Homoallylic *versus* Allylic Carbonium Ion Formation

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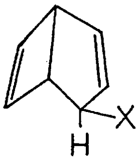
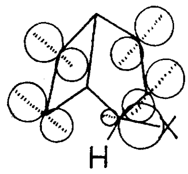
THE rearrangement of quadricyclanone provided easy access to the hitherto unavailable 2-substituted bicyclo[3,2,0]heptadienyl system (I).[1] This system was of particular interest as one which would potentially allow a study of the competitive formation of homoallylic and allylic carbonium ions. Although it seemed most likely that interaction of the incipient carbonium ion with the allylic double bond would largely "swamp-out" any observable homoallylic participation,[2] the apparently more favourable geometrical disposition of the homoallylic π-system in the *exo*-isomer (Ia′) during the early stages of carbonium ion development lends some support to the possibility of important homoallylic interaction. It should also be noted that DePuy found complete stereoselectivity in his study of homoallylic carbonium ions involving two homoallylically situated double bonds contained in the same molecule.[3]

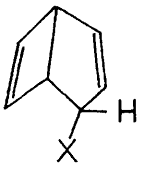
Evidence for homoallylic interaction is provided in the corresponding mono-olefinic system (II) investigated by Whitham.[4] The *exo*-isomer was reported to solvolyse more rapidly than the *endo* in acetic acid and both epimers stereoselectively formed the rearranged *anti*-norbornenyl acetate (III). Whitham suggested, quite reasonably, the intermediacy of the homoallylically delocalized ion (IV).



(Ia)



(Ia′)



(Ib)

The corresponding rearrangement also occurs readily in the dienyl alcohols (I; X = OH). Winstein has shown that the alcohols undergo ring enlargement in fluorosulphonic acid to form 7-norbornadienyl salts.[5] Furthermore, the rearrangement is very easy, being complete in 2 min. at −78°. We report that under solvolytic conditions the *p*-nitrobenzoates of (I) yield results quite different from those obtained by Whitham and by Winstein.

A comparison of solvolysis rates reveals no significant difference in reactivity between the *exo*- and *endo*-*p*-nitrobenzoates, (Ia) and (Ib), in 80% aqueous acetone at 100° [(Ia), $k = 2{\cdot}93 \times 10^{-6}$ sec.$^{-1}$; (Ib), $k = 3{\cdot}59 \times 10^{-6}$ sec.$^{-1}$]. Thus, anchimeric assistance by the homoallylic double bond is not a factor in solvolyses of these derivatives. This conclusion is reinforced by the absence of ring-enlarged products as observed both by Winstein and by Whitham. Furthermore, the solvolyses proceed with only a low degree of

TABLE

Products from solvolyses of bicyclo[3,2,0]*-heptenyl and -heptadienyl derivatives*

Substrate	Conditions	Products[c]	Total yields	Ref.
(IIa) tosylate	HOAc, 98°, 4 hr.	(III) 80%	—	4
(IIb) tosylate	HOAc, 120°, 4 hr.	(III) 80%, (IIb) acetate, 12%	—	4
(Ia) *p*-nitrobenzoate[a]	50% aq. acetone, 4·5 hr.[b]	(Ia)-OH, 87% (Ib-OH, 13%[d]	34%	e
(Ia) *p*-nitrobenzoate ..	HOAc, 4·5 hr.	(Ia)-OAc,[f] 88%; (Ib)-OAc, 12%	63%	e
(Ib) *p*-nitrobenzoate[a]	50% aq. acetone, 6 hr.	(Ia)-OH, 89%; (Ib)-OH, 11%	40%	e
(Ib) *p*-nitrobenzoate ..	HOAc, 6 hr.	(Ia)-OAc, 89%; (Ib)-OAc, 11%	73%	e

[a] *p*-Nitrobenzoates were prepared from the corresponding alcohols by a standard Schotten–Bauman procedure. All new compounds gave satisfactory elemental analyses.

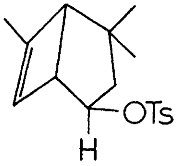
[b] All reactions were carried out at 101°. Reactions did not go to completion.

[c] Products and product ratios were determined by use of analytical and preparative g.l.c. Compounds were identified by comparison of their i.r. and n.m.r. spectra with those of authentic compounds.

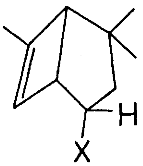
[d] This component was identified by g.l.c. retention time.

[e] This work.

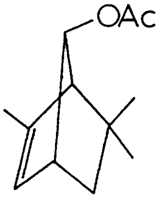
[f] The product ratios were determined by i.r. and g.l.c. analysis of the alcohol mixture after lithium aluminium hydride reduction of the acetate mixture.



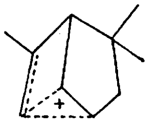
(IIa)



(IIb)



(III)



(IV)

stereoselectivity, as shown by the significant yield of *endo*-products, (Ib).

We conclude that the allylic double bond stabilizes the carbonium ion centre to the extent that participation by the homoallylic double bond furnishes no apparent additional stabilization. The magnitude of this effect cannot be further evaluated in the absence of quantitative rate data from the solvolysis of 2-substituted bicyclo[3,2,0]-hept-6-ene derivatives, but qualitatively, it is clear that the transannular double bond plays no important role under these conditions and that the allylic double bond produces a levelling effect similar to that observed by Gassman in the 7-norbornenyl system.[6]

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