Orientation of a Bridged Quinone System. An Intramolecular Photochemical Cyclisation giving a Cyclobutane Ring, and a Novel Simulation by Non-photochemical Means

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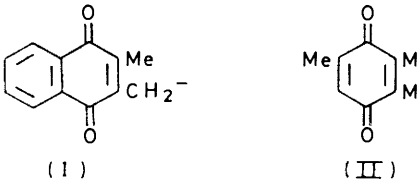
A reinvestigation of the n.m.r. spectrum of the bridged quinone derivative (IVb) confirms that Me^f is correctly placed at position 11a. In support, position 7b must carry a hydrogen atom, because acid-catalysed acetylation opens the bridge and ring B can then aromatise giving the quinol hemiacetal triester (IX).

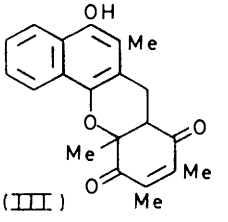
Unlike the phenol (IVa) previously examined, its acetate (IVb) is slowly transformed in daylight into the cyclobutane derivative (VIIb). Remarkably, the propionate is much more sensitive to light. Also remarkably, esterification of the phenol (IVa) by propionic anhydride and pyridine generates some of the cyclobutane derivative (VIIg) even in darkness, although pyridine fails to induce cyclobutane ring formation in the (pre-formed) bridge propionate (IVg).

We showed earlier [1] that interaction of the carbanion (I) with trimethyl-1,4-benzoquinone (II) gives the xanthen derivative (III), which then adds another molecule of the trimethyl-quinone to form a bridged system as in (IVa). Other reasonable bridge structures such as (V) or (VI) differ only in the orientation of the bridging ring B with respect to ring A. A decision in favour of structure (IVa) with the AB orientation head-to-head and *endo* seemed most likely on the basis of the n.m.r. spectra, but there were some discordant facts, especially the failure of the tricyclododecadiene nucleus to undergo photochemical ring closure to the



(I)

(II)



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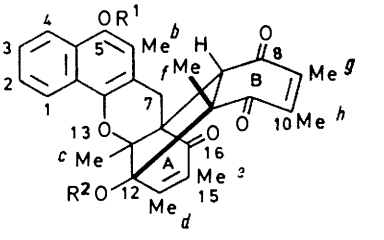
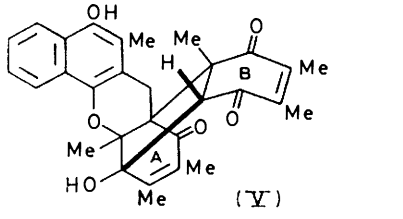
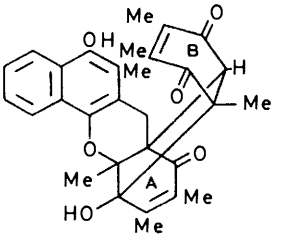


(IV) a; $R^1 = R^2 = H$
b; $R^1 = COMe^a, R^2 = H$
c; $R^1 = CO\cdot CH_2Cl, R^2 = H$
d; $R^1 = SO_2Me, R^2 = H$
e; $R^1 = SO_2Me, R^2 = Ac$
f; $R^1 = SO_2C_7H_7, R^2 = H$
g; $R^1 = MeCH_2\cdot CO, R^2 = H$



(V)



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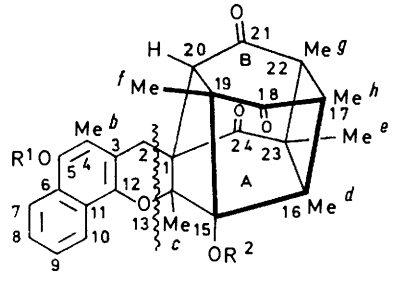
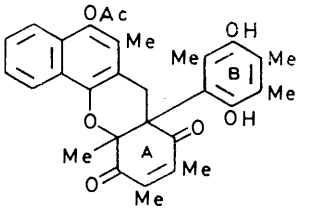
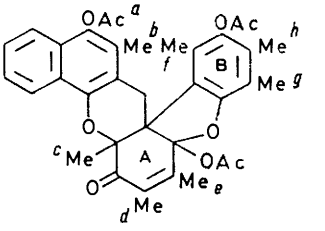


(VII) a; $R^1 = R^2 = H$
b; $R^1 = COMe^a, R^2 = H$
c; $R^1 = SO_2Me, R^2 = H$
d; $R^1 = R^2 = Ac$
e; $R^1 = SO_2Me, R^2 = Ac$
f; $R^1 = PhCO, R^2 = H$
g; $R^1 = MeCH_2\cdot CO, R^2 = H$



(VIII)



(IX)

cyclobutane derivative (VIIa). The present study has resolved the discords and structure * (IVa) is now regarded as certain. Ring closure of the cyclobutane ring can be achieved, although some of the circumstances are unusual.

Since the original structural allocation had depended heavily upon the n.m.r. spectrum of the acetate (IVb), this was reviewed and the results essentially confirmed (Table). Two transpositions in the assignments have been made, however, though these do not affect the structural arguments. The spectrum of the chloroacetate (IVc) lacks a band at τ 7.51, which must therefore be assigned to the acetate methyl group Me^a despite its low field position, and the band at τ 7.70 has to be assigned to the aromatic methyl group Me^b. Specific assignments for the angular methyl groups had been made tentatively because these must be influenced by the naphthalene nucleus to an extent difficult to assess, but now that a number of values for simpler compounds are available from parallel studies it is clear that of the two bands, the one at τ 8.91 is better assigned to Me^f and the one at 8.43 to Me^c. Indeed, this transposition is advantageous, because it shows that it is the Me^f signal that suffers the major downfield shift [1] when the alcohol function is transformed into the trichloroacetylcarbamate,[2] *i.e.* that Me^f is close to the alcohol function. The angular hydrogen atom is hardly affected and is therefore remote. Thus rings A and B should be head-to-head in alignment, and structure (V) must be excluded.

^{1}H N.m.r. spectra * (τ values; solvent $CDCl_3$)

Compound		Me								CH_2		CH (ring B)	Other H
Bridge trione		*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*				
5-acetate †	(IVb)	7.51	7.70	8.43	7.99	8.32	8.91	8.17	8.17	7.24d	6.64d [a]	6.89	
5-propionate †	(IVg)		7.70	8.42	7.97	8.30	8.90	8.14	8.14	7.22d	6.60d [a]	6.87	7.20q, 8.56t (Et, *J* 1.5 Hz)
5-chloroacetate †	(IVc)		7.71	8.44	8.00	8.34	8.92	8.18	8.18	7.24d	6.63d [a]	6.92	5.57 ($ClCH_2$·CO)
5-methanesulphonate †	(IVd)		7.47	8.43	7.98	8.31	8.90	8.15	8.15	7.22d	6.60d [a]	6.92	6.64 (SO_2Me)
5-(toluene-4-sulphonate) †	(IVf)		7.52	8.44	7.99	8.33	8.92	8.16	8.16	7.35d	6.64d [b]	6.98	7.79 ($ArCH_3$)
Hemiacetal triacetate †	(IX)	7.60	7.63	8.65	8.08	8.23	8.13	7.88	7.88	6.70d	6.20d [a]		7.80 (OAc × 2)
Box trione													
5-acetate	(VIIb)	7.54	7.79	8.61	8.66	8.85	9.03	8.81	8.81	7.41d	6.52d [a]	7.35	6.94 (OH)
5,15-diacetate	(VIId)	7.52	7.65	8.73	8.63	8.83	9.05	8.80	8.77	7.37d	6.56d [c]	7.23	7.79 (15-OAc)
5-propionate	(VIIg)		7.81	8.61	8.65	8.86	9.04	8.82	8.82	7.22d	6.52d [c]	7.33	7.22q, 856t (Et, *J* 7.5 Hz)
5-methanesulphonate	(VIIc)		7.57	8.60	8.64	8.86	9.03	8.82	8.82	7.40d	6.53d [a]	7.36	6.66 (SO_2Me)
15-acetate 5-methanesulphonate	(VIIe)		7.57	8.72	8.61	8.83	9.06	8.80	8.76	7.39d	6.58d [a]	7.28	6 66 (SO_2Me) 7.66 (15-OAc)
5-benzoate	(VIIf)		7.74	8.60	8.64	8.83	9.03	8.81	8.78	7.32d	6.48d [a]	7.31	

* Excluding aromatic resonances. † In these compounds there was long-range coupling (<1 Hz) between Me^d and Me^e.
[a] *J* 18 Hz. [b] *J* 17 Hz. [c] *J* 19 Hz.

This conclusion is strongly confirmed by the results of acetylating the bridge trione acetate (IVb) with acetic anhydride and sulphuric acid. Amongst the products was one containing three acetate functions but which, from its n.m.r. spectrum and other properties, could not have been formed merely by esterification of the alcohol function and of the enolic centre, nor by opening of the heterocyclic ring. It must therefore have been derived by a retroaldol reaction opening up the bridge system at one end, which would allow aromatisation to the quinol derivative (VIII). This is possible in head-to-head structures (IV) and (VI) but not in the head-to-tail structure (V), which must again be excluded. The product is not simply an ester of (VIII), however, because the mass spectrum shows ready loss of one of the acetate groupings as acetic acid, and the i.r. spectrum does not fit well with an enedione grouping, being too simple in the ketone region with only one band, of relatively low intensity. However, the quinol (VIII) should form the hemiacetal very readily, and the derived ester (IX) would have the properties described. A hemiacetal of the same type has been more thoroughly studied in a related series.[3]

Brief esterification of the bridge trione (IVa) with acetic anhydride and pyridine affects only the phenolic hydroxy-group giving (IVb), but it was noted that long reaction times produced small amounts of a contaminant. This was ignored until encountered in relatively large amounts following the cleaning of the laboratory windows, when it was recognised as a photochemical product. Diffuse daylight was then shown to convert the acetate (IVb) into the cyclobutane derivative † (VIIb) in high yield, notwithstanding the resistance of the parent naphthol (IVa), the photoconversion of which has now been observed (though it is very slow and the product has not been obtained pure). It seems that the excited enedione system in one molecule is

* For brevity referred to as the bridge trione. For systematic purposes the ring system has been named as an *o*-benzenobenzo[*c*]xanthen,[1] but *Chemical Abstracts* (1971) names the compound (7a*R**,7b*R**,11a*R**,12*R**,12a*S**)-7b,11a,12,12a-tetrahydro-5,12-dihydroxy-6,9,10,11a,12a,14,15-heptamethyl-7*H*-12,7a-propenoindeno[2,1-*b*]naphtho[2,1-*e*]pyran-8,11,16-trione.

† For brevity referred to as the box trione acetate. For systematic purposes the compound is named 5,15-dihydroxy-4,14,16,17,19,22,23-heptamethyl-13-oxaoctacyclo[12.10.0.0^{1,20}.0^{3,12}.0^{6,11}.0^{15,19}.0^{16,23}.0^{17,22}]tetracosa-3(12),4,6(11),7,9-pentaene-18,21,24-trione. Taken alone, the bridge system represents a new combination of two cyclohexane rings and can be regarded as a derivative of the new system pentacyclo[7.3.0.0^{2,7}.0^{4,11}.0^{5,10}]-dodecane.

[2] I. R. Trehan and C. Monder, *Tetrahedron Letters*, 1968, 67.
[3] F. M. Dean, L. E. Houghton, G. H. Mitchell, B. Parvizi, and C. Thebtaranonth, in preparation.

quenched by the naphthol system in another; accordingly, the photochemical cyclisation of the esters (IV) is much slower in the presence of phenol. Since time is required for deactivating collisions to occur, it also seems that the cyclisation does not follow immediately upon activation even though the unsaturated centres cannot separate and appear to line up reasonably well. As remarked earlier, however, the centres may be sufficiently skewed to bring the wrong orbitals into proximity,[1] and thermal agitation may be required to achieve the precise alignment necessary for ring closure.

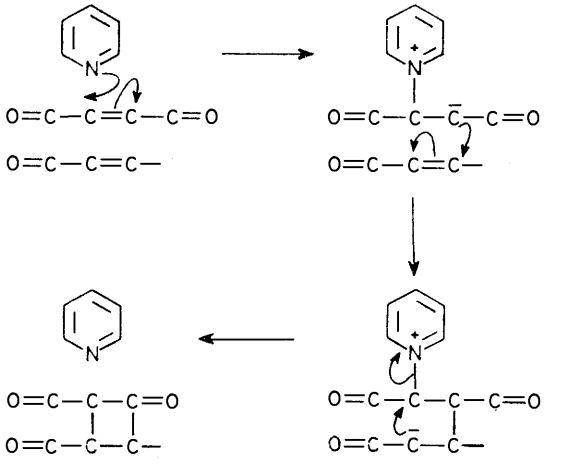
The i.r. and n.m.r. spectra show that enone and dienone groupings are absent from the box trione derivative (VIIb). There are no carbonyl bands at frequencies below 1 700 cm^{-1} but several above; since the acetate band obscures the cyclopentanone band in this spectrum we also examined the corresponding methanesulphonate (VIIc) and found the appropriate absorption at 1 740 cm^{-1}. The n.m.r. spectrum (Table) confirms that what were four vinylic methyl groups are now attached to saturated carbon atoms though the exact assignments are necessarily tentative. Photocyclisation also brings about major changes in the mass spectrum. The cyclobutane isomer shows a much greater tendency to sequential loss of carbonyl groups (as CO). On the other hand the loss of the bridging ring B (as trimethyl-quinone as such or in combination with up to two hydrogen atoms) is much reduced in importance, as would be expected. Loss of keten and then the naphthalene segment as a quinone methide as indicated by the wavy line in structure (VII) is a major feature in box trione derivatives though not in the parent bridge trione acetate. We consider that these observations establish the cyclobutane structure in (VIIb) and hence the *endo*-configuration in (IVa).

The present photoaddition (enedione to enone) is intermediate in character between those found in benzoquinone dimerisations[4] (where enedione adds to enedione) and those found in certain quinone–Diels–Alder adducts[5] (enedione adds to ene); but in none of these examples is there an interfering phenolic substituent and in none of them are the interacting systems geometrically skewed. It is therefore not surprising that we have observed neither the unusually high carbonyl stretching frequencies nor the tendency to hydration that characterise some of the products described previously.[5]

A number of other acyl derivatives of the bridge trione (IVa) were studied, but because the photocyclisation had not been recognised at that time the products were unnecessarily mixed. Thus acid-catalysed acetylation of (IVb) gave not only the triacetate (IX) but also the box trione acetate (VIId), and attempts to acetylate the methanesulphonate (IVd) gave not only the acetate (IVe) but also the box trione ester (VIIe). Even from these results, however, there were indications that not all esters were equally subject to photocyclisation. The toluene-4-sulphonate (IVf) of the bridge trione was obtained by the usual esterification in diffuse daylight, whereas a similar benzoylation gave the box trione benzoate (VIIf) as the only purifiable product.

The mulls used for i.r. spectroscopy showed remarkable differences when exposed to daylight. The acetate (IVb) was completely isomerised in a few hours, the methanesulphonate took more than a day, and the toluene-4-sulphonate was relatively resistant. The most surprising difference, however, was between the acetate and the propionate. In solution, the acetate (IVb) and the propionate (IVg) suffer photocyclisation at about the same speed; as films or in mulls, however, cyclisation of the propionate is almost complete in about 15 min, so that it can only be obtained pure in darkness or under the minimum illumination by filtered (yellow) light. We do not know why the esters differ so much, since it is difficult to understand how the additional methylene group can perturb an intramolecular reaction at so distant a site. Crystal lattice phenomena or relative solubilities in the mulling agent might be implicated.

At first the sensitivity of the propionate to light obscured another curious feature. As stated above, acetic anhydride and pyridine esterify the naphthol. In the absence of light, the box acetate is not formed, but a similar reaction with propionic anhydride and pyridine always produces some box trione propionate (VIIg). Pyridine is involved in the cyclisation, because when sodium propionate is the catalytic base the bridge



SCHEME

propionate is not contaminated by the box propionate. Although the result appears to be a thermal [2 + 2] cycloaddition, orbital symmetry considerations exclude that mechanism, and the Scheme suggests a way in which pyridine might initiate Michael reactions providing the desired result in a series of steps. Certainly there

[4] R. O. Kan, 'Organic Photochemistry,' McGraw-Hill, New York, 1966, p. 170; E. H. Gold and D. Ginsberg, *J. Chem. Soc.* (*C*), 1967, 15.

[5] R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 1964, 3062.

are other factors to be clarified. The Scheme does not explain the absence of cyclisation in the course of acetylation, nor does it explain why we have been unable to induce cyclisation in pre-formed bridge esters by any combination of pyridine, propionic acid, and propionic anhydride.

EXPERIMENTAL

I.r. spectra were determined for mulls in paraffin. Mass spectral analyses are supported by accurate mass measurements and, where necessary, identification by metastable ions.

7b,8,11,11a,12,12a-*Hexahydro*-12-*hydroxy*-6,9,10,11a,12a,-14,15-*heptamethyl*-8,11,16-*trioxo*-7H-12,7a-*propenoindeno*-[2,1-b]*naphtho*[2,1-e]*pyran*-5-*yl Chloroacetate* (IVc) (with M. L. Robinson).—The bridge compound (IVa) (0.14 g) was shaken with benzene (2 ml) containing pyridine (1 drop) and chloroacetic anhydride (1.9 g) for 2 h then left for 20 h. After dilution with benzene (20 ml), the mixture was washed with aqueous sodium hydrogen carbonate until free from acids and then washed with water and dried (Na_2SO_4). Removal of the solvent left a gum that crystallised from ethanol giving the *chloroacetate* as tiny needles (0.10 g), m.p. 248—251°, $\nu_{max.}$ 3 500 (OH), 1 750 (ester C:O), and 1 655 cm^{-1} (conj. ring C:O) [Found: C, 67.9; H, 5.6%; M^+, 562 and 564 (Cl isotopes). $C_{32}H_{31}ClO_7$ requires C, 68.2; H, 5.6%; *M*, 562 and 564].

The Box Trione Acetate (VIIb).—The bridge trione acetate (IVb) (50 mg) was deposited from a solution in dichloromethane on the inner surface of a large Pyrex beaker and exposed to window daylight for 2 days. Crystallisation of the product from ethanol gave the ***box acetate*** as feathery needles (30 mg), m.p. 315—316°, $\lambda_{max.}$ 294infl, 300, 314, and 329 nm (log ε 3.55, 3.71, 3.82, and 3.76), $\nu_{max.}$ 3 450 (OH), 1 750 (acetate and cyclopentanone CO), 1 720 and 1 700 (cyclohexanone CO), 1 640, 1 600, and 1 580 (all weak; aromatic), and 770 cm^{-1} (naphthalene CH) (Found: C, 72.5; H, 6.2%; M^+, 528.218 7. $C_{32}H_{32}O_7$ requires C, 72.7; H, 6.1%; *M*, 528.213 9). The most important peaks in the mass spectrum arise after loss of keten from the molecular ion to give a fragment ion *m/e* 486 which then gives further fragment ions at 458 (486 — CO), 334 (486 — trimethylbenzoquinone — H), 151, 152, and 153 (trimethylbenzoquinone + H), 300 (486 — naphthoquinone methide), and 186 [naphthoquinone methide residue, *cf.* (VII)].

Acetylation of the Bridge Trione Acetate (IVb); *the Box Diacetate* (VIId).—(i) A mixture of the bridge trione acetate (IVb) (200 mg), acetic anhydride (4 ml), and sulphuric acid (4 drops) was kept for several hours in dim daylight; it was then poured into ice–water and the solid collected, washed with water, and crystallised from ethanol. As the product was still a mixture, it was repeatedly chromatographed on thick silica plates from ether–light petroleum (1 : 1), and two compounds were obtained pure.

One compound was the *box diacetate* (VIId), which separated (from cyclohexane) as granules (67 mg), m.p. 304—305° (decomp.), $\nu_{max.}$ 1 755 (aryl acetate), 1 745 (alkyl acetate and cyclopentanone), 1 725 and 1 705 (cyclohexanone), and 1 600 cm^{-1} (weak; aromatic) (Found: M^+, 570. $C_{34}H_{34}O_8$ requires *M*, 570). In the mass spectrum the molecular ion loses keten and then acetyl giving peaks at *m/e* 528 and 485 with associated metastable ions. The latter fragment ion loses CO giving a peak at 457; alternatively it loses the naphthoquinone methide residue as indicated in diagram (VII) giving peaks at 333 and 185.

The other compound separated from ethanol giving the *hemiacetal triacetate* (IX) as needles (34 mg), m.p. 288—291°, $\nu_{max.}$ 1 750 (broad and irregular; acetate carbonyl groups), 1 670 (enone CO), 1 600 (weak; aromatic), and 780 cm^{-1} (naphthalene CH) (Found: M^+, 612. $C_{36}H_{36}O_9$ requires *M*, 612). The mass spectrum shows the sequential losses of three keten units, but there is also a strong peak corresponding to *M* — AcOH, unique in this study. The rest of the spectrum shows further losses of keten or CO units, all with appropriate metastable ions.

(ii) The box trione acetate (VIIb) (59 mg) was heated in refluxing acetic anhydride (1 ml) containing two drops of pyridine for 5 h. T.l.c. showed that little change had occurred. However, after removal of the reagents, thick-layer chromatography on silica from ether–benzene (7 : 93) gave the box trione acetate (4 mg), identical with a sample prepared as in (i).

The Bridge Trione Toluene-4-sulphonate (IVf).—The bridge trione (IVa) (300 mg) and toluene-4-sulphonyl chloride (300 mg) were suspended in benzene (15 ml) and pyridine (60 drops) was added. After being heated under reflux for a few minutes the mixture cleared and after another 4 h was cooled and poured into ice–water. The solid product was purified from ethanol containing a little benzene giving the *toluenesulphonate* as a yellow powder (160 mg), m.p. *ca.* 230° (decomp.), $\nu_{max.}$ 3 510 (OH), 1 660 and 1 650sh (eneone and enedione C:O), 1 615 and 1 600 (weak; aromatic, *etc.*), and 745 cm^{-1} (naphthalene CH) (Found: *M*, 640. $C_{37}H_{36}O_8S$ requires *M*, 640). The two major fragmentations upon electron impact were fission of the sulphonate link giving fragment ions *m/e* 485 (M^+ — $C_7H_7SO_2$) and 91 (C_7H_7) and of the bridge ring B giving fragment ions *m/e* 334 (485 — $C_9H_{11}O_2$) and 152 ($C_9H_{12}O_2$). A signal at *m/e* 149 also appears to be associated with loss of the bridge but has not been identified.

The Box Trione Benzoate (VIIf).—The bridge trione (100 mg) was warmed on the steam-bath with benzoyl chloride (5 ml) containing pyridine (2 drops) until dissolution was complete (*ca.* 10 min) and was then kept at room temperature in daylight for 2 h. A solid separated; the mixture was poured into ice–water and the resulting solid collected, washed with water, and dried in air. Benzoic acid was removed by vacuum sublimation and the residue was purified by thick-layer chromatography on silica from benzene containing 5% ethanol. The major band (purple fluorescence) supplied the *benzoate*, which separated from ethanol as needles (36 mg), m.p. 322—324° (decomp.), $\nu_{max.}$(KBr) 3 580 (OH), 1 740sh (cyclopentanone C:O), and 1 728 and 1 717 cm^{-1} (benzoate and cyclohexanone C:O) (Found: M^+, 590. $C_{37}H_{34}O_7$ requires *M*, 590). In the mass spectrometer the parent ion showed sequential collapse giving fragment ions at 485 (M^+ — PhCO), 457 (485 — CO), 439 (457 — H_2O), 411 (439 — CO), and 105 (PhCO). The only other important fission corresponded to collapse of the ion *m/e* 439 into ions 300 and 137 but cannot be explained precisely with the information available.

The Bridge Trione Methanesulphonate (IVd).—A mixture of the bridge trione (IVa) (500 mg), methanesulphonyl chloride (12.5 ml), and pyridine (25 drops) formed a clear solution when kept in the dark for 4 h and was poured into ice–water and left overnight. The resulting solid separated

from light petroleum (b.p. 60—80°) containing a little benzene giving the *methanesulphonate* as yellow crystals (320 mg), m.p. 250—256° (decomp.), $\nu_{max.}$ 3 450 (OH), 1 670sh and 1 665 (enone and enedione CO), 1 620 and 1 600 (weak; aromatic), and 735 cm^{-1} (naphthalene CH) (Found: M^+, 564.181 2. $C_{31}H_{32}O_8S$ requires M, 564.180 4). Mass spectral fragmentation was mainly into fragment ions m/e 485 and 79 ($MeSO_2$), with signals at 152, 335, and 149 characterising the loss of the bridge ring B as in other examples.

The Box Trione Methanesulphonate (VIIc).—Compound (IVd) (50 mg) was deposited as a film from dichloromethane on the surface of a large Pyrex beaker and exposed to window daylight for 4 days. The resulting gum crystallised from ethanol giving the *methanesulphonate* (20 mg), m.p. 302—307° (decomp.), $\nu_{max.}$ 3 500 (OH), 1 740 (cyclopentanone CO), 1 715 and 1 700sh (cyclohexanone CO), 1 600 (weak; aromatic), and 740 cm^{-1} (aromatic CH) (Found: M^+, 564. $C_{31}H_{32}O_8S$ requires M, 564). After initial ejection of the methanesulphonyl group leaving a fragment ion m/e 485, the mass spectral collapse is characterised by sequential loss of three CO units giving peaks at 457, 429, and 411. Major peaks at m/e 186 and 187 correspond to the naphthoquinone methide, loss of which converts the ion at 411 into one at 235. A number of peaks fall into pairs differing by 136 m.u., and an important peak appears at m/e 137; its identity is uncertain.

Acetylation of the Bridge Trione Methanesulphonate (IVd); *the Acetate Methanesulphonates* (IVe) *and* (VIIe).—The bridge methanesulphonate (IVd) (135 mg) was powdered finely, suspended in acetic anhydride (3 ml) containing sulphuric acid (3 drops), and left for 4 h. The mixture was poured into water and after 1 h the products were collected into dichloromethane and chromatographed on thick silica plates from benzene containing a little ethanol. Two main bands resulted. One contained the *bridge trione acetate methanesulphonate* (IVe), which crystallised from ethanol as yellow prisms, m.p. 249—250°, $\nu_{max.}$ 1 750 (acetate), 1 675 and 1 670sh (enone and enedione CO), 1 600 (weak; aromatic), and 735 cm^{-1} (naphthalene CH) (Found: M^+, 606. $C_{33}H_{34}O_9S$ requires M, 606). In the mass spectrometer the molecular ion can lose 42 m.u. (keten) at once, but the main fragmentation ejects the sulphonyl residue first giving an ion at m/e 527 which then loses 42 m.u. The resulting fragment ion at 485 gives further ions at m/e 335 (by loss of ring B) and 467 (by loss of H_2O). An important peak at 441 has not been accounted for.

The second band contained *box trione acetate methanesulphonate* (VIIe) which separated from ethanol as granules that decomposed without melting at about 230° in a sealed tube and had $\nu_{max.}$ 1 745 (acetate and cyclopentanone CO), 1 725 (cyclohexanone), and 1 600 and 735 cm^{-1} (naphthalene) (Found: M^+, 606.191 0. $C_{33}H_{34}O_9S$ requires M, 606.192 1). The same compound was formed in traces by the prolonged action of acetic anhydride in the presence of pyridine instead of sulphuric acid.

The Bridge Trione Propionate (IVg).—This experiment was conducted in darkness, with the use of a dim yellow safelight only when absolutely essential. A mixture of the bridge trione (IVa) (300 mg), propionic anhydride (7 ml), and sodium propionate (10 mg) was warmed until a clear solution resulted. After 4 h at room temperature, the solution was poured onto ice and the solid formed was purified from benzene giving the *bridge propionate* as light yellow needles (300 mg; stored with exclusion of light), m.p. 155—156°, $\nu_{max.}$ 3 475 (OH), 1 750sh and 1 660 (enone and enedione), 1 620 and 1 600 (aromatic and ene), and 780 cm^{-1} (naphthalene CH) (Found: C, 73.1; H, 6.3%; M^+, 542. $C_{33}H_{34}O_7$ requires C, 73.1; H, 6.3%; M, 542).

The Box Trione Propionate (VIIg).—The propionate (IVg) (100 mg) in chloroform (1 ml) in a sealed tube was exposed to window daylight for 2 days. The product separated from ethanol giving the *box propionate* as needles (92 mg), m.p. 325—327° (decomp.), $\nu_{max.}$ 3 500 (OH), 1 740 (ester and cyclopentanone), 1 720 and 1 700 (cyclohexanone), 1 640, 1 600, and 1 580 (aromatic and ene), and 780 cm^{-1} (naphthalene) (Found: M^+, 542.233 0. $C_{33}H_{34}O_7$ requires M, 542.230 2). In the mass spectrometer, loss of the propionyl residue leaves a fragment ion m/e 485 which then gives further ions at 457 (by loss of CO), 334 (by loss of trimethyl-quinone), and 300 (by loss of the naphthoquinone methide residue), along with a fragment ion at m/e 186 (the naphthoquinone methide residue itself).

Esterifications with Pyridine Catalyst.—In complete darkness, the bridge trione (IVa) (100 mg) was warmed with propionic anhydride (5 ml) containing pyridine until a clear solution was obtained (*ca.* 5 min) and then left in a dark room at ambient temperature for 4 h. Added to ice, the product gave a solid shown by t.l.c. and spectroscopy to be a mixture of bridge and box propionates. A parallel experiment with sodium acetate instead of pyridine showed no formation of box propionate. The bridge and box isomers were separated on thick silica plates with benzene–ethanol (95 : 5) for development. The box isomer was readily obtained pure [25 mg; m.p. 325° (decomp.)] but the bridge isomer fraction still contained some box, probably because too much light had to be admitted while we were detaching the requisite bands, *etc.*

Relative Rates of Cyclisation.—(i) *In chloroform.* Similar solutions (5%) of the bridge trione propionate and acetate in chloroform were placed in i.r. cells (1 mm; NaCl) and exposed to light from a tungsten lamp (200 W; water-cooled). Determination of the i.r. spectra at intervals showed conversions at parallel rates into the box esters, the reaction being almost complete in about 8 h.

(ii) *In mulls.* Similar mulls of the bridge acetate and bridge propionate were prepared for i.r. spectroscopy, and exposed in some experiments to window daylight and in others to a quartz–iodine lamp (60 W) at a distance of 16 cm. Determined at intervals, the i.r. spectra showed that cyclisation of the propionate to the box isomer was complete at about 20 min, at which point the cyclisation of the bridge isomer was only about 10% complete.

(iii) *With phenol.* The bridge trione propionate (20 mg) in chloroform (2 ml) was exposed to daylight or to a tungsten lamp (200 W; water-cooled), at a distance of 20 cm alongside a second similar solution to which phenol (40 mg) had been added. After 8 h t.l.c. and spectroscopy showed that in the first solution cyclisation was virtually complete whereas in that containing phenol there had been hardly any change. The acetate behaved similarly.

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