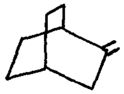
Tetrahedron Letters No.5, pp. 293-296, 1969. Pergamon Press. Printed in Great Britain.

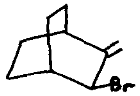
# OBSERVATIONS ON THE ALLYLIC BROMINATION OF SOME BRIDGED POLYCYCLIC OLEFINS

D.I. Davies and L.T. Parfitt.
Department of Chemistry, King's College, Strand,
London W.C.2., England.

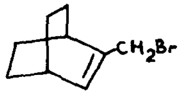
(Received in UK 2 December 1968, accepted for publication 23 December 1968)

The benzoyl peroxide catalysed reaction of N-bromosuccinimide, in boiling carbon tetrachloride, with 2-methylenebicyclo[2,2,2]octane (I) affords an oil, g.l.c. examination of which shows one major peak (~ 85 %), and several minor peaks. N.m.r. examination shows that the major peak corresponds to a mixture of 3-bromo-2-methylenebicyclo[2,2,2]octane (II) and 2-bromomethylbicyclo[2,2,2]oct-2-ene (III) in the ratio 3:2. The identification of (II) is based on the observation of H-3 as a multiplet at τ 5.22, and olefinic protons as two narrow multiplets $W_{\frac{1}{2}}$ 3 c.p.s. at τ 4.90 and 5.04. For compound (III) $-C\underline{H}_2Br$ was observed as a singlet at τ 6.11, and the olefinic proton at τ 3.81 as a doublet (J = 7 c.p.s.), with each peak of the doublet showing additional couplings of ~ 1 c.p.s.

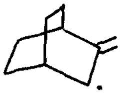

(I)



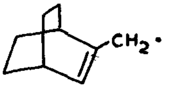
(II)



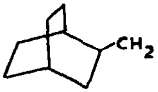
(III)


(IV)

↔



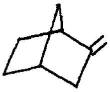
(V)



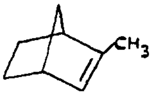
(VI)

The parent olefins 2-methylenebicyclo[2,2,2]octane (I) and bicyclo[2,2,2]oct-2-ene show olefinic proton resonances centred at $\tau$ 5.35 plus 5.48, and 3.82 respectively. The observation of (II) and (III) as products is best rationalised by an initial step involving abstraction of hydrogen from C-3 in (I) to give an allylic radical system, which may be depicted as either (IV) ↔ (V), or (VI). Abstraction of bromine from N-bromosuccinimide, by the allylic radical system, can then give rise to the observed products (II) and (III).

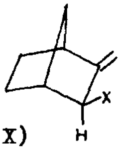
This may be contrasted with the reaction of N-bromosuccinimide with bicyclo[2,2,2]oct-2-ene, which leads to endo-8-bromobicyclo[3,2,1]oct-2-ene as major monobromide product. An ionic mechanism was favoured, although competing ionic and free radical mechanisms are not ruled out.[1] The formation of nortricyclyl bromide from norbornene, in a similar reaction, is also thought to involve an ionic intermediate.[2] However, since both bicyclo[2,2,2]oct-2-ene and norbornene have allylic hydrogens only at bridgehead positions, these atypical reactions of N-bromosuccinimide are perhaps not unexpected.



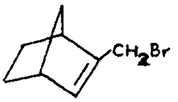
(VII)



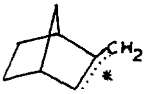
(VIII)



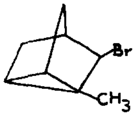
(IX)



(X)



(XI)



(XII)

For (IX) : A, X = Br; B, X = OAc; C, X = $CO_2H$

For (XI) : A, * = · ; B, * = + ; C, * = −

The olefins 2-methylenenorbornane (VII) and 2-methylnorborn-2-ene (VIII), which both possess suitable allylic hydrogens, react with allylic halogenating agents to afford exo-3-bromo-2-methylenenorbornane (IXA), possibly the endo-3-bromo isomer also, but not 2-bromomethylnorborn-2-ene (XA).3) These reactions were interpreted as involving the intermediacy of the allylic radical (XIA), but Jefford4) has put forward an alternative ionic intermediate in the benzoyl peroxide catalysed reaction of N-bromosuccinimide with 2-methylnorborn-2-ene (VIII), since he reports 2-methyl-3-bromonortricyclene (XII) as an additional product, and he considers that both products (IXA) and (XII) should have their origin in a common intermediate, and cannot, therefore, be both derived from the allylic radical (XIA). However, in a reaction that is benzoyl peroxide catalysed it might be expected that at least part of the product formation should occur *via* free radical intermediates. Since competing ionic and free radical reactions can occur, (as for example in the addition of hydrogen bromide to olefins), and in view of the likely intermediacy of the analogous allylic radical (VI) in the reaction of 2-methylenebicyclo[2,2,2]octane (I), it seems perfectly feasible that (IXA) should be formed in a free radical reaction, and (XII) in an ionic reaction from 2-methylnorborn-2-ene (VIII); or rather 2-methylenenorbornane (VII) since olefin isomerisation is reported4) to be faster than reaction with N-bromosuccinimide.

One of the arguments put forward by Jefford against the intermediacy of the allylic radical (XIA) is that the solvolysis of the bromide (IXA), a reaction which presumably involves the analogous allylic carbonium ion (XIB), gives rise to comparable amounts of products having exocyclic and endocyclic double bonds.5) He omits mention of the lead tetraacetate oxidations of 2-methylnorborn-2-ene (VIII) and 2-methylenenorbornane (VII), reactions in which the various products do not have their origin in a common intermediate, but in which the major product derived from the allylic carbonium ion (XIB) is exo-3-acetoxy-2-methylenenorbornane (IXB) having an exocyclic double bond.6) In addition the reaction of 2-methylenenorbornane (VII) with amyl sodium, followed by carbonation, gives the acid (IXC) having an exocyclic double bond, as major product from the intermediate allylic carbanion (XIC). It is therefore clear that most reactions of the olefins (VII) and (VIII) give rise to products having an exocyclic rather than an endocyclic double bond. These are likely to be the thermodynamically more stable, since the highly strained ring system will contain only one $sp^2$ hybridised carbon atom. The failure to observe any 2-bromomethylnorborn-2-ene (XA), in the reaction of (VIII) with N-bromosuccinimide, is therefore scarcely surprising.

## References.

1. N.A. LeBel, J.E. Huber and L.H. Zalkow, J. Amer. Chem. Soc., 84, 2226 (1962).

2. J.D. Roberts, E.R. Trumbull, W. Bennett and R. Armstrong, J. Amer. Chem. Soc., 72, 3116 (1950).

3. C.K. Alden and D.I. Davies, J. Chem. Soc. (C), 709 (1968).

4. C.W. Jefford and W. Wojnarowski, Tetrahedron Letters, 3763 (1968).

5. C.W. Jefford and W. Wojnarowski, Chem. Comm., 129 (1968).

6. W.F. Erman, J. Org. Chem., 32, 765 (1967).

7. R.A. Finnegan and R.S. McNees, J. Org. Chem., 29, 3241 (1964).