Tetrahedron Letters No. 44, pp 4293 - 4296.

0040-4039/78/1029-4293$02.00/0

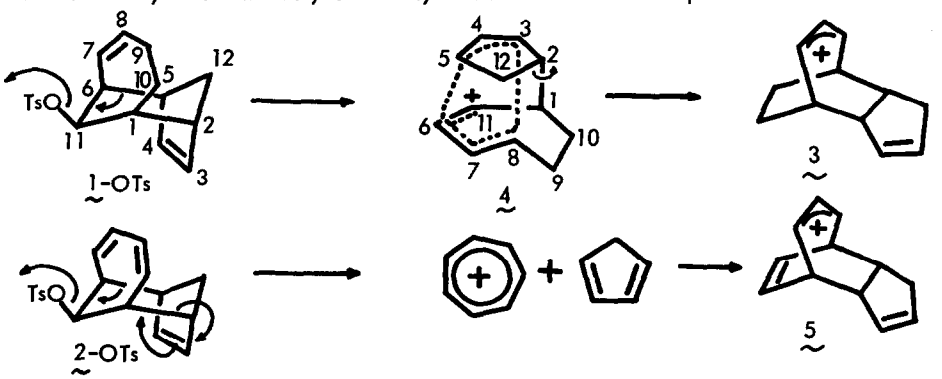
CONCLUSIVE EVIDENCE FOR [3,3] SIGMATROPIC REARRANGEMENT IN THE SOLVOLYSIS OF SOME BRIDGED TRICYCLIC TOSYLATES

Yutaka Fujise, Tetsuo Nakatsu, Akira Nakamura and Shô Itô*

Department of Chemistry, Tohoku University

Sendai 980, Japan

In the previous paper[1] we have reported the solvolysis of exo-tricyclo[4.4.1.1^{2,5}]dodeca-3,7-dien-anti-11-yl and -3,7,9-trien-anti-11-yl tosylates (1-OTs and 2-OTs). In the former reaction, the products derived from the ion 3 were isolated. Since cycloheptatriene and cyclopentadiene do not undergo cycloaddition reaction under the same conditions, the fact is only rationalized by the [3,3] sigmatropy of the ion 1. This rearrangement is unique in that the two three-carbon moieties, $C_3C_4C_5$ and $C_6C_7C_8$, have to interact with each other across the carbon framework (cf. 4), unlike in the reported case[2], and therefore, because of the additional (C_1-C_2) bond connecting them, these moieties have to rotate in opposite direction around C_1-C_2 bond as the reaction proceeds. The reaction of 2-OTs can be explained in the same way to form the delocalized ion 5. However, trapping experiments disclosed the fragmentation pathway to tropylium ion and cyclopentadiene, which are known[3] to undergo cycloaddition to the same ion 5. Thus, we have evidence for two pathways, the intramolecular rearrangement (Path A) and the fragmentation-recombination (Path B), in the solvolysis of two very similar systems. With the anticipation that Path A is also operating



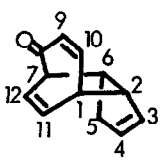
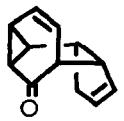
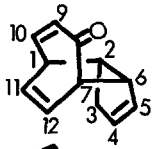
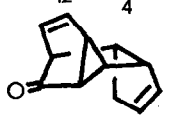
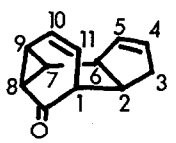
in the latter reaction, we have reinvestigated the reaction using isotopically labelled compound and found that it is indeed the case, although to a less extent than in the former reaction.

In order to determine the product ratios as accurate as possible, we have first developed an analytical procedure[4,5], utilizing the cycloaddition reaction of tropylium ion and cyclopentadiene[3]. By this method, the ratio 6+7:8+9 which reflects that of the nucleophilic attack on the allylic ion 5, was obtained with a reasonable reproducibility. The typical product ratios are shown in Table[6].

The acetolysis products (HOAc, NaOAc, 105°, 48 hr) of 2-OTs were then analyzed after hydrolysis ($LiAlH_4$) exactly in the same way[4] to give the ratios also shown in Table. The ratio 6+7:8+9 in this reaction is apparently larger than that in the cycloaddition. The increase in the ratio in acetolysis implies involvement of a path leading to 6+7 exclusively or preferentially in addition to the Path B revealed before[1], providing the temperature difference between the two reactions does not affect the ratio markedly[7].

In order to determine the extent of Path A, acetolysis of specifically deuterated 2-OTs was examined. The deuterated tosylate 2-d_2-OTs, (D_2 content 94.5%) synthesized[8] from tropone-2,7-d_2, afforded a ketonic

Table. Structures and Ratios of the Products

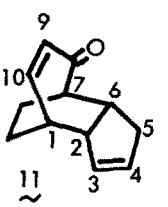
Compd numbers	Structures	Cycloaddition (yield: 72%)	6+7:8+9	Acetolysis (yield: 64%)	6+7:8+9
6		27.4	36.1	36.5	42.8
7		8.7		6.3	
			0.61		0.81
8		53.0	59.3	47.9	53.0
9		6.3		5.1	
10		2.6		4.2	
	others	2		0	

mixture in 83% yield after the same work-up described above. A mixture of 6-d_2 and 8-d_2 was separated from the other products by SiO_2 chromatography and its deuterium content was determined by PMR (100 MHz, Eu(fod)$_3$), using signals due to protons on the 5-membered ring as the internal standards.

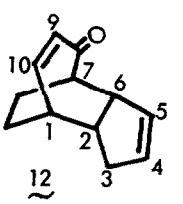
The compound 8 can be formed by path A with the delocalization of the positive charge in the intervening ion 5 and/or by Path B. If the latter is the only pathway operating, the deuterium atoms in 8 should be distributed equally with 27.0% D:H ratio to all carbons originated from tropylium ion, while, if only Path A is operating, the deuterium atoms should be located exclusively at C_1 and C_9. In reality, deuterium content at C_7 and C_9 was found to be 27.1±1.7%, although many other signals overlapped with each other[9]. The result established Path B as the sole pathway to 8 (and 9). At the same time, it eliminated the possibility of delocalization of positive charge in all the intervening ions, suggesting tight ion-pairing during the entire process.

Compound 6 can then only be formed by Path A and by Path B. In the former process, the deuterium atoms should only be located at C_7 and C_9, while in the latter event D:H ratio of 27% is again expected at every hydrogen originated from tropylium ion. Actually, the value 50% was obtained for C_7 and C_9, and 20.8±2.0% for C_1, C_{10}, C_{11} and C_{12}[9], revealing that about 29% of 6 was formed via Path A and the rest via Path B. Since the formation ratio 6:8 is 0.75 (Table), the intramolecular process amounts to about 11% of the whole reaction. Although the consecutive [1,3] sigmatropy which require antarafacial interaction at one of the reacting centers can be eliminated on the basis of geometrical restriction, there are still two symmetry-allowed pathways possible: [3,3] sigmatropy and consecutive [1,5] and [3,3] sigmatropic rearrangements. In view of the recent demonstration[10] of the far-reaching π-π interaction in sigmatropy and the result on 1-OTs[1] (vide infra), the direct [3,3] sigmatropic shift is preferred.

Hydrolysis of 1-OTs was also reexamined using the same analytical procedure[4]. The yield of the tricyclic alcohols derived from the ion 3 amounted to 86%[1]. Intramolecular nature of the reaction was verified by the labelling experiment (56% of D at H_7, 93% at H_9 and 0% at H_{10} starting from 1-1,6-d_2-OTs), establishing Path A as the practically only reaction path. The formation of the isomers 11 and 12, and the presence of only 56% of deuterium at H_7 revealed much weaker ion-pairing in this hydrolysis.



11



12

Thus, the occurrence of sigmatropy was experimentally established in both cases. The difference in its extent in these cases may originate from the relative stability of the respective transition states. The interacting three-carbon moieties in the ion from 2-OTs would have a less favorable geometry for Path A compared with those in 4 because of the reduced flexibility (cycloheptatriene vs. cycloheptadiene), and tend to undergo fragmentation. While thermal [3,3] sigmatropy observed in a very similar situation was rationalized by an intervening diradical intermediate[11], the solvolysis of similar systems is in progress in order to clarify the geometrical factors which control this interesting intramolecular rearrangement.

References and Footnotes

1) S. Itô, I. Itoh, Y. Fujise, T. Nakatsu, C.A. Senkler and P.v.R. Schleyer, Bull. Chem. Soc. Japan, 51, 2379 (1978).

2) R. Breslow and J.M. Hoffman, Jr., J. Amer. Chem. Soc., 94, 2110, 2111 (1972).

3) S. Itô and I. Itoh, Tetrahedron Letters, 2969 (1971).

4) The method consists of the CrO_3 oxidation of whole reaction mixture to the corresponding ketones 6-10[5] after the reaction, and subsequent glc determination of the ratio 6+8:7:9:10[5]. The ratio 6:8 was determined separately by NMR. Since 6 and 8 exhibit their C_{11} and C_{12} signal separated, the ratio was determined by their intensities upon specific irradiation of the bridgehead proton signals.

5) Compound 10 is hitherto unknown liquid. The structure was determined by the following spectral observation in addition to the correct elemental analyses: MS m/e 172 (M^+), 107 ($C_7H_7O^+$), 66 ($C_5H_6^+$, base peak); λ (MeOH) 230 (ε 1440 sh), 297.5 nm (220); ν (liq.) 1695, 1450, 940, 900, 835, 800, 775 cm^{-1}; δ (CCl_4) 1.70-2.20 (3H complex), 2.40-2.68 (3H complex), 3.09 (H_2, tdd, 9.5, 3.2, 1.0), 3.38 (H_6, ddd, 9.5, 7.0, 2.0), 5.48 (H_5, d.sep, 6.0, 2.0), 5.61 (H_{11}, ddd, 9.0, 6.0, 2.0), 5.82 (H_4, dd, 6.0, 2.0), 5.84 (H_{10}, dd, 9.0, 4.2). The sequence of the hydrogens was established by the application of shift reagent and NMDR.

6) The difference in the solvent attack on the allylic ion 5 (ratio 6+7:8+9) can be explained by the asymmetric participation of the double bond in the 5-membered ring (cf. S. Itô, A. Mori, I. Saito, K. Sakan, H. Ishiyama and K. Sasaki, Tetrahedron Letters, 2737 (1973)). The endo:exo ratio is about 95:3, which is somewhat different from that based on the isolated yield[3].

7) When the cycloaddition reaction was carried out at 80° for 20 min., the oxidation of alcohol to the ketone (probably by tropylium ion) occurred extensively which made the product analysis difficult. However, the ratio seemed uneffected. The solvolysis was too slow at room temperature resulting in complete recovery after 1 week.

8) E.E. van Tamelen, P. Barth and F. Lorintzo, J. Amer. Chem. Soc., 78, 5442 (1956).

9) Other signals clearly recognizable are H_{3ex}, H_{3en}, H_5 and H_6 for 8 and H_2, H_{5ex}, H_{5en} and H_6 for 6. All of them contain no deuterium.

10) J.A. Berson and J.M. Janusz, J. Amer. Chem. Soc., 96, 5939 (1974) and private communication from Prof. Berson (Apr. 10, 1978).

11) U. Klinsmann, J. Gauthier, K. Schaffner, M. Pasternak and B. Fucho, Helv. Chim. Acta, 55, 2643 (1972).