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STEREOCHEMISTRY OF CATIONIC ADDITION - π,π TRANSANNULAR CYCLIZATION OF 1,5-CYCLOOCTADIENE

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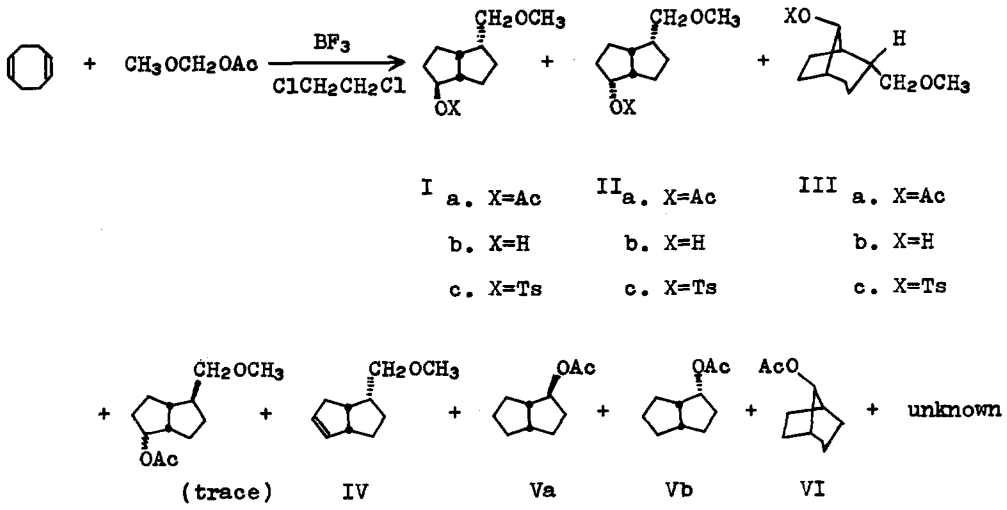
The chemistry of carbonium ion stabilized by means of an appropriately located π-bond or, in some cases, of a σ-bond has been remarkably advanced(1). The observed strong C^+-π interaction suggests that if an unconjugated diene is treated with cationic reagent, transannular cyclization should take place. Cis, cis-1,5-cyclooctadiene seems to be a very favorable unconjugated diene for cationic π-π (concerted) or C^+-π (stepweise) cyclization since 1- and 5-double bond are parallel with only a small angle of Pz axis (39.5°) and ca. 1.74 C-C bond distance apart so that overlap of π-orbitals seems to be very effective. And yet, a little is known on the cationic addition-cyclization of 1,5-cyclooctadiene (COD)(2), although radical addition to COD was investigated somewhat in detail where a transannular cyclization ($C\cdot$ - π) products were obtained in fairly good yield(3).

In this communication, the authors describe the stereochemistry of addition of methoxymethyl acetate or other disubstituted methanes on COD in the presence of boron trifluoride catalyst. Products are shown in Scheme 1.

Scheme 1



I a. X=Ac II a. X=Ac III a. X=Ac

b. X=H b. X=H b. X=H

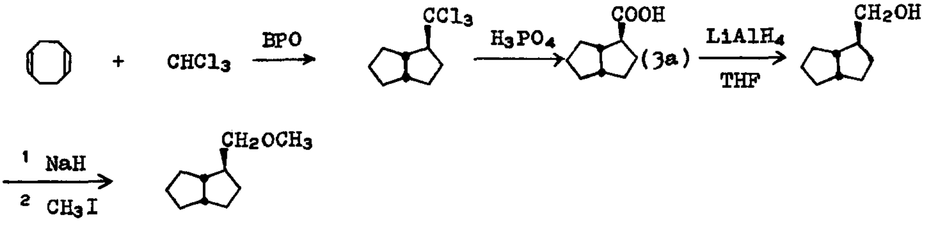
c. X=Ts c. X=Ts c. X=Ts

(trace) IV Va Vb VI

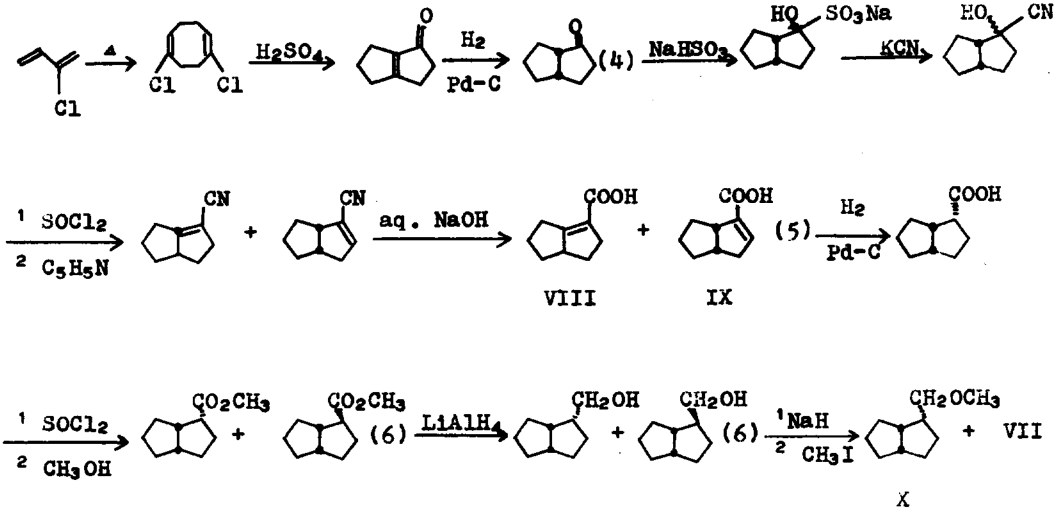
Product Composition, Ia 14.8%, IIa 9.4%, IIIa 10.7%, IV 26.0%, monoacetate 4.9% (V, VI and a small amount of Δ^4-cyclooctenyl acetate), unknown 34.3% (more than 7 compounds)

Structural assignments of I-VI were made on spectral ground (nmr, IR), VPC and elemental analyses. Authentic exo- and endo- cis, cis-bicyclo[3,3,0]oct-2-ylmethyl methyl ether were prepared according to Scheme 2 for the identification purpose.

Scheme 2



VII



Product Ia and IIa (b.p. 128-132°/11mmHg) were hydrolyzed (to Ib and IIb, respectively (b.p. 95-100°/7mmHg)) and the alcohols were converted to the corresponding tosylates Ic and IIc. Then, Ic and IIc were reductively cleaved with $LiAlH_4$, leading to the same ether X, not to VII. Configuration of another saturated ester ether was tentatively assigned as IIIa on the spectral ground and VPC behavior. nmr spectrum of Ia and IIa (CCl_4, TMS) τ 8.1-8.8 multiplet, 8.10 singlet (three protons), 7.2-8.0 very broad multiplet (three protons), 6.80 singlet and 6.65-7.0 thin multiplet (five protons, combined), and the multiplet of proton α to acetoxyl (one proton) centered at 5.35 in the case of Ia and centered at 4.95 in the case of IIa. nmr absorption of a proton α to acetoxyl , especially , affords an useful information of the stereochemistry(7) and IIIa has a higher τ value and less broad shape than Ia or IIa. The nmr absorption is in quite agreement with that of 8-endo-H of bicyclo[3,2,1]octane derivatives. Exo-bicyclo[3,3,0]oct-2-ylacetate (endo H) showed a higher τ value than the endo (exo H) isomer and both have similar broad quartet-like shape.

Additional proof for the position of acetoxyl group in Ia or IIa was obtained from the conversion of corresponding alcohols Ib and IIb to the single ketone by CrO_3-AcOH oxidation. The nmr spectrum of the ketone(CCl_4, TMS) showed that only two methylene protons α to carbonyl were present τ 7.7-8.05

thin multiplet(8). The ketone gave IIb by means of $NaBH_4$ reduction. Identification of IV was made by means of its conversion to the saturated ether X.

Other disubstituted methanes, $AcOCH_2OAc$, $CH_3OCH_2OCH_3$, $ClCH_2OCH_3$ also gave similar products which were identified via conversion to I, II, III, VII or X. Detailed description of the results will appear in a separate paper.

The stereochemistry reported here indicates that cationic reagent approaches almost exclusively from outside (exo-wise) of COD to give 2-endo substituted cis bicyclo[3,3,0]octyl carbonium ion. The finding is contrast to addition-π,π cyclization of COD with CCl_3 and other radicals, where an attacking reagent occupies 2-exo position in a cis bicyclo[3,3,0]octyl derivative(3). Nonconcerted character (at least, in part) of the addition of the disubstituted methanes can be seen by the formation of the proton-elimination product (IV), rearranged product (III) and nonstereoselective addition product (I). The finding is contrast to complete stereoselective cyclization of cis, cis-1,6-cyclodecadiene with Br_2-CH_3OH addition(9). The discrepancy may be partly attributable to the different concentration and/or nucleophilicity of CH_3OH to $[BF_3\cdot OAc]^-$ or CH_3OCH_2OAc. More detailed discussion will be presented.

References

1. See e.g., P.D.Bartlett, "Nonclassical Ions", Benjamin Inc., 1965. π-participation now becomes almost conclusive with many evidence, e.g., H.Tanida et al, J.Am.Chem.Soc., 86, 4904 (1964), but nature of σ-bond participation is still uncertain and some arguments against σ-participation in norbornane system were also presented; e.g, M.Rei and H.C.Brown, J.Am.Chem.Soc., 88, 5335 (1966), H.C.Brown and K.Takeuchi, ibid., 88, 5337 (1966).
2. Limited examples of the reaction are : a) acid catalyzed formic acid addition ; A.C.Cope and P.E.Peterson, J.Am.Chem.Soc., 81, 1940 (1959), b) phosphoric acid-silica gel catalyzed isomerization ; German Patent, 1, 167, 824, Chem.Abstr., 61, 1776 (1964).
3. a) addition of HCOX, $CHCl_3$, $CHClCO_2C_2H_5$ etc. ; R.Dowbenko, Tetrahedron, 20, 1843 (1964), b) addition of HCO_2CH_3 ; L.Friedman, J.Am.Chem.Soc., 86, 1885

(1964), c) addition of acetic anhydride ; G.Pregaglia and G.Gregolio, Chem. Ind. (Milan), 45, 1065 (1963).

4. A.C.Cope and W.R.Schmitz, J.Am.Chem.Soc., 72, 3056 (1950), where only VIII was reported as the product.
5. A.C.Cope and M.Brown, J.Am.Chem.Soc., 80, 2859 (1958).
6. The ester was consisted of 73% endo and 27% exo isomers. The alcohol contained 70% endo and 30% exo isomers.
7. See a separate communication.
8. The corresponding 3-one are not available in the authors laboraty, but a pair of unsubstituted ketone (2-one and 3-one) are available. The former shows quite similar the absorption of two methylene protons α to C=O while the latter shows the absorption of four methylene protons α to C=O (τ 7.65-8.10, relatively thin multiplet). From these chemical and spectroscopic observations, our single ketone should be 2-one so that Ia and IIa were identified as exo-2-OAc and endo-2-OAc, respectively.
9. R.M.Gipson et al, J.Am.Chem.Soc., 88, 5366 (1966).