colorless crystals, m.p. 240° (undepressed when admixed with an authentic sample prepared by the reaction of 9-diazofluorene with thiaxanthione). The product and the authentic sample have identical infrared spectra. It gives a pink color with concd. sulfuric acid.

Reaction of Diphenyldiazomethane with Thiofluorenone.—Thiofluorenone (1.5 g.) was added to a solution of diphenyldiazomethane (1.7 g.) in dry ether (30 ml.). The solid which separated was filtered off, and crystallized from acetone to give VII in colorless crystals, m.p. 227–228° (undepressed when admixed with an authentic sample prepared by the reaction of benzophenone dichloride with fluorene). The product and the authentic sample have identical infrared spectra.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.54; H, 5.45. Found: C, 94.57; H, 5.52.

Action of Sunlight on 9-Diazoxanthene.—A solution of 9-diazoxanthene (1 g.) in dry ether (30 ml.) was exposed to sunlight in a carbon dioxide atmosphere for 6 hr. The pale yellow crystalline product which separated (0.8 g.) was filtered off, crystallized from xylene, and proved to be dixanthylene (melting point and mixed melting point).

When the above experiment was carried out using 9-diazofluorene, dibiphenyleneethylene was produced.

Reactions of Styrene Dimers

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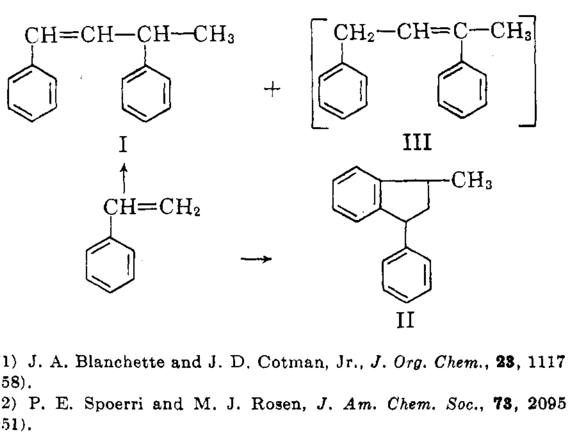
The dimerization of styrene and the structures of its dimers have been described, but little has been reported on their chemical reactions. We have reinvestigated the dimerization of styrene, the isomerization of the linear dimer (1,3-diphenyl-1-butene) to the cyclic dimer (1-phenyl-3-methylindane), and studied several chemical reactions of the dimeric styrenes. We have also shown that the linear dimer contains a small amount of isomeric 1,3-diphenyl-2-butene.

Chemical modification of the higher polymers of styrene has been studied extensively,[1] but very little work has been reported on the chemical reactions of the dimeric styrenes.[2]

The dimerization of styrene by means of sulfuric acid, silica gel, and phosphoric acid absorbed on activated char has been reported[3–8]; also the isomerization of linear styrene dimer (1,3-diphenyl-1-butene) to cyclic dimer (1-phenyl-3-methylindane) by means of sulfuric acid.[3,5,6] We have reinvestigated both of these processes, using several acidic catalysts.

Styrene can be converted in 83–85% yield to an isomer mixture of linear (I) and cyclic (II) dimers by means of aqueous sulfuric and phosphoric acids. The over-all yield of dimer and higher is 96–98%, the higher polymer being essentially trimer.



Styrene is dimerized in sulfuric acid at lower acid concentrations than phosphoric acid, but the latter is more easily separated from the product. By proper choice of conditions the isomer composition of the dimer can be varied from about 10% linear–90% cyclic to about 90% linear–10% cyclic (Table I).

In one experiment, twelve successive batches (fifty volumes) of styrene were dimerized with one volume of 85.8% phosphoric acid, the composition of the dimer being 45% linear–55% cyclic. The acid was as active at the end of the experiment as at the beginning. Phase separation of dimer from phosphoric acid is fast and clean, whereas with sulfuric acid troublesome emulsions are often encountered.

Linear dimer can be isomerized to cyclic dimer by means of various acidic catalysts—*e.g.*, alumina–silica, Filtrol, 100% phosphoric acid, polyphosphoric acid, and phosphoric acid absorbed on activated char. This isomerization is accompanied by the production of varying amounts of higher polymers.

A convenient method of isomerization is to heat a mixture of linear dimer and phosphoric acid under a distilling column at 20 mm. and take off distillate at such rate that the head temperature does not exceed the boiling point (180°) of the cyclic dimer. Starting with 100% linear dimer, a 94% yield of a 25% linear–75% cyclic dimer mixture was obtained.

Gas-liquid chromatography was found to be the

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[2] P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **73**, 2095 (1951).

[3] R. Stoermer and H. Kootz, *Ber.*, **61**, 2330 (1928).

[4] J. Risi and D. Gauvin, *Can. J. Research*, **14B**, 255 (1936).

[5] P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **72**, 4918 (1950).

[6] M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

[7] A. Muller and K. Kormandy, *J. Org. Chem.*, **18**, 1237 (1953).

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Table I

Dimerization of Styrene with Phosphoric and Sulfuric Acids

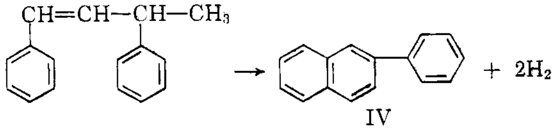
Expt.	Acid Strength, %	Temp.	Min.	Dimer Yield, %	Dimer Composition, % Linear	Dimer Composition, % Cyclic	Trimer, % Yield	Total Dimer-Trimer, % Yield
			Dimerization of Styrene with Phosphoric Acid					
			(A) Fast Addition of Styrene					
1	60.6	110	15	0	..	..	4	4
2	73.2	120	130	82	87	13	14	96
3	85.8	120	48	79	62	38	18	97
4	85.8	150	4	72	62	38	17	89
5	85.8	150	77	83	62	38	15	98
6[a]	114	30–197	2	..	..	..	..	...
			(B) Slow Addition of Styrene					
7	85.8	148	30	81	53	47	15	96
8	93.0	100	38	72	24	76	22	94
9	93.0	150	42	81	28	72	10	91
10	100	55	41	60	4	96	34	94
11	100	86	40	63	7	93	32	95
12	100	152	25	70	11	89	30	100
			Dimerization of Styrene with Sulfuric Acid					
			(C) Fast Addition of Styrene					
13	47.0	120	125	81	91	9	15	96
14	53.1	115	75	81	89	11	15	96
15	58.0	115	45	83	86	14	15	98
16	67.4	100	45	49	70	30	45	94
17[a]	76.6	40–130	5	..	..	..	..	...
			(D) Slow Addition of Styrene					
18	53.1	120	60	78	87	13	11	89
19	53.1	120	90	79	89	11	9	88
20	53.1	120	150	83	87	13	9	92

[a] The exotherm raised the temperature out of control and the product was a gelatinous polymer.

most reliable method for analyzing styrene dimer mixtures, but it was unable to detect the small amount of isomeric linear dimer, 1,3-diphenyl-2-butene (III), which was present. Analysis by bromometric titration (at 10° in the dark) also gave reliable values for differentiating between linear and cyclic dimers. Analytical hydrogenation was less satisfactory.

Epoxidation of linear styrene dimer in acetic acid with peracetic acid gave crude linear styrene dimer glycol monoacetate which was hydrolyzed to a mixture of glycols from which a solid glycol, m.p. 122–122.5°, was isolated. The structure of this glycol was established as 1,2-dihydroxy-1,3-diphenylbutane by oxidative cleavage to a mixture of benzaldehyde and hydratropaldehyde. Oxidation of the mother liquor from crystallizing the glycol mixture yielded a small amount of acetophenone whose precursor was presumably 2,3-dihydroxy-1,3-diphenylbutane. The other oxidation product—phenylacetaldehyde—was not isolated. Previous workers have assumed the linear styrene dimer to be 1,3-diphenyl-1-butene (I), but evidently it is contaminated with a minor amount (perhaps 5%) of isomeric 1,3-diphenyl-2-butene (III).

Linear dimer was dehydrogenated over 1707 catalyst at 550° in the presence of steam to give a 43% per pass yield (70% ultimate) of 2-phenylnaphthalene (IV). This process has preparative possibilities.



IV

Linear dimer was hydrogenated to dihydro dimer (1,3-diphenylbutane), and under more vigorous conditions, to 1,3-dicyclohexylbutane. Similarly, cyclic dimer was hydrogenated to 1-cyclohexyl-3-methylhydrindane. The cyclohexyl derivatives were freed from residual traces of aromatics by percolation through a bed of silica gel.

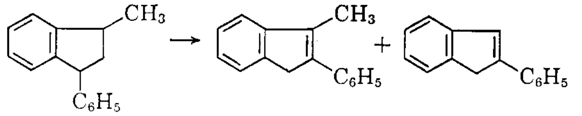
Dihydro linear dimer (1,3-diphenylbutane) was nitrated to mononitro and dinitro derivatives, and these nitro compounds were reduced to the corresponding amines. Chromic acid oxidation of the dinitrodihydro dimer gave a 62% yield of *p*-nitrobenzoic acid.

Dihydro linear dimer was chloromethylated by means of monochloromethyl ether to give bis-(chloromethyl)dihydro dimer which on oxidation by chromic acid gave a 75% yield of terephthalic acid. The chloromethylated dihydro dimer was converted to the corresponding dialdehyde by reaction with hexamethylenetetramine and the dialdehyde was subsequently oxidized to the diacid.

Cyclic styrene dimer was converted to its mono- and diacetyl derivatives and these acetyl derivatives were oxidized to the corresponding carboxy acids. Diacetyl cyclic dimer reacted with isatin to produce its biscarboxyquinoline derivative.

The majority of the products obtained in this work were difficult to purify, as evidenced by poor analytical values, and attempts to prepare analytically pure derivatives often failed.

Passage of cyclic dimer over chromia–alumina catalyst at 560° resulted in dehydrogenation accompanied by rearrangement and rearrangement-demethylation to give 1-methyl-2-phenylindene (10%) and 2-phenylindene (6%), respectively. At 615° only 2-phenylindene (15%) was isolated.



The structures of these indenes were established by comparison (infrared spectra and mixture melting points) with authentic specimens.[9,10a,10b] The thermal rearrangement of 1-phenylindene to 2-phenylindene has been previously reported.[9,10a]

Experimental

Materials.—The styrene monomer (Koppers Co.) contained about 0.2% of *t*-butylcatechol as inhibitor. The various solid catalysts were employed as 5–10 mesh material: alumina–silica catalyst (Houdry Co.) 13% Al_2O_3–87% SiO_2; 1707 catalyst (Standard Oil Development Co.) 72.4% MgO–18.4% Fe_2O_3–4.6% CuO–4.6% K_2CO_3; solid phosphoric acid catalyst No. 2 (Universal Oil Products Co.) about 80% H_3PO_4–20% SiO_2; nickel catalyst (Harshaw Co.) powdered, 65% Ni–35% SiO_2.

Dimerization of Styrene by Phosphoric and Sulfuric Acids. A. Fast Addition of Styrene—Tables I(A) and I(C).—Styrene (88 g.) was added to 100 ml. of stirred acid at room temperature and the mixture heated to the desired temperature in 10–15 min. At the end of the specified reaction time the mixture was cooled to 50° (5 min.). The organic layer was separated and combined with a benzene extract of the acid layer. The benzene solution was freed from acid by water washing, inhibited with 1 g. of *t*-butylcatechol, and concentrated in a rotating film evaporator at 70°/30 mm. The concentrate was distilled through a 15-cm. Vigreux column, collecting dimer fraction at 150–200°/20 mm. The residue was essentially trimer. (Distillation of dimer–trimer mixtures of known composition gave dimer values which were 0.2–0.6% lower than the actual values).

B. Slow Addition of Styrene—Tables I(B) and I(D).—Styrene was added at constant rate during the specified time to the stirred acid at the reaction temperature. The product was worked up as under A.

Linear Styrene Dimer.—A mixture of 1000 ml. of styrene and a solution of 100 ml. of concentrated sulfuric acid in 150 ml. of water was stirred for 4 hr. at 120–125°. (Inhibitor need not be removed from the styrene.) The stirring must be vigorous; otherwise high molecular weight material is produced. After standing for 1 hr. at 50° the hydrocarbon layer was separated, diluted with 250 ml. of benzene, and washed with aqueous sodium chloride and sodium carbonate. Distillation through a 30-cm. Vigreux column yielded 708 g. (77.5%) of linear dimer, b.p. 145–154°/3 mm. Subsequent redistillation through a 27-plate Fenske column at 15:1 reflux ratio gave a heart cut: b.p. 213.7°/50 mm., $n^{20}_{\rm D}$ 1.5928, $n^{25}_{\rm D}$ 1.5913, d^{20}_4 0.9981, d^{25}_4 0.9933.

Cyclic Dimer.—The preparative procedure was essentially that of Rosen,[11] 75.5% yield. A heart cut was obtained by redistillation through a 27-plate Fenske column at 15/1 reflux ratio: b.p. 201.2°/50 mm., $n^{20}_{\rm D}$ 1.5808, $n^{25}_{\rm D}$ 1.5789, d^{20}_4 1.0227, d^{25}_4 1.0182.

Isomerization of Linear Dimer to Cyclic Dimer. A.—A mixture of 100 g. of linear dimer (97% pure by gas-liquid chromatographic analysis) and 10 g. of 100% phosphoric acid was heated under a 23-plate Fenske column at 20 mm. and 94 g. of distillate was removed at such rate that the head temperature did not exceed 180°. Chromatographic analysis showed the composition of the distillate to be 25% linear–75% cyclic.

B.—Linear dimer (200 g.) was passed down through a 90-ml. bed of alumina-silica at 205° during 210 min. The catalyzate (181 g.) was distilled to yield 101 g. (51%) of dimer (b.p. 106–112°/0.5 mm., 12% linear–88% cyclic) plus 80 g. of residue.

C.—Linear dimer (104 g.) was passed down through a 90-ml. bed of UOP solid phosphoric acid catalyst at 200° during 120 min. Distillation of the catalyzate gave 73.8 g. (71%) of dimer (b.p. 105–112°/0 5 mm., 60% linear–40% cyclic).

D.—Linear dimer (200 g.) was added during 1 hr. to 200 g. of stirred polyphosphoric acid at 150° and the mixture stirred for 3 hr. During the second and third hours, 1-ml. samples of the hydrocarbon were removed at 30-min. intervals and analyzed. The isomer compositions of the consecutive samples were (% linear–% cyclic): 14–86, 13–87, 11–89, 8–92, 7–93. The residual reaction mixture was cooled and separated to yield 137 g. of hydrocarbon; dilution of the acid layer with 200 ml. of water gave an additional 45 g. of hydrocarbon. Distillation of the combined hydrocarbon yielded 138 g. (69%) of dimer (b.p. 106–112°/0.5 mm., 8% linear–92% cyclic).

Determination of Isomer Composition of Dimer.—The preferred analytical method was gas-liquid chromatography, using a 4.9-m. polyethylene glycol column. The conditions were: column temperature 206°, column pressure 23 p.s.i., helium flow rate 14 ml./min., flash evaporator temperature 300°. The first and second chromatographic peaks corresponded to the cyclic and linear dimers, respectively, as shown by calibration with pure isomers. Trimer remained on the column. The results were normalized when the sum of the two dimers was less than 100%.

Linear Dimer Glycol.—A mixture of 100 g. (0.48 mole) of linear dimer, 300 ml. of acetic acid and 183 g. (0.96 mole) of 40% peracetic acid was stirred at 25° for 4 hr., then allowed to stand for 15 hr. After destroying excess peracetic acid with bisulfite, the mixture was poured into water and extracted with ether. Concentration of the washed and dried ether solution yielded 110 g. of white paste. This crude glycol monoacetate (Calcd: ester, 3.52 meq./g. Found: ester, 2.85 meq./g.) was mixed with 500 ml. of 95% ethanol and 56 g. of potassium hydroxide and refluxed for 2 hr., then poured into water and extracted with ether. The extract was washed, dried, and concentrated to give 101.5 g. of yellow, waxy solid. Two crystallizations from benzene yielded 17 g. of white needles, m.p. 118–120°; two additional crystallizations gave an analytical sample melting at 122.0–122.5°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 78.92; H, 7.66.

Oxidation of Linear Dimer Glycol. A.—Lead tetraacetate (40 g., 0.09 mole) was added during 0.5 hr. to a stirred mixture (under nitrogen) of 20 g. (0.08 mole) of linear dimer glycol (m.p. 120–121°), 400 ml. of benzene and 30 g. of anhydrous potassium carbonate. The exotherm raised the temperature from 27 to 40°. After stirring for an additional hour the mixture was filtered and the filtrate concen-

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[9] F. Mayer, A. Sieglitz, and W. Ludwig, *Ber.*, **54**, 1397 (1921).

[10] (a) J. Braun and G. Manz, *Ber.*, **62**, 1059 (1929); (b) O. Blum-Bergmann, *Ber.*, **65**, 109 (1932).

[11] M. J. Rosen, *Org. Syntheses*, **35**, 83 (1955).

trated. Distillation of the concentrate through a 10-cm. Vigreux column yielded: (a) 9.2 g., b.p. 72–85°/20 mm. (largely benzaldehyde, 0.08 mole) and (b) 8.8 g., b.p. 85–92°/20 mm. (largely hydratropaldehyde, 0.06 mole). Fraction (a) gave benzaldehyde semicarbazone, melting point and mixture melting point with an authentic sample, 222–223° (lit., m.p. 213–235°,[12] dependent on rate of heating). Fraction (b) gave hydratropaldehyde semicarbazone, m.p. 152–153° (lit., m.p. 153–154°[13]) and hydratropaldehyde, 2,4-dinitrophenylhydrazone, m.p. 137–138° (lit., m.p. 136–137°[14]).

B.—Sixty grams of residue from the mother liquor from crystallizing linear dimer glycol was dissolved in 400 ml. of benzene and oxidized with 120 g. (0.27 mole) of lead tetraacetate as in A. The oxidation product was distilled through a 23-plate Fenske column to give: (a) 7.1 g., b.p. 76–82°/20 mm.; (b) 21.9 g., b.p. 82–100°/20 mm.; (c) 17.0 g. of residue Fraction (a) was shown to be benzaldehyde by melting point and mixture melting point of its semicarbazone, 222–223°. Fraction (b) was stirred with a mixture of 64 g. of sodium bisulfite, 120 ml. of water, and 40 ml. of 95% ethanol. The addition product was filtered and the filtrate extracted with ether. The extract was concentrated and the residue treated with bisulfite. The filtrate from the second bisulfite addition product was extracted with ether and the dried extract concentrated to yield 3.1 g. of oil which gave the semicarbazone of acetophenone; melting point and mixture melting point with authentic acetophenone semicarbazone, 198–199° (lit , m.p. 198–199°[12])

Dehydrocyclization of Linear Dimer over 1707 Catalyst.—Linear dimer and water were vaporized in a preheater (packed with Vycor chips) and the gaseous mixture passed down through a 25-ml. bed of 1707 catalyst. The exit gas was collected; the semisolid organic layer of the catalyzate was dissolved in ether and the ether solution washed with aqueous carbonate, dried, and concentrated. The concentrate was cooled and filtered. The crude 2-phenylnaphthalene (m.p. 99–101°) was washed with a small amount of cold *n*-hexane and crystallized from *n*-hexane or methanol, m.p. 101.5–102°. The filtrate was distilled to determine the amount of unchanged linear dimer. The best results were obtained at a catalyst temperature of 550°; the feed rates of dimer and water were 75 g./hr. and 129 g./hr., respectively (mole ratio of dimer/water, 1:20; the yield of semisolid catalyzate was 74.3 g. from which was obtained 31.4 g. of crude 2-phenylnaphthalene and 28.9 g. of recovered dimer; per pass yield of 2-phenylnaphthalene 42.8%, ultimate yield 69.5%. The yield of gas (25°/740 mm.) was 6.4 l. (water-, carbon dioxide-, and air-free basis); its hydrogen content on the same basis was 98.7%. Under similar feed conditions, but at a catalyst temperature of 450°, there was essentially no dehydro cyclization, whereas at a catalyst temperature of 600° the per pass yield of 2-phenylnaphthalene was 49.5%.

The dehydrocyclization product was shown to be 2-phenylnaphthalene by mixture melting point (101.5–102°) with an authentic specimen[15]; also by oxidation to 2-phenyl-1,4-naphthoquinone. A warm solution of 2 g. of dehydro cyclization product in 40 ml. of acetic acid was poured into a warm solution of 6 g. of chromic acid in 40 ml. of acetic acid. The mixture was boiled for 10 min. then poured into 800 ml. of water. After standing for 3 hr. the mixture was filtered and the solid crystallized from methanol to yield 2.86 g. (62%) of crude quinone, m.p. (109)110–112°. The product was purified by chromatographing over alumina, eluting with petroleum ether–benzene, to obtain a heart cut which was crystallized from *n*-hexane, m.p. 112–113° (lit., m.p. 109°[16]).

Hydrogenation of Styrene Dimers. A. 1,3-Diphenylbutane.—Linear dimer (500 g.) was hydrogenated for 8 hr. at 30°/1500 p.s.i. in the presence of 50 g. of Raney nickel to yield 490 g. (98%) of 1,3-diphenylbutane; b.p. 200.8°/50 mm. $n^{20}\mathrm{D}$ 1.5522, $n^{25}\mathrm{D}$ 1.5502, $d^{20}{}_4$ 0.9697, $d^{25}{}_4$ 0.9655 (lit. values: b.p. 302.5°/760 mm., $n^{20}\mathrm{D}$ 1.5523, $d^{20}{}_4$ 0.9698[17]).

B. **1,3-Dicyclohexylbutane.**—Linear dimer (100 g.) was hydrogenated for 8 hr. at 215°/1700 p.s.i. in the presence of 10 g. of nickel–kieselguhr catalyst. The filtered catalyzate, diluted with an equal volume of petroleum ether (b.p. 30–60°), was percolated through a column of silica gel and the raffinate distilled through a 10-cm. Vigreux column to yield 92.5 g. (87%) of distillate whose infrared spectrum showed it to be free from phenyl rings; b.p. 147.5°/8.5 mm., $n^{20}\mathrm{D}$ 1.4796, $n^{25}\mathrm{D}$ 1.4780, $d^{20}{}_4$ 0.8800, $d^{25}{}_4$ 0.8767 (lit. values: b.p. 303.19°/760 mm., $n^{20}\mathrm{D}$ 1.4797, $d^{20}{}_4$ 0.8801[17]).

C. **1-Cyclohexyl-3-methylhydrindane.**—Cyclic dimer (200 g.) was hydrogenated for 9 hr. at 215°/1700 p.s.i. in the presence of 20 g. of nickel–kieselguhr catalyst. The catalyzate was worked up as in *B* to yield 180 g. (85%) of 1-cyclohexyl-3-methylhydrindane; b.p. 194.5°/50 mm., $n^{20}\mathrm{D}$ 1.4958, $n^{25}\mathrm{D}$ 1.4946, $d^{20}{}_4$ 0.9263, $d^{25}{}_4$ 0.9230.

Anal. Calcd. for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.10; H, 12.51.

Mononitro-1,3-diphenylbutane.—To a stirred solution (at 15°) of 105 g. (0.5 mole) of linear dihydro dimer (1,3-diphenylbutane) in 250 ml. of acetic acid was added a mixture of 100 g. (1.1 moles) of concd. nitric acid and 200 g. (2.2 moles) of concd. sulfuric acid during 1 hr. After stirring for an additional 2.5 hr. the reaction mixture was poured onto ice. The organic layer was washed free from acid, dried, and distilled to yield: (a) 57 g. (45%) of recovered dihydro dimer (b.p. 100–158°/0.3 mm., $n^{25}\mathrm{D}$ 1.5523), (b) 30 g. (12%) of crude mononitrodihydro dimer (b.p. 158–190°/0.3 mm., $n^{25}\mathrm{D}$ 1.5740), and (c) 25 g. of residue. Redistillation of fraction (b) gave a heart cut: b.p. 164–165°/0.5 mm., $n^{25}\mathrm{D}$ 1.5727.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.26; H, 6.71; N, 5.49. Found: C, 74.80; H, 6.47; N, 5.85.

Hydrogenation of the mononitro derivative (11.8 g.) in 200 ml. of ethanol for 0.5 hr. at 30°/50 p.s.i. in the presence of palladium–charcoal (104% of the theoretical hydrogen uptake) yielded 7 g. (68%) of amine; b.p. 143–144°/0.4 mm., $n^{25}\mathrm{D}$ 1.5814.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 84.94; H, 8.58; N, 6.65.

Dinitro-1,3-diphenylbutane.—A mixture of 105 g. (0.5 mole) of dihydro dimer, 144 g. (1.5 moles) of concd. sulfuric acid and 16.4 g. of water was emulsified by stirring for 0.5 hr. at 5°. The temperature was raised to 15° and a mixture of 103 g. (1.1 moles) of concd. sulfuric acid and 108 g. (1.2 moles) of concd. nitric acid was added with stirring during 1 hr. The reaction mixture was subsequently stirred for 1 hr. at 15°, then poured onto 1500 g. of ice and extracted with ether. The extract was washed with water, aqueous carbonate and water, dried, and concentrated to yield 129 g. (86%) of dark brown, viscous oil; $n^{25}\mathrm{D}$ 1.5870, $d^{25}{}_4$ 1.1930.

Eleven grams of dinitro-1,3-diphenylbutane was hydrogenated in methanol at 35°/50 p.s.i. in the presence of platinum. The product, after filtration and evaporation of methanol, was shaken with benzoyl chloride at 25° in the presence of 10% aqueous sodium hydroxide. Trituration of the separated organic material with methanol yielded a solid which was crystallized from aqueous acetic acid, subsequently from ethanol, to give dibenzamido-1,3-diphenylbutane, m.p. 209–211.5°.

Anal. Calcd. for $C_{30}H_{28}N_2O_2$: C, 80.33; H, 6.29; N, 6.25. Found: C, 80.39; H, 6.26; N, 6.26.

Oxidation of Dinitro-1,3-diphenylbutane.—To a stirred mixture of 9.0 g. (0.030 mole) of dinitro-1,3-diphenylbutane and 75 ml. of acetic acid at 20–30° was added 32 g. (0.32 mole) of chromic acid during 1 hr. The reaction mixture

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[12] S. Veibel, *Bull. soc. chim.* (4), **41**, 1410 (1927).

[13] G. Darzens, *Compt. rend.*, **139**, 1216 (1904).

[14] F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953).

[15] W. M. Kutz, J. E. Nickels, J. J. McGovern, and B. B. Corson, *J. Am. Chem. Soc.*, **70**, 4026 (1948).

[16] F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, **65**, 873 (1894).

[17] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **74**, 365 (1952).

was stirred for 4 hr., poured into water, and extracted with ether. The ether solution was washed with aqueous carbonate and the alkaline extract acidified to yield 2.90 g. of *p*-nitrobenzoic acid; melting point and mixture melting point with an authentic sample, 238–239°. The carbonate-washed ether solution was concentrated to yield 4.8 g. (0.016 mole) of dinitro compound (n^{25}_D 1.5845). The 2.90 g. of *p*-nitrobenzoic acid corresponds to a 62% yield, based on the consumed dinitro derivative.

Bis(chloromethyl)-1,3-diphenylbutane.—To a stirred mixture of 277 g. (1.3 moles) of 1,3-diphenylbutane, 359 g. (4.5 moles) of monochloromethyl ether, and 540 ml. of carbon tetrachloride at 0–5° was added 216 g. (0.83 mole) of stannic chloride during 3 hr. The mixture was stirred for an additional hour, poured into water, and separated. The organic layer was washed, dried, and distilled to yield 150 g. (38%) of bis(chloromethyl)derivative; b.p. 205–219°/0.7 mm., n^{25}_D 1.5764, d^{25}_4 1.1402.

Anal. Calcd. for $C_{18}H_{20}Cl_2$: C, 70.36; H, 6.56; Cl, 23.08. Found: C, 70.14; H, 6.53; Cl, 23.16.

Oxidation of Bis(chloromethyl)-1,3-diphenylbutane.—To a stirred mixture of 3.07 g. (0.01 mole) of bis(chloromethyl) derivative and 75 ml. of acetic acid at 30° was added 30 g. (0.30 mole) of chromic acid during 0.5 hr. The reaction mixture was stirred for 4 hr., poured into water, extracted with ether, and the ether solution extracted with aqueous carbonate. Acidification of the carbonate extract yielded 2.50 g. (75%) of terephthalic acid, identified as its dimethyl ester, melting point and mixture melting point with an authentic sample, 141–142°.

Diformyl-1,3-diphenylbutane.—A mixture of 18.3 g. (0.06 mole) of bis(chloromethyl)-1,3-diphenylbutane, 36 g. (0.26 mole) of hexamethylenetetramine, and 108 ml. (0.94 mole) of 50% aqueous acetic acid was refluxed for 3 hr. Dilute hydrochloric acid (150 ml. of 18% acid) was added; the mixture was refluxed for 0.5 hr. and extracted with benzene. The extract was washed, dried, and concentrated to yield 15.4 g. (97%) of crude dialdehyde, whose bis-*p*-nitrophenylhydrazone, yellow crystals from aqueous acetone, melted at 212–213°.

Anal. Calcd. for $C_{30}H_{28}N_6O_4$: C, 67.15; H, 5.26; N, 15.66. Found: C, 67.41; H, 5.27; N, 15.32.

Dicarboxy-1,3-diphenylbutane.—To a stirred mixture of 5.3 g. (0.02 mole) of diformyl-1,3-diphenylbutane and 50 ml. of pyridine at 30–35° was added 8.5 g. (0.054 mole) of potassium permanganate during 10 min. The mixture was stirred for 1 hr., decolorized with acidified bisulfite solution, and extracted with ether. The ether solution was extracted with aqueous carbonate and the alkaline extract acidified to yield 4.9 g. (83%) of crude dicarboxylic acid, m.p. 178–207°. Attempts to purify this material failed.

Anal. Calcd. for $C_{18}H_{18}O_4$: Neut. equiv., 149. Found: Neut. equiv., 159.

Monocarboxy Cyclic Dimer.—To a stirred mixture (0–5°) of 208 g. (1.0 mole) of cyclic dimer and 500 ml. of ethylene dichloride was added a mixture of 146 g. (1.1 moles) of aluminum chloride, 87 g. (1.1 moles) of acetyl chloride, and 400 ml. of ethylene dichloride during 1.5 hr. The reaction mixture was stirred for 0.5 hr., then decomposed by ice–hydrochloric acid. The organic layer was washed with aqueous carbonate, dried, and distilled to yield 125 g. (50%) of monoacetylated dimer; b.p. 151–160°/0.25 mm., n^{25}_D 1.5872. Attempts to derivatize this product failed.

To a warm (*ca.* 60°), stirred mixture of 50 g. (0.20 mole) of monoacetyl cyclic dimer and 350 ml. of dioxane (freshly distilled from solid potassium hydroxide) was added 500 ml. (0.60 mole) of aqueous potassium hypochlorite (1 hr.). The reaction mixture was cooled and extracted with ether, and the ether solution was extracted with aqueous sodium hydroxide. Acidification of the alkaline extract produced a gummy precipitate which was partially purified by solution in aqueous potassium hydroxide, Norit treatment of the solution, and subsequent acidification to yield 37 g. (73%) of a product which was crystallized from cyclohexane; cream-colored solid, m.p. 130–150°. Attempts to purify this product failed.

Anal. Calcd. for $C_{17}H_{18}O_2$: Neut. equiv. 252. Found: Neut. equiv. 254.

Diacetyl Cyclic Dimer.—To a stirred mixture (*ca.* 30°) of 2 l. of carbon disulfide, 314 g. (4.0 moles) of acetyl chloride, and 532 g. (4.0 moles) of aluminum chloride was added 416 g. (2.0 moles) of cyclic dimer (3 hr.). The resulting mixture was stirred for 1 hr., then decomposed by ice–hydrochloric acid. The organic layer was washed with aqueous carbonate, dried, and distilled to yield 370 g. (64%) of diacetyl derivative, b.p. 208–225°/0.5 mm.

The compound was characterized as its biscarboxyquinoline derivative. A mixture of 58.4 g. (0.20 mole) of diacetyl cyclic dimer, 600 ml. of ethanol, 60 g. (0.41 mole) of isatin, 180 g. (3.2 moles) of potassium hydroxide, and 600 ml. of water was refluxed for 12 hr., after which 500 ml. of solvent was distilled off. The residual solution was cooled and poured into excess hydrochloric acid. The precipitate was filtered, washed with water, and dissolved in aqueous carbonate. The alkalin esolution was acidified and filtered to yield 100 g. (90%) of yellow solid, m.p. 180° dec.

Anal. Calcd. for $C_{36}H_{26}N_2O_4$: Neut. equiv., 275. Found: Neut. equiv., 276.

Dicarboxy Cyclic Dimer.—To a warm (*ca.* 60°), stirred mixture of 29.3 g. (0.10 mole) of diacetyl cyclic dimer and 400 ml. of dioxane was added 900 ml. (1.2 moles) of aqueous potassium hypochlorite (0.5 hr.). The reaction mixture was stirred for 2 hr. at 60°, cooled, and acidified with hydrochloric acid. The aqueous layer was decanted and the precipitate dissolved in ether. The ether solution was extracted with aqueous carbonate; the alkaline extract was treated with Norit and acidified to yield 29 g. (95%) of dicarboxy acid, m.p. 110–140°. Attempts to characterize this compound were unsuccessful.

Anal. Calcd. for $C_{18}H_{16}O_4$: Neut. equiv., 148. Found: Neut. equiv., 158.

Reaction of Cyclic Dimer over Chromia–Alumina Catalyst. A.—Cyclic dimer (300 g.) was passed down through a 90-ml. bed of chromia–alumina catalyst at 560° at 0.6 l.h.s.v. (linear hourly space velocity). Filtration of the catalyzate removed 28.5 g. of solid which was crystallized from carbon tetrachloride to yield 16.5 g. (6%) of 2-phenylindene, m.p. 164–167°; recrystallization raised the melting point to 167–168°; identified by mixture melting point (see below). Distillation of the filtrate gave 77 g. of material (b.p. 140–165°/1.3 mm.) which was crystallized from ethanol to yield 31.5 g. (10%) of 1-methyl-2-phenylindene, m.p. 72–75°. Recrystallization raised its melting point to 76–77° (lit., m.p. 76–77°[10b]); its mixture melting point with authentic 1-methyl-2-phenylindene was not depressed.

B.—Cyclic dimer (300 g.) was passed down through a 60-ml. bed of chromia-alumina catalyst at 615° at 1 l.h.s.v. The catalyzate (251 g.), diluted with 1 l. of petroleum ether (b.p. 30–60°), was filtered to give 70 g. of solid plus a filtrate. Distillation of the solid at 0.2 mm. in a short-path distilling apparatus, followed by crystallization of the distillate from carbon tetrachloride, yielded 41 g. (15%) of 2-phenylindene (m.p. 165–167°) plus 2 g. (0.7%) of less pure material (m.p. 160–163°). Recrystallization gave material melting at 167–168°, lit., m.p. 167.5°, 167°, 166–167°[9,10a,10b]; its mixture melting point with authentic 2-phenylindene was not depressed. The initial filtrate was distilled to give a 77.7 g. fraction from which an additional 6 g. (2.2%) of impure 2-phenylindene (m.p. 153–158°) was isolated by crystallization from carbon tetrachloride–petroleum ether.

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