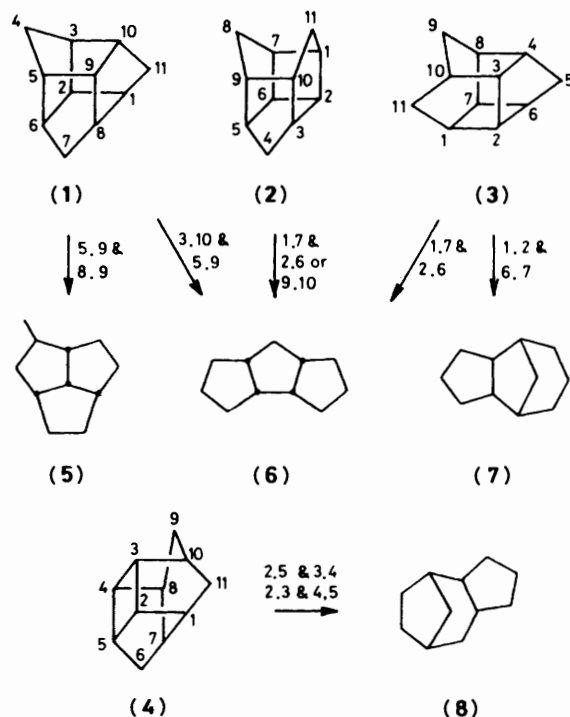


Synthesis and Rearrangements of the Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane [1,2,4-Trishomocubane] Ring System

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Two syntheses of the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane (1,2,4-trishomocubane) system are described. The first synthesis involves intramolecular photochemical [2 + 2]-cycloaddition of the triquinane bisenones (14a—d) to furnish the 1,2,4-trishomocubanediones (15a—d). The second approach is based on a boron trifluoride—diethyl ether-catalysed rearrangement of the readily available Cookson's caged diketones (16a,b) to 1,2,4-trishomocubanediones (17a,b). Thermal and acid-catalysed [2 + 2]-cycloreversions of (15a,c,d) and (17a,b) to linear fused triquinanes (14a,c,d), (20a,b) and tricyclo[5.3.1.0^{2,6}]undecane systems of current synthetic interest are also described.

The C₁₁ derived pentacyclic systems constitute an interesting family.¹ While the total number of possible pentacyclic structures is large, the four trishomocubanes (1)—(4) are the only ones having either one or no cyclobutane ring and formally possessing the homocubane framework.† We became interested in these caged systems since they appeared to us as a veritable repository of five-membered rings from which diverse, convex, quinanes (5)—(8) could be extracted through strategic bond disconnections (see Scheme 1). In this context, the presence of a



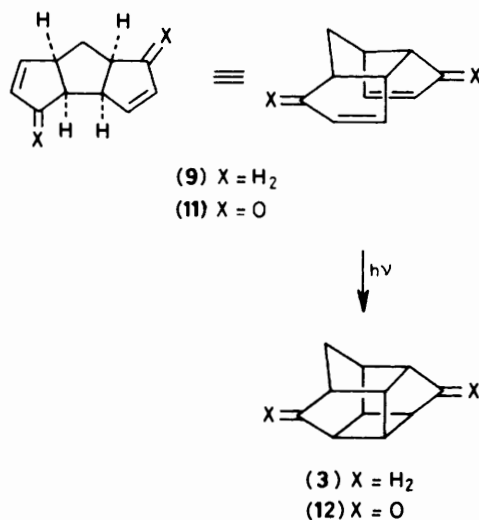
Scheme 1.

cyclobutane ring in (2)—(4) was considered to be particularly advantageous since thermal [2 + 2]-cycloreversion would lead

† These four trishomocubanes (1)—(4) can be differentiated as follows depending on the positions of extra methylene linkages. (1) D₃-Trishomocubane; (2) 1,3,3'-trishomocubane; (3) 1,2,4-trishomocubane; (4) 1,2,3'-trishomocubane.

to uncaging and deliver quinanoid products.² Some of these possibilities are indicated in Scheme 1 and at least one of them, the formation of linear fused triquinanes of the type (6) from the readily available pentacyclic system (2), has been recently established by us as a reaction of considerable synthetic utility.^{2,3} Exploitation of compounds (1)—(4) in meaningful syntheses required that these systems be readily accessible. While many compounds bearing the carbon framework of (1), (2), and (4) have been known for some time⁴ and have received considerable attention in recent years, compound (3) and its derivatives are almost unknown.⁵ Herein, we describe two novel synthetic entries into the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane ring system (3)‡ and also its uncaging through cyclobutane cleavage reactions to provide entry into useful polyquinanes.⁶

In the first approach to the caged system (3), we envisioned an intramolecular $\pi_2^2 + \pi_2^2$ photocycloaddition in a precursor triquinane (9) as the key step (see Scheme 2). Since the

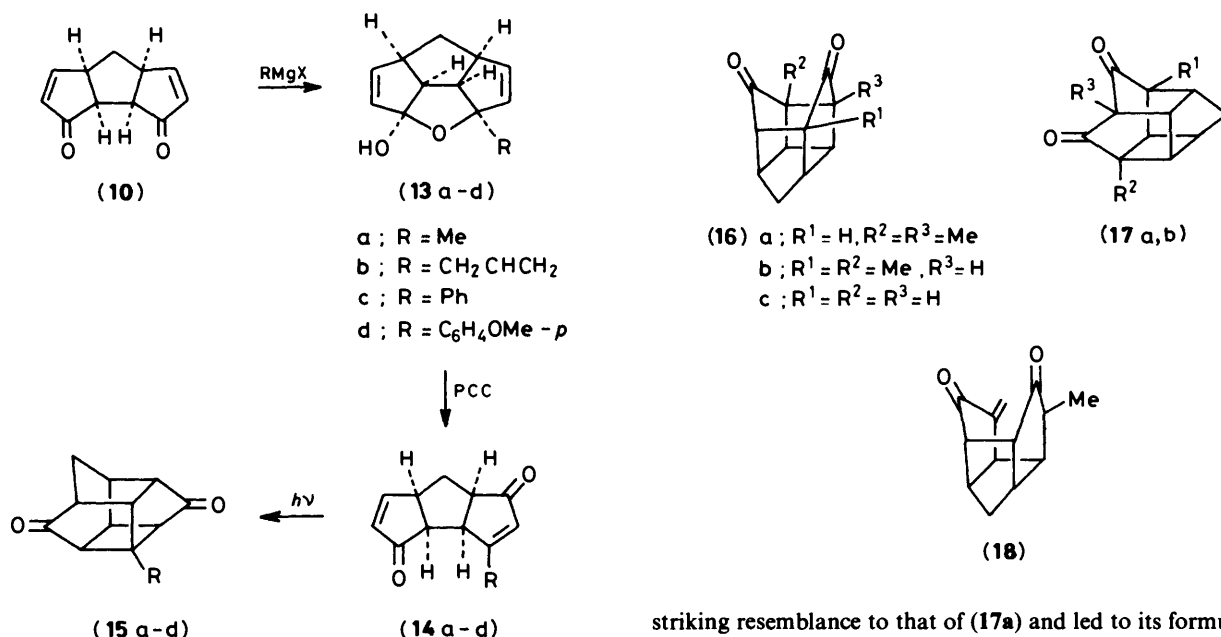


Scheme 2.

symmetrical *cis*, *syn*, *cis*-bis-enone (10) is available readily and in quantity, it seemed to be a suitable starting material for the

‡ I.U.P.A.C. name for this system: 1,3,6-methenocyclopenta[*c,d*]-pentalene. However, in this paper we have used the more familiar von Baeyer system of nomenclature.

projected synthesis.^{2a} Transposition of one of the enone moieties in compound (10) was expected to furnish the precursor (11) of the trishomocubanedione (12). Towards this end, several methodologies for enone transposition were explored. However, all of them, including the usually reliable Wharton reaction⁷ proved unsuccessful. Recourse was then taken to alkylative enone transposition strategy and was implemented as follows. Controlled addition of appropriate Grignard reagents (1–1.2 molar excess) to the dione (10) resulted in the formation of the intermediate hemiacetals (13a–d), which were readily identified by the characteristic carbon signals at δ ca. 120 and δ ca. 100 due to O–C–OH and C–O type functionalities, respectively, in their ¹³C n.m.r. spectra. Oxidation of (13a–d) with pyridinium chlorochromate furnished the required transposed bis-enones (14a–d) (Scheme 3). The structures of (14a–d) were deduced on the basis of



Scheme 3.

unambiguous ¹H and ¹³C n.m.r. spectral evidence summarised in the Experimental section. In particular, the presence of a quaternary sp² carbon signal at δ 170 due to the β -carbon of the cyclopentenone sub-structure proved decisive.

The four desired transposed bis-enones (14a–d) having been obtained, the stage was set for the study of their intramolecular photocycloaddition. Exposure of an ethyl acetate solution of each of the bis-enones (14a–d) to either a 450 W u.v. lamp or sunlight, through a Pyrex filter, resulted in a facile intramolecular $\pi_2 + \pi_2$ cage cyclisation. The photolysis with the u.v. lamp was complete within 1 h and nearly quantitative yields of the pentacyclic diones (15a–d) were realised. Photolysis in sunlight, quite expectedly, required longer reaction times but preparatively was as efficient. The (14a–d) to (15a–d) photocycloaddition also exhibited high quantum efficiency. The quantum yields in the four cases, measured using ferrioxalate actinometry, were 0.80, 0.82, 0.92, and 0.48 respectively. The structures of pentacyclic diones (15a–d) rest secured on their spectral data and further confirmation was derived through single crystal X-ray diffraction studies on (15a).⁸

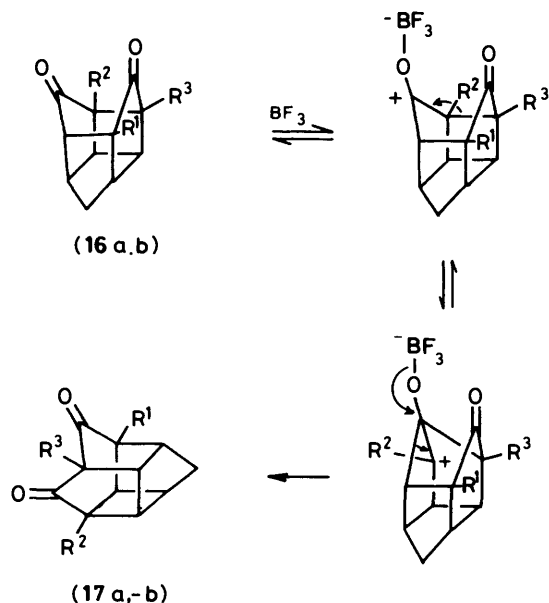
Our second approach to the trishomocubane system (3),

though somewhat fortuitous, was preparatively quite effective. When a benzene solution of the *sym*-dimethyl derivative of Cookson's caged dione (16a) was refluxed with BF₃–Et₂O, two products (2:1), readily separable by column chromatography were obtained in 80% yield. The major product, in its ¹H and ¹³C n.m.r. spectra, still exhibited two quaternary carbon atoms at δ 66.9(s) and 55.6(s) and two quaternary methyl groups at δ 1.38 and 1.3 but the symmetry of the starting material was lost. The presence of a rearranged skeleton was thus indicated and (17a) appeared to be the most probable structure. However, an X-ray diffraction study on (17a) was undertaken and its structure fully secured.* The minor product of the rearrangement was readily recognised as the tetracyclic enone (18) on the basis of its spectral characteristics. Like compound (16a), the unsymmetrical dimethyl derivative (16b), on exposure to BF₃–Et₂O rearranged essentially to a single product (17b) in 50% yield. The ¹H and ¹³C n.m.r. spectra of this product bore a

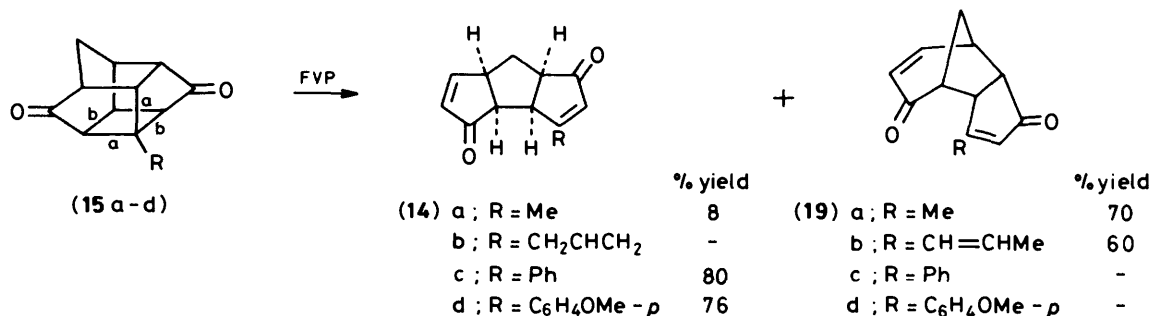
striking resemblance to that of (17a) and led to its formulation as (17b). In this manner, novel trishomocubanediones (17a,b) were obtained in just one step and fair yield from the readily available Cookson's caged dione precursors (16a,b), respectively. We propose that the diones (17a,b) are formed from (16a,b) via a Lewis acid-catalysed ketone–ketone rearrangement depicted in Scheme 4. The role of the methyl substituents in steering the rearrangement is highlighted by the fact that the unsubstituted dione (16c) did not undergo the expected rearrangement.

With the acquisition of six trishomocubane derivatives (15a–d) and (17a,b) attention was turned to the study of their thermal and acid-catalysed rearrangements. Since (15a–d) and (17a,b) have different substitution patterns, in particular the carbonyl disposition, the two series of compounds were expected to behave somewhat differently and this indeed turned out to be the case. On subjecting (15a–d) to thermolysis using the flash vacuum pyrolysis (FVP) technique,^{2a} tricyclic compounds derived through the cyclobutane fragmentation were obtained. Both 'a' and 'b' bond cleavage products were formed, corresponding to the *endo*-tricyclo[5.3.1.0^{2,6}]undecane framework (19) of gymnomitrol-type natural products⁹ and the linear fused *cis*, *syn*, *cis*-tricyclopentanoid framework (14), respectively (Scheme 5). The all-*cis*-triquinane products (14a,c,d) were

* We thank Prof. T. S. Cameron for determining the X-ray crystal structure.^{6b}



Scheme 4.

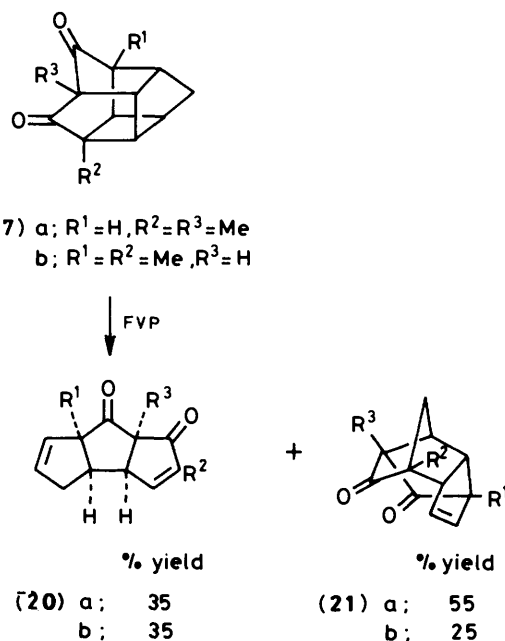


Scheme 5.

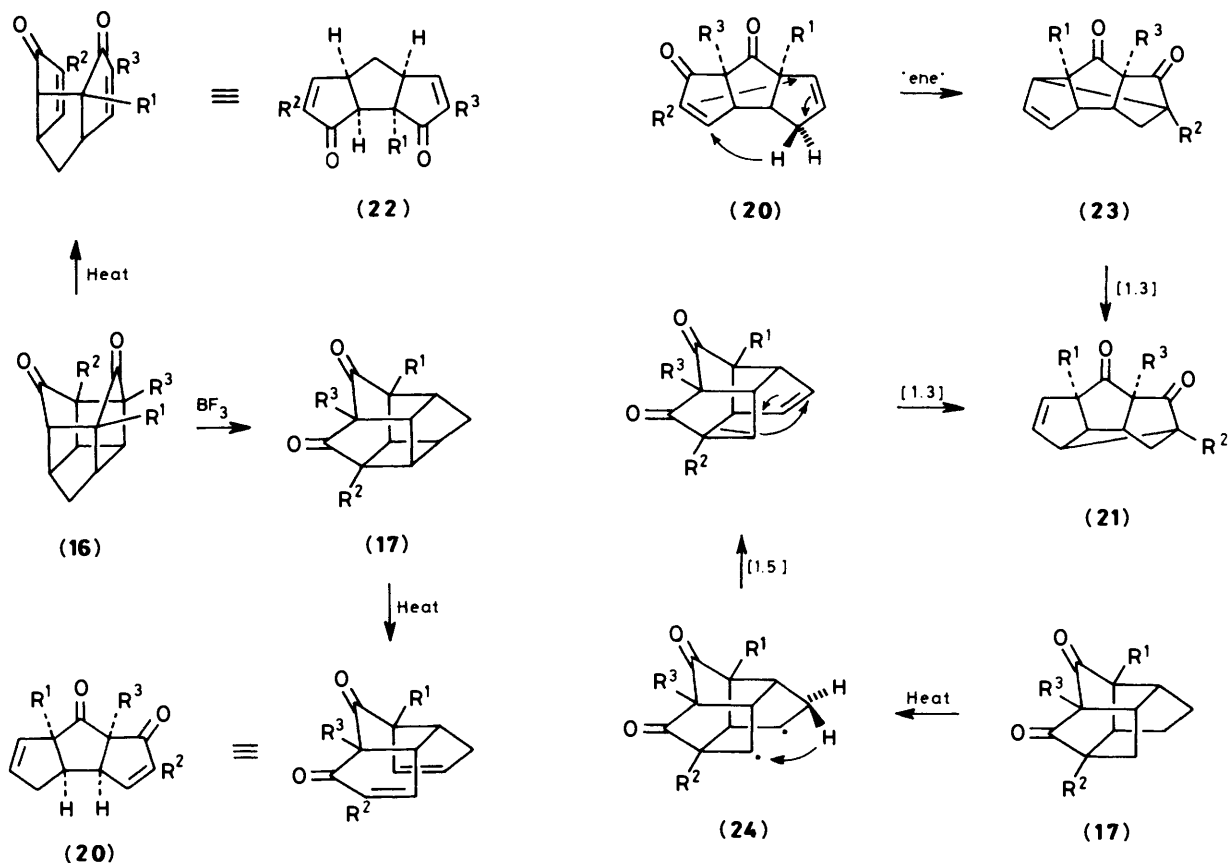
readily identified by comparison with the samples already in hand (*vide supra*). However, assignment of the 5-substituted *endo*-tricyclo[5.3.1.0^{2,6}]undeca-4,9-diene-3,8-dione structure to the new compounds (**19a,b**) required a detailed analysis of their ¹H and ¹³C n.m.r. spectral data (see the Experimental section). For example, the carbon resonances in the ¹³C n.m.r. spectrum due to the unsubstituted enone moiety in (**19a**) at δ 199.6(s), 154.1(s), and 129.4(d) were clearly distinguishable from the corresponding enone moiety in (**14a**) at δ 201.4(s), 168.1(s), and 133.6(d) but had a striking similarity with those of bicyclo[3.2.1]octa-3,6-dien-2-one.¹⁰ The profound effect of the substitution on the regiochemistry of cyclobutane fragmentation with aryl substituents (**15c,d**) favouring the 'b' bond cleavage and alkyl substituents (**15a,b**) promoting 'a' bond cleavage, is noted but its origin remains unclear. A possible explanation could be in terms of the C(2)-C(6) bond lengthening due to the interaction of the phenyl ring with the carbonyl group (7-oxonorbornane type). Indeed, a few instances of abnormal C-C bond lengthening in phenyl substituted cyclobutyl ketones have been recorded recently.¹¹ We, therefore, decided to look at the X-ray crystal structures of (**15a**) and (**15d**); however, owing to enantiomeric and rotational disorders it was not possible to get the geometrical parameters accurately.⁸

The pentacyclic diones (**17a,b**), like their siblings (**15a-d**), on FVP underwent smooth cyclobutane fragmentation to furnish (**20a,b**) and (**21a,b**), respectively (Scheme 6). The *cis*, *syn*, *cis*-triquinane structures of (**20a,b**) followed from a detailed

analysis of the diagnostic spectral parameters summarised in the Experimental section. The all-*cis*-triquinanes (**20a,b**) with a functionality in each of the three rings offer interesting synthetic possibilities. It is also worth mentioning here that through the novel rearrangement (**16**) \rightarrow (**17**) described earlier, it is possible now to obtain all *cis*-triquinanes with two entirely different substitution patterns from the same substrate—Cookson's caged diones (**16**)—depending upon whether the thermal cyclobutane fragmentation is carried out before the (**16**) \rightarrow (**22**)^{2a} or after the (**17**) \rightarrow (**20**) Lewis acid-catalysed rearrangement (Scheme 7). The other products from the thermolysis of (**17a,b**) were the novel tetracyclic structures (**21a,b**). Since unambiguous structures of (**21a,b**) could not be assigned on the basis of spectral data alone, an X-ray crystal structure of (**17a**) was determined. While the formation of (**20a,b**) from (**17**) involved a straightforward, stepwise, [2 + 2]-cycloreversion, the genesis of (**21a,b**) could be considered either in terms of an intramolecular ene reaction in (**20a,b**) and a [1,3]-shift in intermediate (**23**) or a diradical intermediate (**24**) followed by successively an intramolecular [1,5]-hydrogen shift and a [1,3]-shift. But, when compounds (**20a,b**) were heated (*ca.* 250 °C), no evidence of conversion to (**21a,b**) was forthcoming and only double bond isomerised products were detected. The latter mechanism therefore appears to be operative (Scheme 8).



Scheme 6.



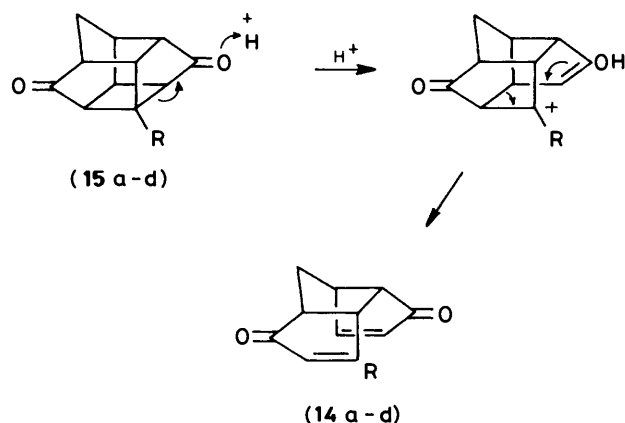
Scheme 7.

Scheme 8.

Table. Acid-catalysed rearrangement of 2-substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane-5,11-diones (15) to 11-substituted tricyclo[6.3.0.0^{2,6}]undeca-4,10-diene-3,9-diones (14)

Substrate	Toluene- <i>p</i> -sulphonic acid ^a		BF ₃ -Et ₂ O ^b		Product
	Time/Temp. °C	Yield (%)	Time/Temp. °C	Yield (%)	
(15a)	6 h/110	20	2 h/80	65	(14a)
(15c)	2 h/80	100	40 min/30	100	(14c)
(15d)	2 h/30	100	5 min/30	100	(14d)

^a 0.2 mol equiv. of acid in either benzene or toluene was used. ^b 0.5M-solution of BF₃-Et₂O in benzene was used (4.5 mol equiv.).



Scheme 9.

Acid-catalysed reactions of the pentacyclic diones (15a—d) and (17a,b) were next investigated. The diones (17a,b) were resistant to any further rearrangement but (15a—d) underwent smooth cycloreversion to the bis-enones (14a—d). While (15d) with catalytic amounts of toluene-*p*-sulphonic acid gave (14d) at ambient temperature (30 °C, 2 h), the use of BF₃-Et₂O proved even more effective, and (15d) reverted to (14d) almost instantly and in quantitative yield. The phenyl and methyl substituted diones (15a,c) also cycloreverted to their precursor bis-enones (14a,c) respectively (Scheme 9 and Table). However, the reaction in the case of the methyl substituted compound was less efficient and there was a clear trend for the propensity towards cycloreversion to decrease with the substitution in the order *p*-methoxyphenyl, phenyl, methyl. The allyl

substituted compound (15b) however, gave a complex mixture because of involvement of the olefinic bond. A plausible mechanism for the facile rearrangement of diones to the triquinane bis-enones is also shown in Scheme 9.

Experimental

All m.p.s were recorded on a Buchi SMP-20 apparatus and are uncorrected. B.p.s refer to bath temperatures. U.v., i.r., ¹H n.m.r. (100 MHz), and ¹³C n.m.r. (25.0 MHz) spectra were recorded on Shimadzu 200S and Perkin-Elmer 297 spectrophotometers, and Jeol MH-100 and Jeol FX-100 spectrometers, respectively. ¹H

N.m.r. and ^{13}C n.m.r. chemical shifts are given in δ using SiMe_4 as the internal standard and CDCl_3 as the solvent. In the ^{13}C n.m.r. spectra, off resonance multiplicities, when recorded, are given in parentheses. Elemental analyses were carried out on a Hewlett-Packard 185-B CHN analyser.

Analytical t.l.c. was performed on (10 \times 5 cm) glass plates coated (250 nm) with Acme silica gel G (containing 13% calcium sulphate as binder). Visualisation of the spots was achieved by exposure to iodine vapour. Acme silica gel (100–200 mesh) was used in the column chromatography. Moisture sensitive reactions were carried out using standard syringe-septum techniques. Dry diethyl ether and tetrahydrofuran (THF) were prepared by distillation over sodium and stored over pressed sodium wire. Dichloromethane was distilled over P_2O_5 . Light petroleum refers to the fraction boiling at 60–80 °C. All solvent extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated on a Buchi-EL rotary evaporator.

11-Methyltricyclo[6.3.0.0 2,6]undeca-4,10-diene-3,9-dione (14a).—To a stirred suspension of magnesium (365 mg, 0.015 mol) in dry ether (15 ml) was added dropwise a solution of methyl iodide (4.54 g, 32 mmol) in dry ether (5 ml). The mixture was stirred at room temperature until all the magnesium had dissolved. The methylmagnesium iodide was added slowly *via* a syringe to a stirred solution of the bis-enone (10) (2 g, 11.5 mmol) in dry THF (20 ml). The reaction mixture was stirred for 20 min at room temperature and quenched by careful addition of saturated aqueous NH_4Cl . The organic layer was separated, the aqueous phase extracted with dichloromethane (50 ml \times 2), and the combined organic extracts washed and dried. Evaporation of the solvent furnished a crude material (3 g) containing *ca.* 30% of the lactol (13a). An analytical sample of the lactol (13a) (in equilibrium with its open ketol form) was prepared by chromatography of the crude lactol on a silica gel column and elution with 15% ethyl acetate in benzene. The product was crystallised from dichloromethane–light petroleum to give a mixture of (13a) and its ketol form in the ratio 1:7, m.p. 100–103 °C; ν_{max} (KBr), 3 400, 1 710w, 1 690w, and 1 620 cm^{-1} ; δ_{H} 7.6 (dd, *J* 6, 3 Hz), 6.18 (br s), 5.96 (dd, *J* 6, 2 Hz), 5.68 (1 H, half AB, *J* 6 Hz), 5.5 (1 H, half AB, *J* 6 Hz), 5.34 (1 H, half AB, *J* 6 Hz), 5.14 (1 H, half AB, *J* 6 Hz), 3.88 (1 H, br s), 2.7–3.3 (4 H, m), 1.76 (2 H, br s), 1.46 (3 H, s), and 1.33 (3 H, s); δ_{C} 139.1(d), 136.3(d), 134.7(d), 133.0(d), 119.9(s), 97.0(s), 60.2(d), 57.9(d), 51.4(d), 50.3(d), 34.3(t), and 26.8(q). The crude lactol (13a) (3 g) obtained above in dichloromethane (15 ml) was added to a stirred suspension of pyridinium chlorochromate (3 g, 14 mmol)¹² in dichloromethane (10 ml). The heterogeneous reaction mixture was stirred vigorously for 4 h at room temperature prior to filtration through a silica gel (20 g) column with large volume of dichloromethane. Evaporation of the solvent furnished the single transposed bis-enone (14a) (650 mg, 30%) which was recrystallised from dichloromethane–light petroleum as white flakes, m.p. 105–106 °C; λ_{max} (MeOH) 223 (ϵ , 14 900) and 315 nm (1 400); ν_{max} (CH_2Cl_2) 1 710, 1 618, and 1 590 cm^{-1} ; δ_{H} 7.46 (1 H, dd, *J* 6, 3 Hz), 5.84 (1 H, dd, *J* 6, 2 Hz), 5.7 (1 H, br s), 3.2–3.65 (2 H, m), 2.7–3.2 (2 H, m), 1.8–2.4 (2 H, m), and 2.24 (3 H, s); δ_{C} 210.4(s), 209.0(s), 178.4(s), 168.1(d), 133.6(d), 129.6(d), 57.1(d), 52.5(d), 51.9(d), 51.3(d), 27.7(t), and 20.5(q) (Found: C, 76.55; H, 6.6. Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43%).

11-Allyltricyclo[6.3.0.0 2,6]undeca-4,10-diene-3,9-dione (14b).—The allylmagnesium chloride prepared from magnesium (365 mg, 0.015 mol) and allyl chloride (2.8 g, 36 mmol) in ether (5 ml), was added slowly *via* a syringe to a stirred solution of the bis-enone (10) (2 g, 11.5 mmol) in dry THF (20 ml). The reaction was worked up after 20 min as described in the previous experiment to furnish crude material (1.4 g) containing *ca.* 60%

of the hemi-acetal (13b). A pure sample of the hemi-acetal was prepared by filtration of the crude material through a silica gel column with 10% ethyl acetate–benzene. Crystallisation from light petroleum furnished (13b) as colourless needles, m.p. 114–115 °C, ν_{max} (KBr) 3 370, 1 640, and 1 625 cm^{-1} ; δ_{H} 4.8–6.04 (7 H, m), 3.74 (1 H, s), 2.6–3.4 (4 H, m), 2.5 (2 H, dd, *J* 7, 1.5 Hz), and 1.76 (2 H, m); δ_{C} 138.8(d), 137.5(d), 133.9(d), 133.3(d, 2 C), 119.9(s), 117.7(t), 99.3(s), 59.8(d), 55.4(d), 51.6(d), 50.3(d), 43.9(t), and 34.3(t).

The above crude hemi-acetal (13b) (1.4 g) was oxidised with pyridinium chlorochromate (2 g, 9.2 mmol)¹² in dichloromethane for 7 h. Work-up as above furnished the single transposed bis-enone (14b) (615 mg, 25% overall in two steps) which crystallised from light petroleum, m.p. 68 °C; λ_{max} (MeOH) 222 (ϵ , 15 350) and 328 nm (100); ν_{max} (KBr) 1 705, 1 685, 1 645, 1 615, and 1 590 cm^{-1} ; δ_{H} 7.48 (1 H, dd, *J* 6, 3 Hz), 5.84 (1 H, d, *J* 6 Hz), 5.68 (1 H, s), 5.4–6.06 (1 H, m), 5.2 (1 H, d, *J* 5 Hz), 5.07 (1 H, s), 2.8–3.8 (6 H, m), 2.3 (1 H, d with fine str, *J* 14 Hz), and 2.03 (1 H, td, *J* 14, 10 Hz); δ_{C} 209.7(s), 209.0(s), 180.1(s), 168.2(d), 133.5(d), 133.0(d), 128.5(d), 118.1(t), 56.8(d), 51.8(d), 51.2(d), 50.8(d), 38.3(t), and 27.8(t) (Found: C, 78.3; H, 6.8. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59%).

11-Phenyltricyclo[6.3.0.0 2,6]undeca-4,10-diene-3,9-dione (14c).—To a suspension of magnesium (365 mg, 0.015 mol) in dry ether (15 ml) was added dropwise a solution of bromobenzene (2.35 g, 15 mmol) in dry ether (7 ml). The mixture was stirred at room temperature until all the magnesium had dissolved. The phenylmagnesium bromide was added slowly *via* a syringe to a stirred solution of the bis-enone (10) (2 g, 11.5 mmol) in dry THF (20 ml). The reaction mixture was worked up after 20 min and extracted with dichloromethane (50 ml \times 2). Evaporation of the solvent furnished crude material (3.2 g) containing *ca.* 25% of the hemi-acetal (13c). An analytical sample of this was prepared by filtration of the crude hemi-ketal through a silica gel column with 10% ethyl acetate–benzene, followed by crystallisation from dichloromethane–hexane, m.p. 134–135 °C; ν_{max} (KBr) 3 410 and 1 625 cm^{-1} ; δ_{H} 6.75–7.5 (5 H, m), 5.6 (2 H, m), 5.34 (1 H, d, *J* 6 Hz), 5.2 (1 H, d, *J* 6 Hz), 4.02 (1 H, s), 2.75–3.5 (4 H, m), and 1.74 (2 H, br s). δ_{C} 145.3, 138.8, 137.6, 134.0, 133.3, 128.0(2C), 126.6, 124.7(2C), 120.5, 100.3, 60.7, 59.8, 51.8, 50.3, and 34.1. The crude hemi-acetal (13c) (3.2 g) was oxidised with pyridinium chlorochromate (3 g, 14 mmol)¹² in dichloromethane (25 ml) for 7 h. The crude product (1.2 g) obtained was loaded onto a silica gel (20 g) column and elution with 20% ethyl acetate–benzene to furnish the single transposed bisenone (14c) (650 mg, 22.5%) which crystallised from carbon tetrachloride, m.p. 111–112 °C; λ_{max} (MeOH) 296 (ϵ , 17 500) and 220 nm (15 500); ν_{max} (CH_2Cl_2) 1 705, 1 602, 1 595, and 1 575 cm^{-1} ; δ_{H} 7.7 (1 H, dd, *J* 6, 3 Hz), 7.3–7.8 (5 H, m), 6.31 (1 H, s), 5.79 (1 H, dd, *J* 6, 2.5 Hz), 4.16 (1 H, dd, *J* 11, 7 Hz), 3.52 (1 H, m), 2.9–3.3 (2 H, m), 2.42 (1 H, half AB, *J* 14 Hz), and 2.1 (1 H, td, *J* 14, 10 Hz); δ_{C} 209(s), 206.9(s), 172.9(s), 167.2(d), 133.5(s), 133.0(d), 130.5(d), 127.9(d, 2C), 127.3(d, 2C), 124.6(d), 56.3(d), 51.4(d), 50.7(d), 47.9(d), and 27.4(t) (Found: C, 81.15; H, 5.7. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 81.58; H, 5.64%).

11-(*p*-Methoxyphenyl)tricyclo[6.3.0.0 2,6]undeca-4,10-diene-3,9-dione (14d).—To a suspension of magnesium (365 mg, 0.015 mol) in dry ether (30 ml) was added dropwise a solution of *p*-bromoanisole (2.8 g, 15 mmol) in dry ether (15 ml). The mixture was stirred at room temperature until all the magnesium had dissolved. The *p*-methoxyphenylmagnesium bromide solution was added slowly *via* a syringe to a stirred solution of the bis-enone (10) (2 g, 11.5 mmol) in dry THF (20 ml) at room temperature. The reaction mixture was quenched and worked up as above after 20 min. Evaporation of the solvent furnished crude viscous material (3.5 g) containing *ca.*

12% of the hemi-acetal (**13d**). A pure sample (quite unstable) of the hemiacetal was prepared by chromatography on a silica gel column. Elution with 20% ethyl acetate–benzene furnished the hemiacetal as viscous material, ν_{\max} (neat) 3 400 cm^{-1} ; δ_{H} 7.26 (2 H, d, J 9 Hz), 6.8 (2 H, d, J 9 Hz), 5.7 (2 H, m), 5.43 (1 H, d, J 5 Hz), 5.26 (1 H, d, J 5 Hz), 3.75 (3 H, s), 3.22 (4 H, m), and 1.82 (2 H, m); δ_{C} 158.5, 139.3, 137.6, 134.0, 133.1, 128.4, 125.9(2C), 113.5(2C), 120.5, 100.2, 60.8, 60.1, 55.2, 51.8, 50.5, and 34.2. The crude hemiacetal (**13d**) (3.5 g) obtained above was taken up in dichloromethane (8 ml) and oxidised with pyridinium chlorochromate (3 g, 14 mmol)¹² in dichloromethane (10 ml). The reaction was terminated after 5 h and the crude product chromatographed on silica gel. Elution with 30% ethyl acetate–benzene furnished the single transposed bis-enone (**14a**) (320 mg, 10%) which crystallised from dichloromethane–light petroleum, m.p. 134–135 °C; λ_{\max} (MeOH) 222 (ϵ , 15 500) and 325 nm (22 200); ν_{\max} (CH_2Cl_2) 1 710, 1 600, and 1 590 cm^{-1} ; δ_{H} 7.65 (2 H, d, J 9 Hz), 7.46 (1 H, dd, J 6, 3 Hz), 6.95 (2 H, d, J 9 Hz), 6.2 (1 H, s), 5.78 (1 H, dd, J 6, 2 Hz), 4.13 (1 H, dd, J 12, 6 Hz), 3.86 (3 H, s), 3.5 (1 H, m), 2.9–3.3 (2 H, m), 2.45 (1 H, half AB, J 12 Hz), and 2.13 (1 H, td, J 12, 9 Hz); δ_{C} 209.1(s), 207.1(s), 172.7(s), 167.1(d), 161.7(s), 133.3(d), 129.4(d, 2C), 126.5(s), 122.7(d), 113.5(d, 2C), 56.4(d), 55.0(l), 51.7(d), 50.9(d), 48.3(d), and 27.6(t).

2-Methylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{4.8}]undecane-5,11-dione (15a).—A solution of the bis-enone (**14a**) (500 mg, 2.66 mmol) in ethyl acetate (120 ml) was carefully purged with a slow stream of nitrogen for 15 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well using a pyrex filter, for 45 min. Alternatively, the photolysis can be carried out in a pyrex flask in sunlight for 2 h. After the completion of the photolysis, the solvent was evaporated and the crude photolysate was crystallised from dichloromethane–hexane. The pentacyclic dione (**15a**) (485 mg, 97%) crystallised as heavy prisms, m.p. 200–201 °C; ν_{\max} (KBr) 1 760 and 1 730 cm^{-1} ; δ_{H} 2.6–3.1 (4 H, m), 2.0–2.55 (5 H, m), and 1.1 (3 H, s); δ_{C} 213.0(s), 212.9(s), 57.0(d), 55.0(d), 51.1(d), 49.7(d), 45.8(d), 43.7(t), 42.6(d), 42.1(s), 38.6(d), and 22.0(q) (Found: C, 76.2; H, 6.1. Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43%).

2-Allylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{4.8}]undecane-5,11-dione (15b).—Photolysis of 11-allyltricyclo[6.3.0.0^{2.6}]undeca-4,10-diene-3,9-dione (**14b**) (320 mg, 1.5 mmol) as described above furnished the pentacyclic dione (**15b**) in quantitative yield, m.p. 69–70 °C (light petroleum); ν_{\max} (KBr) 1 760, 1 735, and 1 640 cm^{-1} ; δ_{H} 5.2–5.8 (1 H, m), 4.8–5.2 (2 H, m), 2.6–3.18 (5 H, m), and 1.9–2.6 (6 H, m); δ_{C} 213.0(s), 212.8(s), 131.0(d), 119.3(t), 55.1(d), 54.8(d), 51.1(d), 47.2(d), 44.6(s), 43.8(2C, t and d), 42.7(d), 39.7(t), and 38.7(d) (Found: C, 78.25; H, 6.5. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59%).

2-Phenylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{4.8}]undecane-5,11-dione (15c).—Photolysis of 11-phenyltricyclo[6.3.0.0^{2.6}]undeca-4,10-diene-3,9-dione (**14c**) (250 mg, 1 mmol) as described above furnished (**15c**) in quantitative yield, m.p. 146–147 °C (CCl_4); ν_{\max} (KBr) 1 765 and 1 740 cm^{-1} ; δ_{H} 7.3 (3 H, m), 6.95 (2 H, m), 2.2–3.5 (9 H, m); δ_{C} 213.1, 212.9, 142.6, 128.8(2C), 127.2, 124.2(2C), 55.9, 54.7, 52.5, 51.2, 46.6, 45.7, 44.1, 42.8, and 38.5 (Found: C, 81.05; H, 5.35. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_2$: C, 81.58; H, 5.64%).

2-(*p*-Methoxyphenyl)pentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{4.8}]undecane-5,11-dione (15d).—Photolysis of 11-(*p*-methoxyphenyl)tricyclo[6.3.0.0^{2.6}]undeca-4,10-diene-3,9-dione (**14d**) (280 mg, 1 mmol) as described above furnished (**15d**) in quantitative yield, m.p. 168–169 °C (CH_2Cl_2 –light petroleum); ν_{\max} (KBr) 1 760, 1 735, and 1 615 cm^{-1} ; δ_{H} 6.5–7.0 (4 H, m),

3.76 (3 H, s), and 2.1–3.5 (9 H, m); δ_{C} 213.3(s), 213.2(s), 158.7(s), 134.9(s), 125.5(d, 2C), 114.3(d, 2C), 56.1(d), 55.2(q), 54.8(d), 52.8(d), 51.3(d), 46.3(s), 45.9(d), 44.2(d), 42.9(d), and 38.4(d) (Found: C, 77.35; H, 5.5. Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_3$: C, 77.12; H, 5.75%).

Boron Trifluoride–Diethyl Ether Reaction of 1,7-Dimethylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{5.9}]undecane-8,11-dione (16a).—To a solution of the dimethyl pentacyclic dione (**16a**) (404 mg, 2 mmol) in dry benzene (15 ml) was added $\text{BF}_3\text{--Et}_2\text{O}$ (1.3 ml, 10 mmol) and the solution refluxed for 10 h. The reaction mixture was cooled, slowly poured into saturated aqueous sodium hydrogen carbonate and extracted with benzene (3 \times 20 ml). The organic layer was washed, dried, and the solvent removed under reduced pressure to yield crude product (400 mg). The crude reaction mixture was loaded onto a silica gel (20 g) column and carefully eluted with benzene to yield rearranged pentacyclic dione (**17a**) (150 mg, 37%) which was crystallised from light petroleum, m.p. 91–92 °C; ν_{\max} (KBr) 1 760 and 1 720 cm^{-1} ; δ_{H} 3.43 (1 H, br s), 2.88 (1 H, br s), 2.62 (2 H, m), 2.4 (2 H, m), 1.74 (2 H, s), 1.38 (3 H, s), and 1.3 (3 H, s); δ_{C} 210.1(s), 208.0(s), 66.9(s), 56.4(d), 55.6(s), 49.3(d), 45.3(d), 44.0(d), 43.1(d), 42.8(d), 37.2(t), 14.5(q), and 10.9(q) (Found: C, 77.45; H, 6.95. Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.22; H, 6.98%). Continued elution with benzene gave unchanged starting material (100 mg, 25%). Further elution of the column with 20% ethyl acetate–benzene mixture furnished the tetracyclic compound (**18**) (80 mg, 20%) which crystallised from ether–light petroleum mixture, m.p. 108–110 °C; ν_{\max} (KBr) 1 740, 1 730, and 1 645 cm^{-1} ; λ_{\max} (MeOH) 239 nm (ϵ , 5 200); δ_{H} 6.04 (1 H, s), 5.34 (1 H, s), 3.18 (1 H, br d), 2.2–3.0 (5 H, m), 1.96 (2 H, ABq, J 11 Hz), 1.68 (1 H, s), and 1.14 (3 H, d, J 6 Hz); δ_{C} 219.0(s), 205.0(s), 147.9(s), 119.7(t), 57.7(d), 56.3(d), 48.8, 48.0, 47.5, 46.8, 45.6, 35.2(t), and 10.2(q) (Found: C, 77.2; H, 7.2. Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.12; H, 6.98%).

Boron Trifluoride–Diethyl Ether Reaction of 1,9-Dimethylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{5.9}]undecane-8,11-dione (16b).—To a solution of the dimethyl pentacyclic dione (**16b**) (2.02 g, 10 mmol) in dry benzene, (25 ml) $\text{BF}_3\text{--Et}_2\text{O}$ (6.5 ml, 50 mmol) was added and the solution refluxed for 10 h. The reaction mixture was cooled, quenched by careful addition to saturated aqueous sodium hydrogen carbonate and extracted with benzene (50 ml \times 3). The organic layer was washed, dried, and the solvent removed under reduced pressure to yield crude product (2 g) which was loaded onto a silica gel (70 g) column and carefully eluted with benzene to furnish the rearranged pentacyclic dione (**17b**) (1.01 g, 50%), m.p. 79–80 °C; ν_{\max} (KBr) 1 760 and 1 710 cm^{-1} ; δ_{H} 3.47 (2 H, half AB, J 3 Hz), 2.76–3.04 (1 H, m), 2.2–2.7 (2 H, m), 1.9 (1 H, m), 1.76 (2 H, br s), 1.36 (3 H, s), and 1.0 (3 H, s); δ_{C} 208.6(s), 207.6(s), 64.8(d), 58.8(s), 55.1(s), 51.6(d), 50.8(d), 43.2(d), 43.0(d), 40.9(d), 35.6(t), and 14.3(q) (Found: C, 77.55; H, 7.05. Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.22; H, 6.98%).

Flash Vacuum Thermolysis of 2-Methylpentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{4.8}]undecane-5,11-dione (15a).—The pentacyclic dione (**15a**) (100 mg, 0.53 mmol) was slowly sublimed at 120 °C/1 mmHg through a preheated (560 \pm 10 °C) quartz tube.^{2a} The condensate in the receiver was found (by n.m.r. analysis) to contain the two bis-enones in the ratio of 7.5:1. The crude mixture was loaded onto a silica gel (10 g) column and carefully eluted with 5% ethyl acetate–benzene. Careful pooling of fractions furnished 5-methyltricyclo[5.3.1.0^{2.6}]undeca-4,9-diene-3,8-dione (**19**) (70 mg, 70%) which crystallised from dichloromethane–light petroleum, m.p. 128–129 °C; λ_{\max} (MeOH): 221 nm (ϵ , 19 500); ν_{\max} (KBr) 1 680 and 1 610 cm^{-1} ; δ_{H} 7.16 (1 H, dd, J 10, 6 Hz), 5.87 (1 H, dd, J 10, 2 Hz), 5.72 (1 H, br s), 3.56 (1 H, m), 3.0–3.44 (3 H, m), 2.33

(1 H, half AB, J 12 Hz), 2.04 (3 H, s), and 1.8—2.2 (1 H, m); δ_C 207.5(s), 199.6(s), 178.3(s), 154.1(d), 133.3(d), 129.9(d), 55.7(d), 51.6(d), 51.5(d), 43.4(t), 36.5(d), and 18.7(q) (Found: C, 76.15; H, 6.75. Calc. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%). Further fractions furnished the triquinane bis-enone (**14a**) (8 mg, 8%) which was identified by comparison (t.l.c., i.r., n.m.r.) with an authentic sample.^{2a}

5-(*Prop-1-enyl*)tricyclo[5.3.1.0^{2,6}]undeca-4,9-diene-3,8-dione (**19b**).—Pyrolysis of the pentacyclic dione (**15b**) (65 mg, 0.3 mmol) as described above and purification by column chromatography (10% ethyl acetate–benzene as eluant) furnished the tricyclic compound (**19b**) (40 mg, 60%), m.p. 98—99 °C (CH_2Cl_2 –light petroleum); λ_{max} (MeOH) 230 (ϵ , 12 800), and 281 (20 455); ν_{max} (KBr) 1 675, 1 640, and 1 575 cm^{-1} ; δ_H 7.12 (1 H, dd, J 10, 7 Hz), 6.42 (1 H, q, J 5 Hz), 6.4 (1 H, s), 5.86 (1 H, dd, J_1 10, 1.5 Hz), 5.75 (1 H, s), 3.84 (1 H, t, J 7 Hz), 3.0—3.5 (3 H, m), 2.35 (1 H, half AB, J 12 Hz), 1.8—2.2 (1 H, m), and 1.95 (3 H, d, J 5 Hz); δ_C 207.0(s), 198.8(s), 172.1(s), 153.5(d), 139.4(d), 130.7(d), 129.9(d), 126.9(d), 55.5(d), 52.5(d), 46.9(d), 43.4(t), 36.2(d), and 19.2(q).

Thermolysis of Phenyl and p-Methoxyphenyl Diones (15c—d).—Thermolysis of the diones (**15c—d**) as described above furnished the triquinane bis-enones (**14c—d**) in 75—80% yield which were identified by comparison (t.l.c., n.m.r., i.r.) with authentic samples.

Thermolysis of 1,10-Dimethylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]-undecane-9,11-dione (17a).—The pentacyclic dione (**17a**) (200 mg, 0.1 mmol) was sublimed at 110 °C/1 mmHg through a Pyrex vigreux column which was pre-heated to 500 °C.^{2a} The pyrolysate (180 mg) was loaded onto a silica gel (10 g) column and elution with benzene furnished the tetracyclic compound (**21a**) (100 mg, 55%) which crystallised from hot light petroleum m.p. 161—162 °C; ν_{max} (KBr) 1 750, 1 715, and 1 605 cm^{-1} ; δ_H 5.72 (2 H, s with fine str), 3.5—3.92 (1 H, ddd, J 8, 10, 6 Hz), 3.12 (2 H, dt, J 10, 2 Hz), 2.75 (1 H, d, J 6 Hz), 2.22 (1 H, dd, J 11, 2 Hz), 1.96 (1 H, half AB, J 11 Hz), 1.2 (3 H, s), and 1.09 (3 H, s); δ_C carbonyls are not seen, 134.6(d), 132.7(d), 65.1(s), 58.8(d), 57.8(d), 57.6(s), 47.8(d), 45.0(d), 44.1(t), 13.7(q), and 13.2(q) (Found: C, 77.0; H, 6.9. Calc. for $C_{13}H_{14}O_2$: C, 77.12; H, 6.98%).

Further elution of the column with 30% ethyl acetate–benzene furnished the tricyclic enone (**20a**) (70 mg, 35%) which was bulb-to-bulb distilled at 160 °C/1 mmHg; ν_{max} (neat) 1 740, 1 700, and 1 640 cm^{-1} ; δ_H 7.25 (1 H, s with st), 5.64 (2 H, m), 3.5 (1 H, br s), 3.3 (2 H, br s), 2.7 (2 H, br s), 1.72 (3 H, s), and 1.36 (3 H, s); δ_C 210.6(s), 156.7(d), 140.0(s), 132.1(d), 129.8(d), 63.6(s), 62.3(d), 52.0(d), 37.5(d), 35.1(t), 18.7(q), and 10.6(q).

Thermolysis of 1,8-Dimethylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]-undecane-9,11-dione (17b). The pentacyclic dione (**17b**) (200 mg 0.1 mmol) was sublimed at 110 °C/1 mmHg through a Pyrex vigreux column which was pre-heated to 500 °C.^{2a} The pyrolysate (180 mg) was loaded onto a silica gel (10 g) column and elution with benzene furnished the tetracyclic compound (**21b**) (50 mg, 25%) which crystallised from hot light petroleum, m.p. 158—159 °C; ν_{max} (KBr) 1 760, 1 715, and 1 605 cm^{-1} ; δ_H 5.7 (1 H, dd, J 6, 3 Hz), 5.48 (1 H, d, J 6 Hz), 3.2—3.52 (1 H, m), 3.14 (1 H, d with st, J 9 Hz), 2.86 (1 H, dd, J 5, 2 Hz), 2.16 (1 H, dd, J 10, 2 Hz), 1.93 (1 H, half AB, J 10 Hz), 1.25 (3 H, s), and 1.23 (3 H, s); δ_C 210.5(s), 208.4(s), 138.7(d), 133.6(d), 65.5(d), 62.1(s), 59.5(d), 56.6(s), 56.5(d), 44.4(t), 37.3(d), 18.5(q), and 13.0(q) (Found: C, 77.0; H, 6.9. Calc. for $C_{13}H_{14}O_2$: C, 77.22; H,

6.98%). Further elution of the column with 10% ethyl acetate–benzene mixture furnished the enone (**20b**) (70 mg, 35%) which crystallised from light petroleum, m.p. 131—132 °C; ν_{max} (KBr) 1 738, 1 690, and 1 630 cm^{-1} ; λ_{max} (MeOH) 216 (ϵ , 8 000) and 241 nm (4 000); δ_H 7.35 (1 H, br s), 5.68 (1 H, d of half AB, J 6, 2 Hz), 5.42 (1 H, d of half AB, J 6, 2 Hz), 3.66 (1 H, m), 3.36 (1 H, d, J 6 Hz), 2.4—3.0 (3 H, m), 1.72 (3 H, dd, J 1 Hz), and 1.16 (3 H, s). δ_C 209.0(s), 200.0(s), 158.1(d), 140.6(s), 135.7(d), 131.3(d), 66.2(s), 61.6(d), 47.0(d), 41.0(d), 34.9(t), 21.2(q), and 10.5(q) (Found: C, 77.0; H, 6.85. Calc. for $C_{13}H_{14}O_2$: C, 77.22; H, 6.98%).

General Procedure for Acid Catalysed [2 + 2]-Cycloreversion of 2-Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]-undecane-5,11-diones (15a,c,d).—A solution of the pentacyclic diones (**15a,c,d**) and either toluene-*p*-sulphonic acid or $BF_3 \cdot Et_2O$ in benzene was stirred either at room temperature or at reflux temperature for the specified time (Table). The reaction mixture was washed with aqueous $NaHCO_3$ followed by brine and the organic layer was dried. Evaporation of the solvent furnished the tricyclic bis-enones (**14a,c,d**) identified by comparison with authentic samples.

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