# Rearrangement of Radicals derived from Bicyclo[5.1.0]octa-2,4-diene, Tricyclo[6.1.0.0²,⁴]nona-6-ene and Tetracyclo[7.1.0.0.²,⁴.0⁵,⁷]decane

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ESR spectra from bicyclo[5.1.0]octadienyl and tricyclo[6.1.0.0²,⁴]nona-6-enyl radicals, and from the rearrangement of tetracyclo[7.1.0.0²,⁴.0⁵,⁷]decanyl radicals have been observed. The rate of ring opening increases in the stated order. The ESR parameters and semiempirical calculations suggest that electron delocalisation into the three-membered rings is insignificant. At temperatures above ambient the bicyclo[5.1.0]octadienyl radical rearranges to the cycloheptatrienylmethyl radical, which in turn rearranges to the norcaradienylmethyl radical and hence to the vinylcyclohexadienyl radical, which gives styrene and products derived therefrom. 1,3-Bromination *via* the S_H2 reaction at the three-membered ring is also an important process for bicyclo[5.1.0]octa-2,4-diene.

Bicyclo[3.1.0]hexenyl radicals (1) can rearrange by β-scission of the exterior cyclopropane bond to give cyclopentadienylmethyl radicals (2), *and* by β-scission of the inter-ring bond to give cyclohexadienyl radicals (3).[1,2] Two similar rearrangements can

(1)

(2)

(3)
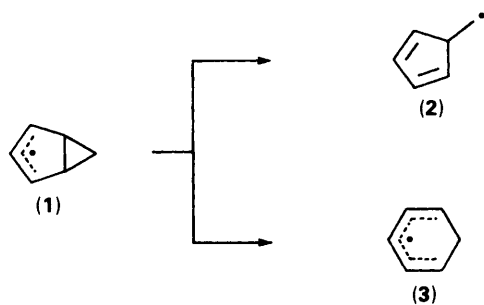
be envisaged for the vinylogous bicyclo[5.1.0]octa-2,4-dienyl radical (4), *i.e.* to give the cycloheptatrienylmethyl radical (5)


(4)

(5)

(6)
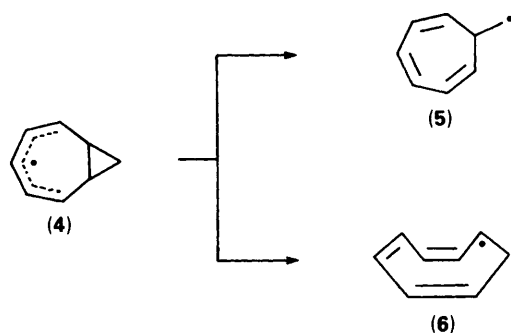
and/or the cyclo-octatrienyl radical (6). It is likely that radical (6) will adopt the non-planar 'tub' conformation in which delocalisation of the unpaired electron is wholly or partly prevented. Thus, there may be little, if any, thermodynamic stabilisation in (6). Furthermore, the bicyclo[5.1.0]octan-2-yl radical, the saturated analogue of (6), is known to rearrange exclusively by exterior bond scission to give the cycloheptenylmethyl radical.[3] The most probable mode of β-scission of (4) is therefore that giving (5) and, in fact, (4) appeared to be a promising alternative source of (5) for which several further interesting rearrangements are possible.[4]

Bicyclo[5.1.0]octa-2,4-diene was used as one precursor of (4) and its synthesis from cycloheptatriene produced several bi- and

tri-cyclopropanated analogues as by-products. An ESR study of the free radical intermediates generated from these molecules as well as an examination of the rearrangements of (4) and (5) by product analysis are reported in this paper.

Results and Discussion

Preparation of Radical Precursors.—We intended to generate the bicyclo[5.1.0]octa-2,4-dienyl radical, with and without a deuterium label, by reduction of the known homotropone[5] (7) with sodium borodeuteride or sodium borohydride and subsequent conversion of the alcohol (8) into the bromide (9a) or chloride (9b) (see Scheme 1). Reaction of (9) with tin-centred radicals would then give (10) and the deuterium label would provide a useful probe of the subsequent rearrangements. In practice, although the alcohol (8) could be obtained

(7)   **(8)**   **(9)**

(11)   **(10)**
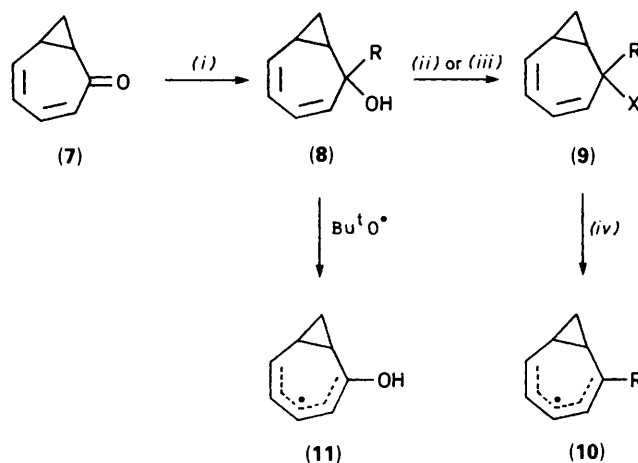
R = H or D
a; X = Br, b; X = Cl

(i) NaBH₄ or NaBD₄, (ii) PBr₃, (iii) Bu₃P/CCl₄, (iv) Bu₃SnH.

Scheme 1

satisfactorily, neither the bromide (9a) nor the chloride (9b) was stable, and mixtures of aromatic halides were formed even under the mildest conditions. Thus, treatment of (8, R = H) with PBr₃ at −78 °C gave monobromostyrenes, dibromoethylbenzenes and a small amount of cyclo-octa-1,3,5-triene.

Hydrogen abstraction from (8, R = H) should yield the hydroxy-substituted radical (11) (Scheme 1). However, when a mixture of (8, R = H) and di(t-butyl) peroxide in t-butylbenzene solvent was photolysed in the cavity of the ESR spectrometer no signals were observed; probably because of the very rapid build-up of a polymer film inside the tube.

Bicyclo[5.1.0]octa-2,4-diene (12) (homocycloheptatriene) was made by cyclopropanation of cycloheptatriene using the standard Simmons–Smith procedure.[6] This reaction gave both possible mono-cyclopropanated products (12) and (13), all four di-cyclopropanated products (14)–(17) and two of the three possible tri-cyclopropanated products (18) and (19). Each
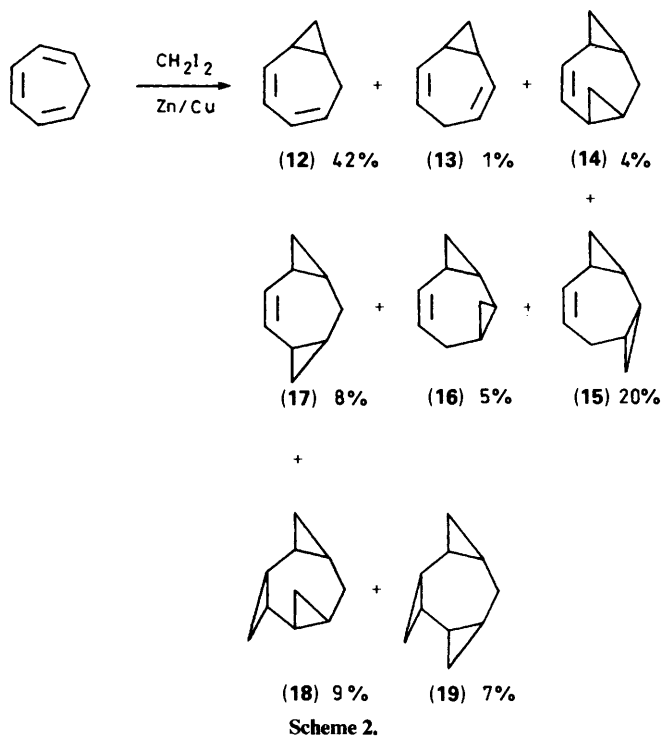
Scheme 2.

component was separated by preparative GLC and the structure confirmed by comparison of its ^{1}H NMR spectrum with those given by Paquette and Detty who developed stereospecific routes to all the bis- and tris-homocycloheptatrienes.[7] Cyclopropanation of cycloheptatriene with diazomethane was previously examined by von Doering and co-workers[8] who found a larger proportion of (13); the di- and tri-cyclopropanated products were not analysed in their study.

8-Ethoxycarbonylbicyclo[5.1.0]octa-2,4-diene (20) was made by the copper(I) chloride catalysed reaction of ethyldiazoacetate with cycloheptatriene. Some di-cyclopropanated products were produced, but difficulties in isolation prevented their identification.

(20)
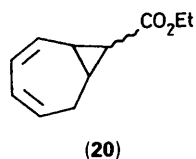
ESR Spectra of Radicals from Homo-, Bishomo- and Trishomo-cycloheptatrienes.—Degassed solutions of the substrate and

di(t-butyl) peroxide in cyclopropane, dichlorodifluoromethane or, at higher temperatures, t-butylbenzene were photolysed in the cavity of the ESR spectrometer. With homocycloheptatriene (12) a complex spectrum was observed with only minor changes in the temperature range 140–320 K. We attribute this spectrum to the homocycloheptatrienyl radical (21); satisfactory simulations were obtained with the hyperfine splittings (hfs) given in the Table. These hfs are similar to those of the open chain pentadienyl radical [$a(H_{1,5}^{anti})$ = 1.04, $a(H_{1,5}^{syn})$ = 0.96, $a(H_{2,4})$ = 0.33, $a(H_3)$ = 1.16 mT][9] and to those of cyclohexa-1,4-dienyl radicals [$a(H_{2,6})$ = 0.91, $a(H_{3,5})$ = 0.27, $a(H_4)$ = 1.37, $a(2H_1)$ = 4.81 mT].[10] The three-membered ring in (21) contains an in-plane set of π-orbitals which could possibly extend the delocalisation of the unpaired electron. However, as shown above, the ESR hfs are very similar to those of the pentadienyl radical and totally unlike the hfs of cycloheptatrienyl [$a(7H)$ = 0.39 mT].[11] The ESR data suggests that this type of homoconjugation is negligible for radical (21).

The structures of radical (21) and its precursor (12) were calculated using the semiempirical MNDO method.[12,13] The computed structure of (21) showed a pentadienyl unit with bond lengths and angles similar to those computed for the penta-1,4-dienyl radical itself.[14] Similarly, the computed structures of the three-membered rings in (12) and (21) were essentially identical. Thus the structure of (21) gives no indication of any delocalisation into the Walsh orbitals of the three-membered ring. The computed angle between the three- and seven-membered rings was 124°, so that the π-orbitals of the former are not well orientated for overlap with the π-orbitals of the pentadienyl unit. The stabilisation energy of (21) relative to the methyl radical, $E_{st}^{CH_4}$ (21), was computed to be 31.8 kcal mol^{-1}.[*] This is close to that computed for the penta-1,4-dienyl radical (29 kcal mol^{-1})[14] so that no 'extra' stabilisation is found for radical (21).
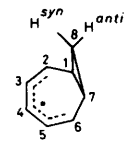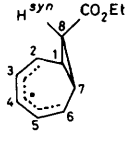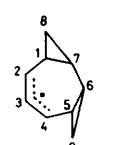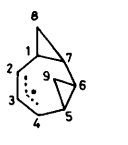
The hfs of radical (21) were calculated by the INDO method,[15] using the optimised MNDO geometry and are recorded in the Table. The correspondence between observed and calculated values was as good as can be expected; INDO usually overestimates the spin density at 'nodal' sites[14,15] such as $H_{3,5}$. The tentative assignment of the experimental hfs to specific hydrogens shown in the Table was made with the guidance of the INDO results. The observation of (21) indicates that the main site of hydrogen abstraction is C(6). This is in accord with expectation because the hydrogens at C(6) are activated by the adjacent π-system. Radical (21) was observed up to ca. 320 K; above this temperature no radicals were detectable. Thus, (21) undergoes β-scission far more slowly than the cyclopropylmethyl radical. This is not unexpected because cyclopropylallyl and other delocalised cyclopropylmethyl type radicals are known to ring-open comparatively reluctantly.[16]

The analogous radical (22) was observed on hydrogen abstraction from 8-ethoxycarbonylbicyclo[5.1.0]octa-2,4-diene (20). The latter was a mixture of two *syn-* and *anti-*isomers probably with the *anti* in large excess. The hfs obtained from the simulation are given in the Table where they are assigned to the *anti-*isomer of the radical. As expected, the electron-withdrawing substituent has only a minor effect on the hfs which are slightly reduced in comparison with (21), except for $a(H_{1,7})$.

On hydrogen abstraction from the *anti-* (15) and *syn-*3,5-bishomocycloheptatriene (16) (tricyclo[6.1.0.0^{2,4}]non-6-ene) the corresponding allyl-type radicals (23) and (24) were observed. Good simulations were obtained, and the hfs are given in the Table. The similarity of these hfs to those of other allyl-type radicals suggests that there is little, if any, delocalisation of the unpaired electron into the three-membered rings in either radical. Both (23) and (24) were observed in the temperature range 200–275 K, the signals weakening and disappearing at the top of this range. This may indicate that β-scission occurs


Table. ESR spectra of radicals derived from homocycloheptatriene, bishomocycloheptatriene, and trishomocycloheptatriene.[a]

Radical	T/K	hfs/mT					
		H_4	$H_{2,6}$	$H_{1,7}$	$H_{3,5}$	H_8^{syn}	H_8^{anti}
(21)	140	1.24	0.87	0.58	0.29	0.09	0.17
	INDO[b]	−1.29	−0.93	0.83	0.62	−0.11	0.33
(22)	217	1.18	0.83	0.64	0.27	0.16	—
		$H_{2,4}$	$H_{1,5}$	H_3	$H_{6,7}$		
(23)	206	1.38	0.43	0.43	0.17		
(24)	206	1.37	0.61	0.35	0.12[d]		
		2H	H				
(26)	128	2.26	3.85[c]				

[a] All g-factors 2.003 ± 0.001. [b] Hfs computed by INDO method (see the text). [c] $\delta a/\delta T = -3.7 \times 10^{-3}$ mT/K. [d] Additional unassigned triplet hfs of 0.06 mT.

at about 275 K, but the rearranged radicals could not be detected spectroscopically.

Enough of the *anti,anti*-trishomocycloheptatriene (18) (tetracyclo[7.1.0.0²,⁴.0⁵,⁷]decane) for an ESR experiment was also obtained. In this case hydrogen abstraction should occur at the C(7) ring methylene to give the trishomocycloheptatrienyl radical (25). In practice the observed radical showed a 'doublet of triplets' spectrum which we attribute to the rearranged species (26).

(18) →(Bu^{t}O•)→ (25) → (26)
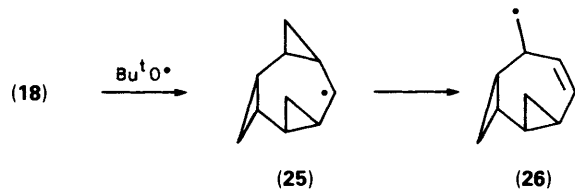
The magnitude of $a(H_8)$ and its large negative temperature coefficient (Table) indicate that in the preferred conformation of (26) the SOMO eclipses the C–H_8 bond. This is characteristic of cycloalkylmethyl and cycloalkenylmethyl radicals with ring sizes of C_6 and greater.[17,18] Even in CF_2Cl_2 solvent at 100 K β-scission was so fast that only (26) was observed. Thus (25) undergoes β-scission much more rapidly than the archetype cyclopropylmethyl radical. As judged from the temperature in the ESR experiments at which the unrearranged radical disappears or at which the rearranged radical appears, the rates

of β-scission are in the order: (25) > cyclopropylmethyl > (23) ~ (24) > (21). This is consistent with the idea that the greater the extent of delocalisation of the unpaired electron, the slower is the β-scission.

Free-radical Reactions of Homocycloheptatrienes.—Compound (12) was treated with *N*-bromosuccinimide (NBS) under the usual free radical conditions. The main products were styrene and two (possibly more) dibromo-adducts $C_8H_{10}Br_2$, accompanied by minor amounts of mono- and di-bromoethyl-benzenes. Analogous products were obtained with the 8-ethoxycarbonyl derivative (20). The most probable route to styrene is shown in Scheme 3. Hydrogen abstraction will lead to (21) [or (22)], as observed by ESR spectroscopy. At 80 °C, where the NBS reactions were carried out, β-scission to give the cycloheptatrienyl radical (5) seems a likely possibility. Cycloheptatriene[19] and derivatives[20] are known to be in equilibrium with norcaradienes, thus, radical (27) will be formed. However, (27) is a cyclopropylmethyl-type radical which is expected to ring-open extremely rapidly to give the resonance stabilised cyclohexadienyl-type radical (28). Radical (28) will be easily oxidised by NBS, or any radical present, to give styrene (29). It is probable that the minor amounts of mono- and di-bromoethylbenzenes are formed by bromination and hydrobromination of this product styrene.

Attempts by preparative GLC, and otherwise, to isolate the other major products, *i.e.* the dibromo-adducts, $C_8H_{10}Br_2$, were

(21, R = H)   (5)   (27)

(22, R = CO$_2$Et)

Mono- and dibromides

(29)   (28)
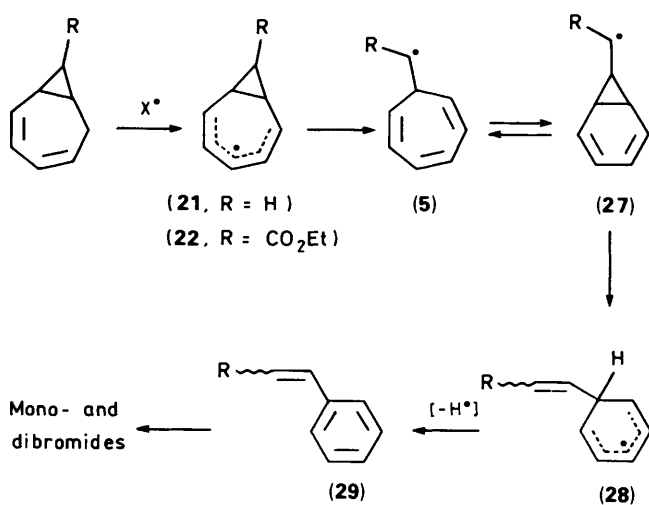
Scheme 3.

unsuccessful. The three main structural possibilities are (30) (or the 1,2-dibromide) formed by direct bromine addition, and (31) or (32) formed by S_H2 attack of bromine atoms on the three-membered ring. The ^{1}H NMR spectrum of the total product

(30)   (31)   (32)
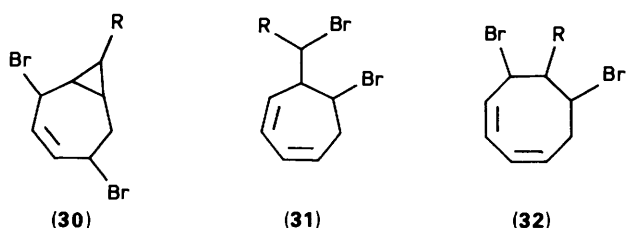
mixtures from (12) and (20) showed the absence of cyclopropane and CH$_2$Br signals, so that the adducts are probably isomeric 1,3-dibromides (32). There is ample precedent for this type of reaction between NBS and substituted cyclopropanes.[21–23]

The reaction of (12) with N-bromobis(trimethylsilyl)amine under radical conditions[24] followed essentially the same course. No styrene was detected, but the proportion of mono- and di-bromoethylbenzenes, which are derived therefrom, was increased. Thus, the reaction proceeded as in Scheme 3, with X = (Me$_3$Si)$_2$N· and this was accompanied by S_H2 attack of bromine atoms to give (32; R = H). Similarly, the photochemical reaction of (12) with CCl$_3$Br was largely explicable by the mechanism of Scheme 3 with X = CCl$_3$·. The presence of chloroform confirmed the hydrogen abstraction step. The same dibromides, probably (32), were formed by the S_H2 reaction of bromine atoms. In addition, this reaction gave several isomeric adducts C$_9$H$_{10}$BrCl$_3$. Since no cyclopropane hydrogens were visible on the ^{1}H NMR spectrum of the product mixture, it is most likely that CCl$_3$· radical addition to the dienyl system in (12) is followed by β-scission to give (33) and isomers, after bromine abstraction from CCl$_3$Br.

(33)
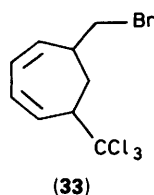
Conclusions

Homocycloheptatrienyl radicals have a similar distribution of

unpaired spin as in pentadienyl radicals, and show negligible delocalisation into the three-membered ring. They probably rearrange to cycloheptatrienylmethyl radicals (5) at temperatures significantly above ambient. The latter are in equilibrium with norcaradienyl radicals (27) which ring-open irreversibly to give cyclohexadienyl-type radicals. Bishomocycloheptatrienyl radicals (23) and (24) also show no homoconjugation and undergo β-scission much more slowly than cyclopropylmethyl radicals which, in turn, ring-open slower than trishomo-cycloheptatrienyl radicals (25).

Experimental

ESR spectra were recorded with a Bruker ER 200D spectrometer on degassed solutions in Spectrosil tubes irradiated with light from a 500W super-pressure Hg arc. Unless otherwise noted, ^{1}H, ^{13}C and ^{2}H NMR spectra were obtained at 300, 75 and 46 MHz respectively on a Bruker AM 300 instrument, utilising CDCl$_3$ solutions at ambient temperature with Me$_4$Si as an internal standard. GC–MS analyses were carried out with a Finnegan Incos instrument fitted with an HP1 methylsilicone capillary column. Preparative GLC employed a Pye–Unicam 105 chromatograph with 5 m × 1 cm glass columns packed with 20% FFAP or Carbowax 20M on Chromosorb WAW.

Bicyclo[5.1.0]octa-2,4-dien-5-ol (8).—To homotropone[5] (7) (1.0 g) in methanol (75 cm^3) cooled in ice was added sodium borohydride (0.3 g) in small portions. The solution was stirred for 30 min then saturated sodium hydrogen carbonate solution (20 cm^3) was added and the methanol partly removed on a rotary evaporator. The mixture was extracted with ether (2 × 50 cm^3) which was washed with water, then dried over sodium sulphate. Evaporation of the ether gave a yellow oil which was purified by chromatography on silica gel using 10% ether in light petroleum as the eluant; yield 52%. The NMR spectra showed two isomers, major (probably *trans*) δ_H 0.83 (1 H, m), 1.27 (1 H, m), 1.81 (1 H, m), 2.10 (1 H, m), 2.39–2.64 (1 H, m), 4.89 (1 H, br s), 5.49 (2 H, m), 5.68 (1 H, m), 6.14 (1 H, dd, *J* 10, 7 Hz); δ_C 6.64, 14.40, 44.15, 69.92, 122.06, 123.58, 131.94, 134.82. Minor isomer (probably *cis*) ^{1}H NMR spectrum badly overlapped by that of the major isomer; δ_C 14.21, 24.22, 44.76, 69.85, 121.81, 127.99, 133.46, 140.44. The alcohols degraded over a few days at room temperature.

Reaction of (8) *with Phosphorus Tribromide.*—To the alcohol (8) (0.5 g, 4.1 mmol) in dry ether (10 cm^3) was added pyridine (0.32 g, 4.1 mmol) and the solution was cooled in a solid CO$_2$–acetone mixture. Then PBr$_3$ (0.39 cm^3, 4.1 mmol) in ether (5 cm^3) was added dropwise. The solution was stirred for 30 min, warmed to room temperature, then washed with water, H$_2$SO$_4$ (2 mol dm^{-3}), NaHCO$_3$ solution, and water again. After drying over Na$_2$SO$_4$ the ether was evaporated and the residue was extracted with pentane. The pentane was evaporated to give a yellow oil (0.2 g). The ^{1}H NMR spectrum and GC–MS analysis showed this to be a complex mixture containing cyclo-octa-1,3,5-triene, monobromides C$_8$H$_7$Br and dibromoethylbenzenes together with several unidentified products.

Reaction of (8) *with Tributylphosphine in Tetrachloromethane.*—The alcohol (8) (0.5 g, 4.1 mmol) in CCl$_4$ (10 cm^3) was cooled in ice under nitrogen and Bu$^n_3$P (0.83 g, 4.1 mmol) in CCl$_4$ (5 cm^3) was added dropwise. The solution was stirred for 4 h, filtered, washed with water, HCl (2 mol dm^{-3}), dried over Na$_2$SO$_4$ and the solvent evaporated. The residue was extracted with pentane which was evaporated to give a brown oil (0.2 g). The GC–MS showed this to contain unchanged alcohol, tributylphosphine oxide and a complex array of products including cyclo-octa-1,3,5-triene.

Cyclopropanation of Cycloheptatriene.—To a freshly prepared Zn/Cu couple (30 g) in dry ether (100 cm^3) was added cycloheptatriene (23 g) and CH$_2$I$_2$ (93.8 g) and the mixture was refluxed for 30 h. The ether was decanted and the residue washed with additional ether which was also decanted. The combined ether layers were poured into 250 cm^3 of HCl (1 mol dm^{-3}) containing ice. The ether layer was washed with water, dried over K$_2$CO$_3$ and distilled. GLC examination indicated *ca.* 20% reactant conversion into eight main products. The GC–MS analysis showed two mono-cyclopropanated products, four di-cyclopropanated products and two tri-cyclopropanated products. The overall and individual component yields were not greatly affected by longer reaction times, excess CH$_2$I$_2$ or ultrasonication. Samples were separated by preparative GLC and identified by comparison of their ^{1}H NMR spectra with those given by Paquette and co-workers[7] at 90 MHz. In order of elution on Carbowax 20M the products were: peak 1 (41.7%), bicyclo[5.1.0]octa-2,4-diene (12), δ_H 0.57 (1 H, m), 1.12 (2 H, m), 1.70 (1 H, m), 2.28 (1 H, m), 2.60 (1 H, dt, *J* 12, 3 Hz), 5.61 (1 H, dd, *J* 7, 12 Hz), 5.69 (1 H, m), 5.85 (1 H, m), 6.17 (1 H, dd, *J* 7, 12 Hz); δ_C 6.53, 15.55, 28.91, 32.28, 124.65, 128.64, 130.70, 135.55; M^+ 106; spectra were similar to those given in the literature.[25] Peak 2 (3.7%), *syn*-1,5-bishomocycloheptatriene (14), δ_H − 0.03 (2 H, m), 0.32 (1 H, m), 0.78 (2 H, m), 1.27 (4 H, m), 2.49 (1 H, m), 5.53 (2 H, s). Peak 3 (20.1%), *anti-* 3,5-bishomocyclohepatriene (15), δ_H 0.13 (1 H, q, *J* 4 Hz), 0.38 (1 H, q, *J* 3 Hz), 0.77–1.12 (5 H, m), 1.21 (1 H, m), 1.92 (1 H, m), 2.28 (1 H, m), 5.63 (1 H, m), 5.76 (1 H, m); M^+ 120. Peak 4 (1.3%), probably bicyclo[5.1.0]octa-2,5-diene (13), δ_H 1.50 (1 H, m), 1.64 (1 H, m), 2.08–2.25 (1 H, m), 2.70–2.83 (1 H, m), 2.90 (1 H, m), 3.22 (1 H, m), 5.22 (2 H, m), 5.98 (2 H, m), *c.f.* W. von E. Doering and co-workers.[8] Peak 5 (5.2%), *syn*-3,5-bishomocycloheptatriene (16), δ_H 0.05 (2 H, m), 0.23 (1 H, m), 0.79 (1 H, m), 0.97 (1 H, m), 1.27 (2 H, m), 2.34 (1 H, m), 2.71 (1 H, m), 5.28 (1 H, m), 5.68 (1 H, dt, *J* 10, 2 Hz), M^+ 120. Peak 6 (8.0%), *anti*-1,5-bishomocycloheptatriene (17), δ_H 0.63 (2 H, q, *J* 4 Hz), 0.78 (2 H, m), 1.00 (2 H, m), 1.18 (2 H, m), 1.93 (2 H, t, *J* 4 Hz), 5.59 (2 H, m). Peak 7 (8.5%) *anti-, anti*-trishomocycloheptatriene (18), δ_H −0.02 (2 H, q, *J* 4 Hz), 0.14 (1 H, m), 0.46 (1 H, dt, *J* 20, 18 Hz), 0.59 (1 H, m), 0.72 (2 H, m), 0.77–0.96 (6 H, m), 2.38 (1 H, dt, *J* 20, 4 Hz), M^+ 134. Peak 8 (7.2%), *anti-, syn*-trishomocycloheptatriene (19), δ_H 0.07 (2 H, m), 0.28 (1 H, m), 0.47 (1 H, m), 0.56 (1 H, q, *J* 4 Hz), 0.72 (2 H, m), 0.81 (3 H, m), 0.97 (1 H, m), 1.22 (1 H, m), 1.48 (1 H, dd, *J* 10, 15 Hz), 2.38 (1 H, dt, *J* 4, 8 Hz), M^+ 134. Several minor unidentified products (total < 5%) were also present but none appeared to be the *syn, syn*-trishomocycloheptatriene. Sufficient bicyclo[5.1.0]octa-2,4-diene (12) for a series of experiments was obtained by a combination of spinning-band distillation and preparative GLC. Small samples (*ca.* 30 mg) of (15), (16) and (18) were isolated by preparative GLC for ESR spectroscopy.

Reaction of (12) with N-Bromosuccinimide.—Compound (12) (89 mg, 0.84 mmol), NBS (0.3 g, 1.7 mmol), and benzoyl peroxide (1 mg) in CCl$_4$ (2 cm^3) were heated at 65 °C and the reaction was monitored by GLC. Fresh peroxide was added periodically and the reaction was stopped after 70 h when all the (12) was consumed. GC–MS examination showed two major and several minor products which were then separated by preparative GLC. In order of elution the components were: peak 1 (major), styrene; peak 2 (minor) 1-bromo-1-phenylethane, peak 3 (minor), 1-bromo-2-phenylethane; peak 4 (minor) unidentified; peak 5 (minor), 1,2-dibromo-1-phenylethane; peak 6 (major) (resolved into at least two components on a capillary column) C$_8$H$_{10}$Br$_2$ (several attempts to separate this product by preparative GLC were unsuccessful, the ^{1}H

NMR spectrum of the whole product mixture showed no signals for cyclopropane hydrogens and no CH$_2$Br doublet in the δ 3–4 region hence this is probably a mixture of dibromo-octadienes (32); peak 7 (trace), C$_8$H$_{10}$Br$_4$, possibly a tetrabromo-octene isomer. Traces of benzoic acid and bromobenzene from the initiator were also detected.

Reaction of (12) with N-Bromobis(trimethylsilyl)amine.—Compound (12) (44 mg), *N*-bromobis(trimethylsilyl)amine (100 mg), 3,3-dimethylbut-1-ene (2 mm^3) and AIBN (5 mg) were dissolved in perdeuteriobenzene and heated at 70 °C. The reaction was monitored by NMR spectroscopy and stopped after 24 h when *ca.* 50% of (12) had been consumed. The reaction produced a complex mixture of mono- and di-bromides in which 1-bromo-1-phenylethane, 1-bromo-2-phenylethane, 1,2-dibromo-1-phenylethane and the bromine adducts C$_8$H$_{10}$Br$_2$ predominated.

Reaction of (12) with Bromotrichloromethane.—(12) (44 mg) was mixed with excess CCl$_3$Br (1 cm^3) and photolysed for 6 h at 25 °C with light from a 250W medium pressure Hg arc. The products were chloroform (minor), styrene (minor), hexachloroethane, the same two C$_8$H$_{10}$Br$_2$ isomers as in the NBS reaction (major), and at least two isomers C$_9$H$_{10}$Cl$_3$Br (major). Attempts to isolate the latter by preparative GLC were not successful. The ^{1}H NMR spectrum of the whole mixture showed the disappearance of the cyclopropane hydrogens, but the δ 3–4 region became very complex and was consistent with the presence of –CH$_2$Br and >CHBr groups.

8-Ethoxycarbonylbicyclo[5.1.0]octa-2,4-diene (20).—Ethyl diazoacetate (20 g, 0.17 mol) was added dropwise to a suspension of copper(I) chloride (0.5 g) in cycloheptatriene (80 cm^3) cooled in ice, under nitrogen. The solution was stirred overnight, filtered and distilled to give (20) as a yellow liquid (10.9 g, 35%) b.p. 115 °C at 1 Torr.* The NMR spectra showed this to be a mixture of *anti-* and *syn*-isomers (81% and 19%; probably the *anti* is the major component); δ_H(major) 1.28 (3 H, t, *J* 7 Hz), 1.83 (1 H, m), 2.18 (2 H, m), 2.31 (1 H, m), 2.66 (1 H, m), 4.12 (2 H, q, *J* 7 Hz), 5.75 (2 H, m) 5.86 (1 H, m), 6.14 (1 H, dd, *J* 5, 12 Hz). The ^{1}H NMR spectrum of the minor component extensively overlapped that of the major δ_C(major) 14.28 (CH$_3$), 21.22 (CH), 26.41 (CH), 27.80 (CH$_2$), 39.11 (CH), 60.54 (CH$_2$), 127.11 (CH), 128.67 (CH), 130.90 (CH), 132.15 (CH), 174.05 (CO); δ_C(minor) 14.36 (CH$_3$), 15.29 (CH), 22.35 (CH$_2$), 23.25 (CH), 27.71 (CH), 59.99 (CH$_2$), 127.89 (CH), 129.02 (CH), 130.63 (CH), 134.32 (CH), 170.95 (CO).

Reaction of (20) with N-Bromosuccinimide.—Bicyclodiene (20) (0.5 g, 2.8 mmol), NBS (0.6 g, 3.3 mmol) and benzoyl peroxide (5 mg) in CCl$_4$ (5 cm^3) were heated at 65 °C for 80 h. The solution was filtered and the solvent evaporated. The residual oil was separated by preparative GLC to give unchanged (20) with *trans-* and *cis*-β-ethoxycarbonylstyrene (29; R = CO$_2$Et) in an 8:1 molar ratio. δ_H(*trans*) 1.34 (3 H, t, *J* 7 Hz), 4.28 (2 H, q, *J* 7 Hz), 6.45 (1 H, d, *J* 16 Hz), 7.40 (3 H, m), 7.54 (2 H, m), 7.69 (1 H, d, *J* 16 Hz). The NMR spectrum of the minor *cis*-isomer overlapped that of the *trans* but the alkene doublets were well resolved at δ_H 5.96 (1 H, d, *J* 11 Hz), 6.97 (1 H, d, *J* 11 Hz). The GC–MS confirmed the β-ethoxycarbonylstyrene identification and showed the presence of trace amounts of dibromides C$_{11}$H$_{14}$Br$_2$O$_2$.

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* 1 Torr = 133.32 Pa

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