the methylene compound VIII. When the methylene compound VIII was dissolved in concentrated sulfuric or perchloric acid, a deep violet-red color was produced, probably due to formation of XIII. The ultraviolet and visible spectra of a perchloric acid solution of VIII show maxima at 268 mμ (ε 2.2 × $10^4$), 332.5 (ε 9.2 × $10^3$) and 549 mμ (ε 6.0 × $10^3$). Minima are evidenced at 243, 295 and 426 mμ.



XIII

## Experimental[6]

**9,10-Dihydro-9,10-dimethyl-9,10-phenanthrenediol** (III).—This was prepared in 50–55% yields by the method of Zincke and Tropp.[2a]

**10,10-Dimethyl-9(10H)-phenanthrone** (IV).—This also was prepared by the method of Zincke and Tropp[2a] by rearrangement of III with sulfuric acid. Purification of the product was facilitated by a rapid distillation in a sausage flask at reduced pressure (2–4 mm.) prior to recrystallization. This compound failed to form an oxime or 2,4-dinitrophenylhydrazone. Its infrared spectrum[7] shows a strong conjugated carbonyl absorption at 1690 cm.$^{-1}$

**9,10-Dihydro-10,10-dimethyl-9-phenylphenanthrol** (V).—To the Grignard reagent prepared from 1.95 g. of magnesium and 13 g. (0.083 mole) of bromobenzene in 100 ml. of ether was added 17.6 g. (0.079 mole) of IV in 100 ml. of benzene. The mixture was refluxed for 6 hours after addition of the ketone was completed. After cooling and decomposing the adduct with sulfuric acid, the mixture was extracted with ether and benzene, the extracts dried and the solvents removed. The resultant sirup was distilled at reduced pressure. The product (18.4 g., 77.5%) was a very viscous, almost glassy, material, b.p. 230–236° (2 mm.). When phenyllithium was substituted for the Grignard reagent in this reaction, the yield was 80.5%.

*Anal.* Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.12; H, 6.72.

**2-Acetyl-2′-benzoylbiphenyl** (VI).—To 7 g. of the carbinol V dissolved in 70 ml. of acetic acid, was added dropwise with stirring, a solution of 14 g. of chromic anhydride in a mixture of 70 ml. of acetic acid and 10 ml. of water. After addition of the chromic acid, the mixture was refluxed 2 hours, then poured onto an equal volume of ice and extracted with ether. The combined ether extracts were washed with dilute sulfuric acid to remove the green color. The extracts were then concentrated to a volume of *ca.* 20 ml., 15 ml. of ethanol added, and the solution cooled. The resultant solid was recrystallized from ethanol to give a white compound melting at 104.5–105.5°. This material gave a positive test with sodium hypoiodite and a positive test with 2,4-dinitrophenylhydrazine.

*Anal.* Calcd. for $C_{21}H_{16}O_2$: C, 83.97; H, 5.35. Found: C, 83.82; H, 5.30.

**2′-Benzoylbiphenyl-2-carboxylic Acid** (VII). **(a) From the Diketone VI.**—Two grams (0.0067 mole) of VI dissolved in 10 ml. of dioxane was added with stirring to an ice-cold solution of sodium hypobromite prepared from 2.2 g. of sodium hydroxide and 1.1 ml. of bromine in 20 ml. of water. Reaction occurred as the mixture was warmed slowly to room temperature. After stirring an additional 30 minutes and standing 10 hours, the aqueous layer was decanted, acidified with hydrochloric acid and extracted with ether. The extracts were evaporated to dryness and the residue recrystallized from a water–ethanol mixture (2:3). After 3 recrystallizations the product melted at 178.5–179.5°.

---

[4] W. E. Bachmann, THIS JOURNAL, **55**, 3852 (1933).

[5] E. J. Chu and F. Wei, *J. Chinese Chem. Soc.*, **7**, 20 (1939); P. G. Seergeev, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1645 (1937).

[6] All melting points are corrected.

[7] The authors are indebted to Dr. K. S. McCallum of the Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, for the determination of the infrared spectra of compounds IV and X. The authors also wish to thank Samuel P. Sadtler and Sons, Inc., Philadelphia, Pa., for the determination of the spectrum of compound IV.

An analytical sample was purified by two sublimations *in vacuo* and melted at 179–180°.

*Anal.* Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.66; neut. equiv., 302.2. Found: C, 79.25; H, 4.42; neut. equiv., 305.5, 306.5.

(b) **From Diphenic Anhydride.**—To a refluxing solution of 26.7 g. (0.118 mole) of diphenic anhydride in a mixture of 175 ml. of anisole and 200 ml. of benzene, was added slowly, over a period of 5.5 hours, the Grignard reagent prepared from 18.7 g. (0.12 mole) of bromobenzene and 2.9 g. of magnesium in a mixture of 80 ml. of ether and 50 ml. of anisole. The Grignard reagent was added through the high-dilution apparatus described by Leonard and Sentz.[8] After addition of the Grignard reagent, refluxing was continued 45 minutes and the mixture then let stand 10 hours. After decomposition of the adduct with dilute sulfuric acid, the reaction mixture was extracted with ether, the extracts extracted with saturated sodium carbonate solution and the aqueous extracts acidified with concentrated hydrochloric acid. The acidified mixture was extracted with ether, the extracts evaporated to dryness and the residue recrystallized successively from an ethanol–water mixture (3:2), an isopropyl ether–petroleum ether mixture (1:1) and then from chloroform. The product weighed 9.2 g. (25.6% yield) and melted at 177.5–178.2°. Admixture with a sample produced by the reaction of sodium hypobromite on VI gave no depression of melting point.

(c) **From 9-Phenylphenanthrene.**—9-Phenylphenanthrene was prepared by the method of Bergmann and Bergmann[9] with the following modification: the 9-cyclohexenylphenanthrene was dehydrogenated by heating for 2.5 hours at 295–360° with 10% palladium-on-charcoal catalyst (the temperature was held at 355–360° for the last 40 minutes of the reaction).

A solution of 1.6 g. of chromic anhydride in a mixture of 15 ml. of acetic acid and 5 ml. of water was added slowly with stirring to 2 g. (0.008 mole) of 9-phenylphenanthrene dissolved in 25 ml. of acetic acid. The mixture was then refluxed 1.5 hours, poured onto twice its volume of crushed ice and extracted with ether. The extracts were evaporated to dryness and the residue recrystallized twice from an alcohol–water mixture (3:2) and then four times from chloroform. The product melted at 178–179.5° and gave no depression of melting point on admixture with either sample of VII prepared as described above.

**Rearrangement of V to 9,10-Dihydro-9-methyl-10-methylene-9-phenylphenanthrene (VIII).**—To 2.4 g. (0.008 mole) of V dissolved in 15 ml. of isopropyl ether and chilled in a Dry Ice–chloroform-bath was added with stirring, 1 ml. of 70% perchloric acid followed by 2 ml. of acetic anhydride. A reddish precipitate formed which disappeared as the mixture warmed to room temperature. The solvent was removed at reduced pressure (water-pump) at room temperature. Fine white crystals remained which were washed with petroleum ether and water and recrystallized from ethanol to give 1.2 g. (47%) of material melting at 87–88°. This compound was also formed in 85% yield when V was refluxed 45 minutes in a mixture of benzene and acetyl chloride. An analytical sample was purified by sublimation *in vacuo* and melted at 88–88.5°, no depression on admixture with the compound reported by Bradsher.[3,10]

*Anal.* Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.43; H, 6.22.

When 3.0 g. of the compound VIII was refluxed 63 hours with a mixture of 150 ml. of acetic acid and 75 ml. of 48% hydrobromic acid, 2.0 g. (80%) of 9-methyl-10-phenylphenanthrene[3] was isolated. The fate of the carbon atom eliminated could not be established.

**9,10-Dihydro-9,10-dimethyl-9-phenylphenanthrene (IX).**—This was prepared by hydrogenation of VIII in the presence of platinum oxide, as reported by Bradsher.[3] An analytical sample melting at 123–123.5°, no depression of melting point on admixture with the material prepared by Bradsher.

*Anal.* Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 93.23; H, 6.87.

**Oxidation of VIII to 10-Methyl-10-phenyl-9(10H)-phenanthrone (X).**—To 5 g. (0.018 mole) of VIII dissolved in 55 ml. of warm acetic acid was added 4.7 g. (0.047 mole) of chromic anhydride dissolved in a mixture of 20 ml. of acetic acid and 15 ml. of water. The mixture was then heated on a steam-bath for 40 minutes, poured onto an equal volume of ice, and filtered. The gummy solid was recrystallized several times from ethanol to yield 2.1 g. (41%) of material melting at 116–118.5°. Further recrystallization raised the melting point to 118.5–119.5°.

*Anal.* Calcd. for $C_{21}H_{16}O$: C, 88.80; H, 5.67. Found: C, 88.68; H, 5.62.

This compound, like IV, did not give a test with 2,4-dinitrophenylhydrazine. Its infrared spectrum shows a strong conjugated carbonyl absorption at 1690 cm.$^{-1}$.

**Reduction of X.**—Eight-tenths gram (0.0028 mole) of X was mixed with 1.0 g. of zinc dust and a solution of 1.0 g. of sodium hydroxide in 40 ml. of ethanol. The mixture was refluxed 10 minutes and then stirred for 5 hours. It was then heated to boiling and filtered while hot through a sintered glass funnel. The residue was washed with two 15-ml. portions of hot ethanol and the filtrate and washings evaporated to dryness. The residue was dissolved in 40 ml. of acetic acid, and 10 ml. of 48% hydrobromic acid was added. The mixture was boiled five minutes, poured into an equal volume of ice-water and neutralized with sodium hydroxide. Extraction with ether and evaporation of the extracts left a solid which was recrystallized thrice from ethanol. The product melted at 97.5–98.5°; no depression on admixture with a sample of 9-methyl-10-phenylphenanthrene prepared by the method of Bradsher and Rosher.[11]

**10-Hydroxy-10-phenyl-9(10H)-phenanthrone (XI).**—To a refluxing solution of 15.3 g. (0.073 mole) of phenanthraquinone in 450 ml. of benzene and 100 ml. of anisole, was added slowly, through the high-dilution apparatus of Leonard,[8] the Grignard reagent prepared from 12.0 g. (0.077 mole) of bromobenzene and 1.8 g. of magnesium in 130 ml. of anisole. After addition of the Grignard reagent was completed (3.25 hours), the reaction mixture was refluxed an additional 15 minutes and then cooled. After decomposition of the adduct with ice and dilute sulfuric acid, the mixture was extracted with benzene, the extracts dried and evaporated to dryness. The residue was recrystallized several times from benzene, chloroform and ethanol. More than 50% (8.4 g.) of the phenanthrenequinone was recovered. A small amount (1.98 g., 9.1%) of a compound whose analysis corresponded to the desired hydroxyketone was isolated. Some 9,10-dihydro-9,10-diphenyl-9,10-phenanthrenediol was also formed (3.4 g.). The hydroxyketone, after purification by sublimation, melted at 118–118.5°.

*Anal.* Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.56; H, 4.86.

**Reaction of XI with Methylmagnesium Iodide.**—To the Grignard reagent prepared from 0.66 g. (0.027 mole) of magnesium and 3.9 g. (0.027 mole) of methyl iodide in 12 ml. of ether, was added, with stirring and cooling, 1.95 g. (0.0068 mole) of XI in 40 ml. of benzene. After addition of the ketone was complete, the mixture was refluxed for 10 hours, cooled, poured onto an equal volume of cracked ice, and shaken with 12 ml. of 6 *M* sulfuric acid. Extraction with chloroform and evaporation of the extracts left a thick sirup which was dissolved in 20 ml. of acetic acid. To this was added 3 ml. of 48% hydrobromic acid and the mixture refluxed 20 minutes. After cooling, the mixture was neutralized with 20% sodium hydroxide solution, and then extracted with benzene and chloroform. The extracts were dried and evaporated to dryness. The residue was slurried with 12 ml. of ethanol and chilled. The resultant crystals, after drying, weighed 1.32 g. (67.5%) and melted at 116–118.5°. A sample purified by sublimation *in vacuo* melted at 118–119°, no depression on admixture with a sample of the material prepared by oxidation of VIII.

**Reaction of X with Methylmagnesium Iodide.**—To the Grignard reagent prepared from 0.6 g. of magnesium and 3.5 g. of methyl iodide in 15 ml. of ether was added 1.8 g. (0.0063 mole) of the ketone X. After standing 45 minutes, the reaction mixture was decomposed with ice and saturated ammonium chloride solution. Extraction with ether and benzene and evaporation of the extracts left a reddish liquid

---

(8) N. J. Leonard and R. C. Sentz, THIS JOURNAL, **74**, 1708 (1952).

(9) E. Bergmann and F. Bergmann, *ibid.*, **59**, 1443 (1937).

(10) The authors wish to thank Prof. C. K. Bradsher of Duke University, Durham, N. C., for the determination of mixed melting points of compounds VIII and IX with the compounds previously prepared in his laboratory.[3]

(11) C. K. Bradsher and R. Rosher, THIS JOURNAL, **61**, 1524 (1939).

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.

IOWA CITY, IOWA

---

[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

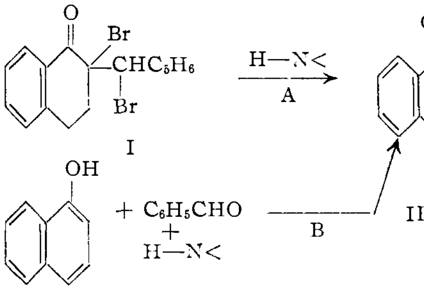
In the presence of an excess of a primary or secondary amine (cyclohexylamine, piperidine, morpholine, N-methylcyclohexylamine), 2-bromo-2-(α-bromobenzyl)-1-tetralone (I) reacted to give good yields of the corresponding 2-(α-aminobenzyl)-1-naphthols (II). The structures of the naphthols were established 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 ($\lambda_{max}$ 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)

---

* Presented at the Midwest Regional Meeting of the American Chemical Society, Ames, Iowa, Nov. 9, 1956.

[1] (a) Monsanto Research Fellow 1954–1955, 1955–1956; (b) to whom correspondence concerning this article should be addressed; (c) National Science Foundation Research Associate, 1954.

[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 G. Drost, *Rec. trav. chim.*, **69**, 1080 (1950).

[5] We have found a similar band for 2-benzalindanone with the $\lambda_{max}$ 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.