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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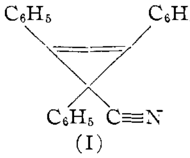
RECEIVED AUGUST 6, 1957

SYNTHESIS OF THE *s*-TRIPHENYLCYCLOPROPENYL CATION

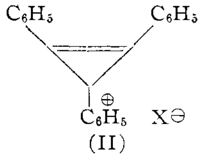
Sir:

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 (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.

OCP has distinctive X-ray and optical properties. It contributed the "additional" lines in Carlström's[3] X-ray pattern for hydroxyapatite. Single-crystal Weissenberg measurements on OCP gave the lattice constants $a = 19.7$ Å., $b = 9.59$ Å., $c = 6.87$ Å., $\alpha \cong \beta = 90.7°$ and $\gamma = 71.8°$. Corresponding hydroxyapatite constants,[7] $2a = 18.84$ Å., $a' = 9.42$ Å., $c = 6.885$ Å., $\alpha = \alpha' = 90°$ and $\gamma = 60°$, resemble closely those of OCP in the values of b, c and α, which lie in the plane of the OCP plates.

Dehydration of OCP at temperatures below 180° shifted the 18.4-Å. line progressively to lower spacings. The line disappeared upon elimination of about two-thirds of the hydrate water. The final pattern was apatitic, intermediate in sharpness between those of tooth enamel and bone. At 220°, $CaHPO_4$ appeared also. At 1000°, the products were β-$Ca_3(PO_4)_2$ and β-$Ca_2P_2O_7$. Boiling water decomposed OCP into an apatite approaching hydroxyapatite in composition, along with a variable amount of $CaHPO_4$. Both thermal and hydrothermal treatments sometimes yielded apatitic single-crystal pseudomorphs after OCP, the c-axes being parallel to the c of the original OCP.

Certainly a distinct crystalline compound, OCP probably has a layer-type structure, the layers perhaps closely resembling those conceivable in hydroxyapatite parallel to (10.0) but separated by water molecules. OCP is not, however, isostructural with hydroxyapatite. The two probably do not form true solid solutions but apparently form interlayered mixtures. Within the layers, the unit-cell constants of hydroxyapatite and OCP resemble those of $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$, $CaClH_2PO_4 \cdot H_2O$ and $Ca_2H_7K(PO)_4 \cdot 2H_2O$.[8] The known ion parameters[9,10] are also similar. Marked stability of $Ca-PO_4$ layers is indicated. Apatites perhaps can accommodate water, carbonates and other materials non-isomorphously between layers parallel to (10.0), thus accounting for carbonation, hydration and "internal surface"[11] of apatites.

The "apatite" obtained by dehydration of OCP apparently is the most acidic that has been prepared and may be another defect apatite.[12] Precipitated calcium phosphates considered as hydroxyapatite by Watson and Robinson[13] have the morphology of either OCP or apatite pseudomorphs after OCP. The morphology of tooth and bone crystallites, as seen in their micrographs, strongly indicates that OCP is involved in the formation of these tissues, probably as a precursor that alters to apatite in place. Determinations of the crystal structures of OCP and acidic apatite thus appear requisite to an understanding of the formation and chemical properties of skeletal tissues.

Our confirmation of the presence of OCP in dental calculus[14] (apparently as a higher hydrate), along with $CaHPO_4 \cdot 2H_2O$ and an apatite, suggests that the transitions $CaHPO_4 \cdot 2H_2O \rightarrow OCP \rightarrow$ apatite occur in calculus.

(7) W. Perdok, *Schweiz. Monatschr. Zahnheilkunde*, **62**, 249 (1952).

(8) Unpublished work by TVA.

(9) G. MacLennan and C. A. Beevers, *Acta Cryst.*, **9**, 187 (1956).

(10) C. A. Beevers and B. Raistrick, *Nature* (London), **173**, 542 (1954).

(11) S. B. Hendricks and W. L. Hill, *Proc. Natl. Acad. Sci. U. S.*, **36**, 731 (1950).

(12) A. S. Posner and A. Perloff, *J. Research Natl. Bur. Standards*, **58**, 279 (1957).

(13) M. L. Watson and R. A. Robinson, *Am. J. Anat.*, **93**, 25 (1953).

(14) Segerman, quoted in ref. 12.

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RECEIVED AUGUST 19, 1957

PAUCIDISPERSE DEOXYRIBONUCLEIC ACID AND ITS USE IN THE STUDY OF GENETIC DETERMINANTS

Sir:

Deoxyribonucleic acid (DNA) prepared by current methods is heterogeneous with respect to both size and shape. We wish to present the results of a new technique which leads to low molecular weight, essentially monodisperse, biologically active DNA.

DNA solutions are passed at various pressures through an all-glass atomizer.[1] The molecular weight of the DNA is decreased and the distribution of sedimentation coefficients is narrowed to near monodispersity. The figure shows the sedimentation distributions[2] of two samples (II, III)

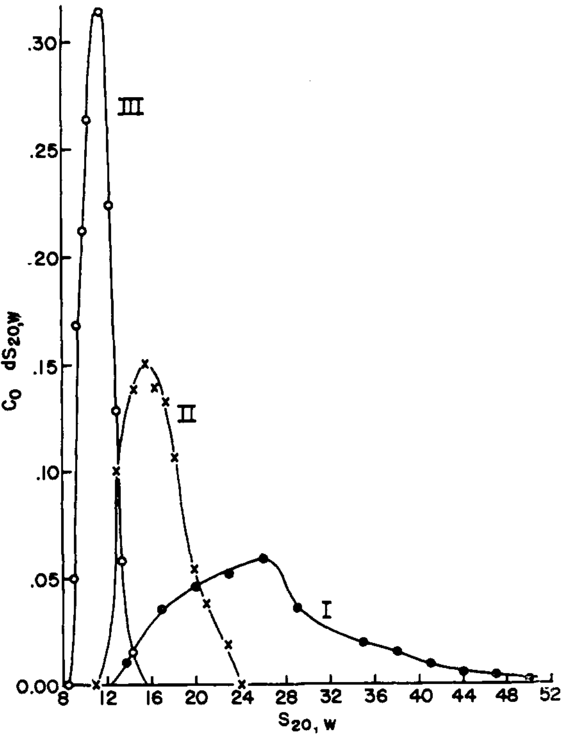

Fig. 1.—Curve I, original DNA; curve II, DNA sprayed at an intermediate rate (liquid flow, 0.1 cc./sec., air pressure, 6.6 cm.): curve III, DNA sprayed at a higher rate (see table).

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(1) A stream of solution issuing from a capillary is allowed to pass through a cone of air formed from the annular space surrounding the outlet of the capillary.

(2) V. N. Schumaker and H. K. Schachman, *Biochim. Biophys. Acta*, **23**, 628 (1956).