[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

The Dimer of 1,3-Diphenyl-1,3-butadiene[1,2]

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A dimer of 1,3-diphenyl-1,3-butadiene has been isolated from the dehydration of 1,3-diphenyl-2-buten-1-ol and 1,3-diphenyl-1-buten-3-ol. 1,3-Diphenyl-1,3-butadiene has been isolated as its maleic anhydride adduct. The structure of the dimer has been shown to be 1,3,4-triphenyl-4-styrylcyclohexene by oxidation and dehydrogenation. A styryl group migration in the tetrachloro-*o*-benzoquinone dehydrogenation of the dimer has been demonstrated.

In the course of another investigation it was found that both 1,3-diphenyl-2-buten-1-ol and 1,3-diphenyl-1-buten-3-ol on dehydration under a variety of conditions gave a hydrocarbon, m.p. 136–137°. From a study of its properties it was obvious that this compound was not 1,3-diphenyl-1,3-butadiene,[3] although it analyzed correctly for $C_{16}H_{14}$. A molecular weight determination indicated that this compound was a dimer of 1,3-diphenyl-1,3-butadiene, but it was apparently not identical with a dimer which Whitby and Gallay[4] reported as being formed by the reaction of benzalacetophenone with methylmagnesium iodide. These authors reported isolation of a dimer of 1,3-dimer of 1,3-diphenyl-1,3-butadiene, m.p. 167°, in 70% yield.

Repetition of Whitby and Gallay's procedure gave as the major product an oil which, in accord with the results of Kharasch and Sayles,[5] consisted mainly of 1,3-diphenyl-1-butanone. Crystalline products obtained in smaller yields were either 1,3,5-triphenyl-4-benzoyl-1,3-hexadiene, m.p. 175.5°, or the 1,3-diphenyl-1,3-butadiene dimer, m.p. 136–137°, and a compound of the formula $C_{31}H_{28}O_2$, 161.5–163°. This last substance is probably 1,3-dibenzoyl-2,4-diphenylpentane on the basis of its spectrum, elemental analysis, and stability toward acids and oxidizing agents. Such a compound could have been formed by a Michael condensation between benzalacetophenone and 1,3-diphenyl-1-butanone. It is to be noted that Kharasch and Sayles[5] report that the product composition of the reaction between benzalacetophenone and the methyl Grignard reagent is sensitive to the concentration of reagent and particularly to the presence of radical sources.

Addition of maleic anhydride to the gummy residues produced 5–10% yields of 3,5-diphenyl-1,2,3,6-tetrahydrophthalic anhydride, m.p. 158–159°, a Diels-Alder adduct of 1,3-diphenyl-1,3-butadiene. This adduct is reported by Cope, Wick, and Fawcett[6] to melt at 142–149°. These authors ascribed the melting point range to the presence of a mixture of stereoisomers. That ours was indeed the same adduct was shown by dehydrogenation to the 3,5-diphenylphthalic acid reported by Cope, Wick, and Fawcett. Decarboxylation of this acid produced *meta*-terphenyl.

The maleic anhydride adduct could be obtained in comparable yields from either 1,3-diphenyl-2-buten-1-ol or 1,3-diphenyl-1-buten-3-ol. This product was formed both with and without a solvent, and by addition of the maleic anhydride both before and after dehydration of the two alcohols.

Dehydration of the two diphenylbutenols in the absence of maleic anhydride gave products of varying homogeneity. A typical dimeric product (usually formed in about 80% yield) melted at 123–140°. The dimer which melted at 136–137° was the principal constituent and was the only one which could be isolated in pure form. The remainder was probably isomeric material. The infrared spectra of various fractions were very similar except for variations in the 900 cm.$^{-1}$ and 970 cm.$^{-1}$ regions. Dehydration of either alcohol with iodine produced mainly a compound which melted at 146–147° This product analyzed correctly for $C_{32}H_{28}$, but differed from the lower melting dimer in the absence of a *trans*-ethylenic band at 970 cm.$^{-1}$ in its infrared spectrum. The higher melting dimer was not further investigated.

The dimer, m.p. 136–137°, showed two hindered non-conjugated double bonds on the basis of microhydrogenation, its ultraviolet spectrum, and various qualitative olefin tests. The ultraviolet spectrum in 95% ethanol showed absorption maxima at 253 mμ (log ε 4.56) and 294 mμ (log ε 3.19) with a minimum at 228 mμ (log ε 4.12), indicative of a slightly modified styrene chromophore. The molec-

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(1) Abstracted from the thesis of Edwin Lewis, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1958.

(2) While this manuscript was in preparation, the isolation and characterization of this dimer was reported by M. H. Goodrow and T. L. Jacobs at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 17, 1958. These authors have come to the same conclusions concerning the structure of the dimer as those presented here. Their results are described in the accompanying paper, *J. Org. Chem.*, **23**, 1653 (1958).

(3) A. V. Dombrovskii, *Doklady Akad. Nauk, S.S.S.R.*, **111**, 827 (1956).

(4) G. S. Whitby and W. Gallay, *Can. J. Research*, **6**, 280 (1932).

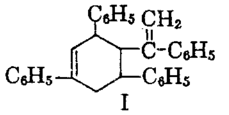
(5) M. S. Kharasch and D. C. Sayles, *J. Am. Chem. Soc.*, **64**, 2972 (1942).

(6) A. C. Cope, E. L. Wick, and F. S. Fawcett, *J. Am. Chem. Soc.*, **76**, 6156 (1954).

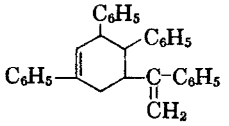
ular weight was 426 as determined ebullioscopically in methyl ethyl ketone. Curiously, the molecular weight as determined by the Rast method was 215 (average of six determinations). Fiesselmann and Ribka[7] have reported an analogous result for the dimer of 2-phenylacrylophenone. It is curious that the tetrahydro derivative (VIII) also showed this same discrepancy. No C-methyl was found on Kuhn-Roth oxidation either of the dimer or its tetrahydroderivative.

Dehydrogenation with sulfur at 230° gave 1,3,5-triphenylbenzene. From oxidation with either ozone or potassium permanganate, the only steam-volatile product was benzaldehyde. The nonvolatile part of these oxidation products consisted of a small, but persistent, amount (5%) of 1,2-dibenzoylethane and an irresolvable mixture of unidentified carbonyl compounds.

Of the four possible Diels-Alder dimers of 1,3-diphenyl-1,3-butadiene, structures I and II are eliminated by the preceding observations. The choice between structures III and IV was inconclusive. III was preferred for theoretical reasons, as discussed below, but this structure required a phenyl migration during the sulfur dehydrogenation. IV required no migration on dehydrogenation, but would require rearrangement to give 1,2-dibenzoylethane on oxidation. Accordingly, dehydrogenations of the dimer at temperatures low enough to preclude rearrangement were explored.



I



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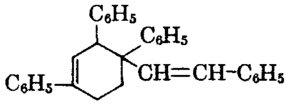
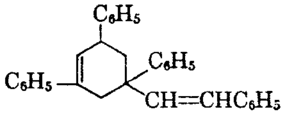


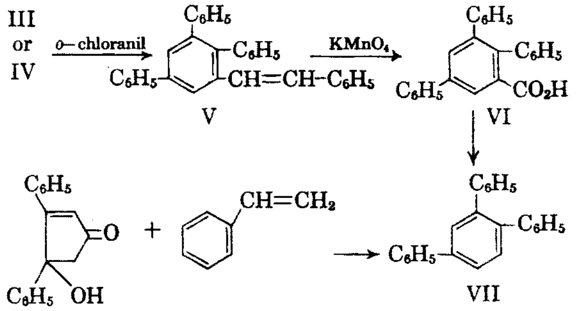
III



IV

Dehydrogenation of the 1,3-diphenyl-1,3-butadiene dimer with selenium dioxide at 75°, or much better, tetrachloro-*o*-benzoquinone at 80° gave a compound of formula $C_{32}H_{24}$ (V), m.p. 178–179°, which from its infrared and ultraviolet spectrum and lack of reaction with maleic anhydride was a triphenylstilbene. This compound was reduced to $C_{32}H_{26}$, m.p. 106–107°, and oxidized to an acid, $C_{25}H_{18}O_2$ (VI), m.p. 219–220° (dec.). This acid had a neutral equivalent of 355, but was not 2,4,6-triphenylbenzoic acid, m.p. 247.5–247.0° (dec.), which was prepared from 2,4,6-triphenylbromobenzene.[8] Decarboxylation of the $C_{25}H_{18}O_2$ acid gave a hydrocarbon $C_{24}H_{18}$, (VII), m.p. 99.5–100.0°. It was assumed that this hydrocarbon was 1,2,4-triphenylbenzene, and attempts were made to synthesize it by the condensation of *trans, trans*-1,4-diphenyl-1,3-butadiene with either styrene, phenylacetylene, or cinnamic acid. All of these failed to give any adduct in agreement with the report that *trans, trans*-1,4-diphenyl-1,3-butadiene is unreactive toward all but the most reactive dienophiles.[9]

1,2,4-Triphenylbenzene was finally prepared by the method of Rose and Statham.[10] This compound was identical with VII. V is therefore 2,3,5-triphenylstilbene produced by the aromatization of the cyclohexene ring, and VI is 2,3,5-triphenyl benzoic acid. This result requires either the migration of a styryl group in structure III or migration of a phenyl group in structure IV. Attempts to prepare VI by the oxidation of what is claimed to be 2,3,5-triphenyltoluene[11] failed. It was found impossible to obtain an oxidation product of this compound.



Catalytic reduction of the 1,3-diphenyl-1,3-butadiene dimer gave a tetrahydro derivative (VIII), m.p. 119–120°, whose ultraviolet spectrum was typical of compounds with isolated benzene rings. In order to make a choice between structures III and IV, it was decided to investigate the dehydrogenation of this substance. There is good evidence for the belief that dehydrogenations using quinones are initiated by hydride abstraction[13] and that blocks to aromatization presented by *gem*-dialkyl groups are overcome by migration processes similar to Wagner-Meerwein shifts. Now although the styryl group of the dimer might compete successfully with a phenyl group in migration from carbon to carbon,[14] it was

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[7] H. Fiesselmann and J. Ribka, *Ber.*, **89**, 40 (1956).

[8] E. P. Kohler and L. W. Blanchard, Jr., *J. Am. Chem. Soc.*, **57**, 367 (1935).

[9] K. Alder in *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers, Inc., New York, 1948.

[10] J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

[11] C. F. H. Allen and J. Van Allan, *J. Org. Chem.*, **10**, 333 (1945). The resistance of their compound, m.p. 131.5–132°, to oxidation is puzzling, and suggests that it is 2,3,6-triphenyltoluene in spite of the evidence cited. Moreover, Ivanov and co-workers[12] have reported that 2,3,5-triphenyltoluene melts at 94–95°.

[12] D. Ivanov, D. Ivanov, and B. Stoianova-Ivanovna, *Compt. Rend.*, **227**, 535 (1948).

[13] R. P. Linstead, E. A. Braude, L. M. Jackman, and A. N. Beames, *Chem. & Ind.* (*London*), 1174 (1954); see also J. D. Loudon, *Ann. Repts.*, 194 (1954).

[14] While there is no theoretical reason why a styryl group should not migrate, possibly through an intermediate analogous to the phenonium ion, no such instance could be found in the literature.

expected that the phenyl group of the tetrahydro dimer VIII would definitely migrate in preference to a saturated aliphatic chain,[15] such as the phenylethyl group. Also, since Dost[16] has shown that 2-phenylpropane is dehydrogenated twice as fast as ethylbenzene with tetrachloro-*p*-benzoquinone, it was reasonable to expect dehydrogenation of the cyclohexane ring with subsequent rearrangement before much dehydrogenation of the phenylethyl group[17] would occur. Steric effects on the course of rearrangement should be negligible, since in IX, the intermediate just prior to rearrangement, the cyclohexadiene ring is very nearly planar and both methylene hydrogens are almost sterically equivalent.

These considerations suggested that if III were the structure of the dimer, dehydrogenation of its tetrahydro derivative should give rise to a substance different from 2,3,5-triphenylstilbene (V) or its dihydro derivative, and that this dehydrogenation product would probably be 2,4,6-triphenylstilbene or 1-(2-phenylethyl)-2,4,6-triphenylbenzene. Although no homogeneous hydrocarbon product, other than starting material, could be isolated from the reaction of VIII with tetrachloro-*o*-benzoquinone in refluxing benzene, xylene, or diethylene glycol dimethyl ether, a 22% of a hydrocarbon, $C_{32}H_{22}$ or $C_{32}H_{24}$ (XI), was obtained when the dehydrogenation was carried out in naphthalene at 140–150°. However, this substance was not oxidized by permanganate and could not be reduced catalytically. This behavior and the infrared spectrum (absence of aliphatic carbon-hydrogen stretching and *trans*-ethylenic bands) argues against the expected structures. This was confirmed by comparison with authentic samples of 2,4,6-triphenylstilbene and 1-(2-phenylethyl)2,4,6-triphenylbenzene (*vide infra*). On the other hand, XI was not identical with 2,2′-binaphthyl. To eliminate the possibility that it was formed from naphthalene in some other fashion, a blank experiment was run in which no trace of XI could be detected.

It was therefore suspected that XI was a substance which resulted from the cyclization of 1-(2-phenylethyl)-2,4,6-triphenylbenzene XIII under dehydrogenating conditions. In order to synthesize this compound the following sequence of reactions was carried out. Phenylacetyl chloride was added to 2,4,6-triphenylphenylmagnesium bromide[8] to give 1-phenylacetyl-2,4,6-triphenylbenzene XII, m.p. 125–126°. Attempts to synthesize this product by a condensation of triphenylbenzene and phenylacetyl chloride failed. Although the reaction of triphenylbenzene and benzoyl chloride with aluminum chloride is reported to give triphenylbenzophenone in almost quantitative yield,[8,18] phenylacetyl chloride gave a low yield of a $C_{32}H_{24}O$ ketone which was quite different from XII, particularly in its carbonyl reactivity. This ketone must be a product of the acylation of one of the end rings, and as such violates the observation made by Allen and Burness[19] that *meta* terphenyl structures are invariably substituted on the central ring.

As noted by Kohler and Blanchard[8] for triphenylphenyl ketones, the carbonyl of XII was quite hindered. No derivative could be obtained with 2,4-dinitrophenylhydrazine, and the lithium aluminum hydride reduction in boiling tetrahydrofuran gave only a 45% yield of 1-(2,4,6-triphenylphenyl)-2-phenylethanol, m.p. 139–140°. This alcohol was dehydrated smoothly with iodine in toluene to give 2,4,6-triphenylstilbene, m.p. 161.5–162°. Catalytic reduction gave a poor yield of 1-(2-phenylethyl)-2,4,6-triphenylbenzene (XIII), m.p. 130.0–130.5°. XIII was also synthesized from XII by a Clemmensen reduction in about the same over-all yield. Dehydrogenation of XIII with tetrachloro-*o*-benzoquinone gave in addition to 61% of recovered starting material, an 8% yield of XI.

This synthesis of the hydrocarbon XI shows that 1-(2-phenylethyl)-2,4,6-triphenylbenzene (XIII) is indeed the initial dehydrogenation product of VIII. Subsequent carbonium ion formation followed by cyclization and another dehydrogenation to complete the aromatization would give either 1,3,9-triphenylphenanthrene or 1,3-diphenyl-9-benzylfluorene.[20] The latter structure was eliminated by synthesis. 1,3-Diphenylfluorenone was reduced to 1,3-diphenylfluorene, m.p. 118–119°, which was condensed with benzyl alcohol to give 1,3-diphenyl-9-benzylfluorene (XIV). The latter differed from XI not only in melting point, but in infrared and ultraviolet spectrum. The formation of 1,3,9-triphenylphenanthrene from VIII and XIII may be rationalized in terms of steric hindrance at the methylene carbon closest to the 2,4,6-triphenylmethyl radical which prevents hydride ion abstraction there and leads exclusively to the formation of ion X.

These results force the acceptance of 1,3,4-triphenyl-4-styrylcyclohexene (III) as the structure of the dimer of 1,3-diphenyl-1,3-butadiene. Therefore, in the Diels-Alder reaction the two molecules of 1,3-diphenyl-1,3-butadiene orient themselves in a manner which would be expected from that shown by the dimerization of 1- and 2-phenylbutadiene.[21,22] This orientation also follows the rule that in the Diels-Alder reaction that terminal car-

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(15) For an analogous case, see ref. 12.

(16) N. Dost, *Rec. trav. chim.*, **71**, 857 (1952).

(17) E. Buchta and W. Kallert, *Ann.*, **573**, 220 (1951).

(18) D. Ivanov and C. Ivanov, *Ber.*, **77B**, 173 (1944).

(19) C. F. H. Allen and D. M. Burness, *J. Org. Chem.*, **14**, 175 (1949).

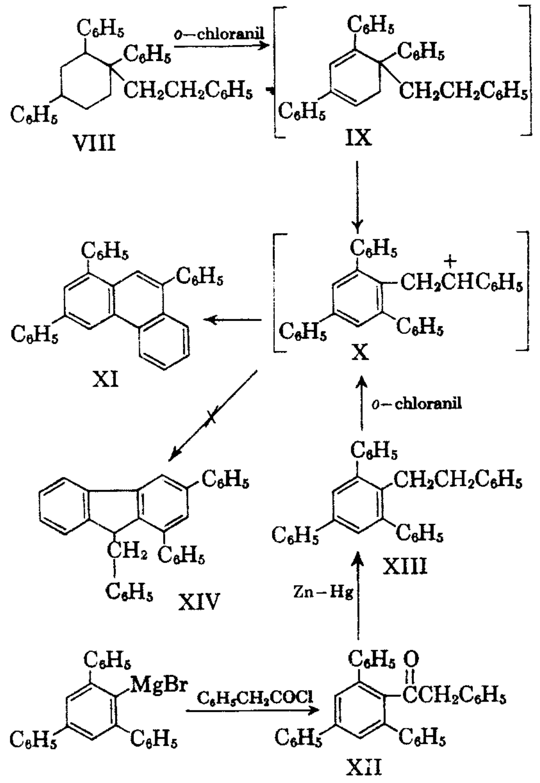
(20) Although these two products differ by two hydrogen atoms, a definite choice between formulae $C_{32}H_{22}$ and $C_{32}H_{24}$ could not be made on the basis of the elemental analysis. The absence of aliphatic carbon-hydrogen stretching in the infrared favored the phenanthrene structure over the fluorene.

(21) K. Alder, J. Haydn, and W. Vogt, *Ber.*, **86**, 1302 (1953).

(22) K. Alder and J. Haydn, *Ann.*, **570**, 203 (1950).

bon atom of the diene whose adjacent carbon atom can best stabilize a positive charge becomes attached to that carbon atom of the dienophile whose adjacent carbon atom can best stabilize a negative charge.[23]

Moreover it has been demonstrated that sulfur dehydrogenation of the dimer results primarily, if not exclusively, in phenyl migration and that *o*-chloranil dehydrogenation results in migration of a styryl group. The mechanism of the phenyl migration is not clear since the synthesis of 1,2,4-triphenylbenzene from 3,4-diphenyl-4-hydroxy-2-cyclopentenone and styrene is carried out under essentially the same conditions.



EXPERIMENTAL[24,25]

1,3-Diphenyl-2-buten-1-ol. To a solution of 10.0 g. (0.045 mole), of dypnone,[26] n_D^{23} 1.6309, in 100 ml. of methanol was added 1.5 g. (0.034 mole) of solid sodium borohydride as rapidly as the frothing allowed. The methanol boiled briefly and then slowly cooled. A smaller amount of sodium borohydride, stirring, or cooling during addition with subsequent reflux invariably resulted in very little reduction. After standing for 2 hr. the methanolic solution was extracted with ether. The ether layer was dried and concentrated at reduced pressure to give a clear green-tinted sirup, n_D^{23} 1.6003 (lit.[27] n_D^{25} 1.5989). The infrared spectrum showed a sharp band at 3655 cm.$^{-1}$ (ϵ = 24). Reduction by normal addition of a 200% excess of lithium aluminum hydride in refluxing ether gave an identical product. Because of extensive decomposition on distillation at 1 mm. the alcohol was used without further purification.

1,3-Diphenyl-1-buten-3-ol. This alcohol was prepared by the method of Cope, Wick, and Fawcett[6] in 25% isolable yield without distillation (the actual yield was 90% by infrared analysis), clumps of small needles from hexane, m.p. 57.5°–59.0° (lit.[6] 57.2–58.0°).

Dimer of 1,3-diphenyl-1,3-butadiene. To a solution of 74.0 g. (0.33 mole) of 1,3-diphenyl-2-buten-1-ol in 50 ml. benzene was added a single crystal of *p*-toluenesulfonic acid. Refluxing this solution for 24 hr. under a water trap produced 5.2 ml. (0.29 mole) of water. Concentration of the benzene solution at reduced pressure gave a yellow sirup. This residue was dissolved in ligroin and chromatographed through an alumina column. Elution with benzene–petroleum ether (1:3) produced a white solid which was separated by recrystallization from ligroin-benzene into 39.0 g. (58%), of a white solid, m.p. 132–134°, and 16.3 g. (24%) of a mixture of white solids m.p. 123–140°. The chloroform eluate produced 12.7 g. (18%) of a yellow oil which was mainly starting material from its infrared spectrum. Several further recrystallizations of fraction I gave large transparent prisms, m.p. 136–137°. Under these same conditions 1,3-diphenyl-1-buten-3-ol gave a 48% yield of material, m.p. 133–136°. The infrared spectrum showed strong absorption bands at 3058 (C—H), 3030 (C—H), 2933 (C—H), 1602 (benzene), 1500 (benzene), 1453 (benzene), 1037 (benzene), and 975 (*trans* double bond) cm.$^{-1}$ The ultraviolet spectrum showed a broad absorption curve with λ_{min} 228 mμ (log ϵ 4.12), λ_{max} 253 mμ (log ϵ 4.56), and a sharp peak at 294 mμ (log ϵ 3.19). The molecular weight (calcd. 406) was 426, determined ebullioscopically in methyl ethyl ketone; 215 (average of six determinations), determined by the Rast method.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found; C, 93.02; H, 7.09.

The absorption of bromine from chloroform was slow, and the decolorization of permanganate in acetone was negligible. The addition of tetranitromethane gave a bright yellow color. The dimer was only partially soluble in cold, concentrated sulfuric acid. Kuhn-Roth oxidation showed the absence of C—methyl groups. Microhydrogenation showed the presence of two double bonds. The dimer was stable to refluxing alcoholic solutions of hydrochloric acid and sodium hydroxide and formed no adduct with maleic anhydride. Slightly over two moles of bromine were absorbed from a chloroform solution with copious evolution of hydrogen bromide. The product was a mixture of bromine-containing compounds.

Dehydration of either 1,3-diphenyl-2-buten-1-ol or 1,3-diphenyl-3-buten-1-ol with iodine in benzene gave a small amount of white solid, m.p. 146–147°. The infrared spectrum showed strong bands at 3063 (C—H), 3034 (C—H), 2911 (C—H), 1603 (benzene), 1500 (benzene), 1462 (benzene), 1038 (benzene), and 906 (unassigned) cm.$^{-1}$ The ultraviolet spectrum showed λ_{max} 245 mμ (log ϵ 4.39) and λ_{min} 227 mμ (log ϵ 4.16).

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.15; H, 6.93.

Reaction of benzalacetophenone with methylmagnesium iodide. The procedure of Whitby and Gallay[4] was followed.

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(23) J. S. Meek, R. T. Merrow, and S. J. Cristol, *J. Am. Chem. Soc.*, **74**, 2667 (1952).

(24) Analyses were performed by Drs. Weiler and Strauss, Oxford, England. Molecular weights were determined by Clark Microanalytical Laboratory, Urbana, Ill. Ultraviolet and infrared spectra were determined by Miss M. A. Esquivel on Beckman Model DK and Perkin-Elmer model 21 spectrometers.

(25) Melting points are uncorrected. Ultraviolet spectra were determined in 95% ethanol solution. The infrared spectra were determined at known concentrations (3–5% solutions) in either chloroform or carbon tetrachloride, unless otherwise specified. The petroleum ether and ligroin referred to are commercial petroleum solvents of boiling range 30–60° and 65–110°, respectively.

(26) We wish to thank the Union Carbide Chemicals Co. for a generous supply of dypnone.

(27) H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955).

One run resulted in a 12% yield of 1,3,5-triphenyl-4-benzoyl-1,3-hexadiene, m.p. 175.5–177.0°, (lit.[5] 176°).

Other runs in which the Grignard reagent was allowed a longer time to form gave 4–17% of a white solid m.p. 161.5–163°, a small amount of 1,3-diphenyl-1,3-butadiene dimer, m.p. 136–137°, and considerable amounts of 1,3-diphenyl-1-butanone. The addition of maleic anhydride to the gummy residues gave 5–10% of the 3,5-diphenyl-1,2,3,6-tetrahydrophthalic anhydride described below. The substance melting at 161.5–163° showed two strong bands at 1666 and 1679 cm.$^{-1}$ (Nujol). The ultraviolet spectrum showed λ_{max} 243 mμ (log ϵ 4.36) and 280 mμ (log ϵ 3.32). It is assumed to be 1,3-dibenzoyl-4-phenylpentane which could have been formed by a Michael condensation between benzalacetophenone and 1,3-diphenyl-1-butanone.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.08; H, 6.53. Found: C. 86.17; H, 6.63.

3,5-Diphenyl-1,2,3,6-tetrahydrophthalic anhydride. A solution of 4.0 g. (0.018 mole) of 1,3-diphenyl-2-buten-1-ol and 1.8 g. (0.018 mole) of freshly sublimed maleic anhydride dissolved in 100 ml. xylene was refluxed under a water trap. On concentration of the xylene solution at reduced pressure 1.9 g. (33%) of a white powder, m.p. 156–157°, separated. Recrystallization from benzene–petroleum ether gave clumps of woolly needles, m.p. 158–159° (lit.[6] 142–149°).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.92; H, 5.51.

3,5-Diphenyl-1,2,3,6-tetrahydrophthalic acid. An aqueous solution of the anhydride was stirred and refluxed for 10 hr. Filtration gave 1.1 g. (80%) of a white solid, m.p. 216–224° (dec.). Recrystallization from acetic acid gave small needles, m.p. 221–224° (dec.). The neutral equivalent was 166 (calcd. 163).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found, C, 74.47; H, 5.64.

3,5-Diphenylphthalic anhydride and 3,5-diphenylphthalic acid. A mixture of 3.4 g. (0.011 mole) of 1,3-diphenyl-1,2,3,6-tetrahydrophthalic anhydride and 2.0 g. (0.062 atom) of sulfur was heated at 190–210° for 6 hr. The cooled mixture was extracted with chloroform, the solvent evaporated, and the residue recrystallized from benzene–petroleum ether. The yield was 2.26 g. (67%) of small needles, m.p. 167–172°. An analytical sample melted at 173–174.5° (dec.), (lit.[6] 176–177°).

Anal. Calcd. for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03. Found, C, 79.70; H, 4.02.

By extraction of the chloroform mother liquors with aqueous bicarbonate there was isolated 0.55 g. (15%) of 3,5-diphenylphthalic acid, m.p. 196–197°. Reprecipitation raised the melting point to 199.0–199.5°. The neutral equivalent was 161 (calcd. 159).

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.53; H, 4.53.

m-Terphenyl. A mixture of 430 mg. of 3,5-diphenylphthalic acid and 1 g. copper-bronze was heated gently with a low flame until no more material formed on the side of the flask. The yellowish, cotton-like material was scraped from the flask and sublimed at 90° (1 mm.). The yield of white powder, m.p. 85–86°, was 31 mg. (10%). The mixed melting point with an authentic sample of *m*-terphenyl showed no depression.

Sulfur dehydrogenation of the dimer. A mixture of 5.0 g. (0.012 mole) of dimer and 2.0 g. of sulfur was heated under nitrogen at 225–230° for 5 hr. The cooled mixture was dissolved in 100 ml. of absolute ethanol and refluxed 2 hr. over W-2 Raney nickel. Evaporation of the alcohol left a brown gum which was dissolved in a small amount of chloroform and chromatographed through an alumina column. Petroleum ether eluted a green oil from which separated 140 mg. (4%) of massive golden tinted needles, m.p. 171.5–172.5°. A mixed melting point with an authentic sample of 1,3,5-triphenylbenzene, prepared by the method of Reddeliens,[28] showed no depression. The infrared and ultraviolet spectra of these two samples were identical.

Ozonolysis of the dimer. A solution of 4.12 g. (0.01 mole) of 1,3-diphenyl-1,3-butadiene dimer dissolved in 150 ml. of ethyl acetate was ozonized at −10° until ozone appeared in the outlet gases (potassium iodide solution). The reaction mixture was quickly removed and added to a spoonful of Raney nickel. After stirring overnight, the faintly green solution was filtered and concentrated to a viscous oil. The oil was dissolved in ligroin (b.p. 60–90°) and a small amount of benzene and chromatographed through an alumina column. From the benzene–petroleum ether fraction was obtained 123 mg. (5%) of 1,2-dibenzoylethane, m.p. and mixed m.p. with an authentic sample,[29] 145–146°. The infrared spectra of these two samples were identical. From the ether fractions was obtained a brown oil which rapidly formed mixtures of carbonyl derivatives with 2,4-dinitrophenylhydrazine and semicarbazide. Only a small portion of this oil was base soluble. The infrared spectrum of the oil showed a broad absorption at 3600–3200 cm.$^{-1}$ (OH), and strong bands at 1775 and 1688 cm.$^{-1}$ (C=O).

In other experiments the reduced ozonide was steam distilled into either an acidic aqueous-alcoholic solution of 2,4-dinitrophenylhydrazine or a saturated aqueous solution of dimedone. The yields of the benzaldehyde derivatives of each were 30–40%. 1,2-Dibenzoylethane was also obtained on oxidation of the dimer with potassium permanganate and sodium bicarbonate in acetone. The yields were slightly lower.

2,3,5-Triphenylstilbene (V). *Dehydrogenation of the dimer with selenium dioxide.* To a well-stirred suspension of 1.11 g. (0.01 mole) of freshly prepared selenium dioxide in 40 ml. of dioxane was added 4.12 g. (0.01 mole) of 1,3-diphenyl-1,3-butadiene dimer. After heating at 75° for 37 hr., the mixture was filtered and the dioxane removed at reduced pressure. The residual yellow gum was dissolved in 20% benzene–petroleum ether and chromatographed through an alumina column. Elution gave yellow oils which showed a carbonyl band (1680 cm.$^{-1}$) in the infrared spectrum, but which were inert toward 2,4-dinitrophenylhydrazine. One of the petroleum ether eluates on standing deposited 64 mg. (2%) of 2,3,5-triphenylstilbene, m.p. 175–177°. Recrystallization from ethanol–ethyl acetate gave long needles, m.p. 178–179°. The infrared spectrum showed a strong band at 970 cm.$^{-1}$ (*trans* double bond). The ultraviolet spectrum showed a broad absorption from 260–320 mμ; λ_{max} *ca.* 270 mμ (log ϵ 4.60) and 310 mμ (log ϵ 4.44).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.00; H, 5.84.

2,3,5-Triphenylstilbene (V). *Dehydrogenation with tetrachloro-o-benzoquinone.* Tetrachloro-*o*-benzoquinone was prepared by the general method of Jackson and MacLaurin.[30] C.P. Nitric acid (dec. 1.42) was found most satisfactory for oxidation of the tetrachlorocatechol. The garnet powder, m.p. 126–128°, was difficult to purify and was used in the crude form.

To a solution of 2.0 g. (0.0048 mole) of the dimer in 40 ml. of benzene was added 3.0 g. (0.012 mole) of tetrachloro-*o*-benzoquinone. The resultant deep red solution was refluxed for 8 hr. Upon cooling the benzene solution was washed through an alumina column with 300 ml. of petroleum ether. Evaporation of the solvent produced 700 mg. (35%) of 2,3,5-triphenylstilbene (V), m.p. 173–175°. The remainder of this product was an irresolvable mixture of solids, m.p. 150–170°, whose ultraviolet spectrum was very similar to that of 2,3,5-triphenylstilbene.

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(28) Described in C. Vorländer, E. Fischer, and H. Wille, *Ber.*, **62**, 2836 (1929).

(29) P. S. Bailey and R. E. Lutz, *J. Am. Chem. Soc.*, **70**, 2412 (1948).

(30) C. L. Jackson and R. D. MacLaurin, *Am. Chem. J.*, **37**, 11 (1907).

1-(2-Phenylethyl)-2,3,5-triphenylbenzene. A solution of 100 mg. (0.00024 mole) of 2,3,5-triphenylstilbene in 50 ml. glacial acetic acid was reduced at three atmospheres with 25 mg. of 10% palladium-on-charcoal, yield 63 mg. (62%) of long needles, m.p. 105.5–106°. An analytical sample recrystallized from ethanol–ethyl acetate melted at 106–107°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.50; H, 6.52.

Reduction in ethyl acetate resulted only in recovery of starting material.

2,3,5-Triphenylbenzoic acid. (VI). To a well-stirred solution of 740 mg. (0.0018 mole) of 2,3,5-triphenylstilbene and 100 mg. of sodium bicarbonate dissolved in 100 ml. acetone was added 4.0 g. potassium permanganate. After stirring at room temperature for 12 hr., methanol was added until the purple color was discharged. The solution was filtered and the manganese dioxide washed thoroughly with 10% sodium hydroxide. Acidification of the combined filtrate and washings produced 458 mg. (71%) of a white acid, m.p. 217–219°. The hexagonal prisms, m.p. 219–220° from acetonitrile, had a neutral equivalent of 355 (calcd. 350).

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.30; H, 4.92.

2,4,6-Triphenylbromobenzene. The method of Kohler and Blanchard[8] gave yields of 79–100% of 2,4,6-triphenylbromobenzene, m.p. 107–108° (lit. 104°;[31] 129–130°[8]). After repeated recrystallizations with no change in melting point, one crop melted at 131–133°. Thereafter recrystallizations gave the higher melting form. Both forms were used interchangeably in subsequent reactions.

2,4,6-Triphenylbenzoic acid. 2,4,6-Triphenylbenzoic acid was formed by the carbonation of 2,4,6-triphenyllithium[32] in low yield. Recrystallization from acetonitrile gave small needles, m.p. 248.5–249.5°.

1,2,4-Triphenylbenzene (VII). *Decarboxylation of 2,3,5-triphenylbenzoic acid* (VI). To a solution of 268 mg. (0.0077 mole) of 2,3,5-triphenylbenzoic acid dissolved in 5 ml. of freshly distilled quinoline was added 40 mg. of copper chromite catalyst.[33] After heating at 213–228° for 2 hr. in a vigorous stream of nitrogen, 40 ml. of benzene was added, and the mixture was extracted with successive 50-ml. portions of 5% HCl, 5% KOH, and water. The benzene layer was dried over sodium sulfate and concentrated to 5 ml. The residue was dissolved in ligroin and chromatographed through an alumina column. Benzene–petroleum ether (1:9) eluted 100 mg. (43%) of a hydrocarbon, m.p. 96–98°. Recrystallization from ethanol gave clumps of needles, m.p. 99.5–100.0°. The ultraviolet spectrum had λ_{max} 248 mμ (log ε 4.52) and 272 mμ (log ε 4.39).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.88; H, 6.06.

1,2,4-Triphenylbenzene (VII). *Preparation from 3,4-diphenyl-4-hydroxy-2-cyclopentenone.* To a mixture of 5.0 g. (0.02 mole) of 3,4-diphenyl-4-hydroxy-2-cyclopentenone[34] and 10.0 g. of freshly fused and pulverized potassium acid sulfate was added 5.0 g. (0.049 mole) of phenylacetylene.[35] This mixture was heated for 7.5 hr. at 180–185°. The potassium bisulfate was filtered and washed with benzene. The combined filtrate and washings were concentrated on a 230–240° bath. After the benzene was removed, the heating was continued for 20 min. The resultant black oil was dissolved in ligroin and chromatographed through an alumina column. Four fractions were obtained from the petroleum ether eluate. The first fraction consisted of 240 mg. (4%) of small prisms, m.p. 118–120°; the second fraction, 260 mg. (5%) of long needles, m.p. 96–99°; the third fraction, 450 mg. (8%) of long needles, m.p. 98–99°; the fourth fraction, 180 mg. (3%) of small prisms, m.p. 117–120°. The infrared spectra of all four fractions were identical. A mixture of fractions I and III gave an opaque melt at 100° which slowly resolidified and melted at 119–120°. Recrystallization of the higher melting form from petroleum ether gave small jewel-like prisms, m.p. 119.5–120°. A mixture of the lower melting form with the 1,2,4-triphenylbenzene (VII) from the dehydrogenation of 2,3,5-triphenylbenzoic acid (VI) melted at 99.5–100°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.34; H, 6.05.

The procedure of Rose and Statham[10] produced the same mixture in 4% over-all yield. These authors report only a single melting point, 109°, for this product.

2,3,5-Triphenyltoluene (?). 2,3,5-Triphenyltoluene, m.p. 131.5–132.5°, was prepared by the method of Allen and Van Allan[11] in 43% yield. A dimer of 2-methyl-3,4-diphenylcyclopentadienone, m.p. 219.5–220.5° (with effervescence), was isolated from the mother liquors in 10% yield. This diketone had carbonyl frequencies at 1690 and 1790 cm.$^{-1}$ Allen and Van Allan[36] report carbonyl frequencies at 177 cm.$^{-1}$ as characteristic for bridged carbonyl compounds.

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73. Found: C, 87.12; H, 5.97.

All attempts to oxidize 2,3,5-triphenyltoluene with permanganate, dichromate, nitric acid, or chromyl chloride resulted either in recovery of starting material or base-insoluble tars.

1-(2-Phenylethyl)-1,3,5-triphenylcyclohexane (VIII). A solution of 1.0 g. (0.0024 mole) of the 1,3-diphenyl-1,3-butadiene dimer dissolved in 40 ml. of ethyl acetate was hydrogenated at three atmospheres with 200 mg. of 10% palladium-on-charcoal for 1 hr. Removal of solvent at reduced pressure yielded 1.0 g. of a white solid, m.p. 116–118°. Subsequent runs gave yields of 75–85%. Recrystallization from ethanol–ethyl acetate produced large prisms, m.p. 119–120°. The molecular weight (calcd. 416) was 375, determined ebullioscopically in methyl ethyl ketone; 266 (average of six determinations) determined by Rast method. No C-methyl was found on Kuhn-Roth oxidation. The ultraviolet spectrum showed absorption maxima at 253 mμ (log ε 2.90), 259 mμ (log ε 2.98), 265 mμ (log ε 2.89), and 268 mμ (log ε 2.80).

Anal. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74. Found: C, 92.26; H, 7.90.

Dehydrogenation of 1-(2-phenylethyl)-1,3,5-triphenylcyclohexane (VIII). A mixture of 2.16 g. (0.0052 mole) of 1-(2-phenylethyl)-1,3,5-triphenylcyclohexane (VIII), 30 g. of naphthalene, and 12.5 g. (0.051 mole) of tetrachloro-o-benzoquinone was heated at 140–150° for 24 hr. in a stream of dry oxygen-free nitrogen. The brown mixture was dissolved in 100 ml. of benzene and passed through an alumina column. The hydrocarbon fraction was completely removed with 300 ml. of benzene. The benzene eluates were reduced in volume and steam distilled until the naphthalene was completely removed. The solid brown residue was taken up in ligroin and chromatographed through an alumina column. The benzene–petroleum ether (1:4) eluate yielded 426 mg. (22%) of a yellowish solid, m.p. 170–175°. Two recrystallizations from benzene-ligroin produced clumps of small needles, m.p. 183.5–184° (XI). This compound was not oxidized by permanganate in acetone solution after 19 hr. It was also inert to catalytic hydrogenation in either ethyl acetate or glacial acetic acid. The infrared spectrum showed no band at 970 cm.$^{-1}$ (*trans* double bond). The ultraviolet spectrum showed λ_{max} 262 mμ (log ε 4.64) with a shoulder

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(31) C. Engler and H. E. Berthold, *Ber.*, 7, 1123 (1874).

(32) J. W. Morton, Dissertation, Iowa State College, 1952.

(33) H. Adkins, E. E. Burgoyne, and H. J. Schneider, *J. Am. Chem. Soc.*, 72, 2626 (1950).

(34) F. R. Japp and J. Knox, *J. Chem. Soc.*, 87, 679 (1905).

(35) J. C. Hessler, *Org. Syntheses*, Coll. Vol. I, 438 (1932).

(36) C. F. H. Allen and J. Van Allan, *J. Org. Chem.*, 20, 306 (1955).

at *ca.* 294 mμ (log ε 4.44). After refluxing with iodine in toluene, this compound was recovered unchanged.

Anal. Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.11; H, 5.43.

A sample of 2,2′-binaphthyl was prepared in low yield by the addition of ferrous chloride to 2-naphthylmagnesium iodide. The purified hydrocarbon, m.p. 181.5–182.5°, on admixture with the above dehydrogenation product melted at 158–167°. Their infrared spectra were different.

A blank dehydrogenation experiment under the same conditions produced, as the only benzene–petroleum ether eluable material, 180 mg. of a halogen-containing white solid. This substance was devoid of benzene bands in its infrared spectrum.

3,5-Diphenyl-4′-phenacetylbiphenyl. To a solution of 7.32 g. (0.055 mole) of anhydrous aluminum chloride dissolved in 30 ml. of dry carbon disulfide was added dropwise with stirring a solution of 15.3 g. (0.05 mole) of 1,3,5-triphenylbenzene and 7.80 g. (0.05 mole) of phenylacetyl chloride in 100 ml. of dry carbon disulfide. The resulting greenish black solution was stirred at room temperature for 8 hr. The reaction mixture was decomposed by the addition of 150 ml. of cold 4*N* hydrochloric acid. The carbon disulfide layer was separated, and the aqueous layer was extracted with three 150-ml. portions of benzene. The combined organic layers were extracted with three 150-ml. portions of sodium bisulfite solution and washed with water. The dried solution was concentrated at reduced pressure and the residual yellow gum was dissolved in ligroin and chromatographed through an alumina column. From the benzene–petroleum ether (1:9) eluate there was recovered 7.0 g. (46% recovery) of 1,3,5-triphenylbenzene. From the benzene–petroleum ether (1:4) eluate there was obtained 1.28 g. (6%) of a yellowish solid, m.p. 146–149°. Recrystallization from benzene-ligroin gave slightly yellow feathery crystals, m.p. 148.5–149.0°. The infrared spectrum showed a strong band at 1680 cm.$^{-1}$ A slow reaction with 2,4-dinitrophenylhydrazine reagent produced orange needles, m.p. 208.5–209.0°, from ethanol–ethyl acetate.

Anal. Calcd. for $C_{38}H_{28}N_4O_4$: C, 75.48; H, 4.67; N, 9.27. Found: C, 74.74; H, 4.83; N, 9.45.

3,5-Diphenyl-4′-(2-phenyl-1-hydroxyethyl)biphenyl. Reduction of 1.21 g. of the preceding ketone with lithium aluminum hydride in ether solution furnished an oil which was chromatographed over alumina. The benzene eluate, wt. 0.82 g., crystallized on trituration with petroleum ether. Slow evaporation of an ethanol solution furnished white crystals, m.p. 130–131.5°.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 89.57; H, 6.44.

3,4-Diphenyl-4′-styrylbiphenyl. A mixture of 0.159 g. of the preceding alcohol, 30 ml. of toluene, and a crystal of iodine was refluxed for 12 hr., cooled, and treated with sodium thiosulfate solution. The toluene layer was dried and concentrated to small volume. The solid, wt. 0.114 g., was recrystallized from ligroin, m.p. 185.5–186°, mixed m.p. with XI 163–175°. The infrared spectrum had the typical *trans*-ethylenic band at 970 cm.$^{-1}$

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.92; H, 5.80.

1-Phenylacetyl-2,4,6-triphenylbenzene (XII). 2,4,6-Triphenylphenylmagnesium bromide was prepared from 1.0 g. of magnesium (0.041 g.-atom) and 15.0 g. (0.039 mole) of 2,4,6-triphenylbromobenzene by the method of Kohler and Blanchard.[8] To the refluxing Grignard solution was added dropwise 6.0 g. (0.039 mole) of phenylacetyl chloride dissolved in 50 ml. of dry benzene. After the addition was complete, stirring was continued for 12 hr. at room temperature. The reaction mixture was poured onto a solution of 30 ml. of hydrochloric acid in 200 ml. of ice water and the layers separated. The organic layer was washed with two 100-ml. portions of 10% sodium hydroxide, water, and saturated calcium chloride solution. The solution was dried and concentrated. The residue was dissolved in ligroin and chromatographed through an alumina column. Petroleum ether eluted 2.7 g. (18%) of triphenylbenzene. From the benzene–petroleum ether (3:7) eluate was isolated 8.6 g. (52%) of a white solid, m.p. 121–124°. Recrystallization from benzene-ligroin produced small plates, m.p. 125–126°. The infrared spectrum showed a carbonyl band at 1702 cm.$^{-1}$ (ε 180) but the substance was inert toward 2,4-dinitrophenylhydrazine. The ultraviolet spectrum showed λ_{max} 245 mμ (log ε 4.64) with a shoulder at ca. 310 mμ (log ε 3.54).

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 91.26; H, 5.72.

1-(2,4,6-Triphenylphenyl)-2-phenylethanol. A solution of 4.0 g. (0.0094 mole) of 1-phenylacetyl-2,4,6-triphenylbenzene (XII) and 0.18 g. (0.0047 mole) of lithium aluminum hydride dissolved in 100 ml. of anhydrous tetrahydrofuran was stirred and refluxed under a stream of dry, oxygen-free nitrogen for 5 hr. Water was added to the reaction mixture, and the organic layer was decanted. The yellow gum obtained on concentration was dissolved in ligroin and chromatographed through an alumina column. The benzene-ligroin eluate yielded 1.7 g. (43% recovery) of starting material. Evaporation of the ether eluate produced 1.8 g. (45%) of a white solid, m.p. 137–140°. Recrystallization from ligroin gave small star-shaped crystals, m.p. 139–140°.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 89.76; H, 5.96.

2,4,6-Triphenylstilbene. A single crystal of iodine was added to a solution of 1.62 g. (0.0038 mole) of 1-(2,4,6-triphenylphenyl)-2-phenylethanol dissolved in 35 ml. of toluene. After refluxing for 21 hr., the solution was poured onto aqueous sodium bisulfite until the iodine color disappeared. The toluene layer was separated, dried, and concentrated. From the residue separated 1.35 g. (87%) of a white solid, m.p. 158–161°. Recrystallization from ligroin yielded fluffy needles, m.p. 161.5–162.0°. The infrared spectrum showed a strong band at 973 cm.$^{-1}$ (*trans* double bond) and the ultraviolet spectrum showed λ_{max} 253 mμ (log ε 4.23) and λ_{max} 314 mμ (log ε 4.54).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.85; H, 5.91.

1-(2-Phenylethyl)-2,4,6-triphenylbenzene (XIII). A solution of 1.35 g. (0.0033 mole) of 2,4,6-triphenylstilbene and 0.2 g. of platinum oxide dissolved in 100 ml. of glacial acetic acid and 50 ml. of ethyl acetate was hydrogenated at four atmospheres for 3 hr. The filtered solution was concentrated to give 0.41 g. (30%) of a white solid, m.p. 123–127°. Recrystallization from petroleum ether yielded long needles, m.p. 130.0–130.5°. The same product was obtained by the reduction of 1-phenylacetyl-2,4,6-triphenylbenzene (XII) with zinc-amalgam,[36] hydrochloric acid, and toluene. The yield after refluxing for 130 hr. was 15%.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.42; H, 6.40.

Cyclization of 1-(2-phenylethyl)-2,4,6-triphenylbenzene (XIII). A mixture of 400 mg. (0.0016 mole) of tetrachloro-*o*-benzoquinone, 590 mg. (0.0015 mole) of 1-(2-phenylethyl)-2,4,6-triphenylbenzene, and 10 g. of naphthalene was heated at 145° for 24 hr. The solid mass was steam-distilled until the naphthalene was completely removed. The brown residue was dissolved in ligroin and chromatographed through an alumina column. From the ligroin eluate was recovered 360 mg. (61%) of 1-(2-phenylethyl)-2,4,6-triphenylbenzene (XIII). Evaporation of the benzene–petroleum ether (1:9) eluate produced 45 mg. (8%) of a white solid, m.p. 179.5–182°. A mixed melting point with XI showed no depression. The infrared spectra of these two samples were identical. A repetition of this reaction with slightly over two equivalents of tetrachloro-*o*-benzoquinone led to a 41% recovery of 1-(2-phenylethyl)-2,4,6-triphenylbenzene (XIII), and a 6% yield of XI. The discrepancy between these yields

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(36) E. L. Martin in *Org. Reactions*, I, 163 (1942).

and the initial yield of XI may be due to slight steam volatility of 2,4,9-triphenylphenanthrene.

1,3-Diphenylfluorene. Reduction of 2.5 g. of 1,3-diphenylfluorenone[8] by the Huang-Minlon modification of the Wolff-Kishner reaction gave an oil which recrystallized on trituration with petroleum ether. Recrystallization from ligroin and petroleum ether yielded 1.7 g. of colorless needles, m.p. 118–119°. The infrared spectrum had a band at 2900 cm.$^{-1}$ (—CH_2—) and no carbonyl absorption, in contrast with 1,3-diphenylfluorenone which exhibited a C═O band at 1708 cm.$^{-1}$ (cyclopentenenone) and had no —CH_2— band.

Anal. Calcd. for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.23; H, 5.83.

9-Benzyl-1,3-diphenylfluorene (XIV). Benzylation of 0.95 g. of 1,3-diphenylfluorene by the method of Sprinzak[38] furnished 0.9 g. of a product which was recrystallized from petroleum ether, m.p. 115–118°, mixed m.p., with 1,3-diphenylfluorene, 95–108°. The infrared spectrum differed considerably from the spectrum of 1,3-diphenylfluorene.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.33; H, 5.74.

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[38] Y. Sprinzak, *J. Am. Chem. Soc.*, **78**, 466 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

1,3-Diphenyl-1,3-butadiene Dimers[1]

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Attempts to prepare 1,3-diphenyl-1,3-butadiene by dehydration of *trans*-2,4-diphenyl-3-buten-2-ol gave two solid dimers. Dimer I, the main product, was shown to be 4-*trans*-styryl-1,3,4-triphenylcyclohexene. Dimer II may be a stereoisomer. Dimer I was also obtained from 2,4-diphenyl-3-buten-1-ol.

In connection with work on the polymerization of phenylacetylene which might be expected to give, at least as an intermediate, a conjugated polyene with phenyl groups on alternate carbons, it was of interest to study conjugated polyenes possessing such a structure. The simplest such compound is 1,3-diphenyl-1,3-butadiene, which was unreported in the literature when our work began. It has since been prepared by the reaction of 2-phenyl-1,3-butadiene with benzenediazonium chloride.[3]

Whitby and Gallay[4] reported that the addition of benzalactophenone to methylmagnesium iodide at −10° gave a 70% yield of a compound, m.p. 167°, which had the composition and molecular weight of a dimer of 1,3-diphenylbutadiene; this compound possessed two double bonds on the basis of bromine addition. The 1,4-addition product, 1,3-diphenyl-1-butanone, was also isolated in 21% yield. Exact experimental details were not given.

In our hands the addition of benzalacetophenone to methylmagnesium iodide under nitrogen using conditions of temperature, etc., as nearly like those of Whitby and Gallay as their directions permitted gave a 60% yield of the 1,4-addition product and 27% of 4-benzoyl-1,3,5-triphenyl-1,3-hexadiene; none of the dimeric material could be isolated. These products are the same as were obtained from benzalacetophenone and methylmagnesium bromide.[5]

Reaction of benzalacetone with phenyllithium essentially as described by Cope and co-workers[6] gave *trans*-2,4-diphenyl-3-buten-2-ol. Dehydration of this carbinol under a variety of conditions gave a yellow gum from which were obtained by chromatography and recrystallization two solid dimers and 2–5% of yellow oily polymeric material. The optimum yield of a solid mixture of the dimers was 95–98%; dimer I, m.p. 137–138°, a crystalline white solid, was readily isolated in 40–50% yield, but dimer II, m.p. 125–126°, an amorphous white solid, was more difficult to purify and may not have been obtained completely pure. A mixture of the two dimers melted over the range 124–135° and the ultraviolet spectra differed only slightly in the intensity of the absorption at the principal band (λ_{max} 254 mμ, dimer I, ϵ 35200; dimer II, ϵ 36000). The infrared spectra of the dimers were identical except for the presence of two additional weak bands at 888 and 1000 cm.$^{-1}$ in the spectrum of di-

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[1] This report is taken from a dissertation submitted by Marvin H. Goodrow to the graduate school of the University of California, Los Angeles, in partial fulfillment of the requirements for the Ph.D. degree, August 1956. The material was presented at the San Francisco meeting of the American Chemical Society, April 1958 (Abstracts of that meeting, p. 78-N). At that meeting Dr. Werner Herz informed us that he and E. Lewis had also investigated this problem; his results will be found in this issue, *J. Org. Chem.*, **23**, 1646 (1958).

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[3] A. V. Dombrovskii, *Doklady Akad. Nauk S.S.S.R.*, **111**, 827 (1956); *Chem. Abstr.*, **51**, 9507 (1957).

[4] G. S. Whitby and W. Gallay, *Can. J. Research*, **6**, 280 (1932).

[5] M. S. Kharasch and D. C. Sayles, *J. Am. Chem. Soc.*, **64**, 2972 (1942).

[6] A. C. Cope, E. L. Wick, and F. S. Fawcett, *J. Am. Chem. Soc.*, **76**, 6156 (1954).