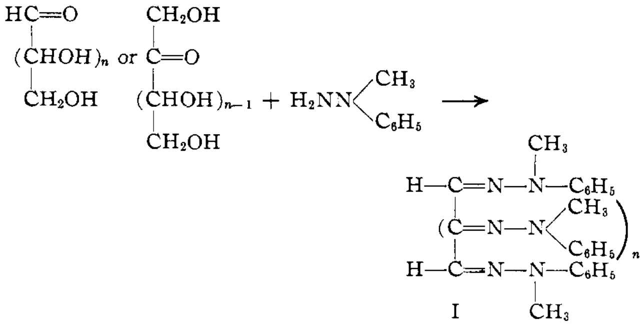
COMMUNICATIONS TO THE EDITOR

Complete Oxidation of Sugars by 1-Methylphenylhydrazine. The Alkazones

Sir:

Since Fischer's classic study of the phenylhydrazine oxidation of sugars,[1] chemists have believed that oxidation of sugars by phenylhydrazine and its derivatives is limited to osazone formation. It has been suggested[2] that this limitation is due to chelate ring formation.[5] If this suggestion is correct, there appears to be no reason why 1-alkylphenylhydrazine oxidation of sugars should not continue beyond the osazone. We have found this to be true, and we now wish to report complete oxidation of sugars by 1-methylphenylhydrazine to a new class of highly unsaturated compounds for which we suggest the name alkazones.[6]

Treatment of 1,3-dihydroxyacetone,[7] erythrose, arabinose, and xylose with excess 1-methylphenylhydrazine in water–ethanol–acetic acid solution gives in each case the corresponding methylphenylalkazone (I) which crystallizes from the solution (Table I). Similar treatment of fructose gives a poor yield of the impure alkazone. It is significant that arabinose and xylose give the same methylphenylalkazone. Evidence for the structures of the alkazones includes chemical analysis, absence of hydroxyl and carbonyl absorption in the infrared spectra, and the n.m.r. spectra (Table II) which show only aldimine protons, aromatic protons, and methyl protons in the proper ratios. The steric problems of the alkazones increase with increasing chain length, and these problems are reflected in the ultraviolet spectra of the alkazones. The complexity of the n.m.r. spectrum also increases with chain length. In arabinose methylphenylalkazone (II) the two ends of the chain are nonequivalent as expected.



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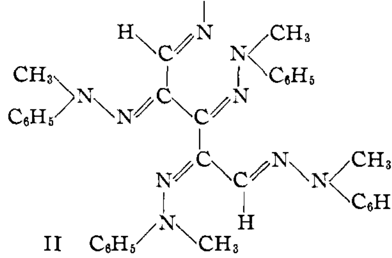

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TABLE I

PROPERTIES OF THE METHYLPHENYLALKAZONES

Source	Alkazone m.p., °C.	Yield of alkazone, %	Ultraviolet absorption $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ (ε), mμ
1,3-Dihydroxyacetone	124.5–127	94	370 (22,250), 335 (22,650, sh.), 255 (22,650)
Erythrose	141–151 156–159.5 Polymorphs	55	357 (52,900), 307 (21,500, sh.), 242 (23,900, sh.), 220 (26,200, sh.)
Arabinose	150–152	30	360 (41,000), 289 (27,900, sh.), 251 (41,000)
Xylose		39	

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE METHYLPHENYLALKAZONES[a]

Length of carbon chain	Aldimine C-H	Aromatic protons	Methyl protons
3	7.62 (2)	7.16 (15)	3.37 (3)
			3.24 (6)
4	7.56 (2)	7.10 (20)	3.44 (6)
			3.24 (6)
5	7.67 (1)	7.12 (25)	3.47 (3)
			3.34 (3)
	7.50 (1)		3.29 (6)
			3.14 (3)

[a] Spectra were obtained on deuteriochloroform solutions using a radiofrequency of 60 Mc. Resonance locations are given as p.p.m. downfield from internal tetramethylsilane. The numbers in parentheses give the area ratio of the resonance.

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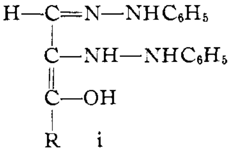
(1) E. Fischer, *Ber.*, **17**, 579 (1884); **20**, 821 (1887).

(2) L. F. Fieser and M. Fieser, "Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1950, pp. 369–372. Evidence pertinent to the chelate structure of sugar osazones has been presented.[3,4]

(3) L. Mester, *J. Am. Chem. Soc.*, **77**, 4301 (1955).

(4) G. Henseke and H. Kohler, *Ann.*, **614**, 105 (1958).

(5) An alternate explanation is that anion formation at C-3 in the phenylosazones is inhibited by formation of delocalized anions by ionization of the N–H bonds. Formation of i is requisite to further oxidation of the osazone.



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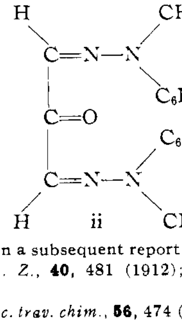
This explanation also suggests that 1-alkylphenylhydrazines should oxidize sugars beyond the osazone stage.

(6) This name is intended to serve the same purpose for per(phenylhydrazones) that the useful term osazone serves for 1,2-bisphenylhydrazones.

(7) Two compounds (m.p. 127–130° and m.p. 147–148°) have been isolated from the reaction of 1,3-dihydroxyacetone with 1-methylphenylhydrazine.[8] The compound melting at 147° has also been obtained from hydroxypyruvaldehyde.[9] Both products have been considered to be the methylphenylosazone of glyceraldehyde.[8,9] In fact, neither is the methylphenylosazone of glyceraldehyde. The compound with m.p. 127–130° is probably the methylphenylalkazone (m.p. 124.5–127°). The compound with m.p. 147° we have obtained by treatment of 1,3-dihydroxyacetone with limited quantities of 1-methylphenylhydrazine. In the n.m.r. spectrum it shows only an aldimine proton (7.63), aromatic protons (7.33), and methyl protons (3.45 p.p.m.). The area ratios are 1:5:3. In the infrared spectrum the compound with m.p. 147° shows a carbonyl absorption at 6.13 μ. The structure of this product is thus not the methylphenylosazone but ii. The significance of the isolation of this product in the oxidation of 1,3-dihydroxyacetone will be discussed in a subsequent report.



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(8) F. Chick, *Biochem. Z.*, **40**, 481 (1912); C. Neuberg, *Ber.*, **35**, 964 (1902).

(9) H. P. den Otter, *Rec. trav. chim.*, **56**, 474 (1937).

The yields of the alkazones are quite good from the three, four, and five carbon sugars. The yield from six carbon sugars is very poor, and the reaction in this case is quite slow. The reason for this difference between the five and six carbon sugars is not clear, but it appears to be associated with side reactions in the slower oxidations of the hexoses.

The complete oxidation of sugars by 1-methylphenylhydrazine explodes a myth based on intuition rather than fact. It also opens new vistas of theoretical and practical consequence and provides a facile synthetic entry to a unique class of highly unsaturated compounds.

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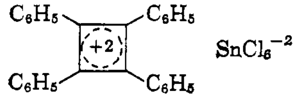
The Crystal and Molecular Structure of a Carbonium Ion. 3-Chloro-1,2,3,4-tetraphenylcyclobutenium Pentachlorostannate

Sir:

The synthesis of the supposed dicarbonium ion salt, tetraphenylcyclobutenium hexachlorostannate (I), has recently been reported.[1] A three-dimensional structure analysis, by X-ray diffraction methods, of crystals of this material[2] has been carried out with the result that, at any rate in the solid state,[3] the compound in question is the isomeric monocation salt 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate (II). Since, as far as the author is aware, the literature contains no reports of structure determinations either of carbonium ions[4] or of pentachlorostannate anions, some details of the structure of this salt may be of interest.



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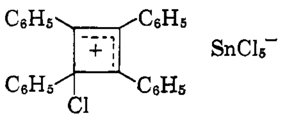

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3-Chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate crystallizes in the orthorhombic system, in space group Pbca, with $a = 19.50 \pm 0.03$, $b = 27.42 \pm 0.05$, $c = 10.55 \pm 0.02$ Å. There is one molecule per asymmetric unit containing 35 atoms, excluding hydrogen.

Some 3560 reflections, representing three-dimensional data to about 1.1 Å.$^{-1}$, were measured from a single crystal, sealed in a thin-walled glass capillary, with Mo Kα radiation. The intensity measurements were converted to structure amplitudes by means of a program specially written to handle the punched card output of the Hilger-Watts linear diffractometer used. No absorbtion corrections were applied.

The position of the tin atom in the unit cell was found from a study of the three-dimensional Patterson function and the rest of the structure determined from successive Fourier approximations to the electron density. The final electron-density distribution is shown in Fig. 1. Refinement was carried through in eight cycles of full matrix least-squares minimalization of the differences between observed and calculated structure amplitudes. All 105 positional parameters, 35 isotropic thermal parameters, and 3 scale factors were varied in alternate cycles to give a value for R of 0.202 for all reflections. The values of the bond lengths and angles derived from the final positional coordinates of the cation are shown in Fig. 2. The standard deviation in

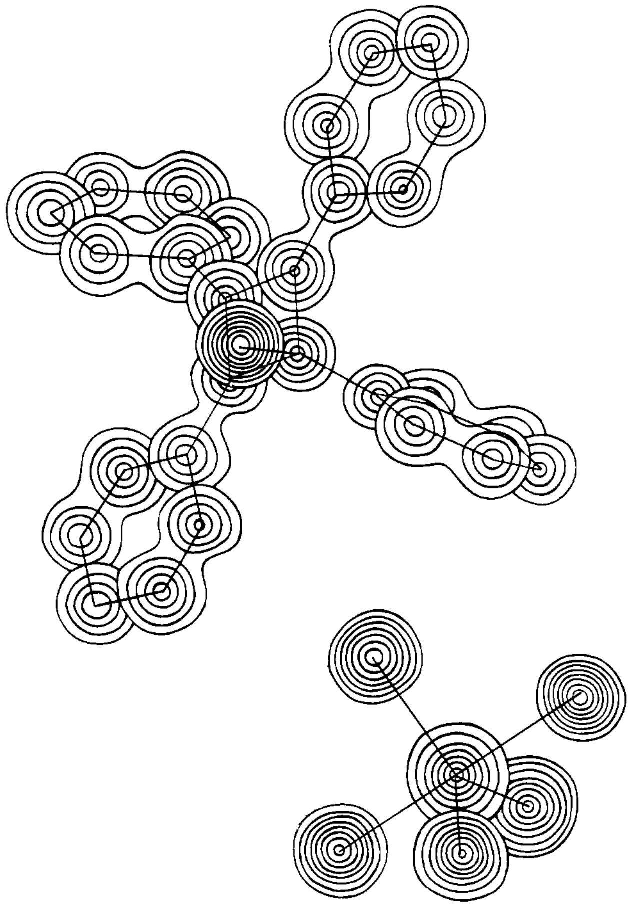

Fig. 1.—The electron density distribution over one formula unit in 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate. The contours are at arbitrary, but equal, intervals for the various atomic species.

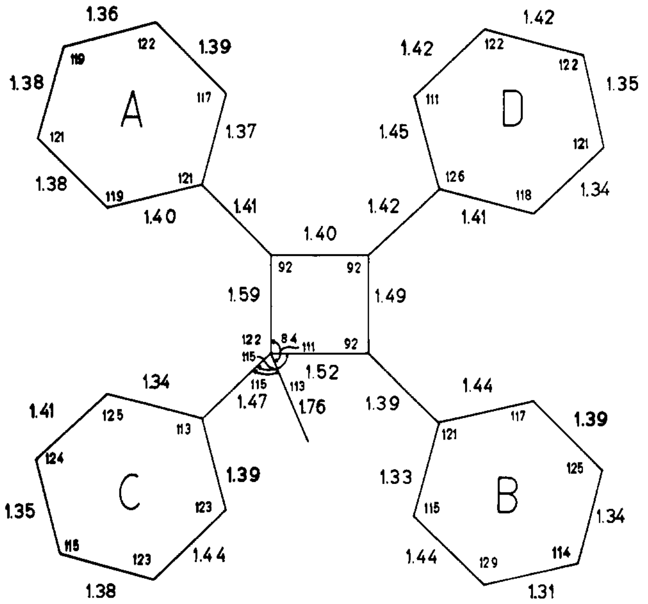

Fig. 2.—Bond lengths and angles in the cation of 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate.

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[1] H. H. Freedman and A. M. Frantz, *J. Am. Chem. Soc.*, **84**, 4165 (1962).

[2] Crystals suitable for X-ray work were kindly supplied by Dr. H. Freedman.

[3] H. H. Freedman and A. E. Young, *J. Am. Chem. Soc.*, **86**, 734 (1964).

[4] NOTE ADDED IN PROOF.—See, however, M. Sundaralingam and L. H. Jensen, *ibid.*, **85**, 3302 (1963).