

Thermogravimetric analysis curves showed that the T_{10} weight-loss values ($10^\circ/\text{min.}$) in air and in nitrogen were 405 and 420° , respectively, although the polymer appears to be susceptible to depolymerization below 200° .

The above procedure has also been extended to the synthesis of soluble, high molecular weight dimethoxy-, diethoxy-, and diphenoxypolyphosphonitriles. These polymers were analytically pure, with weight-average molecular weights close to or above 1×10^6 and glass transition temperatures at -76 , -94 , and -8° , respectively. A related procedure has been employed for the synthesis of aminophosphonitrile high polymers of structure $[\text{NP}(\text{NRR}')_2]_n$. The details of these syntheses will be reported subsequently.

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Halogen Addition to Bicyclo[2.1.0]pentane¹

Sir:

The course of reaction of bicyclo[2.1.0]pentane with electrophilic reagents is now known to be completely dominated by the maximum release of strain as opposed to the electronic and statistical factors which determine the course of cleavage in less strained bicyclo[n .1.0]alkanes. Reactions of bicyclo[2.1.0]pentane with mercuric,^{2a} lead, and thallium acetates^{2b} and *p*-toluenesulfonic acid in acetic acid^{2c} give as the only products those which result from the cleavage of the internal carbon-carbon bond. Bicyclopentane is also known to react readily with bromine,³ but the nature of the product has not been reported. In this communication the unusual mode of bromine and chlorine addition is reported.

The bicyclopentane used was prepared by the method of Criegee³ and gave a single peak on gas chromatography under conditions (10 ft. \times $3/16$ in., 5% squalane on firebrick, 30°) by which the presence of 1% cyclopentene could be determined. The dropwise addition of bromine in anhydrous chloroform to bicyclopentane in chloroform was carried out at -30 and -25° in the dark. Careful removal of the solvent by distillation at 0° and reduced pressure gave in 85–90% yield the crude product which was analyzed directly. Surprisingly, the infrared ($\lambda_{\text{max}}^{\text{CCl}_4}$ 7.62, 7.84, 8.59, 9.59, 9.68, and 11.17 μ) and n.m.r. spectra (doublet of triplets centered at τ 5.30 and complex multiplets in the region of 6.9–8.3) of the product were identical in all respects with the spectra of authentic *trans*-1,2-dibromocyclopentane. However, gas chromatograms (obtained by using a 3 ft. \times $3/16$ in. polyethylene glycol adipate on firebrick column at 135°) demonstrated the presence of two additional materials, one of which was present in 7–9% and was identified by its retention time as cyclopentyl bromide. The third component, emerging at a slightly longer retention time than the predominant component, was always present to the extent of 2% or less and remains unidentified.

(1) Paper VI in a series entitled Carbon-Carbon Bond Fission in Cyclopropanes.

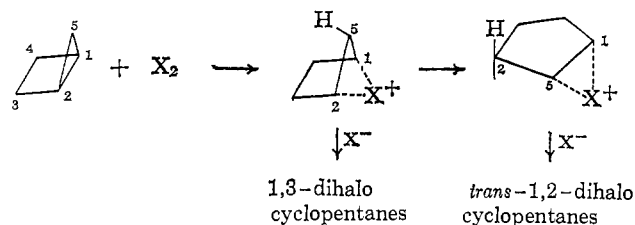
(2) (a) R. Ya. Levina, B. N. Kostin, and T. K. Ustyniuk, *Zh. Obshch. Khim.*, **30**, 359 (1960); (b) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Am. Chem. Soc.*, **87**, 2602 (1965); (c) R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963).

(3) R. Criegee and R. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

Addition of chlorine to bicyclopentane in the dark at -25 to -40° in anhydrous chloroform gave a complex mixture of chlorides but, again, the *trans*-1,2-dihalocyclopentane predominated. Quantitative and preparative scale gas chromatography of the crude product mixture was carried out employing conditions⁴ similar to those used by Russell⁵ in his chromatographic analysis of the isomeric dichlorocyclopentanes. The following, given in the order of increasing retention time, were the identified products present in the amounts specified: cyclopentyl chloride (5%), *trans*-1,2-dichlorocyclopentane (62%), *trans*-1,3-dichlorocyclopentane (8%), and *cis*-1,3-dichlorocyclopentane (5%). Three unidentified components emerge at retention times much longer than the retention times of any of the five isomeric dichlorocyclopentanes. These three components make up 20% of the product mixture. Cyclopentyl chloride and all the dichlorides were identified by matching the retention times of components of the product mixture with the retention time of authentic materials.⁶ The major component was isolated and its identity was confirmed through its n.m.r. and infrared spectra.

The possibility that isomerization of bicyclopentane to cyclopentene takes place under reaction conditions is remote. Bicyclopentane must be heated above 300° ($E_{\text{act}} = 45.6$ kcal./mole)⁷ to effect isomerization to cyclopentene. Moreover, addition of bromine and chlorine to cyclopentene gave cleanly the *trans*-1,2-dihalocyclopentanes at a rate which appears to be at least the same if not slower than the addition of halogen to bicyclopentane under precisely the same reaction conditions. The possibility that initially formed, less stable dihalocyclopentanes could be rearranging to *trans*-1,2-dihalocyclopentanes can be excluded on the basis that *trans*-1,3-dichlorocyclopentane, *cis*-1,2-dibromocyclopentane, and *trans*-1-bromo-3-chlorocyclopentanes all survive the halogen addition conditions.

The predominance of *trans*-1,2-dihalocyclopentane formation can be explained in terms of the scheme depicted below. The transition state for the initial



attack of bicyclopentane by electrophilic halogen would closely resemble the highly strained substrate. The resulting 1,3-halonium ion would still possess much of the strain of the substrate in achieving maximum overlap of the orbitals of halogen with the p-rich sp^3 orbitals of C-1 and C-2. Relief of this strain is the driving force for a 1,2-hydride migration which results in the rapid conversion of the 1,3-halonium ion to a

(4) Di(2-ethylhexyl) sebacate (5–7 ft. \times $3/16$ in., 20%) on Chromosorb P, at 120° .

(5) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, **85**, 2983 (1963).

(6) There can be no doubt about the use of retention times to identify components of the product mixture. The appearance sequence of the five dichlorocyclopentanes has been determined (ref. 5), and similar chromatographic conditions have been employed in the work reported herein.

(7) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 678 (1964).

1,2-halonium ion.⁸ The latter in turn collapses under nucleophilic attack to afford *trans*-1,2-dihalocyclopentane. In the case of chlorination, leakage from the 1,3-bridged intermediate, to give 1,3-dichlorocyclopentanes, occurs because electrophilic attack by chlorine results in a transition state involving a greater development of positive charge on carbon than in the case of the attack by the less electronegative bromine.⁹ The larger size of bromine would also account for its better bridging properties. Apparently the halogen addition to bicyclopentane is sensitive to salt effects. While addition of bromine in the presence of tetraethylammonium bromide (mole ratio $\text{Et}_4\text{N}^+\text{Br}:\text{Br}_2 = 2$) afforded no 1,3-dihalocyclopentanes, the addition of bromine to bicyclopentane in chloroform saturated with the more highly ionic tetraethylammonium chloride gave 2% *cis*- and 13% *trans*-1-bromo-3-chlorocyclopentane. *trans*-1-Bromo-2-chlorocyclopentane and *trans*-1,2-dibromocyclopentane were observed in 27 and 33%, respectively. The formation of an excess of *trans*-1-bromo-3-chlorocyclopentane over the *cis* isomer is another example of the formation of *trans* products resulting from cleavage of strained carbon-carbon bonds.¹⁰

In contrast to the halogen additions reported here, the oxidative cleavage of bicyclopentane with thallium and lead acetates results in no rearrangement.^{2b} This variance is most likely due to differences in the electronegativity and orbital availability of the electrophile as well as the polar character of the solvent. A study of the effect of these variables on the outcome of electrophilic additions to bicyclopentane has been initiated.

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(8) Possibly a 1,3-hydride migration occurs from C-4 to C-2. However, this proposal is less appealing since the migrating hydride ion would move against the *endo* hydrogen on C-5.

(9) The pronounced variation of product composition with the electronegativity of the attacking electrophile has been noted in connection with addition to norbornene derivatives [T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, 85, 2746 (1963)].

(10) However, the formation of *trans* products is by no means general. Examples of *cis* products resulting from the addition of halogen to strained bonds have also been reported. See S. Masamune, *Tetrahedron Letters*, 945 (1965), and W. E. Doering and J. F. Coburn, Jr., *ibid.*, 991 (1965).

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Chlorinolysis of Glycosidic Bonds

Sir:

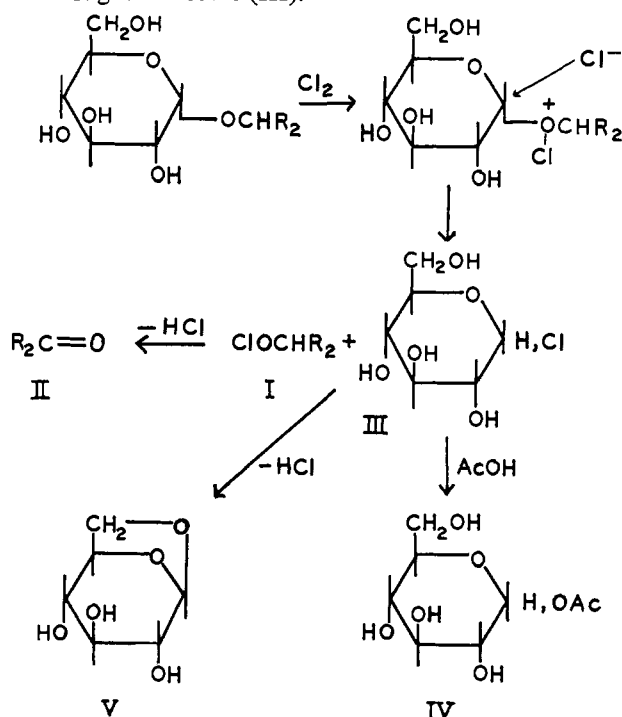
We wish to propose a new mechanism to explain the depolymerization of polysaccharides in the presence of chlorine. This reaction is especially important commercially in the bleaching of cellulose and in the modification of starch. Polysaccharides, often prepared by the use of chlorine, may be degraded in the process.

Treatment of model compounds such as methyl D-glucopyranosides,¹ methyl D-galactopyranosides,² and

methyl β -cellobioside³ with aqueous acidic chlorine solutions has produced aldoses and aldonic acids together with smaller amounts of keto sugars and other products derived from further oxidation at nonacetal sites.⁴ Based on these products it has been proposed that the glycoside is cleaved between the oxygen and the aglycon carbon.^{5,6} These mechanisms would predict that in the aqueous chlorinolysis of oligo- or polysaccharides the glycosidic oxygen is either displaced from the aglycon carbon of the attached sugar by a hydroxyl ion, which would lead to inversion, or a carbonium ion is involved, which would lead to racemization. However, no new sugars have been detected during chlorinolysis of oligo- or polysaccharides. Specifically D-galactose is not found among the aqueous chlorinolysis products of starch⁷ or cellulose.

We have found that starch is extensively depolymerized by gaseous chlorine in the absence of water. This led us to examine the reaction of methyl tetra-O-acetyl- β -D-glucopyranoside with chlorine in carbon tetrachloride solution. Formaldehyde in 22% yield was identified as a reaction product, and a small yield of ethyl β -D-glucopyranoside was obtained when the chlorination reaction mixture was treated with a silver salt in ethanol followed by deacetylation. This result suggests that an acetylated glucosyl chloride was an intermediate and the glycosidic bond was cleaved between the oxygen atom and C-1 of the sugar.

We propose an alternative mechanism which results in the production of a carbonyl compound (II) from the aglycon, by dehydrohalogenation of a hypochlorite ester (I), and the attachment of a chlorine atom on C-1 of the sugar molecule (III).



(1) A. Dyfverman, B. Lindberg, and D. Wood, *Acta Chem. Scand.*, 5, 253 (1951).

(2) B. Lindberg and D. Wood, *ibid.*, 6, 791 (1952).

(3) A. Dyfverman, *ibid.*, 7, 280 (1953).

(4) J. T. Henderson, *J. Am. Chem. Soc.*, 79, 5304 (1957); O. Theander, *Svensk Papperstidn.*, 61, 581 (1958).

(5) N. N. Lichtin and M. H. Saxe, *J. Am. Chem. Soc.*, 77, 1875 (1955).

(6) C. W. Dence, *Tappi Monograph Series*, 27, 51 (1963).

(7) T. R. Ingle and R. L. Whistler, *Cereal Chem.*, 41, 474 (1964).