

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 ⁻	<i>t</i> -BuO ⁻
C ₂ H ₅ CHBrCH ₃	19 (ref. 1)	53.4
C ₃ H ₇ CHBrCH ₃	29 (ref. 1)	66
C ₂ H ₅ CBr(CH ₃) ₂	29 (ref. 1)	72
(CH ₃) ₂ CHCBr(CH ₃) ₂		87
(CH ₃) ₃ CCH ₂ CBr(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
<i>t</i> -Butyl alcohol	72
<i>t</i> -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 (Me₂<Me, Et<Me₃<Me₄<Me₂, *t*-Bu), (2) increasing the steric requirements of the group undergoing elimination (Br⁻<OSO₂R<SMe₂<NMe₃), and (3) increasing the steric requirements of the attacking base (EtO⁻<*t*-BuO⁻).

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

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NUCLEOTIDE SYNTHESIS BY MALT AND PROSTATE PHOSPHATASES

Sir:

In an extension of previous work¹ 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.

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(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 H₂O and HX on a previously cooled KBr plate. The OH₃⁺ must be the source of the four absorption bands at 1050 cm.⁻¹, 1700 cm.⁻¹, 2100 cm.⁻¹ and 2570 cm.⁻¹ in OH₃Cl (similarly, at 1100 cm.⁻¹, 1700 cm.⁻¹, 2100 cm.⁻¹ and 2610 cm.⁻¹ in OH₃Br). In addition, some films of