and attributed this result to steric effects [H. C. Brown and H. L. Berneis, THIS JOURNAL, **75**, 10 (1953)]. We were therefore led to consider the possibility that steric effects might be made to control the direction of elimination and that such steric effects might be the structural basis for eliminations according to the Hofmann rule.

We have now found it possible to control the direction of elimination in alkyl halides by varying the steric requirements of the attacking base. The use of potassium *t*-butoxide gives predominantly the 1-olefin in cases where the ethoxide results in the 2-derivative.

Alkyl halide	% 1-Olefin	
	EtO^-	t-BuO^-
$C_2H_5CHBrCH_3$	19 (ref. 1)	53.4
$C_3H_7CHBrCH_3$	29 (ref. 1)	66
$C_2H_5CBr(CH_3)_2$	29 (ref. 1)	72
$(CH_3)_2CHCBr(CH_3)_2$		87
$(CH_3)_3CCH_2CBr(CH_3)_2$	85	99

Bases with larger steric requirements result in a further increase of the 1-olefin. This may be illustrated by the increasing yields of 3-methyl-1-butene which are obtained from *t*-amyl bromide in bimolecular eliminations utilizing a series of alkoxides of increasing steric requirements.

Potassium salt of	% 1-Olefin
Ethyl alcohol	29
t-Butyl alcohol	72
t-Amyl alcohol	78
Triethylcarbinol	89

Sufficient potassium metal was dissolved in 200 ml. of the alcohol to give a solution approximately 1.5 *M* in the alcoholate. The *t*-halide was then dissolved in the solution, maintaining a 50% molar excess of base. The solution was heated at 75° for two hours to ensure completion of the reaction. The temperature was then raised and the olefin distilled out of the reaction mixture through an efficient micro column. Olefin yields (based on *t*-halide) of 93–99% were obtained. The products were analyzed by refractive index and checked in selected test cases by infrared analysis.

The use of potassium *t*-butoxide and other even more hindered bases should be a valuable synthetic tool in controlling the direction of elimination and should do away with the need to synthesize quaternary ammonium compounds in order to obtain high yields of terminal olefins.

We have now been able to demonstrate a general trend from elimination according to the Saytzeff rule toward elimination according to the Hofmann rule by (1) increasing the steric requirements of the alkyl groups on the incipient double bond ($Me_2 <$ Me, $Et < Me_3 < Me_4 < Me_2$, *t*-Bu), (2) increasing the steric requirements of the group undergoing elimination ($Br^- < {}^-OSO_2R < SMe_2 < NMe_3$), and (3) increasing the steric requirements of the attacking base ($EtO^- < t\text{-}BuO^-$).

These results leave little doubt that steric effect must be the basis of eliminations according to the Hofmann rule.

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RECEIVED JULY 20, 1953

NUCLEOTIDE SYNTHESIS BY MALT AND PROSTATE PHOSPHATASES

Sir:

In an extension of previous work[1] on the phosphorylation of nucleosides by phosphate transfer we have made a search for other transfer systems. As regards the malt enzyme used in the previous experiments, the mononucleotides themselves have been found to be much more efficient donors, as judged by the transfer ratio,[2] than sodium phenylphosphate employed previously.[1] Deoxy- and ribonucleotides, but only the 5′-isomers, were equally effective as donors.

It has, in addition, been found that human prostate phosphatase also is able to catalyze the phosphorylation of nucleosides and that in this case, in contrast to the malt enzyme, which produces only the 5′-nucleotides, all possible nucleotide isomers are formed. In the prostate enzyme system, phenylphosphate served as a donor, but mononucleotides did not. These differences in specificity are summarized below.

Enzyme	Donor	Nucleotides synthesized				
		5′-ribo	3′-ribo	2′-ribo	5′-deoxy	3′-deoxy
Malt	Phenylphosphate	+	−	−	+	−
	Mononucleotide	+	−	−	+	−
Prostate	Phenylphosphate	+	+	+	+	+
	Mononucleotide	−	−	−	−	−

With the use of the prostate enzyme and of phenylphosphate as donor, the three isomers of ribocytidylic acid and the two isomers of thymidylic acid have been synthesized and isolated by ion exchange chromatography.

This work was supported by research grants from the National Institutes of Health, U. S. Public Health Service, and the Rockefeller Foundation. One of us (G. B.) was aided by a Predoctoral Research Fellowship from the U. S. Public Health Service.

[1] G. Brawerman and E. Chargaff, THIS JOURNAL, **75**, 2020 (1953).

[2] B. Axelrod, *J. Biol. Chem.*, **172**, 1 (1948).

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THE INFRARED SPECTRUM OF THE OXONIUM ION

Sir:

The infrared absorption spectra of films of oxonium chloride and oxonium bromide have been observed at −195° and spectra which are typical of those obtained are reproduced in Fig. 1. The films were prepared by condensing an equimolar mixture of gaseous H_2O and HX on a previously cooled KBr plate. The OH_3^+ must be the source of the four absorption bands at 1050 cm.$^{-1}$, 1700 cm.$^{-1}$, 2100 cm.$^{-1}$ and 2570 cm.$^{-1}$ in OH_3Cl (similarly, at 1100 cm.$^{-1}$, 1700 cm.$^{-1}$, 2100 cm.$^{-1}$ and 2610 cm.$^{-1}$ in OH_3Br). In addition, some films of both salts show an absorption maximum near 3200 cm.$^{-1}$ as part of the broad absorption region which extends to frequencies above 3500 cm.$^{-1}$. Very little of the observed spectrum can be attributed to ice, whose intense bands[1] at 812 cm.$^{-1}$ and 3150 cm.$^{-1}$,[2] do not appear. Except for the peaks at 2770 cm.$^{-1}$ in OH_3Cl and 2410 cm.$^{-1}$ in OH_3Br, the halides cannot be responsible either since the same bands occur in both salts.

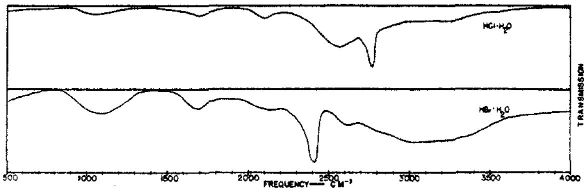

Fig. 1.—The infrared absorption spectrum of oxonium chloride and oxonium bromide at −195°.

To confirm these conclusions we have, in addition to the equimolar compounds, condensed five gas mixtures with composition ranging from 90% HCl-10% H_2O to 20% HCl-80% H_2O, and these showed the expected HCl or ice spectrum superimposed on that of the OH_3^+ ions. The compositions containing excess HCl showed two peaks very close to those reported for pure crystalline HCl at 2704 cm.$^{-1}$ and 2746 cm.$^{-1}$.[3,4] Therefore the HCl responsible for the 2770 cm.$^{-1}$ peak in the OH_3Cl sample must be in a different environment, *e.g.*, as HCl molecules in the OH_3Cl lattice. In this case they may be produced by the equilibrium

$$OH_3Cl \rightleftharpoons H_2O + HCl$$

but we have not yet investigated this possibility. Altogether, the general outlines of the experimental situation seem clear, but some details still need clarification. A number of films have been prepared and the spectra were not completely reproducible, differing chiefly in two respects: (a) the shape of the diffuse absorption region between 2350 cm.$^{-1}$ and 3500 cm.$^{-1}$ and (b) the height of the peak we have ascribed to free HX molecules. Further studies are continuing.

Whereas the observed spectrum is different from either ice or the hydrogen halides, it is closely parallel to that of ammonia. The hydrogen stretching frequencies are lower and the bands broader but both of these features may be attributed to strong hydrogen bonds. It may therefore be concluded that the OH_3^+ ion which is isoelectronic with NH_3, also exists in a symmetrical pyramidal configuration. This conclusion agrees with that derived from proton resonance measurements.[5-6]

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RECEIVED JULY 27, 1953

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(1) F. P. Reding, Thesis, Brown University, 1951.

(2) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A174**, 234 (1940).

(3) G. Hettner, *Z. Physik*, **78**, 141 (1932).

(4) Lee, Sutherland and Wu, *Proc. Roy. Soc.* (*London*), **A176**, 493 (1940).

(5) Y. Kakiuchi, *et al.*, *J. Chem. Phys.*, **19**, 1069 (1951).

(6) R. E. Richards and J. A. S. Smith, *Trans. Far. Soc.*, **47**, 1261 (1951).

A METHOD FOR STUDYING THE MOBILITY OF CHEMISORBED FILMS: OXYGEN ON TUNGSTEN[1]

Sir:

Field emission microscopy has been applied to the above named problem as follows: A small sealed-off field emission tube is immersed in liquid helium kept in an unsilvered Dewar vessel.[2] The tip is cleaned off by electric heating. The resultant clean single crystal emission pattern is stable indefinitely if the tube contains no helium. It is now possible to liberate gas from an auxiliary filament (also heated electrically). If the gas emitter is so placed that it is seen by only a part of the field emitter tip, only that region of the latter will become contaminated with gas. This results from the sufficiently high accommodation coefficient of the internal surface of the tube at 4°K. It is then possible to heat the field emitter electrically and thus to determine how and at what temperature mobility sets in. Field emitter temperature is determinable from its electrical resistance.

Experiments with oxygen on tungsten were carried out with three oxygen sources: A CuO, covered Pt wire, a BaO_2 covered Pt wire, and a rope consisting of ~20 strands of 0.00045 mil W wire on which oxygen condensed on cooling to helium temperatures if the tube contained oxygen at a pressure of 10 mm. The results agree for these sources and are as follows. If small amounts of oxygen are evaporated onto the tip, mobility does not become appreciable below 350°K., and increases with increasing temperature. The phenomenon is definitely not a two-dimensional melting but a gradual, activation-energy-limited diffusion process. Certain regions of the crystal, particularly those in the zone connecting (211) with (211) via (110) hold oxygen most tenaciously. On these regions (the first to show oxygen contamination in this experiment) the oxygen is bound so firmly that desorption seems to precede mobility, setting in at about 1800°K. On other planes mobility seems quite fast at temperatures where these regions cannot retain oxygen for periods of time longer than those required for diffusion to the firmly bonding regions. This is shown by the fact that it is impossible to contaminate regions other than those mentioned above if oxygen is evaporated onto a clean tip kept at 1000°K. or higher. If a previously contaminated tip is heated to these temperatures, however, very complicated patterns result, indicating that desorption is slow and may proceed via the formation of metastable surface oxides.

If oxygen is evaporated in larger amounts onto a tip kept at 4°K. totally different behavior occurs. Under these conditions spreading sets in at 70°K. It is possible to watch the film cover the tip like the unrolling of a carpet. However, the layer thus formed is not itself mobile; if the amount of oxygen initially evaporated is only enough to "unroll the carpet" part way, the sharp boundary thus formed will not change until the tip temperature is 300°K. unless more oxygen is evaporated onto the tip.

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[1] Work supported in part by Contract AF 33(038)-6534 with the U. S. Air Force.

(2) Apparatus very similar to that used is described by R. Gomer and J. K. Hulm, *J. Chem. Phys.*, **20**, 1500 (1952).