Preparation of Tetraphenylbutatriene and Reactions of the Corresponding Dianion

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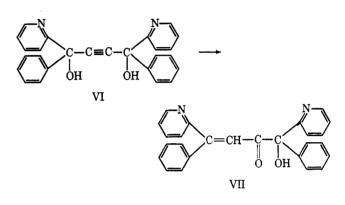
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Improved methods for the preparation of 1,1,4,4-tetraphenylbutatriene and its dianion are presented. Lowtemperature protonation of the dianion gives 1,1,4,4-tetraphenyl-1,2-butadiene (VIII) almost exclusively. Compound VIII is shown to dimerize at moderately low temperatures to 1-diphenylmethylene-2-diphenylmethylmethylene-3,3-diphenyl-4-diphenylmethylcyclobutane (X). At higher temperatures dimer X rearranges to the more stable dimer, 1,2-bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane (XI). Reactions of the two dimers with potassium are reported. 1,1,4,4-Tetraphenyl-2-butyne-1,4-diol and 1,4-diphenyl-1,4-di(2'-pyridyl)-2-butyne-1,4-diol are rearranged by acids to 1,1,4,4-tetraphenyl-1-buten-3-on-4-ol (V) and 1,4-diphenyl-1,4-di(2'pyridyl)-1-buten-3-on-4-ol (VII), respectively.

Zweig and Hoffman¹ and Nahon and Day² studied some of the reactions of tetraphenylbutatriene (III). In view of their conflicting observations, it was decided to pursue the work further in order to arrive at unequivocal conclusions and to extend the work by studying additional reactions. Lithium acetylide-ethylenediamine complex³ was used for the synthesis of 1,1,4,4tetraphenyl-2-butyne-1,4-diol (I) from benzophenone in place of sodium acetylide or acetylenedimagnesium bromide which were used by previous workers.^{1,2} This modified procedure is no more efficient but is more convenient in that fewer steps are involved. Compound I was converted to the tetraphenvlbutatriene dianion (IV) by two methods (Scheme I). Tetraphenylbutatriene has usually been used in the $past^{1,2}$ as the precursor to the dianion but the present study has shown that the diether is a more convenient and efficient source of this ion. The above series of reactions $(I \rightarrow II \rightarrow IV)$ gives better yields of IV and requires less time. This procedure eliminates the necessity for purifying the cumulene required for procedure III \rightarrow IV. The cumulene is more difficult to purify than is the diether (II).

The procedure of Arbuzov⁴ was used for preparing the diether. A small amount of 1,1,4,4-tetraphenyl-1buten-3-on-4-ol (V) was isolated from the filtrate from the diether. Compound V can be isolated in good yields by refluxing a solution of I in tetrahydrofuran with a few drops of concentrated sulfuric acid. The conversion of I to V appears to involve an allylictype rearrangement followed by a tautomeric shift to a keto structure. The structure of V was confirmed by analytical data and by infrared and nmr spectra.

The acid-catalyzed isomerization of acetylenic diols of type I to keto alcohols appears to be general. 1,4-Diphenyl-1,4-di(2'-pyridyl)-2-butyne-1,4-diol (VI) was converted to the corresponding keto alcohol by heating with ethanol alone.



The dianion reacts with alkyl sulfates and carbon dioxide, respectively, to give 1,4-addition products.^{1,2} In the present study it was found that electron acceptors, such as bromine, iodine, and oxygen, react with the dianion to form tetraphenylbutatriene (III). These electron-transfer reactions make it possible to synthesize the triene in excellent yields by a nonacidic pathway $(I \rightarrow II \rightarrow IV \rightarrow III)$. It is our experience that a purer product is obtained by this method. When the cumulene is prepared under acidic conditions, small amounts of polymeric material are also formed.

It had been originally reported¹ that protonation of the dianion, using methanol as the protonating agent, occurred at the 1,4 positions. Under similar conditions Nahon and Day² reported a 25% yield of 1,1,4,4tetraphenyl-1,2-butadiene (VIII). More recently we have found that when the dianion is protonated with methanol or acetic acid at -55° , VIII can be obtained in yields as high as 80% along with small amounts (5-8%) of the conjugated diene, 1,1,4,4-tetraphenyl-1,3-butadiene (IX). Compound VIII is quantitatively isomerized to IX by bases.² The allene is kinetically favored at low temperatures. It may be assumed that the heat of activation for 1,2 addition is less than the heat of activation for 1,4 addition and hence 1,2 addition is greatly favored at lower temperatures. Compound VIII melted at 99°. Kuhn and Fischer⁵ pre-

$$(C_{6}H_{5})_{2}\overline{C} - C \equiv C - \overline{C}(C_{6}H_{5})_{2} \iff$$

$$(C_{6}H_{5})_{2}C \equiv C - \overline{C} - \overline{C}(C_{6}H_{5})_{2} \xrightarrow{2H^{+}}$$

$$(C_{6}H_{5})_{2}C \equiv C \equiv CH - CH(C_{6}H_{5})_{2} \xrightarrow{B^{-}}$$

$$VIII$$

$$(C_{6}H_{5})_{2}C \equiv CH - CH = C(C_{6}H_{5})_{2}$$

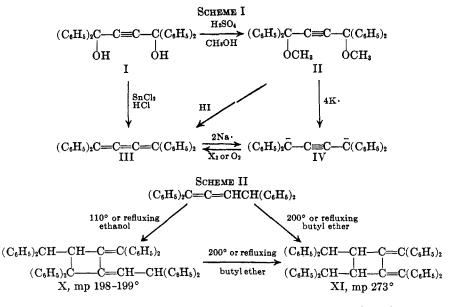
$$IX$$

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⁽¹⁾ A. Zweig and A. Hoffman, J. Am. Chem. Soc., 84, 3278 (1962).

⁽²⁾ R. Nahon and A. R. Day, J. Org. Chem., 30, 1973 (1965).
(3) O. F. Beumel and R. F. Harris, *ibid.*, 38, 2775 (1963); 39, 1870 (1964).

⁽⁴⁾ G. Arbuzov, J. Russ. Phys. Chem. Soc., 53, 293 (1921).



pared the allene from the triene by reduction with aluminum amalgam. They reported a melting point of 107°. Our preparation was repeated several times and the resulting allene always melted at 99°. Our product absorbed in the ultraviolet at λ_{max} 260 m μ (ϵ 19,000) and the infrared spectrum showed characteristic allene peaks at 1945 and 1080 cm⁻¹. The nmr spectrum showed the following peaks: singlet at τ 2.9 (area ~20) for the phenyl protons, doublet at 4.0–4.1 (total area ~1, J = 15 cps) for the olefinic protons, 5.1-5.2 (doublet, ~1) for the benzhydryl protons.

The dimerization of the allene (VIII) has been reinvestigated. Nahon and Day reported the formation of only one dimer (mp 273°) when VIII was heated. We can now report that this is the thermodynamically favored dimer and that a kinetically favored dimer has also been isolated (Scheme II). The structure assigned to XI was based on ultraviolet and nmr.² These data have now been confirmed and additional evidence from ozonolysis experiments has been obtained.

The new dimer (X) absorbed in the ultraviolet at $\lambda_{\max} 305 \text{ m}\mu$ ($\epsilon 15,000$). The nmr spectrum showed the following peaks: multiplet at $\tau 2.8$ (phenyl proton area ~ 40), doublet at 4.4-4.6 (olefinic proton area $\sim 1, J = 14$ cps), doublet at 4.85-5.05 (cyclobutane proton area $\sim 1, J = 14$ cps), doublet at 5.6-5.8 (benzhydryl proton area $\sim 1, J = 14$ cps), doublet at 6.1-6.3 (benzhydryl proton area $\sim 1, J = 14$ cps).

On heating the new dimer above its melting point, it melted (198°), resolidified, and then melted at 273°. The physical data agreed in all respects with the data previously reported for dimer XI.² Obviously, reaction path A is kinetically favored over reaction path B and at lower temperatures is the only path observed. On heating X above its melting point, ring opening occurs followed by an allylic rearrangement and finally by ring closure to the more stable dimer.

Ozonolysis of dimer X yielded both benzophenone and diphenylacetaldehyde while ozonolysis of dimer XI yielded only benzophenone. This evidence serves to confirm the structures of the two dimers.

The dimerization and isomerization reactions can be accounted for on the basis of diradical mechanisms. As in the case of the 1,2 protonation, the kinetically favored formation of dimer X has a lower activation energy and $\begin{array}{c} (C_{6}H_{5})_{2}CH-\dot{C}H-\dot{C}=C(C_{6}H_{5})_{2} \xrightarrow{200^{\circ}} XI \\ (C_{6}H_{5})_{2}CH-\dot{C}H-\dot{C}=C(C_{6}H_{5})_{2} \xrightarrow{XI} \\ A \\ (C_{6}H_{5})_{2}CH-\dot{C}H-\dot{C}=C(C_{6}H_{5})_{2} \xrightarrow{110^{\circ}} X \\ (C_{6}H_{5})_{2}\dot{C}-\dot{C}=CH-CH(C_{6}H_{5})_{2} \xrightarrow{B} \end{array}$

its formation proceeds best at lower temperatures. The conversion of X to XI can also be accounted for by a diradical mechanism (Scheme III). The dimers XI and X corresponding to the diradicals A and B, respectively, were isolated and identified. The dimer corresponding to diradical C has not been isolated.

The reaction of potassium with the two dimers has also been studied. Protonation of the dianion solution produced from XI, by reaction with two atoms of potassium, gave a product which is believed to be 1,2,3,4tetrakis(diphenylmethyl)-1-cyclobutene (XII).

Presumably the 1,4 dianion should be more stable than the other extreme resonance structure, the 1,2 dianion, and this accounts for the formation of XII. No important information could be obtained from the infrared spectrum of XII and its ultraviolet spectrum showed only benzene ring absorptions. The nmr spectrum showed the following peaks: τ 3.00–3.30 (multiplet, area ~20), 5.82 (singlet, area ~1), 6.2–6.3 (doublet, area ~1, J = 6 cps), 6.6–6.7 (doublet, area ~1, J = 6 cps). These absorptions indicate that no olefinic protons are present and that two protons have been added to the dimer to form a symmetrical product. The absorptions at τ 6.2–6.3 represent the benzhydryl protons which split the cyclobutene ring

SCHEME III

protons which absorb at τ 6.6–6.7. The latter have shifted upfield owing to the shielding effect of the electrons of the cyclobutene double bond. The suggested structure (XII) best fits the spectral data, molecular weight, and analytical data.

When dimer X was treated with potassium under similar conditions, and the resulting dianion was protonated, ring cleavage occurred and an open-chain diene appeared to be the final product (XIII). We

$$\begin{array}{c} (C_{e}H_{5})_{2}CH-CH-CH=C=C(C_{e}H_{5})_{2} & \xrightarrow{K} \\ (C_{e}H_{5})_{2}C-C=CHCH(C_{e}H_{5})_{2} & \xrightarrow{K} \\ (C_{e}H_{5})_{2}CH-CH-CH-CH-C-C(C_{e}H_{5})_{2} & \xrightarrow{HOAc} \\ (C_{e}H_{5})_{2}CH-CH=C-CHCH(C_{e}H_{5})_{2} \\ (C_{e}H_{5})_{2}CH-CH=C-CH(C_{e}H_{5})_{2} \\ (C_{e}H_{5})_{2}CH-CH=C-CH(C_{e}H_{5})_{2} \\ (C_{e}H_{5})_{2}CH-CH=C-CHCH(C_{e}H_{5})_{2} \\ (C_{e}H_{5})_{2}CH-CH-C-C-CH(C_{e}H_{5})_{2} \\ XIII \\ (C_{e}H_{5})_{2}C-C-C-CH(C_{e}H_{5})_{2} \\ XIV \end{array}$$

believe that opening of the same bond in X accounts for this ring cleavage as well as for the thermal isomerization of X to XI. Two possibilities appear to exist. The nmr spectrum showed three proton absorptions beside the phenyl protons. This appears to eliminate XIV as a possibility. The nmr spectrum showed the following absorptions: τ 3.0-3.3 (multiplet, area \sim 20), 3.82-4.00 (doublet, ~ 1 , J = 10 cps), 4.6 (singlet, ~1), 5.50-5.68 (doublet, ~1, J = 10 cps). The doublet at τ 3.82-4.00 indicates the presence of an olefinic proton and this is splitting the benzhydryl protons at 5.50–5.68. The singlet at τ 4.6 is due to a benzhydryl proton. The nmr and analytical data definitely support structure XIII. The lack of any significant ultraviolet or infrared absorptions we attribute to the intensity of the ultraviolet absorptions due to the phenyl groups and to the highly hindered nature of the molecule. Diphenylacetaldehyde was obtained by the ozonolysis of XIII (1721 cm⁻¹, mp 2,4-dinitrophenylhydrazone 159°).

Experimental Section

All melting points were taken in a Thomas-Hoover capillary melting point apparatus. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Infrared spectra were measured by a Perkin-Elmer 521 spectrophotometer and nmr spectra were measured in $CDCl_3$ solution using 60-Mc Varian HR-60 or HA-60 spectrometers with tetramethylsilane as an internal reference. For the ozonolysis reaction, the ozone was generated by a Welsbach T-23 Ozonator. 1,1,4,4-Tetraphenyl-2-butyne-1,4-diol (I).—Lithium acetylideethylenediamine complex⁶ (100 g, ca. 1 mole) was refluxed, under nitrogen, with 1000 ml of tetrahydrofuran and 182 g (1 mole) of benzophenone for 2 hr. After cooling, the mixture containing the precipitated lithium glycolate was poured with stirring into 2000 ml of water containing 150 ml of concentrated hydrochloric acid. The diol was then extracted with ether. The ether layer was washed with 10% sodium bicarbonate and dried (MgSO₄). The glycol, obtained by evaporating the ether, was washed with cyclohexane and recrystallized from toluene (yield 76%), mp 192-193° (lit.⁷ mp 193°).

1,4-Diphenyl-1,4-di(2'-pyridyl)-2-butyne-1,4-diol (VI).--Sodium (2.3 g, 0.1 g-atom) and 16 g (0.11 mole) of biphenyl were stirred in 150 ml of dry 1,2-dimethoxyethane under nitrogen for 16 hr. Purified acetylene⁸ was then passed in until decolorization occurred. 2-Benzoylpyridine (18.3 g, 0.1 mole) was added to the slurry with stirring, and the resulting red solution was refluxed for 2 hr. The cooled solution was poured into a solution of 50 ml of concentrated hydrochloric acid in 500 ml of water and the solution was immediately neutralized with sodium hydroxide. The precipitated, colorless diol was removed, washed with water, dried, and recrystallized from tetrahydrofuran-water (yield 87%), mp 179°.

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.55; H, 5.14; N, 7.14. Found: C, 79.35; H, 5.30; N, 7.20.

1,1,4,4-Tetraphenyl-1-buten-3-on-4-ol (V).—Five grams of 1,1,4,4-tetraphenyl-2-butyne-1,4-diol was added to a solution of 5 ml of concentrated sulfuric acid in 50 ml of tetrahydrofuran. Th mixture was refluxed for 30 min and poured into water. The resulting yellow oil was taken up in ether. The ether extract was washed with water, 10% sodium bicarbonate, and water and dried (MgSO₄). Evaporation of the ether left a gummy residue which was solidified by stirring with petroleum ether ($30-60^{\circ}$). The product was recrystallized from hexane (yield 82%), mp 121°. The infrared spectrum (KBr) showed characteristic hydroxy and carbonyl peaks at 3445 and 1680 cm⁻¹.

Anal. Calcd for C₂₈H₂₂O₂: C, 86.15; H, 5.64. Found: C, 86.09; H, 5.72.

1,1-Diphenyl-1,4-di(2'-pyridyl)-1-buten-3-on-4-ol (VII).— Five grams of 1,4-diphenyl-1,4-di(2'-pyridyl)-2-butyne-1,4-diol was dissolved in ethanol and the solution was refluxed for 2 hr. On cooling, a yellow solid separated (yield 83%, mp 181°). The infrared spectrum (KBr) has characteristic hydroxy and carbonyl absorptions at 3290 and 1665 cm⁻¹.

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.55; H, 5.14; N, 7.14. Found: C, 79.66; H, 5.17; N, 7.31.

1,1,4,4-Tetraphenyl-1,4-dimethoxy-2-butyne (II).—1,1,4,4-Tetraphenyl-2-butyne-1,4-diol (10 g) was dissolved in 150 ml of warm methanol. A solution of 1 ml of concentrated sulfuric acid in 10 ml of methanol was added. After shaking for 30 min, the solution was allowed to stand for 24 hr. The solid product was washed with methanol, aqueous ammonia, and again with methanol. It was recrystallized from ethanol (yield 10.4 g), mp 111-112° (lit.⁴ mp 112°).

1,1,4,4-Tetraphenylbutatriene (III). Method A.—This involved treating the acetylenic diol (I) with stannous chloride and hydrogen chloride in ether solution.^{1,2}

Method B.—Potassium iodide (34 g, 0.204 mole) and 34.4 g (0.082 mole) of 1,1,4,4-tetraphenyl-1,4-dimethoxy-2-butyne were added to 200 ml of ethanol and the solution was heated to reflux. A solution of 8 g of concentrated sulfuric acid in 50 ml of ethanol was then added dropwise and the mixture was refluxed for 4 hr. After cooling, the solid was removed, washed with water, ethanol,

⁽⁶⁾ Supplied by the Foote Mineral Co., Exton, Pa.

⁽⁷⁾ G. Dupont, Compt. Rend., 150, 1524 (1910).

⁽⁸⁾ Acetylene was bubbled through four traps containing dilute NaOH, concentrated H₂SO₄, P₂O₅, and KOH pellets, respectively.

and water, respectively, and recrystallized fron xylene (yields 70-75%), mp 235-236°

Dianion from 1,1,4,4-Tetraphenyl-1,4-dimethoxy-2-butyne .--1,1,4,4-Tetraphenyl-1,1-dimethoxy-2-butyne (4.18 g) was dissolved in 250 ml of dry tetrahydrofuran, 1.56 g (0.04 g-atom) of potassium was added, and the mixture was stirred for 16 hr in a nitrogen atmosphere. Disappearance of an esr signal indicated completion of the reaction. The original, colorless solution changed to reddish violet as the anion radical formed and to reddish brown as the dianion formed.

The same procedure was used in preparing the dianion from tetraphenylbutatriene except that only 2 g-atoms of potassium was used for every mole of the butatriene.

Reaction of the Dianion with Electron Acceptors to Form the Cumulene (III).-Bromine (1.6 g, 0.01 mole) was added dropwise to a cold solution of the dianion (0.01 mole) in tetrahydro-The products which separated (tetraphenylbutatriene furan. and potassium bromide) were removed and the filtrate was diluted with water to obtain more product. The combined solids were extracted with chloroform and dried (MgSO₄). The residue obtained by evaporating the chloroform was recrystallized from xylene (yield 78%), mp 235-236°

Addition of iodine as well as the passage of oxygen into the dianion solution gave similar results.

Protonation of the Dianion.—Potassium (15.6 g, 0.4 g-atom) and 2.3 g (0.1 g-atom) of sodium were carefully melted under nitrogen to form a liquid alloy. Dry tetrahydrofuran (600 ml) was added and the mixture was cooled in an ice bath. 1,1,4,4-Tetraphenyl-1,4-dimethoxy-2-butyne (41.8 g, 0.1 mole) was added and the mixture was stirred at room temperature until the esr signal disappeared (16 hr). Dry methanol (15 ml) was added to the cold solution. The clear, yellow solution was removed, under nitrogen from the remaining potassium-sodium alloy. A solution of 20 ml of concentrated hydrochloric acid in 200 ml of methanol was immediately added to the cold solution with stirring. The mixture was then poured into 1000 ml of water and the yellow oil was extracted with ether. The ether extract was washed with water, 10% sodium bicarbonate, and water, respectively. After drying (MgSO₄), the ether was removed The solid and the oily residue was digested with ethanol. residue proved to be 1,1,4,4-tetraphenyl-1,3-butadiene (yield 5%), mp 200°. Slow evaporation of the filtrate gave a 78% yield of 1,1,4,4-tetraphenyl-1,2-butadiene, mp 99°.

When acetic acid was used as the protonating agent in place of the methanol-hydrochloric acid an 82% yield of the allene was obtained. The spectra data for the allene are included in the The conjugated diene (IX) absorbed in the ultradiscussion. violet (CH₃OH) at 345 mµ (\$\epsilon 28,000) and 248 mµ (\$\epsilon 21,000).

Dimerization of 1,1,4,4-Tetraphenyl-1,2-butadiene (VIII) to 1-Diphenvlmethylene-2-diphenylmethylmethylene-3,3-diphenyl-4diphenylmethylcyclobutane (X).—Compound VIII (3 g) was heated at 110° for 4 hr. The cooled residue was dissolved in 10 ml of acetone and the product was precipitated by the addition of 100 ml of ethanol. The product was recrystallized from chloroform-methanol (yield 80%), mp 198-199°. Anal. Calcd for C₅₆H₄₄: C, 93.90; H, 6.10; mol wt, 716.

Found: C, 93.37; H, 6.11; mol wt, 693.

Dimer X was also prepared by dissolving 2 g of the allene (VIII) in 50 ml of ethanol and refluxing the solution for 20 hr. During this time the product precipitated (yield 82%). The spectral data for X are included in the discussion.

Formation of 1,2-Bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane (Dimer XI).-1,1,4,4-Tetraphenyl-1,2-butadiene (3 g) was refluxed in dibutyl ether for 24 hr. The mixture was cooled and the product was removed. After washing with acetone, the product was recrystallized from chloroform-methanol (yield 82%), mp 273° (lit.² mp 273°).

Dimer XI was also obtained by heating dimer X at 200° for hr. The yields were lower (60-70%). The spectral data were 3 hr. identical with those reported by Nahon and Day.²

Ozonolysis of 1,2-Bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane (XI).—A solution of 7.16 g (0.01 mole) of XI in 100 ml of chloroform was ozonized for 1 hr. The chloroform solution was then refluxed with 50 ml of water and 2 g of zinc dust for 15 min. The chloroform layer was separated, washed

with water, and dried (MgSO₄). The dried solution was evaporated to a very small volume and chromatographed on a 72×2.4 cm column containing alumina. Elution with petroleum ether gave no product. Elution with 500 ml of 4:1 cyclohexanecarbon tetrachloride gave 2.7 g of a white solid which was re-crystallized from methanol, mp 181°. Analytical and molecular weight data indicate it to be a diepoxide but its structure is not completely known as yet. Elution with benzene gave an oil which absorbed at 1659 cm⁻¹ and which formed a 2,4-dinitrophenylhydrazone, mp 239°. The major product in the oil was benzophenone. Further elution with chloroform gave a white solid which was recrystallized from cyclohexane, mp 131°. The analytical and spectral data suggested a lactone, possibly 2diphenylmethylene-3,4-bis(diphenylmethyl)butyrolactone. The structural proof is not complete at present.

Ozonolysis of 1-Diphenylmethylene-2-diphenylmethylmethylene-3,3-diphenyl-4-phenylmethylcyclobutane (X).-The ozonation was carried out under conditions which were identical with those used for the ozonation of XI. The reductive hydrolysis step was found to be unnecessary. The chloroform solution was reduced to a very small volume (just short of precipitation) and run through an alumina column.

Elution with cyclohexane gave a white solid which was recrystallized from chloroform-methanol, mp 214°. Again all of the data suggested a diepoxide but more evidence is needed.⁹

Elution with benzene gave an oil which showed the presence of benzophenone (1659 cm⁻¹) and diphenylacetaldehyde (1721 cm⁻¹). This was confirmed by preparing their 2,4-dinitrophenyl-The more soluble 2,4-dinitrophenylhydrazone of hvdrazones. diphenylacetaldehyde was extracted with hot ethanol-water (70:30) and finally recrystallized from the same medium, mp 159°. The less soluble 2,4-dinitrophenylhydrazone of benzophenone was recrystallized from ethyl acetate-ethanol, mp 239°

Final elution with chloroform gave a solid, mp 191°, which is believed to be a lactone.9

Reaction of 1,2-Bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane (XI) with Potassium.-Dimer XI (3.58 g, 0.005 mole) and 0.5 g (0.013 g-atom) of potassium were added to 125 ml of tetrahydrofuran and the mixture was stirred for 48 hr under nitrogen. The contents were cooled to -55° and 6 g (0.1 mole) of acetic acid was added dropwise with stirring. Decolorization occurred and potassium acetate precipitated. The mixture was poured into water and the insoluble component was extracted with ether. The extract was washed with water and dried (MgSO₄). The oily solid, obtained by evaporating the ether, was recrystallized from benzene-methanol. The yield of 1,2,3,4-tetrakis(diphenylmethyl)-1-cyclobutene (XII) was 72%, mp 162°

Anal. Caled for C₅₆H₄₆: C, 93.66; H, 6.34; mol wt, 718. Found: C, 93.55; H, 6.30; mol wt, 690.

The spectral data are included in the discussion.

Reaction of 1-Diphenylmethylene-2-diphenylmethylmethylene-3,3-diphenyl-4-diphenylmethylcyclobutane (X) with Potassium.-The conditions for the reaction of X with potassium were identical with those described above for dimer XI except that the original reaction mixture was stirred for only 20 hr under nitrogen. The yield of 1,1,6,6-tetraphenyl-3,4-bis(diphenylmethyl)-2,4-hexadiene (XIII) was 76%, mp 160°

Anal. Calcd for $C_{55}H_{46}$: C, 93.66; H, 6.34; mol wt, 718. Found: C, 93.42; H, 6.41; mol wt, 698.

The spectral data are included in the discussion.

Registry No.-II, 10487-75-9; III, 1483-68-7; V, 10479-03-5; VI, 10479-04-6; VII, 10479-05-7; VIII, 1483-69-8; IX, 1450-63-1; X, 10487-76-0; XI, 1483-77-8; XII, 10479-08-0; XIII, 10479-09-1; 2-diphenylmethylene - 3,4 - bis(diphenylmethyl)butyrolactone, 10479-10-4; 2,4-dinitrophenylhydrazone of diphenylacetaldehyde, 10479-11-5; 2,4-dinitrophenylhydrazone of benzophenone, 1733-62-6.

(9) Only benzophenone and diphenylacetaldehyde were regarded as important ozonolysis products for the present study. The other products are being included in a broader study of ozonation.