Substituent Effects in the Thermal Rearrangement of Bicyclo[2,1,1]hexenes

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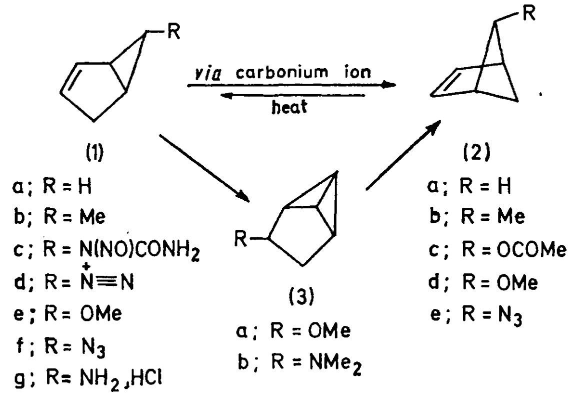
Summary *anti*-5-Methoxy- (**2a**) and 5-azidobicyclo[2,1,1]-hexene (**2b**) rearrange cleanly at 30—50° to give *exo*-6-methoxy- (**1c**) and 6-azidobicyclo[3,1,0]hexene (**1d**) respectively; reduction of (**2b**) below 0° proceeds with rearrangement to 5-aminobicyclo[3,1,0]hexene.

BICYCLO[2,1,1]HEXENE (**2a**) rearranges at 150—200° to bicyclo[3,1,0]hexene (**1a**).[1] A kinetic study[2] of this process afforded the activation parameters log *A* 13·95 and E_a = 35·2 kcal/mol, and the concertedness of the suprafacial 1,3-alkyl shift was checked with *syn-* and *anti*-5-methylbicyclo[2,1,1]hexene (**2b**).[3] The *anti*-isomer (**2b**) rearranged with almost complete inversion of configuration at C-5, compared with *ca.* 25% retention with the *syn*-isomer. *anti*-5-Acetoxybicyclo[2,1,1]hexene (2c) rearranges at 95—110° ($\Delta H\ddagger$ 27·5 kcal/mol; $\Delta S\ddagger$ = — 2 cal K^{-1} mol^{-1}.[4]). We report here on 5-substituted bicyclo-[2,1,1]hexenes which rearrange easily at 30—50° (**2d** and **e**).



These compounds were prepared *via* carbonium-ion rearrangements of the homoallyl–cyclopropylcarbinyl type. Alkaline cleavage of (**1c**) *via* diazonium ion (**1d**) afforded derivatives of bicyclo[2,1,1]hexene (**2**) and/or tricyclo-[3,1,0,$0^{2,6}$]hexane (**3**).[5] (**3a**) was the major product in methanol.[5] When treated with silver perchlorate at 0°, (**3a**) rearranged rapidly to give (**2d**) as the only volatile product (87%). Obviously this reaction does not follow a similar course to the transition-metal promoted isomerizations of simple bicyclo[1,1,0]butanes[6] but rather proceeds by a (Lewis) acid-induced cyclopropylcarbinyl–allylcarbinyl cation interconversion. In accord with this view, we have not been able to induce rearrangement of (**3b**) [obtained from (**1c**) in dimethylamine] under similar conditions.

At slightly elevated temperatures, (**2a**) rearranged quantitatively to *exo*-6-methoxybicyclo[3,1,0]hexene (**1e**). The structure of (**1e**) and the absence (<1%) of the *endo*-isomer were confirmed by comparison with authentic samples.[7] Rates of reaction were measured in CCl_4 by monitoring the well separated n.m.r. signals of the vinyl protons of (**2d**) (δ 6·58 p.p.m.) and (**1e**) (δ 5·3 and 5·6 p.p.m.): *k* (37·5°) = 1·02 × 10^{-4}; *k* (46°) = 2·26 × 10^{-4}; *k* (56°): 9·45 × 10^{-4} s^{-1}; $\Delta H\ddagger$ = 24·5 kcal/mol; $\Delta S\ddagger$ = — 0·5 cal K^{-1} mol^{-1}. 5-Azidobicyclo[2,1,1]hexene (**2e**), obtained from (**1c**) and sodium azide in aqueous dioxan, rearranged with similar ease; *k* (48°) = 2·27 × 10^{-4} s^{-1}.

Attempted reduction of (**2e**) with $LiAlH_4$ in ether below 0°, followed by acid work-up, did not produce the expected 5-aminobicyclo[2,1,1]hexene but rather 6-aminobicyclo-[3,1,0]hexene (**1g**). Some intermediate, or the product, of this reduction must have undergone the (**2**) → (**1**) rearrangement even below 0°.

The remarkable influence of electron-pair donors on the bicyclo[2,1,1] → [3,1,0]hexene rearrangement reported here is reminiscent of similar observations on the norbornadiene → cycloheptatriene rearrangement.[8] In the latter case, the substituent effect has been attributed to the stabilization of diradical intermediates. The stereochemistry of the reactions reported here, *i.e.* *anti*-(**2**) → *exo*-(**1**), suggests a concerted suprafacial 1,3 alkyl shift with inversion of configuration. We hope to obtain additional evidence from a study of suitable *syn*-bicyclo[2,1,1]hexene derivatives.

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