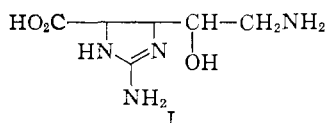


olido)-2-keto-5-acetoxytetrahydrofuran,<sup>24</sup> then sodium borohydride reduction, gave *trans*-1,3-dibenzyl-5-hydroxymethylimidazolid-2-one-4-carboxylic acid, m.p. 160-161.5° (found: C, 66.46; H, 6.42; N, 8.14). Treatment of the latter with sodium in liquid ammonia, then with hot mineral acid, led to formation of *threo*-2,3-diamino-4-hydroxybutyric acid, which was converted into V, m.p. 237-240° (found: C, 37.32; H, 5.54), by treatment with cyanogen bromide. III and V could not be differentiated by paper chromatography in three different systems. The structure of streptolidine (I) is thus 4-(1-hydroxy-2-aminoethyl)-2-aminoimidazoline-5-carboxylic acid.



(24) A gift from Hoffmann-La Roche, Inc.

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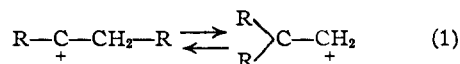
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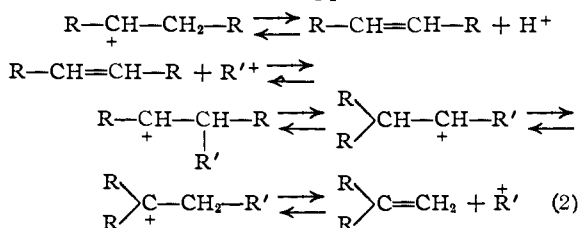
## BIMOLECULAR REACTIONS IN CARBONIUM ION REARRANGEMENTS

Sir:

Primary carbonium ions, arising from intramolecular rearrangements of secondary and tertiary ones, frequently are postulated as intermediates in *liquid phase* isomerizations of paraffins and related compounds. Calculations<sup>1</sup> indicate that at

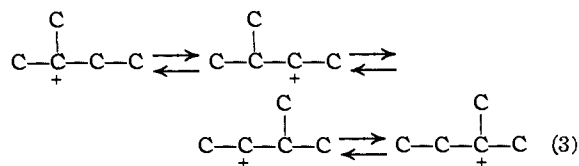


least 22 kcal./mole of activation energy are needed for rearrangements of secondary to primary carbonium ions, and 33 kcal./mole for rearrangements of tertiary to primary. We considered such energies large enough to warrant examination of alternate mechanistic paths, not involving primary carbonium ions. Specifically, rearrangements via *bimolecular* reactions (2) appeared attractive.

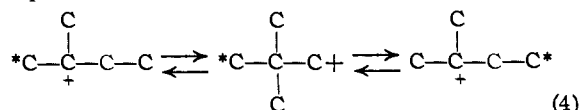


It was demonstrated<sup>2</sup> that isotopic scrambling of C-2  $\rightleftharpoons$  C-3 of 2-methyl-2-chlorobutane-2-C<sup>14</sup> with aluminum chloride does not proceed twice as fast as the scrambling of C-1  $\rightleftharpoons$  C-4 of 2-methyl-

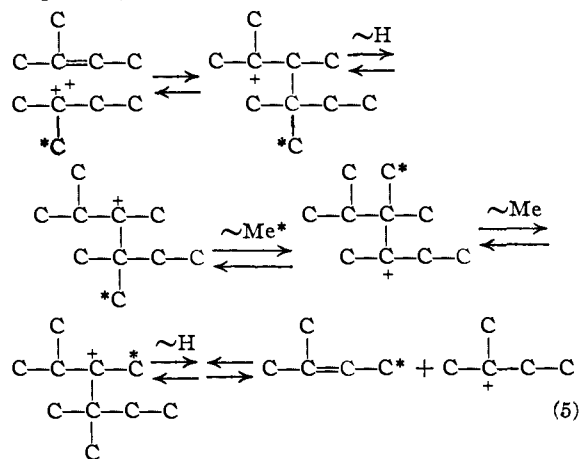
2-chlorobutane-1-C<sup>14</sup> as anticipated if (3) was the only path of isotopic equilibration. Instead, the rate of scrambling of C-2  $\rightleftharpoons$  C-3 versus C-1  $\rightleftharpoons$  C-4 was 1.55. The data necessitated the inter-



pretation that 87% of the rearrangement occurs *via* (3) and 13% *via* (4), since (4) effects C-1  $\rightleftharpoons$  C-4 equilibration, but not C-2  $\rightleftharpoons$  C-3.

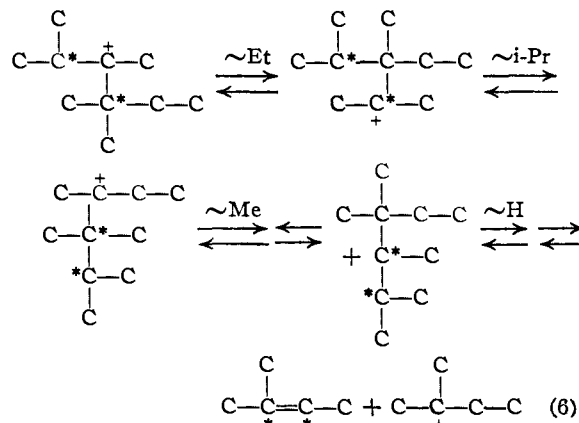


However, the data are also explicable on the basis of bimolecular reactions, without intervention of primary carbonium ions (neopentyl)



Reaction (5), as far as its effect on isotopic equilibration is concerned, is identical with (4). Differentiation between (5) and (4) becomes obvious upon consideration of the implication of (5). If both the cation and the olefin are labeled the recovered *t*-amyl chloride should contain dilabeled species.

Another source of rearrangement and dilabeled species besides (5) is (6).



Reaction (6), unlike (5), leads to dilabeled species from either the C-1 or C-2 labeled chloride (shown

(1) A. G. Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, England, 1946, p. 15.

(2) J. D. Roberts, R. E. McMahon and J. H. Hine, *J. Am. Chem. Soc.*, **72**, 4237 (1950).

