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*-$C_6H_5CR{=}CRC_6H_5$).

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 λ_{max} 288 mμ (log ϵ 4.29) in the ultraviolet, consistent with a disubstituted *cis*-stilbene chromophore, and weak absorption at 6.08 μ in the infrared, attributed to the conjugated tetrasubstituted double bond.

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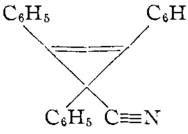
RECEIVED AUGUST 6, 1957

SYNTHESIS OF THE *s*-TRIPHENYLCYCLOPROPENYL CATION

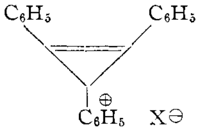
Sir:

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.[1] We wish to report the first preparation of a derivative of this simplest aromatic ring.

Reaction[2] 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 μ ($C\equiv N$) and the ultraviolet spectrum is almost identical with that of 1,2-diphenylcyclopropene-3,3-dicarboxylic ester.[3] The compound is soluble in non-polar solvents such as benzene, and gives no precipitate with ethanolic silver nitrate solution. It is thus covalent.



(I)



(II)

On treatment with boron trifluoride etherate and a trace of water,[4] 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 $C_{21}H_{16}BF_3O$: 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.

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(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).

(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,[1,2] its crystallography is obscure. Its relationship to hydroxyapatite is confused,[3] and even its existence as a "discrete" compound was questioned[4] recently. An awareness of the possible significance of OCP in agriculture[5] and in biochemical processes prompted a study of its crystallography.

Very thin blades of OCP up to 250μ 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 *p*H approached 6.1. The crystals closely approximated the formula $Ca_4H(PO_4)_3{\cdot}3H_2O$ reported by Bjerrum,[6] the average composition of three preparations being $Ca_{3.99}H_{1.02}(PO_4)_3{\cdot}2.88H_2O$.

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

(2) R. Warington, *J. Chem. Soc.*, **19**, 296 (1866).

(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.