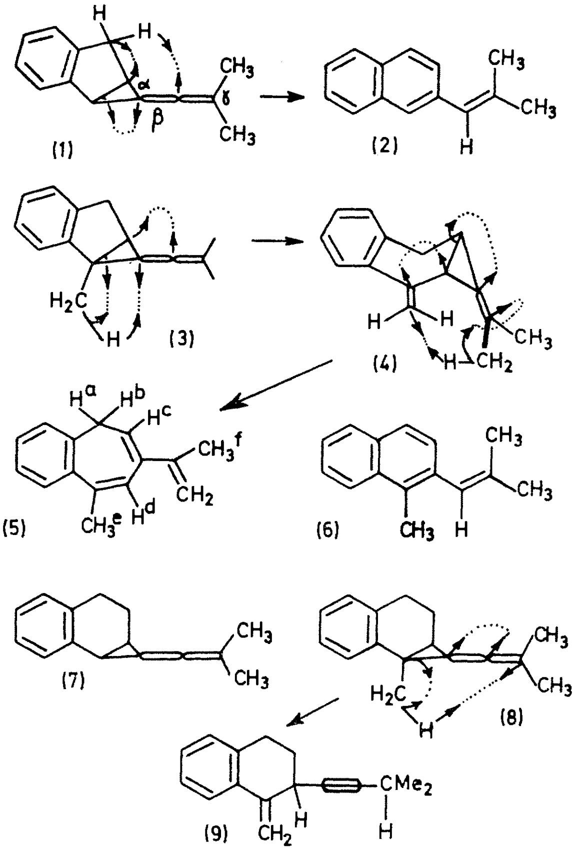
Unusual Rearrangements of Dimethylvinylidene-benzobicyclo[*n*,1,0]alkenes

By I. H. SADLER* and J. A. G. STEWART

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary Thermal rearrangements of dimethylvinylidene-benzobicyclo[n,1,0]alkenes ($n = 3,4$) appear to proceed *via* concerted processes involving hydrogen atom migration from a carbon atom α to the cyclopropane ring to one of the carbon atoms comprising the allene skeleton.

SIMPLE alkyl-vinylidenecyclopropanes rearrange at elevated temperatures to give dimethylenecyclopropanes.[1] This is also true[2] of the aryl analogues; for example, 1-dimethylvinylidene-2-phenylcyclopropane yields 1-isopropylidene-2-methylene-3-phenylcyclopropane. We considered that the formation of products of this type would be rendered unlikely, and that alternative products would be formed, if the structure of the vinylidenecyclopropane was such that the newly formed olefinic group would be located at a bridgehead position in the product. We now report the thermal rearrangement of the dimethylvinylidene benzobicyclo[n,1,0]alkenes (**1**), (**3**), (**7**), and (**8**) conveniently obtained in moderate yield as 1 : 1 adducts† of dimethylvinylidenecarbene with indene, 3-methylindene, 1-2-dihydronaphthalene, and 1,2-dihydro-4-methylnaphthalene, respectively. Their structures were confirmed by spectroscopic data.



Thermal rearrangements of the indene adduct (**1**), effected in refluxing benzene for 24 h (complete disappearance of reactant by i.r.) gave a low yield (20%) of the naphthalene (**2**), identical with an authentic sample. Almost quantitative yields of (**2**), however, were obtained by a low-pressure (*ca.* 0·01 mm Hg) vapour-phase pyrolysis technique in which (**1**) was carried in a stream of nitrogen through a flow system at 450°. Contrary to expectation the 3-methylindene adduct (**3**) readily rearranged in refluxing benzene (12 h) to give the bicycloheptene (**4**)† exclusively, whereas low-pressure vapour-phase pyrolysis (450°) yielded a mixture of the naphthalene (**6**),† identical with a sample synthesised by an independent route, the bicycloheptene (**4**), and the benzocycloheptatriene (**5**),† in the ratio 2 : 3 : 1 (by n.m.r. analysis). Vapour-phase pyrolysis of (**4**) yielded a mixture of (**5**) and unchanged (**4**), but not (**6**).

The identity of (**4**), m.p. 54·5°, was deduced by comparison of the spectroscopic data with that of model compounds [u.v. $\lambda_{\max}$ (EtOH) 250 nm (ϵ 10,600), i.r. $\nu_{\max}$ (Nujol) 1620 and 880 cm^{-1}; n.m.r. τ (CCl$_4$) 2·7—2·9 (m, 1H, ArH), 3·0—3·3 (m, 3H, ArH), 4·85, 5·01 (d, d, 1·5 Hz, 1H, 1H, C : CH_2), 7·00 (d, 3 Hz, 2H, benzylic CH_2), 7·54, 7·81 (m, m, 1H, 1H cyclopropyl-H), and 8·45 (d of d, 1·5 Hz, 6H, C : CMe_2). Compound (**4**) was also isomerised to (**5**) on treatment with 20% aqueous hydrogen chloride.

The structure of (**5**), m.p. 44°, was similarly established, the n.m.r. spectrum (100 MHz) showing a temperature-dependence typical of cycloheptatrienes[3] [τ, at 28° (CS$_2$), 2·5—3·1 (m, 4H, ArH), 3·42 (s, H^a), 4·2 (t, J_{ac} 7·0 Hz, H^c) 5·05, 5·15 (bs, bs, 1H, 1H, C : CH_2), 7·05 (d, J_{ac} 7·0 Hz, 2H, $H^a + H^b$), 7·63 (d, 1·0 Hz, 3H, CH_3^e), and 8·14 (d, 0·5 Hz, 3H, CH_3^f); at −80° (CS$_2$), 4·2 (d of d, 6·6 + 7·8 Hz, H^c), 6·84 (d of d, 12·6 + 7·8 Hz, H^a), and 7·37 (d of d, 12·6 + 6·6 Hz, H^b); remainder of spectrum unchanged. Coalescence occurred at −16° corresponding to $\Delta G^\ddagger = 12$ kcal/mole for ring inversion].

The exclusive formation of (**4**) at low temperatures and its subsequent conversion into (**5**) only at higher temperatures indicate that the initial rearrangement of (**3**) proceeds *via* either of two separate routes, and that the activation energy necessary for the formation of the thermodynamically favoured‡ naphthalene (**6**) is greater than for the formation of the bicycloheptene (**4**).

The formation of the naphthalene derivatives (**2**) and (**6**) can be accounted for in terms of thermally allowed[5] ($\pi^2a + \sigma^2a + \sigma^2s$) processes involving concerted disrotatory ring-opening, double-bond formation, and suprafacial hydrogen atom migration from the carbon α to the cyclopropane ring to the β-carbon of the allene system. The presence of a suitably positioned methyl group, as in compound (**3**), permits an alternative thermally allowed ($\pi^2a + \sigma^2a + \sigma^2s$) concerted process which also involves disrotary ring opening but is accompanied by hydrogen atom transfer

---

† All new compounds gave satisfactory elemental analyses and accurate mass values for the parent ions (MS 902).

‡ The calculated heats of formation of (**3**), (**4**), (**5**), and (**6**) using standard additivity data[4] are 93·3, 73·4, 51·2, and 27·8 kcal/mole, respectively.

from the methyl group, also α to the cyclopropane ring, to the α-carbon atom of the allene system. The ease of this latter process relative to the formation of the naphthalene (**6**) and the absence of products formed by the migration of the hydrogen atoms to the alternative sites of the allene probably result in part from the orientations of the participating C–H bonds in the reactant. Free rotation of the methyl group apparently allows the migrating hydrogen atom to adopt a position which renders the transition state prior to the formation of (**4**) more accessible than that for the formation of (**6**). In this case the position in the reactant of the migrating atom is fixed, such that transfer to the β-carbon atom is favoured. This would also account for the exclusive formation of (**2**) from (**1**).

The formation of the benzocycloheptatriene (**5**) from (**4**) may also be rationalised in terms of a concerted process involving 4 participants and is thermally allowed $(\pi^2a + \pi^2s + \sigma^2s + \sigma^2s)$. Examination of molecular models shows that this complex process has satisfactory overlap of the participating orbitals, the hydrogen migration distance being about 2 Å.

Vapour-phase pyrolysis (450°) of the dihydronaphthalene adduct (**7**) gave an inseparable complex mixture (g.l.c.) of products. By contrast, thermal rearrangement of the corresponding methyl derivative (**8**) under the same conditions gave good yields of the acetylene (**9**).† Rearrangement in solution (180°, 8 h) gave very low yields of (**9**) together with polymeric material. The structure of (**9**) was established from spectral data and by two-stage conversion, using 20% aqueous sulphuric acid followed by *o*-chloranil, into 1-methyl-2-(3-methylbutyryl)naphthalene.

The formation of (**9**) is also in accord with a thermally allowed $(\pi^2a + \sigma^2a + \sigma^2s)$ process where the hydrogen atom migrates to the γ-carbon atom of the allene system and the alternative aryl substituted bond of the cyclopropane is broken. Although, as in (**3**), the orientation of the participating C–H bond is not fixed, migration to the α-carbon is not observed possibly since this would involve formation of a seven-membered ring in the product thereby introducing additional strain in the transition state. It appears that when the methyl group is absent as in (**7**), the molecule cannot adopt the necessary conformation for concerted hydrogen atom transfer and thus no single low-energy pathway is available.

All the initial rearrangements involve cleavage of an aryl substituted bond, suggesting stabilisation of the transition state by the aromatic ring. We consider that the difference in behaviour of these compounds arises from the different geometry in each of the reactant molecules, since this will directly affect the relative ease with which the various possible transition states may be reached. Alternative stepwise pathways for the rearrangements, involving initial cleavage of the cyclopropane ring to form resonance-stabilised diradicals which undergo intramolecular hydrogen abstraction can be excluded, since molecular models make it clear that the shapes of the diradicals are such as to render the hydrogen abstraction step virtually impossible.

We thank the S.R.C. for a maintenance grant (to J. A. G. S.).

(*Received, September 28th*, 1970; *Com.* 1660.)

---

[1] J. K. Crandall and D. R. Paulson, *J. Amer. Chem. Soc.*, 1966, **88**, 4302.
[2] I. H. Sadler, unpublished observation.
[3] J. B. Lambert, L. J. Durham, P. Lapoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3896.
[4] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
[5] R. B. Woodward and R. Hoffman, *Angew. Chem. Internat. Edn.*, 1966, **8**, 781.