

APPORTIONMENTS OF PRODUCTS FROM UNSYMMETRICALLY
SUBSTITUTED MESOMERIC CARBONIUM IONS

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Beltrame, Bunton and Whittaker¹ have reported that the kinetically controlled mixture of products from the methanolysis (via a carbonium ion) of bornyl chloride (endo-IB, X = Cl, see Table I) isobornyl chloride (exo-IB), and camphene hydrochloride (IA) is rich in the thermodynamically unstable tertiary derivative, camphene hydrate methyl ether (IA-OCH₃), products of the bornyl or isobornyl structure being either entirely absent or found in only small amount. These authors have noted that the presumably similar carbonium ion involved in the reactions of camphene hydrochloride in aprotic solvent² (competing exchange of chloride vs. rearrangement to isobornyl chloride) also reacts more rapidly to give product of the camphenehydro structure.

I wish to point out that these are manifestations of a general phenomenon which is of significance to an understanding of the behavior of mesomeric carbonium ions. The generalization may be stated in the following form: Under kinetically controlled circumstances, the carbonium ion intermediate(s) connecting a pair of Wagner-Meerwein related products reacts with nucleophiles predominantly at that one of the two cationic sites which bears the greater number of alkyl substituents. This amounts to Markownikoff-type behavior; like Markownikoff's original rule, the generalization may require modification in special circumstances, e.g., in acyclic systems, when one of the sites bears an unsaturated substituent such as aryl or alkenyl, or when polar substituents (halogen, carboxyl, etc.) are present. The experimental basis for the generalization is given in Table I. As is the case

¹ P. Beltrame, C. A. Bunton and D. Whittaker, Chemistry and Industry 557 (1960).

² T. P. Nevell, E. de Salas and C. L. Wilson, J. Chem. Soc. 1188 (1939).

with system I, the tertiary bicyclic derivatives II-V are unstable with respect to their secondary isomers under equilibrating conditions. Kinetic control of the products in Table I is assured by the reaction conditions (excess of alkali) and/or by control experiments.

A possible exception to the rule may account for the fact that no tertiary derivative (VIII A) has been reported to arise from solvolyses of derivatives of the pinyl-bornyl (VIII A-IB) or pinyl-fenchyl (VIII A-IIIB) systems; the two stereoisomeric alcohols of structure VIII A, for example,



VIII A

are made by alternate means.¹⁰ Because of the strain involved in generating the bicyclo(3.1.1)heptyl ring system, it seems likely that the carbonium ion intermediates connecting the pairs VIII A-IB and VIII A-IIIB would resist attack at the tertiary position.

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- ³ References cited by J. Simonsen and L. N. Owen, "The Terpenes", Vol. II, Cambridge University Press, 1949, p. 355 ff.
- ⁴ H. Meerwein and L. Gérard, Ann. 435, 174 (1924).
- ⁵ N. J. Toivonen, E. Siltanen and K. Ojala, Ann. Acad. Sci. Fennicae Ser. A II, No. 64 (1955).
- ⁶ G. Komppa and S. Beckmann, Ann. 503, 130 (1933); 509, 51 (1934).
- ⁷ P. D. Bartlett, E. R. Webster, C. E. Dills and H. G. Richey, Ann. 623, 217 (1959).
- ⁸ O. Aschan, Öfversigt Finska Vetenskaps-Soc. Förhandl. 53 A, No. 8 (1910/11).
- ⁹ S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, J. Am. Chem. Soc. 74, 1141 (1952).
- ¹⁰ A. Lipp, Ber., 56, 2098 (1923); O. Wallach, Ann. 356, 239 (1907); W. D. Burrows and R. H. Eastman, J. Am. Chem. Soc. 81, 245 (1959).

TABLE I

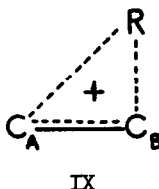
KINETICALLY CONTROLLED PRODUCTS OF SOME CARBONIUM ION REACTIONS

No.	Ref.	Starting material	A	B	Predominant Product
I	1,3,4	C			A
II	5	C			A
III	6	C			A
IV	7	C			A
V	8	C			A
VI	9	D	$\text{CH}_3\text{CHXCH}_2\text{C}_6\text{H}_5$	$\text{CH}_3\overset{\text{C}_6\text{H}_5}{\text{C}}\text{HCH}_2\text{X}$	A
VII	9	D	$\text{CH}_3\text{CHXCH}_2\text{p-C}_6\text{H}_4\text{OMe}$	$\text{CH}_3\overset{\text{p-C}_6\text{H}_4\text{OMe}}{\text{C}}\text{HCH}_2\text{X}$	A

C = chloride prepared from the corresponding olefin, alcohol, or tricyclene and HCl. D = p-toluenesulfonate solvolysis.

The behavior of allylically mesomeric cations suggests the operation of influences that may be related to those responsible for the pattern of Table I. In kinetically controlled reactions, allylic cations give high or even predominant proportions of products resulting from attack of a nucleophile at the more highly substituted carbon of the allylic system, despite the pronounced thermodynamic preference for the allylically isomeric product, which has the more highly substituted double bond.¹¹

The behavior typified by Table I may signify either (i) that the carbonium ion intermediates are unsymmetrically bridged, e.g., IX, or (ii) that the electrical effects of the alkyl groups come into play in the transition states for conversion of the bridged intermediate to products, favoring localization of cationic character at the more highly substituted carbon, C_A.



¹¹ R. H. de Wolfe and W. G. Young, Chem. Revs. 56, 753 (1956).