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THE REACTION OF 2-METHYLNORBORNENE-2
WITH N-BROMOSUCCINIMIDE

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The behaviour of N-bromosuccinimide (NBS) as a brominating agent towards bridged bicyclic olefins is capricious. Although there are few instances, the availability of a suitable allylic position and the overall molecular geometry appear to govern the course of the reaction. For example, when the allylic C-H bond lies in the nodal plane of the double bond, reaction is directed towards the double bond and the homoallylic position. Thus norbornene (1) on treatment with NBS in boiling carbon tetrachloride containing benzoyl peroxide gave solely 3-bromonortricyclane1) (2), whereas bicyclo[2.2.2]octene-2 gave exo and endo 5-bromobicyclo[2.2.2]octene-2 and endo-8-bromobicyclo-[3.2.1]octene-2 as well as dibrominated products.2)

On the other hand, when an allylic position is freely available as is found in isophyllocladene, isokaurene and bicyclo[3.2.1]octene-2, simple bromination occurs at the allylic position, although rather surprisingly, some bridgehead bromination was reported for isokaurene.2-4) Although in the latter cases the products most likely arise via radical intermediates, in the former cases both ionic and radical mechanisms have been proposed.

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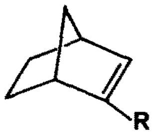
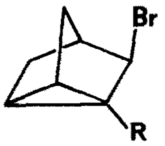


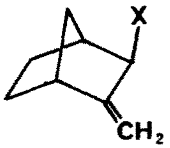
1 R=H

3 R=Me



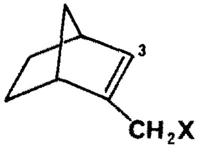
2 R=H

5 R=Me



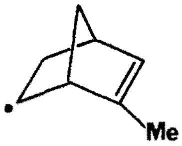
4 X=Br

6 X=H



7 X=Br

8 X= •



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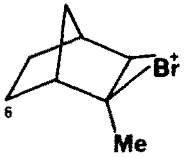

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Accordingly, it seemed to us that 2-methylnorbornene (**3**) would be an appropriate model for study as it embraces both features of the two categories of reactivity described above. Treatment of **3** (0.4 M) with NBS (0.3 M) in boiling carbon tetrachloride containing benzoyl peroxide gave exo-3-bromo-2-methylenenorbornane (**4**) and 2-methyl-3-bromonortricyclene (**5**) in a 3:1 ratio in an overall yield of 69% based on NBS.[‡] The residual non-brominated olefin on recovery was identified as mainly (87%) 2-methylenenorbornane (**6**).[‡] Quite remarkably, no trace of 2-bromomethylnorbornene-2 (**7**) was detected.[5)]

The absence of **7** might be construed as indicating that the related allylic radical **8** does not form, although it could be argued that **8** might undergo attack exclusively at C_3. However, the allylic cation corresponding to **8** undergoes attack at both allylic positions.[6)] Moreover, **8** cannot reasonably

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[‡] The products **4**, **5** and **6** were separated by fractional distillation in vacuo and afforded satisfactory analytical and spectral data.

lead to the other product, the tricyclic structure 5. Conversely, the homoallylic radical 9 could give 5, however 9 cannot lead to the other product 4. Therefore, the simultaneous intervention of both the particular homoallylic radical 9 and allylic radical 8, an unlikely event, would have to be necessary to account for the reaction products. Consequently, it can be concluded that the formation of **4** and **5** are best described as coming from the common bromonium ion, **10**, which has the option of losing a proton from the methyl group or from C_6.

A final point is pertinent. The reductive debromination of 3-bromonortricyclane (2) or exo-5-bromonorbornene-2 with tri-n-butyl- or triphenyltin passes via the nortricyclyl-3 and 2-norbornenyl-5 radicals respectively to give in both cases essentially the same composition of norbornene and nortricyclane.7) Conversely, the absence of exo-5-bromonorbornene-2 on brominating **1** with NBS indicates the absence of a radical process. Accordingly, norbornene and 2-methylnorbornene appear to follow the same mechanism.

The incidental isomerization of 2-methylnorbornene to the exo-methylene compound **6** finds a parallel in the conversion of isokaurene to kaurene during photo-oxidation;8) however, the mechanisms of such endo-exo olefin isomerizations may not be simple.9)

Acknowledgements

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