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CATIONIC TRANSFORMATIONS IN THE TETRACYCLODECENYL SERIES; THE TETRACYCLO$[4.3.1.0^{3,8}.0^{7,9}]$DEC-4-EN-2-YL SYSTEM

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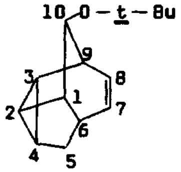
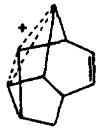
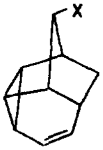
Recently we reported the synthesis of exo-10-*t*-butoxytetracyclo$[4.4.0.0^{2,4}.0^{3,9}]$dec-7-ene (I).[1] Since this compound appeared to be a suitable precursor of a novel trishomocyclopropenyl cation II[**] we undertook the acid cleavage of I. Under the usual conditions[2] only one product, a singly unsaturated acetate (NMR:[***] 6.23 d,d 8.5 Hz, 7 Hz, 1H; 5.75 d,d 8.5 Hz, 7 Hz, 1H; 4.74 d,d 8 Hz, 6.5 Hz, 1H; 3.2 q 7 Hz, 1H; 2.8 m, 2H; 2.2-2.5 m+s, 8H) was obtained in 90% yield. Acetates IIIa - Va resulting from stereospecific attack of acetic acid on carbons 2, 3 or 10 of the presumed intermediate II were considered likely structures of the new compound.



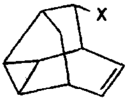
I



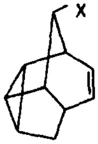
II



III



IV

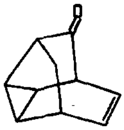


V

a: X = OAc

b: X = OH

c: X = H



VI

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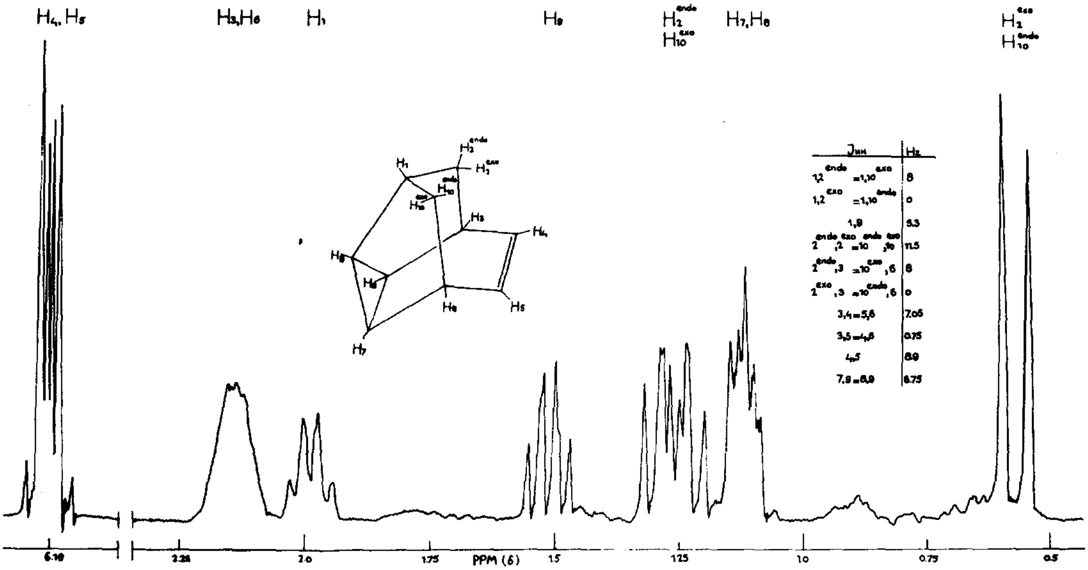
**) Further delocalization of the positive charge by the double bond may be possible (vide infra).

***) 60 MHz NMR spectra were measured in CCl_4 with internal TMS, data are given in ppm(δ).

The following results are incompatible with structures IIIa and Va; they are in accord with structure IVa, exo-2-acetoxytetracyclo[4.3.1.$0^{3,8}$.$0^{7,9}$]dec-4-ene:

- When IVa was treated with $LiAlH_4$ in ether, an alcohol IVb (NMR: 6.35 d,d 8.5 Hz, 7 Hz, 1H; 5.8 d,d 8.5 Hz, 7 Hz, 1H; 4.02 d,d 8 Hz, 6.5 Hz, 1H; 2.9 m, 2H; 2.53 q 6 Hz, 1H; 2.1-1.4 m, 6H) was obtained (83%). Slopes observed on $Eu(dpm)_3$ shift analysis indicated that one methylene proton (part of the 2.1-1.4 multiplet) and the olefinic proton at δ = 5.8 were located in the proximity of the OH-group. This is in accord with structure IVb only.
- Ketone VI obtained from IVb by Jones oxidation (75%) had $\bar{\nu}_{C=O}$ 1738 and 1755 cm^{-1}. Higher values of $\bar{\nu}_{C=O}$ are expected for the ketones derived from IIIb and Vb.[3]
- Huang-Minlon reduction of VI yielded a hydrocarbon (50%) which was different from Vc.[1] Its 220 NMR spectrum indicated a symmetric structure, IVc, the pattern of the olefinic protons resembling that of pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]dec-9-ene.[4]

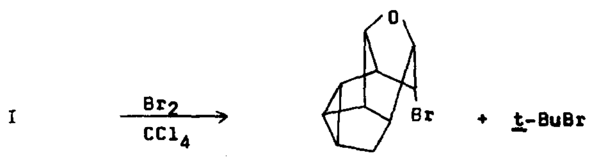


J_{HH}	Hz
$1,2^{endo} = 1,10^{exo}$	8
$1,2^{exo} = 1,10^{endo}$	0
$1,9$	5.3
$2^{endo},2^{exo} = 10^{endo},10^{exo}$	11.5
$2^{endo},3 = 10^{exo},6$	8
$2^{exo},3 = 10^{endo},6$	0
$3,4 = 5,6$	7.05
$3,5 = 4,6$	0.75
$4,5$	8.9
$7,9 = 8,9$	6.75

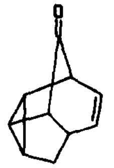
The 220 MHz NMR spectrum of IVc in $CDCl_3$ with internal TMS; coupling constants were obtained from expanded scale spectra.

IVb was converted into its tosylate (81%, m.p. 75-76°) which on buffered acetolysis gave IVa. $LiAlH_4$ reduction of the tosylate in ether gave IVc (80%).

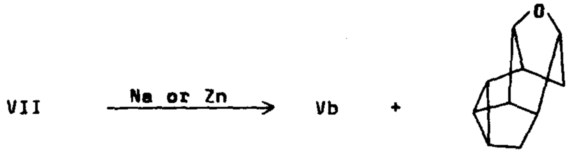
An alcohol which is assigned structure Vb (NMR: 6.35-6.08 m, 1H; 5.75 t 7.5 Hz, 1H; 4.1 m, 1H; 2.7-2.3 m, 3H; 2.2-1.5 m, 4H; 1.4-1 m, 2H) was obtained by a bromination-debromination sequence: Treatment of I with one equivalent of bromine in CCl_4 at room temperature yielded 80% of a bromoether VII (NMR: 5.03 t 5 Hz, 1H; 4.07 t 4 Hz, 1H; 3.75 m, 1H; 3-2.5 m, 4H; 2.1-1.5 m, 3H; 1.3 q 7 Hz, 1H) and t-butyl bromide. Debromination of VII with sodium or zinc gave Vb together with varying amounts of a compound $C_{10}H_{12}O$ (NMR: 4.9 t 5 Hz, 1H; 4.2 t 4.5 Hz, 1H; 2.9-1.1 m, 10H) which is assumed to be VIII (total yield 65%).



VII



IX



VIII

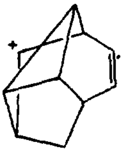
	Vb : VIII
Na/THF	20 : 1
Na/t-BuOH/THF	3 : 2
Zn/HOAc/i-PrOH	1 : 5

Structures VII and VIII are assigned on mechanistic grounds and spectroscopic properties. The assignment of structure Vb to the new alcohol is based on the following arguments:

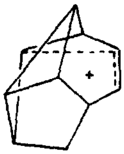
- The NMR spectra of Vb and I are very similar; $Eu(dpm)_3$-induced shifts are of the order expected for structure Vb, e.g. the olefinic protons on C-7 and C-8 are shifted much more than the methylene protons on C-5.
- Jones oxidation of Vb led to ketone IX (75%) which has $\bar{\nu}_{C=O}$ 1762 cm^{-1} and which could be reconverted to Vb with $LiAlH_4$. Treatment of IX with tosylhydrazide gave the tosylhydrazone, which was reduced to Vc[1] by $LiAlH_4$.[5]
- The reactivity of Vb closely corresponds to that of I:

Tosylation followed by buffered acetolysis of the crude tosylate led to IVa; bromination gave VII; refluxing with thionyl chloride in ether as well as treatment with triphenylphosphine in CCl_4[6] led to a chloride $C_{10}H_{11}Cl$, which was also obtained from IVb and which on dechlorination with Na/t-BuOH/THF gave IVc.

The stereospecific formation of IVa from exo-tetracyclo[4.4.0.0^{2,4}.0^{3,9}]dec-7-en-10-yl derivatives I and Vb as well as from exo-tetracyclo[4.3.1.0^{3,8}.0^{7,9}]dec-4-en-2-yl tosylate is compatible with the formation of a common delocalized intermediate II from both types of starting material. Exclusive attack at C-3 of II may be caused by a high contribution of structure X. Models indicate that X is much less strained than ions carrying a positive charge on C-2 or C-10. Also, localization of positive charge on C-3 could be favored by the possibility of additional homoallylic delocalization as depicted by structure X'.



X



X'

Kinetic studies on the solvolyses of suitable esters of IVb, Vb and related compounds will be presented in the future.

References

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