Tetrahedron Letters No. 41, pp 3641 - 3644, 1974. Pergamon Press. Printed in Great Britain.

THE PROTONATION OF "SNOUTENE" (PENTACYCLO$[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]$DEC-9-ENE)

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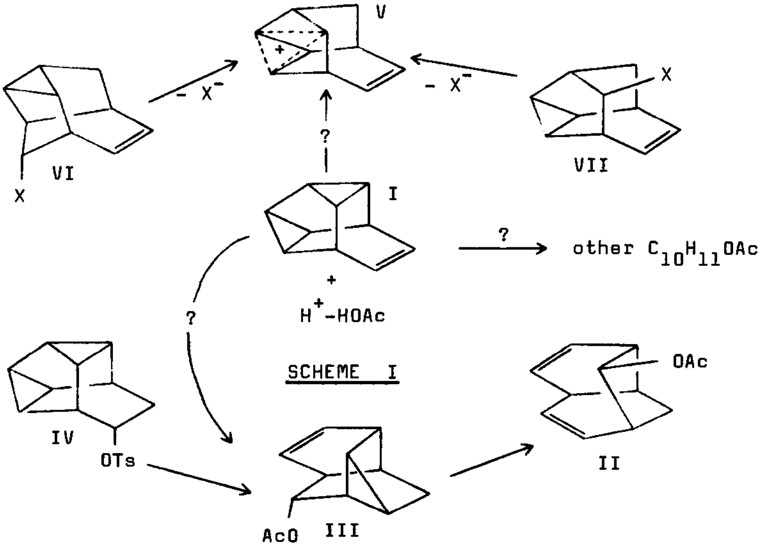
(Received in UK 26 June 1974; accepted for publication 29 August 1974)

Introduction

Our interest in homoaromatic systems led us to consider the possibility that compounds obtained by lengthy routes might be available by protonation of "snoutene" (I)[1]. In scheme I possible modes of protonation of I are indicated by a question-mark, i.e.:

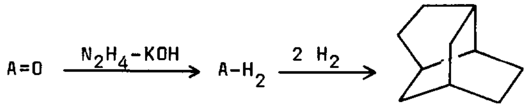
- Does protonation occur at the double bond and does it lead to the same trishomocyclopentadiene derivative II, recently obtained by us[2] from III (which itself had originated from IV)[3]?
- If, instead, one of the cyclopropane rings were attacked by the proton, would this provide a new path to the trishomocyclopropenyl cation V, that is formed upon solvolysis of the very reactive systems VI and VII[4]?
- Which other structures $C_{10}H_{11}^+$ are formed by protonation of I?



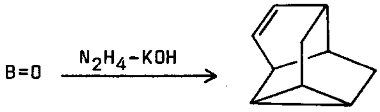
SCHEME I

Results

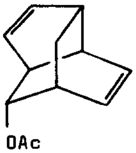
On exposure to acetic acid containing p-toluene sulfonic acid (0.15 M) I readily added one molecule of acetic acid forming three isomeric acetates A-OAc (4-vinyl protons, H-C-OAc doublet, J = 4 Hz at δ [ppm] 4.62), B-OAc (2 vinyl protons, H-C-OAc singlet at δ 5.17), and C-OAc (2 vinyl protons, H-C-OAc triplet, J = 4.5 Hz at δ 5.31). After one hour at 40° the ratio of A-OAc : B-OAc : C-OAc was 42 : 45 : 13; after 40 hours only A-OAc was present. A-OAc was not identical with II and none of B-OAc and C-OAc was identical with VII (X = OAc), the product which is formed from V[4]. II and VII (X = OAc) were stable under the reaction conditions. For further investigation the acetates were isolated by vpc, cleaved with LAH, and the alcohols obtained oxidized with Jones reagent to ketones A=O ($\nu_{C=O}$: 1729 cm^{-1}) and B=O ($\nu_{C=O}$: 1722 and 1739 cm^{-1}). B-OH and C-OH yielded the same ketone B=O, which with LAH regenerated B-OH and C-OH in the ratio 3 : 7. The conversions of A=O to isotwistane (VIII)[5] and of B=O to IX[3] served to identify the carbon skeletons, and, since A=O contained two double bonds and B=O was not identical with the known ketone derived from IX[3], also defined the positions of the oxygen atoms. The configurations of the acetates X - XII could then be assigned on the basis of the H-C-OAc patterns observed in the NMR spectra.



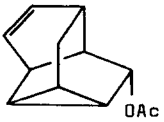
VIII



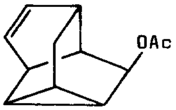
IX



X (≡A-OAc)

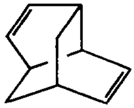


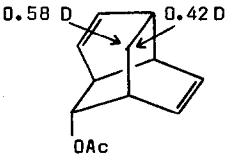
XI (≡B-OAc)



XII (≡C-OAc)

XIII



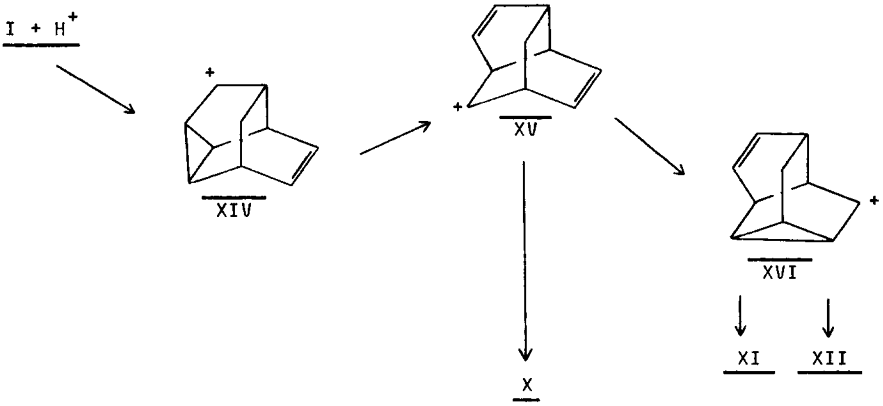


X-D

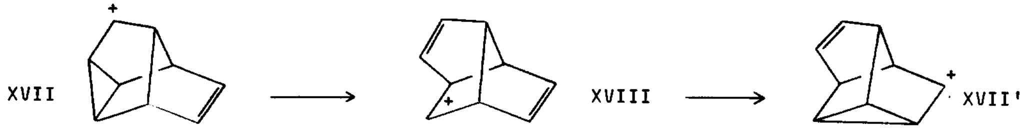
The NMR-spectrum of A-H_2 was in agreement with structure XIII. Reaction of I with DOAc/D$^+$ produced the deuterium distribution shown in formula X-D.

Discussion

Since the experiments were conducted under equilibrating conditions no conclusions regarding favored transition states and structures of related carbonium ions can be drawn from the products found - and from the absence of other possible products. Scheme II therefore contains only canonical structures arranged in a cascade of decreasing energy and leading in a rational way from I to X - XII[6]. Since VII (X = OAc) is stable under the conditions used, its absence indicates that protonation of I does not lead to the trishomocyclopropenyl cation V, but presumably the more stable cyclopropylcarbinyl cation XIV is formed directly through protonation of one of the cyclopropane rings[7,8]. This electrophilic substitution reaction at carbon occurs with slight predominance of retention of configuration (see X-D)[9]. It is interesting to note that the postulated rearrangement XIV → XV → XVI takes place, whereas (in solvolysis) the related doubly degenerate rearrangement XVII → XVIII → XVII' could not be detected[10,11].



SCHEME II



References

1. W.G. Dauben, M.G. Buzzolini, C.H. Schallhorn, D.L. Whalen, and K.J. Palmer, Tetrahedron Letters, 787 (1970).

2. H. Bos, G. Ellen, G.W. Klumpp, and J.J. Vrielink, ibid., 5203 (1973).

3. W.G. Dauben and C.H. Schallhorn, J. Amer. Chem. Soc., 93, 2254 (1971).

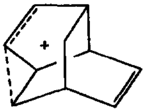
4. G. Ellen and G.W. Klumpp, Tetrahedron Letters, preceding papers.

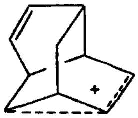
5. M. Tichý and J. Sicher, Coll. Czech. Chem. Comm., 37, 3106 (1972); A. Krantz,

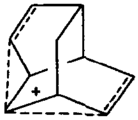
Ph.D. Thesis, Yale University, 1967.

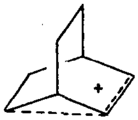
6. a. W.J. Hehre and P.C. Hiberty [J. Amer. Chem. Soc., 94, 5917 (1972)] have calculated that, disregarding solvation, the simple cyclopropylcarbinyl cation is more stable than the homoallyl cation.

   b. Merging of XIV - XVI into delocalized structures is conceivable. Judging from the situation in 7-norbornadienyl cations and in a related cation one would expect partially delocalized structures a and b to be favored over c [M. Brookhart, R.K. Lustgarten, and S. Winstein, J. Amer. Chem. Soc., 89, 6352 (1967); R.M. Coates and J.L. Kirkpatrick, ibid., 92, 4883 (1970)]. The similarity of b to d [N.A. LeBel and J.E. Huber, J. Amer. Chem. Soc., 85, 3193 (1963)] is noted.


a

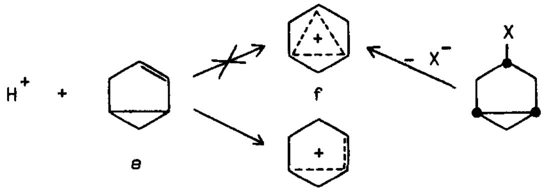

b


c


d

7. Similar preference for cyclopropane protonation over double bond protonation has been observed with other unsaturated cyclopropanes, cf. C.H. DePuy, Fortschr. Chem. Forschg., 40, 74 (1973), see however ref. 8.

8. P.K. Freeman, M.F. Grostic, and F.A. Raymond, J. Org. Chem., 30, 771 (1965), have observed an analogous case of dissimilarity between ionization and protonation in the bicyclo[3.1.0]hexyl system:



In the transition states of the protonations of I and e to V and f less overlap is possible between the cyclopropane bond and the developing empty orbital than in the ionizations of appropriate esters.

9. With a structurally unbiased cyclopropane protonation has been found to take place with predominant (68%) retention: C.H. DePuy, A.H. Andrist, and P.C. Fünfschilling, J. Amer. Chem. Soc., 96, 948 (1974).

10. G.W. Klumpp, Rec. Trav. Chim., 87, 1053 (1968); P.v.R. Schleyer and R.E. Leone, J. Amer. Chem. Soc., 90, 4164 (1968).

11. A. de Meijere and L.-U. Meyer (private communication) have independently studied the protonation of snoutene and have obtained results similar to those reported here.