was removed by distillation and the remaining brown liquid heated with a free flame, under atmospheric pressure, until it distilled. Decomposition accompanied the distillation of a yellow oil which came over at 130–140°. The yield of this oil amounted to 0.25 g. and it was shown to be acetylacetone by its conversion to 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole, m. p. 121–122°, and the comparison of this derivative with an authentic specimen.[19] The 0.25 g. yield of this diketone indicates that the trimer fraction contained at least 50% of the straight chain trimer VIII.

The boiling point of the trimer fraction as well as its content of 1,3,5-triethoxybenzene remained unchanged after a sample of this fraction had been heated at 180° under atmospheric pressure for two hours.

Summary

1. Evidence is presented to show that ketene acetal is converted by cadmium chloride into a white polymer composed of chains having, on an average, 22–23 ketene acetal molecules joined in a head to tail manner. The insolubility of the polymer suggests cross-linking of these chains.

2. The white polymer is converted by acid hydrolysis into an alkali soluble red polymer composed of cross-linked poly-1,3-diketone units which exist in a highly conjugated, enolic form. Molecular weight estimation of this polymer from an end group corresponds fairly well with a similar estimation of the molecular weight of the white polymer.

3. Rapid polymerization of ketene acetal by larger amounts of cadmium chloride produces an open chain dimer and trimer together with 1,3,5-triethoxybenzene. The latter product probably is formed from the cyclic trimer, 1,1,3,3,5,5-hexaethoxycyclohexane.

4. Halogenated ketene acetals cannot be caused to polymerize.

5. An improved method for the preparation of ketene acetal from bromo-acetal is described.

6. The construction and operation of a new apparatus for the determination of the ethoxyl content of the types of acetals encountered in this work are described.

(19) Brady, *J. Chem. Soc.*, 758 (1931).

MADISON, WISCONSIN RECEIVED FEBRUARY 23, 1940

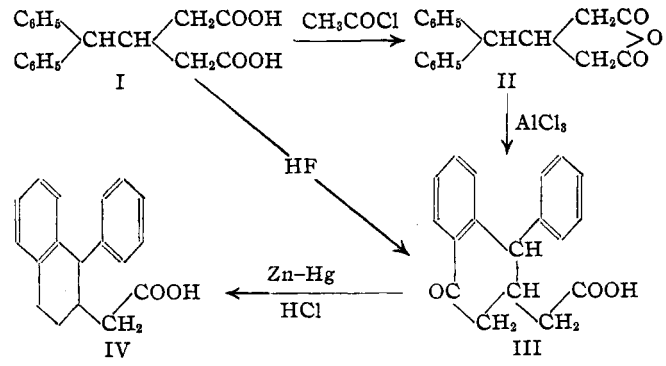
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 2-Methyl-3,4-benzphenanthrene

BY MELVIN S. NEWMAN[1] AND LLOYD M. JOSHEL[2]

Because of the interest in 3,4-benzophenanthrene as a structure possessed of carcinogenic activity, the previously reported synthesis[3] has been modified so that 2-substituted derivatives may be prepared. In this paper is described the synthesis of 2-methyl-3,4-benzphenanthrene[4] and 2-ethyl-3,4-benzphenanthrene.

In the earlier synthesis,[3] β-benzohydrylglutaric acid, I, after conversion to its acid chloride, was cyclized to 1,2,9,10,11,12-hexahydro - 2,9 - diketo - 3,4 - benzphenanthrene from which 2,9-disubstituted derivatives were prepared. The present modification consists in treating the anhydride, II, of β-benzohydrylglutaric acid with aluminum chloride whereby 1,2,3,4-tetrahydro-4-keto-1-phenyl-2-naphthaleneacetic acid, III, was isolated in 63% yield. The same keto-acid was obtained more easily in 89% yield by treatment of the acid, I, with anhydrous hydrogen fluoride.[5] By reduction III was converted into 1,2,3,4-tetrahydro-1-phenyl-2-naphthaleneacetic acid, IV.[4]



The remaining steps required for the synthesis of 2-methyl-3,4-benzphenanthrene and 2-ethyl-

(1) The Elizabeth Clay Howald Scholar at The Ohio State University, 1939–1040.

(2) This material was largely contained in a Dissertation presented by L. M. J. to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, June, 1938. Completing experiments were conducted by L. M. J. at Harvard University under tenure of a Finney-Howell Research Fellowship.

(3) Newman and Joshel, THIS JOURNAL, **60**, 485 (1938).

(4) Hewett, *J. Chem. Soc.*, 596 (1936).

(5) Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).

3,4-benzphenanthrene are similar to those carried out by Hewett.[4]

In conclusion it seems of interest to point out that while 2-methyl-3,4-benzphenanthrene is a very potent carcinogenic agent when tested by painting on the skin,[6] it has proved to be only very slightly active when tested by the injection technique.[7] This finding serves to emphasize the differences in carcinogenic activity of hydrocarbons when estimated by the painting technique as compared to the injection technique. The present instance is one in which the compound is less active when tested by injection whereas in the case of 10-methyl-1,2-benzanthracene,[8] the activity measured by injection was greater than that measured by painting.[9] The following 3,4-benzphenanthrene derivatives have proved inactive when tested by injection[7]: 2,9-dimethyl-[8], 2,9-diethyl-[8], 6,7-dimethyl-[10] and 2-isopropyl-8-methyl-.[11]

Experimental[12]

β-Benzohydrylglutaric Acid, I.—After considerable experimentation the following procedure was found to yield the most consistent results. A solution of 50 g. of diphenylacetaldehyde in 150 cc. of ethyl cyanoacetate was treated with 5 cc. of diethylamine and allowed to stand in a stoppered flask for twelve hours at room temperature. The mixture was then heated for twelve hours on the steam-bath with the further addition of two 5-cc. portions of diethylamine. The resulting cloudy suspension was refluxed for sixty-two hours with a solution of 125 cc. each of water and concentrated sulfuric acid in 350 cc. of acetic acid. The organic acid fraction thus produced was isolated, decarboxylated by heating to 200°, and esterified with methanol and dry hydrogen chloride. A portion of the ester fraction, b. p. about 180° at 2 mm. was crystallized from aqueous methanol yielding colorless needles, m. p. 73.4–74.2°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.91; H, 6.90.

The remaining ester was saponified and 13.4 g. (17.6%) of acid, I, m. p. 172–175°, suitable for use in the next step, was obtained. The pure acid melted at 177.6–178.2°.[3]

1,2,3,4 - Tetrahydro - 4 - keto - 1 - phenyl - 2 - naphthaleneacetic Acid, III.—Twelve grams of the above acid was treated in a metal flask with 150 g. of anhydrous hydrogen fluoride[5] for nine hours at room temperature. The solution was poured on ice and the solids collected. The filtered carbonate extract of this material was acidified and the acid crystallized from benzene–ligroin to yield 9.3 g. of colorless needles, m. p. 115.4–116.2°, and 0.7 g., m. p. 113.0–114.5° (total 89%). The sample for analysis was crystallized from benzene and melted, after thorough heating *in vacuo*, at 115.4–116.2°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75; neut. equiv., 280. Found: C, 77.43; H, 5.84; neut. equiv., 279.

The same acid was prepared in 63% yield from β-benzohydrylglutaric anhydride[3] using aluminum chloride in *sym*-tetrachloroethane solution.

1,2,9,10,11,12 - Hexahydro - 2 - keto - 3,4 - benzphenanthrene.—This compound was prepared either by Hewett's method[4] using *sym*-tetrachloroethane as solvent or by the use of anhydrous hydrogen fluoride,[5] the latter offering no advantage over the former.

1,2,3,4 - Tetrahydro - 1 - phenyl - 2 - naphthaleneacetic Acid, IV.—The keto acid, III, was converted in 74% yield into IV using Martin's modification of the Clemmensen reduction. Our purest sample melted at 140.2–140.8° (lit.[4] 138–139°).

2-Methyl-3,4-benzphenanthrene.—A solution of 1.9 g. of the above ketone in dry benzene was refluxed with an ether solution of methylmagnesium chloride for two and one-half hours. The crude alcohol was heated with 0.2 g. of palladium charcoal[13] for two hours at 290–320° (77% of the theoretical hydrogen collected). By crystallization of the picrate followed by chromatographic adsorption on alumina, there was isolated 1.11 g. (60%) of 2-methyl-3,4-benzphenanthrene, m. p. 69.6–71.0°. The hydrocarbon was recrystallized from benzene–methanol, separating as almost colorless needles, m. p. 70.4–71.0° (lit.[4] leaflets, m. p. 69.5–70.0°). The picrate formed bright orange-red needles, m. p. 141.8–143.2°, from benzene–alcohol.

Anal. Calcd. for $C_{25}H_{17}O_6N_3$: C, 65.93; H, 3.76; N, 9.23. Found: C, 66.11; H, 3.99; N, 9.35.

2-Ethyl-3,4-benzphenanthrene.—A benzene solution of 1.0 g. of 1,2,9,10,11,12-hexahydro-2-keto-3,4-benzphenanthrene was refluxed with an excess of ethylmagnesium bromide, the alcohol thus produced dehydrated by heating with a crystal of iodine, and the tetrahydro derivative aromaticized by heating with 0.26 g. of sulfur at 230° for forty minutes. The distilled crude hydrocarbon was treated with 1 g. of picric acid in benzene–alcohol. A total of 1.00 g. (51%) of picrate, m. p. 78.4–80.0°, was obtained. A portion recrystallized for analysis melted at 80.0–81.0°.

Anal. Calcd. for $C_{26}H_{19}O_7N_3$: C, 64.33; H, 3.95; N, 8.66. Found: C, 64.31; H, 3.78; N, 8.38.

By chromatographic adsorption on alumina, the hydrocarbon was obtained and distilled. Considerable difficulty in crystallization was encountered but by cooling a methanol solution with solid carbon dioxide, seed crystals were obtained. **2-Ethyl-3,4-benzphenanthrene** crystallized from alcohol in colorless needles, m. p. 50.4–51.2°, and had a blue-violet fluorescence in ultraviolet light.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.57; H, 6.16.

(6) Bachmann, Cook, *et al.*, *Proc. Roy. Soc.*, **B123**, 343 (1937).

(7) Private communication from Dr. M. J. Shear.

(8) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).

(9) Shear, *Am. J. Cancer*, **33**, 510 (1938). See also Cook, Robinson and Goulden, *J. Chem. Soc.*, 393 (1937), and reference 6.

(10) Fieser, Fieser and Hershberg, THIS JOURNAL, **58**, 1463 (1936).

(11) Private communication from Professor M. T. Bogert. See Adelson and Bogert, *ibid.*, **59**, 1776 (1937).

(12) All melting points corrected. The authors are indebted to H. S. Clark and J. H. Walker for analyses and to O. Woolfolk for the preparation of a quantity of pure diphenylacetaldehyde. The assistance of Messrs. Walker and Woolfolk was made possible through the Ohio State W. P. A. project No. 65-1-42-89.

(13) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

The *sym*-**trinitrobenzene derivative** formed yellow-orange needles from benzene–alcohol, m. p. 105.6–106.6°.

Anal. Calcd. for $C_{26}H_{19}O_6N_3$: C, 66.52; H, 4.08; N, 8.95. Found: C, 66.37; H, 3.77; N, 9.19.

Summary

The preparation of 1,2,3,4-tetrahydro-4-keto-1-phenyl-2-naphthaleneacetic acid by ring closure of β-benzohydrylglutaric anhydride using aluminum chloride or by direct cyclization of β-benzohydrylglutaric acid using anhydrous hydrogen fluoride is described. The keto group of this keto acid was reduced by the Clemmensen method and the reduced acid cyclized to 1,2,9,10,-11,12-hexahydro-2-keto-3,4-benzphenanthrene. By reaction with the appropriate Grignard reagents followed by dehydration and dehydrogenation 2-methyl-3,4-benzphenanthrene and 2-ethyl-3,4-benzphenanthrene were prepared from the above hexahydroketone.

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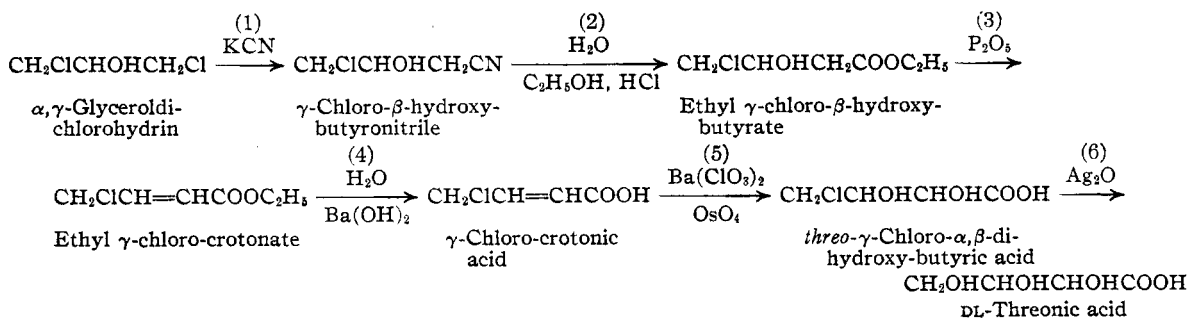
[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

Improvements in the Preparation of DL-Threonic and DL-Erythronic Acids

BY J. W. E. GLATTFELD AND EDWARD RIETZ[1]

The reason for the interest in the two acids mentioned in the title of this article has been recorded several times.[2,3] Briefly, the acids are possible sources of the DL-aldotetroses. These are needed for a proposed study of the saccharinic acid rearrangement of the tetroses which it is hoped to make in these laboratories. Because of the availability of DL-erythronic lactone, definite progress has been made in devising a procedure for its transformation into DL-erythrose.[2] The difficulty of the preparation of DL-threonic acid, however, has prevented corresponding progress with this substance. The main object of the work reported below, therefore, was the simplification and improvement of the known procedure for the preparation of DL-threonic acid.[4] Incidentally, the method of preparation of DL-erythronic lactone was also much improved by the use of vinylacetic acid, an intermediate in the preparation of DL-threonic acid.

DL-Threonic Acid.—The only recorded synthesis of DL-threonic acid is that of Braun.[4b,c]



This process was carried out several times, but great difficulty was experienced at first in inducing the DL-threonic acid sirup to crystallize. The acid is converted into the lactone much more readily, apparently, than Braun's paper[4b] would indicate. To succeed in crystallizing the sirup obtained by concentration of a water solution of the acid, the evaporation must be discontinued before all of the water is removed, that is, while the residue is still a *thin* sirup. If the evaporation is continued at 40° and 2 mm. for four hours after nearly all of the water has been removed, as Braun recommends, the residue will be largely lactone and will not crystallize. That the acid is converted into lactone was demonstrated by the subjection of a sample of crystalline acid to distillation at 3 mm. The distillate, which titration indicated consisted of 87% lactone and 13% free acid, could not be induced to crystallize even when seeded with crystals of DL-threonic acid.

After having succeeded in producing crystalline acid by Braun's procedure, attention was turned

(1) This article is condensed from a dissertation presented by Edward Rietz in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Glattfeld and Kribben, THIS JOURNAL, **61**, 1720 (1939).

(3) Glattfeld and Lee, *ibid.*, **62**, 354 (1940).

(4) Géza Braun, *ibid.*, **52**, (a) 3167, (b) 3176 (1930), (c) **54**, 1133 (1932).