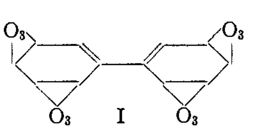
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

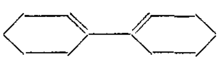
The Ozonation of Certain Hydrogenated Diphenyls

BY C. R. NOLLER AND G. K. KANEKO

During the course of his exhaustive work on the ozonation of organic compounds, Harries found that[1] whereas benzene forms a triozonide in accordance with the Kekulé formula, diphenyl forms only a tetraozonide. He suggested that the tetraozonide had Formula I and that the non-addition of ozone to the double bonds in the 1 and 1′ positions was due to steric hindrance.



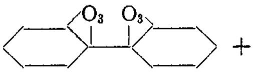
I



II

Because of the difficulty of preparing the tetraozonide, the products formed on decomposition with water have not been identified, but it should be possible to determine whether steric hindrance plays a role by studying compounds such as 1-phenylcyclohexene-1 and dicyclohexenyl-1,1′ (II) in which non-benzenoid double bonds occur in positions similar to those which are supposed to be sterically hindered in benzene.

A review of the literature showed that Brus and Peyresblanques[2] had ozonized 1-phenylcyclohexene-1 and they state that one mole of ozone adds rapidly and quantitatively while benzene adds ozone only slowly. One might be led to believe, however, from the curves given, that the addition was more like that to benzene rather than to an aliphatic double bond. They did not report the decomposition products of the ozonide and it is conceivable as in the case of diphenyl that the ozone is not added to the double bond in the 1- or 1′-position. This work was therefore repeated on 1-phenylcyclohexene-1 and extended to include dicyclohexenyl-1,1′. It was found that phenylcyclohexene adds one mole of ozone as readily as does a simple unsaturated compound such as methyl oleate, and that the ozonide on decomposition with water gives δ-benzoyl-*n*-valeric acid proving that the ozone added to the double bond in the cyclohexene ring. Moreover, dicyclohexenyl-1,1′ was found to add one mole of ozone rapidly while the second double bond added ozone slowly but at a faster rate than benzene. Decomposition of the ozonide did not yield the expected diketo-dibasic acid but adipic acid instead. The reaction may be formulated



$$+ 2H_2O \longrightarrow$$

$$CHO(CH_2)_4-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-(CH_2)_4CHO + 2H_2O_2 \longrightarrow$$

$$HOOC(CH_2)_4COOH + HOOC-(CH_2)_4CHO$$

The aldehyde acid was probably oxidized also to the dibasic acid, due to the exposure to air during the boiling and isolation. Adipic acid could hardly arise from an ozonide other than the diozonide shown and it therefore seems unlikely that steric hindrance, in the sense that there is no room for two ozonide groups to occupy the 1,1′ positions, can account for the non-formation of a diphenylhexaozonide.

During the course of this work the structure of tetrahydrodiphenyl obtained by the reduction of diphenyl with sodium in amyl alcohol[3] also was determined. When diphenyl is reduced by hydrogen in the presence of a nickel catalyst,[4] the products are phenylcyclohexane and dicyclohexyl. This fact led Turner[5] to predict that the tetrahydrodiphenyl of Bamberger and Lodter was a phenylcyclohexene rather than a dicyclohexadiene. Tetrahydrodiphenyl prepared according to the procedure of Bamberger and Lodter was ozonized and found to absorb about 68% of the calculated amount of ozone. Decomposition of the ozonide gave δ-benzoyl-*n*-valeric acid, identical with that obtained from 1-phenylcyclohexene-1. Hence tetrahydrodiphenyl is 1-phenylcyclohexene-1, contaminated with diphenyl or with phenylcyclohexane.

Experimental

Reagents.—1-Phenylcyclohexene-1[6] was prepared by the dehydration of 1-phenylcyclohexanol-1 in 75% yields by distilling 49 g. of the alcohol with 1 g. of potassium bisulfate and 50 cc. of bromobenzene through a 30-cm. Vigreux column as long as water came over (about two hours). The bromobenzene was separated from the distillate and returned to the flask from time to time. Finally all of the bromobenzene was distilled and the product fractionated under a vacuum; b. p. 136–138° (25 mm.).

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(1) Harries and Weiss, *Ann.*, **343**, 337, 374 (1905).

(2) Brus and Peyresblanques, *Compt. rend.*, **190**, 685 (1930).

(3) Bamberger and Lodter, *Ber.*, **20**, 3077 (1887).

(4) Sabatier and Murat, *Compt. rend.*, **154**, 1390 (1912).

(5) Turner, *Rec. trav. chim.*, **48**, 821 (1929).

(6) Sabatier and Mailhe, *Compt. rend.*, **138**, 1321 (1904).

Dicyclohexenyl-1,1′, b. p. 133–135° (23 mm.) was prepared in 68% yields by dehydrating dicyclohexanediol-1,1′[7] using an analogous procedure. The latter compound was prepared in poor yields by following the procedure given in "Organic Syntheses," Coll. Vol. I, p. 448, for pinacol hydrate. This was found to be superior to the sodium reduction method of Zelinsky.[8]

Tetrahydrodiphenyl was prepared by the procedure of Bamberger and Lodter.[3]

Ozonation and Decomposition of the Ozonides.—Oxygen containing 4–5% ozone was passed into a solution of the compound in glacial acetic acid until a sample no longer decolorized a solution of bromine in carbon tetrachloride. To the acetic acid solution of the ozonide was added 25 cc. of water and the solution refluxed for one hour. The acetic acid and water were distilled under reduced pressure and the residue poured into an evaporating dish to solidify. In the cases of phenylcyclohexene and tetrahydrodiphenyl the products were crystallized from ether and melted at 77–78°; the semicarbazones melted at 191–192° and mixed melting points showed no depression. Auwers and Treppmann[9] report the melting point of δ-benzoyl-*n*-valeric acid as 77–78° and the semicarbazone as 187°.

The crude product of the decomposition of the ozonide of dicyclohexenyl-1,1′ was crystallized from ethyl acetate, when it melted at 152–153° and had a neutralization equivalent of 74.6. Adipic acid melts at 153–153.5° and has a neutralization equivalent of 73. A mixed melting point showed no depression.

Summary

1. 1-Phenylcyclohexene-1 adds one mole of ozone to the double bond in the cyclohexene ring and dicyclohexenyl-1,1′ adds ozone to both double bonds. This indicates that steric hindrance in the 1 and 1′ positions is not the factor involved in the failure of diphenyl to form a hexaozonide.

2. Tetrahydrodiphenyl prepared by reducing diphenyl with sodium and amyl alcohol is chiefly 1-phenylcyclohexene-1.

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(7) Wallach and Pauly, *Ann.*, **381**, 112 (1911).

(8) Zelinsky, *Ber.*, **34**, 2801 (1901).

(9) K. v. Auwers and W. Treppmann, *ibid.*, **48**, 1217 (1915).

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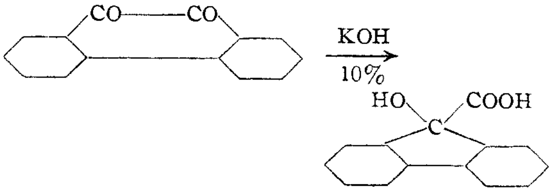
The Higher Benzenoid Hydrocarbons. II. The Isomeric Bromofluorenones[1]

BY HARRY F. MILLER AND G. BRYANT BACHMAN

Of the four possible monobromofluorenones, 2-bromofluorenone is the only one readily available. The preparation of the 4-isomer has never been recorded and the 1- and 3-isomers have been prepared in small quantities only and by way of difficultly accessible intermediates.[2] As a part of our program to elucidate the fundamental chemistry of some of the polycyclic coal tar hydrocarbons it was decided to devise nuclear syntheses for the 3- and 4-bromofluorenones which would make them more readily available and which would serve to establish definitely their structure.

There are five general methods which have been used for the preparation of substituted fluorenones. (1) *Direct substitution.* This serves very well for the preparation of 2-bromo and 2,7-dibromofluorenones. Apparently, however, no other isomers arise in the bromination of either fluorenone or fluorene.[3] (2) *Elimination of hydrogen bromide from substituted o-bromobenzophenones.*

Although this method was used by Montagne to prepare 1- and 3-bromofluorenones, the yields are small and the intermediates difficult to prepare. Furthermore, in view of the high temperatures employed to effect condensation, there is always to be considered the danger of an intramolecular rearrangement. (3) *The rearrangement of phenanthraquinone derivatives.* This is an application of the benzil–benzilic acid rearrangement.



The diphenyleneglycolic acid formed decomposes in the presence of boiling water liberating fluorenone. The method has been used successfully in the preparation of certain nitrofluorenes[4] and of a

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(1) First paper in this series, THIS JOURNAL, **57**, 766 (1935).

(2) Montagne and Van Charante, *Rec. trav. chim.*, **32**, 164 (1913).

(3) Courtot and Vignati, *Bull. soc. chim.*, [4] **41**, 58 (1927).

(4) Schmidt, *et al.*, *Ber.*, **38**, 3737 (1905); **41**, 3679 (1908).