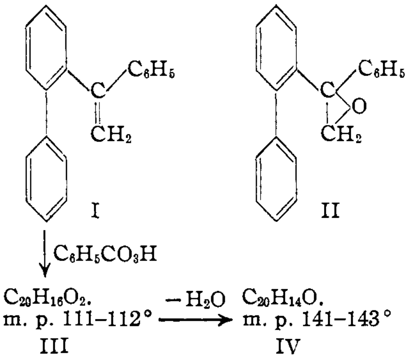
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Anomalous Oxidation of an Ethylene Derivative by Perbenzoic Acid

BY CHARLES K. BRADSHER[1]

The classical reaction of an olefin with perbenzoic acid leads to the formation of an olefin oxide. So well established is this fact, that it forms the basis of a quantitative method for the estimation of olefin linkages.[2]

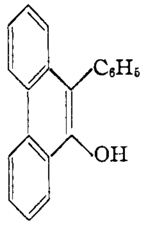
In connection with another problem, we attempted the preparation of the oxide (II) of 1-phenyl-1-(2-biphenylyl)-ethylene by perbenzoic acid oxidation of the corresponding olefin (I).



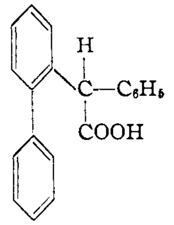
Despite the use of a 32% excess of the oxidizing agent, after three days standing at 0–10° the solution gave a negative test for perbenzoic acid.[3] Worked up in the usual way, there was obtained a quantity of crystals which, upon analysis, proved to be not the expected oxide, but a compound (III) which apparently contained two oxygen atoms. This "dioxide"[4] (III), upon heating with hydrobromic acid, sulfuric acid or potassium bisulfate, lost one molecule of water to yield a compound (IV) melting at 141–143°. When the dehydration product (IV) was refluxed with acetyl chloride, it gave a derivative melting some 20° higher.

The properties and composition of the dehydration product (IV) correspond to those reported by Koelsch[5] for 9-phenylphenanthrol-10 (V) which he had synthesized by cyclization of the acid chloride of (2-biphenylyl)-phenylacetic acid (VI). A sample of the phenanthrol (V) prepared by Koelsch's directions was found to be identical with the dehydration product (IV) obtained from the "dioxide."

It should be pointed out that though (2-biphenylyl)-phenyl-acetic acid (VI) is isomeric, it is not identical with the "dioxide" which has no acidic properties and which melts some 60° lower than the acid.

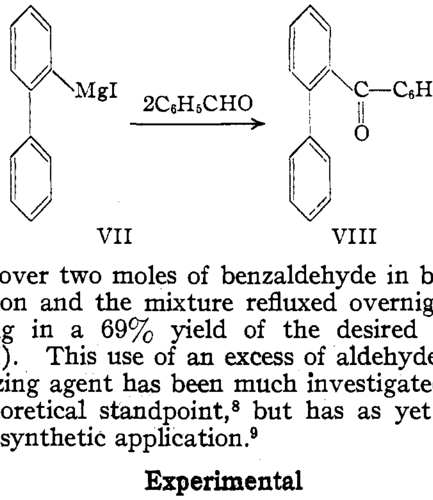


V



VI

The olefin (I) used in the reaction was prepared from *o*-phenylbenzophenone[6] (VIII) by the action of methylmagnesium iodide essentially as described by Bergmann and Bondi.[7] The *o*-phenylbenzophenone has been prepared in a new way which makes possible the use of commercially available starting materials. The Grignard reagent (VII) from 2-iodobiphenyl was treated with over two moles of benzaldehyde in benzene solution and the mixture refluxed overnight, resulting in a 69% yield of the desired ketone (VIII). This use of an excess of aldehyde as an oxidizing agent has been much investigated from a theoretical standpoint,[8] but has as yet found little synthetic application.[9]



VII VIII

Experimental

o-Phenylbenzophenone.—A Grignard reagent was prepared from 56 g. of 2-iodobiphenyl and 4.86 g. of magnesium. A solution of 22 cc. of benzaldehyde in 40 cc. of benzene was added slowly. When addition was complete, two-thirds of the ether was distilled off and 100 cc. of benzene and 40 cc. of benzaldehyde added. The mixture was refluxed for twenty-two hours, after which it was decomposed by the addition of ammonium chloride solution. The ether-benzene layer was dried, concentrated, and the residue distilled under reduced pressure. The entire fraction boiling at 195–232° (19 mm.) was collected and crystallized from methyl alcohol giving 35.8 g. (69.5%)

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[1] National Research Fellow (participating basis) 1941–1942.

[2] Nametkin and Brussoff, *J. prakt. Chem.*, **112**, 169 (1926).

[3] An earlier communication (Bradsher and Rapoport, THIS JOURNAL, **65**, 1646 (1943)) cited an example of an unsaturated hydrocarbon which reacted with more than the theoretical quantity of perbenzoic acid. This cannot be accounted for on the basis of the normal rate for the spontaneous decomposition of perbenzoic acid.

[4] In the use of the term "dioxide," we seek to imply nothing more than the composition of the product. We hope to make the structure of this compound the subject of a further investigation.

[5] Koelsch, THIS JOURNAL, **56**, 482 (1934).

[6] Schlenk and Bergmann, *Ann.*, **464**, 1, 34 (1928).

[7] Bergmann and Bondi, *Ber.*, **64**, 1455, 1476 (1931).

[8] *E. g.*, Marshall, *J. Chem. Soc.*, **105**, 527 (1914); **107**, 509 (1915); **127**, 2184 (1925); Meisenheimer, *Ann.*, **442**, 180 (1925); **446**, 76 (1926); Hess, *ibid.*, **437**, 256 (1924); Rheinholdt, *J. prakt. Chem.*, **109**, 175 (1925); Gomberg and Bachmann, THIS JOURNAL, **52**, 4967 (1930); Shankland and Gomberg, *ibid.*, **52**, 4973 (1930).

[9] A notable exception is to be found in the work of Bachmann, *ibid.*, **56**, 1363 (1934).

of white crystals, m. p. 86–87°. This material was identical with a sample prepared from the nitrile by the method of Schlenk and Bergmann.[6]

1-Phenyl-1-(2-biphenylyl)-ethylene (I) was prepared as described by Bergmann and Bondi[7] with the exception that the product of the reaction between methylmagnesium iodide and *o*-phenylbenzophenone was heated with potassium bisulfate for a half-hour before vacuum distillation. The fraction boiling at 201–202.5° (12 mm.) solidified to a white solid. m. p. 59–61°. The yields were 56–73%. A single attempt was made to prepare the olefin from the product of the reaction of acetophenone with 2-biphenylylmagnesium iodide. Upon distillation, a large fore-run of biphenyl and acetophenone was obtained, followed by a small amount (17.5%) of the desired olefin.

Oxidation of 1-Phenyl-1-(2-biphenylyl)-ethylene.—A solution of 27.9 g. of the olefin (I) was treated with an ethereal solution containing 20 g. of perbenzoic acid. After the solution had stood for three days, it gave a negative test for excess oxidant. The solution was washed free of acid with sodium bicarbonate solution and dried over sodium sulfate. Upon concentration of the solution and addition of petroleum ether. 14 g. (46%) of nearly colorless crystals was obtained, m. p. 107–109°. An analytical sample was prepared by repeated recrystallization. m. p. 111–112°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C. 83.32; H. 5.60. Found: C. 83.37; H. 5.68.

Dehydration of the "Dioxide" (III).—(a) By hydrobromic and acetic acids: one-half gram of the "dioxide" (III) was suspended in a boiling mixture containing 5 cc. of acetic and 5 cc. of 34% hydrobromic acids and the mixture refluxed for twenty-four hours. The product, once recrystallized from alcohol, was nearly white and melted at 139–141°; yield 0.33 g. (35%). In one case in which the "dioxide" had been heated previously for a few minutes at its boiling point (22 mm.) the yield was 56%.

(b) By the action of potassium bisulfate: one gram of the "dioxide" was heated at 170–180° for ten minutes with 2 g. of potassium bisulfate. The product was extracted with ether and recrystallized as above; yield 0.33 g. (35%).

(c) By the action of concentrated sulfuric acid: one-half gram of the "dioxide" was heated on the steam-bath for two minutes with 3 cc. of concentrated sulfuric acid. Poured into water and once recrystallized, it gave 0.30 g. (64%) of white needles, m. p. 141–143°.

The products obtained by all of these methods were shown to be identical by mixed melting point determinations.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C. 88.94. 88.73; H. 5.30, 5.23.

The products were shown to be identical with a sample of 9-phenylphenanthrol-10 (V) prepared from (2-biphenylyl)-phenylacetic acid (VI) by the method of Koelsch.[5]

A crystalline derivative (m. p. 158–159.5°) was obtained by refluxing the cyclization product overnight with acetyl chloride.[10]

Summary

It has been demonstrated, in one case at least, that perbenzoic acid may bring about the addition of two atoms of oxygen to one mole of an olefin.

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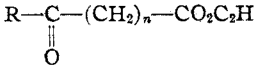
[10] This product is probably the acetate (m. p. 153–155°) prepared previously by Koelsch[5] by the action of acetic anhydride and sulfuric acid on 9-phenylphenanthrol-10.

[Contribution from the Furman Chemical Laboratory, Vanderbilt University]

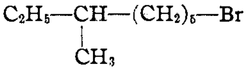
Branched-Chain Fatty Acids. II. Syntheses in the C_{19} and C_{25} Series. Preparation of Keto Esters

By James Cason and Franklin S. Prout[1]

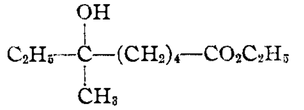
In continuation of the program of synthesizing methyloctadecanoic acids,[2] the 16-methyl isomer has been prepared by the general method used for synthesis of 17-methyloctadecanoic acid.[2] This procedure involves preparation of a keto ester (I) by reaction between a dialkylcadmium compound and an ω-carbethoxyalkoyl chloride, reduction of the keto ester by the Clemmensen method and hydrolysis of the reduced ester. For synthesis of 16-methyloctadecanoic acid the required alkyl halide is 1-bromo-6-methyloctane (II). This bromide has been prepared by Levene and Marker[3] from the corresponding alcohol which was obtained by reduction of ethyl 6-methyloctoate (IV). These workers prepared 6-methyloctoic acid[4] by extending the chain of 1-bromo-4-methylhexane by use of the malonic ester synthesis.


$R—C(=O)—(CH_2)_n—CO_2C_2H_5$

I


$C_2H_5—CH(CH_3)—(CH_2)_5—Br$

II


$C_2H_5—C(OH)(CH_3)—(CH_2)_4—CO_2C_2H_5$

V

Our preparation of 1-bromo-6-methyloctane also utilizes ethyl 6-methyloctoate, which was first prepared by us as in the scheme shown. It was hoped that the small amount of isoamyl alcohol present in the *s*-butylcarbinol[5] used as starting material would not interfere with obtaining a pure product in the final stages of the synthesis; however, such was not the case. Reduction of the keto ester, III, by the Clemmensen method proved more difficult than reduction of the 7-methyl isomer[2]; therefore, the concentration of the undesired 7-methyl isomer, arising from isoamyl bromide, was considerably increased at this step. 16-Methyloctadecanoic

(1) Taken in part from the M.S. thesis of Franklin S. Prout.

(2) Cason, This Journal, **64**, 1106 (1942).

(3) Levene and Marker, *J. Biol. Chem.*, **103**, 299 (1933).

(4) Levene and Marker, *ibid.*, **95**, 153 (1932).

(5) Fractionated through a 3-foot packed column, b. p. 127.5 128.5°.