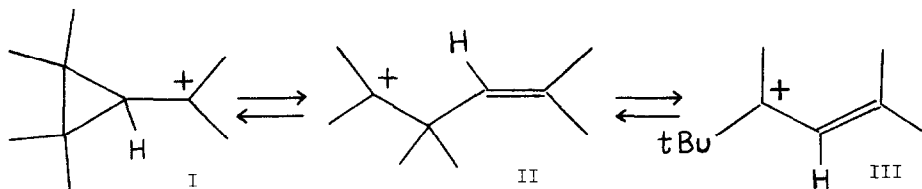


CYCLOPROPYLCARBINYL-ALLYLCARBINYL-ALLYL
CATION REARRANGEMENTS

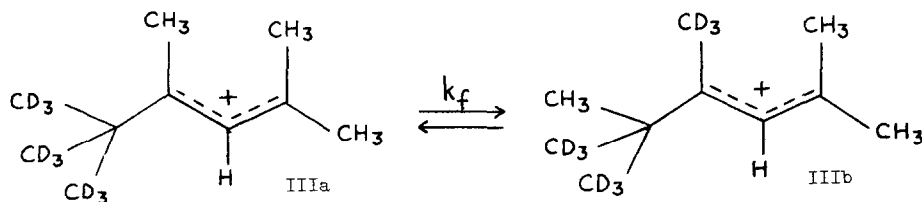
by T.S. Sorensen and K. Ranganayakulu
Department of Chemistry
The University of Calgary
Calgary, Alberta, Canada

(Received in USA 17 October 1969; received in UK for publication 20 January 1970)

Recently, Winstein and Poulter (1) have described a reversible cyclopropylcarbinyl \rightleftharpoons allyl cation rearrangement using the $\alpha,\alpha,2,2,3,3$ -hexamethylcyclopropylcarbinyl \rightleftharpoons 1-t-butyl-1,3,3-trimethylallyl system. We have independently investigated this system and have used a somewhat different approach in order to obtain information relating to a crucial step in this transformation, namely the position (if any) occupied by the "classical homoallyl cation" II, using Winstein's terminology. The following sequence has been used as a simple working model in this work and is identical to that used by the above authors (2).



The reversible nature of the overall reactions was shown by the two following deuterium labelling experiments. Thus, the ion IIIa (3) in FSO_3H solvent rearranges (4) rapidly to put deuterium in the 1-methyl position (IIIb). The forward rate constants for this first order

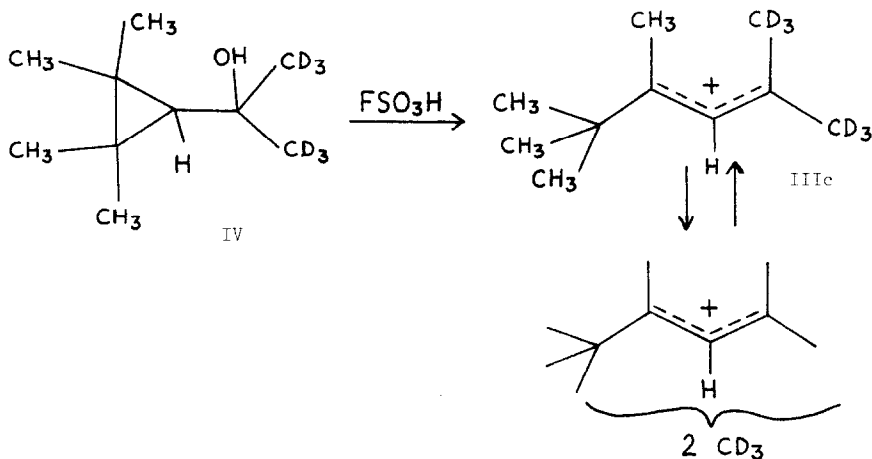


process are reported in Table I. The activation energy for the process is 14.5 ± 1 kcal/mole. Within experimental error, the equilibrium constant is three, showing no measurable isotope effect. Using an n.m.r. line broadening method, Winstein and Poulter report an activation energy of 14.3 kcal/mole.

TABLE I Rates of IIIa - IIIb Reaction

Temp. °C.	-70	-66	-62	-58	-55	-51	-46.5	-44.5	-41.5
$k_f \text{ sec}^{-1}$	5×10^{-5}	9.5×10^{-5}	2.1×10^{-4}	5.1×10^{-4}	6.4×10^{-4}	1.5×10^{-3}	2.1×10^{-3}	3.35×10^{-3}	5.5×10^{-3}

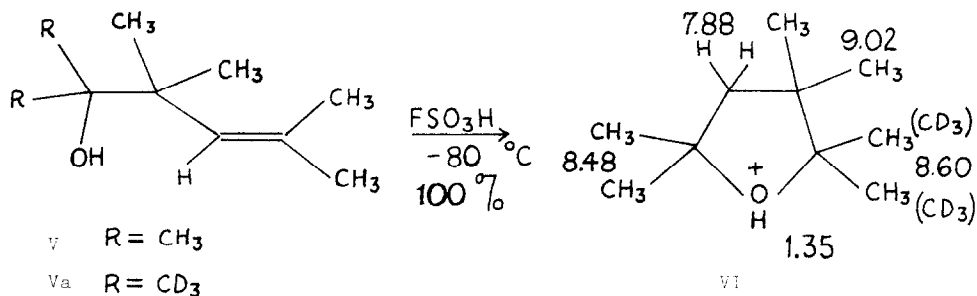
The reported (1) slower six-methyl scrambling in IIIc has been independently observed in this laboratory. This process can be best formulated as proceeding through a degenerate cyclopropylcarbinyl rearrangement of I, as indeed the above authors have also proposed.



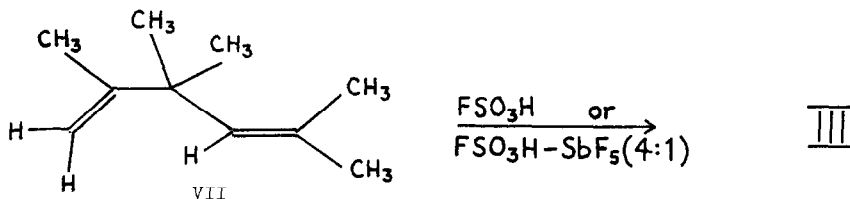
The IIIa \rightleftharpoons IIIb reaction mechanism could conceivably involve:

- Only type II ion(s),
- Only type I ion(s) or,
- Both ion types I and II as intermediates (or II and a symmetrical transition state resembling 1).

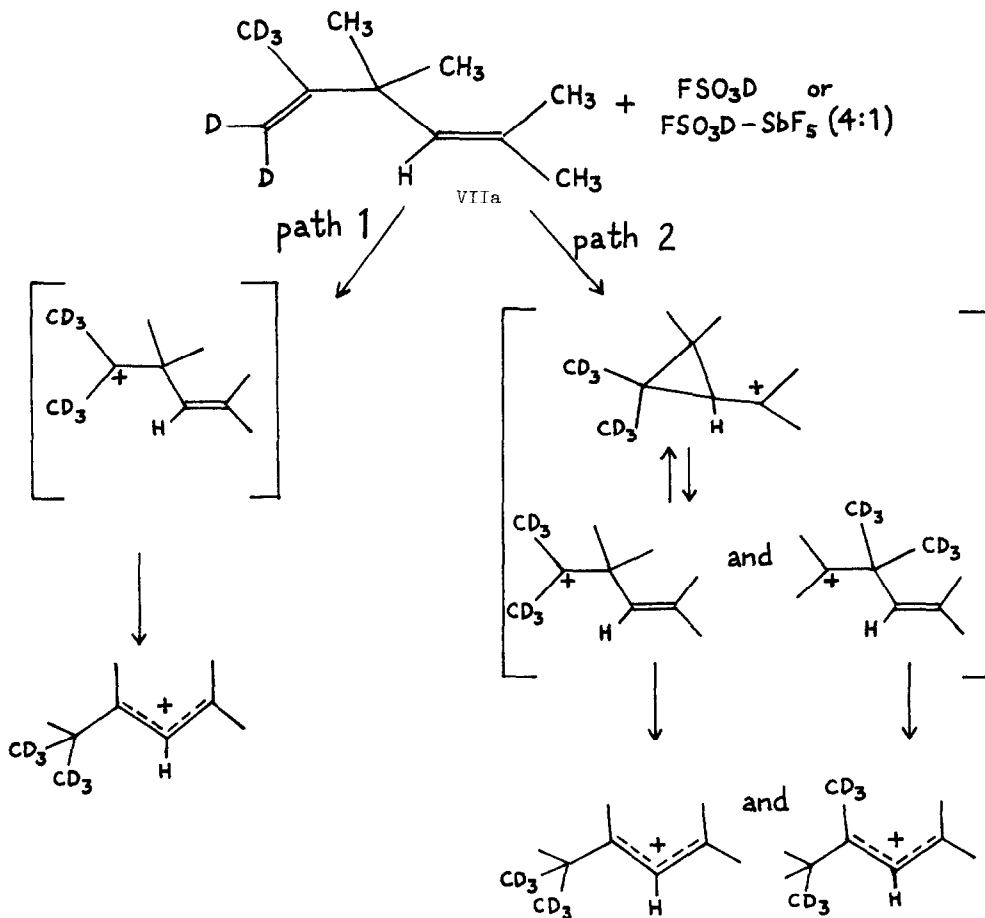
An attempt was made therefore to generate ion II with specific deuterium labelling. The alcohol V could not be used as an ion precursor since the careful addition of this compound to FSO_3H at -80°C yields exclusively the protonated tetrahydrofuran VI (5).



The diene VII, however, in FSO_3H or 4:1 $\text{FSO}_3\text{H-SbF}_5$ yields quantitatively and immediately, at -80°C , the allylic ion III.



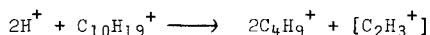
With specific deuterium labelling in the diene (VIIa), the rearranged allylic ion produced contains a completely and evenly scrambled deuterium label between the l-methyl and t-butyl groups. The pathways leading to a scrambled or unscrambled ion (III) are shown below:



The result can be therefore clearly stated: that path 2 is followed, since path 1 leads to an unscrambled ion which has been experimentally shown to be stable (Table I) for short times, under the reaction conditions.

Path 2 is consistent with either mechanism b or c and mechanism a is eliminated. If II is an actual intermediate, then it follows that the $II \rightleftharpoons III$ reaction has the higher activation energy.

Cation III is not indefinitely stable in any of the solvents used in this study. In H_2SO_4 and FSO_3H , III eventually decomposes to yield a product n.m.r. spectrum characteristic of the t-butyl cation disproportionations (6). In 1:1 FSO_3H-SbF_5 , the species formed in about 75% yield appears at τ 4.07 in the n.m.r. spectrum, a position characteristic of the t-butyl cation (7), and the following stoichiometry is probable.



ACKNOWLEDGEMENT

We thank the National Research Council of Canada and the Petroleum Research Fund for generous financial support.

REFERENCES

- (1) C. D. Poulter and S. Winstein, J. Am. Chem. Soc., 91, 3649, 3650 (1969).
See also G. A. Olah and J. M. Bollinger, ibid., 90, 6082 (1968).
- (2) Formula I implies only a symmetrical structure and II an asymmetric one.
- (3) Prepared from 2-t-butyl-4-methylpent-3-en-2-ol (t-butyl d_9).
- (4) (a) Measured in n.m.r. tubes using a Varian HA-100 spectrometer.
(b) Both the increase of t-butyl protons and the decrease of 1-methyl protons can be followed. τ values are reported with reference to external TMS = 10.
- (5) All new compounds were characterized by C, H analysis, i.r. and n.m.r. spectroscopy.
- (6) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, J. Am. Chem. Soc., 86, 1645 (1964).
- (7) G. A. Olah, M. B. Comisarow, C. A. Cupas and C. U. Pittman, Jr., ibid., 87, 2997 (1965).