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 $Et_4N^+Br:Br_2 = 2$) 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

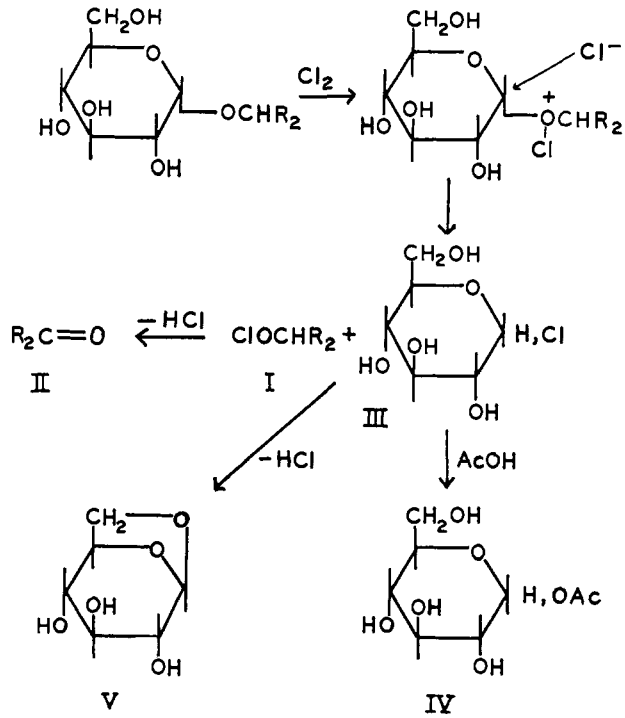
Sir:

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-cellobioside[3] 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 starch[7] 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).
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(5) N. N. Lichtin and M. H. Saxe, *J. Am. Chem. Soc.*, 77, 1875 (1955).
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(7) T. R. Ingle and R. L. Whistler, *Cereal Chem.*, 41, 474 (1964).

We have studied the reaction of chlorine in dry acetic acid on methyl α-D-glucopyranoside. The reaction mixture after removal of any acetyl groups with aqueous potassium carbonate was separated by chromatography on thick paper into D-glucose (52%), unreacted methyl α-D-glucopyranoside (22%), and a third fraction (26%) which is a mixture containing 1,6-anhydro-β-D-glucopyranose and an unknown material. Acetylation of the mixture gave 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-glucopyranose together with an unidentified acetate.

In a similar oxidation of maltose, D-glucose was again the major nonacidic product, and 1,6-anhydro-β-D-glucopyranose was formed in small amounts.

The formation of these reaction products can be rationalized in terms of the proposed intermediate glucosyl chloride (III) undergoing solvolysis in acetic acid to give 1-*O*-acetyl-D-glucopyranose (IV) and also dehydrohalogenation to give 1,6-anhydro-β-D-glucopyranose (V), probably *via* 1,2-anhydro-α-D-glucopyranose.[8]

The oxidation products from anhydrous amylose and chlorine in dry acetic acid also support the proposed mechanism. Chlorinolysis of the 1→4 links followed by reduction with borohydride produces terminal D-galactose residues. Subsequent hydrolysis and reduction to the alditols, and separation of their acetyl derivatives, gave hexaacetylgalactitol and hexaacetyl-D-glucitol. The formation of D-galactose by reduction of the oxidized amylose indicates the presence of a 4-keto end group,[9] which is produced by dehydrohalogenation of the first formed D-glucose 4-hypochlorite.

The above mechanism also explains the major products of oxidation of glycosides with chlorine in an aqueous medium. The glycosyl chloride (III) would be solvolyzed to the aldose which is converted to an aldonolactone by oxidation analogous to the aqueous bromine oxidation of D-glucose to D-glucono-δ-lactone.[10-12]

(8) J. Janson and B. Lindberg, *Acta Chem. Scand.*, **13**, 138 (1959).
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Mechanisms of Photochemical Reactions in Solution. XXX.[1] Photosensitized Isomerization of Azobenzene

Sir:

We have investigated the photosensitized isomerization of azobenzene in isooctane in order to shed further light on the mechanism of the reaction. The choice of suitable sensitizers for these experiments was critical. Azobenzene absorbs light in both the ultraviolet and visible regions of the spectrum, and as a result filters had to be used to exclude the visible radiation. Those sensitizers with a significant quantum yield for fluorescence could not be used because of the possibility that azobenzene might absorb this fluorescent radiation. Similarly, sensitizers excited through n–π* transitions could not be used because the excited states of these sensitizers abstracted hydrogen from the hydrocarbon solvent at a significant rate. The radicals so produced react with the azo linkage of the azobenzene.[2] Sensitizers exhibiting high extinction coefficients above 400 mμ were not used because the 400–450 mμ region of the spectrum was used for azobenzene analysis. Table I lists sensitizers with triplet energies varying from 45 to 66.6 kcal./mole,[3] which were used to effect photoisomerization of azobenzene. The photostationary states were established from both directions. Within experimental error the same stationary state was obtained with each of these sensitizers, indicating that a sensitizer with triplet energy of ~45 kcal./mole still behaves as a high-energy sensitizer with regard to energy transfer to azobenzene.

(1) Part XXIX is A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).

Table I. Photostationary States for Photosensitized Isomerization of Azobenzene

Sensitizer	E_t	*cis*, %
3-Acetylpyrene	~45	1.8
β-Acetonaphthone	59.3	1.5
Triphenylene	66.6	1.6

This latter fact was further substantiated by measurement of the rates of energy transfer from the sensitizers to azobenzene by flash spectroscopy. Using a kinetic analysis based on the reasonable assumption that at low azobenzene concentration the photostationary state is established after only two or three flashes of light, it was found that the energy-transfer step (to either *cis*- or *trans*-azobenzene) was probably diffusion controlled.[4] The rate constants for the energy transfer process are given in Table II.

Table II. Rates of Quenching of Sensitizer Excited States by Azobenzene

Sensitizer	E_t	k_q, M^{-1} sec.$^{-1}$
3-Acetylpyrene	45	4.0×10^9
β-Acetonaphthone	59.3	3.4×10^9

The results are reminiscent of those encountered in the study of the sensitized isomerization of the stilbenes and 1,2-diphenylpropenes[5] where it was also found that high-energy sensitizers produce the same photostationary states with either substrate. These results can be understood if transfer of energy to either stereoisomeric ground state leads to formation of a common excited state (or states) from which decay to ground-state molecules occurs. An abbreviated mechanism is

$$S^{*(3)} + \textit{trans}\text{-A} \xrightarrow{k_1} S + A_T \quad (1)$$

$$S^{*(3)} + \textit{cis}\text{-A} \xrightarrow{k_2} S + A_T \quad (2)$$

$$A_T \xrightarrow{k_3} \textit{trans}\text{-A} \quad (3)$$

$$A_T \xrightarrow{k_4} \textit{cis}\text{-A} \quad (4)$$

At the stationary state

$$\frac{[\textit{trans}]_s}{[\textit{cis}]_s} = \frac{k_2 k_3}{k_1 k_4} \quad (5)$$

(2) J. K. S. Wan, L. D. Hess, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **86**, 2069 (1964).
(3) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).
(4) For discussion of a probable limitation on the significance of "diffusion control" see R. M. Noyes, *ibid.*, **86**, 4529 (1964).
(5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).