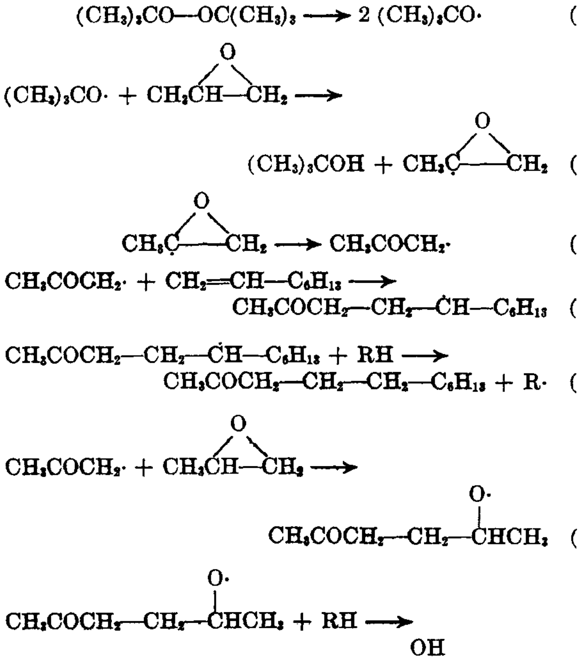
attack and ring opening of the three-membered carbon ring has recently been reported.[2] In support of the latter and to report an interesting electron realignment of a free radical, we wish to describe results obtained from a study of the free radical chemistry of the epoxide ring. It was found that the radical formed from propylene oxide by hydrogen atom abstraction isomerized to a keto-radical and that this keto-radical attacked both a double bond and the epoxide ring.

When propylene oxide, 1-octene, and *tert*-butyl peroxide were heated at 150° for 2 hr., a product, b.p. 50–57° (0.26 mm.), was obtained. This was shown to be a 4:1 mixture of 2-undecanone (8.3% yield based on 1-octene) and 5-hydroxy-2-hexanone (2% yield based on propylene oxide) by gas chromatography. When a similar reaction mixture was heated at 125° for 17 hr. the product was mainly the hydroxy ketone. The 2-undecanone gave a semicarbazone, m.p. 118–120°, reported 119–120°,[3] and the 5-hydroxy-2-hexanone was similar to the authentic compound.[4]

The following reaction scheme seems reasonable:



$$(CH_3)_3CO{-}OC(CH_3)_3 \longrightarrow 2\,(CH_3)_3CO\cdot \tag{1}$$

$$(CH_3)_3CO\cdot + CH_3\overbrace{CH-CH_2}^{O} \longrightarrow (CH_3)_3COH + CH_3\overbrace{\underset{\cdot}{C}-CH_2}^{O} \tag{2}$$

$$CH_3\overbrace{\underset{\cdot}{C}-CH_2}^{O} \longrightarrow CH_3COCH_2\cdot \tag{3}$$

$$CH_3COCH_2\cdot + CH_2{=}CH{-}C_6H_{13} \longrightarrow CH_3COCH_2{-}CH_2{-}\dot{C}H{-}C_6H_{13} \tag{4}$$

$$CH_3COCH_2{-}CH_2{-}\dot{C}H{-}C_6H_{13} + RH \longrightarrow CH_3COCH_2{-}CH_2{-}CH_2{-}C_6H_{13} + R\cdot \tag{5}$$

$$CH_3COCH_2\cdot + CH_3\overbrace{CH-CH_2}^{O} \longrightarrow CH_3COCH_2{-}CH_2{-}\overset{O\cdot}{\overset{|}{C}}HCH_3 \tag{6}$$

$$CH_3COCH_2{-}CH_2{-}\overset{O\cdot}{\overset{|}{C}}HCH_3 + RH \longrightarrow CH_3COCH_2{-}CH_2{-}\overset{OH}{\overset{|}{C}}HCH_3 + R\cdot \tag{7}$$

To test the mode of formation of the hydroxy ketone, propylene oxide was brought into reaction with other compounds which have reactive hydrogen atoms. In support of the postulate, toluene, propylene oxide, and *tert*-butyl peroxide gave bibenzyl, 5-hydroxy-2-hexanone, and 4-phenyl-2-butanol; cyclohexane, propylene oxide, and *tert*-butyl peroxide afforded 5-hydroxy-2-hexanone, 2,5-hexanedione, cyclohexylacetone, and 1-cyclohexyl-2-propanol; and ethanol, propylene oxide, and *tert*-butyl peroxide gave 5-hydroxy-2-hexanone and 2,4-pentanediol. All the product identifications were done by gas chromatography by comparison with authentic compounds.

Studies are in progress to determine if the displacement reaction on the epoxide ring (reaction 6) is a frontside or backside attack, and whether or not the *tert*-butoxy radical also gives the displacement.

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[3] H. D. Dakin, *J. Am. Chem. Soc.*, **44**, 47 (1910).

[4] R. M. Adams and C. D. Vanderwerf, *J. Am. Chem. Soc.*, **72**, 4368 (1950).

[5] From the Ph.D. thesis and some post-doctoral research by T. J. W. whose present address is Esso Research and Engineering Co., Linden, N. J.

Photolysis of Aromatic Iodo Compounds as a Synthetic Tool

Sir:

Our interest in the chemistry of thyroxine and related substances[1] led us to examine the photochemical decompositions of certain iodinated thyronines and iodotyrosines. The behavior of these substances, on irradiation, is complex and the interpretation of the results required a prior study of simpler systems. Hence, we studied the photolysis of model substances, such as iodobenzene, *o*- and *p*-iodophenols, *p*-iodonitrobenzene, and 2,6-di-iodo-*p*-cresol under definitive conditions.

Our initial results suggest that photolysis of a variety of iodoaromatic compounds by essentially monochromatic light (2537Å), at or near room temperature, in dilute solution in an appropriate aromatic solvent, is a reaction which has broad synthetic and theoretical implications. While this work was in progress, reports by Szychlinski[2] and Blair and Bryce-Smith,[3] which deal with related reactions, also appeared, but to our knowledge it has not been previously shown that the reactions could be carried out in a synthetically useful manner and with a variety of substituted iodoaryl compounds (*e.g.*, the iodophenols).

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[3] J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 1788 (1960).

The problem in adapting the photolysis of aromatic iodo compounds for synthetic purposes is to establish conditions which promote the scission of the carbon-iodine bonds without causing subsequent reactions of products, or undesired side reactions. Thus, the use of a quartz housing and a wide-spectrum light source lead to various side reactions.[3] However, by conducting the reaction at or near room temperature and using an ultraviolet source which provides energy at a wave length which essentially cleaves only the carbon iodine bond, the side reactions are minimized.

The synthesis of 2-hydroxybiphenyl in one step, in 60–70% yields of chromatographically pure product, is carried out as follows: *o*-Iodophenol (lg) in 50 ml. pure, dry benzene, was irradiated in a "Vycor"-7100 tube, by a helical cold-cathode, low pressure mercury lamp (manufactured by Dallons Laboratories, Los Angeles, California). After twenty hours of irradiation, the release of iodine, conveniently measured by titration with thiosulfate, was complete. Isolation of the product from the organic layer and purification by two passes through an alumina column gave 0.46 g. (60% yield) of pure 2-hydroxybiphenyl, fully characterized by its m.p.[4] and infrared spectrum.

By similar procedures, in synthetically useful yields, we obtained the following products: diphenyl (from iodobenzene irradiated in benzene); 4-hydroxybiphenyl (from *p*-iodophenol irradiated in benzene); 4-nitrobiphenyl (from 4-iodo-nitrobenzene irradiated in benzene); a separable mixture of 2-methyl-4′-nitrobiphenyl and 4-methyl-4′-nitrobiphenyl (by irradiation of 4-iodonitrobenzene in toluene); and 2-methoxybiphenyl (by irradiation of iodobenzene in anisole). The irradiation of 1 g. of 2,6-di-iodo-*p*-cresol in benzene led to 712 mg. of a highly crystalline, *iodine-free* product, m.p. 66–7°, the infrared spectrum of which showed a phenolic group and polyphenyl absorption, but which has not yet been fully characterized. The structure of the fully-characterized products obtained are those to be expected for free radical attack on the substrates used.[5] These reactions, which occur at the wave lengths where iodoaromatic compounds show continuous absorption, can thus be considered as occurring, undoubtedly, by free radical mechanisms. The effective, low temperature generation of aryl radicals, and specifically of hydroxyaryl radicals, by this means, is novel. The use of diiodoarenes in this synthesis is also illustrated by the formation of *p*-terphenyl from *p*-diiodobenzene and of *p*-quaterphenyl from 4,4′-diiodobiphenyl, irradiated in benzene.

We are continuing studies to determine the scope of these reactions, both as regards sources for aryl radicals, from iodo compounds, as well as solvents capable of capturing the radicals generated by the photochemical technique.

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[4] O. Hönigschmid, *Monatsh.* 22, 568 (1901).

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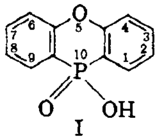
The Phenoxphosphinic Acid Ring System

Sir:

Only a few phosphinic acids are known in which the phosphorus atom is a member of a ring system.[1] In particular, the synthesis of phenoxphosphinic acid (I) or its derivatives has not been previously accomplished. Although phenoxarsinic acid is easily prepared by refluxing phenyl ether with arsenic trichloride and a small quantity of aluminum chloride and then oxidizing the resulting chloroarsine with bromine water,[2] the analogous reaction with phosphorus trichloride yields *p*-phenoxyphenylphosphonic acid.[3] It is not clear why arsenic trichloride preferentially attacks the 2-position of phenyl ether, while phosphorus trichloride attacks the 4-position.



I

Numerous attempts in this laboratory to prepare phenoxphosphinic acid by the intramolecular dehydration of *o*-phenoxyphenylphosphonic acid have met with failure.[4] This compound is unaffected by polyphosphoric acid at 130° and is apparently sulfonated by concentrated sulfuric acid at 100°. The method of Campbell and Way,[5] whereby 2-biphenylylphenylphosphinic acid was cyclized to 9-phenyl-9-phosphafluorene 9-oxide by heating with an excess of phosphorus pentachloride in nitrobenzene, also failed with *o*-phenoxyphenylphosphonic acid. We can not explain the resistance of *o*-phenoxyphenylphosphonic acid to cyclization, but

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(1) *Cf.* L. D. Freedman and G. O. Doak, *J. Org. Chem*, 24, 638 (1959)

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