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NOVEL REARRANGEMENT OF EXO-EPOXIDE OF NORBORNENE

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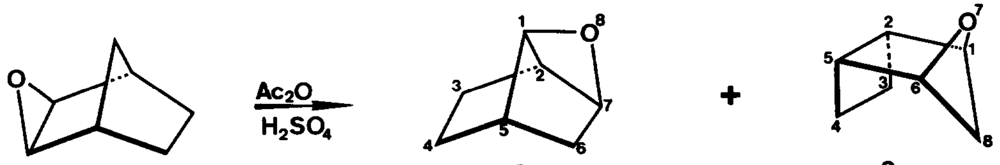
Summary : **Exo-epoxide 1 reacts with Ac_2O in the presence of H_2SO_4 to give two isomeric tricyclic ethers,2 and 3a.**

Starting from the P.von R.Schleyer's ingenious discovery of isomerisation of tetrahydrodicyclopentadiene to adamantane[3],the "stabilomeric" (term see [4]) approach to synthesis of hydrocarbons has been especially fruitful in the area of adamantane-like structures[5]. The key idea of this approach consists in a relief of strain in the course of a transformation of a skeleton via rearrangement/s. As a ramification, we have expanded on this approach to cage ethers : for instance, 2-oxaadamantane can be easily obtained from 2-oxatwistane [6], 2-oxaisotwistane [7] and,what is more,from the readily available bicyclo[3,3,1]nona-2,6-diole [8]. For a long time our groups have been investigating chemistry of strained epoxides [9]. The purpose of the present paper is to describe the stabilomeric rearrangement of exo-epoxide of norbornene,1.

It is well documented,that epoxide 1 [10] (and 8-oxa-analogs [11]) undergoes acid-catalysed epoxide ring opening with Wagner-Meerwein rearrangement. However,the principle products of this rearrangement possess also the norbornane skeleton. We describe here different pathway for that series.

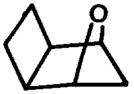
We have found, that the treatment of 1 with Ac_2O in ether in the presence of sulfuric acid proceeds to give the mixture of two isomeric compounds 2 and 3a with their yield and ratio being dependent on the conditions [12,13]. The compound 2 was identified to be 8-oxatricyclo[3,3,0,$0^{2,7}$]octane [14].



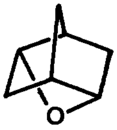
1 **2** **3a**

The ^{13}C NMR data of 3a reveal the presence of four signals [15],and hence of either C_2 or σ. Structural inspection of $C_7H_{10}O$ family and corresponding isomeric interconversions using the computer system FLAMINGOES [16] has shown that only two structures satisfy the spectral requirements, namely stereoisomeric 7-oxatricyclo[4,1,1,$0^{2,5}$]octanes (3a and 3b) and 4-oxatricyclo[3,3,0,$0^{3,7}$]octane, 4. The choice and unambiguous structural assignment has been made using NMR ^{1}H+Eu(fod)$_3$ spectra. Determination of Eu(fod)$_3$ induced chemical shifts permitted to calculate [17] coordinates of hydrogen atoms and position of Eu atom (Fig. 1) and hence, to proove the structure 3a [17].

Taking into account the interrelation of derivatives of 7-substituted norbornane and 2-substituted bicyclo[3,2,0]-



3b



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heptanes[18] we suggest the rationalization presented on Scheme 1. Thus, stabilomeric isomerisation of **1** includes the Wagner-Meerwein rearrangement to give **2** , generation of carbocationic center at C-7 and σ-participation for ion **5**[18] and OH participation in the final step,**6**→**7**, of this unusual rearrangement.

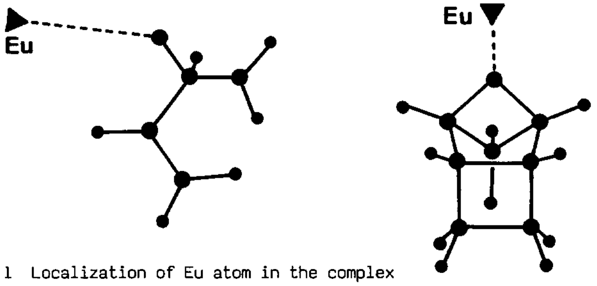
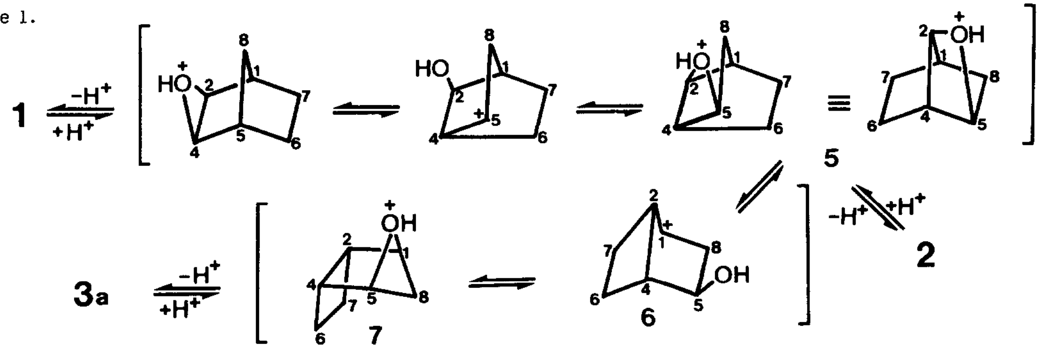


Fig.1 Localization of Eu atom in the complex of Eu(fod)$_3$ + **3a**

Scheme 1.



REFERENCES AND NOTES

1 Kiev State University,Kiev,Ukr.SSR,USSR.

2 Kiev Polytechnical Institute,Kiev,Ukr.SSR,USSR.

3 P.von R.Schleyer,J.Am.Chem.Soc.,**79**,3292 (1957).

4 Z.Majerski and Z.Hamersak,J.Org.Chem.,**49**,1182 (1984) and references therein.

5 A.Greenberg and J.F.Liebman,"Strained Organic Molecules",Acad.Press,M.Y.,SF.,L., chapter 4 (1978).

6 N.S.Zefirov,N.V.Averina,N.K.Sadovaja and Z.A.Rashchupkina,"Chemistry of Polyhedranes",All-Union Conference,Theses,Volgograd,p.104 (1976).

7 This rearrangement has been made by us using the method describing in Refs 6,8.

8 N.V.Averina and N.S.Zefirov,J.Chem.Soc.,Chem.Commun.,197 (1973).

9 N.S.Zefirov and co-workers : Zh.Obshch.Khim.,**36**,197(1966);**37**,2440(1967). L.A.Kas'jan and co-workers : Zh.Org.Khim.,**20**,2295(1984);Tetrahedron Letters,**1979**,949.

10 J.K.Crandall,J.Org.Chem.,29,2830 (1964) and references therein.

11 Yu.K.Yur'ev and N.S.Zefirov,Zh.Obshch.Khim.,**31**,840 (1961);**32**,773 (1962).

12 The mixture of **1** (1g),Ac_2O (10ml) and H_2SO_4 (1ml) in 40ml of ether was stirred 3 min and neutralized Na_2CO_3.The usual work-up gave 0.85g of mixture (1:1) of **2** and **3a**,which were separated with chromatography (silica gel,ether hexane [3:1]).Yields are changeable. Comp.**2** is unstable during purification and storage.

13 Unidentified products were observed if the reaction time and/or amount of the acid was increased.

14 Comp.**2** : m.p.84-85(dec.,from pentane);R_f 0.77;m/e 110 (M^+). ^{13}C NMR (δ,ppm): 90.34(C1),86.87(C7),40.11(C2), 37.98(C5),36.40(C6),23.42(C3),18.96(C4).

15 Comp. **3a** : m.p.42-43.5(from pentane);R_f 0.48;m/e 110·(M^+). ^{13}C NMR (δ,ppm): 85.72(C1,C6),40.19(C2,C5),31.85 (C8),22.70(C3,C4).PMR (200mHz): 4.73(d,2H,J=1.5Hz),2.59(d,2H,J=1.5Hz),2.05(dt,1H,J=1.5,J=11.3),1.69(m,2H),1.44 (dt,1H,J=1.5,J=11.3),1.17(dd,2H,J=2.45,J=8.4).

16 (a) Multipurposed system FLAMINGOES (Ref.16b) permits to perform all types of monocyclic bond redistributions. Computer analysis permitted also to reveal **1**→**2** and **2**→**3a** transformations as possible (and hence,predictable) one-step pathways. (b) N.S.Zefirov and S.S.Tratch,Zh.Org.Khim.,**17**,2465 (1981).

17. M.Yu.Kornilov,T.A.Tolstikov,P.P.Kadzjauskas and E.B.Butkus,Comp.Chem.,**7**,193 (1982);M.Yu.Kornilov,A.V.Titov and V.I.Zamkovoi,Ukr.Khim.Zhur.,**41**,769 (1975). Satisfactory position of Eu for **3b** has not been found at all.

18 J.Wiet and P.Chenier,J.Org.Chem.,**35**,1571 (1970); N.N.Povolotskaja,M.I.Kollegova,A.G.Rumjantseva,A.Yu.Spivak and V.A.Barkhasch,Zh.Org.Khim.,**8**,1037 (1972); W.Kirmse and J.Streu,J.Org.Chem.,**50**,4187 (1985).

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