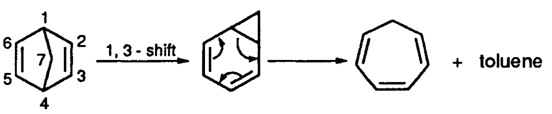
Donor–Acceptor Accelerated Norbornadiene Rearrangements

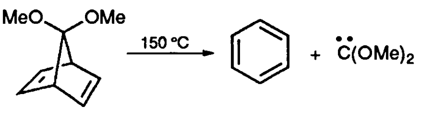
Christine Bleasdale and David W. Jones
School of Chemistry, The University, Leeds LS2 9JT

The norbornadienone acetals **3** with a CO_2Me, $CONMe_2$ or CHO substituent at C-2 undergo rearrangement under very mild conditions; cycloheptatrienes are obtained for CO_2Me and $CONMe_2$ substituents and the furanone acetal **9** for the CHO substituent. The donor–acceptor acceleration is consistent with a formal 1,3-shift to a norcaradiene proceeding either *via* a zwitterionic intermediate or a concerted-forbidden path. Rearrangement *via* a biradical is not consistent with the slower rearrangement of 7-cyano-7-methoxy-2,3-bis(methoxycarbonyl)norbornadiene **16**. The indene **19** racemises rapidly at a temperature 100 °C below that required for **18** establishing that a donor and an acceptor (Me_3SiO and CN) at a potential radical centre promote homolysis to a greater extent than two donor groups (two alkoxy groups).

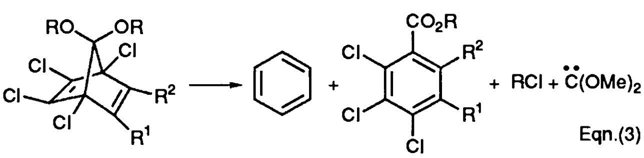
Norbornadiene rearranges to cycloheptatriene and toluene above 325 °C [eqn. (1)][1] and 7-alkoxynorbornadienes undergo similar rearrangements at 170 °C.[2] 7,7-Dialkoxynorbornadienes eliminate dialkoxycarbenes, *e.g.* eqn. (2), but the tetrachloro compounds, *e.g.* **1**, undergo both elimination of dialkoxycarbene and cleavage of the bridge to give an ester, *e.g.* **2**, and alkyl chloride [eqn. (3)].[3] The compound **1** (R = Me, R^1 = H, R^2 = Ph) decomposes above 100 °C, but attempts to produce **1** (R = Me, R^1 = R^2 = CO_2Me) gave mostly the bridge cleavage product **2** (R = Me, R^1 = R^2 = CO_2Me). Herein, we describe in detail the remarkably easy rearrangement (≈40 °C) of the 7,7-dialkoxynorbornadienes **3** to the cycloheptatrienes **4**/**5**.[4] Our observations bear on the long standing problem of the mechanism of these reactions. Although norcaradienes are accepted intermediates in norbornadiene into cycloheptatriene conversions, the mechanism of the 1,3-shift involved [Eqn. (1)] remains a matter of debate.



Eqn.(1)



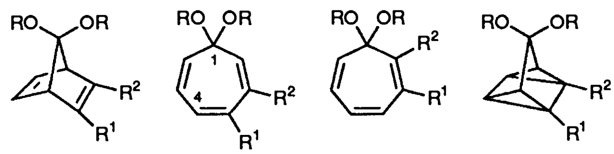
Eqn.(2)



Eqn.(3)

1 **2**

Preparation of Norbornadienes.—The norbornadiene **3a** was first prepared by addition of the metastable cyclopentadienone dimethyl acetal[5] to dimethyl acetylenedicarboxylate. However, a more flexible route to norbornadienone acetals involved the quadricyclanones **6** prepared in quantity by way of Diels–Alder addition of an acetylenic dienophile to 6,6-dimethylfulvene followed by photochemical closure to a quadricyclane and ozonolysis.[6] The quadricyclanones were smoothly converted into their acetals **6** using the method of Noyori *et al.*[7] involving treatment with a silylated alcohol and trimethylsilyl triflate at low temperature. The required silylated alcohols with the exception of methyl trimethylsilyl ether[8] were prepared using



3 **4** **5** **6**

a; R = Me, R^1 = R^2 = CO_2Me
b; R = $CH_2CH{=}CH_2$, R^1 = R^2 = CO_2Me
c; R = Me, R^1 = H, R^2 = CO_2Me
d; R = Me, R^1 = D, R^2 = CO_2Me
e; R = Me, R^1 = H, R^2 = $CONMe_2$
f; R = Me, R^1 = H, R^2 = CHO
g; R = Me, R^1 = H, R^2 = $CH{=}CH_2$
h; R,R = CH_2CH_2, R^1 = H, R^2 = CO_2Me
} throughout

N,*N*′-bis(trimethylsilyl)urea.[9] The conversion of the acetals **6** into the norbornadienes **3** could be accomplished at 20 °C using either palladium acetate in benzene* or 10% palladium on charcoal in ethyl acetate. In all cases isomerisation was slow, as expected in the presence of electron-withdrawing groups in the quadricyclane.[10]

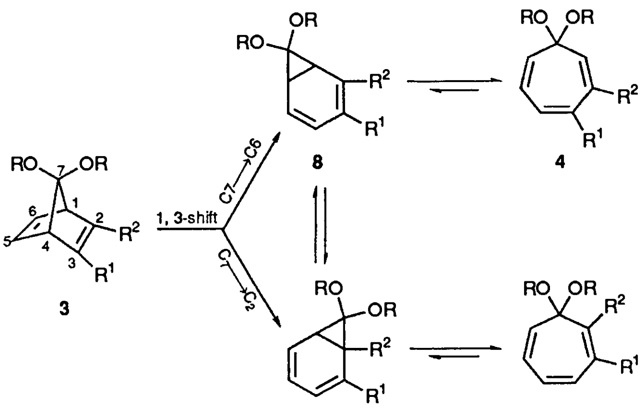
In the case of **6a** isomerisation to **3a** using $[Rh_2(CO)_4Cl_2]$ was too slow below 60 °C for preparative use; at 60 °C rearrangement of **3a** is rapid (see below). With 10 mol % of $Pd(OAc)_2$ in benzene **6a** gave **3a** in 30% isolated yield after 96 h at 20 °C. Our use of $Pd(OAc)_2$ is an extension of the use of palladium on charcoal for quadricyclane isomerisation first noted by Cristol.[11] The sensitive aldehyde **3f** was prepared by Swern oxidation of the alcohol **3** (R = Me, R^1 = H, R^2 = CH_2OH) which was obtained by ring-opening of the quadricyclane **6** (R = Me, R^1 = H, R^2 = CH_2OH) formed by reduction of **6c** with $LiAlH_4$.

The acid formed by alkaline hydrolysis of the ester **6c** gave the dimethylamide **6** (R = Me, R^1 = H, R^2 = $CONMe_2$) by reaction with ethyl chloroformate followed by dimethylamine; ring-opening with $Pd(OAc)_2$ (20 °C) then gave the norbornadiene **3** (R = Me, R^1 = H, R^2 = $CONMe_2$). The aldehyde **3** (R = Me, R^1 = H, R^2 = CHO) reacted with methylenetriphenylphosphorane to give the vinylnorbornadienone acetal **3** (R = Me, R^1 = H, R^2 = CH = CH_2). Full details for the preparation of the norbornadienone acetals are given in the Experimental section.

* Slow liberation of metallic palladium is observed in these reactions suggesting a Pd^0 species may actually be involved.

Rearrangement of Norbornadienes.—Initial attempts to prepare **3a** involved the trapping of cyclopentadienone dimethyl acetal with a large excess of dimethyl acetylenedicarboxylate. Removal of the latter at 100 °C under high vacuum and chromatography then gave **4a** (30%) rather than **3a**. The ease of the rearrangement of **3a** to **4a** was confirmed by work-up of the addition reaction at 20 °C using chromatography alone. This allowed the isolation of pure **3a** which was found to be completely *converted* into **4a** after heating in C_6D_6 (70 °C, 1.5 h). The conversion of **3a** into **4a** at 40–55 °C (C_6D_6) was followed by ^1H NMR spectroscopy (90 MHz) and the rate data recorded in Table 1 was obtained. This gave the following activation parameters: $E_a = 24.0 \pm 0.3$ kcal mol^{-1}, $\Delta H^\ddagger = 23.4 \pm 0.3$ kcal mol^{-1}, $\Delta S^\ddagger = -4.6 \pm 2$ cal mol^{-1} K^{-1}. Subsequently, a short-lived cycloheptatriene **5a** was detected using 400 MHz spectroscopy to monitor the early stage of the reaction. Heating of **3a** at 50 °C for 30 min in deuteriobenzene gave **3a** (56%), **4a** (33%) and **5a** (11%). Spin decoupling experiments allowed the firm assignment of the following spectrum to **5a**; δ 7.22 (1 H, dt, *J* 11 and 1, 3-H), 6.51 (1 H, ddd, *J* 11, 6 and 1, 4-H), 6.07 (1 H, ddd, *J* 10.5, 6 and 1, 5-H), 5.70 (1 H, dt, *J* 10.5 and 1, 6-H), 3.65 (3 H, s), 3.31 (3 H, s) and 3.07 (6 H, s). The presence of the intact acetal unit [C(OMe)$_2$], two different methoxycarbonyl groups and the structural unit -HC=CH-CH=CH-leads to the assigned structure **5a**. Continued heating of the reaction mixture led to complete conversion into **4a**.

The compounds **3a**, **4a** and **5a** are related by the reactions indicated in Scheme 1. 1,3-Shift of C-7 could occur to C-2 or to

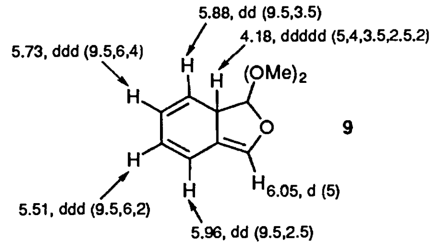


Scheme 1

both C-2 and C-6 to give the norcaradiene **7** or both **7** and **8** the valence tautomers of cycloheptatrienes **5a** and **4a**, respectively. The conversion of **5a** into **4a** involves valence tautomerism **5a**→**7a**, walk rearrangement of **7a** to **8a** and valence tautomerism to **4a** (Scheme 1). The remarkable ease of the walk rearrangement* and the ease of the initial 1,3-shift [**3a** to **7a** or **3a** to **7a** and **8a**] are associated with donor substituents on the migrating carbon atom and acceptor substituents on the migration frame. Rearrangement of the monoester **3c** to **4c** proceeds at about half the rate shown by the diester **3a** [Table 1 entries (v) and (i)] showing that only the methoxycarbonyl group at C-2 is needed for fast rearrangement. A possible rearrangement path for **3c** to **4c** involving migration of C-7 to C-3 rather than to C-6 and/or C-2 was discounted by rearrangement of **3d** to give **4d** with total deuterium integrity at C-3. Attempts to prepare the ethylene acetal **3h** by quadricyclane ring-opening gave instead the rearrangement product **4h**. The implied easier rearrangement of **3h** than of **3c** agrees with better overlap of oxygen lone-pairs in the cyclic acetal either with the migrating σ-bond or a cationic or radical site at C-7. The effectively greater donor ability at C-7 speeds rearrangement.

Reduced electron-accepting ability in the C-2 substituent is expected for the amide **3e** due to more efficient amide resonance and steric inhibition of conjugation between the amide carbonyl group and the C(2), C(3) double bond. The C-3 proton in **3c** appears at δ 7.50 but that in **3e** resonates at δ 6.73. Rearrangement of **3e** proceeds *ca.* 15 times more slowly than for **3c**, and after 3 h at 100 °C both cycloheptatrienes **4e** and **5e** and *N,N*-dimethylbenzamide produced by carbene expulsion (ratio, 9:9:2) are present.

Rearrangement of **3f** with the more powerfully electron-withdrawing formyl group at C-2 was as expected more rapid (*ca.* 4 times) than for the methoxycarbonyl substituted acetal **3c**. However, in this case the major product was not a cycloheptatriene, but a rather unstable compound formulated as **9** on the basis of UV absorption (C_6H_{12}, λ_{max} 325 nm), the 400 MHz



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^1H NMR data (C_6D_6) appended to structure **9**, and conversion into phthalide and related products (55%) on treatment with CF_3CO_2H (see Experimental section).

Discussion of the Reaction Mechanism.—The acetals **3** with a conjugating electron-withdrawing group at C-2 rearrange at temperatures considerably lower than those required for extrusion of dimethoxycarbene from norbornadienone dimethyl acetal itself [eqn. (2)]. Carbene elimination from **3b** becomes important only at higher temperatures, *e.g.* after 5 min at 100 °C **3b** gives 12 parts of cycloheptatriene **4b** and 1 part of dimethyl phthalate but after 2 min at 150 °C the ratio is 1 part of cycloheptatriene to 5 parts of dimethyl phthalate. Direct elimination of carbene from norbornadiene **3a** at 100 °C is *ca.* 10 times faster than from **4a**. In contrast, introduction of a methoxycarbonyl group at C-2 and C-3 in 7-methoxynorbornadiene only slightly accelerates rearrangement to cycloheptatrienes.[13] The minimum structural requirements for very easy rearrangement to cycloheptatrienes are, therefore, two electron-donating oxygen groups at C-7 *and* an electron-withdrawing conjugating group at C-2. It is not sufficient that the C-2 substituent be only a conjugating one; **3g** with a vinyl group at C-2 fails to rearrange below *ca.* 120 °C at which temperature it ejects dimethoxycarbene to give styrene and provides no evidence for cycloheptatriene formation. The same synergistic substituent effect may be responsible for the easy norbornadiene into cycloheptatriene rearrangement and the easy walk rearrangement **7a**→**8a** the key step in the conversion of cycloheptatriene **5a** into its isomer **4a**.

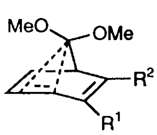
Possible mechanisms for the formal 1,3-shift converting norbornadienone acetals into corresponding norcaradienes are outlined in Scheme 2. Whilst a Woodward–Hoffmann allowed concerted 1,3-shift with inversion at C-7 would be inhibited sterically[13] the forbidden concerted 1,3-shift with retention at C-7 would involve a sterically less demanding transition state (TS), *e.g.* **10**.

Moreover, the concerted forbidden process proceeding by

* Walk rearrangement of norcaradienes has been observed at 100 °C (ref. 12).

way of an anti-aromatic TS characterised by a high-lying HOMO and a low-lying LUMO* is just the kind of TS that would benefit most by appropriately placed donor and acceptor groups.

The small energy gap between the donor HOMO (high-energy) and the low-energy LUMO of the anti-aromatic TS ensures strong interaction and significant stabilisation of the donor lone pair. Similar strong interaction of the high energy TS HOMO with the low-energy acceptor LUMO significantly lowers the energy of the electron pair in the TS HOMO.[14] The other reactions occurring upon thermolysis of the norbornadienone acetals can also be interpreted as concerted reactions. The extrusion of dialkoxy carbenes could be a cheletropic process,[15] and the conversion of norcaradiene **7** into norcoradiene **8** a concerted forbidden 1,5-shift proceeding with inversion at the migrating centre as shown in TS **11**; the ease of this transformation is again explicable in terms of the stabilisation afforded an anti-aromatic TS by appropriate donor–acceptor substitution. A similar explanation could be offered to account for formation of the furanone acetal **9** upon heating **3f**; rate-limiting formation of **7f** could be followed by



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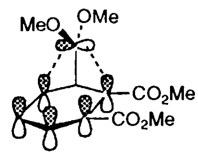

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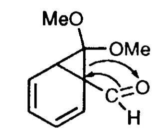

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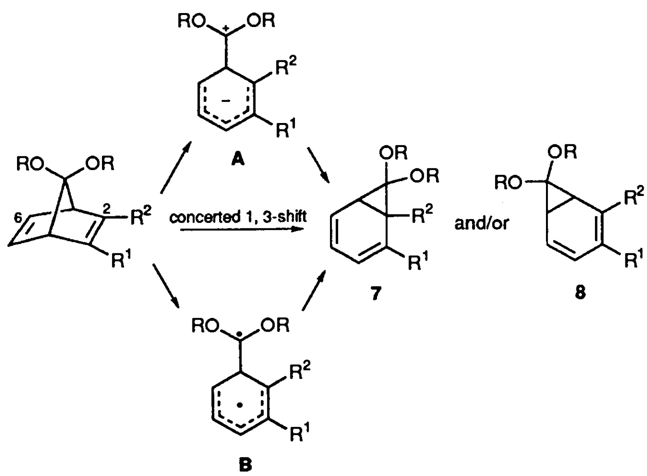
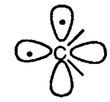
the 1,3-shift depicted in **12** and favoured by the high energy of the migrating σ-bond and the low energy of the carbonyl π*-orbital. The acylcyclopropane to dihydrofuran reaction is well known[16] even if its mechanism has not been established.

Two-step alternatives to any or all of the above mentioned concerted processes are, of course, possible. Most obviously, heterolysis to the zwitterion **A** (Scheme 2) should be favoured by donor–acceptor substitution. The zwitterion **A** could split off dimethoxycarbene, could ring-close either to the norcaradienes **7a** and **8a** or, if R^2 = CHO could give the furanone acetal **9**. The



Scheme 2

aldehyde group is known to participate more readily than the ester group in related ring-closures.[17] Reversible formation of **A** from the cycloheptatriene **5a** *via* norcaradiene **7a** can account for the conversion of **5a** into **4a**. At low temperatures ring-closure of **A** to norcaradienes must have the lower activation energy and is preferred to carbene expulsion. At higher temperatures this selectivity in the decomposition of **A** diminishes as expected and since carbene loss is irreversible but cycloheptatriene formation is reversible the ultimate product is that from carbene expulsion. Although carbene formation was at first formulated as proceeding *via* biradical intermediates **B**[3a,c] more recently Hoffmann and his collaborators[3b] have suggested that bond-breaking in a biradial like **B** would lead to a triplet or excited singlet carbene, *e.g.* **13**. Since dialkoxycarbenes are ground state singlets, *e.g.* **14**, with large S^0/T^1 and S^0/S^1



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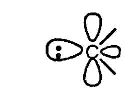

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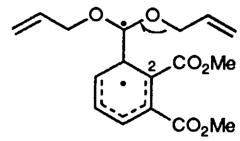

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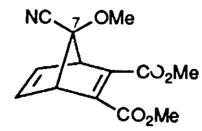

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energy differences they would arise from zwitterions **A** rather than biradicals **B**. On the other hand, carbenes with triplet ground states, *e.g.* cyano-substituted species, can be produced *via* biradicals **B**, although in many cases the formation of cycloheptatrienes and benzylic products (*e.g.* toluene from cycloheptatriene) is preferred. We first sought information for/against biradical intermediates by rearrangement of **3b**. A hypothetical biradical intermediate **15** could lose a resonance-stabilised allyl radical (**15**; arrows) with subsequent transfer of an allyl residue to C-2 or other ring carbon. An intramolecular version of the same process is also feasible. In the event, rearrangement to **4b** was very clean giving **4b** (86%) and a little dimethyl phthalate (3%) after heating at 100 °C (5 min). Further evidence against biradical intermediates was obtained by thermolysis of the 7-cyano-7-methoxynorbornadiene **16**.† A biradical intermediate **17** with a radical site strongly stabilised by CN and further stabilised by the capto-dative effect (merostabilisation) would be expected to be more stable than a biradical of type **B** so that **16** would rearrange particularly rapidly. In fact, **16** rearranged *ca.* 10^3 times more slowly than **3a** [Table 1 entries (vi) and (i)]. The C-7 epimer of **16** was also obtained in our preparation and rearranged at a very similar rate to **16**. [Table 1 entry (viii)]. The much faster rearrangement of **3a** than **16** is not consistent with a biradical intermediate for rearrangement of both **3a** and **16** although a biradical is likely for **16**. This leaves a zwitterionic intermediate or a concerted forbidden 1,3-shift as likely routes for rearrangement of **3a**.

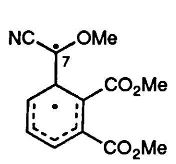
Independent evidence that a radical site is better stabilised by a donor and an acceptor than by two donor groups[18] was obtained by showing that the indene **18** racemised by way of the indicated homolysis only slowly at 220 °C[19a] whereas **19** which provides a merostabilised radical undergoes rapid homolysis at 150 °C.

* Cyclobutadiene, the prototype anti-aromatic molecule is isoelectronic with the TS **10**. In the Hückel approximation square cyclobutadiene has two degenerate non-bonding MOs. As a result of bond localisation the degeneracy is lifted by small Jahn–Teller splitting giving a high HOMO and low LUMO. Cyclobutadienes stabilised by push-pull resonance are isolable, *e.g.* R. Gompper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 824.

† We thank Professor Hoffmann for details of the preparation of this compound prior to their publication; these have now appeared ref. 3*b*. Ring-opening of the quadricyclane corresponding to **16** is much more rapid with Pd/C in boiling EtOAc (see Experimental section).

Table 1 Rearrangement rates of norbornadienes

	Compd.	Solvent	10^5k/s^{-1} (T/°C)
(i)	**3a**	C_6D_6	4.30 ± 0.07 (40)
			7.71 ± 0.26 (45)
			14.70 ± 0.05 (50)
			24.40 ± 0.90 (55)
(ii)	**3a**	CD_3CN	5.20 ± 0.20 (40)
(iii)	**3a**	CD_3OD	51.00 ± 0.20 (50)
(iv)	**3b**	C_6D_6	7.10 ± 0.10 (50)
(v)	**3c**	C_6D_6	12.20 ± 0.05 (55)
(vi)	**16**	C_6D_6	10.70 ± 0.04 (150)
(vii)	**16**	CD_3CN	9.80 ± 0.05 (150)
(viii)	*epi*-**16**	C_6D_6	18.00 ± 0.02 (160)
(ix)	*anti*-7-Methoxy-2,3-bis(methoxycarbonyl)norbornadiene	C_6D_6	*ca.* 13.1 (160)
(x)	*syn*-7-Methoxy-2,3-bis(methoxycarbonyl)norbornadiene	C_6D_6	*ca.* 2.80 (160)
(xi)	7-Methoxynorbornadiene	Decane	1.83 (160)



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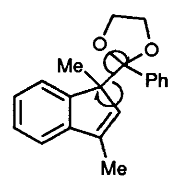

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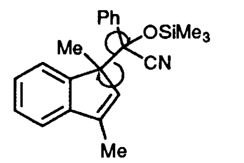

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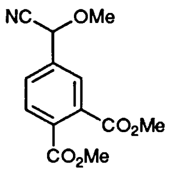

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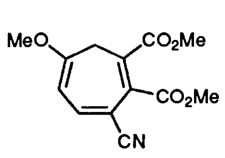

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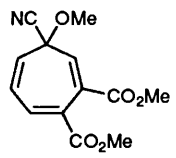

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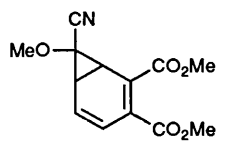

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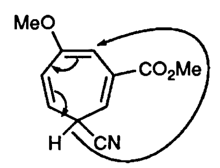

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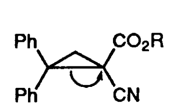

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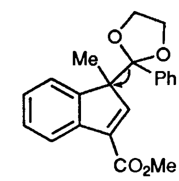

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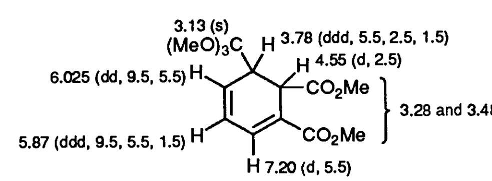

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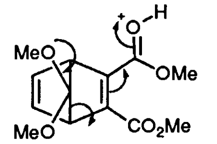
The products of the thermolysis of **16** at 150 °C were the aromatic compound **20** (56%), the cycloheptatriene **21** (16%), unidentified product(s) (8%) and dimethyl phthalate (3%).

Upon milder heating (135 °C, 2.75 h) **16** gave starting material (6 parts), **20** (1 part) and a new cycloheptatriene **22** (1 part). At 150 °C **22** gave **20** (4 parts) and **21** (1 part). A possible route to **21** therefore involves the norcaradiene **23** formed by formal 1,3-shift in **16**. Valence tautomerism of **23** gives **22** which, by a 1,5-cyano shift, which is known to be easy in cycloheptatrienes,[20] and should be accelerated by methoxy at the migration origin, would give **24**. A 1,5-H shift in **24** would then give **21**.

Evidence for/against a zwitterionic intermediate **A** was sought by carrying out rearrangement of **3a** in CD_3CN and CD_3OD. In CD_3CN rearrangement at 40 °C was only 1.21 times faster than in C_6D_6 and in CD_3OD rearrangement at 50 °C was 3.47 times more rapid than in C_6D_6. Such small solvent-rate effects do not favour rate-determining formation of a zwitterion but do not rule out such an intermediate[21a] if the ions are well delocalised and the transition state is early.[21b] Cram and his collaborators have noted a similar small solvent rate effect of 2.3 at 125 °C on going from benzene to acetonitrile for the bond heterolysis shown in **25**.[21c] However the bridge-cleavage process of eqn. (3) leading to compounds **2** has been formulated as involving rate-determining formation of a zwitterion of type **A** and shows a large solvent rate effect $k(CH_3CN)/k(C_6H_{12}) \sim 400$ whilst the competing carbene elimination shows only a modest effect of ~ 4.[3c] In another attempt to model formation of the zwitterionic intermediate **A** we prepared the optically active indene **26**. Heterolysis of **26** should afford ions, as, or even more delocalised than in zwitterion **A** and on that basis might be expected to show a small solvent-rate effect. Racemisation of **26** occurred cleanly in decalin at 125 °C ($k = 6.60 \times 10^{-5}$ s^{-1}) and in acetonitrile at 45 °C ($k = 7.13 \times 10^{-5}$ s^{-1}). In methanol at 45 °C loss of optical activity is also fast ($k = 8.64 \times 10^{-5}$ s^{-1}), *i.e.* $k(CH_3OH)/k(\text{decalin}) \approx 300$.[19b] Racemisation of **26** requires recombination of the two ions on the face of the indenyl anion opposite that from which the carbonium ion departed. The rate of racemisation may underestimate the rate of heterolysis of the indenyl-acetal bond due to internal return in an initial ion-pair. However, the large solvent rate effect shows this to be a true heterolysis and raises again the question why rearrangements of **3a** shows such a small effect if heterolysis is a rate-limiting step.

In the course of our kinetic experiments, rearrangement of **3a** in CD_3OD had been shown to give mainly **4a**. However, a subsequent detailed search for products of possible trapping of an intermediate zwitterion by methanol was more rewarding. Rearrangement of **3a** in CH_3OH at 40 °C was followed by evaporation of CH_3OH and examination of the residue in C_6D_6 by 400 MHz spectroscopy. After the reaction mixture had been heated for 2 h, its spectrum showed the presence of starting material (15.75%), the cycloheptatriene **4a** (66.6%) and a compound tentatively formulated as **27** (17.6%). The NMR data supporting structure **27** are appended to its structure (δ value, multiplicity, J value/Hz); the assignments agree with spin-decoupling experiments and the observation that in the product of reaction in CD_3OD the δ 4.55 signal is absent and the δ 3.78 resonance is simplified. Attempts to isolate **27** or a simple transformation product by silica chromatography failed. Before observation of **27** can be taken as proof for a zwitterionic mechanism two reservations should be mentioned. Firstly, although all our thermolyses were conducted in base-washed glassware it is not inconceivable, though it seems unlikely, that **27** arises *via* an acid-catalysed process (**28**; arrows). As precedent one can mention the conversion of **3a** into **29** in 33% yield upon treatment with methanol and boron trifluoride–ether at 20 °C. Secondly, Sunko and his collaborators[3d] propose that norcaradienes are *primary* intermediates in the reactions of the type shown in eqn. (3). The strain at C* in the norcaradiene **30** derived from **31** may account for the failure of



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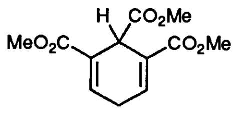

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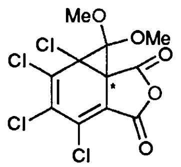

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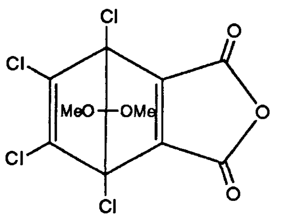

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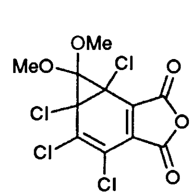

32

31 to rearrange below *ca.* 200 °C. In contrast, the norbornadiene **1** (R = Me, $R^1 = R^2 = CO_2Me$) rearranges as it is formed at > 110 °C.[3d] This explanation presumes C-7 must migrate to C-2 to give **30** and not to C-6 to give unstrained norcaradiene **32** which should be capable of proceeding to products of type **2**; it is possible that concerted-forbidden rearrangement would prefer the more electron-poor double bond. In the mechanism written by Sunko and his collaborators zwitterions are only formed from the *initially produced* norcaradienes. If these ideas are applied to the reactions in Scheme 1 the initial concerted 1,3-shift must occur to C-2 not to both C-2 and C-6. The resulting norcaradiene **7** could ring-open to cycloheptatriene **5** or heterolyse to a zwitterion of type **A** (Scheme 2). The latter could give the trapped product **27** in methanol or could ring-close to the norcaradiene **8** (Scheme 2) and hence give the thermodynamically preferred cycloheptatriene **4**.

Conclusions

The norbornadiene to cycloheptatriene rearrangement is strongly accelerated by the combined action of two alkoxy groups at C-7 and a conjugating electron-withdrawing group at C-2. Related fast rearrangement is not observed either in the absence of the acceptor group at C-2 or of one of the C-7 alkoxy groups. 7-Dimethylaminonorbornadiene, however, does undergo fast rearrangement to a cycloheptatriene despite the absence of an acceptor group at C-2,[3b] and related rearrangement of norbornadien-7-olate is enormously faster than that of norbornadien-7-ol.[22] An acceptor group at C-2 is, therefore, unnecessary for easy rearrangement if the C-7 donor is sufficiently powerful. A good case can be made[3b] for the involvement of zwitterions in all these rearrangements as well as in the higher temperature loss of carbenes from norbornadienes. Whether such zwitterions are produced directly from norbornadienes or only after rearrangement to norcaradienes must await further evidence. A starting point for study would be the mechanisms of the reactions of Eqn. (3) including the stable norbornadienone acetal **31**. At present it would be unsafe to conclude whether the rearrangement of Scheme 2 pursued the concerted-forbidden path or proceeded *via* zwitterion **A**; rearrangement *via* the biradical **B** is much less likely.

Experimental

For general details see ref. 23. Thermolyses were carried out in C_6D_6 in Pyrex tubes (4 × 180 mm or 5 × 180 mm) which had been soaked in aqueous potassium hydroxide (> 24 h), washed several times with distilled water and once with acetone, and dried at 100 °C (6–12 h). Pipettes used for transferring solutions for thermolysis were subjected to the same treatment. The tubes were sealed *in vacuo* (4 to 6 freeze–pump–thaw cycles) and heated by total immersion in a Grant constant temperature bath. Solutions of 10–30 mg of the compound to be thermolysed was dissolved in 0.2–0.5 cm^3 of a deuteriated solvent and thermolysis was followed by ^1H NMR to *ca.* 60–70% conversion.

7,7-Dimethoxy-2,3-bis(methoxycarbonyl)cyclohepta-1,3,5-triene **4a**.—A solution of potassium *tert*-butoxide (3.51 g, 31.3 mmol) in dry dimethyl sulfoxide (15 cm^3) was added to a solution of 2,5-dibromo-1,1-dimethoxycyclopentane (1.5 g, 5.2 mmol) in dimethyl sulfoxide (5 cm^3) at 15 °C. After 5 min the mixture was poured into ice-water and extracted with cold ether (2 × 40 cm^3). The combined ether extracts were added to a solution of dimethyl acetylenedicarboxylate (15 cm^3, 123 mmol) in ether (15 cm^3). The mixture was allowed to stand (16 h) at 20 °C over $MgSO_4$ and then evaporated. Dry benzene (30 cm^3) was added to the residue and the solution gently boiled under reflux (1 h). The solvent and excess of dimethyl acetylenedicarboxylate were evaporated under high vacuum at 100 °C. Chromatography of the product on silica (100 g) in benzene–ether (4:1) gave the *title compound* **4a** (422 mg, 30%) as a colourless oil (Found: M^+, 268.095. $C_{13}H_{16}O_6$ requires *M*, 268.095), ν_{max}(film)/cm^{-1} 1725 and 1625; λ_{max}/nm 230 and 262 (ε 5400 and 4600); $\delta(C_6D_6)$ 7.66 (1 H, d, *J* 6 with fine splitting, 4-H), 6.76 (1 H, d, *J* 1.5, 1-H), 6.02 (1 H, dd, *J* 6 and 10.5, 5-H), 5.75 (1 H, ddd, *J* 10.5, 1.5 and 0.5, 6-H), 3.46 (3 H, s, CO_2Me), 3.41 (3 H, s, CO_2Me) and 2.97 (6 H, s, 2 × OMe); δ_C 167.1 (2 × C=O), 135.7, 135.4, 134.2, 132.2, 128.5, 126.2, (6 × sp^2 C), 97.7 (C-7), 52.5 (Me), 52.33 (Me) and 49.3 (2 × Me); *m/z* 237, 209, 163, 135, 120, 119, 105, 92, 91 and 77 (29.2, 31.7, 100.0, 13.8, 12.8, 11.7, 10.1, 13.4, 12.7 and 26.0%).

7,7-Dimethoxy-2,3-bis(methoxycarbonyl)norbornadiene **3a** *by Addition of* 1,1-*Dimethoxycyclopenta*-2,5-*diene to Dimethyl Acetylenedicarboxylate.*—A solution of potassium *tert*-butoxide (3.51 g, 31.3 mmol) in dry dimethyl sulfoxide (15 cm^3) was added to a solution of 2,5-dibromo-1,1-dimethoxycyclopentane (1.5 g, 5.2 mmol) in dimethyl sulfoxide (5 cm^3) at 15 °C. After 5 min the mixture was poured into ice–water and extracted with ice-cold ether (2 × 40 cm^3). The combined ether extracts were added to a solution of dimethyl acetylenedicarboxylate (15 cm^3, 123 mmol) in ether (15 cm^3). The mixture was allowed to stand (16 h) at 20 °C over $MgSO_4$ and then filtered and evaporated at 20 °C. Chromatography of the product on silica (150 g) in benzene–ether (4:1) [or when performed at *ca.* −20 °C in dichloromethane–ether (19:1)] gave norbornadienone acetal **3a** (358 mg, 26%) containing cycloheptatrienone acetal **4a** (*ca.* 10%). Continued elution of the column gave the title compound **3a** (105 mg, 8%) as colourless crystals, m.p. 49–50 °C (from ether–pentane) (Found: C, 58.05; H, 5.9. $C_{13}H_{16}O_6$ requires C, 58.2; H, 6.0%); ν_{max}(film)/cm^{-1} 1720 and 1625; λ_{max}/nm 227 and 260sh (ε 3800 and 2100); $\delta(C_6D_6)$ 6.5 (2 H, t, *J* 2.5, olefinic), 4.07 (2 H, t, *J* 2.5, bridgehead), 3.45 (6 H, s, 2 × CO_2Me), 3.08 (3 H, s, OMe) and 2.85 (3 H, s, OMe); δ_C 164.9 (C=O), 147.4 (C-2 and

C-3), 137.8 (C-5 and C-6), 132.5 (C-7), 57.2 (C-1 and C-4), 52.1 (OMe) and 51.9 (OMe); *m/z* 237, 209, 163, 135, 105, 92, 91, 79 and 77 (12.9, 16.5, 100.0, 11.4, 15.8, 20.6, 19.1, 11.9 and 44.1%).

Thermolysis of Norbornadiene **3a**.—A solution of the title compound (33 mg) in C_6D_6 (0.6 cm^3) was heated in a sealed tube at 70 °C (1.5 h). The ^1H NMR spectrum of the solution showed only the presence of **4a**. Similar thermolysis in C_6D_6 at 100 °C (25 min) showed the presence of **4a** and dimethyl phthalate in a ratio of 10:1. Under the same conditions thermolysis of **4a** gave starting material and dimethyl phthalate in a ratio of *ca.* 99:1. A solution of **3a** (23 mg) in CD_3OD (0.3 cm^3) in a sealed tube was heated at 50 ± 0.5 °C in a constant temperature water-bath over 1 h to give a rate constant *k* of (5.1 ± 0.2) 10^{-4} s^{-1}. Continued heating (14 h) gave 7,7-di(deuteriomethoxy)-2,3-bis(methoxycarbonyl)cyclohepta-triene [$^2H_6$]-**4a** identified by NMR and TLC [benzene–ether (4:1)] comparison with fully protonated material.

A solution of **3a** (18 mg) in dry MeOH (0.3 cm^3) was heated in a base-washed screw-capped sealed tube at 40 °C. The reaction was monitored at 20 min intervals by removing MeOH at 0 °C in a N_2-stream and then a high vacuum and measuring the 400 MHz ^1H NMR spectrum in C_6D_6. After the mixture had been heated for a total of 2 h the spectrum showed the presence of cycloheptatriene **4a** (66.6%), starting material **3a** (15.75%) and the trapped product **27** (17.6%). Attempted isolation of **27** by silica chromatography in benzene–ether (9:1) gave only **3a** and **4a**. We thank Mr. John Greaves for this experiment.

Allyloxytrimethylsilane.—To a well stirred solution of dry allyl alcohol (2.9 cm^3, 43 mmol) in dry dichloromethane (40 cm^3), *N,N'*-bis(trimethylsilyl)urea (4.4 g, 21.6 mmol) was added in one portion. The mixture was heated under gentle reflux (5 h). The cooled mixture was filtered and the precipitate of urea washed with dry dichloromethane. Most of the dichloromethane was distilled off at atmospheric pressure after which the concentrated solution was filtered and distillation continued to give allyloxytrimethylsilane (3.4 g, 61%) as a colourless liquid (b.p. 95–98 °C, lit.[24] 100–100.2 °C) (Found: M^+, 130.082. $C_6H_{14}OSi$ requires *M*, 130.081); ν_{max}(film)/cm^{-1} 1250, 870 and 845; $\delta(CCl_4)$ 5.8 (1 H, ddt, *J* 16, 9 and 4.5, 2-H), 5.1 (1 H, ddt, *J* 16, 2 and 2, 3-H_{cis}), 4.9 (1 H, ddt, *J* 9, 2 and 2, 3-H_{trans}), 4.03 (2 H, dt, *J* 4.5 and 2, 1-H) and 0.1 (9 H, s, $SiMe_3$).

3,3-Di(allyloxy)-1,5-bis(methoxycarbonyl)quadricyclane **6b**.—A solution of trimethylsilyl triflate (*ca.* 8 mg, 0.04 mmol) in dry dichloromethane (1 cm^3) was stirred at −78 °C under nitrogen with strict exclusion of moisture. Allyloxytrimethylsilane (0.52 g, 4 mmol) was added, followed by a solution of 1,5-bis(methoxycarbonyl)quadricyclan-3-one (0.225 g, 1 mmol) in dichloromethane (1 cm^3). After 0.5 h the temperature of the solution was allowed to rise to −40 °C and maintained at this temperature (2 h). The solution was then stirred at −20 °C (24 h). Dry pyridine (0.2 cm^3) was added at −20 °C and the mixture allowed to warm up to 20 °C. It was then poured into saturated aqueous sodium hydrogen carbonate, extracted with ether and the ether extracts dried (Na_2SO_4) and evaporated (40 °C). Chromatography of the residue on silica (40 g) in benzene–ether (4:1) gave the title compound **6b** (0.195 g, 61%) as a colourless oil (Found: M^+, 320.126. $C_{17}H_{20}O_6$ requires *M*, 320.126); ν_{max}(film)/cm^{-1} 1720br, 1320 and 1075; λ_{max}/nm 237 (ε 1400); δ 5.98 (2 H, ddt, *J* 16, 9 and 4.5, 2 × =CH–), 5.33 (2 H, m, 2 × =CH_{cis}), 5.18 (2 H, m, 2 × =CH_{trans}), 4.25 (4 H, ddd, *J* 5, 3 and 1.5, 2 × OCH_2), 3.7 (6 H, s, 2 × OMe), 2.53 (4 H, AA'BB' system, *J* 5, 2-H, 4-H, 6-H and 7-H); *m/z* 263, 191, 164, 163, 135 and 77 (5.2, 5.6, 9.6, 100.0, 4.6 and 9.1%).

7,7-Di(allyloxy)-2,3-bis(methoxycarbonyl)norbornadiene **3b**.—Palladised charcoal (10%; 0.576 g), was added to a solution of quadricyclane **6b** (0.576 g, 1.8 mmol) in ethyl acetate (25 cm^3). The mixture was stirred at 20 °C (5 days) and then filtered through a pad of Celite and evaporated. Chromatography of the product on silica (40 g) in benzene–ether (9:1) gave the *title compound* **3b** (0.256 g, 44%) as a colourless oil (Found: M^+. 320.126. $C_{17}H_{20}O_6$ requires *M*, 320.126), ν_{max}(film)/cm^{-1} 1720, 1630w and 1100; λ_{max}/nm 227 and 280sh (ε 4670 and 1540); $\delta(C_6D_6)$ 6.52 (2 H, t, *J* 2.5, 5-H and 6-H), 5.77 (2 H, ddt, *J* 17, 11 and 6, 2 × =CH–), 5.19 (1 H, d, *J* 17 with further coupling, =CH_{cis}), 5.11 (1 H, d, *J* 17 with further coupling, =CH_{cis}), 4.96 (2 H, d, *J* 11 with further coupling, 2 × =CH_{trans}), 4.07 (2 H, t, *J* 2.5, 1-H and 4-H), 3.96 (2 H, dt, *J* 6 and 2, OCH_2), 3.7 (2 H, dt, *J* 6 and 2, OCH_2) and 3.44 (6 H, s, 2 × CO_2Me); *m/z* 263, 235, 191, 164, 163 and 77 (11.8, 6.2, 6.3, 11.1, 100.0 and 10.1%).

Thermolysis of the Norbornadiene **3b**.—A solution of the norbornadiene **3b** (88 mg, 0.28 mmol) in deuteriobenzene (0.5 cm^3) was heated in the usual manner at 50.0 ± 0.2 °C for 0.5, 1.5, 3 and 6.5 h, the reaction being followed by NMR to determine its rate constant [k = (7.1 ± 0.1) 10^{-5} s^{-1}]. After a heating period of 19 h the contents of the tube were evaporated; chromatography of the product on silica (15 g) in benzene–ether (19:1) gave 7,7-di(allyloxy)-2,3-bis(methoxycarbonyl)-cyclohepta-1,3,5-triene **4b** (63 mg, 71%) as a colourless oil (Found: M^+, 320.126. $C_{17}H_{20}O_6$ requires *M*, 320.126); ν_{max}(film) cm^{-1} 1730, 1625w and 1260; λ_{max} 228 and 263 nm (ε 18 500 and 13 400); δ 7.65 (1 H, d, *J* 6.5, 4-H), 6.62 (1 H, d, *J* 2, 1-H), 6.48 (1 H, dd, *J* 6.5 and 10, 5-H), 6.05 (1 H, dd, *J* 10 and 2, 6-H), 5.83 (2 H, ddt, *J* 16, 11 and 5.5, 2 × =CH), 5.2 (2 H, ddd, *J* 16, 3 and 2, 2 × =CH_{cis}), 5.1 (2 H, ddd, *J* 11, 3 and 2 Hz, 2 × =CH_{trans}), 3.97 (4 H, d, *J* 5.5 with further coupling, 2 × OCH_2), 3.78 (3 H, s, CO_2Me) and 3.74 (3 H, s, CO_2Me); *m/z* 263, 235, 191, 164 and 163 (26.2, 16.8, 9.5, 10.1 and 100.0%). Similar thermolysis of **3b** (70 mg) in C_6D_6 (0.5 cm^3) at 100 °C (5 min) and chromatography of products on silica in benzene–ether (49:1) gave dimethyl phthalate (3 mg, 7%) and cycloheptatriene **4b** (60.5 mg, 86%). After a similar heating of **3b** in C_6D_6 at 150 °C (2 min) the NMR spectrum showed dimethyl phthalate and cycloheptatriene **4b** in a 2:5 ratio.

The cycloheptatriene **4b** in decalin–benzene (1:1) was heated at 103 ± 2 °C (4 h 7 min) and then at 140 ± 2 °C (85 min) to give dimethyl phthalate in 82% yield after isolation by chromatography on silica in benzene–ether (19:1).

Methoxytrimethylsilane.—Dry aniline (94.5 cm^3, 1.04 mol) was added to trimethylsilyl chloride (59.5 cm^3, 0.47 mol) under nitrogen with stirring. The mixture was shaken and then stirred at 20 °C (15 min). Dry methanol (21.1 cm^3, 0.52 mol) was added to the cooled mixture which was then heated in a boiling water bath (20 min). Methoxytrimethylsilane (21.5 g) containing a trace of methanol was distilled from the reaction vessel (b.p. 49–55 °C, lit.,[8] 57–58 °C). This mixture was quickly washed with water (2 × 5 cm^3) and dried ($MgSO_4$) to give methoxytrimethylsilane (11.11 g, 23%), ν_{max}(film)/cm^{-1} 1250, 1090, 865 and 840; δ 0 (9 H, s, SiMe) and 3.3 (3 H, s, OMe).

3,3-Dimethoxy-1,5-bis(methoxycarbonyl)quadricyclane **6a**.—A solution of trimethylsilyl triflate (40 mg, 0.18 mmol) in dry dichloromethane (2 cm^3) was cooled to −78 °C under nitrogen and methoxytrimethylsilane (1.87 g, 18 mmol) was added to the solution with stirring. 1,5-Bis(methoxycarbonyl)quadricyclan-3-one (1.0 g, 4.5 mmol) in dichloromethane (4 cm^3) was then added and stirring was continued at −78 °C (0.5 h), at −30 °C (4 h), and then at −20 °C (16 h). Dry pyridine (0.4 cm^3) was added to the reaction mixture at −20 °C. The cooling bath was then removed and the solution allowed to warm to 20 °C. The mixture was poured into saturated aqueous sodium hydrogen carbonate, extracted with ether and the extracts were dried (Na_2SO_4) and evaporated. Chromatography of the product on silica (100 g) in benzene–ether (17:3) gave the title compound (0.872 g, 72%) identical with authentic material (m.p. and ^1H NMR spectrum).[25]

The Norbornadiene **3a** *by Catalysed Isomerisation of Quadricyclane* **6a**.—Palladium acetate (32 mg, 0.14 mmol) was added to a solution of the quadricyclane **6a** (380 mg, 1.4 mmol) in dry benzene (10 cm^3). The solution was stirred at 20 °C for 4 days and then filtered through glass fibre paper and concentrated to 1 cm^3 under reduced pressure at 20 °C. Chromatography of the solution on silica (100 g) in benzene–ether (19:1) gave the cycloheptatriene **4a** (50 mg, 13%) followed by a mixture of cycloheptatriene **4a**, trimethyl hemimellitate and norbornadiene **3a** (33 mg, 9%). Continued elution of the column gave norbornadiene **3a** (140 mg, 37%) and recovered starting material **6a** (85 mg, 22%).

3-Deuterio-7-isopropylidene-2-methoxycarbonylnorbornadiene.—A solution of dimethylfulvene (2.27 g, 21.4 mmol) and methyl 3-deuteriopropiolate[26] (3.6 g, 42.8 mmol) in dry toluene (15 cm^3) was heated under reflux (48 h). The toluene was evaporated under reduced pressure at 100 °C and methanol (8 cm^3) added to the residue to give a solution which was set aside at −25 °C (18 h). The precipitate was filtered off and the filtrate evaporated. The residue was distilled (bulb-to-bulb) to give the title compound (0.94 g, 23%), bath-temp. 70 °C/0.2 mmHg. The product was identical with the fully protonated material[6] (b.p. and ^1H NMR spectrum) except that the resonance at δ 7.68 integrated for 0.38 H. [7-Isopropylidene-2-methoxycarbonylnorbornadiene, δ 7.68 (1 H, dd, *J* 4 and 2, 3-H), 7.0 (1 H, ddd, *J* 5, 4 and 2, 6-H), 6.83 (1 H, ddd, *J* 5, 4 and 2, 5-H), 4.4 (1 H, m, 1-H), 4.2 (1 H, m, 4-H), 3.72 (3 H, s, CO_2Me), 1.46 (3 H, s, Me) and 1.44 (3 H, s, Me)].

5-Deuterio-3-isopropylidene-1-methoxycarbonylquadricyclane.—A solution of 3-deuterio-7-isopropylidene-2-methoxycarbonylnorbornadiene (0.93 g, 4.87 mmol) in dry, degassed ether (250 cm^3) was photolysed by internal irradiation through Pyrex (Hanovia 125W, Hg-medium pressure water cooled lamp) (15.5 h). The ether was evaporated and the residue distilled (bulb-to-bulb) to give the title compound, b.p. 102 °C/0.2 mmHg which crystallised with time at −2 °C, m.p. 47–48 °C (from ether–pentane). The product was identical with the 5-protio compound (b.p. and ^1H NMR spectrum) except that the resonance at δ 1.9–2.6 integrated for *ca.* 4.4 H [3-Isopropylidene-1-methoxycarbonylquadricyclane, δ 3.65 (3 H, s, CO_2Me), 1.9–2.6 (5 H, m, 2-, 4-, 5-, 6- and 7-H) and 1.9 (6 H, s, Me)].

5-Deuterio-1-methoxycarbonylquadricyclan-3-one.—Ozone was bubbled through a stirred solution of 5-deuterio-3-isopropylidene-1-methoxycarbonylquadricyclane (0.725 g, 3.8 mmol) in dry dichloromethane (20 cm^3) at −30 °C (10 min). Acetic acid (2.86 cm^3) and then zinc dust (0.77 g) in portions and then water (0.4 cm^3) were added at −30 °C. The mixture was stirred at −30 °C (0.5 h) and then allowed to warm up to 20 °C (over 0.5 h). The mixture was filtered and the residue washed with ether. The combined filtrate and washings were washed with water (2 × 2 cm^3) and then with saturated aqueous sodium carbonate until the washings were neutral, and then with a little more water (1 × cm^3). The ethereal layer was dried ($MgSO_4$) and the evaporated solution chromatographed on silica (10 g) in benzene–ether (19:1) to give the title compound (0.55 g, 87%) as a colourless oil, identical with the 5-protio-analogue [TLC in benzene–ether (19:1) and ^1H NMR spectrum] except that the signal at δ 2.73 integrated for *ca.* 0.38 H [1-methoxycarbonylquadricyclan-3-one, δ 3.72 (3 H, s, CO_2Me), 2.8 (1 H, ddd, *J* 5, 2.5 and 1.5, 7-H), 2.73 (1 H, td, *J* 5 and 1.5, 5-H), 2.40 (1 H, td, *J* 5 and 2.5, 6-H), 1.96 (1 H, dd, *J* 5 and 1.5, 2-H) and 1.4 (1 H, td, *J* 5 and 1.5, 4-H)].

3,3-Dimethoxy-1-methoxycarbonylquadricyclane **6c**. Trimethylsilyl triflate (160 mg, 0.7 mmol) in dry dichloromethane (2 cm^3) was cooled to −78 °C under nitrogen. Methoxytrimethylsilane (7.6 g, 73 mmol) was added, *via* a syringe, to the stirred solution. 1-Methoxycarbonylquadricyclan-3-one (3 g, 18 mmol) in dichloromethane (3 cm^3) was added to the mixture which was then stirred at −78 °C (0.5 h) and then allowed to warm up to −30 °C over an hour; it was then maintained at −35 to −30 °C (1.5 h). Pyridine (1.5 cm^3) was added to the reaction mixture at −30 °C and the mixture allowed to warm up to 20 °C. The mixture was diluted with dichloromethane, washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. Chromatography of the product on silica (100 g) in benzene–ether (7:3) gave the title compound **6c** (3.53 g, 93%) as a colourless oil (Found: M^+, 210.089. $C_{11}H_{14}O_4$ requires *M*, 210.089), ν_{max}(film)/cm^{-1} 1720; λ_{max}/nm 230 (ε 1350); δ 3.66 (3 H, s, CO_2Me), 3.46 (6 H, s, 2 × OMe), 2.53 (1 H, ddd, *J* 6, 3 and 1.5, 2-H), 2.34 (1 H, dd, *J* 6 and 2, 7-H), 2.22 (1 H, ddd, *J* 5, 5.5 and 1.5, 5-H), 1.9 (1 H, ddd, *J* 5.5, 4.5 and 3, 4-H) and 1.66 (1 H, ddd, *J* 4.5, 5 and 2, 6-H); *m/z* 179, 163, 151, 136, 105, 91, 77, 75, 74 and 59 (21.4, 7.9, 17.3, 18.1, 83.6, 20.3, 39.0, 8.2, 28.3 and 100.0%).

5-Deuterio-3,3-dimethoxy-1-methoxycarbonylquadricyclane **6d**.—This compound was prepared as described above for **6c** except that stirring at −78 °C was continued for 1 h and then at −30 °C (5 h) before addition of pyridine. The yield was 72% and the product showed a signal at δ 2.22 for 0.38 H.

7,7-Dimethoxy-2-methoxycarbonylnorbornadiene **3c**.—Palladised charcoal (10%; 130 mg) was added to a solution of the quadricyclane **6c** (130 mg, 0.62 mmol) in ethyl acetate (20 cm^3) under nitrogen. The mixture was stirred at 20 °C (87 h) filtered through a pad of Celite and evaporated at 20 °C. Chromatography of the product on silica (35 g) in benzene–ether (9:1) gave dimethyl phthalate (9 mg, 7%). Continued elution of the column gave **3c** (82.5 mg, 63%) as colourless crystals, m.p. 79–80 °C (from ether) (Found: C, 63.05; H, 6.95. $C_{11}H_{14}O_4$ requires C, 62.9; H, 6.7%); ν_{max}(Nujol)/cm^{-1} 1695 and 1600; λ_{max}/nm 226 and 268 (ε 3560 and 1600); δ(C_6D_6) 7.43 (1 H, dd, *J* 4 and 1.5, 3-H), 6.11 (1 H, ddd, *J* 6, 4 and 1.5, 5-H), 6.34 (1 H, ddd, *J* 6, 4 and 1.5, 6-H), 4.21 (1 H, dt, *J* 4 and 1.5 with further coupling, 1-H), 3.47 (1 H, m, partially hidden, 4-H), 3.43 (3 H, s, CO_2Me), 2.94 (3 H, s, OMe) and 2.89 (3 H, s, OMe); *m/z* 179, 163, 151, 136, 105, 91, 77, 75, 74 and 59 (26.6, 10.4, 22.0, 12.8, 100.0, 24.5, 76.6, 11.1, 36.6 and 98.4%).

3-Deuterio-7,7-dimethoxy-2-methoxycarbonylnorbornadiene **3d**.—This compound was prepared as described above for **3c** except that stirring with Pd/C was continued for 168 h. The product **3d** was obtained in 65% yield; the δ 7.43 signal integrated for 0.38 H.

Thermolysis of Norbornadiene **3c**.—A solution of norbornadiene **3c** (20 mg, 0.095 mmol) in deuteriobenzene (0.3 cm^3) was heated at 55.0 ± 0.5 °C (constant temperature water bath). NMR spectra recorded after 0.5, 1.25, 2, 2.75 and 4 h enabled a rate constant to be determined. After 9 h 12 min at 55 °C the contents of the tube were evaporated and chromatographed on basic alumina (grade 1) (20 g) in benzene–petroleum (9:1) to give 7,7-dimethoxy-2-methoxycarbonylcyclohepta-1,3,5-triene **4c** (19 mg, 95%) as a colourless oil (Found: M^+, 210.089.

$C_{11}H_{14}O_4$ requires *M*, 210.089), ν_{max}(film)/cm^{-1} 1720; λ_{max}/nm 227 and 260 (ε 7900 and 4700); δ 7.46 (1 H, d, *J* 12, 3-H), 6.94 (1 H, s, with fine splitting, 1-H), 6.49 (1 H, dd, *J* 12 and 6.5, 4-H), 6.1 (1 H, dd, *J* 6.5 and 10.5, 5-H), 5.59 (1 H, d, *J* 10.5, with fine splitting, 6-H), 3.36 (3 H, s, CO_2Me) and 3.0 (6 H, s, 2 × OMe); *m*/*z* 179, 164, 135, 105 and 77 (12.1, 18.8, 9.8, 100.0 and 62.4%).

Chromatography of the cycloheptatrienone acetal **4c** (20 mg, 0.095 mmol) on silica (20 g) in benzene–ether (9:1) gave 3-*methoxycarbonyltropone* (8 mg, 51%) as pale yellow crystals, m.p. 63–64 °C (from ether) (Found: C, 65.5; H, 4.65. $C_9H_8O_5$ requires C, 65.9; H, 4.9%); ν_{max}(Nujol)/cm^{-1} 1720 and 1635; λ_{max}/nm 230 and 315 (ε 9500 and 6600); δ(C_6D_6) 7.79 (1 H, dd, *J* 2 and 1.5, 2-H), *ca.* 7.2 (1 H, m, partially obscured, 4-H), 6.7 (1 H, m), 6.1 (2 H, m) and 3.27 (3 H, s, CO_2Me); *m*/*z* 164, 105, 86, 84 and 77 (33.7, 100.0, 22.7, 38.9 and 37.1%).

Thermolysis of 3-*Deuterio*-7,7-*dimethoxy*-2-*methoxycarbonylnorbornadiene* **3d**.—A solution of 3-deuterio-7,7-dimethoxy-2-methoxycarbonylnorbornadiene (25 mg, 0.12 mmol) in deuteriobenzene (0.3 cm^3) was heated at 60.0 ± 0.5 °C (6.25 h) (constant temperature water bath). The solution was evaporated and the residue chromatographed on basic alumina (grade 1; 20 g), in benzene–light petroleum (7:3) to give 3-deuterio-7,7-dimethoxy-2-methoxycarbonylcycloheptatriene **4d** (20 mg, 80%) identical with the fully protonated material [TLC in benzene–light petroleum (7:3) and ^{1}H NMR] except that the resonance at δ 7.46 integrated for 0.38 H.

3,3-*Dimethoxyquadricyclane*-1-*carboxylic Acid.* A solution of sodium hydroxide in water–ethanol (1:1; 7.15 cm^3, 14.3 mmol) was added to the quadricyclane **6c** (0.6 g, 2.86 mmol) and the solution was stirred at 20 °C (14 h). The pH of the solution was lowered to 5 with cold dilute hydrochloric acid and the mixture extracted with ethyl acetate; more acid was added and the pH gradually reduced to 1, extracting with ethyl acetate between each addition. The combined extracts were dried ($MgSO_4$) and concentrated. The title compound (447 mg, 80%) crystallised from the solution, m.p. 147–148 °C (from acetone) (Found: C, 60.95; H, 6.3. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%), ν_{max}(Nujol)/cm^{-1} 2600br and 1665br; λ_{max}/nm 220 (ε 2950); δ 7.77 (1 H, br s, CO_2H), 3.47 (6 H, s, 2 × OMe), 2.65 (1 H, m, 2-H), 2.43 (1 H, dd, *J* 6 and 2, 7-H), 2.25 (1 H, ddd, *J* 5, 5.5 and 1.5, 5-H), 1.94 (1 H, ddd, *J* 5.5, 4.5 and 3, 4-H) and 1.7 (1 H, ddd, *J* 4.5, 5 and 2, 6-H); *m*/*z* 105, 91, 77, 74, 59 and 52 (27.8, 13.4, 38.3, 21.4, 100.0 and 20.4%).

N,N-*Dimethyl*-3,3-*dimethoxyquadricyclane*-1-*carboxamide* **6e**.—A solution of 3,3-dimethoxyquadricyclane-1-carboxylic and (1.2 g, 6.1 mmol) in chloroform (100 cm^3) was cooled to 0 °C and dry triethylamine (0.89 cm^3, 6.4 mmol) added in one portion by syringe. The mixture was stirred for 5 min and then ethyl chloroformate (0.61 cm^3, 6.4 mmol) was added in one portion. After it had been stirred for 30 min dimethylamine was bubbled through the solution for 20 min. The solution was stirred at 0 °C for an additional 30 min after which time the mixture was allowed to warm to 20 °C and stirring continued (16 h). The remaining dimethylamine was allowed to evaporate by stirring in an open flask at 30 °C. The chloroform solution was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated. Chromatography of the product on silica (40 g) in ethyl acetate gave the title compound **6e** (0.99 g, 72%) as a colourless oil (Found: M$^+$, 223.118. $C_{12}H_{17}NO_3$ requires *M*, 223.121); ν_{max}(film)/cm^{-1} 2815w and 1630; δ 3.47 (6 H, s, 2 × OMe), 3.01 (6 H, br s, 2 × NMe), 2.46 (1 H, ddd, *J* 6, 3, 1.5, 2-H), 2.10 (1 H, ddd, *J* 5, 5.5 and 1.5, 5-H), 1.97 (1 H, dd, *J* 6 and 2, 7-H), 1.90 (1 H, ddd, *J* 4.5, 5.5 and 3, 4-H) and 1.60 (1 H, ddd, *J* 4.5, 5 and 2, 6-H); *m*/*z* 163, 118, 105, 77, 72, 59 and 51 (15.8, 74.9, 92.5, 100.0, 83.8, 77.9 and 53.0%).

N,N-*Dimethyl*-7,7-*dimethoxynorbornadiene*-2-*carboxamide* **3e**. Palladium acetate (100 mg, 0.45 mmol) was added to a solution of the carboxamide **6e** (1.0 g, 4.5 mmol) in deuteriobenzene (5 cm^3) under nitrogen. The solution was stirred at 20 °C (24 h), concentrated to *ca.* 1 cm^3 under reduced pressure at 20 °C and chromatographed on silica (30 g) in ethyl acetate to give the *title compound* **3e** (0.665 g, 67%) as colourless crystals, m.p. 79–79.5 °C (from ether–pentane) (Found: C, 64.45; H, 7.75; N, 6.1. $C_{12}H_{17}NO_3$ requires C, 64.6; H, 7.6; N, 6.3%); ν_{max}(film)/cm^{-1} 1630, 1595 and 1560; λ_{max}/nm 225 and 265sh (ε 3700 and 1930); δ 6.8 (1 H, ddd, *J* 6, 9 and 2, 5-H) 6.73 (1 H, dd, *J* 5 and 2, 3-H), 6.66 (1 H, ddd, *J* 6.9 and 2, 6-H), 3.95 (1 H, m, 1-H), 3.83 (1 H, m, 4-H), 3.2 (3 H, s, OMe), 3.14 (3 H, s, OMe) and 3.05 (6 H, br s, 2 × NMe); *m*/*z* 164, 163, 133, 118, 105, 77, 72 and 59 (26.4, 24.9, 16.6, 100.0, 54.2, 49.5, 40.0 and 43.3%).

Thermolysis of N,N-*Dimethyl*-7,7-*dimethoxynorbornadiene*-2-*carboxamide* **3e**.—A solution of the carboxamide **3e** (100 mg, 0.45 mmol), in deuteriobenzene (0.5 cm^3) was heated at 100 °C (3 h). Analysis by highfield NMR indicated that the product consisted of *N*,*N*-dimethyl-7,7-dimethoxycyclohepta-1,3,5-triene-1-carboxamide **5e**, *N*,*N*-dimethyl-7,7-dimethoxycyclohepta-1,3,5-triene-2-carboxamide **4e**, and *N*,*N*-dimethylbenzamide in the ratio 9:9:2; δ(400 MHz, C_6D_6) 7.3 (2 H, m), 7.08 (3 H, m) and 3.11 (6 H, s) (*N*,*N*-dimethylbenzamide), 6.77 (1 H, d, *J* 11 with fine coupling to 1-H and 6-H, 3-H), 6.45 (1 H, dd, *J* 11 and 6.5, with fine coupling to 1-H, 4-H), 6.13 (1 H, dd, *J* 11 and 6.5, 5-H), 5.73 (1 H, d, *J*, with fine coupling to 4-H and 3-H, 1-H), 5.68 (1 H, dd, *J* 11 and 2 with fine coupling to 3-H, 6-H), 3.02 (6 H, s, 2 × OMe), 2.65 (3 H, br s, NMe) and 2.27 (3 H, br s, NMe) [*N*,*N*-dimethyl-7,7-dimethoxycyclohepta-1,3,5-triene-2-carboxamide **4e**], 6.42 (1 H, dd, *J* 10.5 and 6, with fine coupling to 6-H, 4-H), 6.36 (1 H, dd, *J* 10.5 and 6, with fine coupling to 5-H and 6-H, 3-H), 6.28 (1 H, d, *J* 6.5, 2-H), 6.2 (1 H, dd, *J* 6 and 10.5, with fine coupling to 3-H and 2-H, 5-H), 5.58 (1 H, d, *J* 10.5, with fine coupling to 3-H, 6-H), 3.2 (3 H, br s, OMe), 3.15 (3 H, br s, OMe), 2.75 (3 H, s, NMe) and 2.43 (3 H, s, NMe) (*N*,*N*-dimethyl-7,7-dimethoxycyclohepta-1,3,5-triene-1-carbox amide **5e**). The contents of the tube were evaporated and chromatographed by preparative TLC on alumina (4 plates) [4 elutions in benzene–ether (7:3)] to give, *N*,*N*-dimethylbenzamide (5 mg) as the least polar fraction. This was followed by a mixture of *N*,*N*-dimethylbenzamide and cycloheptatriene **5e** (15 mg) and then N,N-*dimethyl*-7,7-*dimethoxycyclohepta*-1,3,5-*triene*-1-*carboxamide* **5e** (5 mg) (Found: M$^+$, 223.118. $C_{12}H_{17}NO_3$ requires *M*, 223.121), ν_{max}(film)/cm^{-1} 1630; λ_{max}/nm 222 and 266 (ε 1680 and 1690); δ(C_6D_6) 6.40–6.05 (4 H, m, 2-H, 3-H, 4-H and 5-H), 5.55 (1 H, d, *J* 10, 6-H), 3.2 (6 H, s, 2 × OMe), 2.75 (3 H, s, NMe) and 2.38 (3 H, s, NMe); *m*/*z* 192, 151, 133, 118, 105, 91, 90 and 77 (43.3, 42.3, 29.1, 66.5, 100.0, 28.7, 29.0 and 87.8%).

1-*Hydroxymethyl*-3,3-*dimethoxyquadricyclane.*—3,3-Dimethoxy-1-methoxycarbonylquadricyclane **6a** (1.94 g, 9.2 mmol) in dry ether (5 cm^3) was added dropwise over 10 min to a stirred suspension of lithium aluminium hydride (0.26 g, 6.9 mmol) in ether (45 cm^3) at 0 °C under nitrogen. After 1.5 h, the ice-bath was removed and pulverised sodium sulfate decahydrate (15 g) added; stirring was continued at 20 °C (3.25 h). The mixture was dried ($MgSO_4$) and evaporated. Chromotography on silica (40 g) eluting with ethyl acetate gave the *title compound* (1.4 g, 84%) as a colourless oil (Found: M$^+$, 182.091. $C_{10}H_{14}O_3$ requires *M*, 182.094); ν_{max}(film)/cm^{-1} 3400br; δ 3.73 (2 H, br m, CH_2), 3.48 (6 H, s, 2 × OMe), 2.1 (1 H, br s, OH), 1.9 (3 H, m) and 1.54 (2 H, m); m/z 151, 91, 79, 77 and 59 (25.8, 47.3, 26.8, 34.0 and 100.0%).

2-Hydroxymethyl-7,7-dimethoxynorbornadiene.—Palladised charcoal (10%; 1.3 g) was added to a solution of 1-hydroxymethyl-3,3-dimethoxyquadricyclane (1.3 g, 7.1 mmol) in ethyl acetate (35 cm^3). The mixture was heated under reflux and stirred (1.25 h). The cooled mixture was filtered through glass fibre paper and evaporated to dryness at 20 °C. Chromatography on silica (40 g) in ethyl acetate–light petroleum (3:1) gave the *title compound* (1.17 g, 90%) (Found: M^+, 182.093. $C_{10}H_{14}O_3$ requires M, 182.094); ν_{max}(film)/cm^{-1} 3400br and 1560; δ 6.68 (2 H, t, J 2.5, 5-H and 6-H), 6.34 (1 H, m, 3-H), 4.29 (2 H, br s, CH_2), 3.63 (2 H, m, 1-H and 4-H), 3.14 (3 H, s, OMe), 3.12 (3 H, s, OMe) and 1.75 (1 H, br s, OH); m/z 151, 91, 77, 74 and 59 (22.9, 35.7, 24.0, 28.7 and 100.0).

2-Formyl-7,7-dimethoxynorbornadiene **3f**.—A solution of oxalyl chloride (134 mg, 1.06 mmol) in dry dichloromethane (1 cm^3) was stirred at −50 °C under nitrogen and dry dimethyl sulfoxide (165 mg, 2.11 mmol) in dichloromethane (1 cm^3) was added dropwise to it, *via* a syringe over 5 min, and stirring continued for an additional 10 min. 2-Hydroxymethyl-7,7-dimethoxynorbornadiene (175 mg, 0.96 mmol) in dichloromethane (1 cm^3) was added dropwise to the mixture and stirring continued (15 min). Dry triethylamine (0.66 cm^3, 4.8 mmol) was then added to the mixture and stirring continued for 5 min. The cooling bath was then removed and the mixture allowed to warm to 20 °C. Water (2 cm^3) was then added to it and stirring continued (10 min). The mixture was extracted with ether (25 cm^3), and the extracts washed with a little water (5 cm^3), dried ($MgSO_4$) and evaporated. Chromatography of the residue on a short silica column (0.5 in, 10 g) in benzene–ether (9:1) gave the *title compound* **3f** (140 mg, 80%) as a colourless oil (Found: M^+, 180.079. $C_{10}H_{12}O_3$ requires M, 180.079); ν_{max}(film)/cm^{-1} 1675 and 1590; λ_{max}/nm 282 and 240 (ε 1400 and 2900); $\delta(CCl_4)$ 9.59 (1 H, s, CHO), 7.4 (1 H, dd, J 5 and 2, 3-H), 6.65 (1 H, ddd, J 7, 4 and 2, 5-H), 6.45 (1 H, ddd, J 7, 4 and 2, 6-H), 4.04 (1 H, m, 1-H), 3.76 (1 H, m, 4-H), 3.05 (3 H, s, OMe) and 3.02 (3 H, s, OMe); m/z 180, 149, 136, 133, 121, 106, 105, 104, 92, 91 and 77 (14.7, 23.5, 14.9, 31.3, 18.1, 19.3, 76.2, 15.9, 15.3, 41.8 and 100.0%).

Thermolysis of 2-Formyl-7,7-dimethoxynorbornadiene.—(a) A solution of the norbornadiene **3f** (30 mg) in deuteriobenzene (0.3 cm^3) was heated at 100.0 ± 0.2 °C in the usual manner for 15 min, to give *1,1-dimethoxy-2-oxabicyclo*[4.3.0]*nona-3,5,7-triene* **9** as the major product, δ(400 MHz, C_6D_6) 6.05 (1 H, dt, J 5 and 1, 3-H), 5.96 (1 H, ddt, J 9.5, 2.5 and 1, 5-H), 5.51 (1 H, dddd, J 9.5, 6, 1 and 2, 6-H), 5.73 (1 H, dddd, J 1, 6, 9.5 and 4, 7-H), 5.88 (1 H, ddt, J 9.5, 3.5 and 1, 8-H), 4.18 (1 H, ddddd, J 5, 2.5, 2, 4 and 3.5, 9-H), 3.15 (3 H, s, OMe) and 3.09 (3 H, s, OMe).

(b) 2-Formyl-7,7-dimethoxynorbornadiene was dissolved in degassed cyclohexane and transferred to a silica UV cell which had previously been subjected to the usual basic wash. The cell was sealed *in vacuo* (three freeze–thaw cycles) and heated by total immersion in a constant temperature water-bath at 60.0 ± 0.5 °C for 15 min. A new absorption bond had appeared in the UV spectrum at λ 325 nm. The seal was broken and a solution of 4-phenyl-1,2,4-triazole-3,5-dione in benzene was added; the peak at λ 325 nm disappeared instantaneously.

(c) A solution of freshly prepared 2-formyl-7,7-dimethoxynorbornadiene (70 mg, 0.39 mmol) in deuteriobenzene (0.5 cm^3) was heated in an NMR tube at 65 °C for 1 h. Trifluoroacetic acid (15 mg, 0.13 mmol) was added and after 1 min at 20 °C the solution was diluted with benzene and neutralised with solid sodium hydrogen carbonate. The solution was evaporated and the residue chromatographed on silica (20 g) in benzene–ether (5:1) to give the trifluoroacetate of methyl 2-(hydroxymethyl)benzoate (11 mg, 12%), $\nu_{max}(CCl_4)$/cm^{-1} 1790 and 1725; δ 8.05 (1 H, m), 7.5 (3 H, m), 5.8 (2 H, s) and 3.9 (3 H, s). Continued elution of the column gave 2-methoxycarbonylbenzaldehyde (4 mg, 6%); δ(90 MHz) 10.7 (1 H, s, CHO), 7.85 (4 H, m, aromatic) and 4.0 (3 H, s, CO_2Me); and phthalide (19 mg, 37%) identical with authentic material by NMR, TLC and m.p. comparison.

7,7-Dimethoxy-2-vinylnorbornadiene **3g**.—Butyllithium (hexane solution; 1.1 cm^3, 1.64 mmol) was added to a solution of methyltriphenylphosphonium bromide (644 mg, 1.8 mmol) in dry ether (20 cm^3) at 0 °C under nitrogen. The solution became intensely yellow and was stirred (2 h). 2-Formyl-7,7-dimethoxynorbornadiene (150 mg, 0.82 mmol) in ether (5 cm^3) was added to it and stirring continued (0.75 h). Water (10 cm^3) was added to the mixture and the product was extracted into ether. The ethereal layer was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the product on silica (30 g) in benzene–ether (49:1) gave the title compound **3g** (27 mg, 19%) as a colourless oil (Found: M^+, 178.098. $C_{11}H_{14}O_2$ requires M, 178.099); ν_{max}(film)/cm^{-1} 1620w; δ 6.65 (2 H, m, 5-H and 6-H), 6.53 (1 H, dd, J 16 and 10, =CH), 6.37 (1 H, m, 3-H), 5.2 (1 H, d, J 16 with further coupling, =CH_{cis}), 5.02 (1 H, dd, J 10 and 1, =CH_{trans}), 3.72 (1 H, m), 3.55 (1 H, m) (1-H and 4-H) and 3.11 (6 H, s, 2 × OMe); m/z 147, 121, 104, 103, 91, 77, 74 and 59 (18.1, 28.5, 29.9, 21.6, 24.8, 21.1, 22.8 and 100.0%).

Thermolysis of the Norbornadiene **3g**.—A solution of the norbornadiene **3g** (18 mg) in deuteriobenzene (0.3 cm^3) was heated in the usual manner at 50 °C (0.5 h), at 70 °C (0.5 h) and at 90 °C (0.5 h). ^1H NMR monitoring indicated that there was no reaction. The thermolysis was continued at 100 °C (0.5 h) and at 110 °C (0.5, 2 and 4.5 h). Since the reaction was progressing only slowly the temperature was raised to 120 °C and after heating periods of 2.75, 4.75, 6.75 and 17 h the reaction was complete. The major product was identified as styrene by comparison with an NMR spectrum of authentic material in deuteriobenzene. Chromatography of the product on silica (20 g) in benzene–ether (19:1) gave two other unidentified products.

1,2-Bis(trimethylsilyloxy)ethane.—A solution of ethylene glycol (3 g, 48 mmol) in dry dichloromethane (50 cm^2) was stirred under nitrogen. *N,N'*-Bis(trimethylsilyl)urea (9.87 g, 48 mmol) was added in one portion to the mixture which was then heated under reflux for 5 h. The cooled mixture was filtered and evaporated. Bulb-to-bulb distillation gave the title compound (7.67 g, 78%) as a colourless liquid (bath temperature 80 °C/0.35 mmHg) identical with authentic material (NMR and b.p.).

1-Methoxycarbonylquadricyclan-3-one Ethylene Acetal **6h**.—Trimethylsilyl triflate (5 mg, 0.024 mmol) in dry dichloromethane (5 cm^3) was cooled to −78 °C under nitrogen and 1,2-bis(trimethylsilyloxy)ethane (0.5 g, 2.44 mmol) was added to it. 1-Methoxycarbonylquadricyclan-3-one (200 mg, 1.22 mmol) in dichloromethane (2 cm^3) was then added to the mixture which was allowed to stand at −78 °C (3 h), at −40 °C (2 h) and at −20 °C (15 h). Dry pyridine (0.2 cm^3) was added at −20 °C to the mixture which was then allowed to warm to 20 °C. The mixture was poured into saturated aqueous sodium hydrogen carbonate and extracted with ether. The ether layer was dried (K_2CO_3) and evaporated. Chromatography of the product on silica (30 g), in benzene–ether (9:1) gave the title compound **6h** (0.145 g, 57%) as colourless crystals, m.p. 113–114 °C (from benzene) (Found: C, 63.5; H, 6.0. $C_{11}H_{12}O_4$ requires C, 63.5; H, 5.8%); ν_{max}(Nujol)/cm^{-1} 1710; λ_{max}/nm 230 (ε 2800); δ 4.1 (4 H, s, 2 × OCH_2), 3.68 (3 H, s, CO_2Me), 2.56 (1 H, ddd, J 6, 3 and 1.5, 2-H), 2.27 (1 H, ddd, J 5, 5.5 and 1.5, 5-H), 2.08 (1 H, dd, J 6 and 2, 7-H), 1.93 (1 H, ddd, J 5.5, 4.5 and 3, 4-H) and 1.4 (1 H, ddd, *J* 4.5, 5 and 2, 6-H); *m/z* 207, 163, 149, 136, 105 and 77 (12.7, 10.8, 22.1, 11.6, 100.0 and 46.2%).

Ring-opening of the Ethylene Acetal **6h** *with Palladised Charcoal.*—Palladised charcoal (10%) (30 mg) was added to a solution of the ethylene acetal **6h** (30 mg, 0.14 mmol) in ethyl acetate (5 cm^3) and the mixture was stirred at 20 °C (52 h). It was then filtered through a pad of Celite and the filtrate evaporated at 20 °C. The product was chromatographed on basic alumina (20 g) in benzene–light petroleum (4:1) to give *3-methoxycarbonyltropone ethylene acetal* **4h** (6 mg, 21%) as a colourless oil (Found: M^+, 208.072. $C_{11}H_{12}O_4$ requires *M*, 208.074; ν_{max}(film)/cm^{-1} 1720; λ_{max}/nm 263 (ε 8900); $\delta(C_6D_6)$ 7.4 (1 H, d, *J* 11, 4-H), 7.06 (1 H, s, with fine splitting, 2-H), 6.45 (1 H, dd, *J* 7 and 11, 5-H), 6.12 (1 H, dd, *J* 7 and 11, 6-H), 5.79 (1 H, d, *J* 11 with fine splitting, 1-H), 3.42 (4 H, s, 2 × OCH_2) and 3.35 (3 H, s, OMe); *m/z* 163, 149, 136, 133, 106, 105 and 77 (6.9, 11.9, 8.9, 8.0, 7.0, 100.0 and 66.1%). Continued elution of the column gave an aromatic compound (6 mg, 20%) tentatively assigned as 2-hydroxyethylmethyl phthalate; δ 7.64 (4 H, m, ArH), 4.45 (2 H, m, OCH_2), 3.93 (3 H, s, OMe), 3.93 (2 H, m, CH_2OH, hidden) and 2.53 (1 H, m, exch. D_2O, OH); *m/z* 194, 164, 163, 149, 104 and 77 (17.3, 12.8, 100.0, 49.4, 12.9 and 14.8%).

3-*Cyano*-3-*methoxy*-1,5-*bis(methoxycarbonyl)quadricyclane.*—1,5-Bis(methoxycarbonyl)quadricyclan-3-one (0.9 g, 4.05 mmol) in methanol (5 cm^3) was added dropwise to a solution of potassium cyanide (0.32 g, 4.86 mmol) in water (5 cm^3) at 0 °C followed by dropwise addition of dimethyl sulfate (0.47 cm^3, 4.86 mmol). After the mixture had been stirred at 0 °C for 10 min, the cooling bath was removed and the mixture stirred at 20 °C. After 45 min the crystalline precipitate was filtered off and recrystallised from ether–pentane to give *anti*-3-cyano-*syn*-3-methoxy-1,5-bis(methoxycarbonyl)quadricyclane (0.26 g, 25%), identical with authentic material[3b] (NMR and m.p. comparison). The filtrate was extracted with ether (50 cm^3), and the ether extract washed with water (2 × 15 cm^3), dried ($MgSO_4$) and evaporated. Chromatography of the oily residue on silica (60 g) in benzene–ether (4:1) gave *syn*-3-cyano-*anti*-3-methoxy-1,5-bis(methoxycarbonyl)quadricyclane (113 mg, 11%) as colourless crystals, m.p. 104–105 °C (from ether–pentane) (Found: C, 59.3; H, 5.1; N, 5.2. $C_{13}H_{13}NO_5$ requires C, 59.3; H, 4.9; N, 5.3%); ν_{max}(Nujol)/cm^{-1} 2240, 1715 and 1707; δ 3.73 (6 H, s, 2 × CO_2Me), 3.62 (3 H, s, OMe) and 2.68 (4 H, AA′BB′ system, 2-H, 4-H, 6-H and 7-H); *m/z* 232, 204, 163, 77 and 59 (37.2, 65.6, 100.0, 57.8 and 53.0%).

anti-7-*Cyano*-syn-7-*methoxy*-2,3-*bis(methoxycarbonyl)norbornadiene* **16**.—Palladised charcoal (10%; 300 mg) was added to a solution of *anti*-3-cyano-*syn*-3-methoxy-1,5-bis(methoxycarbonyl)quadricyclane (300 mg, 1.14 mmol) in ethyl acetate (15 cm^3) and the mixture was stirred under reflux (5 h). The cooled solution was filtered through glass fibre paper and evaporated. Crystallisation of the residue from ethyl acetate–petroleum gave the title compound **16** (105 mg) identical with authentic material[3b] (m.p. and NMR comparison). Chromatography of the mother liquors on silica (30 g) in ethyl acetate–petroleum (1:4) gave a further quantity (142 mg, 82% total) of the same norbornadiene.

Ring-opening of the 7-epimer proceeded similarly to give, after chromatography on silica in ethyl acetate–light petroleum (1:4), syn-7-*cyano*-anti-7-*methoxy*-2,3-*bis(methoxycarbonyl)-norbornadiene* (*epi*-**16**) (78%) as colourless crystals, m.p. 67–68 °C (from ether–pentane) (Found: C, 59.1; H, 5.2; N, 5.15. $C_{13}H_{13}NO_5$ requires C, 59.3; H, 4.9; N, 5.3%); ν_{max}(Nujol)/cm^{-1} 2235, 1725, 1715 and 1634; δ 6.96 (2 H, t, *J* 2.5, 5-H and 6-H), 4.21 (2 H, t, *J* 2.5 1-H and 4-H), 3.83 (6 H, s, 2 × CO_2Me) and 3.34 (3 H, s, OMe); *m/z* 232, 216, 204, 163, 77 and 59 (25.2, 46.0, 95.3, 100.0, 23.0 and 24.4%).

Thermolysis of the Norbornadiene **16**.—(a) *At* 150 °C. A solution of norbornadiene **16** (95 mg, 0.36 mmol) in deuteriobenzene was heated at 150.0 ± 0.2 °C, in the usual manner (0.5, 1.75, 3, 5.5 h, 8 h 10 min and 12.5 h), the progress of the reaction being followed by ^{1}H NMR spectroscopy. The contents of the tube were evaporated and the residues chromatographed on silica (20 g) in ethyl acetate–light petroleum (1:4) to give dimethyl phthalate (2 mg, 3%) identical with authentic material [NMR and TLC in ethyl acetate–light petroleum (1:4)]. Continued elution of the column gave dimethyl 4-(cyanomethoxymethyl)phthalate **20** (53 mg, 56%), identical with authentic material[3b] (NMR and m.p. comparison). Further elution gave an impure unidentified cycloheptatriene (7 mg, 8%), $\delta(C_6D_6)$ 7.39 (1 H, dd, *J* 1.4 and 2.3), 6.4 (1 H, dd, *J ca.* 1 and 8), 5.2 (1 H, s), 5.06 (1 H, dd, *J* 2.3 and 8), 3.23 (3 H, s), 3.05 (3 H, s) and 2.84 (3 H, s). Continued elution of the column gave 4-cyano-1-methoxy-5,6-bis(methoxycarbonyl)cyclohepta-1,3,5-triene **21** (15 mg, 16%), m.p. 107–110 °C (from ether–pentane) (*cf.* m.p. 107–108 °C[3b]); $\delta(C_6D_6)$ 6.84 (1 H, d, *J* 7.5, 3-H), 4.65 (1 H, d, *J* 7.5, 2-H), 3.6 (3 H, s, OMe), 3.26 (3 H, s, OMe), 2.77 (3 H, s, OMe) and 2.48 (2 H, s, 7-H).

(b) *At* 135 °C. A solution of the norbornadiene **16** (170 mg, 0.65 mmol) in deuteriobenzene (0.7 cm^3) was heated, in the usual manner, at 135.0 ± 0.2 °C (2.75 h). The contents of the tube were evaporated and the residue chromatographed on silica (30 g) in benzene–ether (3:17) to give a mixture of dimethyl 4-(cyanomethoxymethyl)phthalate **20** and cycloheptatriene **22** (30 mg), followed by unchanged starting material (100 mg, 59%). The mixture of aromatic compound **20** and cycloheptatriene **22** products was chromatographed on alumina (30 g) in benzene–light petroleum (4:1) to give *7-cyano-7-methoxy-2,3-bis(methoxycarbonyl)cycloheptatriene* **22** (15 mg, 9%) as a colourless oil (Found: M^+, 263.079. $C_{13}H_{13}NO_5$ requires M^+, 263.079); $\nu_{max}(CCl_4)$/cm^{-1} 1730 and 1620w; λ_{max}/nm 261 (ε 7200); $\delta(C_6D_6)$ 7.76 (1 H, d, *J* 6, 4-H), 6.53 (1 H, d, *J* 1.5, 1-H), 5.82 (1 H, dd, *J* 6 and 10, 5-H), 5.48 (1 H, dd, *J* 10 and 1.5, 6-H), 3.52 (3 H, s, OMe), 3.45 (3 H, s, OMe) and 3.17 (3 H, s, OMe); *m/z* 232, 216, 204, 163, 77 and 59 (36.0, 33.3, 100.0, 96.3, 22.8 and 27.9%). Further elution of the column gave a mixture of the aromatic compound **20** and cycloheptatriene **22** products (2 mg, 1%) followed by dimethyl 4-(cyanomethoxymethyl)phthalate **20** (12 mg, 7%). The latter was identical with authentic material (NMR and m.p. comparison).[3b]

Thermolysis of 7-Cyano-7-methoxy-2,3-bis(methoxycarbonyl)cyclohepta-1,3,5-triene.—A solution of cycloheptatriene **22** (10 mg, 0.04 mmol) in deuteriobenzene (0.3 cm^3) was heated at 149.0 ± 0.2 °C (1 h 40 min). Analysis of the mixture by ^{1}H NMR spectroscopy indicated complete conversion into dimethyl 4-(cyanomethoxymethyl)phthalate **20** and 4-cyano-1-methoxy-5,6-bis(methoxycarbonyl)cyclohepta-1,3,5-triene **21** in the ratio 4:1, respectively.

1-(α-*Cyano*-α-*trimethylsilyloxybenzyl*)-1,3-*dimethylindene* **19**.—Potassium cyanide–18-crown-6 complex[27] (1.3 mg, 0.004 mmol) was added to a solution of (+)-1-benzoyl-1,3-dimethylindene[28] (50 mg, 0.2 mmol) in dry benzene (1 cm^3) and the solution was stirred under nitrogen at 20 °C (20 min). A solution of trimethylsilyl cyanide (30 mg, 0.3 mmol) in dry benzene (1 cm^3) was added to the reaction mixture and stirring was continued (18 h). The product was chromatographed on silica (10 g) in benzene to give a diastereoisomeric mixture (*ca.* 3:1) of the title compound **19** (62 mg, 90%); $\delta(C_6D_6)$ 7.24–6.54 (9 H, m, ArH), 5.9 (major) and 4.7 (1 H, q, *J* 1.5, olefinic), 1.62 and 1.5

(major) (3 H, d, *J* 1.5, Me), 1.55 (major) and 1.4 (3 H, s, Me) and 0.0 (9 H, s, $SiMe_3$).

Hydrolysis of the Indene **19**.—Silver fluoride[29] (10 mg, 0.75 mmol) was added to a solution of a diastereoisomeric mixture (*ca.* 3:1) of the indene **19** (30 mg, 0.086 mmol) in tetrahydrofuran–water (15:1; 2 cm^3). The mixture was protected from light and stirred at 20 °C (20 h). The filtered mixture was diluted with dichloromethane, washed with water (2 × 15 cm^3) and saturated brine (2 × 15 cm^3), dried (Na_2SO_4), and evaporated. Chromatography of the product on silica (10 g) in light petroleum–benzene (2:3) gave colourless crystalline (+)-1-benzoyl-1,3-dimethylindene (20 mg, 94%), $[\alpha]_D^{22}$ +234 (*c* 0.30, in $CHCl_3$) identical with authentic material by NMR and by TLC in light petroleum-benzene (2:3).

Thermolysis of the Indene **19**.—A solution of a diastereoisomeric mixture (*ca.* 3:1) of the indene **19** (33 mg, 0.1 mmol) in deuteriobenzene (0.35 cm^3) was heated at 150.0 ± 0.2 °C (0.5 h). The thermolysis mixture was evaporated and the product dissolved in tetrahydrofuran–water (15:1) (2.5 cm^3). Silver fluoride (12 mg) was added to the solution which was then protected from light and stirred at 20 °C (18 h). The filtered solution was diluted with dichloromethane, washed with water (2 × 15 cm^3) and with saturated brine (2 × 15 cm^3), dried (Na_2SO_4), and evaporated. Chromatography of the residue on silica (15 g) in light petroleum–benzene (4:1 to 2:3) gave first *meso*-1,1′,3,3′-tetramethyl-1,1′-biindenyl (1.6 mg, 6%) identical with authentic material[19a] (NMR comparison). Continued elution of the column gave a mixture of the *meso*- and *racemic*-1,1′,3,3′-tetramethyl-1,1′-biindenyl (1 mg, 4%). The mixture was identical with an authentic mixture[19a] (NMR and TLC comparison). Further elution of the column gave 1-benzoyl-1,3-dimethylindene (18 mg, 73%) ($[\alpha]_D^{22}$ +4.3, *c* 2.34 in $CHCl_3$) as colourless crystals, identical with authentic material[28] [NMR and by TLC in petroleum–benzene (2:3)].

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