Divalent Carbon: Some Reactions in the Diphenylmethyl Series

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Attempts have been made to produce diphenylmethylene by pyrolysis of benzhydryl acetate, by desulfurization of thiobenzophenone, by dechlorination of dichlorodiphenylmethane, and by dehydrochlorination of benzhydryl chloride with *n*-butyllithium. Reactions were observed in each case with 1,1-diphenylethylene to form 1,1,3,3-tetraphenylpropene or 1,1,3-triphenylindene. From none of the reactions could 1,1,2,2-tetraphenylcyclopropane, the characteristic product of diphenyldiazomethane and 1,1-diphenylethylene, or its rearrangement product 1,1,3-triphenylindane, be isolated. A new preparative method for 1,1,3-triphenylindene is described.

Various reactions have been described[1a–h] in which methylene is suspect as an intermediate. Utilization of similar reaction types on the corresponding diphenyl substituted compounds, which might yield the more stable diphenylmethylene, has not been surveyed. We have studied the pyrolysis and photolysis of diphenyldiazomethane,[2] pyrolysis of benzhydryl acetate, dehydrochlorination of benzhydryl chloride with *n*-butyllithium, dechlorination of diphenyldichloromethane with copper, mercury, and zinc, and the desulfurization of thiobenzophenone with zinc. Fig. 1 outlines our results. Fig. 2 shows the ultraviolet spectra of the isomeric substances prepared in this work.

Credit must be given to Nef[3] and Bacon[4] who first pyrolyzed benzhydrol and benzhydryl acetate. They both proposed diphenylmethylene as a reactive intermediate but made no attempt to "trap" this intermediate with an olefin. Reaction 13 is a repetition of the procedure described by Schlenk and Bergmann[5] and the oxidations of V, VI, and IX to VII followed the procedure described by Kohler.[6]

A complete mechanistic scheme has been devised for the formation of each of the compounds shown in Fig. 1 not involving the intermediacy of divalent carbon atoms.[7] The interesting features of this scheme involve the heterolytic cleavage of *sym*-tetraphenylethane to form either the indene derivative (cationic reaction with the aromatic nucleus) (reaction 8) or to react with acetic acid to give benzhydryl acetate which subsequently forms IV (reaction 7); and, homolytic cleavage of benzhydryl acetate to give, after reaction with 1,1-diphenylethylene, 1,1,3,3-tetraphenylpropene (IV). This latter fact is supported by the isolation of 1,1-diphenylethane, formed probably *via* decomposition of the acetoxyl radical to methyl radical which subsequently reacts with diphenylmethyl radical[8] (see Table I in Experimental).

The principal justification for assuming that this series of reactions does not involve a divalent carbon atom is that *in the reaction of the diazo compound such an intermediate does form and it reacts characteristically with 1,1-diphenylethylene to give the cyclopropane derivative.* If, however, the cyclopropane derivative is formed in the diazo reaction from an unstable pyrazoline (or nitrogen-containing) intermediate, then it is possible that all the others (except the dechlorination reaction) represent carbon–hydrogen insertion reactions of diphenylmethylene.

Reaction 12 proceeds at room temperature and gives 1,1,3-triphenylindene in 70% yield. This is a good preparative procedure since the previous synthesis of this compound was by the acid-catalyzed rearrangement of tetraphenylallene.[9]

Experimental

The infrared spectra were obtained with a Perkin–Elmer Infracord Model 137 using sodium chloride optics. A potassium bromide disk was made of all solids. Ultraviolet spectra were obtained with a Beckman spectrophotometer Model DK-2. An F & M gas chromatograph Model 127, using a 6-ft. copper column packed with Apiezon L grease on Chromosorb and held at 260°, was used for gas chromatographic analysis. The carrier gas was helium.

The pyrolyses were run in a bomb made from a piece of 1-in. steel stock machined to hold a 15 × 150 mm. test tube. The bomb was heated in an electric furnace maintained at 300 ± 5°.

Alcoa F-20 alumina, activated 4 hr. at 180°, was used for elution chromatography. Eluents used in the work were principally petroleum ether (b.p. 30–60°), 3:1 petroleum ether–benzene, 1:1 petroleum ether–benzene, and finally benzene. Melting points and boiling points are uncorrected.

1,1-Diphenylethylene was prepared from bromobenzene and ethyl acetate by the method of Allen and Converse[10] in 64% yield and from bromobenzene and acetophenone by

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(1)(a) H. Staudinger and R. Endle, *Ber.*, **46**, 1437 (1913); H. Staudinger, *ibid.*, **49**, 1886 (1916); (b) F. O. Rice and A. C. Glasebrook, *J. Am. Chem. Soc.*, **55**, 4329 (1933); **56**, 2381 (1934); (c) H. M. Frey and G. B. Kistakowsky, *ibid.*, **79**, 6373 (1957); (d) M. Burton, T. W. Davis, A. Gordon, and H. A. Taylor, *ibid.*, **63**, 1956 (1941); (e) T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J. Chem. Soc.*, 409 (1938); (f) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); **82**, 5723 (1960); (g) W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 6162 (1954). This procedure has been applied, without success, to chlorodiphenylmethane, S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959); (h) see also ref. cited in J. Houben, "Die Methoden der Organischen Chemie," Verlag Georg Thieme, Leipzig, 1925, Edwards Brothers, Inc., Ann Arbor, Mich., Vol. 4, 1943, p. 891.

(2) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959); H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(3) J. U. Nef, *Ann.*, **298**, 231 (1897).

(4) R. F. Bacon, *Am. Chem. J.*, **33**, 68 (1905).

(5) W. Schlenk and E. Bergmann, *Ann.*, **463**, 223 (1928).

(6) E. P. Kohler, *Am. Chem. J.*, **40**, 217 (1908).

(7) M. P. Hughes, M.A. thesis, Texas Christian University, 1961.

(8) Suggested by Dr. W. B. Smith of this department.

(9) D. Vorlander and C. Siebert, *Ber.*, **39**, 1024 (1906).

(10) C. F. H. Allen and S. Converse, "Organic Synthesis," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 226.

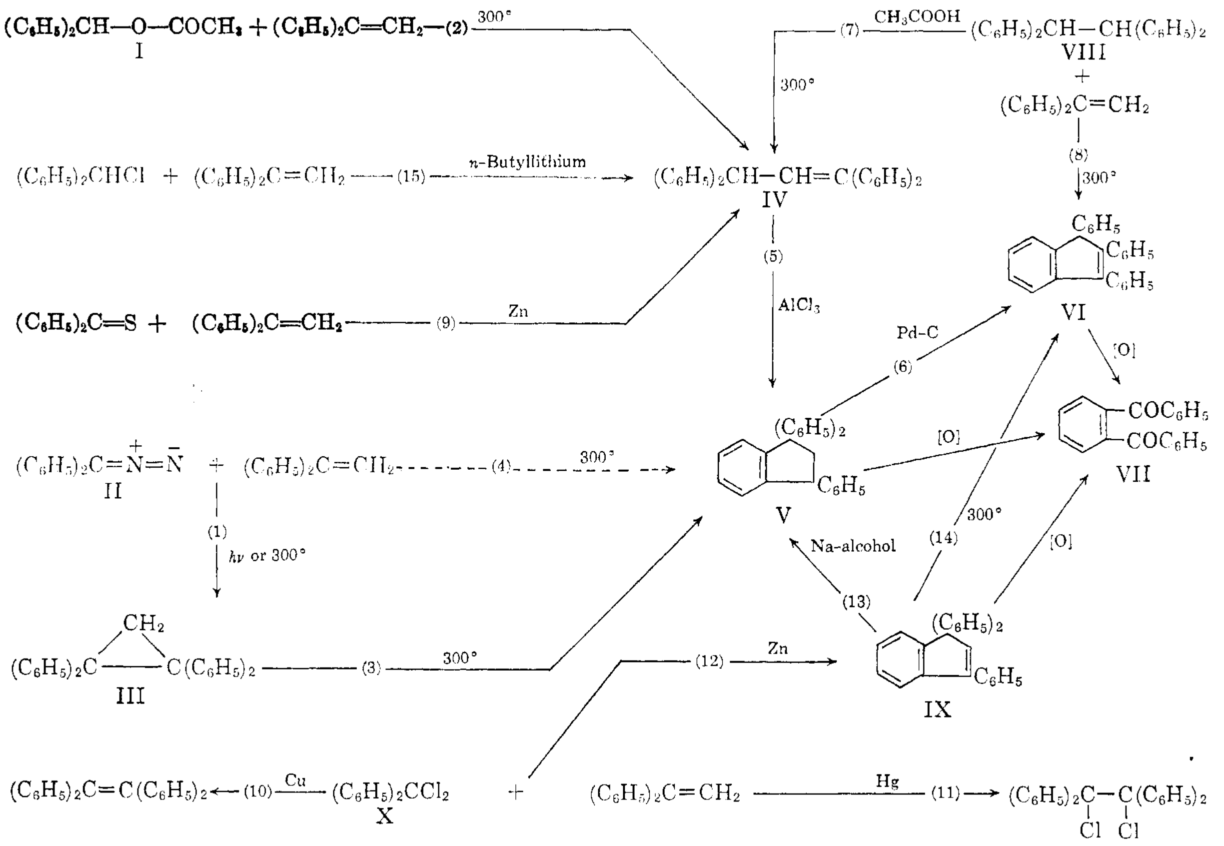

Fig. 1.—Reaction scheme. The dashed line in reaction 4 indicates that this reaction is experimentally observed but actually proceeds *via* reactions 1 and 3.

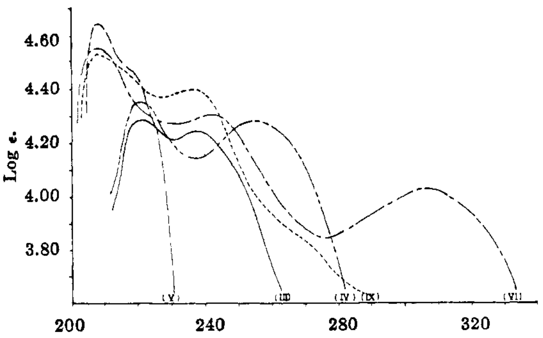

Fig. 2.—Ultraviolet absorption spectra. III, 1,1,2,2-tetraphenylcyclopropane; IV, 1,1,3,3-tetraphenylpropene; V, 1,1,3-triphenylindane; VI, 1,2,3-triphenylindene; IX, 1,1,3-triphenylindene.

a similar type Grignard reaction in 60% yield. The clear liquid boiled at 140–142° (13 mm.), $n^{21}\text{D}$ 1.6052 (lit.,[5] b.p. 113°/2 mm.).

Benzhydryl Acetate.—Sixty grams of benzhydrol was dissolved in 100 ml. of glacial acetic acid, 100 ml. of acetic anhydride was added, and the mixture was refluxed for 24 hr. The mixture was then poured into 1 l. of crushed ice and the water solution was extracted with four 50-ml. portions of ether. The combined ether extracts were washed with 10% sodium hydroxide until the wash remained basic and then the ether layer was dried over calcium chloride. After removing the ether the residual oil was vacuum distilled, collecting the fraction boiling 193–197° at 30 mm. The clear oil solidified upon cooling, m.p. 40–41°. The yield was 50 g. (81%) (lit.,[11] m.p. 41–41.5°[6]; b.p. 184°/23 mm.).

Pyrolysis of Benzhydryl Acetate and 1,1-Diphenylethylene.—The reaction was run under various conditions. A typical run is given as follows: ten grams (0.044 mole) of benzhydryl acetate was dissolved in 15.0 g. (0.084 mole) of 1,1-diphenylethylene in a test tube, the mouth of the test tube plugged with glass wool, and the test tube sealed in the bomb. The bomb was heated for 6 hr. at 300°. After slow cooling the bomb was opened and the black reaction mixture dissolved in 25 ml. of boiling benzene. The reaction was worked up by two methods.

A. The benzene solution was filtered and the filtrate vacuum distilled. Seven and three-tenths grams of a clear liquid, b.p. 137–141°/13 mm., was collected and shown by vapor phase chromatography and infrared analysis to contain 2.1 g. (30%) of diphenylmethane, 1.1 g. (14%) of 1,1-diphenylethane and 4.1 g. of unchanged 1,1-diphenylethylene. The solid residue was dissolved in 25 ml. of benzene, filtered through a short column (25 × 100 mm.) of alumina and the filtrate evaporated to dryness. The residue was recrystallized twice from 4:1 ethanol-benzene. Six grams (40%) of 1,1,3,3-tetraphenylpropene, m.p. 127–128°, was isolated.

B. The benzene solution was chromatographed on an alumina column (25 × 500 mm.). The petroleum ether fractions contained a clear liquid shown by vapor phase chromatography and its infrared spectra to contain 3.4 g. (37%) of diphenylmethane, 0.8 g. (10%) of 1,1-diphenylethane, and 5.7 g. of unchanged 1,1-diphenylethylene. The petroleum ether–benzene fractions, after evaporation to dryness and crystallization of the residue from 4:1 ethanol–

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(11) B. K. Morse and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 416 (1952).

TABLE I

PYROLYSIS OF BENZHYDRYL ACETATE IN 1,1-DIPHENYLETHYLENE

Time heated, hr.	IV, %	Diphenylmethane, %	Tetraphenylethane, %	1,1-Diphenylethane, %
0.5[a]	5	...	5	0
2.0	23	...	15	0
4.0[a]	28	...	11	0
6.0	36–40	30–37	0	10–14
12.0	36	...	0	...
24.0	37	..	0	...

[a] Refluxed in 1,1-diphenylethylene (285°).

benzene, contained 5.4 g. (36%) of 1,1,3,3-tetraphenylpropene, m.p. 127–127.5°. The results of other reactions are given in Table I.

Preparation of 1,1,3,3-Tetraphenylpropene. Benzalacetophenone was prepared from benzaldehyde and acetophenone.[12] The product, in 89% yield, melted at 54–55°.

β,β-Diphenylpropiophenone was prepared by 1,4-addition of phenylmagnesium bromide to benzalacetophenone. Phenylmagnesium bromide, prepared in the usual manner from 3.05 g. of magnesium turnings and 18.02 g. of bromobenzene, was added to 20.0 g. of benzalacetophenone. Fifteen grams (55%) of product, crystallized from ethanol, m.p. 94°, was obtained (lit.,[13] m.p. 96°, lit.,[14] 96°).

1,1,3,3-Tetraphenylpropene was prepared by dehydration of the alcohol obtained from addition of phenylmagnesium bromide to β,β-diphenylpropiophenone. One and five tenths grams of magnesium turnings and 9.25 g. of bromobenzene were used to prepare the Grignard compound. To this solution was added 15.0 g. of β,β-diphenylpropiophenone. The resulting alcohol was refluxed for 4 hr. in 20% hydrochloric acid. White needles were obtained from 4:1 ethanol–benzene. The yield was 5.5 g. (30%) of 1,1,-3,3-tetraphenylpropene, m.p. 127–127.5° (lit.,[15] m.p. 127°). Infrared bands (potassium bromide disk) were observed at 3.3–3.35 (m-doublet), 6.3 (s), 6.9–7.0 (s-doublet), 7.4 (m), 9.35 (m), 9.75 (s), 11.1 (s), 12.8 (s), 13.0 (vs), 13.5 (vs) and 13.8 (vs), and 14.3 (vs) μ. The ultraviolet spectrum (absolute ethanol) showed bands at 255 mμ (ε 19,700) and 220 mμ (ε 22,800).

Preparation of 1,1,2,2-Tetraphenylcyclopropane.—Diphenyldiazomethane was prepared from 15.0 g. of benzophenone hydrazone and 41.0 g. of yellow mercuric oxide by the method of Miller.[16] The resulting material was dissolved in 30.0 g. of 1,1-diphenylethylene and placed in a quartz flask mounted under an ultraviolet light (Hg) source. The flask was irradiated until the purple color disappeared (*ca.* 48 hr.). The white solid (m.p. 149–153°) was filtered, washed well with chilled petroleum ether, dissolved in 50 ml. of benzene, and chromatographed on an alumina column (50 × 500 mm.). The column was developed with 500 ml. of 9:1 petroleum ether–benzene. Similar fractions were combined, evaporated to dryness and the solid crystallized from absolute ethanol. Nine grams of 1,1,2,2-tetraphenylcyclopropane, m.p. 165–165.5°, was obtained (lit.,[15] m.p. 165–165.5°). Infrared bands (potassium bromide disk) were observed at 3.3–3.35 (m-doublet), 6.3 (s), 6.75 (s), 6.95 (s), 8.3–8.4–8.5 (w-triplet), 9.3 (m), 9.7 (m), 9.9 (m), 12.6 (s), 13.3 (vs), 14.0 (vs), and 14.3 (vs) μ. The ultraviolet spectrum (absolute ethanol) exhibited bands at 239 mμ (ε 18,200) and 220 mμ (ε 19,800).

Reaction of Diphenyldiazomethane and 1,1-Diphenylethylene.—A. Five grams of diphenyldiazomethane and 10.0 g. of 1,1-diphenylethylene were mixed in a test tube, the test tube was sealed in a bomb and was heated to 300° for 1 hr. After rapid chilling of the bomb, the yellow oil was subjected to chromatography. Seven and three-tenths grams of 1,1-diphenylethylene was obtained from the petroleum ether fractions. The 1:1 petroleum ether–benzene fractions contained 4.8 g. (57%) of 1,1,3-triphenylindane, m.p. 111–112°. (A mixed melting point with an authentic sample was not depressed.) Benzophenone azine (0.90 g.), m.p. 157–161°, was obtained from the combined benzene fractions (lit.,[17] m.p. 162–163°).

B. Procedure A was repeated heating the bomb for 30 min. Chromatography of the product gave 2.8 g. (32%) of 1,1,2,2-tetraphenylcyclopropane, m.p. 165–165.5°.

Rearrangement of Tetraphenylcyclopropane. A. In 1,1-Diphenylethylene and Acetic Acid.—Five grams of tetraphenylcyclopropane, 10.0 g. of 1,1-diphenylethylene, and 1.0 g. of acetic acid were mixed in a test tube. The test tube was sealed in the bomb and heated to 300° for 1 hr. The products were separated by chromatography. The petroleum ether fractions contained 9.4 g. of 1,1-diphenylethylene. The 1:1 petroleum ether–benzene fractions, after evaporation to dryness and crystallization of residue from 4:1 ethanol–benzene, contained 3.5 g. (70%) of 1,1,3-triphenylindane m.p. 111–112°. The filtrate from the crystallization was evaporated and 0.30 g. (6%) of 1,2,3-triphenylindene, m.p. 132–133°, was obtained.

B.—Procedure A was repeated except that the bomb was heated for 2 hr. Careful elution chromatography gave 2.75 g. (50%) of 1,1,3-triphenylindane and 1.4 g. (28%) of 1,2,3-triphenylindene.

C.—Procedure A was repeated except that the bomb was heated for 4 hr. Elution chromatography gave 27% 1,1,3-triphenylindane and 61% of 1,2,3-triphenylindene.

D. In 1,1-Diphenylethylene.—Procedure A was repeated except that the acetic acid was omitted. Elution chromatography gave 2.2 g. (41%) of 1,1,3-triphenylindane.

1,1,3-Triphenylindane.—Five grams (0.0145 mole) of 1,1,3,3-tetraphenylpropene was dissolved in 50 ml. of anhydrous carbon disulfide, 2.0 g. (0.015 mole) of aluminum chloride was added and the solution let stand for 24 hr. Fifty milliliters of concentrated hydrochloric acid was then added and the two-phase solution separated. The carbon disulfide layer was washed with 10% sodium hydroxide and dried over anhydrous sodium sulfate. Evaporation to dryness gave a thick red oil which was chromatographed on an alumina column. The benzene fractions were combined, evaporated to dryness and the residue crystallized from 4:1 ethanol–benzene. Two grams (40%) of 1,1,3-triphenylindane, m.p. 111–112°, was obtained (lit.,[8] m.p. 111–112°). Infrared bands (potassium bromide disk) were observed at 3.24–3.3 (m-doublet), 3.35 (m), 3.35 (w), 6.25 (m), 6.7 (s), 6.8 (m), 6.9–6.95 (s-doublet), 9.7 (m), 13.0–13.15–13.3 (vs-triplet), and 14.3 (vvs) μ. The ultraviolet spectrum (absolute ethanol) gave a band at 208 mμ (ε 44,500).

Conversion of 1,1,3-Triphenylindane to 1,2,3-Triphenylindene.—One gram of 1,1,3-triphenylindane and 0.2 g. of 5% palladium on charcoal were mixed in a test tube, a thermometer was inserted, and the mixture was heated at 350° for 20 min. When cool, the melt was dissolved in 5 ml. of benzene, then filtered and the filtrate evaporated to dryness. The light yellow residue was recrystallized twice from absolute ethanol. A 0.35-g. yield (35%) of 1,2,3-triphenylindene, m.p. 131–132°, was obtained (lit.,[18] m.p. 132°). Infrared bands (potassium bromide disk) were observed at 3.24–3.3 (m-doublet), 6.2 (ms), 6.7 (s), 6.8 (s), 6.85–6.9 (s-doublet), 7.4 (w), 12.6 (s), 12.9 (vs), 13.1 (s), 13.3 (vs), 13.8 (s), and 14.2 (vvs) μ. The infrared spectrum was identical to an infrared spectrogram of 1,2,3-triphenylindene

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(12) E. P. Kohler and H. M. Chadwell, "Organic Synthesis," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 78.

(13) E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904); **38**, 511 (1907).

(14) A. Luttringhaus and K. Scholtis, *Ann.*, **557**, 70 (1945).

(15) G. Wittig and B. Obermann, *Ber.*, **67B**, 2053 (1934).

(16) J. P. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(17) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

(18) R. E. Lutz and E. H. Rinker, Jr., *ibid.*, **77**, 366 (1955).

kindly furnished by Samuel P. Sadtler & Son, Inc., of Philadelphia, Pa. The ultraviolet spectrum (absolute ethanol) showed bands at 306 mμ (ε 10,500), 241 mμ (ε 20,300), and 208 mμ (ε 37,200).

Oxidation of 1,1,3-Triphenylindane.—One gram of 1,1,3-triphenylindane was dissolved in 15 ml. of boiling glacial acetic acid and a solution of 2.0 g. of chromium trioxide in 2 ml. of water was added dropwise. The mixture was refluxed for 30 min. The acetic acid solution was then poured into 50 ml. of water and the water solution extracted with two 25-ml. portions of ether. The ether extracts were combined, washed with 10% sodium hydroxide until the wash remained basic, and dried over calcium chloride. The ether was removed under vacuum and the solid crystallized from acetone–ethanol. A 0.12-g. yield (14%) of *o*-dibenzoylbenzene, m.p. 146–147°, was obtained (lit.,[9] m.p. 146–148°).

Oxidation of 1,2,3-Triphenylindene.—One gram of 1,2,3-triphenylindene was oxidized by the above procedure using 0.7 g. of chromium trioxide. The yield was 0.35 g. (41%) of *o*-dibenzoylbenzene, m.p. 146–147°.

Tetraphenylethylene was prepared by the method of Buckles and Matlack[19] using dichlorodiphenylmethane and copper powder. White needles (53%), m.p. 222–223°, from 1:1 benzene–ethanol were obtained (lit.,[19] m.p. 223–224°).

***sym*-Tetraphenylethane** was prepared by the two methods described below.

A. Tetraphenylethylene was reduced by sodium in liquid ammonia by the method of Wooster and Mitchell[20] in 74% yield. White prisms were obtained from chloroform, m.p. 208–209° (lit.,[21] m.p. 208–209°).

B. Chlorodiphenylmethane (27.2 g.) and zinc dust (20.0 g.) were refluxed in benzene for 4 hr. The solution was filtered while hot and the filtrate evaporated to dryness. The residue was recrystallized from chloroform. The yield was 40% of product, m.p. 208–210°.

Reaction of *sym*-Tetraphenylethane, 1,1-Diphenylethylene and Acetic Acid.—Two grams of *sym*-tetraphenylethane, 11.3 g. of 1,1-diphenylethylene, and 1.0 g. of acetic acid were mixed in a test tube, the test tube sealed in a bomb and heated at 300° for 20 hr. When cool the bomb was opened and the products separated by chromatography. The petroleum ether fractions contained 0.85 g. (43%) of diphenylmethane and 7.8 g. of 1,1-diphenylethylene, as determined by gas chromatography. The benzene fractions contained, after recrystallization twice from 4:1 ethanol-benzene, 0.8 g. (39%) of 1,1,3,3-tetraphenylpropene, m.p. 126–127°. A mixed melting point with an authentic sample was not depressed.

Reaction of *sym*-Tetraphenylethane and 1,1-Diphenylethylene.—Five grams (0.015 mole) of *sym*-tetraphenylethane and 16.0 g. (0.089 mole) of 1,1-diphenylethylene were heated as above for 6 hr. at 300°. The reaction mixture was chromatographed. The petroleum ether fractions contained 1.0 g. of diphenylmethane and 13.0 g. of 1,1-diphenylethylene. The benzene fractions contained, after crystallization from ethanol, 4.9 g. (47%) of 1,2,3-triphenylindene, m.p. 132–133°. A mixed melting point with an authentic sample melted 131–132°.

Thiobenzophenone was prepared by the method of Westheimer and Staudinger[22,23] using benzophenone, anhydrous hydrogen chloride, and anhydrous hydrogen sulfide. The yield was 70% of deep blue crystals, m.p. 52.5–53.3° (lit.,[23] m.p. 51–52°). The infrared spectrum showed only traces of benzophenone.

Reaction of Thiobenzophenone, 1,1-Diphenylethylene, and Zinc Dust.—Five grams (0.025 mole) of freshly prepared thiobenzophenone and 27.7 g. (0.154 mole) of 1,1-diphenylethylene were mixed in a 100-ml. flask fitted with stirrer, a nitrogen purge system, and a condenser. Eleven grams (0.17 mole) of zinc dust was added through the condenser, the stirrer was started, and the mixture heated to 145° for 96 hr. or until the blue color disappeared. The brown solution was diluted with petroleum ether and filtered to remove zinc salts. After removing the petroleum ether under vacuum, the oil was chromatographed. All benzene fractions were combined, evaporated to dryness and the residue chromatographed on a second column. Again all benzene fractions were combined and evaporated to dryness. The residue was crystallized from chloroform–petroleum ether and from ethanol–benzene. Eight-tenths of a gram (9.3%) of 1,1,3,3-tetraphenylpropene, m.p. 125–127°, was obtained. A mixed melting point with an authentic sample melted 125–127°.

Dichlorodiphenylmethane (benzophenone dichloride) was prepared by refluxing equal weights of benzophenone and phosphorus pentachloride for 5 hr. The product was purified by vacuum distillation. The yield was 90% of clear oil, b.p. 185–187° at 22 mm., $n^{21}\text{D}$ 1.6044 (lit.,[24] b.p. 180–181°/17 mm.).

Reaction of Dichlorodiphenylmethane, 1,1-Diphenylethylene and a Metal. A. Reaction Using Copper Powder.—Twenty-five grams of dichlorodiphenylmethane, 24.9 g. of 1,1-diphenylethylene, and 50 ml. of benzene were mixed together in a 100-ml. flask. Copper powder (18.0 g.) was added and the solution refluxed for 5 hr. The solution was filtered while hot and the filtrate chilled in a Dry Ice–acetone bath. The resulting crystals were filtered and recrystallized from 1:1 ethanol–benzene. Nine grams (50%) of tetraphenylethylene, m.p. 220–222°, was obtained. Vacuum distillation of the filtrates gave 19.8 g. of 1,1-diphenylethylene, b.p. 170–173°/45 mm.

B. Reaction Using Zinc Dust.—Ten grams of dichlorodiphenylmethane, 10 g. of 1,1-diphenylethylene, and 30 ml. of benzene were mixed together and 10 g. of zinc dust added. Immediately after the zinc was added the solution darkened and an exothermic reaction began. After 1 hr. the temperature began to fall; then the mixture was refluxed for four additional hours. The reaction was worked up as above. Five and eight-tenths grams (40%) of 1,1,3-triphenylindene, m.p. 135–135.5°, was obtained (lit.,[18] m.p. 135°). Infrared bands (potassium bromide disk) were observed at 3.3 (m), 6.3 (m), 6.8 (s), 6.9–7.0 (s-doublet), 7.45 (w), 8.7 (m), 9.3–9.4 (m-doublet), 9.8 (s), 10.9 (w), 11.0 (w), 12.1 (m), 12.9 (s), 13.1 (vvs), and 13.4 (vs) μ. The ultraviolet spectrum (absolute ethanol) gave bands at 236 mμ (ε 25,500) and 208 mμ (ε 34,000).

C.—Twelve grams of dichlorodiphenylmethane and 18.0 g. of 1,1-diphenylethylene were mixed in a flask fitted with stirrer, nitrogen inlet, and condenser. The flask was purged well with dry nitrogen, the motor started, and 10 g. of zinc dust added. The reaction was stirred for 5 hr. Fifty millliters of petroleum ether was added, the flask was chilled in a Dry Ice–acetone bath and then the reaction mixture was filtered. The precipitate was dissolved in 50 ml. of benzene, filtered again to remove zinc salts, and the filtrate was evaporated to dryness. The residue was crystallized twice from 1:1 benzene–ethanol. Twelve grams (70%) of 1,1,3-triphenylindene, m.p. 135–135.5°, was obtained.

D.—The above reaction was repeated using 10 g. of carefully dried zinc chloride instead of zinc dust. Five and four-tenths grams (31%) of 1,1,3-triphenylindene was obtained.

E. Reaction with Mercury.—Procedure B was followed exactly using mercury instead of zinc dust. Twenty-four

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(19) R. E. Buckles and G. M. Matlack, *Org. Syntheses*, **31**, 104 (1951).

(20) C. H. Wooster and N. W. Mitchell, *J. Am. Chem. Soc.*, **52**, 6881 (1930).

(21) W. H. Zartman and H. Adkins, *ibid.*, **54**, 668 (1932).

(22) R. H. Abeles, R. F. Hutton, and F. H. Westheimer, *ibid.*, **79**, 712 (1957).

(23) H. Staudinger and H. Freundenberger, *Ber.*, **61B**, 1576 (1928).

(24) H. Staudinger and H. Freundenberger, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 573.

hours were needed for reaction. Four and nine-tenths grams (48%) of *sym*-dichlorotetraphenylethane, m.p. 184–185°, was obtained (lit.,[25] m.p. 185°).

Reduction of 1,1,3-Triphenylindene.—One gram of 1,1,3-triphenylindene was dissolved in 50 ml. of distilled *n*-amyl alcohol.[8] Two grams of sodium metal was cut in small cubes and slowly added to the refluxing solution. After all the sodium had reacted, 5 ml. of water was added and the mixture chilled in an ice bath. The cream-colored precipitate was filtered and crystallized twice from 4:1 ethanol–benzene. Seven-tenths of a gram (70%) of 1,1,3-triphenylindane, m.p. 111–112°, was obtained.

Oxidation of 1,1,3-Triphenylindene.—One gram of 1,1,3-triphenylindene was oxidized with 1 g. of chromium trioxide in 25 ml. of acetic acid following the procedure used for oxidation of 1,1,3-triphenylindane. Crystals of *o*-dibenzoylbenzene were obtained, m.p. 145–146°.

Rearrangement of 1,1,3-Triphenylindene to 1,2,3-Triphenylindene.—Two grams of 1,1,3-triphenylindene was placed in a test tube, a thermometer inserted into the mixture, and the mixture heated at 350° for 2 hr. When cool the solid mass was recrystallized twice from 4:1 ethanol–benzene. 1,2,3-Triphenylindene (80%), m.p. 130–132°, was obtained. A mixed melting point with an authentic sample melted at 131–132°.

Reaction of Chlorodiphenylmethane, 1,1-Diphenylethylene, and *n*-Butyllithium.[26]—Chlorodiphenylmethane (20 g.) and 1,1-diphenylethylene (18.0 g.) were placed in a 100-ml. flask fitted with a thermometer, dropping funnel, condenser, stirrer, and nitrogen purge system. The motor was started and 40 ml. of *n*-butyllithium was slowly added, keeping the temperature between 25–35°. After addition, 20 ml. of water was added, the two-phase solution was separated and the organic layer dried over sodium sulfate. The dried products were separated by chromatography. The 3:1 petroleum ether–benzene fractions, after recrystallization from 4:1 ethanol–benzene, contained 1.7 g. (5%) of 1,1,3,3-tetraphenylpropene, m.p. 126–127°. A mixed melting point with an authentic sample melted at 126–126.5°. Careful chromatography of two reaction mixtures failed to reveal any cyclopropane derivative.

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[25] H. Staudinger, K. Clar, and E. Czako, *Ber.*, **44**, 1644 (1911).

[26] *n*-Butyllithium (19.8% weight in *n*-heptane) from Lithium Corporation of America, Inc.

Iodo Substituents and the Decomposition of Diacyl Peroxides. IV.[1] Bis(β-iodopropionyl) Peroxide

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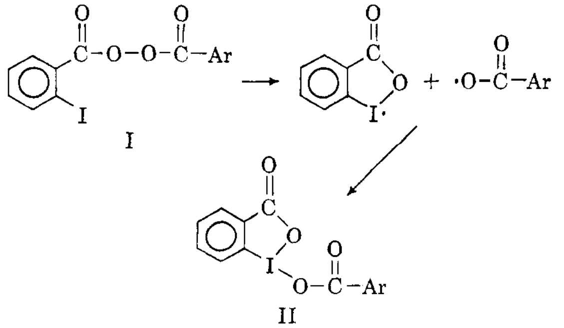
The decomposition of bis(β-iodopropionyl) peroxide owes its comparatively rapid rate to the presence of the β-iodo substituents. The products of the reaction are β-iodoethyl β-iodopropionate, iodine, ethylene, and carbon dioxide. Evidence is presented for a trivalent iodine compound and a carbonic ester anhydride as transient intermediates. A tentative mechanism is proposed for the reaction.

In *o*-iodo substituted benzoyl peroxides[1a,b] the *o*-iodo substituent accelerates the decomposition of the peroxide by what is probably a free radical analog of the neighboring group effect well known in ionic reactions. Thus the decomposition of *o*-iodobenzoyl peroxide (I) leads to the formation of radicals capable of initiating vinyl polymerization and ultimately to the rearrangement product (II).



Similar effects have not been reported in aliphatic diacyl peroxides, although bis(2-iodophenylacetyl) peroxide has been investigated.[1c] The absence of acceleration by *o*-iodine in the decomposition of the latter peroxide has no implications for aliphatic peroxides in general, however, since the competing decomposition mechanisms of the parent compound, bis(phenylacetyl) peroxide, are extremely fast.[3]

Therefore, we decided to investigate the effect of introducing β-iodo substituents on the rate and mechanism of decomposition of dipropionyl peroxide. The parent peroxide decomposes at a moderate rate typical of its homologous series, and the mechanism appears to be a straightforward radical one with no unusual features.[4]

Results and Discussion

The β-iodo substituent in bis(β-iodopropionyl) peroxide does alter the reaction mechanism, but to one somewhat more complicated than had been

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[1] For previous papers in this series see: (a) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958). (b) W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961). (c) J. E. Leffler and A. F. Wilson, *ibid.*, **25**, 424 (1960).

[2] This research was supported in part by the National Science Foundation.

[3] P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950).

[4] J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956).