

SYNTHESIS AND REACTIVITY OF THE ENDO-TRICYCLO[4.2.0.0^{2,8}]OCT-3-EN-7-YL SYSTEM;
A σ -ROUTE TO THE BICYCLO[3.2.1]-OCTA-2,6-DIEN-8-YL CATION

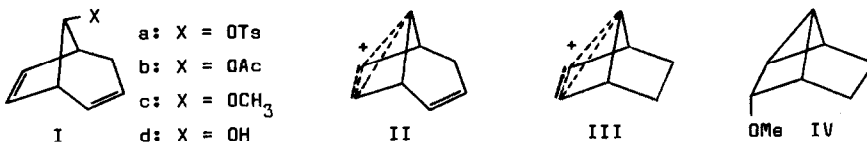
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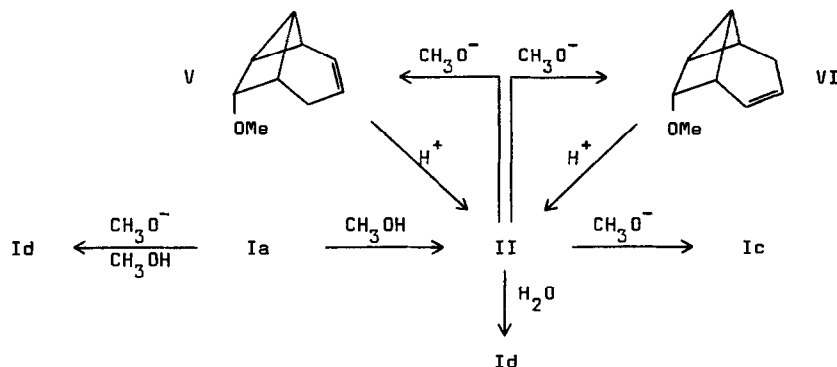
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It had been observed that buffered acetolysis of Ia is anchimerically assisted and that only unrearranged acetate Ib is formed¹. Both observations were rationalized by assuming that ionization of Ia had led to the bishomocyclopropenyl cation II. In order to provide further evidence on this ion we now report upon:

- the methanolysis of Ia in the presence of sodium methoxide, which produced all three methyl ethers expected from the tridentate ion II,
- the synthesis of one (V) of the novel methyl ethers by di- π -methane rearrangement of Ic,
- the kinetics of the acid catalyzed hydrolysis of V.



Methanolysis of Ia in the presence of sodium methoxide was studied, because in the related anti-7-norbornenyl system evidence for the intermediacy of the bishomocyclopropenyl cation III was obtained from the stereospecific production of the tricyclic methyl ether IV under these circumstances². Subjecting Ia to the same conditions also yielded two new tricyclic ethers V and presumably VI together with the unrearranged ether Ic and the unrearranged alcohol Id (see scheme 1). Results obtained at various concentrations of sodium methoxide are collected in table 1.



Scheme 1. Methanolysis of Ia in the presence of sodium methoxide and acid catalyzed hydrolysis of V and VI.

Table 1. Products of methanolysis^a of Ia at 50°

$[\text{NaOCH}_3], \text{ M}$	%Ic	%V	%VI	%Id	% other products
— ^b	90	0	0	0	10 ^c
2	85	8	4	3	—
3.2	60	10	5	25	—
4	19	4	2	75	—

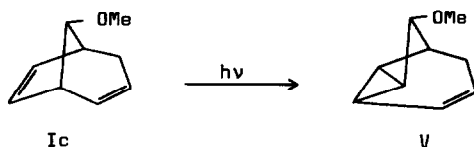
a. The solutions ($[\text{Ia}]$: 0.02 M) were kept at 50° for 72 hours; after work up the products were analyzed by GLC (2 m 20% DEGS, 100°),

b. Solution allowed to become acidic,

c. This product (mol.wt. 168 = Ic + CH_3OH) was not further investigated.

The behaviour of Ia closely resembles that of anti-7-norbornenyl tosylate (VII): Raising the concentration of sodium methoxide leads to an increase of the relative amount of V + VI and to a decrease of the relative amount of Ic in the mixtures formed. A feature not encountered with VII is the production of unrearranged alcohol Id. Because of the relatively low rate of ionization of Ia bimolecular nucleophilic substitution at sulfur leading to Id can become competitive^{3,4}. Since this side-reaction prevented the preparation of V and VI in amounts sufficient for complete spectral and chemical characteriza-

tion V was synthesized in an alternative way via di- π -methane rearrangement of Ic. Irradiation of a cyclohexane solution of Ic at 2537 Å for 65 h gave besides 65% of unreacted starting material about 30% of V, whose IR-spectrum was superimposable upon that of the material obtained from the methanolysis⁵.



The structure of V was deduced from its two modes of formation, its highly specific and very fast (*vide infra*) reversion into Id by dilute aqueous acid (see scheme 1), and from its NMR-spectrum [100 MHz, CDCl_3 , δ (ppm); 5.85 m, 1H; 5.55 m, 1H; 4.1 dd 8.5 Hz and 4 Hz, 1H; 3.2 s, 3H; 2.75 m, 1H; 2.3-2.0 m, 2H; 1.85-1.5 m, 2H; 1.32-1.1 q 5 Hz, 1H]. The multiplicity of the δ 4.1 signal (H-7 coupled to H-6 and H-8) indicates the endo-position of the methoxy group. The same pattern has been observed with IV². Insufficient material was available for NMR identification of VI, however IR-absorptions at 3040, 1007 and 690 cm^{-1} and the close parallelism between its chemistry and that of its congener V [see the dependence of its formation upon $[\text{NaOCH}_3]$ in table 1; VI is converted into Id as readily as is V (scheme 1)] leave little doubt about the structure assigned.

The stereospecific conversions involving the three endo-ethers Ic, V, and VI are completely compatible with the assumption of the bishomocyclopropenyl cation II as the common intermediate of all ionizations shown in scheme I.

Further information about the σ -route to II was gained from a study of the kinetics of the acid catalyzed hydrolysis of V in 80% acetone. First order rate constants obtained at various concentrations of perchloric acid are given in table 2.

Under the same conditions V is about 100 times less reactive than IV^{2a}. This ratio is contrasted with the rate ratio of ca. 8500 observed for VII and Ia⁶ from which III and II are formed by the π -route. Of the several explanations that can be given for this convergence of reactivities the notion that most of the reactivities of IV and V resides in their very similar endo-2-methoxybicyclo[2.1.0]pentyl moieties and that their transi-

tion states leading to III and II have very similar properties seems most attractive⁸.

Table 2. Kinetics^a of hydrolysis of V in 80/20 (v/v) acetone-water at 25^o

$10^3 \times [\text{HClO}_4], \text{ M}$	$10^5 \times k, \text{ sec}^{-1}$	$10^3 \times k/[\text{HClO}_4], \text{ l.mole}^{-1}.\text{sec}^{-1}$
1.72	16.2	94
0.85	8.08	95
0.32	2.90	91

a. Reactions were followed by GLC for about 4 half lives. Only Id was produced.

References

- G.W. Klumpp, G. Ellen, and F. Bickelhaupt, *Rec. Trav. Chim. Pays-Bas*, **88**, 474 (1969).
- a. A. Diaz, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3133 (1966).
b. M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).
- P.G. Gassman, J.M. Hornback, and J.M. Pascone, *Tetrahedron Letters*, 1425 (1971).
- Under the same conditions cleavage of 7-norbornyl tosylate occurred to a much lesser extent. This shows that special factors, which are still unknown, must play a role in the O-S cleavage reaction of Ia.
- R.R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968), have described the same reaction of bicyclo[3.2.1]octa-2,6-diene.
- Values used^{7a}: Ia: k_{25} , acetolysis: $1.12 \times 10^{-7} \text{ sec}^{-17b}$,
 k_{25} , acetone-H₂O (60/40, v/v): $2.29 \times 10^{-6} \text{ sec}^{-1}$; VII: k_{25} , acetolysis:
 $9.04 \times 10^{-4} \text{ sec}^{-17c}$, k_{25} , acetone-H₂O (60/40, v/v): $2.01 \times 10^{-2} \text{ sec}^{-1}$.
- a. G. Ellen, Thesis, Vrije Universiteit, Amsterdam, 1974.
b. This new value differs slightly from that given in ref. 1.
c. S. Winstein, M. Shatavsky, C. Norton, and R.B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).
- Further studies of ionizations of endo-bicyclo[2.1.0]pent-2-yl derivatives and comments on the nature of the various transition states involved: J.J. Tufariello and R.J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969); K.B. Wiberg, V.Z. Williams, Jr., and L. Friederich, *J. Amer. Chem. Soc.*, **92**, 564 (1970); J.J. Tufariello and D.W. Rowe, *Chem. Comm.*, 1066 (1972).