A Trimer of 1,3-Diphenylcyclobutadiene

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In an earlier paper² we reported the isolation of tricyclic compounds II and III from the reaction of 1,3diphenyl-2,4-cyclobutanebis(trimethylammonium) iodide (I) with base; presumably a dimerization of 1,3diphenylcyclobutadiene (IV) was involved (Chart I).³



We now report on several minor products from the reaction: a trimer (V) of IV, a butadiene (VI), and an uncharacterized polymer of IV.

The trimer to which we assign structure V (1,2,5,7,8,-11-hexaphenylpentacyclo [8.2.0.0.^{2,9}0.^{3,8}0^{4,7}] dodeca-5,11diene) was obtained by chromatography of the total reaction product on alumina. The fraction containing both compounds V and the cyclooctatetraene derived from III² was triturated with cold hexane, leaving V as a white residue. The elemental analysis and molecular weight determination led to the formula C₄₈H₃₆, a trimer of the elements of diphenylcyclobutadiene.

Compound V is thermally stable at room temperature, but at elevated temperatures in the solid state ($\geq 200^{\circ}$) it is quantitatively converted into 2 mol of 1,2,4triphenylbenzene.⁴ Pyrolysis experiments in sealed capillaries indicated intermediate species in the conversion but they were not characterized. Compound V is readily hydrogenated with the uptake of 2 molar equiv of hydrogen, indicating by inference four other units of unsaturation. The nmr spectrum shows vinyl signals at τ 3.82 (2 H, d, J = 2.5 cps), an allylic doublet at 6.54 (2 H, J = 2.5 cps), and a broad singlet for the methine hydrogens at 6.73 (2 H). The pair of doublets

(1) Author to whom all inquiries should be addressed.

(2) E. H. White and H. C. Dunathan, J. Amer. Chem. Soc., 86, 453 (1964).

(4) In several runs using potassium *tert*-butoxide as base in the treatment of I, 1,2,4-triphenylbenzene was isolated directly as a reaction product.

with weak 1,3 coupling (AX system) is similar to those found for dimer III⁵ and they can be assigned to the a and b hydrogens of V. The lack of strong coupling is consistent with the dihedral angle between these protons of >70° as indicated by models. The ultraviolet maximum at 263 nm (log ϵ 4.59) is also consistent with structure V, which contains two phenylcyclobutene chromophores.⁶

Unlike dimer III, which readily isomerizes into the cyclooctatetraene form in solution $(t_{1/2}^{25^{\circ}} = 12 \text{ hr}),^2$ compound V is stable under similar conditions. This difference may result from the fact that in III the thermal opening of one cyclobutane ring leads to a system with only a single σ bond to be cleaved to form the cyclooctatetraene and this σ bond is weakened by a double allylic interaction. Compound V, on the other hand, can undergo the initial ring opening (VII), but a further "unzipping" is not as facile as in III because of the strong bonds remaining to be cleaved. If each bond but the last is broken reversibly, a statistical factor would also favor the closed form of V.



The second compound isolated was assigned structure VI (1,3-diphenyl-4-*tert*-butoxy-1,3-butadiene). The formation of this butadiene can be accounted for by a displacement reaction on a ring atom of the cyclo-butene intermediate VIII,⁷ followed by a conrotatory ring opening of the product (eq 2).



The nmr spectrum of VI shows the expected aromatic multiplet at τ 2.3–3.0 (10 H), the *tert*-butyl protons as a singlet at 8.76 (9 H), a vinyl singlet corresponding to the isolated proton H_c at 3.28 (1 H), and an AB pair of doublets at 3.15 and 3.82 (1 H each) with a coupling constant of 16 cps (trans)⁸ corresponding to protons H_a and H_b.⁹ The infrared spectrum shows strong

⁽³⁾ Dimers formed via cyclobutadienes have been extensively reported (see M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, for references through 1966), but evidence indicates that in some cases other reaction paths are involved: E. K. G. Schmidt, L. Brener, and R. Pettit, J. Amer. Chem. Soc., 92, 3240 (1970), and M. Avram, I. G. Dinulescu, T. Marica, G. Matesson, E. Sliam, and C. D. Nenitzescu, Chem. Ber., 97, 382 (1964).

⁽⁵⁾ Compound III has its vinyl and allyl hydrogens at τ 3.30 and 6.20, respectively, with a coupling constant at 2.5 cps.²

^{(6) 1-}Phenyloyclobutane has λ_{max} at 255 nm (log ϵ 4.02) [J. W. Wilt and J. D. Roberts, J. Org. Chem., **27**, 3430 (1962)] and compound III, containing two phenylcyclobutene chromophores, has λ_{max} at 261 nm (log ϵ 4.57).² (7) The chloride salt of VIII has been prepared and characterized.²

⁽³⁾ cis-1,3-Diphenylbutadiene has been synthesized [M. H. Goodrow and T. L. Jacobs, J. Org. Chem., 23, 1653 (1958)], but the trans isomer has not been reported. The best model we have found for the absorption spectrum is 1,3-diphenyl-1,3-cyclohexadiene, which has its uv absorption maxima at 255 and 311 nm (log ϵ 4.39) (private communication from Professor G. F. Woods, University of Maryland).

⁽⁹⁾ L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

vinyl ether bands at 1630, 1260, and 1150 $\rm cm^{-1.10}$ A long-wavelength absorption at 304 nm (log ϵ 4.51) in the ultraviolet is consistent with the assigned structure and inconsistent with the presence of only styrene type chromophores.

In a few runs, a highly fluorescent polymer $(C_{16}H_{12})_n$ was also found. It melted sharply at $\sim 273^{\circ}$ and it was thermally stable to about 225°, but pyrolysis at 285° yielded 1,3,5-triphenylbenzene together with several other unidentified products.

Experimental Section

The nmr spectra were run on a Varian A-60 spectrometer with tetramethylsilane (TMS) as an internal standard. Ultraviolet spectra were determined on a Cary 14 spectrophotometer. Infrared spectra were taken in potassium bromide discs on either a Perkin-Elmer 337 or 521 spectrophotometer. Melting points were taken on a Kofler hot stage apparatus and are uncorrected.

1,2,5,7,8,11-Hexaphenylpentacyclo [8.2.0.0^{2,9}.0^{3,8}.0^{4,7}] dodeca-5,11-diene (V).-The crude product (8.0 g) from the potassium tert-butoxide driven elimination reaction of 25.0 g (43.4 mmol) of 1,3-diphenyl-2,4-cyclobutanebis(trimethylammonium) iodide (I)^{2,11} was carefully chromatographed on an alumina column using increasing amounts of ether in benzene as the eluent. From the early fractions (0.5-10% ether), 0.369 g (1.3 mmol, 3%) of butadiene VI was isolated; from the middle fractions (15-19% ether), 3.46 g (8.4 mmol, 39.2%) of the cyclooctatetraene formed from II was obtained; and from the fractions with 20-25% ether, 2.55 g (6.3 mmol, 28%) of the cyclooctatetraene derived from III containing some V was obtained. Recrystallization of this material from methylene chloride-ethanol followed by trituration of the solid with cold hexane gave a residue of 0.54 g (0.89 mmol, 2.0%) of compound V as white microcrystals. In other runs, yields of 0-2% were obtained. Crystallization of V from methylene chloride-ethanol gave tiny white plates: mp 220.5° dec; uv $\lambda_{max}^{\text{ether}}$ 263 nm (log ϵ 4.59), 255 sh (4.56), 271 (4.56), 285 sh (4.20), 293 (3.60); nmr, see text.

Anal. Calcd for $C_{48}H_{36}$: C, 94.08; H, 5.92; mol wt, 612.8. Found: C, 94.08; H, 5.81; mol wt, 608 (Signer-Barger).

Pyrolysis of Compound V.—Compound V (38.89 mg, 0.0636 mmol) was sublimed at 200° (15 μ). The total sublimate was then carefully washed from the cold finger of the sublimator and the solvent was removed to give 39.5 mg (0.129 mmol, 101%) of 1,2,4-triphenylbenzene. Ultraviolet and infrared comparisons as well as melting points and mixture melting points proved the identity of the product. Thin layer chromatography (silica gel) using 1:4 benzene-petroleum ether (bp 30-60°) gave a single spot, $R_{\rm f} 0.46$.

Small amounts of the trimer V were heated in evacuated capillaries at various temperatures for different time intervals to detect possible intermediates. At 155° for 15 min, no change was found by tlc but at 180°, three compounds were observed: a possible intermediate at R_1 0.22, starting material V, and 1,2,4-triphenylbenzene. At 240° for 30 hr, only 1,2,4-triphenylbenzene was detected.

Hydrogenation of Compound V.—V (25 mg, 0.041 mmol) was hydrogenated in 5 ml of ethyl acetate containing 20 mg of prereduced 10% Pd/C. Uptake of hydrogen (corrected) was 1.6 equiv in 15 min and 1.95 equiv in 1 hr. At the end of 17 hr, no additional hydrogen had been absorbed.

1,3-Diphenyl-4-tert-butoxy-1,3-butadiene (VI).-From the earliest fractions of the chromatography above (5--10% ether in liest fractions of the chromatography above to 10% cannot hexane), 369 mg (1.3 mmol, 3.0%) of compound VI was isolated after removal of the solvent. Crystallization from isopentane here receives mp 101-103°; uv $\lambda_{\rm max}^{\rm MeoH}$ 230 nm gave colorless needles: mp 101-103°; uv λ_{max}^{MeOH} 230 nm (log ϵ 4.12) and 303 (4.51); ir 3030 (w), 2980 (s), 2940 (w), 1630 (s), 1260 (s), 1150 (vs), and 1105 cm⁻¹ (s). A qualitative test for nitrogen was negative.

Anal. Calcd for C₂₀H₂₂O: C, 86.28; H, 7.97. Found: C, 86.33; H, 8.03.

Miscellaneous Products .--- In several runs, a highly fluorescent white solid was isolated in the chromatography fractions immediately following the elution of 1,3,5,7-tetraphenylcyclooctatetraene (derived from II) with yields up to 1.5% (based on a trimeric structure). After crystallization from dichloromethane-ethanol to a constant melting point, white plates were obtained, mp 273.0-273.5°. The ultraviolet spectrum had a single maximum at 267 nm (log ϵ 4.32 based on the molecular weight for a trimer, 612.8).

Anal. Calcd for $(C_{16}H_{12})_n$: C, 94.08; H, 5.92. Found: C, 94.10; H, 6.02; mol wt, 426, 508 (micro Rast).

The compound sublimed unchanged at 225° (15 μ) but at 285° it was converted into at least four different compounds; one was identified as 1,3,5-triphenylbenzene by tlc (color formation and $R_{\rm f}$ at 0.48; silica gel with 1:4 benzene-petroleum ether).

In later chromatographic fractions using solvent containing more than 25% ether, extremely viscous, highly colored oils remained on evaporation of the solvent. In the infrared, these oils showed strong carbonyl absorption at $1700-1750 \text{ cm}^{-1}$. A random fraction from one run was chosen for analysis (100%)ether fraction).

Anal. Found: C, 90.70; H, 6.08; N, 0.00.

Registry No.-IV polymer, 36812-97-2; V, 36789-10-3; VI, 36789-11-4.

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Thallium in Organic Synthesis. XXXI. Oxidative Cleavage of Glycols by Thallium Salts¹

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Glycol cleavage reactions are of considerable utility in both synthesis and degradation, and from a practical point of view periodate and lead(IV) acetate are generally the oxidants of choice.^{2,3} A wide range of oxidants has been investigated with respect to glycol cleavage and Rigby has defined the efficiency of such reagents as oxidants "which concern elements which (a) can reasonably be envisaged as capable of forming a preliminary cyclic compound with the glycol, and (b) exist in two stable oxidation states which are two valence units apart, the lower representing a substance which is not an oxidizing reagent under ordinary conditions [Pb(II) or Bi(III)] or which no longer fulfills condition a (the IO_3^- ion)."⁴ According to this def-inition, thallium(III) salts, which are isoelectronic with lead(IV) salts, should function as efficient glycol

(4) W. Rigby, J. Chem. Soc., 1907 (1950).

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⁽¹¹⁾ R. L. Stern, Ph.D. Thesis, The Johns Hopkins University, 1963; Earl W. Friend, Jr., Ph.D. Thesis, The Johns Hopkins University, 1967.

⁽¹⁾ Part XXX: E. C. Taylor, R. L. Robey, and A. McKillop, Angew.

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⁽³⁾ C. A. Bunton in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 367-407.