Tetrahedron. Vol. 30, pp. 3945 to 3952. Pergamon Press 1974. Printed in Great Britain

REACTION OF BENZYNE WITH CYCLOHEPTATRIENE PREPARATION AND THERMOLYSIS OF SOME BENZO(C_9H_{10}) HYDROCARBONS

L. LOMBARDO and D. WEGE*
Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009

(*Received in the UK* 13 *June* 1974; *accepted for publication* 28 *June* 1974)

Abstract—The title reaction gave a 2 + 2 cycloadduct, 8,9-benzo-*cis*-bicyclo[5.2.0]nona-2,4,8-triene **7**, together with ene product, 7-phenylcycloheptatriene. The structure of **7** was confirmed by catalytic reduction to give 8,9-benzo-*cis*-bicyclo[5.2.0]non-8-ene, which was also obtained in the reaction of benzyne with cycloheptene, and by reduction of the known 8,9-benzobicyclo[5.2.0]nona-1,8-diene. Other benzo(C_9H_{10}) hydrocarbons which have been synthesised are 7,8-benzobicyclo[4.2.1]nona-2,4,7-triene **5**, 2,3-benzobicyclo[6.1.0]nona-2,4,6-triene **28** and 4,5-benzobicyclo[6.1.0]nona-2,4,6-triene **29**. The thermolysis of **7**, **28**, **29** and of 3,4-benzo-*exo*-*endo*-tetracyclo[4.3.1.$0^{3,4}$.$0^{7,9}$]dec-3-en-10-one, **25**, is described.

INTRODUCTION

The reactive intermediate *o*-benzyne (1,2-dehydrobenzene) **1** has been generated in the presence of a large number of olefinic substrates. In general[1], three main classes of reaction are observed: (a) Diels-Alder addition with 1,3-dienes; (b) ene reaction[2] with alkenes possessing a suitable allylic H atom; and (c) 2 + 2 cycloaddition. In some cases, reactions (a)–(c) are competitive, and only recently has an attempt been made to delineate the factors which favour one reaction mode over another with certain cyclic dienes.[3]

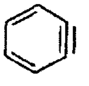
Cycloheptatriene **2** reacts with powerful dienophiles such as maleic anhydride,[4] tetracyanoethylene[5] and 4-phenyl-1,2,4-triazoline-3,5-dione[6] to give adducts **4** formally derived from norcaradiene (bicyclo[4.1.0]hepta-2,4-diene) **3**, although it has not been possible to demonstrate the existence of an equilibrium concentration of **3** in cycloheptatriene either spectroscopically[8a] or by kinetic means.[8b]

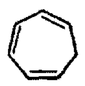
During 1971 we commenced an investigation of the reaction of benzyne with cycloheptatriene. In principle, the possible cycloadducts from such a reaction are **4** (X–X = C_6H_4), **5**, **6**, and the 2 + 2 cycloadducts **7** and **26** (see later). While our work was in progress, a preliminary communication appeared[9] in which structure **5** was assigned to a cycloadduct formed in this reaction. We[10] and others[11] have shown this to be in error. We now present full details, and further evidence for the correct structure **7** for this cycloadduct. In addition, we have also synthesised **5**, and have investigated the thermolysis of **7** and a number of related benzo(C_9H_{10}) hydrocarbons.

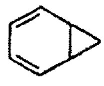
RESULTS AND DISCUSSION

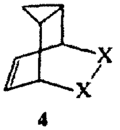
Reaction of benzyne with cycloheptatriene 1,3-cycloheptadiene and cycloheptene

Reaction of benzyne, generated from *o*-benzenediazonium carboxylate, with cycloheptatriene gave two $C_{13}H_{12}$ hydrocarbons in a ratio of

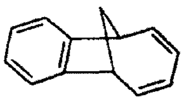

1

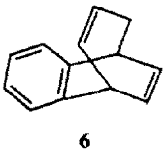

2


3

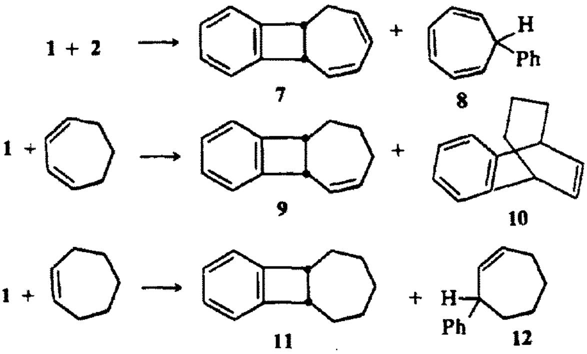


4


5

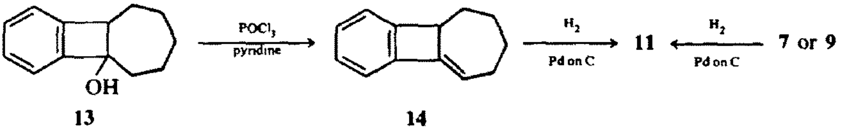

6

42:58 by VPC analysis. These could be separated on a small scale by chromatography on silver nitrate impregnated alumina. The less abundant product was readily identified as the ene product, 7-phenylcycloheptatriene **8** from its spectral properties. The other product was assigned structure **7** on the basis of the evidence outlined below. Hydrocarbon **7** could readily be obtained pure in gram quantities by treating the distilled reaction mixture with 0·5 molar equivalents of tetracyanoethylene, which resulted in the selective removal of 7-phenylcycloheptatriene as a sparingly soluble adduct. The failure of cycloadduct **7** to react with tetracyanoethylene under these conditions is no doubt due to the badly skewed diene system of **7**.



SCHEME 1.

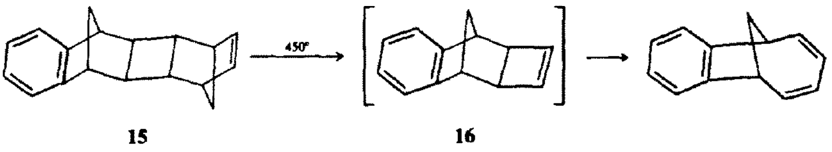
The presence of two double bonds in **7** was evident from its NMR spectrum,[10] and from quantitative catalytic hydrogenation experiments, which yielded a single product **11**. Reaction of benzyne with 1,3-cycloheptadiene gave in addition to the expected Diels-Alder adduct **10** an isomeric hydrocarbon **9**. Catalytic hydrogenation of **9** also gave **11**. The nature of the ring skeleton of **11**, and hence of **7** and **9** was firmly established when it was found that **11** was formed, together with 3-phenylcycloheptene **12**, in the reaction of benzyne with cycloheptene (Scheme 1). Additional evidence for the structure of **11** is shown in Scheme 2. The tertiary alcohol **13**, prepared by the reaction of benzyne, generated from sodium amide, with the enolate anion of cycloheptanone,[12] was dehydrated with phosphoryl chloride in pyridine to give **14**. Catalytic hydrogenation of **14** gave **11**. Addition of hydrogen to **14** should occur to the less hindered face of the π-bond to give the *cis*-fused ring junction shown for **11**.



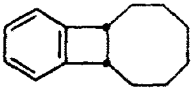
SCHEME 2.

Structure **5**, erroneously suggested[9] for the cycloadduct of benzyne and cycloheptatriene was further discounted by synthesis of **5**. Pyrolysis of the "crossed dimer" **15**, obtained from benzonorbornadiene and norbornadiene,[13] gave **5**, presumably *via* **16** (Scheme 3). This reaction has precedent in the formation of bicyclo[4.2.1]nona-2,4,7-triene by thermolysis of the analogous norbornadiene dimer.[14] Hydrocarbon **5** has recently also been prepared by another route.[15] The spectral data (Experimental) and the thermal stability (see below) of **5** are quite different from those of **7**.

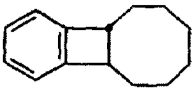
The 2 + 4 cycloaddition of benzyne with 1,3-dienes has been shown to be stereospecific, while the 2 + 2 cycloaddition of benzyne to acyclic alkenes proceeds with loss of stereochemistry.[17] The reaction of benzyne with *trans*-cyclooctene[16] also proceeds with loss of stereochemistry to give a mixture of *cis*- and *trans*-fused cycloadducts **17** and **18**. These observations are most simply inter-



SCHEME 3.



17



18

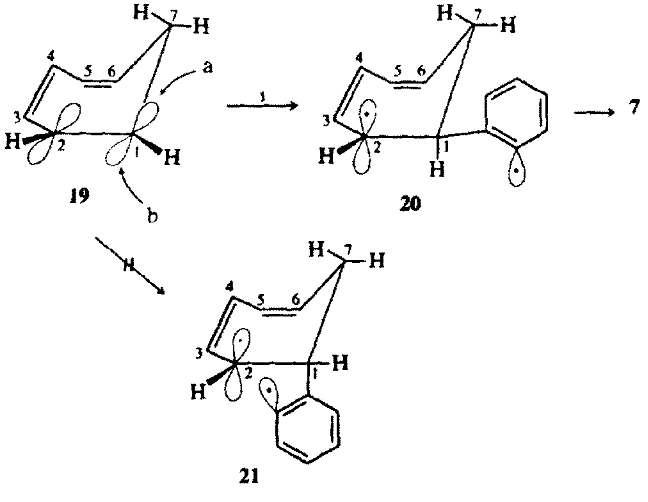
preted[17] in terms of benzyne being in the symmetric, singlet ground state,[18] and that 2 + 4 cycloaddition is concerted (i.e. $\pi^2s + \pi^4s$), and 2 + 2 cycloaddition is step-wise. With non-polar alkenes, the 2 + 2 cycloaddition probably proceeds *via* a diradical, rather than a zwitterionic intermediate. A diradical mechanism can also be assumed for the formation of **7**, **9** and **11**.

Hückel MO and SCF MO calculations on cycloheptatriene both indicate that the order of reactivity towards free radical attack is C − 1 > C − 2 > C − 3.*Cycloheptatriene is known to exist in a non planar conformation[19], **19** which undergoes rapid ring inversion.[20,7] Molecular models indicate that the π-lobe at C − 1 is sterically more accessible from the top of the "boat" (direction a) than the bottom (direction b). Attack of benzyne, acting as a diradical, from direction a would give conformer **20**, having the bulky aryl group in a pseudo-equatorial position, while attack from direction b would give conformer **21** in which the aryl group is in the more crowded pseudo-axial position. Hence formation of **20** should be favoured over **21**. Radical coupling in **20** would yield **7**, while abstraction of a hydrogen atom from C − 7 would give the ene product **8**. Alternatively, the ene product could be formed by a concerted mechanism operating in competition with that shown in Scheme 4. The absence of cycloadducts **5** and **6**[11] in the reaction product rules out conformer **21** as a product-determining intermediate. Bonding of the aromatic radical to C − 6 or to C − 4 could yield **5** or **6** readily. The formation of **7** as the only cycloadduct can therefore be explained in terms of diradical **20** as the key intermediate.

Preparation of other benzo(C_9H_{10}) *hydrocarbons.* An attempt to prepare the remaining possible benzyne-cycloheptatriene cycloadduct **26** is summarised in Scheme 5. Reaction of benzyne with the tricyclic hydrocarbon **22**[21] gave the (2 + 2) cycloadduct **23** and ene product **24**. Ozonolysis of **23** readily afforded ketone **25**. Thermal extrusion of carbon monoxide from **25** at 180° did not yield **26**, but products of further rearrangement (see below).

Finally, hydrocarbons **28** and **29**, required for thermolysis studies, were prepared from benzocyclooctatetraene **27** by conversion into the dianion followed by alkylation with dichloromethane (Scheme 6).

Thermolysis of hydrocarbons **7, 28, 29** *and ketone* **25**. When cycloadduct **7** was heated at 200° for 3½ hr, the dihydrobenzindene **31** was cleanly obtained. At lower temperatures (175°), the hydrocarbon **28** was also detected, and synthetic **28** was found to rearrange to **31** at 200°. After this portion of our work had been completed, the reaction of **7** to give **28** and **31** was also reported by Kato *et al.*[22] The reaction sequence (Scheme 7) can be rationalised in terms of a symmetry-allowed [1, 5] suprafacial sigmatropic shift, (**7** → **28**), followed by a non-concerted (diradical mechanism) ring opening (**28** → **30**), and a thermally allowed disrotatory electrocyclic reaction (**30** → **31**). Thermolysis of ketone **25**



SCHEME 4.

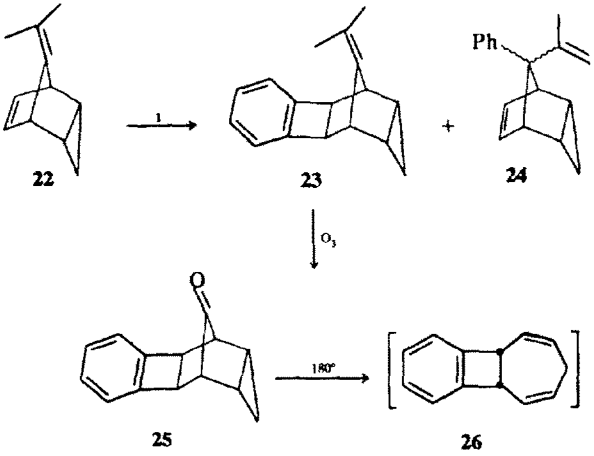
---

*G. S. Chandler and M. D. Morris, unpublished results; M. D. Morris, Honours Thesis, University of Western Australia, 1972.

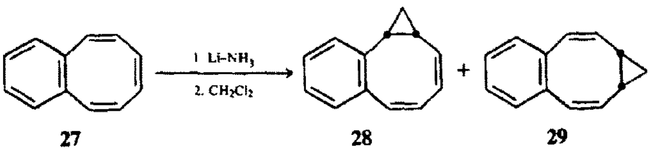
gave a mixture of **29** and the dihydrobenzindene **33**. Synthetic **29** was also found to be smoothly converted into **33**. The structures of the isomeric dihydrobenzindenes **31** and **33** follow from their NMR spectra (Table), and from the fact that catalytic hydrogenation of **31** and **33** gave the known[23] hydrocarbon **34**.

The conversions **28**→**31** and **29**→**33** thus occur without cross-over, and each is completely analogous to the much-studied[24] *cis*-bicyclo[6.1.0]nona-2,4,6-triene-*cis*-dihydroindene rearrangement (**35**→**36**).

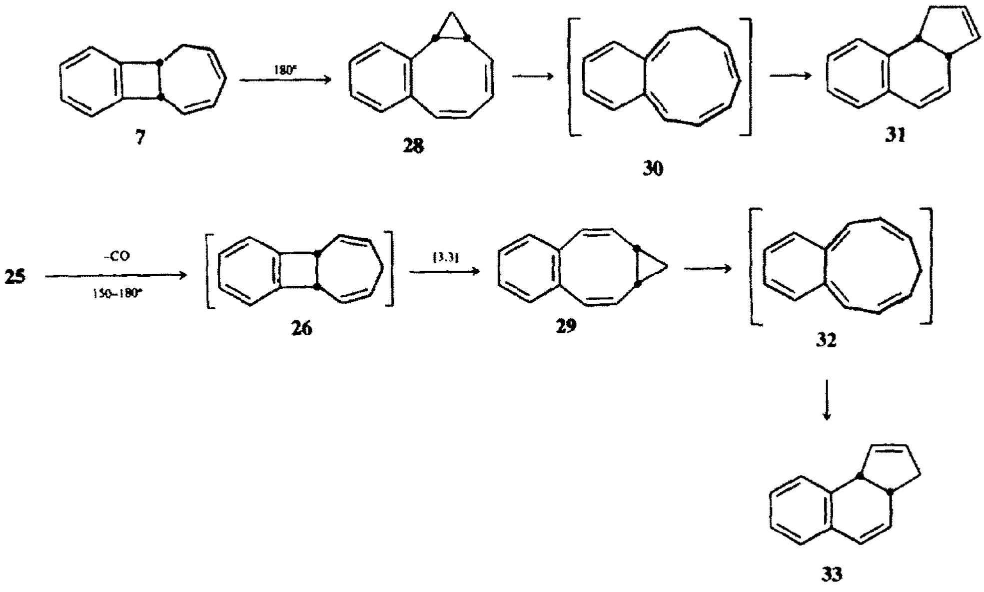
The thermolysis of ketone **25** (Scheme 7) can be rationalised in terms of decarbonylation with



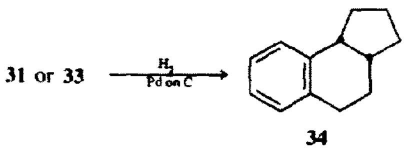
SCHEME 5.



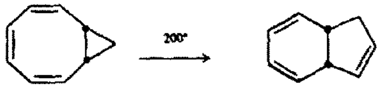
SCHEME 6.



SCHEME 7.



34



35 36

cyclopropyl participation (**25**→**26**) followed by a rapid [3, 3] sigmatropic shift (**26**→**29**). Non-concerted ring opening (**29**→**32**) followed by a disrotatory ring closure would give **33**. Hydrocarbon **26** cound not be detected experimentally in the decarbonylation of ketone **25** at 150°. Hydrocarbon **26** can be expected to be highly reactive since the related hydrocarbon 2,6-diphenylbicyclo[5.2.0]-nona-2,4,6-triene[25] is converted into 2,7-diphenylbicyclo[6.1.0]nona-2,4,6-triene in an analogous [3, 3] sigmatropic change at temperatures above −25°.

The benzo(C_9H_{10}) hydrocarbons described in this paper thus lie on two distinct energy surfaces, which do not cross over. The first energy surface involves **7**, **28**, and **31**, with **31** lying at the lowest level. The second connects **26**, **29**, and **33**; the dihydrobenzindene, in this case **33**, is again the most stable species. Hydrocarbon **5** was found to be thermally stable; no change was observed when **5** was heated at 250° for 21 hr. In principle, a suprafacial [1, 5] sigmatropic shift of the C_1–C_9 bond of **5** would give **28**. The fact that this symmetry-allowed reaction is not observed under the above conditions can be attributed to the geometry of **5**. Molecular models reveal that the axis of the C_1–C_9 bond is badly aligned with the axis of the diene π-orbital system, and that the C_1–C_9 bond is rather remote from the potential migration terminus C_5. This poor orbital overlap should hinder stabilisation of the transition state for the **5**→**28** rearrangement, and probably accounts for the stability of **5**.

EXPERIMENTAL

M.ps and b.ps are uncorrected. Microanalyses were carried out by Australian Microanalytical Service, Melbourne. NMR spectra were determined with either a Varian A60 instrument at 60 MHz, or a Bruker instrument at 90 MHz, using CCl_4 as solvent and TMS as internal reference. UV spectra were recorded with a Perkin Elmer 137 U spectrometer, and IR spectra with a Perkin Elmer 337 grating spectrometer. Mass spectra were measured using an Atlas CH_7 at 70 eV. Analytical VPC was carried out with a Perkin Elmer 880 gas chromatograph, equipped with a flame ionisation detector and using N_2 as carrier gas, while preparative VPC was performed using a Wilkins Autoprep, with He as carrier gas. The columns used were A: 10′ × 1/8″ column of 5% Carbowax 4000 on Chromosorb W (80 − 100 mesh); B: 10′ × 1/8″ column of 5% TCEP on Chromosorb W (80 − 100 mesh); C: 10′ × 3/8″ column of SE 30 on Chromosorb W (60 − 80 mesh); D: 9′ × 3/8″ column of Carbowax 20M on Chromosorb W (60 − 80 mesh).

Reaction of benzyne with cycloheptatriene. A slurry of *o*-benzene diazonium carboxylate,[26] prepared from anthranilic acid (15 g, 0·11 mol), in CH_2Cl_2 (75 ml) and cycloheptatriene (30 g, 0·33 mol) was refluxed (bath 70°) until gas evolution ceased (2½ hr). The dark mixture was adsorbed onto Al_2O_3 (50 g) and placed onto a column of Al_2O_3 (150 g), which was then eluted with light petroleum. Evaporation of the first 3 fractions (100 ml each) followed by distillation gave a 58 : 42 mixture (column A, 145°) (6·8 g, 37%), b.p. 91–4° (0·8 mm). Redistillation of a portion of the mixture through a 3′ spinning band column gave early fractions rich in **7**, and later fractions rich in **8**. Pure samples of **7** and **8** were obtained by careful chromatography of the appropriate enriched fractions on 10% $AgNO_3$–Al_2O_3.[27] *8,9-Benzo-*cis*-bicyclo*[5.2.0]*nona-2,4,8-triene* **7** was obtained as a clear oil, b.p. ~56° at 0·05 mm. (Found: C, 92·66; H, 7·20. $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%). Molecular weight (mass spectrum) 168; NMR δ 7·30–6·75 (m, 4H, ArH), 6·50–5·55 (m, 4H, vinyl), 4·40–4·03 (m, 2H, methine), 2·60–2·20 (m, 2H, methylene); UV (cyclohexane) 218 (log ϵ = 3·54), 245 (3·54), 259 (3·44), 265 (3·34), 272 (3·22) nm.

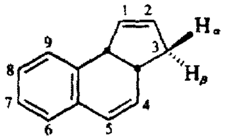
7-Phenylcycloheptatriene **8** was obtained as a clear liquid, b.p. ~70° (bath) at 0·1 mm and identified by its NMR spectrum.[28]

To obtain larger quantities of cycloadduct **7**, the distilled reaction mixture (3·9 g, 0·023 mol) was stirred at room temp for 10 min with a soln of tetracyanoethylene (1·65 g, 0·013 mol) in CH_2Cl_2 (100 ml). The resulting white solid was filtered off to give the *adduct* (3·7 g), m.p. 207–9° (dec) from MeCN. (Found: C, 77·09; H, 4·17. $C_{19}H_{12}N_4$ requires: C, 77·01; H, 4·08%). The mother liquors were concentrated, and washed through a short column of Al_2O_3 to give pure **7** as a clear oil (1·85 g).

Reaction of benzyne with 1,3-*cycloheptadiene. o*-Benzenediazonium carboxylate, from anthranilic acid (3·0 g, 0·013 mol) was added portionwise over 1·5 hr to a soln of 1,3-cycloheptadiene 0·96 g, 0·013 mol) in dioxane (20 ml) at 70°. The mixture was finally heated on a steam bath for 5 min, and volatile material was evaporated and the residue washed through Al_2O_3 in light petroleum to give a 67 : 33 mixture (column A, 148°) of hydrocarbons **10** and **9** (0·97 g). The mixture was chromatographed on 10% $AgNO_3$-Al_2O_3 (50 g). Elution with 15% benzene-light petroleum gave *8,9-benzo-*cis*-bicyclo*[5.2.0]*nona-2,8-diene* **9** as a clear oil (0·31 g). (Found: C, 91·94; H, 8·32. $C_{13}H_{14}$ requires; C, 91·71; H, 8·29%); molecular weight (mass spectrum) 170; NMR δ 7·30–6·82 (m, 4H, ArH), 5·95–5·26 (m, 2H, vinyl), 4·49–4·24 (m, 1H, allylic cyclobutyl), 3·75–3·35 (5 line m, 1H, cyclobutyl) 2·52–1·40 (m, 6H, methylene); UV (cyclohexane) 261 (3·28), 267 (3·37), 274 (3·29) nm; elution with benzene gave *6,7-benzobicyclo*[3.2.2]*nona-6,8-diene* **10** as a clear oil (0·49 g). (Found: C, 91·11; H, 8·24; $C_{13}H_{14}$ requires: C, 91·71; H, 8·29%); Molecular weight (mass spectrum) 170; NMR δ 7·02 (s, 4H, ArH), 6·37 (apparent d of d, J_{obs} = 4·8, 3·1 Hz, 2H, vinyl), 3·58–3·18 (m, 2H, bridgehead), 1·82–1·20 (m, 6H, methylene). Double irradiation of the bridgehead signal caused the vinyl multiplet to collapse to a singlet; UV (Cyclohexane) 220 (3·61), 264 (2·61), 272·5 (2·56) nm.

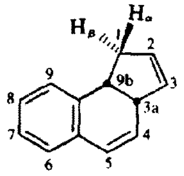
Reaction of benzyne with cycloheptene. o-Benzenediazonium carboxylate, prepared from anthranilic acid (12 g, 0·087 mol), was refluxed with cycloheptene (8·4 g, 0·087 mol) in THF (60 ml) until gas evolution ceased (1·5 hr). The crude product was adsorbed directly onto Al_2O_3 (50 g) was placed onto a column of Al_2O_3 (100 g),

Table 1. Proton chemical shifts and coupling constants for hydrocarbon **33**. Parameters for $H_{3\alpha}$, $H_{3\beta}$, H_{3a}, H_{9b} were obtained by decoupling followed by analysis of the four-spin system by computer using the LAOCN3 program. The coupling constants were accurate to ± 0·05 Hz.



Chemical shift (ppm) relative to TMS	Proton assignment	Coupling constant (Hz)
2·313	$H_{3\beta}$	$J_{3\beta,3\alpha} = -15{\cdot}6$ $J_{3\beta,3a} = 3{\cdot}8$ $J_{3\beta,9b} = 2{\cdot}2$
2·788	$H_{3\alpha}$	$J_{3\alpha,3\beta} = -15{\cdot}6$ $J_{3\alpha,3a} = 8{\cdot}3$ $J_{3\alpha,9b} = 2{\cdot}3$
3·282	H_{3a}	$J_{3a,3\alpha} = 8{\cdot}3$ $J_{3a,3\beta} = 3{\cdot}8$ $J_{3a,9b} = 9{\cdot}3$
3·967	H_{9b}	$J_{9b,3a} = 9{\cdot}3$ $J_{9b,3\alpha} = 2{\cdot}3$ $J_{9b,3\beta} = 2{\cdot}2$
5·629	H_4	$J_{4,5} = 9{\cdot}8$
5·457–5·867	H_1H_2	complex multiplet
6·249	H_5	$J_{5,4} = 9{\cdot}8$ $J_{5,3a} = 2{\cdot}1$
6·744–7·133	$H_6H_7H_8H_9$	multiplet

Table 2. Proton chemical shifts and coupling constants for hydrocarbon **31**. Parameters for $H_{1\alpha}$, $H_{1\beta}$, H_{9b}, H_{3a} were obtained by decoupling followed by computer analysis of the four-spin system using the LAOCN3 program. The coupling constants were accurate to ± 0·15 Hz. Parameters for other protons were obtained by decoupling experiments.



Chemical shift (ppm) relative to TMS	Proton assignment	Coupling constant (Hz)
2·282	$H_{1\alpha}$	$J_{1\alpha,1\beta} = -16{\cdot}0$ $J_{1\alpha,9b} = 9{\cdot}5$ $J_{1\alpha,3a} = 2{\cdot}2$
2·624	$H_{1\beta}$	$J_{1\beta,1\alpha} = -16{\cdot}0$ $J_{1\beta,9b} = 9{\cdot}2$ $J_{1\beta,3a} = 0{\cdot}3$
3·423	H_{9b}	$J_{9b,1\alpha} = 9{\cdot}5$ $J_{9b,1\beta} = 9{\cdot}2$ $J_{9b,3a} = 10{\cdot}7$
3·549	H_{3a}	$J_{3a,1\alpha} = 2{\cdot}2$ $J_{3a,1\beta} = 0{\cdot}3$ $J_{3a,9b} = 10{\cdot}7$
5·526	H_4	$J_{4,5} = 9{\cdot}5$
5·677–5·944	H_2,H_3	complex multiplet
6·237	H_5	$J_{5,4} = 9{\cdot}5$ $J_{5,3a} = 2{\cdot}2$
6·677–7·077	$H_6H_7H_8H_9$	multiplet

which was eluted with light petroleum. Evaporation of the first fraction (120 ml) gave an oil (3·7 g), shown to contain two components in a ratio of 77:23 (column B, 140°). Portion of this material (0·76 g) was chromatographed on 10% $AgNO_3$–Al_2O_3 (60 g), and the column was eluted with penthane. The first 50 ml fraction gave an oil (0·48 g), shown to be a 1:1 mixture by VPC. The second 50 ml fraction yielded 3-*phenylcycloheptene* **12** as an oil (0·22 g), having an NMR and mass spectrum identical with those reported.[29] The first fraction was rechromatographed on $AgNO_3$–Al_2O_3 (60 g), and the minor reaction product, 8,9-*benzo*-cis-bicyclo[5.2.0]non-8-ene **11** was obtained as a colourless solid (0·15 g), m.p. 30–32°, from the early pentane fractions. The material was identical with that prepared in the hydrogenation experiments below.

8,9-Benzo-cis-*bicyclo*[5.2.0]*non-8-ene* **11**. (i) To a soln of alcohol **13** (3·74 g) in pyridine (25 ml) at 0° was added $POCl_3$ (18 ml). The mixture was kept at room temp for 17 hr, and then heated on a steam bath for 15 min. The cooled mixture was cautiously poured onto crushed ice containing conc HCl (20 ml). Work-up by ether extraction, followed by short path distillation gave 8,9-*benzobicyclo*[5.2.0]*nona*-1,8-*diene* **14** as a clear liquid (1·80 g, 53%), b.p. 80° (bath) 0·5 mm (lit.[12] 130°/11 mm). The NMR spectrum was identical with that reported.[12] Catalytic hydrogenation of **14** (1·80 g) in MeOH using 10% Pd-C catalyst at room temp and pressure proceeded with the uptake of a molar equivalent of H_2, to give, after short path distillation, 8,9-benzo-*cis*-bicyclo[5.2.0.]non-8-ene **11** (1·52 g), b.p. 64–70° (bath)/0·1 mm, m.p. 30–2°. (Found: C, 91·00; H, 9·27. $C_{13}H_{16}$ requires: C, 90·64; H, 9·36%); *M* (mass spectrum) 172; NMR δ 7·25–6·83 (m, 4H, ArH), 3·82–3·42 (m, 2H, benzylic), 2·42–1·00 (m, 10H, methylene); UV (cyclohexane) 261 (3·18), 267 (3·36), 274 (3·31) nm. (ii) Catalytic hydrogenation of **7** as above proceeded with the uptake of two molar equivalents of H_2, while **9** took up one mol of H_2, to give **11** having spectral properties identical with those given in (i).

Thermolysis of "crossed dimer" **15**. Hydrocarbon **15** (80 mg) was placed in a tube (8 mm × 100 cm), sealed at one end. The open end was connected to a water aspirator. The middle of the tube was heated with a tubular furnace to 450°, and the tube was then slowly drawn through the hot zone while a gentle vacuum was applied. The product (62 mg) which collected near the open end of the tube was sublimed to give 7,8-*benzobicyclo*[4.2.1]*nona*-2,4,7-*triene* **5** as a colourless solid (50 mg, 88%), m.p. 75–6° (Found: C, 92·57; H, 7·16. $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%); *M* (mass spectrum) 168; UV (cyclohexane) end absorption to 243, 232 sh (3·60), 254 (3·47), 262 (3·60), 272 (3·67), 284 (3·47) nm; NMR (90 MHz) δ 1·88 (d, one arm of AB pattern, J = 11·4 Hz, H_9 anti to benzene ring), 2·45 (d of t of t, other arm of AB pattern, J = 11·4, 6·6, 1·2 Hz, H_9 syn to benzene ring), 3·67 (d of d, J = 7·6, 6·6 Hz, 2 Hz, bridgehead protons), 5·46–5·47 (m, 2H, H_3 and H_4), 5·96–6·33 (m, 2H, H_2 and H_5), 7·05 (s, 4H, aromatic).

Reaction of benzyne with 8-*isopropylidene*-endo-*tricyclo*[3.2.1.$0^{2,4}$]-*oct*-6-*ene* **22**. A suspension of *o*-benzenediazonium carboxylate, prepared from anthranilic acid (2·4 g, 0·0175 mol), in dioxane (10 ml) was added portionwise over 1·5 hr to a soln of **22** (2 g, 0·0148 mol) in dioxane (4 ml) at 70°. Solvent and volatile material was evaporated, and the residue washed through a short column of Al_2O_3. Short path distillation of the eluate gave an oil (0·83 g), b.p. (bath) 110° (0·1 mm), shown to be a 63:37 mixture (column B, 140°). This material was chromatographed on 10% $AgNO_3$–Al_2O_3. Elution with light petroleum gave the more abundant component 3,4-*benzo*-10-*isopropylidene*-exo-endo-*tetracyclo*[4.3.1.$0^{2,5}$.$0^{7,9}$]*dec*-3-*ene* **23** as a colourless solid, m.p. 96–7° (Found: C, 92·06; H, 8·22. $C_{17}H_{18}$ requires: C, 91·84; H, 8·16%). *M* (mass spectrum) 222. NMR δ 7·18–6·67 (symm. m, 4H, ArH), 3·14 (s, 2H, benzylic), 2·86–2·68 (m, 2H, bridgehead), 1·50–0·15 (m, 10H, remaining H); UV (cyclohexane) 222 (3·36), 262 (3·06), 268 (3·29), 274 (3·28) nm. Elution with 10% benzene–light petroleum gave 8-*phenyl*-8-(2-*propenyl*)-endo-*tricyclo*[3.2.1.$0^{2,4}$]*oct*-6-*ene* **24** as a clear liquid, b.p. (bath) 80° (0·1 mm) (Found: C, 91·55; H, 8·20; $C_{17}H_{18}$ requires: C, 91·84; H, 8·16%); *M* 222 (mass spectrum).

3,4-*Benzo*-exo-endo-*tetracyclo*[4.3.1.$0^{3,4}$.$0^{7,9}$)*dec*-3-*en*-10-*one* **25**. Ozonised O_2 was bubbled through a soln of **23** (0·637 g) in CH_2Cl_2 (40 ml) cooled in an ice-salt bath until O_3 was no longer absorbed (KI trap). The soln was allowed to warm to room temp, treated with AcOH (3·5 ml), H_2O (a few drops) and Zn powder (3·4 g). After 1 hr at room temp, the CH_2Cl_2 layer was separated, washed with H_2O, K_2CO_3 soln and dried. The crude product was chromatographed on Al_2O_3 (100 g). Elution with ether gave **25** as a colourless solid (0·303 g, 54%), m.p. 170–1° (dec) (Found: C, 85·67; H, 6·18. $C_{14}H_{12}O$ requires: C, 85·68; H, 6·16%); NMR δ 7·45–6·90 (symm. m, 4H, ArH), 3·29 (s, 2H, benzylic), 2·84–2·44 (m, 2H, bridgehead), 1·55–0·79 (m, 4H, cyclopropyl); IR 1765 cm^{-1}.

Thermolysis of ketone **25**. A soln of **25** (112 mg) in ether was injected onto column C at 180°, and the liquid product (67 mg) collected as one peak. Analytical VPC (column A, 155°) showed two components in a ratio of 4:5, which were separated on column D at 155° to yield pure samples of **29**, (17·5 mg) and **33** (38·5 mg), each spectroscopically identical to independently prepared material (see later).

Reaction of the dianion of benzocyclooctatetraene with CH_2Cl_2. To Na-dried liquid NH_3 (100 ml) was added Li (20 mg), followed by benzocyclooctatetraene[30] (800 mg). The dry ice-acetone condenser was replaced by KOH guard tube, and excess Li (230 mg) was added in small portions over 5 min. The resulting red-brown mixture was stirred for 10 min, and then CH_2Cl_2 (5 ml) in ether (25 ml) was added dropwise over 15 min. The guard tube was replaced by a dry ice-acetone condenser, and stirring was continued over 2 hr, after which the ammonia was allowed to evaporate. The residue was treated with NH_4Cl aq (40 ml) and worked up by ether extraction to give an oil (860 mg) shown by VPC (column A, 120°) to consist of derivatives **28** (61%) and **29** (17%), and another product (22%), apparently a reduced derivative of benzocyclooctatetraene. The mixture was chromatographed on 2% $AgNO_3$–Al_2O_3 (60 g). Elution with pentane and 10% benzene–pentane gave a mixture of **28** and the unknown reduced material. Elution with benzene gave 4,5-*benzobicyclo*[6.1.0]*nona*-2,4,6-*triene* **29** (80 mg), as a white solid, m.p. 49–50° (after sublimation). (Found: C, 92·41; H, 7·33. $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%). NMR (90 MHz) δ 7·22–6·95 (m, 4H, ArH), 6·48 (d, one arm of AB pattern, J = 11·0 Hz, H–3, H–6) 5·84 (d of t, other arm of AB pattern, J = 11·0 Hz, J = 1·6 Hz, H–2, H–7), 1·50–1·22 (br. t, 2H, cyclopropyl methine), 0·84–0·43 (m, 2H, cyclopropyl methylene); UV (cyclohexane)- end absorption to 300 nm.

The contaminated sample (450 mg) of **28** which was obtained in the previous chromatography was chromatographed on 10% $AgNO_3$–Al_2O_3 (20 g). Elution with 20% benzene-pentane gave 2,3-*benzobicyclo*[6.1.0]*nona*-2,4,6-*triene* **28** (60 mg) as a clear oil, b.p. 50° at 0·01 mm (Found: C, 92·30; H, 7·55. $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%); *M* (mass spectrum) 168; NMR (90 MHz) δ 7·44–6·86 (m, 4H, aromatic), 6·54 (d, one arm of AB pattern J = 11·7, 1·2 Hz, H_5), 5·72 (narrow m, 2H, H_6H_7), 2·01 (6 br. lines, J = 9·0, 8·2, 5·8 Hz, cyclopropyl methine H_1), 1·56 (m, J = 9·0, 9·2, 6·0 Hz, cyclopropyl methine H_8), 1·05 (6 lines, J = 9·2, 8·2, −4·0 Hz, H_9 anti to 4,5-double bond), 0·52 (6 lines, J = 6·0, 5·8, −4·0 Hz, H_9 syn to 4,5-double bond); UV (cyclohexane) end absorption to 240, 251 (3·75) nm.

Thermolysis of 4,5 - *benzobicyclo*[6.1.0]*nona* - 2,4,6 - *triene* **29**. The hydrocarbon, **29** (24 mg) was sealed at 0·05 mm pressure in an ampoule (25 ml capacity) which has previously been flushed with N_2. The hydrocarbon was kept at 200° for 2 hr to give *cis* - 3a,9b - *dihydro* - 3*H* - *benz*[*e*]*indene*, **33** (24 mg), as a clear oil, b.p. (bath) 55° at 0·05 mm (Found: C, 92·53; H, 7·48; $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%); NMR (90 MHz) (Table I); UV cyclohexane) 250 sh (3·76), 261 (3·94), 270 (3·96), 279 sh (3·74), 293 sh (2·79), 297 sh (2·61), 307 (2·20), 310 (2·15), 317 (2·06), 323 (1·93) 331 (1·46) nm.

Thermolysis of 2,3 - *benzobicyclo*[6.1.0]*nona* - 2,4,6 - *triene*. **28** The hydrocarbon **28** (45 mg) was kept at 200° for 2 hr as in the previous case to give *cis* - 3a,9b - dihydro 1H - *benze*[e] - *indene* **31** (45 mg) as a clear oil, b.p. (bath) 65° at 0·05 mm. (Found: C, 92·62; H, 7·34; $C_{13}H_{12}$ requires: C, 92·81; H, 7·19%; NMR (90 MHz) (Table 2); UV (cyclohexane) 261 (3·90), 270 (3·91), 279 sh (3·70), 313 (2·66), 323 sh (2·57), 327 sh (2·51), 331 sh (2·29) nm.

Thermolysis of 8,9 - *benzo* - cis - *bicyclo*[5.2.0]*nona* - 2,4,8 - *triene*. **7** The hydrocarbon **7** (1·0 g) was kept at 200° for 3½ hr as in the previous case to give *cis*-3a,9b-*dihydro*-1H-*benz*[e]*indene* **31** (1·0 g) as the only product. The spectral data were identical to those of the synthetic material.

When hydrocarbon **7** (100 mg) was kept at 175° for 2½ hr it gave a mixture (100 mg). Analytical VPC (column A, 130°) showed two major components in the ratio of 5:4 which were separated on column D at 150° to yield **28** (39 mg) and *cis* **31** (24 mg). The spectral data of each compound were identical to those of the synthetic samples.

(i) Catalytic hydrogenation of **31** (190 mg) in MeOH using 10% Pd-C catalyst at room temp and pressure proceeded with the uptake of 2 molar equiv of H_2 to yield after short path distillation, *cis* - 2,3,3a,4,5,9b - *hexahydro* - 1H - *benz*[e]*indene* **34** (180 mg), b.p. 80° (bath) at 1·0 mm. The spectral properties were identical with those of the reported[23] compound.

(ii) Catalytic hydrogenation of **33** as above proceeded with the uptake of two molar equiv of H_2 to give **34** with spectral properties identical to those obtained in (i).

Acknowledgements—We thank Dr. R. Muneyuki for spectral data of compound **34**. We thank the Australian Research Grants Committee for financial support and the Commonwealth Government for a postgraduate award to L.L.

REFERENCES

[1] R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes*. Academic Press, New York (1967)

[2] H. M. R. Hoffmann, *Angew. Chem.* (Internat. Ed.), **8**, 556 (1969); G. Wittig and H. Durr, *Liebigs Ann* **672**, 55 (1964)

[3] P. Crews and J. Beard, *J. Org. Chem.* **38**, 522 (1973); P. Crews and J. Beard, *Ibid.* **38**, 529 (1973)

[4] H. Ishitobi, H. Tanida, K. Tori and T. Tsuji, *Bull. Chem. Soc. Japan* **44**, 2993 (1971)

[5] G. H. Wahl, Jr., *J. Org. Chem.* 33, 2158 (1968)

[6] R. C. Cookson, S. S. H. Gilani and I. D. R. Stevens, *J. Chem. Soc.* C, 1905 (1967)

[7] F. R. Jensen and L. A. Smith, *J. Am. Chem. Soc.* **86**, 956 (1964)

[8a] e.g. H. Günther and T. Keller, *Chem. Ber.* **103**, 3231 (1970); M. Görlitz and H. Günther, *Tetrahedron* **25**, 4467 (1969)

[8b] T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Japan* **42**, 2033 (1969)

[9] I. Tabushi, H. Yamada, Z. Yoshida and H. Kuroda, *Tetrahedron Letters* 1093 (1971)

[10] L. Lombardo and D. Wege, *Ibid.* 3981 (1971)

[11] P. Crews, M. Loffgren and D. J. Bertelli, *Ibid.* 4697 (1971)

[12] P. Caubère, N. Derozier and B. Loubinoux, *Bull. Soc. Chim. Fr*, 302 (1971)

[13] L. Lombardo, D. Wege and S. P. Wilkinson, *Aust. J. Chem.* **27**, 143 (1974)

[14] L. G. Cannell, *Tetrahedron Letters* 5967 (1966)

[15] R. C. Hahn and R. P. Johnson, *Ibid.* 2149 (1973)

[16] P. G. Gassman and H. P. Benecke, *Ibid.* 1089 (1969)

[17] M. Jones, Jr., and R. H. Levin, *J. Am. Chem. Soc.* **91**, 6411 (1969)

[18] R. Hoffmann, A. Imamura and W. J. Hehre, *Ibid.* **90**, 1499 (1968)

[19] M. Traetterberg, *Ibid.* **86**, 4265 (1964)

[20] F. A. L. Anet, *Ibid.* **86**, 458 (1964)

[21] R. Muneyuki, T. Yano and H. Tanida, *Ibid.* **91**, 2408 (1969)

[22] M. Kato, T. Sawa and T. Miwa, *Chem Comm.* 1635 (1971)

[23] R. Muneyuki and H. Tanida, *J. Am. Chem. Soc.* **90**, 656 (1968)

[24] e.g. J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Ibid.* **94**, 5845 (1972) and refs therein; S. W. Staley, *Intra-Science Chemistry Reports* **5**, 149 (1971)

[25] L. A. Paquette and M. J. Epstein, *J. Am. Chem. Soc.* **95**, 6717 (1973)

[26] F. M. Logullo, A. H. Seitz and L. Friedman, *Org. Synth.* **48**, 12 (1968)

[27] R. Wolovsky, *J. Am. Chem. Soc.* **87**, 3638 (1965)

[28] H. Günther, M. Görlitz and H. H. Hinrichs, *Tetrahedron* **24**, 5665 (1968)

[29] A. C. Cope and S. S. Hecht, *J. Am. Chem. Soc.* **89** 6920 (1967)

[30] J. A. Elix and M. V. Sargent, *Ibid.* **91**, 4734 (1969)