B. *With 2-hydroxy-2-(α-chlorobenzyl)-4,4-dimethyl-1-tetralone* (VII). With 2.5 mg. of VII/ml. in a 5 mm. cell, γ_{OH}, 3545/20 and 3490/20; $\gamma_{C=O}$, 1696/70 and 1682/65; with 10 mg./ml. in a 1.0 mm. cell with sodium chloride optics, γ_{OH}, 3550/20 and 3500/23, $\gamma_{C=O}$, 1695–1683/80.

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LINCOLN, NEB.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

An Indone to Naphthol Ring Expansion

C. F. KOELSCH

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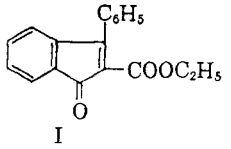
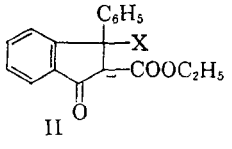
2-Carbethoxy-3-phenylindone (I) adds phenacyl chloride in a Michael reaction, and the resulting anion at once eliminates chloride forming a cyclopropane (III). This product is attacked further by bases, which cause it to rearrange into a naphthol (IV).

After 2-carbethoxy-3-phenylindone (I) was found to add certain anions forming II,[1] it became of interest to alkylate the products, but all attempts to do this failed. In explanation it may be noted first that anions II are weakly basic, the corresponding acids dissolving in carbonate, and second that C_2 in II is flanked by bulky groups on C_3, and it is well known that analogous mono-*tert*-alkylated malonic or acetoacetic esters are resistant to alkylation.

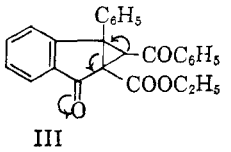


I

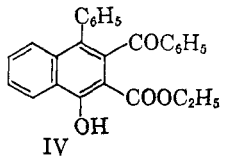


II

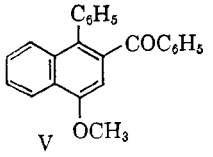
These inhibiting effects would be less important in an intramolecular reaction, and accordingly conditions were arranged so that a Michael reaction leading to II could be followed by an intramolecular alkylation. This was done by treating I with phenacyl chloride. In accordance with expectation, the cyclopropane III was formed smoothly.



III



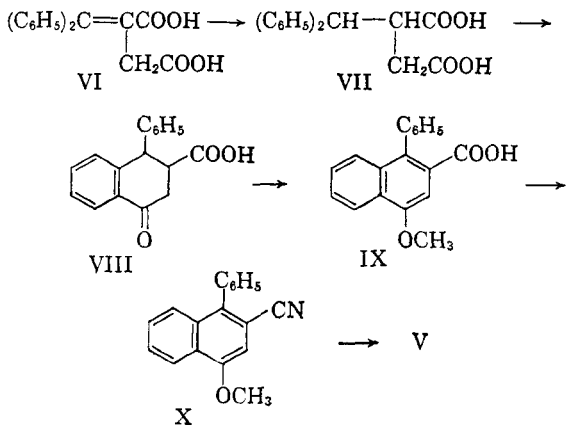
IV



V

Compound III was found to be quite sensitive to alkali. Although it could be isolated in good yield when proper conditions prevailed, use of excess base in the Michael reaction or treatment of isolated III with base led to formation of IV. The mechanism for the isomerization is indicated by arrows in formula III, and it is seen that the process is analogous to one studied recently by Wawzonek and Morreal.[2]

Structure IV for the rearrangement product was confirmed; hydrolysis, decarboxylation and methylation yielded V, and this substance was synthesized by the route indicated in formulas VI–X.



Diphenylitaconic acid (VI) was reduced by use of Raney alloy and sodium hydroxide[3] as recommended by Drake and Tuemmler[4] but the product was found to be not VII, but an aluminum complex of this acid, a fact which accounts for the low yield obtained by Drake and Tuemmler in their further use of the substance. The complex was remarkably stable; its clear solution in dilute bicarbonate deposited it unchanged on acidification; it was boiled with concentrated hydrochloric acid without change and it crystallized as described from ethyl acetate-benzene. Isolation of VII from the complex was accomplished by esterification (methanol-sulfuric acid) followed by saponification, or better by precipitation of the barium salt of VII directly from

(1) C. F. Koelsch, *J. Org. Chem.*, 25, 2088 (1960).

(2) S. Wawzonek and C. E. Morreal, *J. Am. Chem. Soc.*, 82, 439 (1960).

(3) D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, 7, 587 (1942).

(4) N. L. Drake and W. B. Tuemmler, *J. Am. Chem. Soc.*, 77, 1209 (1955).

the reduction mixture, the barium salt being subsequently freed of barium with hydrochloric acid.

EXPERIMENTAL

Compound III. A mixture of 2.5 g. of ethyl 3-phenylindone-2-carboxylate, 1.5 g. of phenacyl chloride and 12 ml. of *tert*-butyl alcohol was warmed, then cooled rapidly to 25° to give a fine suspension and treated with 0.75 g. of 85% potassium hydroxide in 1.5 ml. of water. After the mixture had been shaken for 15 min., it was evaporated at 95° under reduced pressure and then taken up in water and ether. The ether solution was washed with 5% sodium carbonate, then mixed with ligroin, giving 2.6 of nearly pure *ethyl 1-benzoyl-2-oxo-6b-phenyl-1a,6b-dihydrocycloprop[b]indene-1a-carboxylate*, III, colorless flat needles from dilute alcohol, m.p. 115–116°. The compound was insoluble in 10% sodium hydroxide and gave no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.09. Found: C, 79.0; H, 5.21.

Compound IV. When 2.6 g. of III was added to a solution of 0.17 g. of sodium in 5 ml. of absolute alcohol, a deep yellow solution resulted that soon set to a solid crystalline magma. The mixture was heated for 15 min. on a water bath, then neutralized with acetic acid and taken up in water and ether. Crystallization from alcohol gave 2.4 g. of *ethyl 3-benzoyl-1-hydroxy-4-phenyl-2-naphthoate*, IV, faintly tan prisms, m.p. 120–121°. The compound gave a deep blue color with alcoholic ferric chloride; its yellow sodium salt was somewhat soluble in water.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.09. Found: C, 78.7; H, 5.11.

Saponification by boiling IV with excess 5% sodium hydroxide for 1 hr. gave *3-benzoyl-1-hydroxy-4-phenyl-2-naphthoic acid* in quantitative yield, nearly colorless needles from dilute acetic acid that sintered at 195° and melted at 215–217° with effervescence; alcoholic ferric chloride gave a deep green color that became blue on addition of water.

Anal. Calcd. for $C_{24}H_{16}O_4$: C, 78.2; H, 4.38. Found: C, 77.7; H, 4.47.

Compound V. When 0.4 g. of the above acid was heated at 220° for 5 min. it was converted into *3-benzoyl-4-phenyl-1-naphthol*, V, faintly yellow prisms from toluene, m.p. 226° with previous sintering. The sodium salt was bright yellow, difficultly soluble in cold water.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.2; H, 4.97. Found: C, 85.0; H, 5.01.

Methylation of the phenol was effected with methyl sulfate in 5% aqueous sodium hydroxide; the resulting *3-benzoyl-1-methoxy-4-phenylnaphthalene* formed coarse colorless plates from alcohol, m.p. 148–149°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.36. Found: C, 85.0; H, 5.37.

Compound VII. A solution of 15 g. of diphenylitaconic acid in 450 ml. of hot 10% sodium hydroxide was treated with 30 g. of Raney alloy in portions, then boiled for 30 min. and filtered. Addition of a concentrated solution of 20 g. of barium chloride dihydrate in hot water gave an easily filterable precipitate of the barium salt, less soluble in hot than cold water. This was removed and boiled for 15 min. with 150 ml. of water containing 25 ml. of hydrochloric acid. Cooling gave 14.9 g. of pure benzhydrylsuccinic acid, needles m.p. 180–183°; the product gave no color with concd. sulfuric acid (unreduced diphenylitaconic acid gives a deep green).

The aluminum complex which resulted when the reduction mixture from 10 g. of diphenylitaconic acid was poured into excess hot hydrochloric acid was dried and boiled for 1 hr. with 50 ml. of methanol containing 5 ml. of sulfuric acid. Water and ether were added, and the ether solution was extracted with dilute sodium carbonate. This gave 5.8 g. of *methyl hydrogen benzhydrylsuccinate*, needles from ethyl acetate-ligroin, m.p. 150–152°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.08. Found: C, 72.3; H, 6.11.

Methyl benzhydrylsuccinate remained in the ether, and separated from 60–68° ligroin (b.p. 60–68°) in the form of prisms (3.0 g.), m.p. 84–85°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.1; H, 6.45. Found: C, 73.2; H, 6.70.

Saponification of both the acid ester and the neutral ester gave benzhydrylsuccinic acid.

Cyclization of 8.4 g. of benzhydrylsuccinic acid by the method of Hewitt[5] gave 7.3 g. of crude 1-phenyl-4-oxo-1,2,3,-4-tetrahydro-2-naphthoic acid (VIII), and when this was boiled for 1 hr. with 35 ml. of methanol containing 3 ml. of sulfuric acid it gave 4.5 g. of pure *methyl ester*, coarse needles from methanol, m.p. 115–117°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.75. Found: C, 77.1; H, 5.77.

Compound IX. When a solution of 4.5 g. of the preceding ester in 10 ml. of benzene was treated with 2.6 g. of bromine, rapid reaction took place with evolution of hydrogen bromide. The solvent was removed and the crystalline residue was taken up in 30 ml. of collidine and boiled for 4 min. Collidine was then removed with dilute hydrochloric acid and the resulting *methyl 4-hydroxy-1-phenyl-2-naphthoate* was crystallized from methanol, giving 3.8 g. of hexagonal plates, m.p. 173–174°,[6] that fell to a powder on drying.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.07. Found: C, 77.7; H, 5.18.

Methylation of the above ester with excess methyl sulfate in aqueous alkali gave *methyl 4-methoxy-1-phenyl-2-naphthoate*, colorless needles from 80% acetic acid, m.p. 118–119°; yield 86%.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.0; H, 5.52. Found: C, 77.6; H, 5.48.

A solution of 1.5 g. of the methoxy ester and 0.7 g. of sodium hydroxide in 6 ml. of glycol was boiled for 1 min., then diluted with water and acidified. The resulting *4-methoxy-1-phenyl-2-naphthoic acid*, IX, formed colorless prisms from acetic acid, m.p. 217–219°; yield 1.4 g.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.07. Found: C, 77.9; H, 5.18.

Compound. X. When a suspension of 1.4 g. of the methoxy acid in 5 ml. of benzene containing 1.2 ml. of thionyl chloride was boiled for 5 min., a clear solution resulted. Benzene and excess thionyl chloride were then removed at 100° under reduced pressure, and the remaining crystalline acid chloride was redissolved in 10 ml. of benzene and shaken with 10 ml. of concd. ammonium hydroxide for 10 min. The product was removed by filtration and recrystallized from alcohol giving 1.35 g. of *4-methoxy-1-phenyl-2-naphthamide*, colorless needles, m.p. 210–212°.

Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 78.0; H, 5.45. Found: C, 77.8; H, 5.38.

The amide dissolved when it was boiled with thionyl chloride in benzene, but subsequent addition of water gave it back unchanged. In order to prepare *4-methoxy-1-phenyl-2-naphthonitrile* X, 1.1 g. of the amide was boiled with 5 ml. of phosphorus oxychloride for 10 min. Volatile materials were then removed at 100° under reduced pressure, and the residue was treated with water and benzene. A small amount of black amorphous substance was removed by filtration, and the product was crystallized from acetic acid, giving pink needles, m.p. 162°; yield 1 g.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.4; H, 5.05. Found: C, 83.2; H, 5.12.

A solution of 0.9 g. of the nitrile in 5 ml. of benzene was added to ethereal phenylmagnesium bromide prepared from 0.5 g. of magnesium. No apparent reaction took place, but after the mixture had been boiled for 30 min. a dense white precipitate formed. The mixture was then shaken with iced

(5) C. L. Hewitt, *J. Chem. Soc.*, 596 (1936).

(6) Reported m.p. 174–175°, Borsche and Kettner, *Ann.*, 526, 1 (1936).

hydrochloric acid, and the resulting *4-methoxy-1-phenyl-2-naphthylphenylketimine hydrochloride* was removed by filtration. To remove bromide anion, the salt was dissolved in alcohol and made basic with ammonium hydroxide. Addition of water then gave a colorless oil which was taken up in ether and reconverted to the hydrochloride by shaking with dilute hydrochloric acid. The salt was nearly insoluble in hot water, ethyl acetate, or benzene. It was easily soluble in chloroform and crystallized from a mixture of methanol and ether as deep yellow prisms, m.p. 235–240°; yield 1 g.

Anal. Calcd. for $C_{24}H_{20}ClNO + CH_3OH$: C, 74.0; H, 5.92. Found: C, 74.11; H, 5.37.

The ketimine salt was quite resistant to hydrolysis, but when 0.6 g. of it was boiled for 15 min. with 5 ml. of 50% acetic acid containing a few drops of hydrochloric acid, it gave 0.5 g. of 3-benzoyl-1-methoxy-4-phenylnaphthalene, identical (mixed melting point and infrared spectrum) with the compound obtained before.

Acknowledgment. The author thanks Mrs. O. Hamerston for analytical results.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Cleavage of 10-Substituted 1,2-Benzanthracenes[1-3]

FRANK A. VINGIELLO AND THOMAS J. DELIA

Received August 17, 1960

The acid-catalyzed cleavage of 10-substituted 1,2-benzanthracenes has been observed and investigated.

Since a recent publication[4] noted the physiological activity of 10-phenyl-1,2-benzanthracene, and since 10-methyl-1,2-benzanthracene is a carcinogen, we thought it would be interesting to prepare 10-cyclohexyl-1,2-benzanthracene and have it screened for possible carcinogenic or carcinolytic activity. In view of the extensive use made of aromatic cyclodehydration reactions to prepare *meso*-substituted 1,2-benzanthracenes,[5] we chose to attempt the preparation of 10-cyclohexyl-1,2-benzanthracene (IIa) *via* the aromatic cyclodehydration of 2-(1-naphthylmethyl)phenyl cyclohexyl ketone (Ia). This ketone was prepared by the Grignard reaction between cyclohexylmagnesium bromide and 2-(1-naphthylmethyl)benzonitrile[6] followed by acid hydrolysis.[7] The first attempts at cyclization of the ketone involved the use of the often used boiling hydrobromic–acetic acid mixture. Although 14% of the expected 10-cyclohexyl-1,2-benzanthracene (IIa) was obtained, 32% of 1,2-benzanthracene (III) was also isolated. Apparently cleavage of the cyclohexyl group occurred during the course of the reaction. We also observed cleavage in the anthracene series. The acid-catalyzed cyclization of 2-benzylphenyl cyclohexyl ketone gave 29% of the expected hydrocarbon, 9-cyclohexylanthracene, and 23% of anthracene. Several instances of the loss of aromatic groups had been observed previously in this laboratory. Vingiello and Borkovec[8] reported cleavage during the attempted preparation of some di-*ortho* substituted *meso* phenyl-1,2-benzanthracenes and Vingiello and Stevens[4] reported loss of a methoxyphenyl group when 2-(1-naphthylmethyl)-4′-methoxy benzophenone or 2-(1-naphthylmethyl)-2′-methoxy diphenyl ketimine hydrochloride was treated with a strong acid. In either case, 1,2-benzanthracene was the only product isolated. Just recently Zajac[9] observed cleavage during the acid-catalyzed cyclization of 2-(2-naphthylmethyl)-2′-chloro-5′-methylbenzophenone which gave 1,2-benzanthracene. Bradsher and co-workers[10] reported the loss of an isopropyl group during the acid-catalyzed cyclization of ketones to give 9,10-dialkylphenanthrenes. They also showed that an olefin oxide which might be expected to yield 9-isopropyl-10-isobutylphenanthrene afforded instead 9-isobutylphenanthrene. They suggested that the loss of the isopropyl group in 9-isopropyl-10-alkylphenanthrenes was probably due to the strain introduced by crowding the two groups into the rather restricted space at the 9- and 10-positions. Our observations in

(1) This paper has been abstracted in part from the Master's thesis of Thomas J. Delia presented to the Virginia Polytechnic Institute in 1959.

(2) This investigation was supported in part by a research grant (S-73) from the Bureau of State Services (Division of Sanitary Engineering Services and Division of Special Health Services) of the National Institutes of Health, Public Health Service.

(3) Presented before the Chemistry Section at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., November 1960.

(4) F. A. Vingiello and R. K. Stevens, *J. Am. Chem. Soc.*, 80, 5256 (1958).

(5) See F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, 78, 1240 (1956), and references listed there.

(6) F. A. Vingiello, A. Borkovec, and J. Shulman, *J. Am. Chem. Soc.*, 77, 2320 (1955).

(7) Again it was found that the yield of the ketone was 15–20% higher if the ketimine hydrochloride was not isolated; see Ref. 5.

(8) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, 78, 3205 (1956).

(9) W. W. Zajac, Jr., Ph.D. Dissertation, Virginia Polytechnic Institute, 1959.

(10) C. K. Bradsher and D. J. Beavers, *J. Am. Chem. Soc.*, 78, 3193 (1956); C. K. Bradsher and W. J. Jackson, Jr., *J. Am. Chem. Soc.*, 76, 4140 (1954); S. T. Amore, Ph.D. Dissertation, Duke University, 1944.