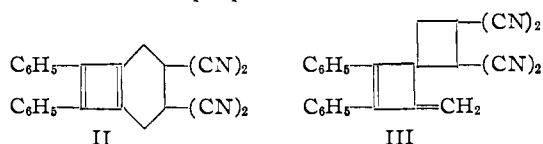
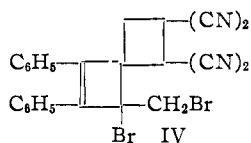


respectively. Only structure III was in accord with all of the observed properties of the adduct.



In the ultraviolet the adduct, in isoöctane, showed  $\lambda_{\max}$  245  $m\mu$  (broad) ( $\log \epsilon$  4.30) and  $\lambda_{\max}$  308  $m\mu$  ( $\log \epsilon$  4.07). The infrared spectrum showed weak absorption at 4.46  $\mu$  ( $-\text{C}\equiv\text{N}$ ), characteristic aromatic absorption and absorption at 5.97, 11.40 and 11.60  $\mu$  characteristic of the methylenecyclobutene system.<sup>4</sup> In carbon tetrachloride at room temperature the adduct absorbed one molar equivalent of bromine to give a crystalline dibromide IV, m.p. 162.5–163°. *Anal.* Calcd. for  $\text{C}_{24}\text{H}_{14}\text{N}_4\text{Br}_2$ : C, 55.62; H, 2.72; N, 10.81; Br, 30.84. Found: C, 55.92; H, 2.92; N, 10.73; Br, 31.07. The infrared and ultraviolet spectra of IV were similar



to those of the tetrabromide of I.<sup>1</sup> IV showed weak absorption at 6.06  $\mu$  in the infrared and  $\lambda_{\max}$  285  $m\mu$  ( $\log \epsilon$  4.25) in the ultraviolet (chloroform solution).

Finally, the nuclear magnetic resonance spectrum of the adduct in hexadeuteroacetone solution shows three peaks approximately in the weight 5:1:1 and at about the correct positions for phenyl hydrogen ( $\text{C}_6\text{H}_5$ ), exomethylenic hydrogen ( $=\text{CH}_2$ ) and saturated ring methylene hydrogen ( $-\text{CH}_2-$ ) respectively.

This unique cycloaddition of tetracyanoethylene to form a four-membered carbon ring under such mild conditions is attributed to the extreme reactivity of the reactants and their refusal to form a stable, isolable cyclobutadiene. Further study of the triene I and related compounds is in progress.

**Acknowledgment.**—Support of this investigation by a Research Grant from the National Science Foundation is gratefully acknowledged. The authors also wish to express their thanks to Dr. T. L. Cairns of the du Pont Co. for supplying a quantity of tetracyanoethylene.

(4) D. E. Applequist and J. D. Roberts, *THIS JOURNAL*, **78**, 4012 (1956).

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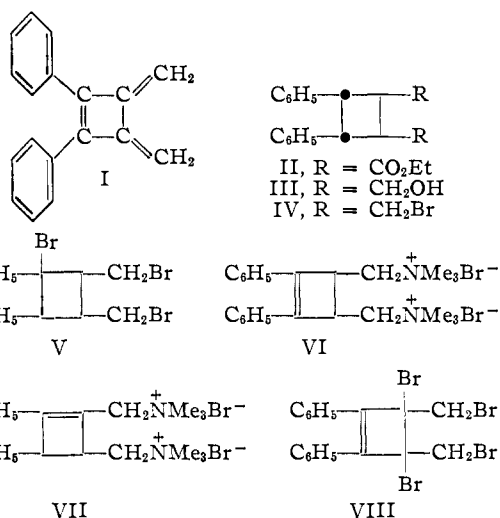
### DIPHENYLDIMETHYLENOCYCLOBUTENE

Sir:

We wish to report the synthesis of diphenyldimethylenecyclobutene (I), the most highly unsaturated four-membered ring hydrocarbon known.<sup>1</sup>

(1) For an interesting theoretical discussion of this system see J. D. Roberts, A. Streitwieser and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952).

It is isoelectronic with the recently reported "Cyclobutadienoquinones."<sup>2</sup>



Diethyl  $\beta$ -truxinate<sup>3</sup> (II) was reduced with lithium aluminum hydride to give the glycol III, m.p. 110–111°. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_2$ : C, 80.56; H, 7.51. Found: C, 80.83; H, 7.23. Treatment of III with phosphorus tribromide gave the dibromide IV, m.p. 95.5–96.5°. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{Br}_2$ : C, 54.85; H, 4.60; Br, 40.55. Found: C, 55.04; H, 4.64; Br, 40.40. IV reacted smoothly with one equivalent of N-bromosuccinimide in refluxing carbon tetrachloride yielding the tribromo compound V, m.p. 105–105.5° (dec). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{17}\text{Br}_3$ : C, 45.70; H, 3.62; Br, 50.68. Found: C, 45.74; H, 3.61; Br, 49.96. Simultaneous elimination and displacement could be brought about by treatment of V with excess trimethylamine at 50°. The bis-quaternary salts, VI and VII, were separated by virtue of their differing solubility in methylene chloride. The more soluble isomer was recrystallized from water to give colorless needles, m.p. 185–187° (dec). *Anal.* Calcd. for  $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Br}_2$ : 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. The less soluble isomer, m.p. 200–202° (dec.), was characterized as its dipicrate, m.p. 228–230° (dec.). *Anal.* Calcd. for  $\text{C}_{36}\text{H}_{38}\text{O}_{14}\text{N}_8$ : C, 53.60; H, 4.75; N, 13.89. Found: C, 53.73; H, 4.61; N, 13.95. Either isomer, when converted to the bis-quaternary hydroxide and subjected to Hofmann degradation at 120–140° (0.5 mm.), yielded the triene I as a colorless crystalline solid. After resublimation at 40° (0.3 mm.), I showed m.p. 44–45°. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{14}$ : C, 93.87; H, 6.13. Found: C, 93.65; H, 6.05. The triene I could be kept at 0° under nitrogen for several days without visible change. However, at room temperature it rapidly turned yellow within a few hours and eventually formed a polymer. In the ultraviolet I (isoöctane soln.) showed the following maxima ( $\log \epsilon$ 's in parentheses): 237  $m\mu$  (4.42); 262  $m\mu$  (4.50); 328  $m\mu$  (4.20). The infrared spectrum revealed

(2) E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955); M. P. Cava and D. R. Napier, *ibid.*, **79**, 3606 (1957).

(3) H. I. Bernstein and W. C. Quimby, *ibid.*, **65**, 1845 (1943).

peaks at 3.29, 5.89 and 11.56  $\mu$  ( $>C=CH_2$ ), at 3.34 and 6.33  $\mu$  ( $C_6H_5^-$ ) and at 6.10  $\mu$  (*cis*- $C_6H_5CR=CRC_6H_5$ ).

Upon quantitative hydrogenation over Adams catalyst I absorbed three equivalents of hydrogen simultaneously. Formaldehyde, isolated as its dimedone derivative, was obtained upon reductive ozonolysis of I. The triene rapidly added two equivalents of bromine at room temperature, giving rise to the tetrabromide VIII, m.p. 118–119° (eff.). *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. VIII in  $CHCl_3$  showed  $\lambda_{max}$  288  $m\mu$  ( $\log \epsilon$  4.29) in the ultraviolet, consistent with a disubstituted *cis*-stilbene chromophore, and weak absorption at 6.08  $\mu$  in the infrared, attributed to the conjugated tetrasubstituted double bond.

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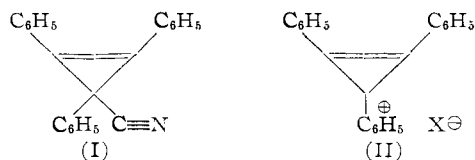
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#### SYNTHESIS OF THE *s*-TRIPHENYLCYCLOPROPENYL CATION

*Sir:*

Much of the interest in the field of non-benzenoid aromatic compounds centers around attempts to verify theoretical predictions that certain conjugated systems will be especially stable, or "aromatic," while others will not. These predictions indicate that, in addition to well-known aromatic systems containing six electrons and more, a three-membered ring containing two electrons, the cyclopropenyl cation, should also be aromatic.<sup>1</sup> We wish to report the first preparation of a derivative of this simplest aromatic ring.

Reaction<sup>2</sup> of diphenylacetylene with phenyldiazoacetonitrile yields 1,2,3-triphenyl-2-cyclopropene carboxylic acid nitrile (I); m.p. 145–146° (calcd. for  $C_{22}H_{15}N$ : C, 90.07; H, 5.15; N, 4.77; mol. wt., 293. Found: C, 90.22; H, 5.43; N, 4.91; mol. wt. (Rast), 286). The infrared spectrum of (I) contains a band at 4.5  $\mu$  ( $C\equiv N$ ) and the ultraviolet spectrum is almost identical with that of 1,2-diphenylcyclopropene-3,3-dicarboxylic ester.<sup>3</sup> The compound is soluble in non-polar solvents such as benzene, and gives no precipitate with ethanolic silver nitrate solution. It is thus covalent.



(1) J. D. Roberts, A. Streitwieser, Jr. and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952).

(2) This is one example of a new method for synthesis of cyclopropenes, to be reported shortly.

(3) S. F. Darling and E. W. Spanagel, *THIS JOURNAL*, **53**, 1117 (1931). We have also prepared this compound by our new method (R. Breslow and R. Winter, *Am. Chem. Soc. Meeting Abstracts*, New York, 1957, in press).

On treatment with boron trifluoride etherate and a trace of water,<sup>4</sup> however, it is converted to a white crystalline solid, m.p. 300° (d.). This new substance is insoluble in ether, chloroform or benzene, but can be dissolved in methanol and subsequently recovered. It is reconverted by potassium cyanide to (I). The analysis of the compound indicates that it is 1,2,3-triphenylcyclopropenyl fluoborate (II,  $X=BF_4$ ) contaminated with the hydroxyfluoroborate (II,  $X=BF_3OH$ ); (calcd. for  $C_{21}H_{15}BF_4$ : C, 71.21; H, 4.27; F, 21.46. Calcd. for  $C_{21}H_{15}BF_3O$ : C, 71.62; H, 4.58; F, 16.18. Found: C, 71.03, 71.18; H, 4.56, 4.38; F, 17.80, 18.31).

Consequently, the fluoroborate has been converted to a picrate, m.p. 195–196° (II,  $X=C_6H_2N_3O_7$ ); (Calcd. for  $C_{27}H_{17}N_3O_7$ : C, 65.45; H, 3.46; N, 8.48. Found: C, 65.50, 65.67; H, 3.55, 3.59; N, 8.59, 8.71). This compound is bright yellow, indicating the presence of picrate ion, and is insoluble in benzene or ether. It is quite soluble in ethanol or methanol, however. While it can be recovered from these solutions, prolonged standing leads to some decomposition.

Thus the *s*-triphenylcyclopropenyl cation is relatively stable, due of course in part to conjugation of the three phenyl rings with the positive charge. That it has some reactivity, as evidenced by the slow decomposition in alcohols, may be in part due to the strain resulting from the presence of three trigonal carbons within a three membered ring.

**Acknowledgment.**—The author wishes to acknowledge generous financial support by the du Pont Company.

(4) This procedure is based on a known method for preparing the cycloheptatrienyl cation (M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 2026 (1956)).

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#### CRYSTALLOGRAPHY OF OCTACALCIUM PHOSPHATE

*Sir:*

Although octacalcium phosphate (OCP) was described long ago,<sup>1,2</sup> its crystallography is obscure. Its relationship to hydroxyapatite is confused,<sup>3</sup> and even its existence as a "discrete" compound was questioned<sup>4</sup> recently. An awareness of the possible significance of OCP in agriculture<sup>5</sup> and in biochemical processes prompted a study of its crystallography.

Very thin blades of OCP up to 250 $\mu$  long were prepared by slow hydrolysis of  $CaHPO_4 \cdot 2H_2O$  in a quiescent 0.5 *M* solution of sodium acetate at 40°. The acetate solution was renewed when its pH approached 6.1. The crystals closely approximated the formula  $Ca_4H(PO_4)_3 \cdot 3H_2O$  reported by Bjerrum,<sup>6</sup> the average composition of three preparations being  $Ca_{3.99}H_{1.02}(PO_4)_3 \cdot 2.88H_2O$ .

(1) J. J. Berzelius, *Ann.*, **53**, 286 (1845).

(2) R. Warington, *J. Chem. Soc.*, **19**, 296 (1886).

(3) P. W. Arnold, *Trans. Faraday Soc.*, **46**, 1061 (1950).

(4) D. Carlström, *Acta Radiol.*, Supplement 121 (1955).

(5) J. R. Lehr and W. E. Brown, *Soil Sci. Soc. Am. Proc.*, in press.

(6) N. Bjerrum, "Selected Papers," Einar Munksgaard, Copenhagen, 1949, p. 245.