of *p*-bis(bromoacetyl)benzene, m.p. 160–165°. Recrystallization from ethanol (Darco) increased the m.p. to 176–178° (lit.,[13] m.p. 177–178°), λ_{max} 265 mμ, ε 17,800.

Preparation of 1,4-bis(2-ethyl-4-thiazolyl)benzene (IV). A solution of 1.0 g. (0.011 mole) of thiopropioamide and 1.77 g. (0.0056 mole) of *p*-bis(bromoacetyl)benzene in 40 ml. of dimethylformamide was refluxed overnight. After removal of most of the solvent under reduced pressure, there was obtained 1.1 g. of crude product, m.p. 94–97°. Two recrystallizations from dimethylformamide (Darco) gave 1.0 g. (44%) of IV, m.p. 114–116°. See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{16}H_{16}N_2S_2$: C, 64.0; H, 5.33; N, 9.33. Found: C, 63.75; H, 5.29; N, 9.13.

Preparation of 1,4-bis(4-phenyl-2-thiazolyl)benzene (I). A solution of 3.270 g. (0.0166 mole) of dithio-1,4-benzenedicarboxamide and 6.637 g. (0.0333 mole) of phenacyl bromide in 150 ml. of purified dimethylformamide was heated under reflux for 18 hr. After cooling the product crystallized in the form of plates. More solid was obtained by diluting the mother liquor with 500 ml. of water. The combined solids were washed with methanol and dried in a vacuum oven at 60° to give 4.77 g. (96.9%) of I, m.p. 225–226°. One recrystallization raised the m.p. to 229–230° (lit.,[7] m.p. 225°). See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{24}H_{16}N_2S_2$: C, 72.69; H, 4.04; N, 7.08. Found: C, 72.48; H, 3.86; N, 6.89.

Preparation of 1,3-bis(4-phenyl-2-thiazolyl)benzene. A solution of 1.635 g. (0.0083 mole) of dithio-1,3-benzenedicarboxamide and 3.318 g. (0.0166 mole) of *p*-bis(bromoacetyl)benzene in 75 ml. of purified dimethylformamide was heated under reflux for 18 hr. Working up the product in the same manner as described above for compound I, there was obtained a 3.21 g. (97.5%) yield of II, m.p. 167–169°, which, after recrystallization from carbon tetrachloride, had m.p. 170°. See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{24}H_{16}N_2S_2$: C, 72.69; H, 4.04; N, 7.08. Found: C, 72.55; H, 4.17; N, 6.84.

Preparation of thiazole polymer III. To a hot solution of 3.700 g. (0.0210 mole) of dithioadipamide in 425 ml. of acetic acid, there was added 6.720 g. (0.0210 mole) of *p*-bis(bromoacetyl)benzene in 250 ml. of hot acetic acid. A yellow precipitate began to form immediately. After heating with stirring at 80° for 24 hr., the solid was collected on a filter and reprecipitated twice from formic acid into a large excess of ethanol. The solid powder was ground and dried at 60° (1 mm.). Ultraviolet spectra and other properties of this polymer are mentioned in the discussion section of this paper.

Anal. Calcd. for $(C_{16}H_{14}N_2S_2)_n$: C, 64.41; H, 4.72; N, 9.38; S, 21.45. Found: C, 63.65; H, 4.75; N, 9.04; S, 20.59; Br, 1.25, 1.26.

Preparation of thiazole polymer V. A solution of 3.200 g. (0.01000 mole) of *p*-bis(bromoacetyl)benzene and 1.963 g. (0.01000 mole) of dithio-1,4-benzenedicarboxamide in 300 ml. of purified dimethylformamide was refluxed for 105 hr. with stirring. The reactants were initially soluble, but a fine yellow powder began to form within a few minutes after mixing. At the end of the reaction period, the solid was collected on a filter, washed with methanol, and dried overnight in a vacuum oven yielding 2.810 g. of fine yellow powder. The inherent viscosity was 0.12 in sulfuric acid at 25° (0.24 g./100 ml.). Ultraviolet spectra and other properties of this polymer are mentioned in the discussion section of this paper.

Anal. Calcd. for $(C_{18}H_{10}N_2S_2)_n$: C, 67.90; H, 3.17; N, 8.80. Found: C, 66.46; H, 3.92; N, 8.69; Br, 1.38, 1.65.

Preparation of thiazole polymer VI. A solution of 3.200 g. (0.0100 mole) of *p*-bis(bromoacetyl)benzene and 1.963 g. (0.0100 mole) of dithio-1,3-benzenedicarboxamide in 300 ml. of dimethylformamide was heated under reflux with stirring for 216 hr. Although the reactants were initially miscible, a fine yellow powder began to form shortly after they were mixed. At the end of the reaction period, 2.58 g. of a fine yellow powder was obtained by filtration. Addition of the mother liquor to 1 l. of methanol caused the precipitation of an additional 0.278 g. of yellow powder. This material showed the same ultraviolet maxima as the initial precipitate.

Anal. Calcd. for $(C_{18}H_{10}N_2S_2)_n$: C, 67.90; H, 3.17; N, 8.80. First precipitate: C, 64.90; H, 3.60; N, 8.44; Found: Br, 1.38. Second precipitate: C, 66.01; H, 3.68; N, 8.46; Br, 2.37.

The inherent viscosity in sulfuric acid was found to be 0.095 at 25° (0.24 g./100 ml.).

Acknowledgment. This work was carried out under the sponsorship of Contract AF-33(616)5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. This paper may be reproduced for any purpose of the United States Government.

It is a pleasure to acknowledge the help of Mrs. N. S. Fan, Mr. R. R. Haynes, and Mr. H. Schauble in the synthesis of intermediates.

URBANA, ILL.

---

[13] F. Kröhnke and I. Vogt, *Chem. Ber.*, **86**, 1132 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Reactions of 2-Benzhydrylphenylacetic Acid; A New Pyrone Synthesis[1]

R. L. LETSINGER, J. D. JAMISON,[2] AND A. S. HUSSEY

Received April 20, 1960

In contrast to 8-benzhydryl-1-naphthoyl chloride, which isomerizes with 1,5-phenyl migration under Friedel-Crafts conditions, 2-benzhydrylphenylacetyl chloride cyclizes to a seven-membered cyclic ketone (IV) in the presence of aluminum or stannic chloride. When heated with a mixture of acetic acid and polyphosphoric acid both 2-benzhydrylphenylacetic acid and ketone IV afford a substituted 4-pyrone (VI) in good yield.

In a previous paper it was reported that 8-benzhydryl-1-naphthoyl chloride (Ib) rearranged in the presence of stannic chloride to a substance which on hydrolysis gave (>90%) 1-phenylhydroxy-

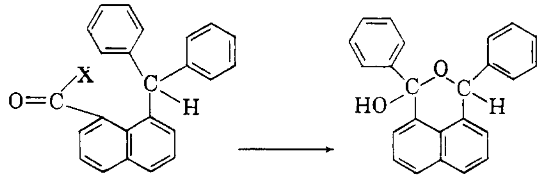
---

[1] Presented at the 137th Meeting of the American Chemical Society, Cleveland, April 1960.

[2] Standard Oil Co. of Indiana Fellow, 1958–59.

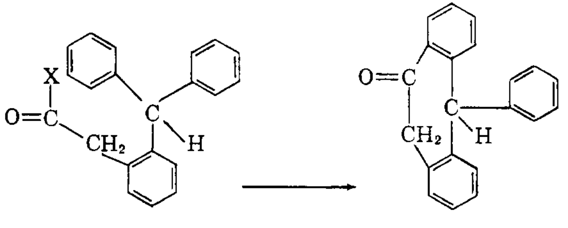
methyl-8-benzoylnaphthalene hemiketal (II).[3] A similar transformation ensued when 8-benzhydryl-1-naphthoic acid (Ia) was dissolved in concentrated sulfuric acid.

In order to extend our knowledge of systems capable of exhibiting such 1-5-aryl migrations we synthesized 2-benzhydrylphenyl-acetic acid (III) and subjected it and the corresponding acid chloride to the action of a variety of acidic reagents. Although the carboxyl and benzhydryl groups in compound III may assume a relative position very close to that obtaining in compound I, no evidence was found of products resulting from a 1,5-phenyl migration. Instead, the seven-membered cyclic ketone (IV) and substances derived from it were isolated. The reactions leading to these products were slow relative to the rearrangement of I. It therefore appears that the structural requirements for the 1,5-aryl migration are very stringent, that little deviation from the structure of I can be tolerated.



Ia. X = OH
b. X = Cl

II

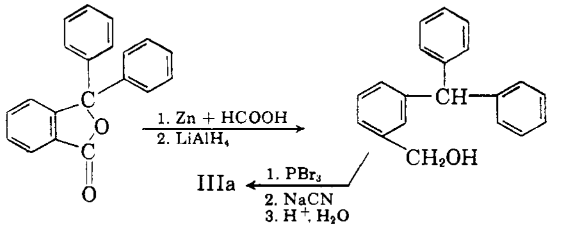


IIIa. X = OH
b. X = Cl

IV

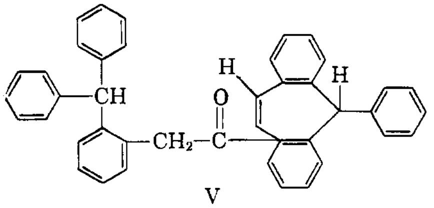
The synthesis of 2-benzhydrylphenylacetic acid is indicated by sequence 1. Yields were high throughout. Acid IIIa and its chloride (IIIb) reacted normally with alcohols (methanol and ethanol) to give the esters.

Sequence I



Ketone IV was best obtained (65% yield) by the action of aluminum chloride on 2-benzhydrylphenylacetyl chloride in carbon disulfide. It absorbed at 5.99 μ (C=O) in the infrared, gave a 2,4-dinitrophenylhydrazone derivative, and afforded an enolacetate (VIII) when treated with acetic anhydride and potassium acetate. In confirmation of the structure the NMR spectrum of IV (40 Mc./sec.) showed, in addition to the expected aromatic hydrogen bands at low field, a sharp band attributable to the tertiary hydrogen and a quartet of bands attributable to the two non-equivalent methylene hydrogens[4] ($\nu_0\delta$, 18.6 cycles/sec.; J, 17.6 cycles/sec.).[5]

With stannic chloride as a catalyst the reaction products were in general more complex. Under mild conditions (sixty hours at room temperature) ketone IV was formed (18%); however, most of the acid chloride remained unaffected and was recovered as 2-benzhydrylphenylacetic acid. A similar reaction under more strenuous conditions (fourteen hours in refluxing benzene) gave as the principal product (45%) a new, high melting, nonsublimable crystalline solid. This substance was identified as an enolacylate derivative (V) of compound IV by the analysis, the hydrolytic products (2-benzhydrylphenylacetic acid and ketone IV) and the marked similarity of the infrared and ultraviolet spectra with the spectra of the enolacetate of ketone IV. From a twenty-hour reaction of IIIb with stannic chloride in boiling carbon disulfide was obtained IIIa (45% recovery, subsequent to hydrolysis) and a neutral oil from which a small amount of V was isolated. By contrast, under similar conditions the rearrangement of Ia was essentially complete within an hour.



V

Attempts to cyclize acid IIIa directly to ketone by mineral acids were unsuccessful. Sulfuric acid either left IIIa unchanged or converted it to water-soluble products. Hydrogen fluoride proved ineffective and hot polyphosphoric acid slowly transformed it to a complex mixture of ketones from which no pure compounds could be isolated.

In the course of these studies a sample of 2-benzhydrylphenylacetic acid was heated with a mixture of acetic acid and polyphosphoric acid. From this mixture was obtained a good yield of a new crystalline substance, VI, the analysis of which agreed with the formula $C_{26}H_{18}O_2$. Compound VI failed to react with 2,4-dinitrophenylhydrazine in alcohol solution but did condense with hydrazine

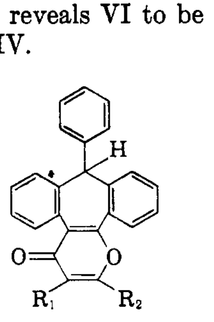
---

[3] R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, 78, 2649 (1956); 81, 940 (1959).

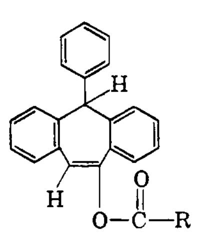
[4] See J. A. Pople, W. G. Schneider, and H. J. Berstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Co., New York (1960), p. 119.

[5] We are grateful to Mr. C. Creswell for the spectral determination and interpretation. Carbon tetrachloride was used as a solvent for these measurements.

under forcing conditions. The information described below reveals VI to be a pyrone derived from ketone IV.



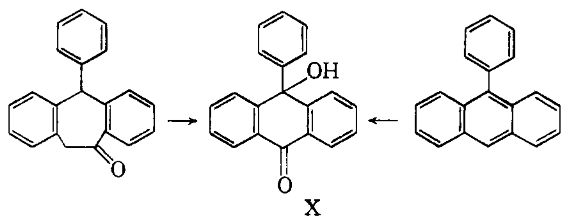
VI. $R_1 = H$; $R_2 = CH_3$
VII. $R_1 = CH_3$; $R_2 = C_2H_5$



VIII. $R = CH_3$
IX. $R = CH_2Cl$

Hydrolysis of compound VI by potassium hydroxide in refluxing ethylene glycol solution afforded a 95% yield of ketone IV, indicating that the acetic acid residues were joined at the methylene and carbonyl carbon atoms rather than to the aromatic rings. On the assumption that VI might be a pyrone, the hydrolysis was repeated under conditions that any acetone liberated would be trapped as the 2,4-dinitrophenylhydrazone. In agreement with the pyrone structure, acetone 2,4-dinitrophenylhydrazone was obtained in 60% yield (based on one mole of acetone liberated per mole of VI).

Oxidation of compound VI by alkaline permanganate yielded (84%) 10-hydroxy-10-phenylanthrone, identical with a sample of this substance prepared for comparison purposes by oxidation of 9-phenylanthracene. Since ketone IV also underwent ring contraction under similar oxidation conditions to give 10-hydroxy-10-phenylanthrone, this observation is compatible with the structure proposed for VI. Formation of the anthrone may be rationalized on the assumption that IV and VI are oxidized to a seven-membered ring vicinal diketone which subsequently undergoes a benzilic acid type rearrangement and oxidative decarboxylation. An analogous ring contraction occurs in the oxidation of phenanthrenequinone to dibenzofluorenone.[6]



X

Conclusive evidence that VI was a 4-pyrone rather than a 2-pyrone was provided by the infrared spectrum. Compound VI exhibited a triplet of bands between 6.0 and 6.3 μ which is characteristic for the 4-pyrone structure.[7,8] The 2-pyrones absorb near 5.8 μ.[8]

Propionic acid reacted with 2-benzyhydrylphenylacetic acid in polyphosphoric acid in a manner similar to acetic acid. A high melting compound was obtained which had the characteristic 4-pyrone triplet in the infrared spectrum, had an ultraviolet spectrum almost identical with that of VI, and gave an analysis consistent with the formula $C_{27}H_{22}O_2$. In view of the mode of formation this substance may be regarded as the substituted pyrone, VII. Under similar conditions chloroacetic acid reacted with 2-benzhydrylphenylacetic acid to give the enolchloroacetate (IX) as the only isolable pure compound. It was also found that pyrone VI could be obtained in good yield by heating together ketone IV, acetic acid, and polyphosphoric acid. The scope of this new pyrone synthesis will be discussed in more detail in a subsequent publication.

EXPERIMENTAL

The infrared spectra were recorded with a Baird Model AB-2 spectrophotometer with the sample in potassium bromide. Ultraviolet spectra were taken with a DK-2 Beckman ratio recording instrument. Carbon, hydrogen, and nitrogen analyses were performed by Miss Hilda Beck.

2-Benzhydrylbenzoic acid. A mixture of 19.73 g. of 3,3-diphenylphthalide, 160 g. of formic acid, 40 g. of zinc, and 40 g. of water was refluxed for 5 hr. and then poured into water. The precipitate was separated and dissolved in alcohol. After filtration to remove unchanged zinc, excess ethanol was distilled and the residue recrystallized from ethanol-water to give 7.1 g. (92%) of 2-benzhydrylbenzoic acid; m.p. 158–162°. After two further recrystallizations the sample melted at 161–162°; lit.,[9] m.p. 161°.

Anal. Cacld. for $C_{20}H_{16}O$: C, 83.33; H, 5.55. Found: C, 83.50; H, 5.50.

2-Benzylhydrylbenzyl alcohol. 2-Benzhydrylbenzoic acid (30 g., 0.104 mole) in 300 ml. of ether was added slowly with stirring to 8 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of ether, the addition rate being sufficient to keep the ether refluxing. Thereafter the mixture was warmed for 2 hr., cooled with an ice bath, and hydrolyzed by additions of 15 ml. of 95% ethanol (in 80 ml. of ether) and 4 ml. of water. The ether solution was separated from the insoluble cake and washed successively with 6*M* hydrochloric acid, 10% sodium bicarbonate solution, and water. On drying and evaporation of the ether it yielded 26 g. (94%) of 2-benzhydrylbenzyl alcohol. The analytical sample (recrystallized from ligroin) melted at 108–108.5°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.62; H, 6.56. Found: C, 87.83; H, 6.58.

2-Benzhydrylbenzyl bromide was prepared by dropwise addition of 10 g. (0.037 mole) of phosphorus tribromide into a cold, stirred ether solution containing 20 g. (0.073 mole) of 2-benzhydrylbenzyl alcohol. The mixture was allowed to stand at ice temperature for 24 hr.; then it was filtered to remove the bromide which had separated. Additional product was obtained from the mother liquor by adding water, washing the ether layer with sodium bicarbonate solution, and evaporating the ether. The total yield of crystalline 2-benzhydrylbenzyl bromide was 23.7

---

(6) R. Anschutz and F. R. Japp, *Ber.*, **11,** 211 (1878).

(7) We are grateful to Professor C. D. Hurd for pointing out this property of 4-pyrones and for helpful discussions concerning the chemistry of these substances. A number of spectra of 4-pyrones are reproduced in the Ph.D. dissertation of S. Trofimenko, Northwestern University, 1958.

(8) R. H. Wiley and C. H. Jarboe, *J. Am. Chem. Soc.*, **78,** 2398 (1956).

(9) L. W. Jones and F. B. Root, *J. Am. Chem. Soc.*, **48,** 189 (1926).

g. (96.5%); m.p. of the analytical sample (recrystallized from ether), 123-124°.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.23; H, 5.05. Found: C, 71.22; H, 4.90.

2-Benzhydrylphenylacetonitrile was prepared by heating 17 g. (0.050 mole) of the bromide with a solution of 4 g. of sodium cyanide, 25 ml. of water, and 100 ml. of ethanol at reflux temperature for 24 hr. On addition of water and cooling the nitrile (11.94 g., 83.5%) separated; m.p. 96-97° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{17}N$: C, 89.04; H, 6.00; N, 4.95. Found: C, 88.55; H, 6.06; N, 4.89.

2-Benzhydrylphenylacetic acid (IIIa) formed quantitatively when 11 g. of the nitrile was heated for 4 hr. with a refluxing solution of 20 ml. of acetic acid, 20 ml. of water, and 20 ml. of sulfuric acid. It was collected by filtration and washed with water; m.p. 209-212°. After recrystallization from ethyl acetate a sample melted at 212-213°; infrared band, 5.9 μ.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96. Found: C, 83.25; H, 6.07.

Methyl 2-benzhydrylphenylacetate formed when a solution of 2-benzhydrylphenylacetic acid (2.0 g.) in 50 ml. of methanol and 2 ml. of sulfuric acid was refluxed for 7 hr. Concentration followed by addition of 100 ml. of water precipitated the ester. It was taken up in ether and the solution was washed with aqueous alkali, dried, and evaporated. The ester, 1.86 g. (89%), melted at 76-78°; after recrystallization from ethanol the analytical sample melted at 77-78°, infrared bands (carbon disulfide solvent) 3.30, 3.37, 5.78, 6.22, 7.5 μ.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.56; H, 6.33. Found: C, 83.93; H, 6.09.

Reactions of 2-benzhydrylphenylacetyl chloride (IIIb). In each case, unless otherwise noted, the acid chloride was prepared by heating the carboxylic acid with excess thionyl chloride, distilling the residual thionyl chloride, adding dry benzene, and then removing the benzene by vacuum distillation. The acid chloride was left as a white solid; infrared band at 5.6 μ: no absorption in hydroxyl region.

(*a*) *Ethanol.* The acid chloride, prepared from 1.45 g. of 2-benzhydrylphenylacetic acid, was warmed with 35 ml. of ethanol. The solution was then concentrated by distillation, water was added, and the oil taken up with ether. Evaporation yielded *ethyl 2-benzhydrylphenylacetate,* which crystallized from pentane as a white solid; 1.20 g. (76%); m.p. 57.5-58.5°; infrared bands (potassium bromide), 3.38, 3.45, 5.8, 6.25, and 6.70 μ.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.57; H, 6.71. Found: C, 83.77; H, 6.30.

(*b*) *Aluminum chloride in carbon disulfide.* A mixture of the acid chloride (from 3.9 g. of acid) and 5 g. of aluminum chloride in carbon disulfide was heated at reflux for 17 hr. Carbon disulfide was then removed by distillation and the residue taken up in ether, hydrolyzed, and washed with a sodium hydroxide solution (no carboxylic acid resulted on acidification). On concentration of the ether solution 2.37 g. (69%) of the cyclic ketone, *compound IV,* crystallized; m.p. 140-152°. After sublimation it melted at 151-152°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.73; H, 5.64. Found: C, 88.94; H, 5.60.

The *2,4-dinitrophenylhydrazone* derivative melted with decomposition at 240° when heated rapidly.

Anal. Calcd. for $C_{27}H_{20}N_4O_4$: C, 69.90; H, 4.31. Found: C, 70.05; H, 4.53.

(*c*) *Stannic chloride in benzene (compound V).* The acid chloride from 3.00 g. of acid was heated with 5 ml. of stannic chloride in 40 ml. of benzene at reflux for 14 hr. The resulting mixture was hydrolyzed with 50 ml. of ice water and the products were separated by conventional extraction procedures. From an alkaline extraction was obtained 0.385 g. of 2-benzhydrylphenylacetic acid (m.p. 201-208°) and from the portion containing neutral products was isolated by crystallization from ether 1.10 g. (45% calcd. as $C_{42}H_{32}O_2$) of a white solid, m.p. 188-195°. The residual oil appeared to be a mixture of IV and VI from the infrared spectrum. Several recrystallizations of the solid from ethanol-ethyl acetate yielded the analytical sample, m.p. 201-203°. This substance, *compound V,* did not sublime when heated at reduced pressure, did not react with 2,4-dinitrophenylhydrazine, and was insoluble in concd. sulfuric acid at room temperature. It absorbed strongly at 5.7 μ in the infrared, as did the enolacetate of *III*. The ultraviolet spectra of V and the enolacetate of III were almost identical ($\lambda_{max}^{cyclohexane}$ 289 mμ in both cases).

Anal. Calcd. for $C_{42}H_{32}O_2$: C, 88.73; H, 5.67. Found: C, 88.68; H, 5.55.

Hydrolysis of the compound melting at 201-203° (0.334 g.) by boiling ethanolic potassium hydroxide (15 hr.) afforded 0.182 g. of 2-benzhydrylphenylacetic acid, m.p. 203-208°, and 0.135 g. of ketone IV (identified by the infrared spectrum), in agreement with the proposed structure.

(*d*) *Stannic chloride in benzene at room temperature.* In this case the acid chloride was prepared by heating 3.00 g. of 2-benzhydrylphenylacetic acid with 25 ml. of phosphorus trichloride for 2 hr. Excess phosphorus trichloride was removed by distillation and 5 ml. of stannic chloride in 25 ml. of benzene was added. After standing for 60 hr. at room temperature the mixture was hydrolyzed and worked up as in the previous case. Under these mild conditions relatively little reaction occurred and 2.38 g. of 2-benzhydrylphenylacetic acid (m.p. 198-205°) was recovered. None of compound V was obtained but 0.501 g. (86% calculated on the basis of the carboxylic acid not recovered) of ketone IV was isolated; m.p. 140-147°. After a recrystallization this material melted at 147-150° and the melting point was not depressed on admixture with compound IV prepared by the aluminum chloride reaction.

(*e*) *Stannic chloride in carbon disulfide.* The acid chloride (from 3.00 g. of the acid and thionyl chloride) was heated with excess stannic chloride in refluxing carbon disulfide for 20 hr. In contrast to the reaction of 8-benzhydryl-1-naphthoyl chloride,[8] which rapidly produced an insoluble complex of the rearranged product, no heterogeneous phase was formed. Hydrolysis and conventional work-up afforded 1.37 g. (45%) of recovered 2-benzhydrylphenylacetic acid, 0.32 g. of compound V, and an oil which could not be separated by chromatography or crystallization. The infrared spectrum of the oil indicated the presence of compounds IV and V and the absence of any hydroxy compounds.

Reactions of 2-benzhydrylphenylacetic acid with mineral acids. (*a*) *Hydrogen fluoride.* A suspension of IIIa (1.99 g.) in 20 g. of liquid hydrogen fluoride was stirred for an hour at 0° and an hour at room temperature. The mixture was poured onto ice and processed in a conventional manner to yield 1.71 g. of recovered acid (m.p. 208-212°) and no other isolable products.

(*b*) *Sulfuric acid.* Compound IIIa (1.0 g.) was allowed to stand an hour in 25 ml. of concd. sulfuric acid (during which time it dissolved) and then poured onto ice. No organic material separated; all products were soluble in water. Similarly, only water-soluble products were obtained when 0.375 g. of ethyl 2-benzhydrylphenylacetate was allowed to stand for an hour at room temperature in concd. sulfuric acid. Only unchanged ester was recovered when a solution of 0.5 g. of the ethyl ester in 24.5 g. of sulfuric acid and 0.5 g. of water was allowed to stand 20 min. at 0°.

(*c*) *Polyphosphoric acid.* Acid IIIa (0.5 g.) was heated for 2 hr. with 20 g. of polyphosphoric acid[10] at 120-130°. The dark green mixture was then poured into water. Ether extraction and alkaline extraction of the ether solution yielded 0.37 g. of recovered acid. The neutral oil obtained from the ether layer amounted to 0.13 g. and showed carbonyl absorption at 5.7 and 6.0 μ, but no hydroxyl absorption.

---

(10) The polyphosphoric acid was kindly donated by the Victor Chemical Co.

Chromatography on silica gel failed to separate any solid products.

Reaction of 2-benzhydrylphenylacetic acid with acetic acid in polyphosphoric acid. (Compound VI). 2-Benzhydrylphenylacetic acid (1.00 g.) was added to a mixture of 25 ml. of acetic acid and 20 g. of polyphosphoric acid[10] and heated rapidly to 130°. The mixture was allowed to reflux at this temperature for 10 min., then acetic acid was removed by distillation at the rate of 1 ml. every 5 min. until 15 ml. of acetic acid had been collected. During this time the pot temperature rose to 160° and the mixture acquired a brown-black appearance. After an additional 5-min. period of refluxing the mixture was cooled and poured into water.

The organic suspension was taken up in ether and the ether solution extracted three times with 10% potassium carbonate. On acidification 0.103 g. (m.p. 205–211°) of the carboxylic acid (IIIa) was recovered. From the ether layer was obtained 0.672 g. of compound VI (58%), m.p. 225–230°, and 0.235 g. of an oil. This pyrone melted at 235–236° after recrystallizations from benzene and ethanol; infrared bands to 7 μ; 3.30, 6.03, 6.17, 6.22, 6.70, and 6.90 μ. The bands near 6 μ are characteristic of 4-pyrones.[7] The ultraviolet spectrum (in cyclohexane) showed a general decrease in absorption as the wave length increased, with plateaus centered at 242 mμ (ε 1.4 × 10^4) and 283 mμ (ε 8.1 × 10^3).

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.70; H, 5.15. Found: C, 85.82; H, 4.96.

Reaction of 2-benzhydrylphenylacetic acid with propionic acid in polyphosphoric acid (VIII). A mixture containing 3.00 g. of 2-benzhydrylphenylacetic acid, 50 ml. of propionic acid, and 30 g. of polyphosphoric acid was refluxed at 145° for 10 min. Propionic acid (35 ml.) was then withdrawn over a 2-hr. period, during which the temperature rose to 170°. The mixture was cooled and poured into water. Work-up as in the previous experiment yielded 1.40 g. of base soluble material (crude recovered III, m.p. 206–211°) and 0.40 g. of neutral product, VII, m.p. 190–195°. The analytical sample of VII, recrystallized from an ethyl acetate–ethanol mixture, melted at 197–198°. The infrared spectrum was markedly similar throughout to that for compound VI, with bands (to 7 μ) at 3.28, 3.38, 3.42, 6.04, 6.18, 6.23, 6.70, and 6.90 μ (note, however, the extra bands at 3.38 and 3.42 μ due to the increased number of aliphatic C—H). Likewise the ultraviolet spectrum of VII was very close throughout to that of VI; the plateau centers for VII occurred at 243 mμ (ε 1.4 × 10^4) and 285 mμ (ε 7.4 × 10^3).

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.71; H, 5.82. Found: C, 86.03; H, 5.80.

Reaction of 2-benzhydrylphenylacetic acid with chloroacetic acid and polyphosphoric acid (IX). A mixture of 2.00 g. of 2-benzhydrylphenylacetic acid, 15 g. of chloroacetic acid, and 20 g. of polyphosphoric acid was refluxed at 190° for 20 min. and then cooled and poured into water. Conventional work-up yielded 0.64 g. (27%) of the enol-chloroacetate, m.p. 176–183°. The analytical sample melted at 189–190° (from benzene); infrared spectrum: 5.70 μ (C=O), 6.08 (C=C), 6.22 μ, 6.70 μ and 6.90 μ; ultraviolet spectrum; $\lambda_{max}^{cyclohexane}$ 288 (ε 1.23 × 10^4). Both the infrared and ultraviolet spectra were quite similar to the spectrum of the enol-acetate of compound IV.

Anal. Calcd. for $C_{23}H_{17}ClO_2$: C, 76.55; H, 4.72. Found: C, 76.50; H, 4.83.

Enolacetate VIII. A mixture of 0.81 g. of compound IV, 0.5 g. of potassium acetate, and 15 ml. of acetic anhydride was heated at reflux for 8 hr. It was then poured into water and the oil taken up in ether and washed with potassium hydroxide solution. From the ether layer was obtained 0.893 g. (96%) of product, m.p. 172–174°. After recrystallization from ethanol–ethyl acetate it melted at 175°; infrared bands: 5.72 (C=O), 6.10 (C=C), 6.23, 6.72, and 6.95 μ; ultraviolet spectrum; $\lambda_{max}^{cyclohexane}$ 289 mμ (ε 1.28 × 10^4).

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.27; H, 5.58.

Miscellaneous experiments in acetic acid–polyphosphoric acid. Experimental conditions and procedures were the same as in the reaction of *o*-benzhydrylphenylacetic acid with acetic acid and polyphosphoric acid. In each case 1 g. of the aromatic compound was employed.

From ketone IV was obtained 0.905 g. (76%) of VI, m.p. 225–230°. The infrared spectrum was identical with that for VI prepared directly from III.

From a similar reaction with 1 g. of triphenylmethane was obtained only slightly impure triphenylmethane, 0.99 g., m.p. 82–87°; m.p. after recrystallization from ethanol, 92–94°. This experiment shows that acylation does not occur at the aromatic rings or the tertiary hydrogen under the conditions for which 2-benzhydrylphenylacetic acid and also ketone IV were converted to VI.

Alkaline cleavage of compound VI. (a) A solution of 50 ml. of ethylene glycol, 10 g. of potassium hydroxide, and 0.65 g. of compound VI was refluxed 4 hr., cooled, and poured into water. The precipitate weighed 0.50 g. (95%) and melted at 143–149°. Recrystallization afforded a sample, m.p. 150–151.5°, identical (infrared spectrum) with compound IV.

(b) A solution of 2.00 g. of compound VI and 1.25 g. of potassium hydroxide in 25 ml. of ethanol was refluxed for 4 hr. Most of the solution was then distilled through a Vigreux column into an ethanolic solution of 2,4-dinitrophenylhydrazine (300% excess). Fresh ethanol (15 ml.) was added to the alkaline solution to replace that which had been removed and the mixture refluxed an additional 20 hr. and again partially distilled into a dinitrophenylhydrazine solution. The acetone dinitrophenylhydrazine from the two distillations weighed 0.85 g. (60% yield based on 1 mole of acetone per mole of VII and melted at 124–126°). The infrared spectrum was identical with that of an authentic sample.

In a control run, identical with the above except that compound VI was omitted, no precipitate formed in the dinitrophenylhydrazine solution.

Reaction of compound VI with hydrazine hydrate. A solution containing 0.60 g. of compound VI, 5.0 ml. of 85% hydrazine hydrate, and 35 ml. of ethylene glycol was refluxed for 5 hr., cooled, and poured into 100 ml. of water. An ether extract of this mixture was washed with dilute hydrochloric acid, dried, and evaporated to give 0.58 g. of a solid derivative; m.p. 245–257°; after recrystallization from ethanol the pale yellow product melted with decomposition (rapid heating) at 261–264°; infrared bands: 2.90, 3.30, 6.18, 6.22, 6.70, 6.91, 7.12 μ.

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.45; H, 5.50; N, 7.70. Found: C, 81.96; H, 5.52; N, 8.09.

The analysis indicates that an oxygen in VI has been replaced by NNH_2. The derivative was not further characterized, however, an *N*-amino-4-pyridone structure appears plausible.

Oxidation of compound VI. Compound VI (1.00 g.) was heated with 3 g. of potassium permanganate and 5 g. of potassium hydroxide in 100 ml. of water at reflux for 5 hr. After cooling and acidification, sodium bisulfite was added to reduce excess permanganate and the organic products were extracted with ether. The ether-soluble portion gave on fractional crystallization two fractions; *A*, 0.50 g., m.p. 210–215°, and *B*, 0.3 g., m.p. 197–198°.

Substance *A* melted sharply at 215.5–216° after two recrystallizations from ethanol. The infrared spectrum showed hydroxyl (2.95 μ) and carbonyl (6.05 μ) groups. With sulfuric acid *A* gave a deep purple color, indicative of a hydroxyanthrone. Substance *A* was shown to be *10-hydroxy-10-phenylanthrone* by a mixture melting point with an authentic sample and by the identity of the infrared spectrum with the spectrum of the authentic sample.

Spectral data indicated that fraction *B* was a mixture of 10-hydroxy-10-phenylanthrone and the starting material (VI), and indeed, 0.062 g. of 10-hydroxy-10-phenylanthrone was isolated from a reaction of 0.10 g. of *B* with excess hydrazine hydrate in ethylene glycol. After the reaction mixture had refluxed for 70 hr. it was cooled, diluted with water, and extracted with ether. Recrystallization of the residue left from evaporation of the ether afforded the anthrone. The yield of anthrone from *A* was 61%; with the added material from *B* the total yield amounted to 84%.

For comparison purposes 10-hydroxy-10-phenylanthrone was prepared by oxidation of 9-phenylanthracene by the procedure of Baeyer.[11] The purified product melted at 215–216° and gave a purple color with sulfuric acid as reported.[11] Baeyer reported a m.p. of 208°; Barnett and Cook,[12] a m.p. of 214°.

The 9-phenylanthracene was obtained by heating for 70 hr. 15 g. of 3,3-diphenylnaphthalide, 2.5 g. of red phosphorus, 50 g. of hydriodic acid, and sufficient acetic acid to give a homogeneous solution. Two recrystallizations of the organic product gave 5.0 g. (37%) of 9-phenylanthracene; m.p. 152–153°; lit. m.p. 152–153°.[11] The ultraviolet spectrum showed five peaks, as reported for 9-phenylanthracene: $\lambda_{max}^{ethanol}$ 2540 (log ϵ 5.16); 3295 (3.55); 3463 (3.90); 3638 (4.11); 3825 (4.07); reported[13]: λ_{max} 2555 (5.16); 3305 (3.56); 3465 (3.90); 3645 (4.10), and 3840 (4.08). Baeyer prepared 9-phenylanthracene by reduction of 3,3-diphenylphthalide with zinc dust in acid.[11]

Oxidation of ketone IV to anthrone X. Ketone IV (0.200 g.) was heated with a solution of 0.75 g. of potassium permanganate and 1.25 g. of potassium hydroxide in 25 ml. of water for 3.5 hr. at reflux. Dilution with water, acidification, treatment with sodium bisulfite, ether extraction, and recrystallization gave 0.10 g. (50%) of 10-hydroxy-10-phenylanthrone (identified by mixture m.p. and infrared spectrum); m.p. 213–216°.

EVANSTON, ILL.

---

[11] A. Baeyer, *Ann.*, **202**, 58 (1880).

[12] E. B. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2638 (1923).

[13] E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **74**, 6235 (1952).

[CONTRIBUTION FROM THE VERONA RESEARCH CENTER OF KOPPERS CO., INC.]

The Reduction of the Carbazole Nucleus. Some Derivatives of Hydrocarbazoles[1]

HANS DRESSLER AND MELVIN E. BAUM

Received May 16, 1960

Improved methods for the preparation of tetrahydrocarbazole and dodecahydrocarbazole in high yields by the catalytic hydrogenation of carbazole are described. 3-Amino-1,2,3,4-tetrahydrocarbazole and 3-amino-9-methyldodecahydrocarbazole were made by the hydrogenation of the appropriate aminocarbazoles. The reduction of carbazole with lithium in *n*-propylamine gave a 90% yield of 1,2,3,4-tetrahydrocarbazole. The latter was resistant to further reduction by this reagent, as was 1,2,3,4,10,11-*cis*-hexahydrocarbazole. 9-Methylcarbazole was reduced by lithium in *n*-propylamine to 9-methyl-1,2,3,4,10,11-hexahydrocarbazole in 71% yield. A number of new derivatives of the hydrocarbazoles, such as the pyridylethylation products, are described.

In the past, the reduction of the carbazole nucleus by chemical agents or by catalytic hydrogenation has been difficult. Thus, compared with aromatic compounds and certain other nitrogen heterocyclics such as acridine, indole, and phenylpyrrole, carbazole is much more resistant to catalytic hydrogenation. The first report[2] of the catalytic hydrogenation of carbazole claimed the formation of 2,3-diethylindole as the main product. However, none of the subsequent investigators were able to substantiate this claim. von Braun and Ritter[3] were actually unable to hydrogenate purified carbazole in the presence of a nickel catalyst at 260° and 450 p.s.i.g., and obtained only fair yields of 9-methyl-1,2,3,4-tetrahydrocarbazole and 1,2,3,4,5,6,7,8-octahydro-9-methylcarbazole from 9-methylcarbazole. The perhydrogenation of carbazole in an organic solvent at 160–220° and 590–1200 p.s.i.g., using a nickel catalyst, was reported in a 1930 German patent[4] with little detail. The best data were obtained by Adkins and Coonradt[5] who hydrogenated carbazole in the presence of Raney nickel at 230° to obtain an 87% yield of dodecahydrocarbazole; when they used a copper chromite catalyst under these conditions, a 72% yield of 1,2,3,4-tetrahydrocarbazole was obtained. However, this procedure required rather high pressures (of 3600–4400 p.s.i.g.) and highly purified materials.

Prior work on the chemical reduction of carbazole was limited to the sodium-alcohol system. In 1907, the preparation of 1,4-dihydrocarbazole from carbazole by this reagent was reported.[6] Later it was shown that the product of this reaction is a mixture containing at least 50% of carbazole, tetrahydrocarbazole, plus unknowns.[7] Surprisingly, a 1950 publication again claimed the isolation of 1,4-dihydrocarbazole from this mixture.[8] 1,2,3,4-Tetrahydrocarbazole can indeed be prepared in fair

---

[1] Based upon a paper presented at the 137th National Meeting of the American Chemical Society, Cleveland, April 1960.

[2] M. Padoa and C. Chiaves, *Atti reale accad. Lincei*, **16**, 762 (1908); *Gazz. chim. ital.*, **38**, 236 (1903).

[3] J. v. Braun and H. Ritter, *Ber.*, **55**, 3792 (1922).

[4] German pat. **514,822** (1930).

[5] H. Adkins and H. L. Coonradt, *J. Am. Chem. Soc.*, **63**, 1563 (1941).

[6] J. Schmidt and R. Schall, *Ber.*, **40**, 3225 (1907).

[7] B. M. Barclay, N. Campbell, and R. S. Gow, *J. Chem. Soc.*, 997 (1946).

[8] G. Sanna, *Gazz. chim. ital.*, **80**, 572 (1950).