a drying tube filled with magnesium perchlorate, then into a prefluorinated metal vacuum line, and frozen into a cold trap at $-195°$. When the trap was warmed to $-78°$, it was demonstrated that the radon moved readily under vacuum into other parts of the line which were cooled to $-195°$. The position of the radon was determined by counting the 1.8 Mev. gamma activity of the daughter Bi^{214}. The Bi^{214} ($T_{1/2}$ = 19.7 min.), following Pb^{214} ($T_{1/2}$ = 26.8 min.), grew into equilibrium with the radon wherever it appeared and decayed where it disappeared, within several hours. The measurements were made with a 400-channel pulse height analyzer and two sodium iodide scintillation detectors, shielded by lead bricks.

In the first experiment in which the fluoride was prepared, a 5.1 microcurie amount of radon was condensed into a 5 cc. nickel reaction tube, fluorine was added to a pressure of 300 mm. and the mixture was heated to 400° for 30 minutes. The tube was cooled to $-78°$, and the excess fluorine was pumped off through a trap at $-195°$. It was found that a marked reduction in the volatility of the radon had occurred. The radon remained fixed in the tube, in a vacuum of 2×10^{-6} mm., when warmed in slow stages to 150°. At 230 to 250°, part of the radon moved out of the tube and condensed in the exit valve, which was at approximately 100°.

To ascertain whether the behavior of the trace radon was the same in the presence of macroscopic amounts of carrier, a mixture of xenon and radon next was fluorinated. A new 7-cc. nickel vessel, provided with a capillary inlet tube, was charged with 110 mm. partial pressure of xenon. 87 microcuries of radon, and 1200 mm. partial pressure of fluorine and heated to 400° for 25 minutes. The vessel was cooled to $-78°$ while the excess fluorine was pumped off, then was warmed to 50° to allow the xenon fluoride formed to sublime under vacuum into a trap at $-195°$. The less volatile radon fluoride remained behind. When the vessel was heated gradually to 250°, the radon fluoride moved into the cooler section of capillary tubing.

We have found that radon alone, when heated to 400° in a nickel vessel, shows no evidence of reaction with the walls. When the vessel is cooled to room temperature or to $-78°$, the radon can be distilled as usual into a trap at $-195°$. In this respect our results are in agreement with the very early work of Rutherford and Soddy[4] and of Ramsay and Soddy,[5] who demonstrated that radon does not react with metals and a large number of other reagents.

The composition of the radon fluoride has not yet been determined. Attempts are being made to introduce samples of the fluoride into a time-of-flight mass spectrometer for stoichiometric analysis.

The fluoride can be reduced with hydrogen to quantitatively recover elemental radon. At 200° the compound appears to be stable in hydrogen, but at 500° and a hydrogen pressure of 800 mm. it is completely reduced within 15 minutes.

The tracer quantities of radon fluoride prepared thus far have shown no evidence of radiation de-

composition from alpha particle emission. Samples have been stored for several days at room temperature without evolving any measurable amounts of elemental radon. The compound has been present in such dilute form on the inner surfaces of the container vessels that most of the energy of the alpha particles has been absorbed by the metal walls rather than by the compound. The radiation decomposition may be significant when larger amounts of the compound are prepared.

We wish to express our deep appreciation to Dr. W. M. Manning, Director of the Chemistry Division, for encouraging us to undertake this research and for his continued enthusiastic support. We also wish to thank Dr. J. E. Gindler for supplying the radium chloride solution.

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TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. V.[1] THE TETRAPHENYLCYCLOBUTENIUM DICATION

Sir:

The isolation of true carbonium-ion salts has been limited mainly to the monocations derived from polyarylmethanes and those singly charged species incorporated in "Hückel aromatic" systems. We wish now to report the first example of a stable, crystalline dicarbonium-ion salt, formally bearing adjacent positive charges, whose stability derives from an unusual combination of the above mentioned systems.

Bromination of tetraphenylcyclobutadiene-nickel bromide complex[2] with excess pyridinium hydrobromide perbromide yields (65%) 3,4-dibromotetraphenylcyclobutene[3] (II), (m.p. 173-174°; calcd. for $C_{28}H_{20}Br_2$: C, 65.1; H, 3.9; Br, 31.0; mol. wt., 517.2. Found. C, 64.9; H, 3.9; Br, 31.0; mol. wt. (osmometer) 540), whose structure is assigned on the basis of its spectral ($\nu_{Raman}^{C=C}$ 1627 cm.$^{-1}$(s), $\lambda_{max}^{CH_2Cl_2}$ 305 mμ (20.000)) and chemical properties.[4]

In contrast to the inert character of the vinylic bromine atoms of its valence isomer, cis,cis-1,4-dibromotetraphenylbutadiene,[2] the allylic bromines of II are extremely labile and give an instantaneous precipitate with alcoholic silver nitrate. In common with the trityl halides, II is un-ionized in solvents of moderate polarity,[5] but in liquid sulfur dioxide II dissolves sparingly to yield a red solution from which unchanged, colorless II is recovered on evaporation. Dissociation in anhydrous acids occurs readily, the strength of the acid determining whether one or both bromines undergo ionization. In hot glacial acetic or formic acid, solution occurs with evolution of one mole of hydrogen bromide,

(1) Part IV, H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962).

(2) H. H. Freedman, *ibid.*, **83**, 2194 (1961).

(3) Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 26-O.

(4) II undergoes a number of remarkable chemical transformations some of which have been briefly summarized in the abstract cited in reference 3. Further details will be given in a forthcoming publication.

(5) This is indicated by the identity of the ultraviolet spectrum of II in tetrahydrofuran and in n-hexane.

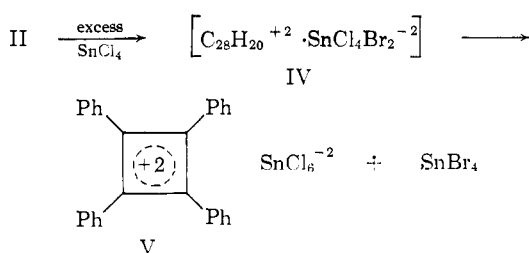(4) E. Rutherford and F. Soddy, *Phil. Mag.*, [6] **4**, 580 (1902).

(5) W. Ramsay and F. Soddy, *Proc. Roy. Soc.* (London), **72**, 204 (1903).

and addition of water to the colorless solution affords (80%) 1-bromo-1,2,3-triphenyl-3-benzoyl-propene-1 (III), (m.p. 143–145°; calcd. for $C_{28}H_{21}BrO$: C, 74.2; H, 4.7; Br, 17.6. Found: C, 73.9; H, 4.7; Br, 17.8: $\lambda_{max}^{EtOH} \sim 245$ mμ (shoulder): $\lambda_{max}^{CCl_4}$ 5.92μ; n.m.r. (CCl$_4$): 1 proton at $\delta = 5.57$, 20 phenyl protons at $\delta = 6.7$–7.5).

II

III
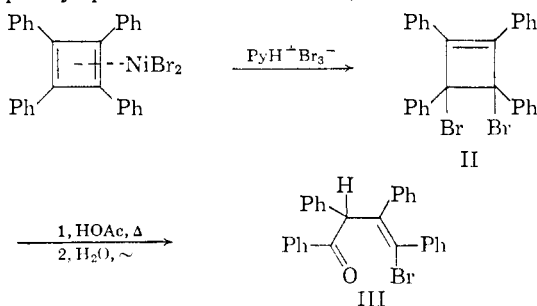
Solution of II in cold 96% H_2SO_4 occurs with evolution of more than one mole of hydrogen bromide[6] and results in an intense red solution ($\lambda_{max}^{96\% H_2SO_4}$ 482 mμ (50,000)) which on hydrolysis gives none of III, but yields bromine-free products characteristic of the dication.

Treatment of one mole of II in dry benzene or methylene chloride with two moles of an anhydrous, monovalent silver salt (perchlorate, hexafluoro-antimonate, tetrafluoroborate, etc.) rapidly causes precipitation of two moles of silver bromide. Though this evidence strongly supports the formation of a dication in solution, the isolation of a crystalline solid of known composition by this technique has eluded us to date.[7] The dicarbonium ion was obtained by the treatment of an anhydrous benzene solution of II with excess tin tetrachloride; the resulting brick-red, crystalline solid, obtained in 75% yield, proved to be substantially bromine-free (calcd. for $C_{28}H_{20}Cl_8Sn$: C, 48.9; H, 2.9; Cl, 30.9; Sn, 17.3; Br, 0.0. Found: C, 49.1; H, 3.3; Cl, 30.1; Sn, 17.0; Br, 0.4) and must have arisen by ionization of *both* bromines and then disproportionation of the unstable dibromotetrachlorostannate intermediate IV in the presence of excess tin tetrachloride, yielding the dication, 1,2,3,4-tetraphenyl-cyclobutenium hexachlorostannate (V).

$$\text{II} \xrightarrow[\text{SnCl}_4]{\text{excess}} \left[C_{28}H_{20}^{+2} \cdot SnCl_4Br_2^{-2}\right] \longrightarrow$$

IV

$$SnCl_6^{-2} \;+\; SnBr_4$$

V

Hart[8] has proved elegantly the existence of stable dicarbonium ions in solution, but a crystalline

(6) Attempts to measure the evolved HBr led to irreproducible results, perhaps due to the slow oxidation of the HBr by the acid.

(7) Subsequent investigation of the solid product derived from the reaction of II with two moles of AgClO$_4$ suggests that it is a monocation, resulting from a disproportionation involving the second mole of perchlorate.

(8) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, (a) **80**, 5894 (1958); (b) **82**, 5419 (1960); (c) **82**, 4460 (1961). It is pertinent that Prof. Hart has noted that a cyclobutene ring with two positive charges may be stable due to its incipient aromaticity (ref. (b) above).

species has not been reported hitherto and it is therefore of importance to rule out the possibility that our product may be the isomeric monocation, 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate (Va), even though very few examples of stable, crystalline pentachlorostannates (in contrast to hexachlorostannates) are known.


Va
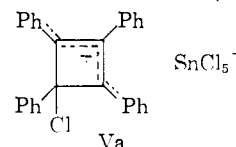
The spectroscopic properties of the salt support the Huckel-aromatic structure V, rather than the allylic monocation, Va. Delocalization of the positive charges of V must occur with all four of the phenyl groups to an equal extent, whereas the single positive charge of Va can be delocalized only over two of the four available phenyls. This difference should affect strongly its spectroscopic properties and, to a first approximation, equivalent distribution of charge over all four phenyls should yield spectra analogous to those of the trityl salts in which ring equivalence has been demonstrated.[9] This is apparent from the ultraviolet, infrared, and, in particular, the n.m.r. spectrum of the dicarbonium ion which closely resembles that of the trityl cation[10] and shows no absorption in the usual phenyl range of $\delta = 6.5$–7.5, but only the expected low field absorption of $\delta > 7.5$ is observed.[11]

The absence of skeletal rearrangement in V was demonstrated unambiguously by the hydride exchange reaction of V with tropylidene, according to the method of Dauben.[12] Addition of excess tropylidene to 555 mg. of V in methylene chloride gave an immediate precipitate of ditropylium hexachlorostannate (433 mg. 100%) [$\lambda^{2N\ HCl}$ 277 mμ (max.), 259 mμ (min.); lit.,[13] $\lambda^{2N\ HCl}$ 276–277 mμ

(9) R. Dehl, W. R. Vaughan and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959).

(10) R. B. Moodie, T. M. Connor and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

(11) It has been pointed out by Prof. R. Breslow that if the equilibration between Vb and Vc were rapid compared to the time scale of the n.m.r. experiment, then this would account for the observed spectrum. Though halide tautomerism of this type is without precedent

Vb   Vc

Vd   Ve
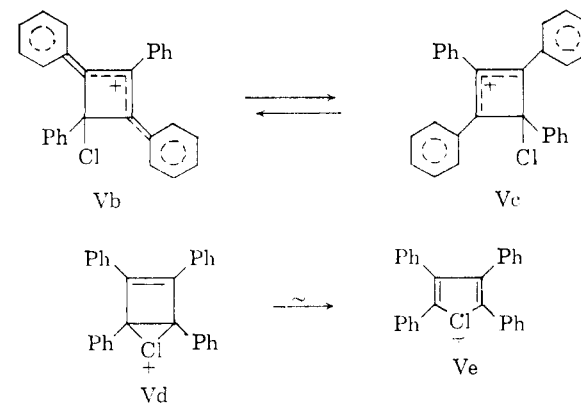
and would be of unusual interest *per se*, it seems likely that such an equilibrium mixture would tend to stabilize as the bicyclic chloronium-chloride Vd, which in turn would rapidly revert to its strain-free valence tautomer, Ve; this latter structure is ruled out by the chemistry of our dication.

(12) H. J. Dauben, Jr., *et al.*, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(max.) 258-259 mμ (min.)] and from the filtrate there was obtained 193 mg. (67%) of 1,2,3,4-tetraphenylcyclobutene (VI) (calcd. for $C_{28}H_{22}$: C, 93.8; H, 6.2. Found: C, 93.6; H, 6.3), identified by its spectral properties (λ_{max}^{EtOH} 303 mμ (19,500) n.m.r. [CCl₄]: 2 proton singlet at δ = 4.62, 10 Ph protons at δ = 6.78, 10 Ph protons at δ = 7.0–7.5; νRaman 1635 cm.⁻¹) and by its conversion to II on bromination.[14]

The solid dication V is stable to light and dry air but reacts instantly when its solution is exposed to water or other weak nucleophiles. Paralleling the known chemistry of tropylium, aqueous solvolysis of V yields a mixture of products including tetraphenylfuran, cis-dibenzoylstilbene and didesyl.[15]

(13) D. Bryce-Smith and N. A. Perkins, Chem. and Ind., 1022 (1959).

(14) The unambiguous proof of structure of VI reopens the question of the identity of the hydrocarbon C₂₈H₂₂, m.p. 122–123°, obtained from the hydrogenation of the tetraphenylcyclobutadiene-nickel bromide complex.² The similarity of the δ values for the nonphenyl protons of VI and the 122° hydrocarbon (two singlets at δ = 4.10 and 5.97)² suggests certain environmental similarities for these protons, but the non-identity of the proton singlet of VI (δ = 4.62) to either of these latter bands makes untenable our previous conclusion that the 122° hydrocarbon is a mixture of the cis and trans isomers of VI. (However, the importance of the proof of structure of the 122° hydrocarbon as evidence for the presence of a four-membered ring in the tetraphenylcyclobutadiene-nickel bromide complex, became an academic one in the light of the preparation of II).

(15) The fact that tropylium¹⁶ and cyclopropenium¹⁷ salts can be recovered from their acidified, aqueous solutions, whereas the dication V cannot be so recovered, reflects the reversibility of the solvolysis of the former two species (eq. [1]) and the nonreversibility of the latter (eq. [2]). The formation of tetraphenylfuran is the expected intra-

$$R^+ + 2H_2O \rightleftharpoons ROH + H_3O^+ \qquad (1)$$

(2)
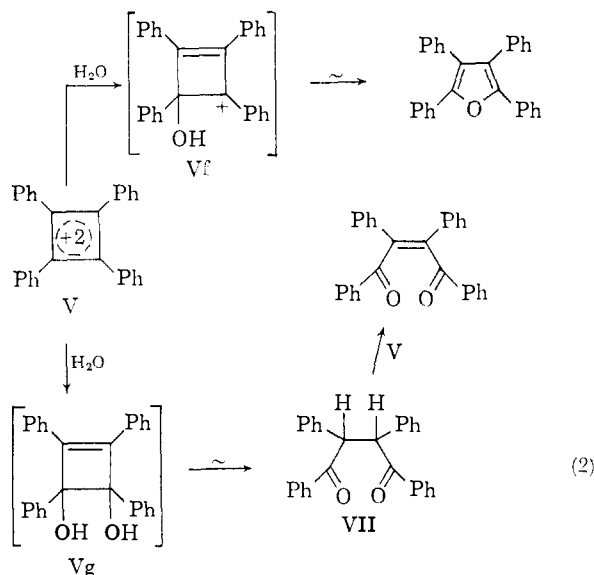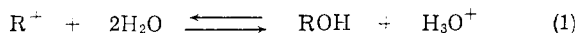
molecular solvolysis product of the mono-hydroxy carbonium ion Vf, analogous to the formation of ditropyl ether by the intermolecular attack of tropylium on the initially formed tropyl alcohol.¹⁸ It is also conceivable that the unstable glycol Vg is also formed which gives rise by tautomeric rearrangement to didesyl (VII). The latter may account for the presence of cis-dibenzoylstilbene, which by analogy with the disproportionation of tropylium to cycloheptatriene and tropone,¹⁹ probably arises by hydride abstraction from VII by excess V. This also accounts for the variation in production composition, which would be markedly dependent on the availability of excess dication V. A detailed study of this reaction is in progress.

(16) W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 79, 352 (1959).

Solution of V in glacial acetic acid causes rapid deposition of colorless crystals, containing active halogen, tentatively identified as 3,4-dichlorotetraphenylcyclobutene (75%) (m.p. 193–195°; calcd. for $C_{28}H_{20}Cl_2$: C, 78.7; H, 4.7; Cl, 16.6. Found: C, 79.0; H, 4.5; Cl, 16.7), presumably by chloride attack on the unstable 3,4-diacetoxytetraphenylcyclobutene. V is stable to approximately 150°, at which temperature it decomposes to yield tin tetrachloride and 1,4-dichlorotetraphenylbutadiene, m.p. 181–183°, identical with the product obtained from the thermal decomposition of tetraphenylcyclobutadiene-palladium chloride complex.²⁰ Further studies on the fundamental nature of the dication are in progress.

(17) R. Breslow, J. Lockhart and Hai Won Chang, ibid., 83, 2375 (1961), and refs. cited therein.

(18) W. von E. Doering and L. H. Knox, ibid., 76, 3203 (1954).

(19) K. Ikemi, T. Nozoe and H. Sugiyama, Chem. and Ind., 932 (1960); K. M. Harmon, et al., J. Am. Chem. Soc., 84, 120 (1962).

(20) A. T. Blomquist and P. M. Maitlis, ibid., 84, 2329 (1962).

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FORMATION OF IMINES BY ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON IN THE BECKMANN AND SCHMIDT REACTIONS¹

Sir:

Although the insertion of neutral, electron-deficient nitrene intermediates into unactivated C–H bonds is well known,² the replacement of paraffinic hydrogen by a cationic nitrogen species has not been noted.³ We now wish to report such an electrophilic substitution involving intramolecular attack by an iminium ion,⁴ generated under Beckmann or Schmidt reaction conditions, on a non-adjacent saturated carbon atom.

The key model compound, 4-bromo-7-t-butyl-1-indanone,⁵ was chosen because normal Beckmann rearrangement of its oxime (I) would be expected to proceed with great difficulty⁶ and also because

(1) This research was supported by Grant No. 550-A of the Petroleum Research Fund, American Chemical Society. Grateful acknowledgment is made to the donors of this fund for their generous support.

(2) (a) D. H. R. Barton and L. R. Morgan, J. Chem. Soc., 622 (1962); (b) G. Smolinsky, J. Am. Chem. Soc., 82, 4717 (1960); (c) J. W. ApSimon and O. E. Edwards, Can. J. Chem., 40, 896 (1962).

(3) In two cases, acid-catalyzed reactions of ketoxime sulfonates have yielded as minor products pyrazines, which are allegedly derivable from azacyclopropenes (P. A. S. Smith, J. Am. Chem. Soc., 70, 323 (1948)). Such possible intermediates could result from an insertion of the type discussed here or by cyclization of a vinyl nitrene (cf. G. Smolinsky, ibid., 83, 4483 (1961)).

(4) The term "iminium ion" is used here essentially for brevity and is not meant to infer that polyphosphate ion is first lost from the esterified oxime, yielding a discrete cationic intermediate which inserts in a subsequent step. It has been pointed out, however (D. E. Pearson and R. M. Stone, ibid., 83, 1715 (1961)), that bond-breaking is well advanced in the rearrangement of oxime polyphosphates; moreover, aryl participation is not of importance in the indanone system (ref. 6). Thus, usage of the term iminium ion appears justified.

(5) L. F. Fieser and D. K. Snow, ibid., 60, 176 (1938).

(6) L. G. Donaruma and W. Z. Heldt, "Organic Reactions," R. Adams, Ed., Volume 11, John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 11–12.