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.

Acknowledgment. This work was supported in part by grants from the Research Corp. and the National Science Foundation, for which we express our thanks. We are indebted to Dr. H. M. Walborsky for stimulating discussions.

TALLAHASSEE, FLA.

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

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

THOMAS L. JACOBS AND MARVIN H. GOODROW[2]

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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).

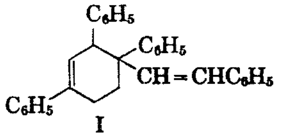
(5) M. S. Kharasch and D. C. Sayles, *J. Am. Chem. Soc.*, **64**, 2972 (1942).

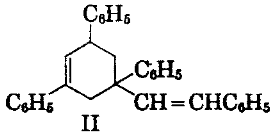
(6) A. C. Cope, E. L. Wick, and F. S. Fawcett, *J. Am. Chem. Soc.*, **76**, 6156 (1954).

mer II. The best evidence that these dimers are different arises from chromatography experiments: Dimer II is more tightly held on alumina, and during elution an intermediate, low melting mixture comes off between the dimers. It is possible that these two dimers are stereoisomers.

Preliminary attempts were also made to synthesize 1,3-diphenyl-1,3-butadiene from 2,4-diphenyl-3-buten-1-ol.[7] The carbinol was prepared by reduction of methyl 2,4-diphenyl-3-butenoate with lithium aluminum hydride, but the product was a mixture containing approximately 18% of unchanged ester. Attempts to purify the alcohol by saponification of the ester were not successful, but some of the alcohol was apparently dehydrated in the process since a low yield of dimer I was isolated from the reaction mixture. The 3,5-dinitrobenzoate of 2,4-diphenyl-3-buten-1-ol was prepared, but attempts to pyrolyze the very small amounts of this derivative that were available yielded neither the diene nor its dimer.

trans-1,3-Diphenyl-1,3-butadiene would be expected to dimerize by a Diels-Alder reaction to give one of structures I–IV. By analogy with the behavior of other 1,3-disubstituted butadienes,[8,9] of 1-phenyl-1,3-butadiene[10] and of 2-phenyl-1,3-butadiene,[11] I would be the most probable structure.


I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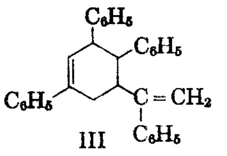
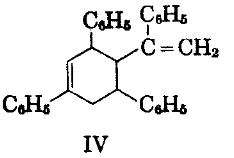

III


IV

Dimer I, although somewhat resistant to hydrogenation, gave a tetrahydro derivative with the ultraviolet and infrared spectra expected for a tetrahydro derivative of I–IV. Partial hydrogenation with absorption of one mole of hydrogen or reduction with hydroiodic acid gave impure dihydro derivatives that could not be purified successfully. An attempt to rearrange the double bonds in dimer I by refluxing for 16 hr. in ~0.9*M* sodium ethoxide in ethanol was unsuccessful. The dimer absorbed bromine in carbon tetrachloride very slowly. A Kuhn-Roth determination showed that C—methyl groups were absent.

The infrared spectrum of dimer I is that expected for structure I and makes structures III and IV unlikely. The absence of a band in the 1420–1410 cm.$^{-1}$ region, characteristic of in-the-plane deformation of the CH_2 of RR′C = CH_2[12] is a significant feature. Although there is a weak band at 905 cm.$^{-1}$ not far from the position expected for the out-of-plane deformation band of the CH_2 group of $R_1R_2C = CH_2$ (892–887 cm.$^{-1}$), such a band should be strong if the group = CH_2 were present. A weak band at 1635 cm.$^{-1}$ and a medium band at 1595–1600 cm.$^{-1}$ might be expected for phenyl conjugated double bonds. Very strong bands at 690 and 735 cm.$^{-1}$ as well as four evenly spaced bands in the 2000–1700 cm.$^{-1}$ region suggest the presence of only mono-substituted phenyl groups.[13] A strong band at 968 cm.$^{-1}$ indicates that one of the two double bonds is *trans*. The ultraviolet spectrum of dimer I shows typical β-substituted styrene absorption with the principal maximum at 254 mμ (log ϵ 4.546) and a small but sharp side peak at 294 mμ (log ϵ 3.250). The principal band has several small inflections and one small side peak at 271 mμ (log ϵ 4.342). The position of the principal maximum and the high extinction coefficient indicate that both double bonds are present as styryl functions, and a comparison with the spectrum of *trans*-1,3-diphenyl-1-butene,[14] which displays maxima at 294 (log ϵ 3.100), 286 (log ϵ 3.240), and 253 mμ (log ϵ 4.250), suggests that the dimer contains two 1,3-diphenyl-1-butene systems. The ultraviolet absorption is evidence against structures III and IV because the α-substituted styryl chromophore absorbs in the 242–244 mμ region and has extinction coefficients lower than 10,000.[15,16]

The evidence discussed above makes structures III and IV improbable, but does not permit a choice between structures I and II. Dimer I is somewhat resistant to oxidative degradation except under conditions so vigorous that benzoic acid is the principal product. Ozonization followed by either reductive or oxidative decomposition of the ozonide gave up to 5% yields of 1,2-dibenzoylethane in addition to benzoic acid, polymeric material, and small amounts of carbonyl compounds which were never isolated as pure compounds in sufficient amounts for structural determination. Structure II cannot give 1.2-dibenzoylethane without an unlikely rearrangement; structure I is therefore believed to be correct for dimer I, although the results of dehydrogenation studies described below tend to confuse the matter.

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[7] These experiments were carried out by E. Staggs, *An Attempted Synthesis of 1,3-Diphenyl-1,3-butadiene*, M.S. thesis, University of California, Los Angeles, June 1955.

[8] K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949).

[9] J. S. Meek and J. W. Ragsdale, *J. Am. Chem. Soc.*, **70**, 2502 (1948).

[10] K. Alder, J. Haydn, and W. Vogt, *Chem. Ber.*, **86**, 1302 (1953).

[11] K. Alder and J. Haydn, *Ann.*, **570**, 201 (1950).

[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954.

[13] C. W. Young, R. B. Du Vall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

[14] M. Grumez, *Ann. chim.* [11], **10**, 378 (1938).

[15] American Petroleum Institute Research Project No. 44, Ultraviolet Spectral Data, Carnegie Institute of Technology, June 30, 1952, No. 119.

[16] Y. Hirschberg, *J. Am. Chem. Soc.*, **71**, 3241 (1949).

Sulfur dehydrogenation of dimer I gave a mixture which was difficult to separate. Pure 1,3,5-triphenylbenzene and a sulfur-containing compound, $C_{18}H_{14}S$, whose structure was not determined, were isolated by chromatography. Dehydrogenation over a palladium-on-carbon catalyst at 300° gave ethylbenzene, 1,3,5-triphenylbenzene, and small amounts of 1,2,4-triphenylbenzene. It was difficult to separate the unsymmetrical derivative from the symmetrical, and the former was not isolated in a completely pure state, but melted at 96–99.5°. Pure 1,2,4-triphenylbenzene, prepared for comparison,[17] melted at 101.5–102°. A mixture melted between these values. The ultraviolet and infrared spectra indicated that the compound from the dehydrogenation was mainly *uns*-triphenylbenzene contaminated with small amounts of the *sym.* isomer. An attempt to isomerize the *uns.* to the *sym.* compound under the conditions of the dehydrogenation was unsuccessful. Dehydrogenation of dimer I with chloranil was not attempted at first because when this dehydrogenation was applied to dimer II, only very low yields of crystalline products were obtained. After learning that Herz and Lewis had obtained 2,3,5-triphenylstilbene from dimer I by dehydrogenation with tetrachloro-o-benzoquinone, we dehydrogenated dimer I with chloranil and isolated 34% of 2,3,5-triphenylstilbene, m.p. 176–179°.

Dimer II was not investigated in any detail. Its spectra are very similar to those of dimer I, and catalytic dehydrogenation gave ethylbenzene and 1,3,5-triphenylbenzene. Hydrogenation with Adams' catalyst gave mixtures of dihydro compounds as with dimer I; the more active catalyst which gave the tetrahydro derivative with dimer I was not tried with dimer II.

Dehydrogenation with chloranil gave mixtures from which very low yields of two crystalline products were isolated. The first of these, m.p. 81–82°, had approximately the composition and molecular weight of $C_{32}H_{26}$; the second, m.p. 179–179.5° also gave an unsatisfactory analysis which corresponded to $C_{32}H_{26}$. In the light of the results obtained by Herz and Lewis, this second material was probably 2,3,5-triphenylstilbene.

On the basis of the above evidence it is concluded that dimer I is 4-*trans*-β-styryl-1,3,4-triphenylcyclohexene, I. Dimer II may be a stereoisomer. The rearrangement that occurs during the dehydrogenation is interesting and has been discussed in greater detail by Herz and Lewis[1] and in the thesis of Marvin H. Goodrow.[1]

EXPERIMENTAL[18]

The reaction of benzalacetophenone with methylmagnesium iodide. To 3.9 g. (0.16 g.-atom) of magnesium turnings in a 200-ml. flask was added dropwise under nitrogen with stirring 6.9 ml. (0.17 mole) of methyl iodide in 75 ml. of anhydrous ether so that the mixture refluxed gently. After the addition, the mixture was refluxed for 30 min., cooled, and 15.3 g. (0.074 mole) of benzalacetophenone in 100 ml. of anhydrous ether was added dropwise with vigorous stirring. The reaction mixture was kept at −12° to −7° throughout the addition, then allowed to warm to room temperature and decanted into 100 ml. of a solution containing 10% sulfuric acid and 50 g. of ice. The ethereal solution was separated, washed with 5% sodium hydroxide, 5% sodium bisulfite, and water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give a light yellow gum. This gum was dissolved in 300 ml. of ether and the solution cooled to −80° to yield 9.0 g. (60%) of light yellow 1,3-diphenyl-1-butanone. Long white crystals, m.p. 72–73° were obtained after several recrystallizations from ethanol (reported[5] m.p. 72°). These were sublimed at 60–70° and 1 to 2 mm. before analysis.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.48; H, 7.14.

Infrared spectrum (10% solutions in carbon tetrachloride and carbon disulfide): strong bands at 3065, 3030, 2960, 1691, 1600, 1587, 1500, 1457, 1272, 1217, 1203, 1180, 1101, 990, 749, 695, and 686 cm.$^{-1}$ Ultraviolet spectrum (in ethanol): λ_{max} 276–278 (log ϵ 3.00), 243 mμ (log ϵ 4.123).

The ethereal filtrate was concentrated to half volume and allowed to stand for several days. A powder separated and was recrystallized from ethanol to give 4.4 g. (27%) of 4-benzoyl-1,3,5-triphenyl-1,3-hexadiene, m.p. 177–178° (reported[5] 176°). As reported earlier,[5] difficulties were encountered in the analysis.

Anal. Calcd. for $C_{31}H_{26}O$: C, 89.83; H, 6.28. Found: C, 89.23, 89.16, 89.10; H, 7.52, 7.27, 7.21.

Infrared spectrum (10% solutions in carbon tetrachloride and carbon disulfide): strong bands at 1650, 1600, 1498, 1455, 1358, 1273, 1157, 1102, 1076, 1067, 1050, 1030, 1016, 760, 741, and 695 cm.$^{-1}$ Ultraviolet spectrum (in ethanol): λ_{max} 265 (log ϵ 4.068), λ_{min} 240 mμ (log ϵ 3.709).

trans-1,3-Diphenylbuten-1-ol-3. The procedure of Cope[6] was employed and the alcohol obtained in 84–89% yield, m.p. 57.0–57.8° (reported 57.2–58.0°). The ultraviolet spectrum in 95% ethanol showed λ_{max} 292 (log ϵ 3.098), 284 (log ϵ 3.295), and 252 mμ (log ϵ 4.328). Infrared spectrum (6% solution in carbon tetrachloride and 7% solution in carbon disulfide): strong bands at 3550, 3420, 3020, 3005, 2950, 1597, 1494, 1450, 1370, 1325 (broad), 1160, 1095, 1065, 1028, 968, 762, 746, and 689 cm.$^{-1}$ The band at 968 cm.$^{-1}$ gives evidence that the double bond is *trans.*[12]

The residue that remained in the flask after distilling the alcohol was chromatographed on neutral alumina and eluted with 20% ether–80% pentane to give a yellow oil. The ultraviolet spectrum of this oil in 95% ethanol showed a strong maximum at 251.5 mμ and a weak maximum at 292 mμ; minima were observed at 291 and 232 mμ.

Dehydration of trans-1,3-diphenylbuten-1-ol-3. A. With acetic anhydride. Twenty grams (0.09 mole) of the alcohol was refluxed for 8 hr. with 10 g. of acetic acid and 20 g. of acetic anhydride. Thereafter, the solution was concentrated and the yellow residue (a gum) was chromatographed on neutral activated alumina. A white solid was obtained (96% yield) by eluting with 10% ether-pentane. Crystallization from 95% ethanol at room temperature provided 7.8 g. (42%) of a crystalline product which when further purified had a melting point of 137.0–138.0°.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84; mol. wt. 412. Found: C, 92.95; H, 6.92; mol. wt. 424 (cryoscopic in benzene).

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[17] F. R. Japp and N. H. J. Miller, *J. Chem. Soc.*, **47**, 11 (1885).

[18] Melting points were taken with total immersion Anschutz thermometers but otherwise not corrected. Analyses were carried out by Miss Heather King. Infrared spectra were determined on a Perkin-Elmer Model 21 instrument with sodium chloride prism and ultraviolet spectra on a Cary Recording Spectrophotometer, Model 11.

Infrared spectrum (10% solutions in carbon tetrachloride and carbon disulfide). In addition to the bands described in the discussion above, the following strong bands were observed: 3050, 3020, 2915, 1495, 1448–1455, 1075, and 1030 cm.$^{-1}$

The filtrate from the crystallization of the above dimer (Dimer I), when placed in the refrigerator overnight, deposited 5.9 g. (32%) of a white amorphous solid, m.p. 124–126°. One gram of this material was chromatographed on neutral activated alumina and eluted with 10% ether-pentane to give an 0.4 g. fraction of dimer melting at 124.5–127.5°. Several recrystallizations of this fraction from 95% ethanol provided a pure sample of the second dimer (Dimer II), m.p. 125.0–126.0°.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84; mol. wt. 412. Found: C, 93.17; H, 6.87; mol. wt. 396 (Rast).

Additional dimer I was isolated from this chromatogram which brought the total yield of this compound to 50%. The mixed melting point of dimers I and II was 124–135°.

B. With iodine. trans-1,3,-Diphenylbuten-1-ol-3, 3.22 g. (0.002 mole), 35 mg. of iodine and 300 ml. of toluene were refluxed for 7 hr. The toluene solution was washed with saturated sodium bisulfite solution and water, and dried. After concentration of the solution, there remained a yellow residue which was chromatographed on neutral alumina and yielded 2.95 g. (98%) of a white solid. Crystallization from 95% ethanol at room temperature gave 1.23 g. (42%) of dimer I, m.p. 137–138°, and upon cooling, 0.90 g. (31%) of crude dimer II.

C. With phosphorus trichloride. To a solution of 5.0 g. (0.0223 mole) of the *trans* alcohol in 20 ml. of dry pyridine was added slowly 3.15 g. (0.0229 mole) of phosphorus trichloride while maintaining the temperature at 0–5°. The mixture was stirred for 30 min. and then 100 g. of ice was added. The organic material was extracted with 100 ml. of ether and the ethereal layer was washed thoroughly with water and dried. Removal of the ether provided a yellow oil which was chromatographed on neutral alumina to yield dimer I as the only apparent product.

Hydrogenation of dimer I. Catalytic reduction of 0.700 g. (0.002 mole) of dimer I with Baker's 10% palladium-on-carbon in 20 ml. of ethyl acetate resulted in the absorption of 1.97 moles of hydrogen per mole of dimer. The solution was filtered through Celite and the solvent removed. Crystallization of the oily residue from 95% ethyl alcohol gave 0.62 g. (88%) of transparent needles, m.p. 119–120°.

Anal. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74. Found: C, 92.04; H, 7.89.

Infrared spectrum (15% solutions in carbon tetrachloride and cyclohexane): strong bands at 3057, 3026, 2930, 2865, 1600, 1495, 1475, 1450, 1068, 1030, 745, and 693 cm.$^{-1}$ Ultraviolet spectrum (ethanol) similar to that of *tert.* butylbenzene: λ_{max} 268.5 (log ϵ 2.757), 264.5 (log ϵ 2.838), 259 (log ϵ 2.947), 253.5 (log ϵ 2.863) and 248.5 mμ (log ϵ 2.718); $\lambda_{infl.}$ 261 (log ϵ 2.907) and 243 mμ (log ϵ 2.521).

Catalytic dehydrogenation of dimer I. A mixture of 2.00 g. of dimer I and 400 mg. of 10% palladium-on-carbon was heated at 300° for 2 hr. The residue was taken up in ether and the catalyst removed by filtration. The filtrate was concentrated by heating under reduced pressure and the yellow residue chromatographed on neutral alumina. The first fraction was eluted with pentane and consisted of 347 mg. of crude ethyl benzene which was identified by its infrared and ultraviolet spectra. The material (730 mg.) eluted with 4% ether-pentane crystallized upon evaporation of the solvent, m.p. 173–175°. This material proved to be 1,3,5-triphenylbenzene by a comparison of melting points and spectra with authentic material prepared according to Bernhauer.[19]

With further evaporation of the solvent from the above filtrate there was deposited an amorphous solid (about 20 mg.), m.p. 96–99.5°. This material proved to be 1,2,4-triphenylbenzene with trace amounts of the symmetrical isomer from which it was inseparable. The ultraviolet spectrum (in ethanol) of this material is identical with that of authentic 1,2,4-triphenylbenzene,[17] m.p. 101.5–102°. It has a maximum at 249 mμ, a minimum at 228 mμ, and high absorption in the range 280–325 mμ; by contrast 1,3,5-triphenylbenzene displays a maximum at 252 mμ, a minimum at 225 mμ, and absorption that falls considerably more rapidly in the range 260–325 mμ. The infrared spectra of authentic 1,3,5- and 1,2,4-triphenylbenzene and of the material m.p. 96–99.5° were determined in potassium bromide disks. The latter had all of the bands of the 1,2,4-isomer and weak bands *corresponding to the strongest* unique peaks of the 1,3,5-isomer. Particularly significant were bands at 1473, 1442, 1385, 1006, 895, and 835 cm.$^{-1}$ which are shown by the 1,2,4-isomer but not by the 1,3,5-isomer. Peaks at 1493, 1410, 910, and 876 cm.$^{-1}$ show that the impurity is the 1,3,5-compound.

Dehydrogenation of dimer I *with sulfur.* One gram of dimer I and 155 mg. of sulfur were mixed and immersed in a Wood's metal bath at 125°. The temperature was raised until the evolution of hydrogen sulfide commenced (260°) and then increased slowly and maintained at 270° for 30 min. The amount of hydrogen sulfide evolved was 0.8 mole per mole of dimer. The residue was chromatographed several times on neutral alumina with no success in resolving the components. Concentration and crystallization from ether-pentane of the combined fractions from the unsuccessful chromatogram eventually gave 145 mg. of 1,3,5-triphenylbenzene, m.p. 175.5–176.6°. Crystallization of the residue obtained from this filtrate from methanol then gave 66 mg. of an amorphous sulfur-containing compound, m.p. 107–109°. An analytical sample was prepared by recrystallization from methanol with considerable loss to give colorless crystals, m.p. 110.5–111.5°.

Anal. Calcd. for $C_{18}H_{14}S$: C, 82.40; H, 5.38. Found: C, 82.77; H, 5.39.

Dehydrogenation of dimer I *with chloranil.* A solution of 2.00 g. (0.0048 mole) of dimer I and 3.00 g. (0.012 mole) of chloranil in 35 ml. of benzene was heated under reflux for 24 hr. The solution was then cooled, diluted with an equal volume of pentane, and concentrated after filtering the insoluble material. The resulting brown residue was chromatographed on alumina using 5% ether-petroleum ether (b.p. 30–60°) to elute the column. Upon evaporation of the solvent there remained 670 mg. (34%) of crude 2,3,5-triphenylstilbene, m.p. 176–179°. An analytical sample was obtained by three recrystallizations from ether to yield small white needles, m.p. 180.5–181.5°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.96; H, 5.93.

Terminal methyl determination on dimer I, when carried out by conventional methods[20,21] gave values ranging from 0.97 to 1.44 methyl groups. This would be expected from styryl derivatives.[22] Dr. C. W. Koch[23] found a value of 0.2 by a variation of the Kuhn-Roth procedure which involves a 20-hr. digestion period with chromic anhydride–sulfuric acid solution. Essentially all of the benzoic acid is destroyed by this procedure.

Oxidation of dimer I *with potassium permanganate.* To a solution of 2.0 g. (0.002 mole) of dimer I in 50 ml. of pyridine, was added 4.08 g. (0.03 mole) of potassium permanganate in 50 ml. of water over a period of 3 hr. The mixture had to be heated to 45° where it reacted at a mod-

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(19) K. Bernhauer, P. Müller, and F. Neiser, *J. prakt. Chem.* (2), **145**, 301 (1936).

(20) R. Kuhn and F. L'Orsa, *Z. angew. Chem.*, **44**, 847 (1931).

(21) W. F. Barthel and F. B. La Forge, *Ind. Eng. Chem., Anal. Ed.*, **16**, 434 (1944).

(22) E. J. Eisenbraun, S. M. McElvain, and B. F. Aycock, *J. Am. Chem. Soc.*, **76**, 607 (1954).

(23) We wish to thank Dr. Koch, University of California, Berkeley, for this determination.

erate speed. Solid sodium bisulfite was added to decompose the manganese dioxide and the solution was steam distilled to remove the pyridine. The residue was extracted with ether and the ether layer was extracted with dilute base. The basic extract was worked up in the usual manner to yield 560 mg. of crystalline benzoic acid, m.p. 123.2–124.2°. The mixed melting point with authentic benzoic acid was undepressed.

The neutral material from the oxidation was chromatographed on neutral alumina to separate 863 mg. of a yellow crystalline material. This was crystallized from methanol-ether mixtures for analysis, m.p. 206.0–207.2°.

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 81.05; H, 5.48.

The infrared spectrum suggested that this compound contained a hydroxyl function (3525 cm.$^{-1}$) and an *alpha-beta*-unsaturated ketone (1692 cm.$^{-1}$). Its identity could not be determined.

Oxidation experiments using more vigorous conditions always resulted in degradation of the dimer to benzoic acid and inseparable, unidentifiable oils.

Oxidation of dimer I *with acidic potassium permanganate.* To 1.00 g. (0.002 mole) of dimer I in 50 ml. of nitrobenzene was added over a period of 2 hr. a solution containing 11.3 g. of potassium permanganate, 13 ml. of concentrated sulfuric acid, and 90 ml. of water. After stirring this mixture for 4 hr. at room temperature, sodium bisulfite was added to remove the manganese dioxide; the solution was then made basic with 6*N* sodium hydroxide and steam distilled to remove the nitrobenzene. The residue was worked up in the usual way to give 25 mg. of crude benzoic acid, m.p. 115–118°. The neutral material was chromatographed on neutral alumina to give 50 mg. of a white solid. Crystallization from 95% ethanol provided 10 mg. of a white crystalline product, m.p. 187°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 86.98; H, 5.99.

The infrared spectrum indicated that this compound had the structure of an *alpha-beta*-unsaturated, five-membered ring ketone. The small amount of this material precluded further examination.

Ozonization of dimer I, *oxidative decomposition.* A solution of 4.12 g. (0.01 mole) of dimer I in 70 ml. of chloroform was ozonized with excess ozone. The chloroform solution was then shaken for 48 hr. with 30 ml. of water and 7.5 ml. of 30% hydrogen peroxide. Thereafter, the organic material was separated and extracted with 1% sodium hydroxide. Acidification of this basic solution and continuous extraction with ether for 16 hr. provided 248 mg. of a yellow solid. This solid was chromatographed on silicic acid to remove the yellow impurity, and sublimed to yield 61 mg. of benzoic acid, m.p. 121–122°, neutralization equivalent 126. The mixed melting point with authentic material was not depressed.

The neutral organic fraction from above was concentrated and chromatographed on neutral alumina.

Fraction 1 (360 mg.), eluted with ether, was a yellow oil from which 30 mg. of a white solid, m.p. 74.5–75.5°, was obtained when it was dissolved in 95% ethanol.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.73; H, 6.43.

The infrared spectrum suggested that this compound contained a carbonyl group; however, the small amounts precluded a careful examination of its structure.

Fraction 2 (300 mg.), eluted with 1% methanol-ether, deposited a white crystalline solid upon evaporation of the solvent. Crystallization from ether yielded 72 mg. of 1,2-dibenzoylethane, m.p. 147.0–147.4°. Literature[24] m.p. 145–147°. A mixed melting point with authentic material was undepressed.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; mol. wt. 238. Found: C, 80.70; H, 6.24; mol. wt. 231 (Rast).

The ultraviolet spectrum, λ_{max} 279 mμ (log ϵ 3.330) and 244 mμ (log ϵ 4.423) was identical with that in the literature.[25]

Fraction 3 (883 mg.), eluted with 2% methanol-ether and fraction 4 (813 mg.), eluted with methanol, were yellow oils which resisted crystallization and purification. Both gave positive carbonyl tests with 2,4-dinitrophenylhydrazine.

Ozonization of dimer I; *reductive decomposition.* A solution of 4.12 g. of dimer I in 50 ml. of ethyl chloride was ozonized with an excess of ozone. The solvent was removed and 15 ml. of chloroform and 5 ml. of glacial acetic acid were added. The ozonide was decomposed with zinc dust. The solution was then filtered, washed with 2% sodium bicarbonate solution, and dried. There remained 4.44 g. of a yellow viscous oil which was chromatographed on neutral alumina.

Fraction 1 (300 mg.), eluted with ether, was a yellow oil. This was rechromatographed on neutral alumina to yield two major fractions; neither could be induced to crystallize. Each fraction was converted to its 2,4-dinitrophenylhydrazine derivative. The first compound was crystallized from ethanol with considerable loss of material to give 5 mg. of derivative, m.p. 184–186°.

Anal. Calcd. for $C_{28}H_{23}O_4N_4$: C, 70.13; H, 4.83. Found: C, 70.42; H, 4.83.

This analysis corresponded to a carbonyl compound with the formula $C_{22}H_{20}O$. Its structure was not determined.

It was necessary to chromatograph the second 2,4-dinitrophenylhydrazone on neutral alumina to obtain a product with an acceptable melting point. From the chromatograph was obtained 13 mg. of product which was crystallized from 95% ethanol for analysis, m.p. 99–101°.

Anal. Calcd. for $C_{29}H_{26}O_4N_4$: C, 70.43; H, 5.30. Found: C, 70.66; H, 5.27.

The above analysis corresponded to a carbonyl compound with the formula $C_{23}H_{22}O$; however, its structure was not elucidated.

Fraction 2 (125 mg.), eluted with 2% methanol-ether, proved to be 1,2-dibenzoylethane as determined by its melting point and mixed melting point with authentic material.

Fraction 3 (1.175 g.), eluted with 4% methanol-ether, was the same polymeric material as obtained in the oxidative decomposition and remained an inseparable mixture.

2,4-Diphenyl-3-butenoic acid.[7] 1,3-Diphenyl-2-propanol was prepared by reducing 1,3-diphenyl-2-propanone with magnesium and methanol[26] or with lithium aluminum hydride. This alcohol has been dehydrated to 1,3-diphenylpropene by several methods.[27–31] In our work it was dehydrated by heating with and then distilling from potassium acid sulfate, but the product was not easily purified and crude yields were only 44–79%; the product after redistillation had a b.p. of 184–185°/20 mm., n_D^{25} 1.5932.

The olefin was converted to its sodium derivative by reaction with amylsodium in *n*-pentane by a procedure used for phenylallylsodium,[32] and carbonation was accomplished by siphoning the slurry of organometallic compound onto excess

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Dry Ice. The reaction mixture was worked up by conventional methods, but the yield of 2,4-diphenyl-3-butenoic acid, m.p. 123.5–124.5°, was only 9%. Recrystallization from ligroin (b.p. 90–95°) gave pure acid, m.p. 125–126°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92, neutral equivalent, 238.3. Found: C, 80.71; H, 6.06; neutral equivalent, 243. Ultraviolet spectrum (95% ethanol): λ_{max} 252 (log ϵ 4.352), 283.5 (log ϵ 3.318), 292.5 mμ (log ϵ 3.121).

This acid is relatively stable to a temperature of 150° for a short time, but after heating at 100–115° for 2 hr. in a capillary tube, the m.p. was 118–119°.

Methyl 2,4,-diphenyl-3-butenoate was prepared from the acid with diazomethane; after recrystallization from ethanol at low temperatures, the ester melted at 35–36°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.71; H, 6.37.

2,4-Diphenyl-3-buten-1-ol.[7] Methyl 2,4-diphenyl-3-butenoate was reduced with excess lithium aluminum hydride in ether, the reaction mixture worked up as usual and the product distilled, b.p. 175–185°/1.4 mm. The yield was 70%, but the distillate was a mixture containing about 82% of 2,4-diphenyl-3-buten-1-ol on the basis of combustion analysis. The infrared spectrum was that expected of such a mixture.

Attempts were made to remove the ester by saponification with aqueous methanolic potassium hydroxide or sodium ethylate, but neutral material recovered from the reaction still gave a low carbon analysis even though the ester group appeared to have disappeared on the basis of the infrared spectrum. The product was a viscous red oil which deposited a solid. The solid was purified by chromatography on neutral, activated alumina and recrystallization from alcohol, m.p. 137–138°. It was shown to be dimer I by analysis, ultraviolet absorption and a mixed melting point determination. The yield was about 10% based on 2,4-diphenyl-3-buten-1-ol in the reaction mixture used.

The residual red oil would not distill below 200° at 1 to 2 mm., and did not give a correct analysis for 2,4-diphenyl-3-buten-1-ol.

Crude 2,4-diphenyl-3-buten-1-ol from the lithium aluminum hydride reduction was treated with 3,5-dinitrobenzoyl chloride in pyridine and gave a 3,5-dinitrobenzoate in 27% yield, m.p. 125–126° after recrystallization from aqueous acetone.

Anal. Calcd. for $C_{23}H_{18}O_6N_2$: C, 66.02; H, 4.34. Found: C, 66.28; H, 4.23.

The small amount of the 3,5-dinitrobenzoate that was available was pyrolyzed under nitrogen, but neither 1,3-diphenyl-1,3-butadiene nor its dimer was obtained.

Crude 2,4-diphenyl-3-buten-1-ol was refluxed with 2.5*N* aqueous alcoholic sulfuric acid but no dimer was obtained.

Although the experiments described here are only preliminary, this method to 1,3-diphenyl-1,3-butadiene does not appear promising and further work in this direction is not planned.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

2-Phenyl-1,3-butadiene and Related Compounds[1]

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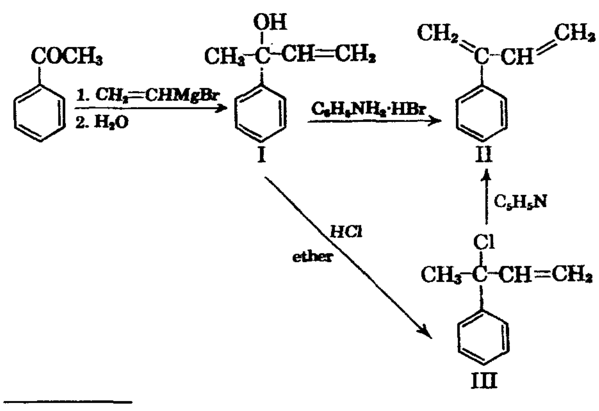
2-Phenyl-1,3-butadiene (II) has been prepared from acetophenone and vinylmagnesium bromide in a two-step synthesis. The synthesis and properties of several new and related compounds are given.

Recently, Normant discovered[2] that vinylmagnesium bromide could be prepared and used in reactions quite easily in tetrahydrofuran solvent. This work suggested a convenient route for the synthesis of 2-aryl-substituted dienes which are sometimes difficult to obtain in good yield by other methods. Thus, treatment of acetophenone with vinylmagnesium bromide gave methylphenylvinylcarbinol (I) in 75% yield. This carbinol (I) has been prepared previously by reaction[3] of acetophenone and the di-Grignard reagent of diacetylene, followed by hydrolysis and catalytic hydrogenation,[4] and by the action[5] of phenylmagnesium bromide on methyl vinyl ketone. However, the present method produced considerably better yields than previously reported. Dehydration of the carbinol (I) by slow distillation from aniline hydrobromide gave 2-phenyl-1,3-butadiene (II) in 61% yield. This represents an over-all yield of 46% from acetophenone for a two-step synthesis, and is possibly the best route presently available for preparing 2-phenyl-1,3-butadiene. All previous methods[6] involved numerous steps or poor yields or both. Treatment of methylphenylvinylcarbinol with an-



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