

For conversion to 4-phenanthroic acid, 0.1 g. of 4-acetylphenanthrene was boiled for one and one-half hours with a sodium hypochlorite solution prepared from 1 g. of the commercial calcium salt (H. T. H.). After cooling, filtering and destroying the excess reagent, the product was precipitated by acidification and crystallized from dilute alcohol. It formed glistening, colorless plates, and after thorough drying at 130° to remove solvent, the acid melted at 171.5–173°. Kruber³ reports the value 170–171°, uncorr.

Cleavage of 1',3'-Diketo-1,2-cyclopentenophenanthrene.—After refluxing a solution of the diketone (1.2 g.) in 1 *N* sodium hydroxide for ten hours the light brown solution was filtered from a small amount of purple material and acidified. The acidic product which precipitated was crystallized from benzene, giving 0.96 g. of material. After a second crystallization the substance, m. p. 190–193°, had approximately the composition of a mixture of acetylphenanthroic acids.

Anal. Calcd. for C₁₇H₁₂O₃: C, 77.24; H, 4.58. Found: C, 77.63, 77.40; H, 5.22, 5.36.

In further recrystallizations the melting point of the less soluble portion rose to about 216°, but an assuredly homogeneous product was not obtained.

Summary

The condensation of the 1,2- and 3,4-dicarboxylic esters of phenanthrene with ethyl acetate proceeds smoothly, affording diketocyclopentenophenanthrenes of interest in the study of oestrogenic activity. The alkaline cleavage of the 1,2-derivative proceeds in both possible directions, whereas with the 3,4-diketone steric hindrance at the 4-position is so pronounced that the reaction affords pure 4-acetyl-3-phenanthroic acid. This on decarboxylation yields the new 4-acetylphenanthrene.

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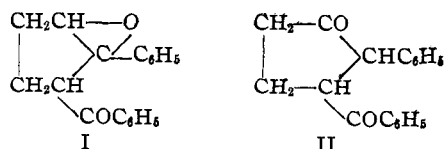
RECEIVED AUGUST 12, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Rearrangement of 1-Phenyl-5-benzoylcyclopentene Oxide

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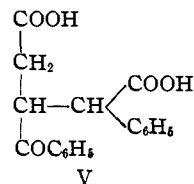
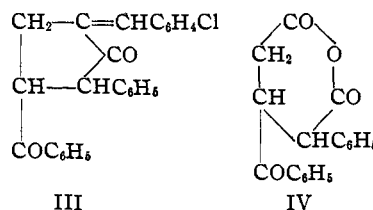
The chief product in the reduction of 1,4-dibromo-1,4-dibenzoylbutane with zinc dust and sodium iodide has been shown to be 1-phenyl-5-benzoylcyclopentene oxide (I).¹ The oxide was accompanied by an isomer which appeared to be derived from it by rearrangement. This isomer was obtained also (1) by the action of alcoholic hydrogen chloride on the oxide; (2) by treatment of a solution of the oxide in glacial acetic acid with ozone; and (3) together with I by the action of perbenzoic acid on 1-phenyl-5-benzoylcyclopentene. It has now been shown that the oxide readily undergoes rearrangement when dissolved in hot glacial acetic acid, and that the rearrangement product is identical with that reported by Fuson and Farlow. The compound has proved to be 2-phenyl-3-benzoylcyclopentanone (II).



The structure of this compound has been established by a degradation process leading to the formation of α -phenyl- β -benzoylglutaric acid (V).

(1) Fuson and Farlow, *THIS JOURNAL*, **56**, 1593 (1934).

The ketone condensed readily with *p*-chlorobenzaldehyde to give a chlorobenzal derivative (III).



When treated with ozone this compound gave *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid and an anhydride (IV) corresponding to that of α -phenyl- β -benzoylglutaric acid (V). By hydrolysis of the anhydride the acid was obtained in the two forms required by theory. One of these melted at 176–177°, and, when heated in the presence of alkali, isomerized to the other, which melted at 135–136°.

Mention should be made of the fact that under certain conditions the rearrangement of the oxide

to the cyclopentanone could be interrupted at an intermediate state. The intermediate compound has not been investigated fully, but it appears likely that it is the theoretically possible geometrical isomer of II.

Experimental

1-Phenyl-5-benzoylcyclopentene Oxide.—The general procedure of Conant and Lutz,² and Fuson and Farlow³ was followed. It was found, however, that the reactants could be used in more nearly equivalent quantities—a modification which increased the yield of oxide by rendering its purification less troublesome. From 200 g. of 1,4-dibromo-1,4-dibenzoylbutane, 40 g. of zinc dust and 186 g. of hydrated sodium iodide was obtained 44 g. of the pure oxide.

Rearrangement of 1-Phenyl-5-benzoylcyclopentene Oxide

(a) **By the Action of Hydrogen Chloride in Alcohol.**—One gram of the oxide was shaken for ten minutes with 25 cc. of absolute alcohol saturated with dry hydrogen chloride. The mixture was then quickly filtered and poured onto 100 g. of cracked ice. The product, after crystallization from methanol, melted at 159–159.5° (corr.) and, when mixed with the sample prepared by Fuson and Farlow, showed no lowering of the melting point.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 81.8; H, 6.1; mol. wt., 264. Found: C, 81.7; H, 6.2; mol. wt. (Rast), 260, 270.

(b) **By Heating with Glacial Acetic Acid.**—A solution of 1 g. of the oxide in 25 cc. of glacial acetic acid was heated in such a manner that at the end of two minutes the temperature had reached 100°. It was then poured onto 50 g. of ice. After repeated recrystallization from methanol the product melted at 123.5–124.5°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.8; H, 6.4.

This method of treatment usually gave a product melting at 116–119° which was very difficult to purify. This substance was dissolved in boiling glacial acetic acid, and the solution was then diluted with hot water until a slight cloudiness was noted. This was discharged by heating, and the solution was allowed to cool. The product softened at 110–113°, and melted at 152–154°. This compound, when subjected to a second treatment similar to that just described, melted at 153–155°. A mixture of this with the oxide melted at 154–157°.

That the substance melting at 116–119° was an intermediate in the conversion of the oxide to the cyclopentanone was further supported by the fact that a hot, slightly alkaline solution of alcohol converted it into the pure cyclopentanone.

(2) Conant and Lutz, *THIS JOURNAL*, **49**, 1090 (1927).

(3) Fuson and Farlow, *ibid.*, **56**, 1593 (1934).

Reactions of 2-Phenyl-3-benzoylcyclopentanone

(a) **With Alcoholic Hydrogen Bromide.**—Treatment with this reagent for four days at 0° produced no change.

(b) **With Bromine.**—Bromination in chloroform solution gave a product which crystallized from alcohol in the form of yellow-orange needles melting at 136.5–137.5°.

Anal. Calcd. for $C_{13}H_{14}O_2Br_2$: C, 51.0; H, 3.3. Found: C, 51.4; H, 3.0.

Attempts to dehalogenate the dibromide by treatment with pyridine, zinc dust or sodium iodide all failed to give products which could be characterized.

(c) **With *p*-Chlorobenzaldehyde.**—One-half gram of the ketone and 0.5 g. of the aldehyde gave 1 g. of a solid which, after two recrystallizations from benzene and high-boiling petroleum ether, melted at 207–207.5°.

Anal. Calcd. for $C_{25}H_{19}OCl$: C, 77.6; H, 5.0. Found: C, 77.5; H, 4.9.

Ozonization of 8 g. of the *p*-chlorobenzal derivative gave a mixture of *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid and 5.5 g. of α -phenyl- β -benzoylglutaric anhydride. The anhydride crystallized from benzene in needles melting at 183–184°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 73.4; H, 4.8. Found: C, 73.3; H, 5.1.

The anhydride was dissolved in a 10% sodium hydroxide solution and the solution was filtered and acidified. The free α -phenyl- β -benzoylglutaric acid, after recrystallization from a mixture of ethyl acetate and petroleum ether, melted at 176–177°.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 69.3; H, 5.1; neut. equiv., 156. Found: C, 69.0; H, 5.3; neut. equiv., 156.

Concentration of the mother liquors yielded an isomeric acid melting at 135–136° (from benzene).

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 69.3; H, 5.1; neut. equiv., 156. Found: C, 69.3; H, 5.4; neut. equiv., 155, 159.

The acid melting at 176–177° was heated for six hours with a 6% solution of alcoholic potassium hydroxide. Acidification of the resulting mixture gave the isomeric acid (melting at 135–136°).

Summary

It has been shown that 1-phenyl-5-benzoylcyclopentene oxide (I) rearranges to 2-phenyl-3-benzoylcyclopentanone (II) when treated with alcoholic hydrogen chloride.

The structure of the rearrangement product has been established by a degradation process leading to the formation of α -phenyl- β -benzoylglutaric acid which has been obtained in the two forms predicted by theory.

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RECEIVED JUNE 22, 1936