a titre of more than 0.1 ml. of 0.1N sodium hydroxide per aliquot. A correction also was made for the quantity of amine removed in the course of analysis. The extracted samples were analyzed by titration with 0.1N hydrochloric acid in 1:1 ethylene glycol-isopropyl alcohol solvent.[3] The end points were determined potentiometrically.

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A Dimer of Styrene: 1,2-Diphenylcyclobutane

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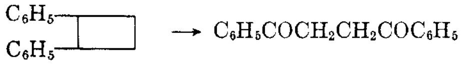
The treatment of styrene with refluxing aqueous sulfuric acid yields two dimeric hydrocarbons, the linear, unsaturated 1,3-diphenyl-1-butene, and the cyclic, saturated 1-methyl-3-phenylindan.[2,3] The free radical or thermal polymerization of stryene, on the other hand, leads to high molecular weight polymers. If the thermal reaction is conducted, however, in the presence of polymerization inhibitors such as picric acid,[4] iodine,[5] or *sym*-trinitrobenzene,[5] one again observes the formation of cyclic, saturated dimeric hydrocarbons.[6] These dimers are structurally different from 1-methyl-3-phenylindan. The present paper presents evidence that one of the dimers produced from the free radical inhibited thermal polymerization of styrene is 1,2-diphenylcyclobutane, a head-to-head dimer of styrene. Thus, the chromic oxide oxidation of the dimeric mixture yields 1,2-dibenzoylethane (diphenacyl, succinophenone).[7] This represents the first definite evidence for the preparation[4,5] and presence of 1,2-diphenylcyclobutane.



EXPERIMENTAL

Styrene. Commercial styrene was washed free of inhibitor with aqueous sodium hydroxide, dried, and distilled through a 1-meter packed column at reduced pressure.

Dimerization reaction. A solution of 0.4 g. iodine in 200 g. styrene was refluxed for 16 hr. (146°). Vacuum distillation separated the amber-colored reaction product into 100 g. of recovered monomer, 77 g. solid polymer, and 19 g. liquid oligomer. The latter was washed with aqueous sodium bisulfite and mercury to remove codistilled iodine and then distilled to yield 7 fractions (b.p. 124–160°/0.5 mm., n_D^{20} 1.5864–1.5961).[8]

Fraction 3 (n_D^{20} 1.5913) was submitted for analysis.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.1; H, 7.8; mol. wt. 208; H_2 absorption, 0.00 mole. Found: C, 92.5; H, 7.9; mol. wt. 196 (benzene); H_2 absorption, 0.03 mole.

The infrared spectra of the individual fractions differed from that of the separately prepared sulfuric acid dimer.[2] Significant differences are the presence in the latter of the methyl group absorption at 1376 cm.$^{-1}$ and the *trans*-unsaturation band at 966 cm.$^{-1}$

Oxidation of the dimer. Chromium trioxide (4 g.) was added over a period of 40 min. to a solution of dimer (1 g.) in 40 ml. glacial acetic acid at 50°. The temperature rose to 73° during the oxidation. Extraction with aqueous sodium bicarbonate gave no acidic product. After numerous washings, chromatograms on silica gel, and fractional sublimations of the residue, a small yield of colorless crystals of diphenacyl (m.p. 143–145°, lit.,[9] m.p. 144–145°) was obtained. It gives the described green color in concd. sulfuric acid solution.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.9; H, 5.5.

The diketone reacts with 2,4-dinitrophenylhydrazine to yield a brilliant crimson derivative (m.p. 219–221°). This may be the pyridazine which can arise by the condensation of the —$NHNH_2$ function with both carbonyl groups.

Anal. Calcd. for $C_{22}H_{16}N_4O_4$: N, 14.0. Found: N, 14.0.

The *bis*-2,4-dinitrophenylhydrazone of 1,2-dibenzoylethane is reported to be orange-yellow in color and to melt at 250° dec.[10]

Conclusive identification of the oxidation product as 1,2-dibenzoylethane was established by an independent synthesis of the diketone by the zinc dust–acetic acid reduction of 1,2-dibenzoylethylene.[10] The latter was prepared by the Friedel-Crafts condensation of fumaryl chloride with benzene.[11] An attempted synthesis of the diketone involving the sulfur dehydrogenation of the methyl groups of two acetophenone molecules was not successful.

The infrared spectrum (potassium bromide) of the oxidation product was identical with that of the authentic sample of 1,2-dibenzoylethane. Absorption bands are observed at 3060, 2905, 1680, 1598, 1582, 1445, 1396, 1372, 1352, 1256, 1220, 1178, 1074, 1062, 1024, 988, 946, 927, 918, 858, 775, 736, and 692 cm.$^{-1}$

Other reactions. Attempts to isolate definite products from the dimers by (a) ozonization in carbon tetrachloride solution

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(1) Present address: Texas-U. S. Chemical Co., TEXUS Research Center, Parsippany, New Jersey.

(2) M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

(3) B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954).

(4) F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).

(5) F. R. Mayo, personal communications.

(6) The author has observed a similar oligomerization of α-methyl styrene in the presence of iodine and ultraviolet radiation.

(7) M. Pailer and U. Müller, *Monatsh-Chemie*, **79**, 615 (1948) have shown that the chromic oxide oxidation of 1,2,3,4-tetraphenylcyclobutane (isolated from the photochemical dimerization of stilbene) yields 1,2-diphenyl-1,2-dibenzoylethane (bidesyl).

(8) A recent personal communication from F. R. Mayo and K. Griggs states that the application of gas chromatographic and infrared techniques reveals that a typical dimer obtained from the iodine-inhibited thermal polymerization of styrene consists of a mixture of 1,2-diphenylcyclobutane, 1-phenylnaphthalene, 1-phenyltetralin, and other components. The 1-phenyltetralin is isolated in greatest yield.

(9) W. Borsche, S. Kettner, M. Gilles, H. Kühn, and R. Manteuffel, *Ann.*, **526**, 1 (1936).

(10) C. F. H. Allen, D. M. Young, and M. R. Gilbert, *J. Org. Chem.*, **2**, 235 (1937).

(11) R. E. Lutz, C. F. H. Allen, and F. P. Pingert, *Org. Syntheses*, **Coll. Vol. III**, 248 (1955).

at −78°, (b) bromination with *N*-bromosuccinimide followed by dehydrobromination, (c) nitration with nitric acid–sulfuric acid at 0°, and (d) oxidation with basic aqueous potassium permanganate were unsuccessful in spite of detailed crystallization, chromatographic, and sublimation techniques. These results are in keeping with the now-determined complexity of the dimeric mixture.[8]

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