

the position of a carbon atom, as calculated by the least-squares program ORFLS, is 0.04 Å., giving a standard error in a C-C bond length of about 0.06 Å. This high value, although not exceptional for a molecule of this complexity, is disappointing since it means that little significance attaches to the actual values found for the bond lengths in the cyclobutenium moiety. The observed values, however, do coincide closely with what might be expected in such an arrangement. Further refinement, now in progress, using anisotropic thermal parameters may well allow a more precise definition of the geometry of the molecule. At the present stage it is better to consider only the over-all structure of the molecule as significant.

The carbon atoms of the phenyl group A and the attached carbon atom of the four-membered ring lie in a plane given by the equation

$$0.6579X - 0.2730Y - 0.7018Z - 0.8697 = 0$$

Those of group B and the attached carbon atom lie in a plane of equation

$$0.6601X - 0.2545Y - 0.7067Z - 0.9817 = 0$$

effectively parallel to the first but separated from it by 0.11 Å. The phenyl group C and the corresponding carbon atom lie in a plane inclined at 83° to the previous two. The 3-chloro atom lies some 0.12 Å. from this plane. The corresponding group D forms a plane inclined at 57° to planes A and B and at 26° to ring C. The average deviation of atoms from these mean planes is 0.03 Å., the greatest 0.05 Å. There is no significant distortion of any of the phenyl groups from regular planar hexagons of side 1.39 Å.

The molecular shape implies that the delocalization of the positive charge in the cation takes place primarily over the two rings A and B. The tilt of ring D is that commonly found where overcrowding of phenyl rings is avoided by free rotation. The inclination of ring C is remarkable in that no free rotation has occurred about the single C-C bond linking it to the four-membered ring. It may be that this is dictated by the crystal packing or there may be some electronic interaction between the chlorine atom and the ring.

All the angles in the cyclobutenium ring are reduced from strain-free values by equal amounts. The bonds from the ring to the phenyl groups A, B, and D effectively bisect the external angles (C-C-C = 134 ± 7°).

The pentachlorostannate anion is in the form of a regular trigonal bipyramid. The Sn-Cl bond lengths are, in-plane, 2.30, 2.40, and 2.38 Å., perpendicular, 2.37 and 2.39 Å. ($\sigma = 0.025$ Å.). The in-plane Cl-Sn-Cl angles are 114, 120, and 126°. The other angles lie in the range 90 ± 4°.

All intermolecular contacts are between anions and cations. The shortest intermolecular approach is between a chlorine atom of the SnCl_5^- anion and the 3-chloro atom where the separation is only 3.67 Å. This, however, is not significantly different from the sum of the van der Waals radii of the atoms concerned. The shortest C-Cl approach is 3.61 Å.

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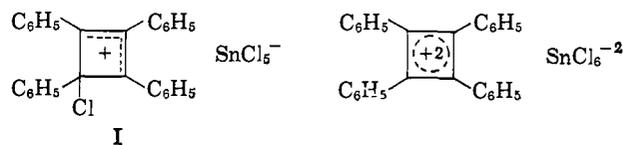
ROBERT F. BRYAN

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Tetraphenylcyclobutenium Difluoroborate¹

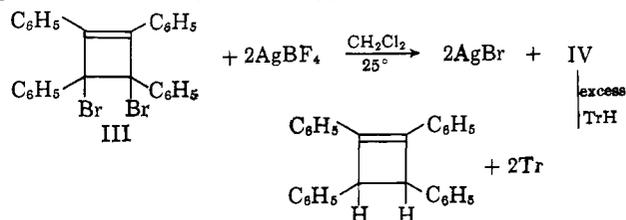
Sir:

The recent X-ray investigation by Bryan² leaves no doubt that the crystalline product obtained from 3,4-dibromotetraphenylcyclobutene (III) and tin tetrachloride is in fact the chloromonocation pentachlorostannate (I) and not the dication hexachlorostannate (II).³ The possibility that solvation forces, absent

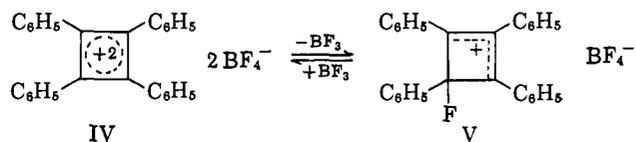


in the solid state, could be the decisive factor in the formation of the potential Hückel aromatic system II, coupled with the difficulties in clearly discriminating between penta- and hexacoordinate chlorostannate, led us to investigate fluoroborate as the stabilizing anion.

Reaction of III in methylene chloride solution with two moles of silver fluoroborate affords *two* moles of silver bromide (97%, >95% pure by X-ray) and a deep red solution (IV) which on treatment with excess tropilidene (TrH) yields tropylium fluoroborate (80%



of 2 equiv.) and tetraphenylcyclobutene³ (70%). It is clear that both bromines have been displaced by fluoroborate and the transfer of hydride from two moles of tropilidene proves the absence of skeletal rearrangement and is consistent with the presence of the dication (IV).⁴ However, this chemical evidence does not rule out the presence of the monofluorocation (V), formed at the expense of IV. The formation of V implies that IV is an exceedingly energetic species with a pK_R -comparable to that of boron trifluoride, and in view of



the previous report that 3,4-dichlorotetramethylcyclobutene forms only the monocation in solution⁵ and the present finding of Bryan,² it becomes obligatory to clearly demonstrate that dication IV is the major species present.

Experimental access to such a demonstration is available from the F^{19} n.m.r. spectrum of IV.⁶ A methylene chloride solution of IV exhibits one singlet at +70.9 p.p.m. (relative to external CF_3CCOH) and

(1) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).

(3) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(4) It has been established that hydride exchange with TrH occurs only with fully ionized carbonium ions, and we have verified this for the case of III, which undergoes no detectable exchange with TrH in CH_2Cl_2 solution even after 3 days. However, structural evidence based on this hydride exchange reaction with the chlorostannate carbonium ion, which also forms cyclobutene in good yield,³ becomes ambiguous inasmuch as the formation of (Tr)₂⁺ SnCl_6^- from I requires the liberation of a mole of SnCl_4 .

(5) T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

(6) We are greatly indebted to Dr. E. B. Baker, Physical Research Lab., The Dow Chemical Company, Midland, Michigan, for the F^{19} spectra.

integration with the aid of an internal standard reveals the presence of 8.0 ± 0.5 fluorines. The position of this peak is in complete accord with that expected for the fluoroborate anion: thus, triphenylmethyl fluoroborate in methylene chloride appears at $+71.7$ p.p.m. and aqueous fluoroboric acid is at 71.3 p.p.m.⁷

For this data to be consistent with the presence of V as the major species, a rapid time-averaged exchange of the ring fluorine, boron trifluoride, and fluoroborate anion is required. Since the boron trifluoride resonance is found at $+47.8$ p.p.m. in methylene chloride, the fortuitous appearance of the exchange-averaged resonance at the exact chemical shift of authentic fluoroborate dictates that the ring fluorine of V, in the absence of exchange, appear at $+140$ p.p.m., a region in which apparently only aliphatic primary fluorine has been observed.⁸ The absence of $F^{19}-B^{11}$ splitting⁹ in the spectrum of IV could be interpreted as evidence for the presence of exchange averaging. However, this splitting is also absent in the trityl fluoroborate spectrum in which rapid equilibration of chemically different fluorines (as required for V) does not occur. At low temperatures the peak in question does broaden, perhaps due to a restoration of the $F^{19}-B^{11}$ splitting.

It now appears that differentiation between mono- and dication, as for example I and II, by its proton n.m.r. spectrum cannot be accomplished on an *a priori* basis, and details of these investigations will be reported in due course.

Acknowledgment.—We are particularly indebted to Dr. V. R. Sandel for many helpful discussions.

(7) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(8) W. D. Phillips, "Determinations of Organic Structures by Physical Methods," Academic Press, New York, N. Y., 1962, p. 406.

(9) $F^{19}-B^{11}$ splitting of the BF_4^- resonance into a poorly resolved quartet has been observed in a concentrated aqueous solution of $NaBF_4$ by R. D. Chambers, *et al.*, *Can. J. Chem.*, **39**, 258 (1961).

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Strained Systems. I. The Tricyclo[1.1.1.0^{4,5}]pentane System

Sir:

It is well known that the photolysis of an α -diazomethyl ketone effects a reaction analogous to the Wolff rearrangement.¹ We have found, however, that an α -ketocarbene generated by ultraviolet irradiation undergoes an intramolecular addition to a double bond at a greater rate than the rearrangement.² Thus, the photolysis of 1,2-diphenyl-3-diazomethylketocyclopropene (I) has led to the formation of a hitherto unknown ring system. We now wish to report the synthesis and properties of this extremely strained tricyclo[1.1.1.0^{4,5}]pentane system.

Compound I, m.p. 115° dec., was prepared from the corresponding acid chloride, m.p. $101-102^\circ$. A 0.5% solution of I in tetrahydrofuran was irradiated at room temperature with a Hanovia 450-w. mercury lamp, using a Pyrex filter.^{3,4} Evolution of nitrogen sub-

(1) P. de Mayo, "Advances in Organic Chemistry, Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 407. For comparison with the silver-catalyzed rearrangement, see K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **78**, 1640 (1956).

(2) Addition of an α -ketocarbene to a double bond is also effected with copper-catalyzed thermal decomposition of the diazomethyl ketone. For instance, see G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961). However, in cases where the products are thermally unstable, this method is not applicable.

(3) Treatment of I with silver benzoate in triethylamine effected the Wolff rearrangement and provided the methyl ester of the homologated acid in good yield.

(4) The photolysis of 1,2-di-n-propyl-3-diazomethylketocyclopropene provided a ketone which corresponds to II. The n.m.r. spectrum of this

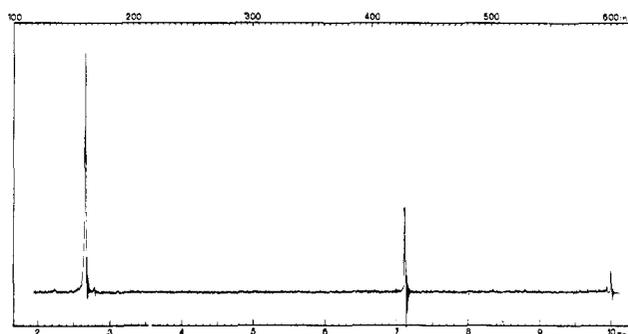


Fig. 1.—The n.m.r. spectrum of II.

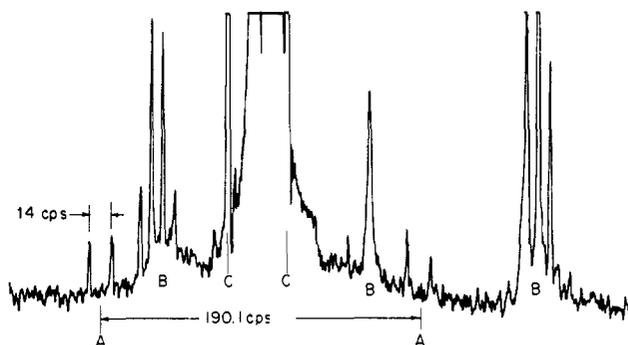
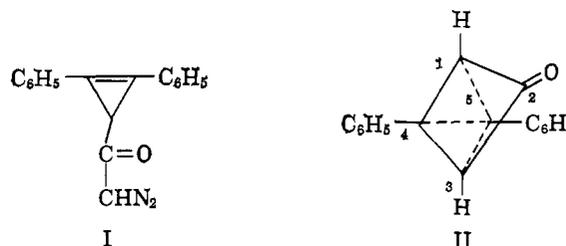


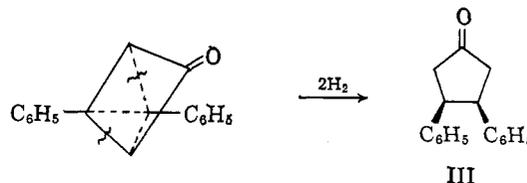
Fig. 2.—The n.m.r. spectrum of the ^{13}C satellite of II (A); added ethanol (B); spinning side bands (C).

sided within 2 hr. and silicic acid chromatography of the photolysate easily separated a new ketone (II), m.p. $139-140^\circ$ dec. (*Anal.* Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21; mol. wt., 232. Found: C, 87.88; H, 5.39; mol. wt., 230 (thermoelectric osmometer)).



While the infrared spectrum indicated the presence of a four-membered ketone (1785 cm^{-1}), the n.m.r. spectrum in $CDCl_3$ (Fig. 1) showed two equivalent aliphatic protons at 7.12τ and a phenyl absorption at 2.65τ (10 protons). These analytical and spectral results are in complete agreement with the structure shown in II.

Catalytic hydrogenation of II proceeded with the uptake of two moles of hydrogen and provided in excellent yield *cis*-3,4-diphenylcyclopentanone (III),⁵ m.p. $106-107^\circ$, identified by direct comparison with an authentic sample. Since the bicyclobutane system is



known to undergo hydrogenolysis,⁶ the formation of di-n-propyl derivative showed a singlet (2 protons) at 8.13τ in addition to a typical n-propyl absorption. This experiment was carried out by Mr. N. T. Castellucci.

(5) D. Y. Curtin, *et al.*, *J. Am. Chem. Soc.*, **83**, 4838 (1961), and references cited therein.

(6) K. B. Wiberg and R. P. Ciula, *ibid.*, **81**, 5261 (1959); J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963). The course of hydrogenolysis of II is somewhat different from those of 1-carboethoxybicyclo-