Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.31; H, 5.16. Found: C, 78.50; H, 5.14.

***trans*-2-Chlorostilbene.**—One gram of *cis-o*-chlorostilbene was isomerized with 10 ml. of nitrobenzene and a few crystals of iodine at reflux temperature for twenty minutes. The solvent was removed and the *trans*-2-chlorostilbene was distilled, b.p. 138–140° at 2 mm. The oil solidified and was recrystallized from methanol giving colorless prisms, m.p. 39–40°; reported[5] m.p. 40°.

Attempted Synthesis of *cis*-Stilbene-2-carboxylic Acid. (1).—In a dry nitrogen-flushed 200-ml. three-necked round-bottomed flask provided with a stirrer, dropping funnel and a reflux condenser, the latter two protected with calcium chloride drying tubes was placed 1 g. (0.14 mole) of lithium metal ribbon cut into small pieces. A solution of 20 g. (0.097 mole) of *cis*-2-chlorostilbene in 50 ml. of anhydrous ether was then added dropwise at room temperature with vigorous stirring over a period of three hours; the brown reaction mixture was stirred for another half hour at room temperature. It was then poured into a beaker containing 50 g. of crushed Dry Ice. The acidic material was extracted with 10% potassium hydroxide. The crude acidic fraction, 1.5 g. (7% yield), had a m.p. of 135–155°; it was dissolved in 10% sodium hydroxide, decolorized, acidified and then recrystallized from aqueous acetic acid (80%) to give 1.3 g. of long colorless needles, m.p. 158.5–160.5°; the reported[6] m.p. of *trans*-stilbene-2-carboxylic acid is 158–160°. The infrared curve has a band at 10.35 μ as expected for a *trans* isomer.

From the neutral fraction there was recovered 15 g. of *cis*-2-chlorostilbene (identified by its infrared curve); a small amount of solid material was also obtained which on crystallization from methanol gave 0.2 g. of colorless needles, m.p. 117–120°. This is impure *trans*-stilbene; the reported m.p. of stilbene is 124°.

(2).—Fifteen grams of recovered *cis*-2-chlorostilbene was again treated with lithium. The reaction mixture was refluxed gently throughout the reaction, and for 12 hours longer. The deep red solution was poured onto 50 g. of crushed Dry Ice and worked up as before. The crude acid was brown and rubbery. It was purified through its sodium salt and recrystallized from methanol, m.p. 156–160°; yield 1.6 g., 10%. A larger amount of the solid neutral material was obtained; on recrystallization from ethanol soft colorless plates, m.p. 123–124°, were obtained. The infrared curve was identical with that of the by-products of the previous run.

Acknowledgment.—We wish to express our appreciation to the National Science Foundation for a research grant.

[5] A. Klages and F. Tetzner, *Ber.*, **35**, 3970 (1902).

[6] S. Gabriel and T. Posner, *ibid.*, **27**, 2506 (1894).

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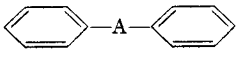
ITHACA, NEW YORK

The Thermal Decomposition of 2-Phenoxybenzoyl Peroxide

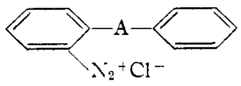
BY DELOS F. DETAR[1] AND ALEX HLYNSKY[2]

RECEIVED APRIL 7, 1955

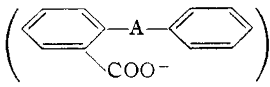
In order to obtain information about the mechanisms of the reactions of free radical intermediates with aromatic rings, a number of compounds have been studied in which an intermediate free radical of structure I is expected. If the bridge group A is C=O or O, then an intramolecular free radical substitution reaction will lead to fluorenone or to dibenzofuran and the formation of the five-membered ring should exert an appreciable driving force in favor of ring closure. If A is a *cis*-ethylenic bridge, then the ring closure to phenanthrene is perhaps even more favored. The two methods of producing the free radical intermediate I that seem to have been studied most thoroughly are the action of alkali upon the diazonium salt II or the thermal decomposition of the peroxide III.



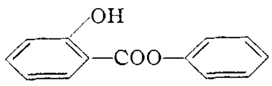
I



II



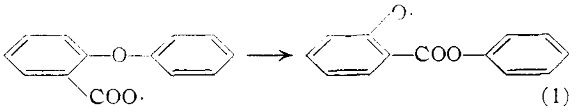
III



IV

Previous work[3] has been carried out for the most part with the diazonium salts, for the desired peroxides have so far proved rather troublesome.

In the present work the peroxide of 2-phenoxybenzoic acid was obtained by treatment of the acid chloride in toluene with an aqueous solution of sodium peroxide. On thermal decomposition of the peroxide in benzene decarboxylation amounted to less than 1%. The major identified product was phenyl salicylate (IV), found in 25% yield. It is reasonable to consider that this product arises by cleavage of the peroxide to 2-phenoxybenzoyloxy radicals (V) which then undergo the intramolecular reaction (eq. 1) to give 2-(carbophenoxy)-phenoxy radicals (VI). This hypothesis has a certain amount of supporting evidence: (1) the thermal decomposition appears to afford no anomalous behavior[4]; (2) the peroxide initiates vinyl polymerization; and finally (3) there seems reason to believe that ionic intermediates would give different products—the *o*-phenoxybenzoate anion should be inert, and the *o*-phenoxybenzoyloxy cation should rearrange[5] to give an *o*-hydroxydiphenyl ether derivative.



V VI (1)

The other reaction products of the thermal decomposition in benzene were a high-melting acid, possibly a dimer of 2-phenoxybenzoic acid (9%); 2-phenoxybenzoic acid (8–12%); ether-insoluble red tar (6%, by weight); unidentified acidic components (18%); neutral components insoluble in ethanol (30–40%). The phenyl ester of phenylsalicylate appeared to be absent.

Attempts were made to modify the phenyl salicylate yield by carrying out the decomposition in other solvents. The peroxide is not very soluble in isoöctane. In an isoöctane–carbon tetrachloride mixture (3:1 by volume) the phenyl salicylate yield was 19%; in chloroform the yield was 20%; and in a benzene–bromotrichloromethane mixture (88:22 by weight) the yield was 21%. The yield of this product was therefore insensitive to the solvents investigated.

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[1] Department of Chemistry, University of South Carolina, Columbia, South Carolina.

[2] Rohm and Haas Research Assistant, Cornell University, 1949–1950.

[3] D. F. DeTar and D. I. Relyea, THIS JOURNAL, **76**, 1680 (1954); D. F. DeTar and Y. W. Chu, *ibid.*, **76**, 1686 (1954).

[4] A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

[5] J. E. Leffler, *ibid.*, **72**, 67 (1950).

In one experiment a sample of 2-methoxybenzoyl peroxide[6] was decomposed in benzene, but no methyl salicylate could be found.

Experimental[7]

2-Phenoxybenzoic Acid.—The preparation of this acid has been described previously,[8] but since devising a procedure for the formation of a pure product in good yield proved troublesome, the procedure is given. Phenol (18.8 g., 0.20 mole), 16.5 g. of 85% potassium hydroxide (0.25 mole), 15.7 g. of *o*-chlorobenzoic acid (0.10 mole), and approximately 0.5 g. of copper bronze were heated with stirring in a 250-ml. three-necked flask (foaming) equipped for distillation. While the temperature was gradually increased a sudden reaction occurred at about 150° and the color of the mixture changed from brown to brick red; phenol began to distil at 180° and by slowly raising the temperature between 200 and 220° a yield-reducing exothermic reaction was avoided. The mixture was cooled to 115° and 20 ml. of water added cautiously to prevent the troublesome caking which occurs in the absence of water. The solution was acidified with sulfuric acid and excess phenol removed by steam distillation. The solid was filtered, dissolved in benzene, and the acidic materials extracted into aqueous sodium bicarbonate. Acidification gave a somewhat reddish solid; this crude 2-phenoxybenzoic acid was dissolved in about 10 ml. of benzene, kept at 55° while 40 ml. of petroleum ether (b.p. 60–70°) was added slowly and with stirring to prevent separation of an oil; then 50 ml. of petroleum ether was added rapidly precipitating a small amount of red oil that quickly solidified. The hot solution was filtered and the pure 2-phenoxybenzoic acid, m.p. 111–112°, crystallized out in 70% yield (15.2 g.). This purification method removes the red-colored impurity and a colorless solid, m.p. 187–198°, possibly diphenic acid.

2-Phenoxybenzoyl Chloride and 2-Phenoxybenzoyl Peroxide.—2-Phenoxybenzoic acid (13 g.) and 7 ml. of thionyl chloride were heated at 50–55° for 40–60 min.; 15 ml. of *n*-heptane was added, the solution filtered and cooled in a Dry Ice bath to cause the acid chloride to crystallize. Sometimes a non-crystallizable oil settled out; in this case the heptane was decanted and replaced by a fresh portion. The 2-phenoxybenzoyl chloride is an almost colorless solid, m.p. 39–40°, and obtained in 94% yield.

To a stirred solution of 2.40 g. of sodium peroxide in 75 ml. of water maintained at 5° was added in dropwise fashion over a half-hour period a solution of 14.9 g. of 2-phenoxybenzoyl chloride in 100 ml. of toluene. Stirring was continued for an additional three hours at 0–5°. After drying the toluene layer, most of the solvent was removed at 30° and 20 min., and the resulting oil triturated with successive portions of *n*-heptane until it solidified to a light-yellow powder (containing 97.5% of peroxide as determined iodometrically); yield 88%. The product on crystallization from an ether-heptane mixture was obtained in the form of colorless crystals, m.p. 66–67°. The product slowly decomposed at room temperature over a period of several weeks.

Anal. Calcd. for $C_{26}H_{18}O_6$: C, 73.25; H, 4.25. Found: C, 73.16; H, 4.37.

Polymerization of Monomers.—Ten-ml. samples of freshly distilled styrene were placed in each of four test-tubes. To the first tube was added 0.1 g. of 2-phenoxybenzoyl peroxide (2.3 mmoles), to the second was added 0.057 g. of benzoyl peroxide (2.3 mmoles), to the third 0.1 g. of 2-phenoxybenzoyl peroxide plus 0.138 g. (1.25 mmoles) of hydroquinone; the fourth tube contained just styrene. After seven days in the dark at room temperature the contents of the first two tubes had become viscous, but the latter two tubes appeared unchanged.

In a similar experiment with methyl methacrylate the benzoyl peroxide tube had hardened, the 2-phenoxybenzoyl peroxide tube was somewhat viscous, and the other two tubes were still mobile.

Thermal Decomposition of 2-Phenoxybenzoyl Peroxide.—In two experiments 1-g. samples of 2-phenoxybenzoyl peroxide were refluxed with 100-ml. portions of benzene for seven hours while swept with a slow stream of high-purity nitrogen to determine carbon dioxide yields. In the first experiment the Ascarite tube gained 5.5 mg., equivalent to a carbon dioxide yield of 1.4%, but the large quantity of benzene found in the cold trap indicated that the nitrogen sweep rate was too high. The second experiment gave a gain of only 0.3 mg.; the carbon dioxide yield was nil.

Evaporation of the benzene from a run in which 5.4 g. of the peroxide had been refluxed for 15 hours in 500 ml. of reagent grade benzene gave a viscous oil. This was extracted with isoöctane, one portion of which was diluted and the ultraviolet absorption spectral curve obtained, and the other portion of which was evaporated and the infrared curve obtained. The absorption curve of the oil had all the absorption peaks of phenyl salicylate (more than 28 significant peaks) and only one peak at 5.73 μ that was clearly extraneous. Attempts to get the oil to solidify were unsuccessful. This extract was missing some of the peaks characteristic of the phenyl ester of 2-phenoxybenzoic acid. 2-Phenoxybiphenyl has strong peaks at 12.99, 13.33 and 13.57μ; the above oil lacks peaks in these regions. The absence of dibenzofuran was indicated by the ultraviolet spectra; dibenzofuran has peaks at about 250 mμ and at 282 mμ and a minimum at about 259 mμ. The ultraviolet curve of the oil had maxima at 241 and at 310 and a minimum at 278 mμ with no indication of perturbations expected for dibenzofuran. Moreover, the formation of these products would require decarboxylation. Their absence therefore seems well established.

A small amount of solid material, m.p. 271–273°, could be isolated from a benzene concentrate of the decomposition products. It may be some sort of dimer (or polymer) of *o*-phenoxybenzoic acid as indicated by analysis and by the high melting point. The material was recovered unchanged from refluxing sodium hydroxide.

Anal. Calcd. for $C_{26}H_{18}O_6$: C, 73.25; H, 4.25; neut. equiv., 214. Found: C, 73.22; H, 4.89; neut. equiv., 217.5.

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(6) We are indebted to Dr. A. J. Buselli for this sample.[4]

(7) All melting points are corrected.

(8) F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2111 (1905); R. Q. Brewster and F. Strain, THIS JOURNAL, **56**, 117 (1934).

Saturation of Acetyldehydroalanine with Benzylamine

BY S.-C. J. FU AND JESSE P. GREENSTEIN

RECEIVED APRIL 20, 1955

The unsaturated character of the dehydropeptides, RCHCONHC(=CHR′)COOH, is revealed in part by several types of addition reactions such as the decolorization of bromine and permanganate,[1,2] and the addition of catalytic hydrogen,[1] of mercaptans,[3] of amides[4] and of amines.[2,5] Not all of the dehydropeptides react alike toward these reagents. Thus, whereas acetyldehydroalanine readily reacts quantitatively with bromine[2] and with amines,[2,5] acetyldehydrovaline reacts only partially, and acetyldehydrophenylalanine not at all with bromine, and neither compound reacts with amines.[2]

Saturation of acetyldehydroalanine (N-α-acetaminoacrylic acid) with benzylamine has led to the identification of α-acetamino-β-benzylaminopropionic acid as one of the products.[2] The low yield obtained made it desirable to study the reaction in more detail, and it was further considered of interest to see if it might serve as a method for the preparation of the relatively difficultly accessible

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(1) M. Bergmann and F. Stern, *Ann.*, **448**, 20 (1926).

(2) I. Z. Eiger and J. P. Greenstein, *Arch. Biochem.*, **19**, 467 (1948).

(3) B. H. Nicolet, *Science*, **81**, 181 (1935).

(4) D. Shemin and R. Herbst, THIS JOURNAL, **60**, 1954 (1938).

(5) V. E. Price and J. P. Greenstein, *J. Biol. Chem.*, **173**, 337 (1948).