the equatorially oriented bromide of III by pyridine with inversion of the anomeric center. If so, this reaction would have to be very rapid as compared to the formation of II from I since the results require the formation of III to be rate-controlling in the sequence of reactions leading to VII. Also, the concentration of III must be very small throughout the course of the reaction since, although it is the anomer with the bromine in equatorial orientation, it is the thermodynamically less stable anomer.[4,5] The driving force for this condition has been termed the "anomeric effect."[6,7]

It seemed more likely that the rapid formation of VII by way of III would involve participation of the 2-acetoxy group in the reaction of III to lead to a 1,2-acetoxonium ion. In fact, the β-bromide (III) has recently been isolated[8] and its reaction properties correspond to those previously established for tetra-*O*-acetyl-β-D-glucopyranosyl chloride.[9] Since the reaction of the latter compound in pyridine containing an alcohol leads to the formation of α-D-glucopyranose 1,2-(alkyl orthoacetate) triacetate,[9,10] these observations related to the formation of VII led to the prediction that the addition of the α-bromide (I) to pyridine containing methanol would result in the formation of the 1,2-methyl orthoacetate (VI).[11] In fact, the reaction of I in pyridine containing 3 moles of methanol per mole of I, under conditions (30% of I) which in the absence of the methanol provided the α- and β-pyridinium glucosides in the ratio 3:2, gave as the product a mixture of the methyl orthoacetate (VI) and β-pyridinium glucoside (II) in the ratio 3:2. That is, the presence of the methanol blocked the route to the formation of the α-pyridinium compound (VII), precisely the result expected should the latter compound arise from the 1,2-acetoxonium ion intermediate (IV). The n.m.r. spectrum of the 1,2-orthoacetate (VI) in chloroform showed the presence of the two possible diastereoisomers arising from a change in the configuration of the new asymmetric center in the dioxolane ring.[12] The isomer, which produced signals for the methoxy and orthoacetyl groups at 3.30 and 1.72 p.p.m. (trimethylsilane), respectively, and believed on the basis of n.m.r. to have structure VIII, was formed in approximately 6.2 times greater amount than that with the corresponding signals at 3.46 and 1.57 p.p.m.

In order to confirm these notions, the reaction of tetra-*O*-acetyl-β-D-glucopyranosyl chloride with pyridine was examined. As expected, *N*-(tetra-*O*-acetyl-α-D-glucopyranosyl)-pyridinium chloride was formed but none of the β-isomer. It is therefore concluded that the driving force for the ready formation of VII from III is derived from the anchimeric assistance provided by the participation of the 2-acetoxy group and that, consequently, the last stage of the reaction involved an intramolecular rearrangement of a transient 1,2-orthoacetyl pyridinium bromide (Vb). The plausibility of such a migration is well supported through the consideration of a molecular model and the fact that the rupture of the Cl-to-oxygen bond in the dioxolane ring of Vb must involve participation by the oxygen of the pyranose ring. The latter type of participation is clearly involved in the first stage of all displacement reactions at the anomeric center of sugar structures.

The occurrence of the above migration without doubt explains the stereochemical routes of reaction observed in the synthesis of 3-carboxamidopyridinium nucleosides.[2,13,14] Also, the discovery likely has an important bearing on the formation of both the anomeric forms in the syntheses of other types of nucleosides by way of *O*-acylated glycosyl halides.[15-17]

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Electrophilic and Nucleophilic Substitution of Allylic Mercurials[1,2]

Sir:

Organomercurials have been studied extensively as substrates for electrophilic substitution at saturated carbon,[3] and more recently for generation of carbonium ions[4] by so-called "demercuration." The corresponding carbon–mercury bond cleavages are depicted by R:|Hg and R|:Hg, respectively. Both substitutions, electrophilic as well as nucleophilic, are especially interesting with allylic mercurials, and we report on this matter in the present communication. The present observations on the behavior of crotyl- and cinnamylmercuric derivatives furnish considerable insight into the competition between the two kinds of substitution and the mechanistic preferences displayed by each of them.

Crotylmercuric bromide,[5] prepared from the butenyl Grignard reagent and mercuric bromide, was recrystallized from pentane–acetone; m.p. 90.8–91.2° dec. The *trans*-crotyl structure was confirmed by the presence of only two vinyl protons as indicated by the n.m.r. spectrum in chloroform solvent, the absence of infrared bands at 905–915 cm.$^{-1}$ and 985–995 cm.$^{-1}$ for terminal methylene, and the presence of an infrared band at 965 cm.$^{-1}$ for a *trans*-olefinic group. Crotylmercuric and cinnamylmercuric bromide,[6] on treatment with silver acetate in acetone, gave rise to the corresponding crotylmercuric acetate,[5] m.p. 76–77°, and cinnamylmercuric acetate,[5] m.p. 98.0–98.5°.

The predominant result from treatment of the allylic mercurials with acidic media depends on the nature of the anionic ligand in RHgX. Halide as the ligand is relatively unfavorable to nucleophilic substitution and, therefore, electrophilic cleavage of the mercurial is predominant. Thus, at room temperature crotylmercuric bromide is converted essentially quantitatively to olefin by excess hydrogen chloride in ethyl acetate

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(2) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.
(3) *E.g.*, O. A. Reutov, *Rec. Chem. Progr.*, **22**, 1 (1961).
(4) (a) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363 (1963); (b) S. Winstein, E. Vogelfanger, K. C. Pande and H. F. Ebel, *ibid.*, **84**, 4994 (1962); (c) S. Winstein, E. Vogelfanger and K. C. Pande, *Chem. Ind.* (London), 2061 (1962).
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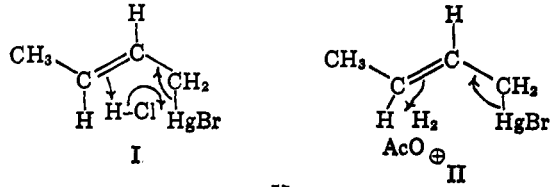
in a few minutes, or by 0.02 *M* perchloric acid in acetic acid solvent in 0.5 hr. Olefin is also the product from crotylmercuric acetate and hydrogen chloride in ethyl acetate, ligand exchange presumably being sufficiently rapid so that crotylmercuric chloride is the species cleaved to yield olefin. On the other hand, treatment of crotylmercuric acetate in acetic acid with dilute perchloric acid gives rise essentially exclusively to solvolysis products, the butenyl acetates, by way of the crotylmercuric ion.

Two noteworthy features of the acid cleavages of the allylic mercurials are the high rates of reaction compared to saturated mercurials and the relatively complete allylic rearrangement which accompanies them. Thus, crotylmercuric bromide reacts with hydrogen chloride more rapidly than does the *n*-butyl analog[7] by a factor which is roughly 10.[7] From this cleavage, as well as from the crotylmercuric acetate cleavage with hydrogen chloride, the butene obtained is very nearly pure 1-butene (Table I). This is true also of the butene from crotylmercuric bromide and perchloric acid in acetic acid solvent. Cinnamylmercuric derivatives behave similarly to the crotylmercuric analogs, hydrogen chloride cleavage leading nearly exclusively to allylbenzene.

TABLE I
OLEFINS FROM RCH=CHCH$_2$HgX

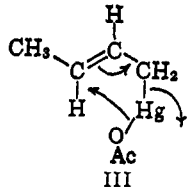
R	X	Solvent	Reagent	% Olefins: $RCH_2CH{=}CH_2$	$RCH{=}CHCH_3$ *trans*	$RCH{=}CHCH_3$ *cis*
CH_3	OAc	EtOAc	HCl	>99.2	0.3	<0.5
CH_3	Br	EtOAc	HCl	>99.3	.2	< .5
CH_3	Br	AcOH	$HClO_4$	>98.9	.6	< .5
C_6H_5	OAc	Et_2O	HCl	98.4	.9	.7
C_6H_5	Br	Et_2O	HCl	98.4	1.1	.5

Both the high rate and the complete allylic rearrangement are explained by an SE′ path for the acid cleavages. With hydrogen chloride in ether or ethyl acetate, the SEi′ designation (I) seems most likely, while the SE2′ description (II) seems best for the cleavage with perchloric acid in acetic acid solvent.



I

II



III

Partial neutralization (11–16%) of *ca.* 0.05 *M* crotylmercuric acetate with perchloric acid in acetic acid solvent causes very rapid formation of mercury. The first order rate constant for the crotylmercuric perchlorate is (1.7 ± 0.3) × 10^{-2} sec.$^{-1}$ at 25.0°, some seven powers of ten greater than that for the *n*-butyl analog.[4a] The product of this demercuration is a 71:29 mixture of α-methylallyl and γ-methylallyl acetates, respectively, a result in accord with a carbonium ion description for the solvolysis. It is interesting that the crotyl component of the acetate product is nearly pure *trans*, in line with preservation of the *trans*-configuration by the crotyl cation[8] IV.

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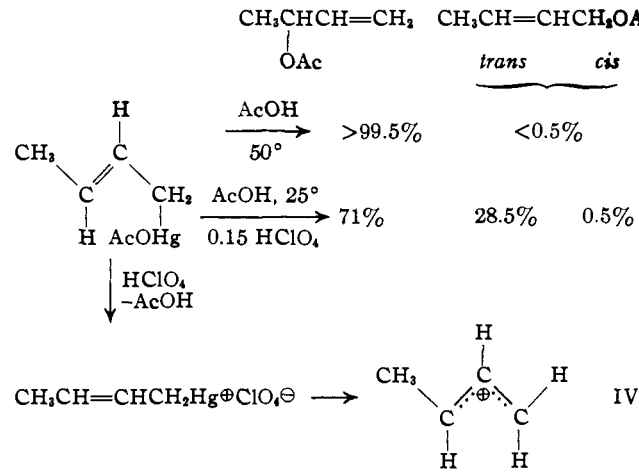

The behavior of crotylmercuric acetate in neutral acetic acid makes an interesting contrast with that in the presence of perchloric acid. In neutral acetic acid, slow solvolysis occurs along with some butene formation[9] (*ca.* 16% at 50°.) The kinetics of this reaction are not well behaved,[9] the solvolysis rate constant at 50° being *ca.* 5 × 10^{-6} sec.$^{-1}$. This figure is at least 10^6 times a value for *n*-butylmercuric acetate which can be deduced from data reported by Jensen.[4a] The product from neutral acetolysis of crotylmercuric acetate at 50° is entirely the rearranged secondary acetate, at least 99.5% pure.

The strict SNi′ type result in the neutral acetolysis of crotylmercuric acetate suggests that this type of demercuration is another example in the whole spectrum of merging ion pair and non-ionic cyclic mechanisms of allylic rearrangements (see III). The present example is reminiscent of allylic azide,[10a] thiocyanate[10b] and thionbenzoate[10c] isomerizations.[11]

(9) This and other features of the neutral reaction have not yet been clarified.

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(11) Allylmercuric acetate in neutral acetic acid yields more propylene than allyl acetate, the rate of the latter reaction being slower than the corresponding one for the crotyl analog by a factor of *ca.* 4–5 at 75°. If one assesses carbonium ion character of the transition state by the effect of the γ-methyl group on reactivity, neutral demercuration may be judged comparable to the above-mentioned isomerizations as regards ionic character.

(12) Standard Oil Company of California Fellow in Chemistry, 1959–1962.

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Base-Catalyzed Isomerization of Trihalobenzenes

Sir:

The unprecedented isomerization of 1,2,4-tribromobenzene to 1,3,5-tribromobenzene, in 33% yield through the action of sodium amide in liquid ammonia, was reported by Wotiz and Huba.[1] A 24% yield of 3,4-dibromoaniline was also reported.

Using potassium amide as the base and with careful attention to the purity and identity of reactant and product, we have been able to confirm that this unusual isomerization does occur, although conversions were only about 12% in our hands. However, when potassium anilide was employed instead of potassium amide, conversions of 1,2,4- to 1,3,5-tribromobenzene of 50–80% were observed. Rearrangement was never complete, and some products presumed to be diphenylamine derivatives were formed.

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