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ACETOLYSIS OF PENTACYCLO[7.5.0.0^{2,7}.0^{5,13}.0^{6,12}]TETRADECA-3,10-DIEN-8-YL TOLUENE-p-SULFONATE

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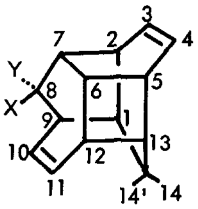
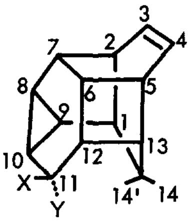
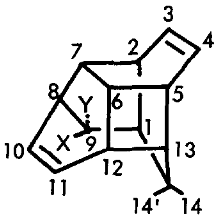
In the previous paper (1), we have reported the formation of the cage molecule, pentacyclo-[7.5.0.0^{2,7}.0^{5,13}.0^{6,12}]tetradeca-3,10-dien-8-one (Ia), by the double cycloaddition reaction of tropone and cycloheptatriene. As considerable internal strain in the molecule was clearly revealed by the X-ray crystallographic study of its 7-chloro derivative (2,3), we are interested in the fate of the corresponding geometrically-fixed homoallylic ion and have undertaken the solvolytic study of tosylate of the corresponding alcohol Ib.



I a: X,Y=O
b: Y=H, X=OH
c: Y=H, X=OTs
d: Y=OH, X=H



II a: X=OH, Y=H
b: X=H, Y=OH
c: X,Y=O



III a: X=H, Y=OH
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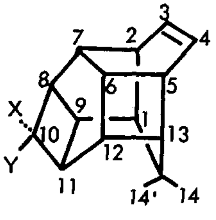
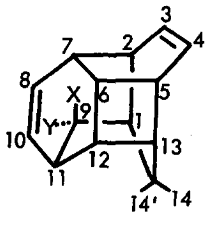
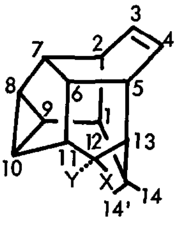


IV a: X=H, Y=OH
b: X,Y=O



V a: X=H, Y=OH
b: X,Y=O



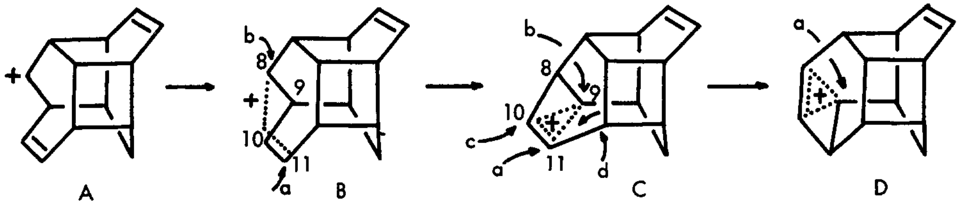
VI a: X=OH, Y=H
b: X,Y=O

The tosylate (Ic), m.p. 122-123°, derived from Ib (1) was subjected to acetolysis at 118° for 11 hrs. The resulted acetate mixture, after treatment with lithium aluminum hydride and separation by silica-gel column chromatography, yielded four isomeric alcohols: IIa, m.p. 163° (d.) (17%), IIb, m.p. 153° (d.) (33%), IIIa, m.p. 170° (9%), IVa, m.p. 130-134° (14%) (4). All the products were formed in the 1st order process as was revealed by glc. The tropylidene moiety remains intact in all of these compounds, since mass spectra of ketone derivatives exhibit the most intense peaks at m/e 92 and m/e 91, corresponding to tropylidene and tropylium ion, respectively, besides the molecular ion (m/e 198) (5).

The structure of the alcohol IIa rests on its IR (ν 3285, 1044, 1014 cm^{-1}) and NMR spectra [$\delta_1,\delta_7,\delta_{13}$:~2.4, δ_2: 2.76, δ_3: 6.15, δ_4: 5.62, δ_5:~3.00, δ_6:~2.7, $\delta_8,\delta_9,\delta_{10}$: 1.00, δ_{11}: 4.13, δ_{12}: 1.33, δ_{14}: 1.15, $\delta_{14'}$: 1.54, $J_{1,2}=8$, $J_{1,14}=3.5$, $J_{1,14'}=1.6$, $J_{2,3}=8$, $J_{2,7}=4$, $J_{3,4}=8.5$, $J_{4,5}=7$, $J_{5,6}=8$, $J_{5,13}=8$, $J_{6,12}=4$, $J_{10,11}=1$, $J_{11,12}=3.2$, $J_{12,13}=6$, $J_{13,14}=2$, $J_{13,14'}=4$, $J_{14,14'}=13$ (6,7)], and its chromic acid oxidation to the cyclopropyl ketone IIc, m.p. 163° (d.) [λmax 280 nm (ϵ 95), ν 1678 cm^{-1}, δ_1,δ_{13}: ~2.60, $\delta_2,\delta_5,\delta_6,\delta_7$: 2.84-3.30, $\delta_{3 \text{ or } 4}$: 5.25, $\delta_{4 \text{ or } 3}$: 5.65, $\delta_8,\delta_9,\delta_{12}$: 1.75-2.1, δ_{10}: 1.48, δ_{14}: 1.32, $\delta_{14'}$: 1.66, $J_{1,14}=5$, $J_{1,14'}=1.6$, $J_{2,3}=6.5$ or 7.2, $J_{3,4}=9$, $J_{4,5}=7.2$ or 6.5, $J_{8,10}=7$ or 8, $J_{9,10}=8$ or 7, $J_{13,14}=2.7$, $J_{13,14'}=4$, $J_{14,14'}=13$]. The second alcohol IIb [ν 3265, 1049, 1007 cm^{-1}, δ_{11}: 4.07 (dd, J=4.6, 4.1)] is the epimer of IIa as it is oxidized to IIc by chromic acid.

Spectra of the third alcohol IIIa revealed the presence of secondary hydroxyl group [ν 3500, 1092 cm^{-1}, δ_9: 3.77 (dd, J=4.2, 1.5)], two cis double bond [ν 1627, 683 cm^{-1}, $\delta_{3 \text{ or } 4}$: 6.09, $\delta_{4 \text{ or } 3}$: 5.82, $\delta_{10 \text{ or } 11}$: 6.32, $\delta_{11 \text{ or } 10}$: 6.40] and a methylene group (δ_{14}: 1.19, $\delta_{14'}$: 1.47, $J_{14,14'}=12.0$). The configuration of the hydroxyl group was deduced from the coupling constants of the carbinyl hydrogen, H_9. Chromic acid oxidation of IIIa gave the β,γ-unsaturated 5-membered ring ketone IIIb, m.p. 188-190°, [λmax 288 nm (ϵ 110), ν 1740 cm^{-1}]. Although the NMR spectrum of IIIb was very complicated, NMDR experiment revealed that the methylene group [δ_{14}: 1.33 (t, J=12.2, 4.5), $\delta_{14'}$: 1.74 (br.d, J=12.2)] was separated at least by three single bonds from any of the olefinic linkage.

The fourth alcohols IVa [ν 3500, 1127, 686 cm^{-1}, $\delta_{14},\delta_{14'}$: 1.33 (2H, br.t), δ_{10}: 4.21 (t, J=5.5)] contains only one double bond [δ_3,δ_4: 5.5-6.5 (2H, m)]. On chromic acid oxidation, IVa yielded the 4-membered ring ketone IVb [m.p. 134-136°, λmax 285 nm (ϵ 120), ν 1768 cm^{-1}, $\delta_{14},\delta_{14'}$: 1.38 (2H, t, J=3.2), δ_3,δ_4: 5.7-6.4 (2H, m)] (8).



From the product analysis described above, it is clear that only the homoallyl-cyclopropylcarbinyl-cyclobutyl type rearrangement and no cleavage nor simple 1,2-shift of C-C single bond have occurred during the acetolysis. Therefore, initially-formed homoallyl cation A with the fixed geometry would change immediately to the asymmetrically-participated nonclassical ion B which is stabilized by the participation of C=C, since C_{10}-C_{11} double bond is situated closely to C_8. The acetate of IIb would be resulted by the stereospecific attack of nucleophile on the ion B (attack a). The absence of the product corresponding to the epimer Id of Ib (attack b) suggests the formation of IIb acetate be concerted (9). Subsequent participation of C_9-C_{10} bond results in the formation of the delocalized ion C with less internal strain. The formation of the acetates of IIa, IIIa and IVa would be the result of the stereospecific attack of nucleophile on the ion C at all the three possible positions, C_{11} (attack a), C_9 (attack b), and C_{10} (attack c) (10). Thus, all the products can be rationalized by the intervening ion B and C. In this connection, it is of interest that IIc and IIIb was found among the product of the cycloaddition reaction of tropylium ion and cycloheptatriene after subsequent oxidation (11).

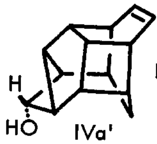
When the acetolysis was carried out at higher temperature (150°, 24 hrs) the product distribution changed completely. After the separation of the acetate mixture by preparative glc [two peaks due to acetates (12)] followed by the hydrolysis, IIIa was obtained in 11% yield, along with two new alcohols, Va and VIa, which were separated partially by SiO_2 chromatography. Most pure alcohols were oxidized to the corresponding ketones Vb, m.p. 124-127° (subl.) and VIb, m.p. 174-180° (subl.). The yield of ketones was 30% and 16% from Ic, respectively.

Va contains a tropylidene moiety [m/e 198 (M^+), 92, 91, $\delta_{14}, \delta_{14'}$: 1.90 (2H, s), β,γ-unsaturated 6-membered carbonyl group [λmax 284 nm (ε 272), ν 1725 cm^{-1}] and two olefinic linkage [δ_{10}: 5.60 (dd, J=9.0, 6.0), δ_8: 6.01 (dd, J=9.0, 5.5), δ_4: 6.24 (dd, J=7.5, 6.3), δ_3: 6.42 (ddd, 7.5, 6.3, 1.6)], while VIb has a 5-membered carbonyl [λmax 282 nm (ε 37), ν 1745 cm^{-1}], a double bond [δ_3: 6.09 (dd, J=9.2, 6.7), δ_4: 6.32 (dd, J=9.2, 6.7)] and a cyclopropane ring [$\delta_8, \delta_9, \delta_{10}$: 0.95-1.20 (3H, complex) as well as the tropylidene moiety [m/e 198 (M^+), 92, 91, $\delta_{14}, \delta_{14'}$: 1.55 (2H, br.s)]. The structures of the ketones were elucidated by NMDR coupled with the use of $Eu(fod)_3$ shift reagent. Stereochemistry of the hydroxyl groups in Va and VIa was determined from the coupling patterns of their carbinyl protons at δ_9: 4.17 (s) for Va and δ_{12}: 3.90 (br.s, $W_{1/2h}$=8) for VIa.

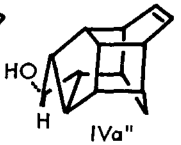
This experiment clearly disclosed the involvement of one more ionic species D for the formation of Va acetate, while the formation of VIa acetate only needs 1,2-migration of C_6-C_{12} bond to C_{11} with the subsequent stereospecific nucleophilic attack. Such a skeletal rearrangement needs the activation energy and therefore higher temperature. However, the cause of the whole reaction sequence can only be rationalized by the strain energy present in the original molecule Ic, which would be released by the skeletal rearrangement. Apparently, the localization of the positive charge in C by the 1,2-bond migration (path d) would be unfavored unless the strain in 4-membered ring is released.

References and Footnotes

1) S. Itô, Y. Fujise and M.C. Woods, Tetrahedron Letters, 1059 (1967).
2) Y. Fukazawa, S. Itô and Y. Iitaka, Acta Cryst., B25, 665 (1969).
3) The identity of the skeleton of both compounds has been rigorously established when reduction of ethylene ketal of the chloro compound was found to produce the derivative of Ia (Y. Fujise, Ph.D. Thesis, Tohoku University, 1967).
4) A few more minor alcohols are present in the reaction mixture, but not studied further. Their yields are less than 1%.
5) S. Itô, Y. Fujise and M. Sato, Tetrahedron Letters, 691 (1969).
6) Spectra were measured in the following status: UV, in methanol: IR, as KBr pellet: NMR, in $CDCl_3$. All the NMR parameters were determined by the aid of NMDR.
7) The numbering system in these alcohols and ketones should follow the IUPAC rule. However, in this paper the numbering in Ia is followed for the convenience of comparison and discussion.
8) The alternative structures IVa', IVa" were eliminated from the following observations. i) The coupling pattern (t, J=5.5) of the carbinyl proton suggests the presence of two vicinal hydrogens in cis disposition, ii) the chemical shift of methylene hydrogens is identical both in IVa IVb and, on going from IVa to IVb, the signal exhibits a down field shift. Those observations suggest that the hydroxyl group is not in the vicinity of the methylene hydrogens.



IVa'



IVa"

9) Since Id acetate is stable under the solvolytic condition, its absence in the solvolysis products suggests that the nucleophilic attack at C_8 of the ion A had not occurred.
10) Although IIa might have been formed by the nucleophilic attack on the ion B (attack with poor stereoselectivity), we prefer the stereospecific attack on the ion C, because the stereospecificity is held at all other attacks.
11) S. Itô, A. Mori, I. Saito, K. Sakan, H. Ishiyama and K. Sasaki, Tetrahedron Letters, 2737 (1973).
12) The intensity ratio was 64:25. Although another peak (ca. 10%) was present in glc, it was not studied further, because its mass spectrum showed it to be a mixture of compounds with no acetoxyl group.