Norbornan-7-ylidene

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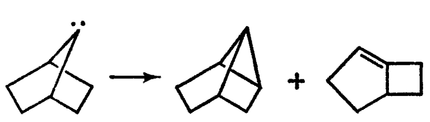
Summary The intramolecular reaction products of norbornan-7-ylidene are bicyclo[3,2,0]hep-1-ene and tricyclo[3,2,0,$0^{2,7}$]heptane.

NORBORNAN-7-YLIDENE has been of interest since 1962,[1] and more recently of theoretical concern.[2] We now report initial observations of the generation and fate of norbornan-7-ylidene (I).

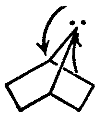
The toluene-*p*-sulphinhydrazone (m.p. 153—155° from NeOH,† norbornan-3-one[3] was converted into its lithium salt[4] and this was pyrolysed (185°, 20 torr.); the products (80%) were collected at −70°.

The three components of the mixture (1·18 : 1·00 : 6·16) were isolated by v.p.c. (QF-1) and identified as norbornane, tricyclo[3,2,0,$0^{2,7}$]heptane (II)[5] and bicyclo[3,2,0]hept-1-ene (III).

Norbornane and (II)[6] were identified by comparison with authentic samples. Structure (III)† is confirmed as follows: M^+ 94; i.r. (CCl_4) 6·08 μm. (C=C): n.m.r. (CCl_4) δ 5·13 (envelope, 1H, vinyl and 3·15—1·30 p.p.m. (m, 9H). Hydrogenation (10% Pd–C 1 mol. of H_2) gave bicyclo[3,2,0]-heptane, identical with material produced by hydrogenation of bicyclo[3,2,0]hepta-2,6-diene.[7] Ozonolysis of (III) (MeOH, −70°) led, after hydrolysis, to a product whose i.r. showed *inter alia* absorption at 5·63 μm., indicative of a cyclobutanone carbonyl group.[8]



(I) (II) (III)



(IV)

Our results are best explained in terms of the intermediate, norbornan-7-ylidene (I); (II) is a 1,3-insertion product of (I), while (III) can arise by the 1,2 rearrangement (IV). This latter process finds analogies in carbonium ion chemistry.[9,10]‡

Examination of models suggests that the architecture of (I) is far from optimal[12] for a 1,3 (or 1,2) insertion reaction; rearrangement to (III) appears to be geometrically favourable. The small yield of norbornane probably does not come from (I)

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† Satisfactory elemental analyses have been obtained for all new compounds.

‡ At least formally, (II) can be converted to (III) by a cyclopropane–propene rearrangement.[11] The (II)/(III) distribution was unchanged, however, after treatment of crude product mixture with lithium toluene-*p*-sulphinate at 185° and 20 torr. Thus (III) is not being formed from (II) under our reaction conditions.

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[12] See W. Kirmse and G. Wächterhäuser, *Tetrahedron*, 1966, **22**, 62, and references therein.