(2.96 g.) and water (5 ml.) were heated on the steam-bath with stirring for six hours. The reaction mixture was processed and distilled at reduced pressure to yield 3 g. of starting material and 0.75 g. of a ketonic fraction, b.p. 170–200° (20 mm.). This fraction was treated with 2,4-dinitrophenylhydrazine and after five recrystallizations from ethanol–ethyl acetate the product melted at 142–143° alone or when mixed with a sample of IV obtained in part B.

Michael Additions to VII.—The procedure of Bachmann and Fornefeld[5] was followed using ethyl malonate (5 g.), unsaturated ketone VII (0.928 g.) and a solution of sodium (0.138 g.) in absolute ethanol (10 ml.). After processing there was obtained 0.825 g. (53%) of product which boiled at 188–190° (0.58 mm.).[10] This product formed a semicarbazone which melted at 164–165°.

Anal. Calcd. for $C_{22}H_{31}O_7N_3$: C, 58.5; H, 6.9. Found: C, 59.38; H, 7.14.

Four experiments using different temperatures, reaction times and ratios of sodium ethoxide were carried out in attempts to cause the addition of ethyl acetamidomalonate to VII. In all cases the starting materials were recovered unchanged.

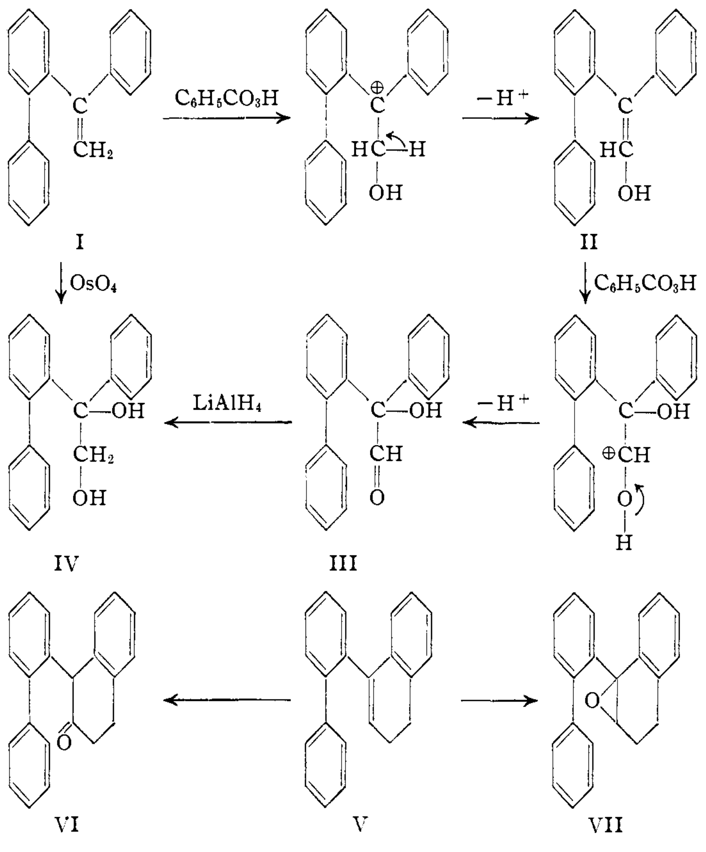
NEW BRUNSWICK, NEW JERSEY RECEIVED AUGUST 2, 1951

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Perbenzoic Acid with Certain Olefins

BY FRANK L. WEISENBORN[1] AND DAVID TAUB[2]

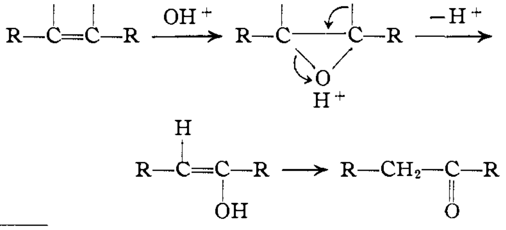
The product of the reaction of perbenzoic acid with 1-phenyl-1-(2-biphenylyl)-ethylene has been shown to be phenyl-(2-biphenylyl)-glyoxal and a mechanism for its formation is suggested. 1-(2-Biphenyl)-3,4-dihydronaphthalene has been shown to give the normal oxide by reaction with monoperphthalic acid to give 1-(2-biphenylyl)-2-tetralone by reaction with perbenzoic acid.



In the course of studying methods of synthesis of substituted phenanthrene derivatives Bradsher[3] reported the formation of a neutral "dioxide," $C_{20}H_{16}O_2$, by the reaction of perbenzoic acid with 1-phenyl-1-(2-biphenylyl)-ethylene (I). In connection with another investigation of the reactions of peracids it was of interest to us to determine the structure of this compound.

A number of reactions have previously been reported in which the action of perbenzoic acid on systems similar to I has given rise to a ketone rather than an oxide. Thus from 3,4-dihydro-6-methoxynaphthalene Salzer[4] obtained 6-methoxy-β-tetralone. Newbold and Spring[5] have also recorded the formation of diphenylacetaldehyde in 35% yield by treatment of 1,1-diphenylethylene with perbenzoic acid. Zaugg, Freifelder and Horrom[6] have obtained 1-phenyl-2-tetralone from 1-phenyl-3,4-dihydronaphthalene by perbenzoic acid oxidation followed by treatment with sulfuric acid.[7] In addition, we have found that 1-(2-biphenylyl)-3,4-dihydronaphthalene (V) reacts with perbenzoic acid in chloroform to give 1-(2-biphenylyl)-2-tetralone (VI), m.p. 165–166°. Evidence for the presence of a carbonyl group is given by the infrared spectrum (Fig. 1C). Bradsher and Rapoport,[8] on the other hand, have reported that monoperphthalic acid in ether reacts with this same olefin (V) to give a different substance, m.p. 99°. Actually, this latter compound is the normal oxide (VII) as shown by the absence of any carbonyl absorption in the infrared spectrum (Fig. 1B).

The mechanism of formation of these ketones by reaction with perbenzoic acid may be formulated



$$\mathrm{R{-}\overset{H}{C}{=}\overset{H}{C}{-}R \xrightarrow{OH^+} R{-}\overset{H}{C}{-}\overset{H}{C}{-}R\ (\underset{H^+}{O}) \xrightarrow{-H^+}}$$

$$\mathrm{R{-}\overset{H}{C}{=}\underset{OH}{C}{-}R \longrightarrow R{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}R}$$

---

(1) Public Health Service Postdoctoral Fellow, 1950–1951; Riker Laboratories, Inc., Los Angeles, California.

(2) Public Health Service Postdoctoral Fellow, 1950–1951.

(3) C. K. Bradsher, THIS JOURNAL, **66**, 45 (1944).

(4) W. Salzer, *Z. physiol. Chem.*, **274**, 39 (1942).

(5) G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 247 (1945).

(6) H. E. Zaugg, M. Freifelder and B. W. Horrom, *J. Org. Chem.*, **15**, 1197 (1950).

(7) Although the character of the product obtained before treatment with sulfuric acid was not investigated by these authors it was probably the ketone.

(8) C. K. Bradsher and Lorence Rapoport, THIS JOURNAL, **65**, 1646 (1943).

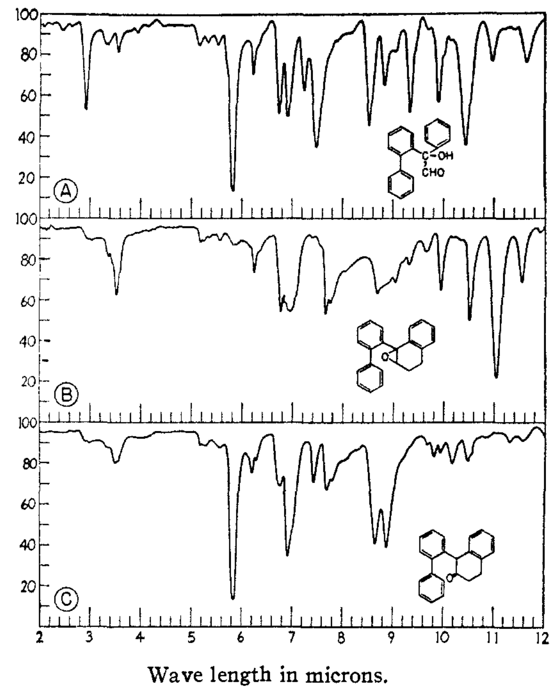


Fig. 1.—Infrared absorption spectra (in chloroform).

The product of the reaction of two moles of perbenzoic acid on 1-phenyl-(2-biphenylyl)-ethylene, designated as "Bradsher's dioxide," has been shown to be phenyl-(2-biphenylyl)-glyoxal (III). The infrared spectrum (Fig. 1A) of the "dioxide" showed bands at 2.85 and 5.80 μ characteristic of a hydroxyl group and carbonyl function, respectively. The compound gave a positive test with Tollens reagent and Fehling solution, indicative of an aldehyde and also formed a 2,4-dinitrophenylhydrazone. Confirmatory evidence for structure III was obtained by reduction of the "dioxide" to a glycol (IV), m.p. 88°. This compound was found to be identical with the glycol obtained by oxidation of 1-phenyl-2-(2-biphenylyl)-ethylene (I) with osmium tetroxide.

The formation of phenyl-(2-biphenylyl)-glyoxal (III) is easily accounted for by consideration of the above mechanism. Thus the initial product from the reaction of one mole of peracid is the aldehyde (II) and since this compound exists predominantly in the enol form it is susceptible to attack by a second mole of perbenzoic acid to form the hydroxyaldehyde (III).

The acid cyclization of III to 9-hydroxy-10-phenylphenanthrene reported by Bradsher[3] is consistent with other related cyclizations described by Bradsher himself[9] and by Berliner.[10]

Experimental

Phenyl-(2-biphenylyl)-glyoxal (III).—This compound was prepared by a modification of the procedure of Bradsher.[3] 1-Phenyl-(2-biphenylyl)-ethylene (I) (1.00 g., 0.0039 mole) was dissolved in a mixture of 10 ml. of chloroform and 14.2 ml. of 0.54 M (0.0078 mole) perbenzoic acid in chloroform. The solution was allowed to stand 12 hours; the excess acid was then decomposed with potassium iodide solution and the trace of iodine present reduced with sodium thiosulfate. The chloroform layer was washed with bicarbonate, then water, dried over sodium sulfate and concentrated. The residue of 1.2 g. of oil was taken up with a little ether and on dilution with petroleum ether (30–60°), 0.74 g. (65.5%) of hard clusters of colorless crystals was obtained, m.p. 108–110°. Recrystallization from ether–petroleum ether gave colorless prisms, m.p. 112–113°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.32; H, 5.60. Found: C, 83.39; H, 5.57.

The substance reduced Tollens reagent and Fehling solution.

The 2,4-dinitrophenylhydrazone prepared in cold alcoholic–hydrochloric acid solution was obtained as orange prisms, m.p. 211–212°.

Anal. Calcd. for $C_{26}H_{20}O_5N_4$: C, 66.66; H, 4.30; N, 11.96. Found: C, 66.72; H, 4.45; N, 11.99.

Phenyl-hydroxy-(2-biphenylyl)-ethyl Alcohol (IV). A. From (I).—1-Phenyl-1-(2-biphenylyl)-ethylene (I) (1.04 g.) dissolved in 25 ml. of anhydrous ether was cooled to 0° and added to a solution of osmium tetroxide (1.04 g.) in 25 ml. of ether at 0°. The mixture was allowed to stand at room temperature for 5 days and the precipitate was filtered and washed with ether to give 1.53 g. (73.5%) of the black osmic ester. The ester was dissolved in 30 ml. of methylene chloride and stirred with a solution of 5 g. of mannitol and 1.5 g. of potassium hydroxide in 50 ml. of water. After eight hours of stirring the colorless methylene chloride layer was separated and the aqueous layer saturated with sodium chloride and extracted with chloroform. The combined extracts were washed with ammonium chloride solution, dried with calcium sulfate and concentrated, leaving 0.80 g. of colorless glass. The residue was dissolved in petroleum ether (60–90°) containing a little ethyl acetate and on standing 0.59 g. (50%) of colorless needles was obtained, m.p. 87°. Recrystallization from ethyl acetate–ligroin gave fluffy, long needles, m.p. 88°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.74; H, 6.25. Found: C, 82.52; H, 6.29.

B. From (III).—Three hundred milligrams of III dissolved in 10 ml. of ether was added to 200 mg. of lithium aluminum hydride in 20 ml. of ether. After stirring for ten minutes the excess hydride was decomposed with ethyl acetate and the alkoxides decomposed with ammonium chloride solution. The ether layer was dried and evaporated leaving 0.30 g. of gum. The residue was taken up in ligroin (60–90°) containing a little ethyl acetate and, on scratching, 0.28 g. of colorless, fluffy needles was obtained, m.p. 86–87°. Mixed melting point with the substance obtained by oxidation of (I) with osmium tetroxide was undepressed. The infrared spectra were also identical.

Oxide of 1-(2-Biphenylyl)-3,4-dihydronaphthalene (VII). This material was prepared by the method of Bradsher and Rapoport.[8]

1-(2-Biphenylyl)-2-tetralone (VI).—1-(2-Biphenylyl)-3,4-dihydronaphthalene (V)[8] (1.00 g.) was treated with one molar equivalent of perbenzoic acid in 15 ml. of chloroform. After standing 12 hours the chloroform solution was extracted with bicarbonate, washed with water, dried over sodium sulfate and then concentrated. The crude oily residue which showed strong carbonyl absorption in the infrared spectrum was chromatographed on 5 g. of alumina. The column was eluted first with 150 ml. of ligroin (60–90°) and then with 100 ml. of 25% benzene–ligroin from which 0.25 g. of solid was obtained. Recrystallization from ethyl acetate–petroleum ether gave colorless plates of 1-(2-biphenylyl)-2-tetralone, m.p. 164–165°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.57; H, 6.08. Found: C, 88.90; H, 5.61.

CAMBRIDGE, MASSACHUSETTS

RECEIVED SEPTEMBER 19, 1951

---

(9) C. K. Bradsher and E. Smith, THIS JOURNAL, **65**, 854 (1943).

(10) E. Berliner, *ibid.*, **64**, 2894 (1942).