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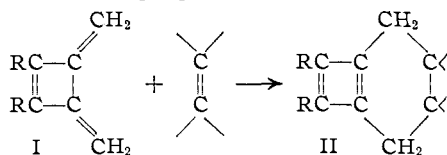
Synthesis of Some Conjugated Cyclobutane Polyolefins and their 1,2-Cycloaddition to Tetracyanoethylene^{1,2}

BY A. T. BLUMQUIST AND YVONNE C. MEINWALD

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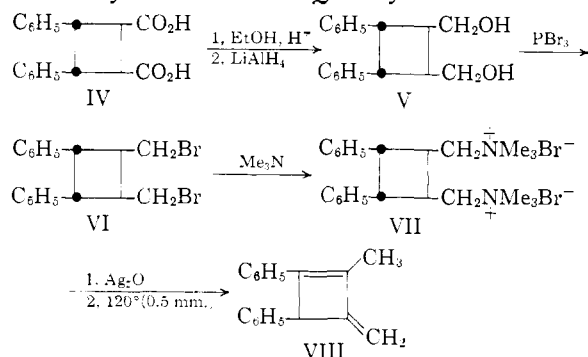
3-Methylene-1,4-diphenyl-2-methylcyclobutene and diphenyldimethylenecyclobutene have been synthesized from β -truxinic acid by a series of conventional transformations which included Hofmann degradation of appropriate bis-quaternary hydroxides in the final steps. The structures of the hydrocarbons were confirmed by chemical and spectral properties. Both olefins reacted with tetracyanoethylene *via* 1,2-cycloaddition to give spiro-cyclobutane derivatives. Similar 1,2-cycloaddition was observed for 3-methylenecyclohexene. Interestingly, tetracyanoethylene and norbornadiene also formed a 1:1 adduct, presumably a tricyclic derivative.

The observation that 1,2-dimethylenecyclobutane easily undergoes normal Diels-Alder reactions at room temperature to form cyclobutene derivatives³ suggested that it might be possible to realize *bona fide* cyclobutadienes *via* the addition of dienophiles to suitable derivatives of dimethylenecyclobutene. For the purpose of exploring this route to



cyclobutadienes of the type II it seemed desirable to examine first the behavior of the diaryl-substituted triene diphenyldimethylenecyclobutene (III). Such a triene, relative to the parent hydrocarbon (I, R = H), should be less prone to polymerize. Further, a cyclobutadiene derivative resulting from it, by the path indicated above, should be more stable under ordinary conditions than those of type II in which the substituents R are hydrogen atoms or alkyl groups. Finally, synthesis of the triene III from the readily available β -truxinic acid (IV) was envisioned as being fairly straightforward.

The first approach to the triene III is outlined in the diagram which follows. β -Truxinic acid (IV) was obtained easily in quantity by photodimerization of freshly precipitated cinnamic acid as described by Bernstein and Quimby.⁴ Lithium alu-



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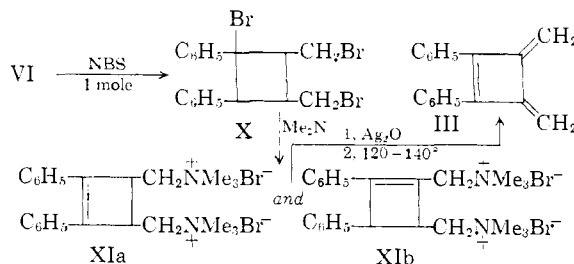
(2) For preliminary communications of portions of this work see A. T. Blomquist and Y. C. Meinwald: (a) *THIS JOURNAL*, **79**, 5316, 5317 (1957); (b) Abstracts of Papers Presented at the National Meeting of the American Chemical Society at San Francisco, Calif., April 13-18, 1958, p. 77-N.

(3) A. T. Blomquist and J. A. Verdol, *THIS JOURNAL*, **77**, 1806 (1955).

(4) H. I. Bernstein and W. C. Quimby, *ibid.*, **65**, 1845 (1953).

minum hydride reduction of the diethyl ester of IV gave the solid glycol V, m.p. 110-111°, in 92% yield. The dibromide VI, m.p. 95.5-96.5°, was obtained (77% yield) by reaction of the glycol V with phosphorus tribromide. Conversion of the dibromide VI to the bis-quaternary ammonium bromide VII was quantitative. The latter was characterized as its dipicrate derivative, m.p. 255-256°. Transformation of the salt VII to the corresponding bis-quaternary ammonium hydroxide followed by thermal decomposition at 120° (0.5 mm.) in a vacuum sublimation apparatus afforded the rearranged diene VIII, 3-methylene-1,4-diphenyl-2-methylcyclobutene, in 65-80% yield, as a colorless crystalline solid, m.p. 63-64°.

Structure VIII for the diene is postulated on the basis of spectral and chemical properties. The diene showed absorption maxima at 5.97 and 11.60 μ in the infrared (See Fig. 1) consistent with the presence of a methylenecyclobutene structure.⁵ Its ultraviolet spectrum possessed the following absorption maxima (log ϵ 's in parentheses): 228 m μ (4.08), 235 m μ (3.96), 292 m μ (4.43), 302 m μ (4.40) and a shoulder at 316.5 m μ (4.12) [λ_{\max} 280 m μ for 1-phenylbutadiene⁶]. The diene failed to give a Diels-Alder adduct with maleic anhydride. Upon quantitative hydrogenation in ethyl acetate at room temperature over Adams catalyst the diene VIII absorbed only one equivalent of hydrogen to give 2,3-diphenyl-1,4-dimethylcyclobutene (IX). The latter (IX) in isoöctane solution showed the following maxima in its ultraviolet spectrum (log ϵ 's in parentheses): 255 m μ (4.06), 261 m μ (4.10), and a shoulder at 270 m μ (3.90) [λ_{\max} 244 m μ for a substituted styrene⁶]. The infrared spectrum of IX had a weak absorption band at 6.03 μ ($>C=C<$ stretching). Reductive ozonolysis of the diene gave formaldehyde (25%), isolated as its dimedone derivative.⁷



(5) D. F. Applequist and J. D. Roberts, *ibid.*, **78**, 4012 (1956).

(6) E. A. Braude, *Ann. Reports*, **42**, 105 (1945).

(7) This was the result of a single experiment. The yield could undoubtedly be improved by further work.

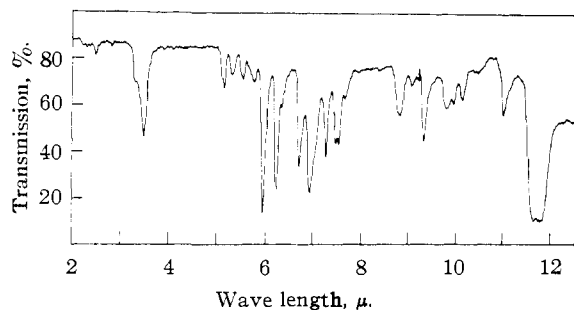


Fig. 1.—Infrared spectrum of 3-methylene-1,4-diphenyl-2-methylcyclobutene, chloroform solution.

The second and successful approach to the triene III is illustrated by the accompanying chart. The dibromide VI reacted smoothly with one equivalent of *N*-bromosuccinimide in carbon tetrachloride at reflux temperature to give a single crystalline tribromide X, m.p. 105–105.5°, in 74% yield. Treatment of X with excess trimethylamine at 50° gave the mixture of isomeric unsaturated bisquaternary ammonium salts XIa and XIb separable by virtue of their differing solubility in methylene chloride. However, this separation was not necessary since either salt when converted to its bisquaternary ammonium hydroxide and heated at 120–140° (0.5 mm.) gave the triene III in 46–85% yield. Pure triene III, m.p. 42–43°, was obtained by resublimation *in vacuo*.

The triene III showed infrared absorption maxima at 3.29, 3.34, 5.89, 6.10 and 11.56 μ (see Fig. 2). In the ultraviolet, absorption maxima ($\log \epsilon$'s in parentheses) at 237 $m\mu$ (4.42), 262 $m\mu$ (4.50) and 328 $m\mu$ (4.20) were observed. Upon quantitative hydrogenation over Adams catalyst III absorbed three equivalents of hydrogen without any break in the rate of hydrogen uptake. This behavior on hydrogenation in contrast to that of the diene VIII may be attributed to the planarity of the triene which would permit particularly easy adsorption on the catalyst surface. Reductive ozonolysis of III yielded formaldehyde (34% of the theoretical amount isolated as its dimedone derivative) and titration of III with bromine in carbon tetrachloride afforded a crystalline tetrabromide XII, m.p. 118–119°. The compound XII possessed a maxima in its ultraviolet spectrum at 288 $m\mu$ ($\log \epsilon$ 4.29) which is consistent with the presence of a *cis*-stilbene chromophore⁶ (λ_{\max} 280 $m\mu$).

Both the diene VIII and the triene III exhibited moderate stability when pure. They could be kept in the refrigerator under nitrogen for 2–3 days without visible change. However, the triene III deteriorated rapidly at room temperature. It became yellow within a few hours and eventually polymerized.

Unlike the parent hydrocarbon 1,2-dimethylcyclobutane³ the triene III was unreactive toward maleic anhydride, *N*-phenylmaleimide and acetylenedicarboxylic ester at moderate temperatures (25–75°). At elevated temperatures polymerization occurred in all cases and no crystalline products could be isolated. From reaction with acetylenedicarboxylic ester at 150°, for example, an amorphous product, m.p. 160–170° dec., was obtained in low

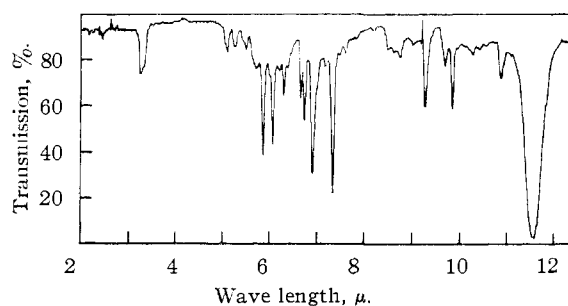
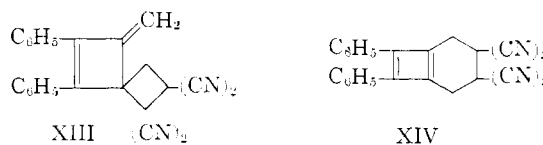
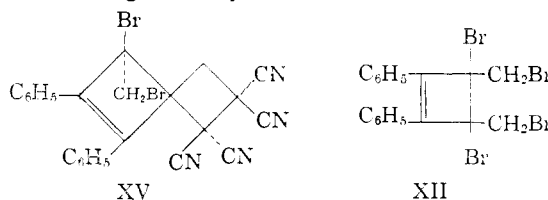


Fig. 2.—Infrared spectrum of diphenyldimethylenecyclobutene, chloroform solution.

yield. However, the triene III and tetracyanoethylene in benzene solution reacted smoothly at room temperature to give a colorless crystalline stable 1:1 adduct (XIII), m.p. 175–176° dec., in 40% yield. Physical and chemical properties of the adduct indicated that it was the spiran XIII and not the cyclobutadiene XIV.



The infrared spectrum of the adduct showed weak absorption at 4.46 μ ($-\text{C}\equiv\text{N}$), characteristic aromatic absorption and absorption at 5.97, 11.40 and 11.60 μ characteristic of the methylenecyclobutene system.⁵ In the ultraviolet the adduct, in isoöctane, showed λ_{\max} 245 $m\mu$ (broad) ($\log \epsilon$ 4.30) and λ_{\max} 308 $m\mu$ ($\log \epsilon$ 4.07). The nuclear magnetic resonance spectrum of the adduct in hexadeuterioacetone showed three peaks approximately in the weight 5:1:1 and at about the correct position for phenyl hydrogen (C_6H_5-), exomethylene hydrogen ($=\text{CH}_2$) and saturated ring methylene hydrogen ($-\text{CH}_2-$), respectively. In carbon tetrachloride solution the adduct absorbed one equivalent of bromine to give a crystalline dibromide XV, m.p.

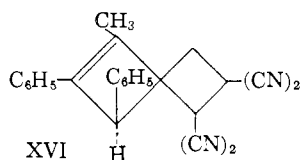


162.5–163°. The dibromide XV showed weak absorption at 6.06 μ in the infrared ($\text{C}=\text{C}$ stretching) and ultraviolet λ_{\max} 285 ($\log \epsilon$ 4.25) in good agreement with the maximum observed for the tetrabromide XII (*supra vide*).

Although the stereochemistry was not established, the configuration written above would seem to be preferred on the assumption that Br^+ attack should occur on the least hindered side of the spiro molecule XIII, *i.e.*, *cis* to the methylene group.

In view of the unusually facile 1,2-cycloaddition of tetracyanoethylene to the triene III it seemed desirable to examine the behavior of the diene VIII when treated with tetracyanoethylene at room temperature. It was found that a crystalline 1:1 adduct (XVI), m.p. 139–140°, formed in 3 hours. The adduct XVI showed a maximum in its ultra-

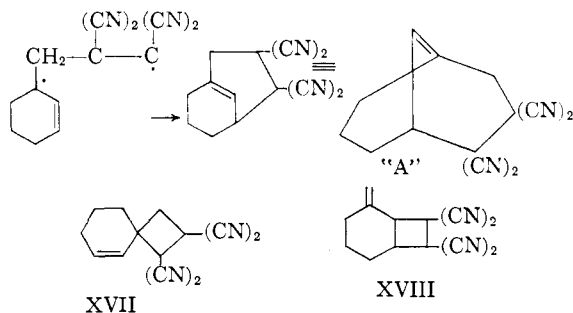
violet spectrum at 265μ ($\log \epsilon$ 4.33) very similar to that observed in the ultraviolet spectrum of the cyclobutene IX (*supra vide*). The configuration shown for the adduct XVI is based on the as-



sumption that in the addition reaction, the tetracyanoethylene molecule would approach the least hindered side of the diene VIII, *i.e.*, *trans* to the phenyl group.

At this point it is pertinent to comment on the fact that the triene III reacts with but one equivalent of tetracyanoethylene to form the adduct XIII. Although XIII possesses the methylenecyclobutane structural feature of the diene VIII, the additional spiro group probably serves as a steric barrier to the approach of a second tetracyanoethylene molecule. There is, of course, no such steric problem in the diene VIII.

With the discovery of the second instance of facile 1,2-cycloaddition of tetracyanoethylene to conjugated olefinic systems leading to new cyclobutane structures, an effort was made to explore to some extent the "scope and limitations" of the reaction. Accordingly, the behavior of a variety of mono- and diolefins was examined. It was observed generally that simple olefins of the reactive type exemplified by Fiest's acid, methylenecyclobutane, methylenecyclohexane and norbornene do not add to tetracyanoethylene under the mild conditions described above. Also, the compound allene failed to react at $25-90^\circ$, although a number of allene-substituted olefin 1,2-cycloadditions have been reported by Cripps and co-workers⁸ to occur at $175-225^\circ$. It was noted, however, that the *transoid* hydrocarbon 3-methylenecyclohexene gave a simple 1:1 adduct with tetracyanoethylene under mild conditions. Adduct formation was accompanied here with the formation of some polymeric product. Since the infrared spectrum of the adduct possessed no absorption band characteristic of an exomethylene group it would seem to have structure XVII and not XVIII.⁹



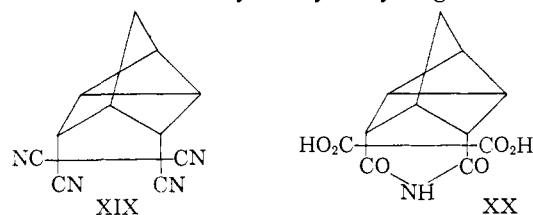
An especially interesting case observed was that of norbornadiene which, like the *transoid* conju-

(8) H. N. Cripps, J. K. Williams and W. K. Sharkey, *THIS JOURNAL*, **80**, 751 (1958).

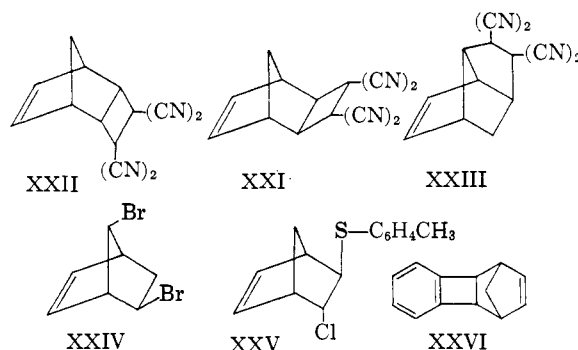
(9) It should be pointed out that any other structure resulting from rearrangement of the double bond after initial addition of tetracyanoethylene could only give rise to a bicyclic compound such as "A" which violates Bredt's rule.

gated diene, gave a quantitative yield of a crystalline 1:1 adduct (XIX) with tetracyanoethylene. The adduct was obtained in two polymorphic modifications, depending upon the reaction conditions; m.p. $158-160^\circ$ and m.p. $184-185^\circ$. The lower melting modification, formed in benzene at room temperature, transformed on standing at room temperature for several days to the higher melting form. Although the infrared spectra of the two forms in their solid states were different, their solutions in chloroform and in acetone showed identical spectra.

The following observations support the assignment of structure XIX to the adduct. Its infrared spectrum showed a band at 12.3μ , characteristic of the nortricyclic system.¹⁰ The adduct failed to add bromine in carbon tetrachloride or to add hydrogen over Adams catalyst in ethyl acetate. Alkaline hydrolysis of the adduct gave a cyclic imide dicarboxylic acid (XX), m.p. $205-207^\circ$, which also could not be reduced by catalytic hydrogenation.



Other structures considered for the adduct were XXI-XXIII. Such compounds would be expected



to add hydrogen and bromine readily. Thus, 5,7-dibromo-2-norbornene (XXIV) and the adduct of *p*-toluenesulfonyl chloride to norbornadiene (XXV) add hydrogen readily.^{10b-12} Similarly the hydrogenation of 1,4-endomethylene-1,4,11,12-tetrahydrobiphenylene (XXVI) occurs with ease.¹³

If structure XIX is accepted for the norbornadiene adduct, the addition of tetracyanoethylene must have followed an unprecedented course. All previously reported additions, ionic and free radical, for the norbornadiene system have involved approach of the adding reagent from the *exo* side of the molecule.^{10b-12} In this case, however, *exo* addition could lead only to XXI or XXIII, depending

(10) (a) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *THIS JOURNAL*, **72**, 3116 (1950); (b) L. Schermerling, J. P. Luvisi and R. W. Weld, *ibid.*, **78**, 2819 (1956).

(11) S. Winstein and M. Shatevsky, *Chemistry & Industry*, 56 (1956).

(12) S. J. Cristol, R. P. Organbright, G. D. Brindell and R. M. Heitz, *THIS JOURNAL*, **79**, 6335 (1957).

(13) C. D. Nenitzescu, M. Avram and D. Dinu, *Ber.*, **90**, 2541 (1937).

upon whether or not rearrangement occurred. In either case, the product would be tricyclic and olefinic. The conclusion that the reaction at hand involves *endo* addition appears therefore to be unavoidable.

Experimental Part¹⁴

Diethyl β -Truxinate.¹⁵— β -Truxinic acid⁴ (64 g., 0.216 mole) was esterified with 300 ml. of absolute ethanol, 150 ml. of toluene and 3 ml. of concd. sulfuric acid by the azeotropic distillation method. There was obtained 71.9 g. (94.5%) of the diester which had m.p. 51° (lit.¹⁵ m.p. 50°).

1,2-Bis-(hydroxymethyl)-3,4-diphenylcyclobutane (V).—A solution of 67.7 g. (0.192 mole) of diethyl β -truxinate in 100 ml. of anhydrous ether was reduced with 14.8 g. (0.39 mole) of lithium aluminum hydride in 750 ml. of anhydrous ether in the usual manner. After completion of the addition of the ester, the mixture was stirred for 4 hr. and then decomposed by the addition of 60 ml. of water. The inorganic salts were separated by filtration, dissolved in dilute hydrochloric acid and extracted with ethyl acetate. From the combined ethereal filtrate and ethyl acetate extract there was obtained 47.5 g. (92.5%) of the crystalline glycol V, m.p. 108–110°. After recrystallization from methanol the glycol V had m.p. 110–111°.

Anal. Calcd. for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.83; H, 7.23.

1,2-Bis-(bromomethyl)-3,4-diphenylcyclobutane (VI).—The solid glycol V described above (13.4 g., 0.05 mole) was added in several portions with stirring to 13.7 g. of phosphorus tribromide at ice-bath temperature. The mixture, protected from atmospheric moisture, was stirred at room temperature until solution was complete. It was then heated at 80° for 8 hr. The mixture was then cooled with an ice-bath and 25 ml. of water was added carefully. The mixture was extracted with benzene and the benzene extract washed with dilute sodium carbonate, water and dried over magnesium sulfate. Evaporation of the solvent and recrystallization of the crystalline residue from carbon tetrachloride-pentane gave 15.2 g. (77%) of the pure dibromide VI, m.p. 95.5–96.5°.

Anal. Calcd. for C₁₈H₁₈Br₂: C, 54.85; H, 4.60; Br, 40.55. Found: C, 55.04; H, 4.64; Br, 40.40.

1,2-Bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane Dimethobromide (VII).—A mixture of 3.94 g. (0.01 mole) of the above dibromide VI, 4.8 g. of trimethylamine and 2 ml. of methanol was sealed in a Pyrex tube and held at room temperature for one week. Evaporation of the reaction mixture *in vacuo* gave 5 g. (98%) of the bis-quaternary ammonium bromide VII which was characterized as its dipicrate. The dipicrate derivative, recrystallized from ethanol, showed m.p. 255–256° dec.

Anal. Calcd. for C₂₆H₃₀N₄O₈: C, 53.46; H, 4.98; N, 13.86. Found: C, 53.33; H, 4.83; N, 13.84.

3-Methylene-1,4-diphenyl-2-methylcyclobutene (VIII).—To a solution of 2.56 g. of the bis-quaternary ammonium bromide VII in 10 ml. of water was added freshly prepared silver oxide (from 3.4 g. of silver nitrate and 1.4 g. of potassium hydroxide) with stirring for 2 hr. The mixture was filtered into a vacuum sublimation apparatus and the filtrate evaporated to dryness at room temperature, first by passing a stream of dry air over it and finally by the application of reduced pressure. The residue, a glassy solid, was pyrolyzed directly in the sublimer at 120–140° (0.4–0.5 mm.). At the end of the pyrolysis the hydrocarbon (0.75–0.9 g.) had deposited on the cold finger as colorless needles, m.p. 58–62°. The yield, from several runs, ranged from 60–80%. After purification by sublimation at 55° (0.4 mm.) or recrystallization from methanol the hydrocarbon VIII had m.p. 63–64°. In the infrared VIII showed absorption at 5.97, 6.26, 11.60 and 11.75 μ . In the ultraviolet VIII (isooctane solution) showed the following maxima (log ϵ 's in parentheses): 228 m μ (4.08), 235 m μ (3.96), 292 m μ (4.43), 302 m μ (4.40), shoulder at 316.5 m μ (4.12).

Anal. Calcd. for C₁₈H₁₆: C, 93.06; H, 6.94. Found: C, 92.93; H, 6.98.

(14) All b.p.'s are uncorrected; all m.p.'s are corrected.

(15) R. Stoermer and E. Laage, *Ber.*, **54**, 96 (1921).

2,3-Diphenyl-1,4-dimethylcyclobutene (IX).—The diene VIII was hydrogenated in ethyl acetate with pre-reduced Adams catalyst at 25° and 736.5 mm. pressure in a semi-micro hydrogenation apparatus. Uptake of hydrogen was rapid and the reduction was complete at the end of one hour (101% of the theoretical amount of hydrogen required for one double bond was absorbed). After the catalyst and solvent had been removed, a light yellow viscous oil was obtained which failed to crystallize. The hydrocarbon IX was further purified by chromatography on alumina, with pentane used as an eluent. The pure IX thus obtained was a colorless liquid, *n*_D²⁰ 1.5892. In the infrared IX showed weak absorption at 6.03 μ . The ultraviolet spectrum of IX, isooctane solution, showed the following maxima (log ϵ 's in parentheses): 255 m μ (4.06), 261 m μ (4.10) and a shoulder at 270 m μ (3.90).

Anal. Calcd. for C₁₈H₁₈: C, 92.26; H, 7.74. Found: C, 92.03; H, 7.72.

Ozonolysis of the Diene VIII.—Ozonized oxygen was passed through a solution of 114.3 mg. (0.49 mmole) of VIII in 30 ml. of methylene chloride at Dry Ice temperature for 0.5 hr. The solution of the ozonide was added to a stirred mixture of 0.2 g. of zinc dust in 10 ml. of acetic acid. After the resulting mixture had been stirred 0.5 hr. at room temperature, it was distilled into a receiver containing a solution of 200 mg. of dimedone, a drop of piperidine and 10 ml. of 75% ethanol. The mixture thus collected was heated until all the methylene chloride had been removed. Upon cooling, 35 mg. (25%) of the dimedone derivative of formaldehyde separated as long needles m.p. 190–191°.

1,2-Bis-(bromomethyl)-3-bromo-3,4-diphenylcyclobutane (X).—A mixture of 3.94 g. (0.01 mole) of the dibromide VI, 1.78 g. (0.01 mole) of N-bromosuccinimide, a few crystals of dibenzoyl peroxide and 100 ml. of carbon tetrachloride was refluxed one hr. The succinimide was removed by filtration and the filtrate concentrated to a volume of ca. 10 ml. Upon the addition of pentane to this solution 3.4 g. (72%) of the crystalline tribromide X, m.p. 103–105°, separated. Recrystallization of X from ether-pentane afforded X as colorless plates, m.p. 105–105.5° dec.

Anal. Calcd. for C₁₈H₁₇Br₃: C, 45.70; H, 3.62; Br, 50.68. Found: C, 45.74; H, 3.61; Br, 49.96.

1,2-Bis-(dimethylaminomethyl)-3,4-diphenylcyclobutene Dimethobromides (XIa and XIb).—The tribromide X obtained in the preceding experiment was sealed in a Pyrex tube together with excess trimethylamine in methanol and kept at 50° for 2 days. Work-up of this reaction mixture gave 4.5 g. of a mixture of bis-quaternary salts XIa and b. Extraction of this mixture with methylene chloride left 1.5 g. of one of the salts (XIa and b), m.p. 200–204°, which was very soluble in water and in ethanol. The picrate derivative of this salt was prepared and showed m.p. 228–230° dec. when recrystallized from ethanol.

Anal. Calcd. for C₂₆H₃₀O₁₄N₈: C, 53.60; H, 4.75; N, 13.89. Found: C, 53.73; H, 4.61; N, 13.95.

Evaporation of the methylene chloride extract gave the other bis-quaternary salt which was recrystallized from water m.p. 185–187°. The picrate derivative of this salt could not be obtained in solid crystalline form. The salt itself was analyzed.

Anal. Calcd. for C₂₄H₃₄N₂Br₂: C, 56.48; H, 6.71; N, 5.49; Br, 31.32. Found: C, 56.23; H, 6.76; N, 5.49; Br, 31.46.

Either of the methobromides, XIa or XIb, or the mixture of bis-quaternary salts as originally obtained could be used in the subsequent pyrolysis which afforded the triene III.

Diphenyldimethylenecyclobutene (III).—The conversion of the bis-quaternary salts XIa and XIb to the corresponding bases was carried out exactly as described in the preparation of the diene VIII. From 2.04 g. (0.003 mole) of the mixture of XIa and XIb 1.21 g. of the crude bis-quaternary bases was obtained. Pyrolysis of this material in a vacuum sublimation apparatus at 120–140° (0.3–0.5 mm.) gave 0.28–0.35 g. (46%–58%) of almost colorless crystals, m.p. 40–43°, or a light yellow oil which solidified upon scratching. Resublimation at 40° (0.3 mm.) gave colorless crystalline triene III, m.p. 42–43°. The triene III could be kept at 0° under nitrogen for several days without visible change. At room temperature it turned yellow within a few hours and eventually transformed to a polymer. In the ultraviolet, III (isooctane solution) showed the following maxima (log ϵ 's

are in parentheses): 237 $m\mu$ (4.42), 262 $m\mu$ (4.50), 328 $m\mu$ (4.20). The infrared spectrum revealed peaks at 3.29, 5.89 and 11.56 μ ($>C=CH_2$), at 3.34 and 6.33 μ (C_6H_5) and at 6.10 μ (*cis*- $C_6H_5CR=CRC_6H_5$); see Fig. 2.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.65; H, 6.05.

In all pyrolyses about 0.25–0.3 g. of a dark colored, non-volatile polymeric residue was formed. It was soluble in benzene and could be reprecipitated with hexane.

Anal. Calcd. for $(C_{18}H_{14})_n$: C, 93.87; H, 6.13. Found: C, 91.37; H, 6.05.

Upon quantitative hydrogenation over Adams catalyst the triene III absorbed 90% of three equivalents of hydrogen simultaneously. Reductive ozonolysis of III gave 34% of the theoretical amount of formaldehyde, isolated at its dimedone derivative.

Addition of Bromine to the Triene III. Formation of 1,2-Dibromo-1,2-bis-(bromomethyl)-3,4-diphenyl-3-cyclobutene (XII).—A solution of 0.32 g. of the triene III in 2 ml. of carbon tetrachloride was titrated at 0° with a 10% solution of bromine in carbon tetrachloride. The end-point for the consumption of 2 moles of bromine per mole of triene was quite sharp. The solvent was removed *in vacuo* and the residue (0.75 g.) was recrystallized from ether to give the tetrabromide XII as colorless dense crystals, m.p. 118–119° (eff.). In the ultraviolet XII showed $\lambda_{max}^{CHCl_3}$ 288 $m\mu$ (log ϵ 4.29). The infrared spectrum of XII showed a weak band at 6.08 $m\mu$, attributed to the conjugated tetrasubstituted double bond.

Anal. Calcd. for $C_{18}H_{14}Br_4$: C, 39.31; H, 2.57; Br, 58.13; mol. wt., 549.9. Found: C, 39.01; H, 2.37; Br, 58.36; mol. wt., 509.2.

Attempted Reactions of the Triene III with Conventional Dienophiles.—The triene III was unreactive toward maleic anhydride, N-phenylmaleimide and acetylenedicarboxylic ester at moderate temperatures (25–27°). At higher temperatures polymerization occurred in all instances and no crystalline products could be isolated. For example, upon heating the triene III with acetylene-dicarboxylic ester at 150° there was obtained in low yield, after careful chromatography, an amorphous product which decomposed at 160–170°. The infrared spectrum of this polymeric product indicated that it comprised combined III and dienophile.

Anal. Calcd. for $(C_{24}H_{20}O_4)_n$: C, 77.40; H, 15.41. Found: C, 77.60; H, 15.53.

Reaction of the Triene III with Tetracyanoethylene.¹⁶ Formation of XIII.—A solution of 0.34 g. (0.0015 mole) of the triene III obtained directly from the pyrolysis and dissolved in a few ml. of benzene was added, under nitrogen atmosphere, to a benzene solution of 0.35 g. of tetracyanoethylene. The reaction mixture, which instantly became deep green in color, was either refluxed for 0.5 hr. or allowed to stand at room temperature overnight. The dark colored residue obtained, after removal of the benzene *in vacuo*, was extracted several times with boiling ether to leave an insoluble polymeric residue which was not examined. The ether extract was decolorized with Norite and upon concentration 0.18 g. (34%) of the adduct XIII, 1,1,2,2-tetracyano-5,6-diphenyl-7-methylenespiro[4,4]-5-heptene, separated as colorless needles, m.p. 175–176° dec. In the ultraviolet the adduct XIII, in isoöctane, showed λ_{max} 245 $m\mu$ (broad) (log ϵ 4.30) and λ_{max} 308 $m\mu$ (log ϵ 4.07). The infrared spectrum showed weak absorption at 4.46 μ ($-C\equiv N$), characteristic aromatic absorption and absorption at 5.97, 11.40 and 11.60 μ , characteristic of the methylenecyclobutene system.⁵

Anal. Calcd. for $C_{24}H_{14}N_4$: C, 80.43; H, 3.94; N, 15.63; mol. wt., 358.4. Found: C, 80.73; H, 4.08; N, 15.39; mol. wt., 340.

Addition of Bromine to XIII. Formation of 1,1,2,2-Tetracyano-5-bromo-5-bromomethyl-6,7-diphenylspiro[4,4]-6-heptene (XV).—A solution of 47 mg. of the adduct XIII in 0.5 ml. of chloroform was titrated with a solution of bromine as described for the triene III. The residue of crude bromo derivative XV obtained upon removal of the solvent showed m.p. 161–162° dec. after recrystallization from ether. A sample recrystallized again from ether had m.p. 162.5–163° dec. The infrared spectrum of XV possessed a weak

absorption band at 6.06 μ and showed no absorption at 5.97 and 11.5 μ . In the ultraviolet a chloroform solution of XV had a maximum at 285 $m\mu$ (log ϵ 4.25).

Anal. Calcd. for $C_{24}H_{14}N_4Br_2$: C, 55.62; H, 2.72; N, 10.81; Br, 30.84. Found: C, 55.92; H, 2.92; N, 10.63; Br, 31.07.

Addition of Tetracyanoethylene to VIII. Formation of 1,1,2,2-Tetracyano-5,7-diphenyl-5-methylspiro[4,4]-5-heptene (XVI).—The diene VIII (0.2144 g., 0.93 mmole) in 5 ml. of anhydrous ether was added to a solution of 0.120 g. (0.93 mmole) of tetracyanoethylene in 10 ml. of ether. The deep blue color, which developed instantly, disappeared after the mixture had been shaken for 3 hr. at room temperature. Removal of solvent *in vacuo* gave a light yellow glassy solid which, after recrystallization from ether–petr. ether, had m.p. 139.5–140.5° dec. In ethanol solution the adduct XVI showed a maximum in its ultraviolet absorption spectrum at 265 $m\mu$ (log ϵ 4.33).

Anal. Calcd. for $C_{24}H_{16}N_4$: C, 79.98; H, 4.48; N, 15.55. Found: C, 80.17; H, 4.50; N, 15.32.

3-Methylenecyclohexene.—The diene was obtained by pyrolysis of 2-cyclohexenemethanol acetate. A sample of impure 2-cyclohexenemethanol¹⁷ (13 g.) was heated with phthalic anhydride (17.3 g.) in refluxing toluene (15 ml.) for 3 hr. The mixture was left at room temperature overnight, diluted with ether and filtered from the precipitated excess phthalic anhydride. The filtrate was extracted thoroughly with dilute sodium carbonate solution. Acidification of the aqueous alkaline extract gave the crude acid phthalate of the alcohol as an oil which was taken up in methylene chloride. Some insoluble phthalic acid present was removed by filtration. The residue of acid phthalate obtained upon evaporation of the dried methylene chloride solution showed m.p. 73.5–75.5° after recrystallization from hexane–ether.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.25; H, 6.20. Found: C, 69.40, 69.51; H, 6.18, 6.17.

The acid phthalate derivative of 2-cyclohexenemethanol (32 g.) was hydrolyzed by refluxing with 180 ml. of 25% sodium hydroxide solution for 2 hr. Distillation of the alcohol regenerated from this saponification gave 12.7 g. (45%) which had b.p. 95° (8 mm.) and n_D^{20} 1.4820. This alcohol (12.7 g.) was acetylated with acetic anhydride and pyridine at room temperature. There was obtained 16.7 g. (96%) of 2-cyclohexenemethanol acetate, b.p. 95–96° (15 mm.), n_D^{20} 1.4575.

This acetate was pyrolyzed at $525 \pm 15^\circ$ as described previously.¹⁸ Distillation of the crude hydrocarbon obtained gave 6.9 g. (68%) of a fraction having b.p. 55–110°. Vapor phase chromatography of this fraction indicated that it contained about 80% 3-methylenecyclohexene and two other components. Fractional distillation of this sample through a spinning band column gave pure 3-methylenecyclohexene, b.p. 109–110° (atm.), n_D^{20} 1.4895 (lit.¹⁹ b.p. 109°, n_D^{20} 1.4894–1.4897).

Reaction of Tetracyanoethylene with 3-Methylenecyclohexene. Formation of 1,1,2,2-Tetracyano-5-nonenone (XVII).—3-Methylenecyclohexene (1.6 g.) was added to a solution of 1.6 g. of tetracyanoethylene in benzene. The dark red color which instantly developed disappeared when the mixture was either refluxed for 10 min. or allowed to stand at room temperature overnight. After filtering a white, amorphous, benzene-insoluble precipitate, the benzene solution was evaporated at room temperature. Recrystallization of the residue from ether gave 1.4 g. of the adduct XVII which showed m.p. 121–122° dec. This adduct began to soften and became yellow in color at 100–116° depending upon the rate of heating. The infrared spectrum of the adduct had a medium absorption band at 3.32 μ and weak bands at 4.45 and 6.04 μ .

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21; mol. wt., 222.2. Found: C, 70.53; H, 4.77; N, 25.02; mol. wt., (Rast), 211.

Reaction of Tetracyanoethylene with Norbornadiene. Formation of 8,8,9,9-Tetracyanoquadricyclo[2,2,1,0^{2,6},2^{3,5}]nonane (XIX).—This reaction was carried out exactly as de-

(17) A. T. Blomquist, J. Verdol, C. L. Adami, J. Wolinsky and D. D. Phillips, *This Journal*, **79**, 4976 (1957).

(18) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, *ibid.*, **78**, 6057 (1956).

(19) W. J. Bailey and J. C. Goosens, *ibid.*, **78**, 2804 (1956).

(16) We are indebted to Dr. T. L. Cairns of the du Pont Co. for the initial supply of tetracyanoethylene. See T. L. Cairns, *et al.*, *This Journal*, **80**, 2775 (1958), for the preparation of tetracyanoethylene.

scribed for the formation of XVII. Upon refluxing the dark red solution of norbornadiene and tetracyanoethylene in benzene for 0.5 hr. the adduct XIX was obtained in quantitative yield; m.p. 186–188° dec. from benzene. The infrared spectrum of the adduct XIX possessed a weak, sharp band at 4.45 μ and a strong band at 12.30 μ .

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44; mol. wt., 220. Found: C, 71.14; H, 3.88; N, 25.38; mol. wt., 219.

A lower melting form of the adduct, m.p. 158–160°, was obtained in quantitative yield when the addition reaction was carried out at room temperature over a period of 3–4 days. The infrared spectra of the two forms were identical in chloroform solution in the 2–12 μ region and in acetone solution in the 12–15 μ region. The form which had m.p. 158–160° was also analyzed.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44; mol. wt., 220. Found: C, 71.19; H, 4.05; N, 25.16; mol. wt., 229.

After standing at room temperature for more than a week the lower melting form transformed to the higher melting modification as indicated by m.p. and infrared spectrum in Nujol mull.

Hydrolysis of the Adduct XIX.—The adduct XIX (1.3 g.) was refluxed 24 hr. in a solution of 10 g. of sodium hydroxide in 12 ml. of water and 30 ml. of ethanol. Ammonia was liberated slowly during this period. The reaction mixture was acidified, most of the ethanol removed by distillation, diluted with 10 ml. of water and finally extracted thoroughly

with ether. A glassy residue (1.6 g.) was obtained from the ether from which 1.25 g. of the imide XX, 8,9-dicarboxy-quadracyclo[2,2,1,0^{2,5}, 2^{3,6}]nonane-8,9-dicarboximide, m.p. 205–207° (eff.), was obtained after recrystallization from benzene-ether. This imide XX showed absorption maxima at 5.60 and 5.82 μ (broad) in its infrared spectrum.

Anal. Calcd. for $C_{13}H_{11}O_5N$: C, 56.32; H, 4.00; N, 5.05. Found: C, 56.58; H, 4.10; N, 5.06.

Attempted Reactions of Tetracyanoethylene with Certain Monoolefins.—The olefinic compounds methylene-1,2-cyclopropanedicarboxylic acid (Feist's acid),²⁰ methylene-cyclobutane,²¹ methylenecyclononane²² and norbornene were examined with respect to their behavior when treated with tetracyanoethylene. All tests were run in the same fashion. The olefinic compounds were added to a saturated solution of tetracyanoethylene in benzene. (The mixture was contained in a sealed Pyrex tube if a low boiling olefin was used.) All solutions became orange in color immediately. This color persisted when solutions had been kept at room temperature overnight and subsequently heated at 80–90° for several hours. In all instances starting materials were recovered unchanged.

(20) We are indebted to D. T. Longone for the sample of Feist's acid.

(21) J. D. Roberts and C. W. Sauer, *THIS JOURNAL*, **71**, 3927 (1949).

(22) Dr. A. D. Josey very kindly furnished a sample of this compound.

ITHACA, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Many-membered Carbon Rings. XVIII. Synthesis and Acyloin Cyclization of δ,δ -Diphenylazelaic Ester¹

BY A. T. BLOMQUIST AND C. J. BUCK²

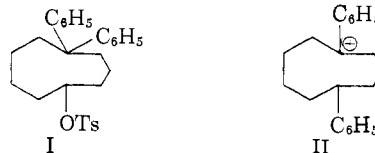
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The *gem*-diphenylazelaoin, 2-hydroxy-6,6-diphenylcyclononane, has been obtained in 35% yield by acyloin cyclization of diethyl δ,δ -diphenylazelaate. The azelaic ester was synthesized from diphenylmethane in five steps (55% yield) *via* dialkylation with γ -bromopropyl ethyl ether followed by a suitable bis-homologation of the di-alkylated intermediate.

In recent years there have been numerous exemplifications of transannular hydride migration in medium size rings.³ Transmigration of alkyl or aryl groups has not, however, been observed to occur. Thus, Prelog and K \ddot{u} ng³ⁱ found that 1,6-dimethyl-1,6-cyclodecanediol did not undergo a transannular pinacol rearrangement to 6,6-dimethylcyclodecanone. Additionally, we observed no prod-

ucts of rearrangement in the acetolysis of 5,5-dimethylcyclononyl tosylate,⁴ a solvolysis which proceeded at half the rate observed for the acetolysis of cyclononyl tosylate.⁵

In view of the fact that there have been no reported studies of reactions of medium size carbocycles possessing *aryl* annular substituents, it was of interest to examine the acetolysis of 5,5-diphenylcyclononyl tosylate (I). In this tosylate a phenyl group is well situated conformationally for 1,5-migration while anchimerically assisting, as a bridged phenonium ion,⁶ in the rate-determining step of the tosylate ionization. The formation of the tertiary benzyl-type carbonium ion II could provide the driving force for the transmigration.



Since a convenient route to the tosylate I required the *gem*-diphenylazelaoin, 2-hydroxy-6,6-di-

(4) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **80**, 630 (1958).

(5) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956); V. Prelog and R. Heck, *Helv. Chim. Acta*, **38**, 1541 (1955).

(6) For numerous examples and references to the literature see D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

(1) For the preceding paper in this series see A. T. Blomquist and F. Jaffe, *THIS JOURNAL*, **81**, 3405 (1959).

(2) This article is an abstract of part of the dissertation presented by C. J. Buck in February, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); (b) A. C. Cope, S. W. Fenton and C. F. Spencer, *THIS JOURNAL*, **74**, 5884 (1952); (c) V. Prelog, K. Schenker and W. K \ddot{u} ng, *Helv. Chim. Acta*, **36**, 471 (1953); (d) K. Schenker and V. Prelog, *ibid.*, **36**, 896 (1953); (e) A. C. Cope and W. N. Baxter, *THIS JOURNAL*, **76**, 279 (1954); (f) V. Prelog, H. J. Urech, A. A. Bothner-By and J. W \ddot{u} rsch, *Helv. Chim. Acta*, **38**, 1095 (1955); (g) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955); (h) V. Prelog and M. Speck, *ibid.*, **38**, 1786 (1955); (i) V. Prelog and W. K \ddot{u} ng, *ibid.*, **39**, 1394 (1956); (j) A. C. Cope, T. A. Liss and G. Wood, *Chemistry & Industry*, 823 (1956); (k) A. C. Cope, H. E. Johnson and J. S. Stephenson, *THIS JOURNAL*, **78**, 5599 (1956); (l) H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957); (m) A. C. Cope and G. W. Wood, *THIS JOURNAL*, **79**, 3885 (1957); (n) A. C. Cope and H. E. Johnson, *ibid.*, **79**, 3889 (1957); (o) A. C. Cope and B. C. Anderson, *ibid.*, **79**, 3892 (1957); (p) A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957); (q) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., *ibid.*, **79**, 3900 (1957); (r) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957).