# Ene Reactions of Indane-1,2,3-trione (a Super-enophile) and Related Vicinal Tricarbonyl Systems

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Indane-1,2,3-trione **1** is conveniently prepared in quantitative yield by the azeotropic drying of ninhydrin **2** using chlorobenzene as solvent. The central C=O group of the trione is extremely electrophilic and ene addition occurs at this site with a wide range of alkenes and with terminal alkynes in aprotic solvents at moderate temperatures (70–130 °C). The reactivity of trione **1** is somewhat attenuated by the solvent, and the ene additions are consistently faster in chloroform than in tetrahydrofuran. Stereoselectivity, when relevant, appears largely to be dictated by steric factors. Regiochemical control can be exercised if the ene contains two reaction sites. Isoprene and 2,4-dimethylpenta-1,3-diene, however, react by Diels–Alder rather than by ene addition; the adducts are the expected regioisomers **18** and **20**, respectively. Attempts to catalyse the ene reactions with Lewis acids were unsuccessful. The analogous ene reactions of 4,4,5,5-tetramethylcyclopentane-1,2,3-trione **44**, 4,4,6,6-tetramethylcyclohexane-1,2,3-trione **45**, and 2,2-dimethyl-1,3-dioxane-4,5,6-trione ('oxo-Meldrum's acid') **46** were also briefly investigated.

Ene reactions[1] may be regarded as the central members of a pericyclic series of intermolecular reactions that ranges from the well known Diels–Alder reactions at one extreme to the relatively rare homogeneous hydrogen transfers at the other. In comparison with Diels–Alder processes, ene reactions are more difficult to promote as they are attended by less favourable stereoelectronic factors (*e.g.*, a larger HOMO–LUMO gap, lower charge-transfer contribution, larger steric effects and poorer orbital overlap) and activation energies are likely to be greater in consequence of the necessary cleavage of an allylic C–H σ-bond instead of a conjugated π-bond.

The enophile is generally the electron acceptor, and reactive species possess a low LUMO energy. When the reaction site lacks symmetry (as in $R^3R^4C{=}X$, X = electronegative atom) then the LUMO orbital possesses a large coefficient at the carbon atom and a small coefficient at the X atom. The ene component is the electron donor and, apart from an allylic H-atom, needs to have a high HOMO energy. 1,1-Dialkylethylenes are among the most reactive enes; β-pinene is especially reactive since the C(3)-H σ-bond *anti* to the $CMe_2$ bridge is co-parallel with the adjacent p-π orbitals, an essential feature for concerted reaction. The HOMO orbitals of these olefins possess a large coefficient at the unsubstituted carbon atom of the C=C and a small coefficient at the other carbon. Hence, transition states for ene reactions are often likely to be highly unsymmetrical with C–C bonding being more advanced than X–H bonding (Fig. 1). Even in a concerted process the transition state may possess appreciable dipolar or diradical character and, in some cases, it is clear that stepwise mechanisms are involved.[1,2]

There is generally more scope for reducing enophile LUMO energies than for increasing ene HOMO energies. Hence, the attachment of electron-withdrawing groups to the reactive C=X bond in the enophile is beneficial, but much larger effects accrue from the use of enophiles X=Y where both X and Y are electronegative heteroatoms (*e.g.*, O and N), such as in singlet oxygen[3] and in acylnitroso compounds[4] which are highly reactive enophiles. The much lower p-orbital energies of these atoms appreciably reduces the LUMO energy of X=Y. A reduction in strain as a consequence of the ene addition can also greatly accelerate the reactions (*e.g.*, benzyne[5] and hexafluorocyclobutanone[6] are both powerful enophiles). The reaction of hexafluorocyclobutanone benefits from the $sp^2 \rightarrow sp^3$ change at the reaction centre and other aldehydes and

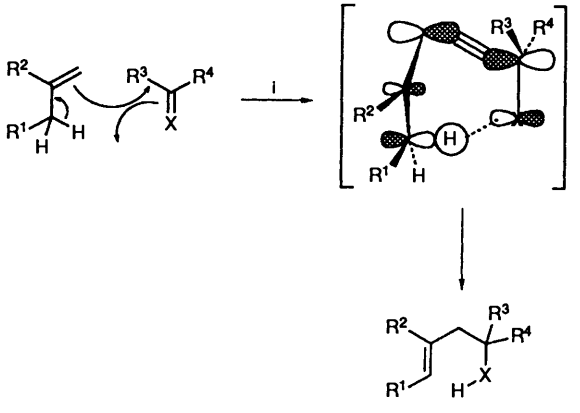
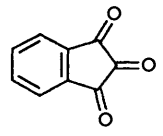



**Fig. 1** i, heat

ketones that form stable hydrates also show enhanced reactivity. The catalysis of ene reactions by Lewis acids[2,7] has also proven to be of benefit in certain cases where the enophile is of only moderate reactivity. It is necessary for the Lewis acid to co-ordinate an electron pair close to the reaction site in order to affect the LUMO energy significantly; such sites, for example, are available in chloral[7] and in acrylate esters.[8]

In the continuation of our studies of carbonyl compounds as potential enophiles,[7,9] we became interested in vicinal tricarbonyl systems. All such systems form stable hydrates through the addition of water to the central C=O, hence they should all show enhanced enophile reactivity. Indeed, Salomon, Pardo and Salomon[10] have reported on the thermal and Lewis acid-catalysed ene reactions of diethyl oxomalonate which proved to be a fairly reactive molecule. We reasoned that reactivity would be further enhanced if the central C=O were flanked by two keto-carbonyl groups rather than by ester-carbonyl groups, and would be maximised in cyclic 1,2,3-triketones if the three C=O groups were coplanar. Indane-1,2,3-trione **1** was chosen as a suitable, readily available model for these studies.†

† Related work on the enophiles alloxan and *N*,*N*-dimethylalloxan will be published separately.



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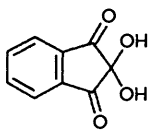

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## Results and Discussion

*Preparation of Indane*-1,2,3-*trione*.—We found Schonberg and Moubacher's method[11] (ninhydrin **2** in a large excess of boiling $SOCl_2$) gave the trione **1** in high yield, but it is contaminated with traces of acidic impurities which are difficult to remove. The procedure is wasteful since the thionyl dichloride has to be carefully redistilled before it can be re-used satisfactorily; a second re-cycle is generally not practicable. The sublimative dehydration of ninhydrin **2** (140 °C/1 mmHg)[12] is slow and tends to produce thin, needle-like crystals of **1** which are extremely sensitive to moisture, reverting to ninhydrin **2**. Solutions of ninhydrin **2** are slowly dehydrated to give the trione **1** when kept over molecular sieves.[13] Unfortunately, both compounds have a very low solubility in simple, volatile aprotic solvents at room temperature. Hence it is difficult to prepare the trione in quantity by any of these routes.

Although we achieved some success with chemical dehydration [*e.g.*, **2**, $Ac_2O$, and catalytic $CF_3CO_2H$ (TFA) in boiling chloroform], the simple expedient of azeotropic drying (toluene or, preferably, chlorobenzene as solvent) proved to be the method of choice since high quality indane-1,2,3-trione **1** was obtained rapidly in essentially quantitative yield. The crystals were prismatic and could be stored in a simple plastic stoppered vial without deterioration for several weeks, recovered solvent could be recycled several times without detriment and reasonable quantities of the trione could be prepared (see Experimental section).

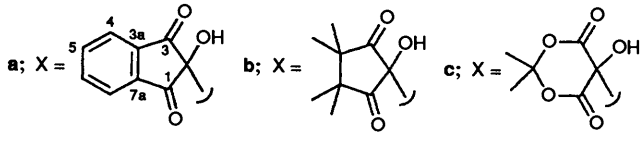
*Procedures*.—On the basis of the present and our previous[7] studies, we have shown that enes may be placed in the following 'reactivity series': **Type 1** $RCH_2C(R^1)=CH_2 \geq RCH_2C(R^1)=CHR^2$ > **Type 2** $RCH_2CH=CH_2$ > **Type 3** $RCH_2CH=CH-CH_2R^1 \geq$ **Type 4** $RCH_2C\equiv CH$ > **Type 5** $ZCH_2CH=CH_2 \geq RCH_2C(Z)=CH_2$, where R is hydrogen, alkyl or aryl, $R^1$ is alkyl or aryl, $R^2$ is alkyl and Z an electron-withdrawing group. Our previous results had indicated an *approximate* order of magnitude fall in reactivity between adjacent members as this series is traversed.

For reactive enes of higher b.p. than that of toluene or chlorobenzene, the dehydration of ninhydrin *2* and the ene reaction were conducted as a tandem one-pot procedure in a simple reflux apparatus (General Method A). Volatile enes, or those of low reactivity, were heated with pre-formed indane-1,2,3-trione **1** in dry solvent (*e.g.*, ethanol-free $CHCl_3$) in heavy-walled Schlenk tubes[14] (General Method B). In both cases progress of the reactions was monitored by the fading of the coloured indanetrione solutions (green in PhMe, PhCl or $CHCl_3$, red in THF); the reactions were deemed complete when fading to colourless, pale yellow or pale brown had been reached. Since the processes are bimolecular reaction rates, of course, are dependent on reactant concentrations; however, there is a pronounced solvent effect (see below). The results are summarised in Table 1.

*Type* 1 *Enes*.—Typical examples are given in entries 1–9 of Table 1. The hindered olefin 2,3,3-trimethylbut-1-ene (entry 6) undoubtedly gave the ene adduct **8a** (from analysis of the $^1H$ NMR spectrum) as the major component of a mixture which could not be separated. The other component(s) appeared to be of substantially higher molecular mass by mass spectrometry. 1-Methylcyclohexene also reacted with indanetrione, but the mixture of products obtained could not be separated. The reaction of β-pinene was especially clean and rapid; even at 70 °C the colour of the trione was discharged within 20 min when initial reactant concentrations were reasonably high. The crude adducts (**3a–9a**, **11a–13a**) were generally obtained in essentially quantitative yields, and purification was effected by simple crystallisation. Structural assignments are in accord with the analytical and spectroscopic data.

The $^1H$ and $^{13}C$ NMR spectra of the β-pinene adduct **3a** are interesting since they both indicate that an appreciable stereoelectronic interaction exists in solution between the pinene and 2-hydroxyindane-1,3-dione moieties. Particularly notable is the appreciable shielding ($\delta_H$ 0.12, d) of the pinene 7-$H^a$ by both the pinene π-bond and the aromatic ring (*i.e.*, 7-$H^a$ is *syn* to the double bond, 7-$H^b$ is *anti* to the double bond). Molecular models indicate approximate 90° dihedral angles for $H^{7a}$–C–C–$H^1$ and $H^{7a}$–C–C–$H^5$, and the observed splitting of 8.7 Hz therefore is the two-bond coupling with 7-$H^b$.

(−)-Carvone (entry 4) reacted entirely at the more nucleophilic exocyclic π-bond to give adduct **6a** resulting from the preferential transfer of an allylic H-atom from the primary ($CH_3$) site. However, 2-methylbut-1-ene (entry 7) gave a 75:25 mixture of double-bond isomers **12a**:**9a**, indicating preferential transfer of H from the secondary allylic site. (*E*)-3-Methylpent-2-ene (entry 8) was more reactive than the *Z*-isomer. The *E*-olefin afforded only adduct **13a**, indicating preferential H-transfer from the (secondary) allylic site which is *syn* to the vinylic H, whereas the *Z*-olefin afforded a 30:70 mixture of isomers **13a**:**11a**; H-transfer therefore occurred predominantly from the (primary) allylic site *syn* to the vinylic H.



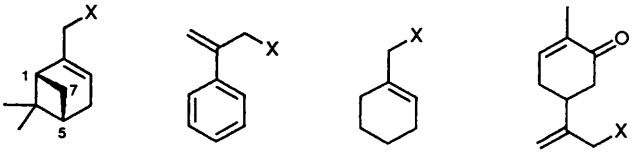
**a**; X =



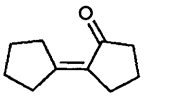
**b**; X =



**c**; X =



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



**7**; R = Me, $R^1$ = H
**8**; R = Bu$^t$, $R^1$ = H
**9**; R = Et, $R^1$ = H
**10**; R = OAc, $R^1$ = H
**11**; R = Et, $R^1$ = Me

**12**; R = H
**13**; R = Me

**14**

The differences in reactivity and regioselectivity are probably a result of steric factors. The lack of rearrangement products characteristic of carbonium ion or radical processes implies concerted mechanisms for the ene reactions of these olefins. On this basis, the two approach topologies for the reactions of 2-methylbut-1-ene and (*E*)- and (*Z*)-3-methylpent-2-ene are indicated in Fig. 2. Molecular models indicate that the major steric interactions (in decreasing order of importance) appear to be: (i) between C-1 and any underlying alkyl group of the olefin (*i.e.*, $R_b$ or $R_a$), (ii) between the C-3/C-3a/C-4 unit and any underlying alkyl group of the olefin (*i.e.*, $R_a$ or $R_b$) and (iii)

**Table 1** Ene addition reactions of indane-1,2,3-trione **1**

| Entry | Ene | Adduct | Method ($T$ °C/$t$/h) | Recryst. solvent[a] | Yield (%) | M.p. (°C) | Found (%) C | Found (%) H | Requires (%) C | Requires (%) H | Formula* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | β-Pinene | **3a** | A2 (80/0.3) | He | 94 | 82–83 | 76.9 | 6.8 | 77.0 | 6.8 | $C_{19}H_{20}O_3$ |
| 2 | α-Methylstyrene | **4a** | A2 (110/6) | He, Ca | 75 | 148–150 | 78.0 | 5.3 | 77.7 | 5.1 | $C_{18}H_{14}O_3$ |
| 3 | Methylenecyclohexane | **5a** | A2 (110/6) | P-E | 90 | 134–135 | 75.0 | 6.3 | 75.0 | 6.3 | $C_{16}H_{16}O_3$ |
| 4 | (−)-Carvone | **6a** | A2 (110/7) | Ch | 74 | 162–163 | 73.9 | 6.0 | 73.5 | 5.85 | $C_{19}H_{18}O_4$ |
| 5 | 2-Methylpropene | **7a** | B1 (80/2) | Ca | 92 | 116–117 | 72.1 | 5.6 | 72.2 | 5.6 | $C_{13}H_{12}O_3$ |
| 6 | 2,3,3-Trimethylbut-1-ene | **8a** + ? | B1 (80/21) | P-E | 39[b] | 225–226 | | | | | |
| 7 | 2-Methylbut-1-ene | **9a** + **12a** | B1 (80/4) | P-E | 68[b] | 102–103 | 73.2 | 6.4 | 73.0 | 6.1 | $C_{14}H_{14}O_3$ |
| 8 | (*E*)-3-Methylpent-2-ene | **13a** | B1 (80/6) | P-E | 94 | 109–110 | 73.95 | 7.0 | 73.75 | 6.6 | $C_{15}H_{16}O_3$ |
| 9 | (*Z*)-3-Methylpent-2-ene | **11a** + **13a** | B1 (80/9) | P-E | 91[b] | 208–209 | 73.8 | 6.7 | 73.75 | 6.6 | $C_{15}H_{16}O_3$ |
| 10 | 3-Methylbut-1-ene | **21a** | B1 (80/5) | P-E | 71 | 84–86 | 72.9 | 6.4 | 73.0 | 6.1 | $C_{14}H_{14}O_3$ |
| 11 | Hex-1-ene | **22a** | B1 (80/4) | He, Ca | 93[c] | 47–48 | 74.0 | 6.5 | 73.75 | 6.6 | $C_{15}H_{16}O_3$ |
| 12 | Hept-1-ene | **23a** | A2 (110/24) | *d* | 90[c] | oil | * | * | * | * | $C_{16}H_{18}O_3$ |
| 13 | Oct-1-ene | **24a** | A2 (110/24) | *d* | 92[c] | oil | * | * | * | * | $C_{17}H_{20}O_3$ |
| 14 | Octa-1,7-diene | **25a** | A2 (110/7) | *d* | 82[c] | oil | * | * | * | * | $C_{17}H_{18}O_3$ |
| 15 | Methyl undec-10-enoate | **26a** | A2 (110/11) | *d* | 83[c] | oil | 70.4 | 7.4 | 70.4 | 7.3 | $C_{21}H_{26}O_5$ |
| 16 | Ethyl nona-3,8-dienoate | **27a** | B1 (80/24) | *d* | 60[c] | oil | * | * | * | * | $C_{20}H_{22}O_5$ |
| 17 | Allylbenzene | **28a** | A2 (110/7) | P-E | 77[c] | 124–125 | 77.8 | 5.3 | 77.7 | 5.1 | $C_{18}H_{14}O_3$ |
| 18 | Allyltrimethylsilane | **29a** | A2 (110/2) | P-E | 76[c] | 92–93 | 66.0 | 6.9 | 65.7 | 6.6 | $C_{15}H_{18}O_3Si$ |
| 19 | Hex-5-en-2-one | **33a** | A2 (110/8) | chrom.[e] | 34[c] | oil | 69.4 | 5.6 | 69.8 | 5.5 | $C_{15}H_{14}O_4$ |
| | | **34a** | | | 10[f] | oil | | | 69.8 | 5.5 | $C_{15}H_{14}O_4$ |
| 20 | Cyclopentene | **36a** | B1 (100/16) | Ca | 75 | 104–105 | 73.6 | 5.3 | 73.7 | 5.3 | $C_{14}H_{12}O_3$ |
| 21 | Cyclohexene | **37a** | B1 (100/16) | Ca | 84 | 120–121 | 74.4 | 5.9 | 74.4 | 5.8 | $C_{15}H_{14}O_3$ |
| 22 | Cycloheptene | **38a** | A2 (110/48) | *d* | 63 | oil | * | * | * | * | $C_{16}H_{16}O_3$ |
| 23 | Cyclooctene | **39a** | A2 (110/48) | Ca | 72 | 118–120 | 75.7 | 6.9 | 75.5 | 6.7 | $C_{17}H_{18}O_3$ |
| 24 | Hex-1-yne | **40a** | B1 (80/26) | He | 58 | 64–65 | 74.2 | 5.9 | 74.4 | 5.8 | $C_{15}H_{14}O_3$ |
| 25 | Octa-1,7-diyne | **41a** | A2 (110/23) | P-E | 62 | 74–75 | 76.5 | 5.5 | 76.7 | 5.3 | $C_{17}H_{14}O_3$ |
| 26 | Benzyl pent-4-ynoate | **42a** | A2 (110/144) | chrom.[e] | 49 | oil | * | * | * | * | $C_{21}H_{16}O_5$ |
| 27 | Pent-4-ynyl *p*-nitrobenzoate | **43a** | A2 (110/120) | chrom.[e] | 56 | oil | | | 64.1 | 3.8 | $C_{21}H_{15}NO_7$ |
| 28 | Isopropenyl acetate | **10a** | B1 (105/48) | Ca | 50 | 117–118 | 64.4 | 4.7 | 64.6 | 4.65 | $C_{14}H_{12}O_5$ |
| 29 | Allyl cyanide | **30a** | A2 (110/72) | E | 66[c] | 128–129 | 68.55 | 4.15 | 68.7 | 4.0 | $C_{13}H_9NO_3$ |
| 30 | Methyl but-3-enoate | **31a** | A2 (110/120) | E | 45[c] | 104–105 | 64.6 | 4.7 | 64.6 | 4.65 | $C_{14}H_{12}O_5$ |
| 31 | Allyl phenyl ether | **32a** | A2 (110/72) | P-E | 73[c] | 128–129 | 73.7 | 5.1 | 73.5 | 4.8 | $C_{18}H_{14}O_4$ |

* Electron impact *m/z*: Found (M requires): **3a** 296.1409 (296.1412); **4a** 278.0927 (278.0943); **6a** 310.1166 (310.1205); **7a** 216.0823 (216.0786); **13a** 244.1114 (244.1099); **11a** + **13a** 244.1097 (244.1099); **22a** 244.1073 (244.1099); **23a** 258.1251 (258.1256); **24a** 272.1411 (272.1412); **25a** 270.1250 (270.1256); **27a** 342.1462 (342.1467); **28a** 278.0963 (278.0943); **29a** 274.1013 (274.1025); **30a** 227.0602 (227.0582); **31a** 260.0692 (260.0685); **32a** 294.0872 (294.0892); **33a** 258.0885 (258.0892); **38a** 256.1097 (256.1099); **40a** 242.0919 (242.0943); **41a** 266.0958 (266.0943); **42a** 348.0983 (348.0998).
[a] Solvents: He = hexane, Ca = carbon tetrachloride, Ch = chloroform, E = diethyl ether, P-E = light petroleum (60–80 °C)–diethyl ether. [b] Mixture of compounds which could not be separated; see text for isomer ratios. [c] Mixture of stereoisomers; the following ratios were obtained for the crude (unpartitioned) product mixtures from the average of $^1H$ and $^{13}C$ NMR analyses (excluding C atoms with long relaxation times). Values given are in the sense *E*:*Z*. **22a** 81.0:19.0; **24a** 80.0:20.0; **28a** and **31a** > 95: < 5 (*Z*-isomer not detected); **29a** 65.5:34.5; **30a** 70.0:30.0; **32a** 64.5:35.5. [d] These oils were purified by dissolution of the crude adduct in hexane; the impurities were hexane-insoluble. The solvent was then removed under reduced pressure. The adducts decompose upon attempted distillation under reduced pressure. [e] Chromatography over flash silica gel. Solvent: chloroform–ethyl acetate (9:1). [f] Appreciable loss of material and contamination occurs on chromatography owing to retro-aldol cleavage; the true chemical yield is nearer 65%.

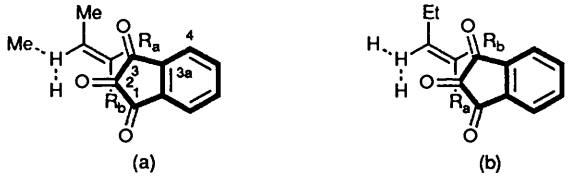



**Fig. 2**

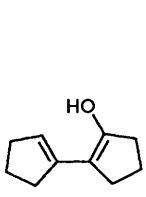
between the C-3 carbonyl oxygen atom and the underlying alkyl group of the olefin (*i.e.*, Me or Et). For 2-methylbut-1-ene ($R_a$ = $R_b$ = H) steric factors (i) and (ii) are more or less identical in approach geometries (a) and (b), Fig. 2, and the difference lies in factor (iii). This leads to the conclusion that topology (a) should be favoured, and that H-transfer should occur preferentially—as observed—from the secondary allylic site.

In the case of (*E*)-3-methylpent-2-ene ($R_a$ = Me, $R_b$ = H) steric factors (i) and (iii) are minimised in topology (a) and, again, predominent transfer of the H-atom from the secondary allylic site is expected—as observed. For (*Z*)-3-methylpent-2-ene ($R_a$ = H, $R_b$ = Me) it is more difficult to see a clear distinction between (a) and (b) [*i.e.* (i) + smaller (iii) in (a) *versus* (ii) + larger (iii) in (b)], although approach topology (b) should be favoured. Indeed, preferential H-transfer was observed to occur from the primary allylic site.

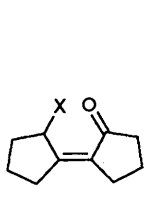
In the reaction of (−)-carvone the exclusive H-transfer from the primary allylic site to give adduct **6a** contradicts the model given in Fig. 2. However, H-transfer from the tertiary allylic site, and consequent movement of the double bond to form an alkylidenecyclohexane, may be disfavoured by an increase in strain.

The reaction of 2-cyclopentylidenecyclopentanone **14**, an electron-deficient tetrasubstituted ethylene, with indanetrione was extremely rapid. It is clear that the product (**16**; stereochemistry unknown) arises from reaction of the enol **15**, the keto–enol equilibrium probably being catalysed by ninhydrin. Diels–Alder addition to the trione would give spiro pentacycle **17**, the hemiketal form of enone **16**, which therefore should possess the *Z*-stereochemistry shown. However, a stepwise electrophilic addition process cannot be ruled out, and hence the product could possess the *E*-stereochemistry.

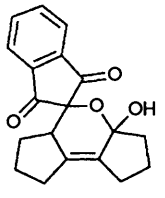
We found previously in studies of Lewis acid-activated chloral that isoprene in part reacted as a Type 1 ene and in part as a Diels–Alder diene.[7] In the thermal addition to trione **1**, however, only a ~14:1 mixture of the two Diels–Alder adducts **18** and **19** was formed. Frontier orbital theory predicts a kinetic preference for the formation of isomer **18**. Analysis of the $^1$H NMR spectra obtained from selective decoupling experiments indicated that the major product had structure **18**, in accord with a previous conclusion.[15] The regiochemistry of the Diels–Alder addition has been more rigorously proven for the closely related reaction of isoprene with *N*,*N*-dimethylalloxan.* 2,4-Dimethylpenta-1,3-diene likewise afforded only a Diels–Alder addition product with trione **1**, the reaction being completely regiospecific. Structure **20** follows from the chemical shift of the



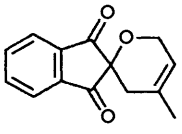
**15**



**16**



**17**



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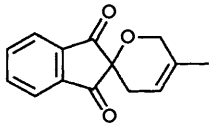

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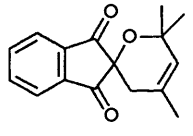
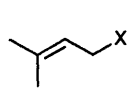
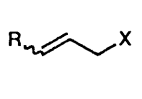
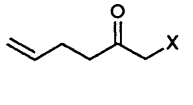


**20**



**21**





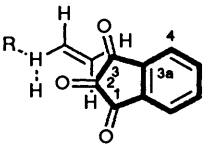
**34**

**22**; R = Pr
**23**; R = Bu
**24**; R = $C_5H_{11}$
**25**; R = $[CH_2]_3CH{=}CH_2$
**26**; R = $[CH_2]_7CO_2Me$
**27**; R = $[CH_2]_2CH{=}CHCH_2CO_2Et$
**28**; R = Ph
**29**; R = $SiMe_3$
**30**; R = CN
**31**; R = $CO_2Me$
**32**; R = OPh
**33**; R = $CH_2COMe$

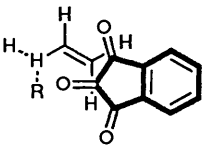
$CH_2$ group ($\delta_H$ 2.23, s). The green solutions of trione **1** in toluene changed immediately to purple on addition of either anthracene or 9,10-dimethylanthracene, indicating appreciable charge-transfer interactions.[12] However, the purple colourations were not discharged during 2 days at the reflux temperature, and starting materials were recovered unchanged.

*Type* 2 *Enes.*—Simple terminal alkenes (Table 1, entries 10–13) all reacted with remarkable ease to give adducts **21a–24a**. The presence of a remote C=C or ester function had little effect on the rate of the addition either singly (entries 14, 15) or in combination (entry 16). Likewise, substitution at the allylic site by phenyl or trimethylsilyl (entries 17, 18), had no deleterious effect on the rate. Hence, all of these olefins should be regarded as Type 2 enes. Hex-5-en-2-one (entry 19) which is also in this category afforded, quantitatively, a mixture of adducts; the $^1$H NMR spectrum indicated an approximate 1:2 ratio of **33a**:**34a**.

* Related work on the enophiles alloxan and *N*,*N*-dimethylalloxan will be published separately.



(a)

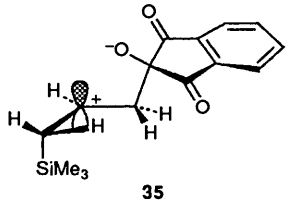


(b)

**Fig. 3**

The latter presumably arose from the attack on trione **1** by the enol –CH=C(OH)–, and the former from ene addition of **1** to the $-CH{=}CH_2$ bond. Reaction with the enol (a high-energy π-HOMO) could occur by a concerted pericyclic mechanism with H-transfer from the 'allylic' O-atom, but a stepwise electrophilic addition/proton-transfer mechanism cannot be discounted. The production of adduct **34a** is presumably limited by the rate of formation of the enol. This adduct is labile (retro-aldol cleavage), and heavy losses occurred during purification.

The products of the alk-1-ene reactions are generally *E*:*Z* mixtures with compositions varying from ~ >95:<5 to 65.5:34.5, depending on the nature of the substitution at the allylic site (see Table 1 footnotes). Assuming concerted reaction, suitable modification of the above steric model results in the two approach topologies shown in Fig. 3. The allylic substituent R can be placed either in the W-type conformation (a), or in the more congested U-type conformation (b). Topology (a) should be favoured, and the *E*-adducts should predominate. For the hydrocarbons (*i.e.*, R = Pr, n-$C_5H_{11}$ and Ph) there is indeed a strong bias towards the *E*-isomer (*i.e.*, 6.4–19:1). However, the *E*-bias should be very pronounced for the bulky trimethylsilyl substituent (R = $SiMe_3$), whereas it falls to 1.9:1. Similar loss of stereoselectivity was found in the case of the less reactive Type 5 alk-1-enes discussed below. Since we were unable to secure a pure sample of, for example, either *E*-**29a** or *Z*-**29a**, the possibility of *E*/*Z* equilibration under the reaction conditions cannot be ruled out. If equilibration is not responsible for the loss in stereoselectivity, then the concerted mechanism of some of these ene reactions is open to question. With allyltrimethylsilane (R = $SiMe_3$), for example, the reaction could proceed *via* the zwitterionic intermediate **35** in which the carbocationic centre at C-2 of the olefin is stabilised by electron donation from the C–Si bond. The collapse of this intermediate to products requires a 60° rotation about C-2/C-3, and hence could generate both the *E*- and *Z*-adducts.



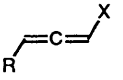
**35**

*Type* 3 *Enes.*—Simple cycloalkenes (Table 1, entries 20–23) were chosen as convenient representatives of this class. All were appreciably less reactive than the above alk-1-enes, but good yields of adducts **36a–39a** were obtained. Cycloocta-1,5-diene, however, afforded only a complex mixture of products.

It is our experience that with enophiles of moderate reactivity, the Type 3 enes usually mark the limits for successful reaction.

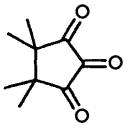
*Type* 4 *Enes.*—By the appropriate choice of reaction conditions the addition of hex-1-yne could be accomplished in *ca.* 24 h (Table 1, entry 24). The rather unpromising, dark-coloured reaction solution afforded colourless crystalline adduct **40a** in reasonable yield after the standard work-up. The

IR spectrum (1960 $cm^{-1}$) and the $^{13}C$ spectrum ($\delta_C$ 197.0 ppm) clearly establish the presence of the allene unit. Octa-1,7-diyne (entry 25) reacted with trione **1** at a similar rate to give adduct **41a**. Remote substitution relative to the $HC{\equiv}CCH_2$ unit (entries 26, 27) led to a sharp decrease in the rate of the ene addition. However, prolonged contact (*i.e.*, 5–6 days) gave the adducts, respectively **42a** and **43a**, in fair yield after chromatographic purification of the resulting dark oils.

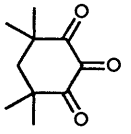


**36**; R = $CH_2$
**37**; R = $[CH_2]_2$
**38**; R = $[CH_2]_3$
**39**; R = $[CH_2]_4$

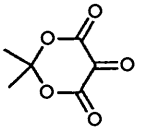
**40**; R = Pr
**41**; R = $[CH_2]_3C{\equiv}CH$
**42**; R = $CH_2CO_2CH_2Ph$
**43**; R = $[CH_2]_2OCOC_6H_4NO_2$-*p*



**44**



**45**



**46**

*Type* 5 *Enes.*—We had anticipated that the limits of reactivity had been reached with the Type 4 enes, but nevertheless decided to investigate a number of representatives of the Type 5 class since ene additions to such systems have been achieved very rarely. Indeed, allyl bromide, methacrylonitrile and methyl methacrylate all proved to be unreactive towards trione **1** under relatively forcing conditions (*e.g.*, 110 °C/7 days). In view of the failure with allyl bromide, it was surprising to find that allyl cyanide, methyl but-3-enoate and allyl phenyl ether (Table 1, entries 29–31) all afforded ene adducts, respectively **30a**–**32a**, in moderate to good yield (100 °C/3–5 days). The products are mixtures of *E*- and *Z*-isomers, and analysis of the NMR spectra indicated a bias towards the *E*-adducts of 2.3 : 1 for allyl cyanide, > 19 : 1 for methyl but-3-enoate (*i.e.*, *Z*-isomer not detected) and 1.8 : 1 for allyl phenyl ether. It is difficult to account for all of these observations in terms of the concerted addition pictured in Fig. 3. The low steric requirement of the C≡N group might make the approach topology (b) rather more favourable, leading to an increase in the *Z*/*E* ratio, but the greater bulk of the OPh group rules out a similar consideration in the case of allyl phenyl ether. Although equilibration or non-concerted addition (*cf.* **35**) remain as distinct possibilities, it is difficult in those terms to reconcile the differences between allyl cyanide and methyl but-3-enoate in which electronic effects should be similar.

Isopropenyl acetate (Table 1, entry 28) could be regarded as a Type 1 ene (R = H, $R^1$ = OAc) or a Type 5 ene (R = H, Z = OAc), depending on the nature of the electronic interaction between the O atom and the C=C. Its reactivity towards trione **1** proved to be somewhat intermediate between these two extremes. The adduct **10a** was isolated in fair yield by crystallisation. As expected of an enol ester, adduct **10a** is relatively labile and in some preparations a yellow residual material remained after the crystallisation. This residue contained three compounds (by TLC analysis) which were not identified.

The successful reaction of trione **1** with at least some of the Type 5 enes leads to our conclusion that indane-1,2,3-trione should be regarded as a super-enophile.

*Effect of Solvent on Reaction Rate.*—The results summarised in Table 1 hide the large reactivity differences among the Type 1–5 enes. It was discovered at a fairly late stage of these studies that there is an appreciable solvent effect. Tetrahydrofuran (THF) was employed to increase reaction scale through the appreciably greater solubility of indanetrione in this solvent. It was expected that reaction rates would also increase because of the higher initial concentrations of indanetrione. However, solutions of substrate **1** in THF are red rather than green, indicating a change in the substrate–solvent electronic interaction. This is reflected in appreciable changes in the UV/VIS spectra (see Experimental section) and in a distinct decrease in rate for reactions run in THF.

Table 2 summarises the relative effects of the four solvents. The time required for colour-fading was observed for a series of identical reactions of trione **1** with both β-pinene (at 70 °C) and hex-1-ene (at 100 °C). Estimation of the 'end-point' by eye was very subjective and open to appreciable error, especially when the final result ($t_\infty$) was a pale yellow or brown solution. Nevertheless, results of qualitative value were obtained which indicated that the ene additions are fastest in chloroform and slowest in THF. Chlorobenzene and toluene gave intermediate values for the reaction time, although the additions were distinctly faster in chlorobenzene.

Table 3 summarises the times for colour-fading for additions of represenative Type 1–4 enes to trione **1** in chloroform at 100 °C under identical conditions.

*Comparison of the Reactivities of Trione* **1** *and Diethyl Mesoxalate.*—The additions of these enophiles to β-pinene are sufficiently rapid for the reactions to be monitored spectrophotometrically (sealed under $N_2$ in 1 cm silica cells at 553 nm for trione **1** and 366 nm for diethyl mesoxalate) at near room temperature (30 °C). For reasons of solubility and solution stability, it was necessary to conduct the reaction of trione **1** in dry dimethylformamide (DMF), while diethyl mesoxalate was studied in THF. Examination of the results for a range of concentrations for both enophile and ene (to ~70% completion) indicated that consistent pseudo-first-order rate constants were obtained for an enophile concentration of ~0.2 mol $dm^{-3}$ and a β-pinene concentration of ~2.5 mol $dm^{-3}$. Thus, for trione **1** $k_{obs} = 3.1 \times 10^{-4}\ s^{-1}$, and for diethyl mesoxalate $k_{obs} = 1.3 \times 10^{-5}\ s^{-1}$. Part of this difference may arise from differences in the nature of the two solvents; nevertheless, it would appear that trione **1** as an enophile is approximately an order of magnitude more reactive than is diethyl mesoxalate.

*Attempted Lewis Acid Catalysis of the Ene Additions of Trione* **1**.—It is usual in these reactions to add the Lewis acid to a solution of the enophile in a suitable aprotic solvent (*e.g.*, $CH_2Cl_2$, $CHCl_3$ or $C_6H_6$) at room temperature, followed by the addition of the ene.[2,7] Cooling may be necessary, and a temperature rise on the addition of the ene is a useful indicator of a successful reaction. Unfortunately, however, trione **1** has a very low solubility in the usual solvents at room temperature. Its higher solubility in, for example, 1,2-dimethoxyethane has to be balanced against the preferential, or exclusive complexation of the Lewis acid by the solvent itself—hence ether solvents are usually avoided.

A suspension of trione **1** in dry $CH_2Cl_2$ at room temperature was treated with 1 mol equiv. of either β-pinene or hex-1-ene followed by 0.05 mol equiv. of anhydrous $AlCl_3$, and the mixtures were stirred under $N_2$. Fading of the green colour was slow (*ca.* 24 h), presumably because of the low concentration of dissolved trione **1**. Standard work-up afforded mixtures of products containing the ene adducts, respectively **3a** and **22a**, and hence the conventional method for catalysis offers no advantages over the thermal process.

*Other* 1,2,3-*Tricarbonyl Systems.*—We were interested to discover if the high ene reactivity of trione **1** was typical of

**Table 2** Effect of solvent on the time for completion of the ene additions of β-pinene and hex-1-ene to compound **1**[a]

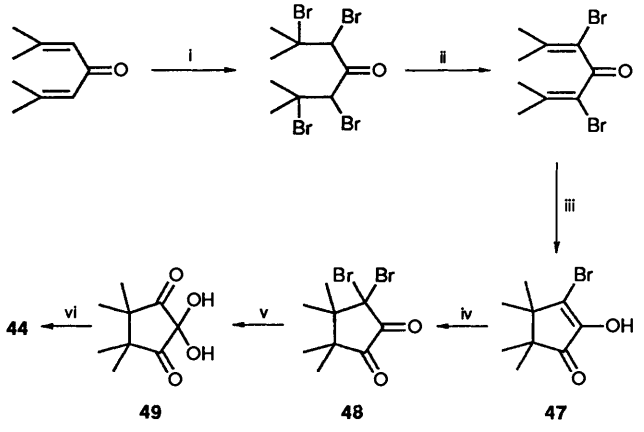
| Solvent | β-Pinene | | Hex-1-ene | |
|---|---|---|---|---|
| | Temp. ($T$/°C) | Time ($t$/min) | Temp. ($T$/°C) | Time ($t$/min) |
| Chloroform | 70 | 2 | 100 | 450 |
| Chlorobenzene | 70 | 12 | 100 | 510 |
| Toluene | 70 | 18 | 100 | ~960 |
| THF | 70 | 30 | 100 | ~1980 |

[a] Indanetrione (0.11 g, 0.687 mmol), ene (1.47 mmol), solvent (3 $cm^3$), Method B1–4 (tube capacity 8 $cm^3$).

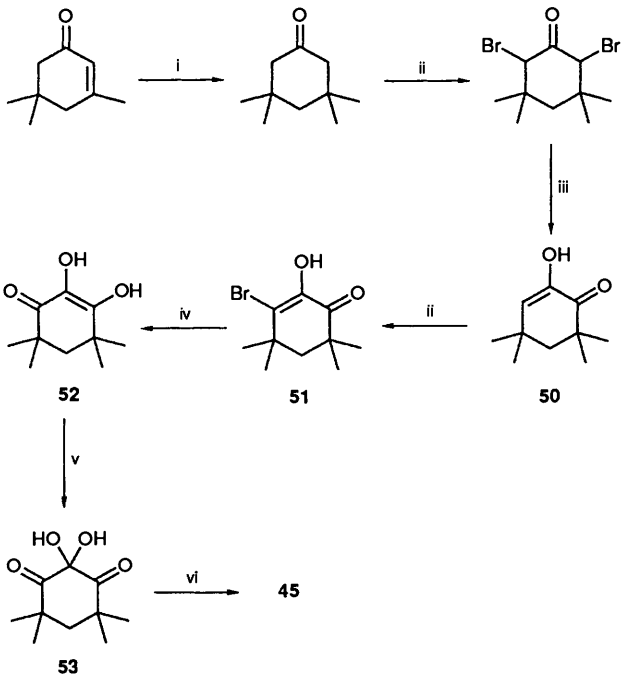
**Table 3** Relative reactivities: times for completion of the ene additions of Type 1–4 enes to **1** in chloroform at 100 °C[a]

| Ene | β-Pinene | Hex-1-ene | Cyclohexene | Hex-1-yne |
|---|---|---|---|---|
| Time ($t$/h) | 0.054 | 7.25 | 28 | 18 |

[a] Indanetrione (0.11 g, 0.687 mmol), ene (2.25 mmol), solvent (3 $cm^3$), Method B1 (tube capacity 8 $cm^3$).




**Scheme 1** *Reagents and conditions:* i, $2Br_2$, AcOH; ii, pyridine, 0 °C; iii, $H_2SO_4$, 0 °C; iv, $Br_2$, AcOH; v, AcONa, MeOH; vi, $P_2O_5$




**Scheme 2** *Reagents and conditions:* i, MeMgI, $Cu^I$; ii, $Br_2$, AcOH; iii, KOH; iv, 1 mol $dm^{-3}$ NaOH, 110 °C; v, $I_2$, KI; vi, $P_2O_5$

other representative vicinal tricarbonyl systems[15,16]* such as 4,4,5,5-tetramethylcyclopentane-1,2,3-trione **44**, 4,4,6,6-tetramethylcyclohexane-1,2,3-trione **45** or 2,2-dimethyl-1,3-dioxane-4,5,6-trione ('oxo-Meldrum's acid') **46**.

The published procedure for the preparation of **44** (Scheme 1) lacks essential experimental detail and spectroscopic data for intermediate compounds.[17] In this route it is worth noting that the bromohydroxy ketone **47**, which separated as needles, tends to decompose upon storage—even at 0 °C. In order to obtain trione **44** in optimum yield, it is essential to work with fresh samples of intermediates **47**–**49**. The trione was isolated as a moisture-sensitive, blue, crystalline solid in 39% yield overall for the six steps from phorone (2,6-dimethylhepta-2,5-dien-4-one). The trione **45** was prepared in a seven-step sequence (Scheme 2) from isophorone (3,5,5-trimethylcyclohex-2-enone); this route is a compilation of individual steps or general procedures from a number of sources.[18] The trione **45** was obtained as a red, crystalline solid in 13% yield overall, and again proved to be highly unstable. The Schlenk tube procedure (Method B, above) was used for the ene reactions of triones **44** and **45**; the triones were handled using dry-bag techniques.[14]

The preparation of the dioxanetrione **46** in two steps from Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) followed the published procedure.[19] We were unsuccessful in attempts to isolate the trione; colour-fading occurred rapidly during manipulation, and the addition of molecular sieves to remove adventitious water seemed to promote decomposition. Hence, the dichloromethane solution of crude trione **46** (presumably also containing the hydrate as well as iodobenzene, a co-product) was boiled overnight ($N_2$ atmosphere) after addition of the ene (2 mol equiv.). Reaction temperature (40 °C) was therefore limited by the solvent used in the preparation of compound **46**.

Results for the reactions of trione **45** were disappointing. For example, reaction with β-pinene in various dry solvents, temperatures in the range 0–60 °C, and reaction times in the range 2 h–3 days generally afforded an orange oil which contained at least six components that could not be separated. It appears that the trione is insufficiently stable to survive even these mild conditions. When an old sample of the hydrate **53** was employed for the preparation of **45**, an orange crystalline solid was obtained instead of the deep red triketone. This solid proved to be 3,3,5,5-tetramethylcyclopentane-1,2-dione which is presumably formed by the benzilic acid rearrangement of **53**, followed by stepwise decarboxylation and oxidation.[18d] The presence of this compound in the mixture obtained from the attempted ene reaction therefore seems likely, but was not proven.

Studies of the reactivity of 'oxo-Meldrum's acid' **46** were constrained by difficulties in preparation and handling.

* Related work on the enophiles alloxan and *N*,*N*-dimethylalloxan will be published separately.

Although addition to β-pinene was successful (affording compound **3c** in 40% yield), the similar reaction with α-methylstyrene gave an unstable product.

The cyclopentanetrione **44** proved more easy to handle. Addition to β-pinene occurred within 24 h at room temperature to give product **3b** in 89% yield. Reaction with hex-1-ene (80 °C; 5 h) also proceeded smoothly to give compound **22b** (60%), but TLC analysis of the crude product and the greater difficulty in product purification indicated that slow decomposition of substrate **44** had occurred under the reaction conditions. Hence, it was not surprising to find that in attempted addition to a Type 3 ene, cyclohexene, that a multi-component mixture of products was obtained.

The following paper shows that indane-1,2,3-trione **1** may be regarded as an enophile equivalent of carbon dioxide since the adducts are readily cleaved to give allyl carboxylic acids. The other vicinal tricarbonyl systems investigated in this study are very much less useful for synthetic purposes because of difficulties in both preparation and handling, as well as their instability.

## Experimental

*General Procedures.*—The enes and all solvents were distilled before use. THF was distilled freshly from sodium under nitrogen. Chloroform was washed thoroughly with water, dried for several days over anhydrous calcium chloride in the dark under nitrogen, distilled and stored in the dark under nitrogen. DMF was dried over anhydrous magnesium sulphate, then over 4Å molecular sieves, followed by distillation under reduced pressure (b.p. 76 °C/40 mmHg). Light petroleum refers to the fraction boiling in the range 40–60 °C.

Fluka Kieselgel G or Merck Kieselgel 60 (9385) were used for column chromatography, and Camlab plastic-backed $UV_{254}$ silica gel plates were used for TLC analyses. A Reichert Kofler micro hot stage was used for m.p. determinations other than for moisture-sensitive compounds, when the sealed capillary tube procedure was used. IR spectra were recorded in a Perkin-Elmer 710B spectrometer and were calibrated using a standard polystyrene film. UV spectra were determined with either a Unicam SP 1700 or a Philips PU 8720 spectrophotometer. Unless stated otherwise, solutions in deuteriochloroform were used for the determination of NMR spectra. Shifts are expressed in ppm downfield from $Me_4Si$(TMS) as internal standard. The $^1H$ and $^{13}C$ spectra were recorded on a Perkin-Elmer R32 90 MHz, JEOL JNM-PS-100, Bruker WM250 or a Bruker AM400 instrument. Signals were singlets unless specified otherwise. *J*-values are given in Hz. Assignments in the $^1H$ spectra were consistent with signal intensities, and in the $^{13}C$ spectra with the results of the DEPT pulse sequence. Mass spectra were by electron impact and were recorded with an AEI MS-902 or VG Micromass 7070E spectrometer.

*Preparation of Indane-1,2,3-trione* **1**.—A mixture of ninhydrin **2** (11.7 g, 65.7 mmol) and chlorobenzene (400 $cm^3$) was boiled under gentle reflux in subdued light for about 30 min; the ninhydrin gradually dissolved and the solution assumed a deep green colour. The majority of the chlorobenzene was removed by distillation (a small fore-run containing all of the water was discarded, the remainder of the recovered solvent was used in subsequent preparations of compound **1**) until ~20 $cm^3$ remained. The residue was cooled in ice–water ($N_2$ atmosphere), the supernatant very pale-green solvent was removed with the aid of a pipette, the red crystals of compound **1** were then rinsed with a little dry diethyl ether or hexane, and the wash solvent was then removed with a pipette. Last traces of solvent were then removed under reduced pressure to give indane-1,2,3-trione **1** (10.41 g, 99%), m.p. 256 °C (lit.,[11,12] 255, 255–257 °C), as lustrous red prisms with a violet tinge: $\lambda_{max}(CH_2Cl_2)$/nm 607 ($\varepsilon_{max}$ 24.7), 336 (4146), 269 (20 980), 265 (21 320), 262 (21 630), 259 (21 835) and 257 (21 800); $\lambda_{max}$(THF)/nm 563 ($\varepsilon_{max}$ 15.7), 319 (2860) and 254 (22 830). The material could be stored in a plastic capped vial, without any visible surface deterioration, for several months.

With toluene (~100 $cm^3$/g of **2**) as the solvent the dehydration could be achieved with the aid of a Dean and Stark water separator (reflux overnight). The product **1** was obtained in similar yield and quality, but the method is slower, and reaction scale (on account of the lower solubilities of both compounds **1** and **2** in toluene) is limited.

*Methods for Performing Ene Additions to Substrate* **1**.—Variations of two basic procedures were used, depending upon the reactivity and b.p. of the ene. General Method A is applicable to all Type 1 and 2 enes of b.p. > 100 °C, and can be conducted on a moderate scale. General Method B is applicable to all enes, but the scale is limited by the dimensions of the Schlenk tube and safety considerations. Although a 1:1 molar ratio of trione **1**:ene may be used, it is better to employ a 1:2–3 ratio to increase the rate and to prevent the addition of substrate **1** to the product.

*Method A*1. A solution of trione **1** in chlorobenzene was prepared as above up to and including the removal of the water–chlorobenzene azeotrope. The distillation was then stopped, the apparatus was rearranged for reflux, the ene (1–3 mol equiv.) then added, and the mixture was boiled until the green colour had disappeared. The mixture was allowed to cool somewhat and the solvent was then removed by rotary evaporation. The residue was recrystallised from the appropriate solvent (Table 1) to give the *ene adduct*.

*Method A*2. A mixture of ninhydrin **2**. the ene (1–3 mol equiv.) and toluene (~100 $cm^3$/1 g of **2**) was boiled under a Dean and Stark water separator. The solution soon assumed a deep green colour which gradually faded as the ene addition proceeded towards completion. When colour-fading was complete, the mixture was worked up as in Method A1.

*Method B*1. Solid indane-1,2,3-trione **1** (1.0 g, 6.3 mmol) was introduced by means of a long-necked funnel into a heavy-walled Schlenk tube (equipped with a high vacuum Teflon screw valve)[14] of about 80–100 $cm^3$ total capacity. The ene (1–3 mol equiv.) was then introduced together with ethanol-free dry chloroform (5–50 $cm^3$) and a small magnetic follower. The tube was flushed with nitrogen, sealed and immersed in a magnetically stirred, pre-heated oil-bath (70–110 °C). After completion of the colour-fading, the tube was removed from the heating bath and allowed to cool to room temperature before being opened. The reaction solution was then worked up as in Method A1. Both scaled-up and scaled-down (see Tables 2 and 3) versions of this basic procedure have been used successfully.

(**Safety Note:** We have not experienced the rupture of a single tube in over a hundred such reactions. However, it is essential that these processes be conducted behind suitable safety screens. Handling of the hot sealed tube can be avoided by clamping it in such a way that lifting of the clamp stand allows the tube to clear the oil-bath. Otherwise, heavy gloves should be worn).

*Methods B2, B3 and B*4. These were identical with Method B1 except that dry THF (Method B2, 5–50 $cm^3$; 80–110 °C), chlorobenzene (Method B3, 50 $cm^3$, 110–130 °C) or toluene (Method B4, 50 $cm^3$, 110–130 °C) were employed as solvents.

*Preparation of* 4,4,5,5-*Tetramethylcyclopentane*-1,2,3-*trione* **44**. *Tetrabromophorone.*—A solution of bromine (32.2 g, 145 mmol) in carbon tetrachloride (50 $cm^3$) was added dropwise to a stirred solution of phorone (10.0 g, 72.5 mmol) in carbon tetrachloride (50 $cm^3$) at such a rate as to keep the temperature

below 30 °C. The mixture was then stirred at room temperature for 30 min, after which time the solvent was removed under reduced pressure. The residue was recrystallised from ethanol to give crystals of the product (28 g, 86%), m.p. 90–91 °C (lit.,[17a] 88–89 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 1720; $\delta_H$ 5.12 (3- + 5-H) and 2.04 (4 × Me).

*Dibromophorone.*—Tetrabromophorone (20.0 g, 50 mmol) was dissolved in ice-cooled pyridine (30 cm$^3$) and the solution was left at 0 °C for 24 h. Water (300 cm$^3$) was then added and the lower oily layer which separated was isolated, and extracted successively with water (50 cm$^3$), 30% sulfuric acid (3 × 20 cm$^3$), and water (20 cm$^3$). The slightly yellowish oil thus obtained was then dried *in vacuo* at 0 °C over phosphorus(v) oxide for 24h to give the product as pale yellow crystals (12.2 g, 82%), m.p. 31–32 °C (lit.[17b] m.p. 32 °C); $\nu_{max}$(film)/cm$^{-1}$ 1655 and 1610; $\delta_H$ 2.08 (2 × Me) and 2.00 (2 × Me).

3-*Bromo*-2-*hydroxy*-4,4,5,5-*tetramethylcyclopent*-2-*enone* **47**.—Ice-cooled conc. sulfuric acid (9.93 g, 101 mmol) was added carefully to stirred, ice-cooled dibromophorone (10.0 g, 33.8 mmol). The mixture was kept at 0 °C for 24 h and was then added dropwise to a stirred, crushed ice–water mixture (~100 g). The pale yellow solid that separated was isolated by filtration, crystallised from ethanol and dried under reduced pressure at 0 °C over phosphorus(v) oxide to give the product as needle-like crystals (6.43 g, 83%), m.p. 116 °C (lit.,[17b] 116 °C; N.B. the structure was mis-assigned by Francis and Willson); $\nu_{max}$(KBr)/cm$^{-1}$ 3300, 1700, 1660, 1380 and 1060; $\delta_H$ 5.92 (br s, exchanged with $D_2O$, OH), 1.18 (2 × Me), 1.14 (2 × Me); $\delta_C$ 22.4 (Me), 22.6 (Me), 24.8 (Me), 24.9 (Me), 46.4 (C-5), 51.7 (C-4), 139.4 (C-2), 147.6 (C-3) and 205.0 (C-1).

3,3-*Dibromo*-4,4,5,5-*tetramethylcyclopentane*-1,2-*dione* **48**.—A solution of bromine (5.23 g, 26.4 mmol) in acetic acid (30 cm$^3$) was added dropwise to a stirred, cold solution of *freshly prepared* compound **47** (6.0 g, 26.4 mmol) in acetic acid (30 cm$^3$). The mixture was stirred for a further 2 h at 20 °C, and then the mixture was poured, in small portions, onto stirred, crushed ice (~100 g) and then kept for 10 min. The resulting orange crystals were isolated by filtration, washed thoroughly with ice-cold water and were then dried under reduced pressure at 0 °C over phosphorus(v) oxide for 24 h to give compound **48** (7.7 g, 94%), m.p. 179–180 °C (lit.,[17b,c] 182 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 1745 and 1620; $\delta_H$ 1.40 (2 × Me) and 1.36 (2 × Me).

4,4,5,5-*Tetramethylcyclopentane*-1,2,3-*trione Hydrate* **49**.—A modification of Shoppee's method[17c] was employed whereby a mixture of the *freshly prepared* dibromo compound **48** (7.0 g, 22.4 mmol), fused sodium acetate (7.0 g) and absolute methanol (120 cm$^3$) was boiled under reflux for 6 h. The majority of the methanol was removed by rotary evaporation, and the yellow-orange residue thus obtained was then extracted with diethyl ether (3 × 50 cm$^3$). The combined extracts were extracted successively with 3 mol dm$^{-3}$ sodium carbonate (20 cm$^3$) and water (2 × 20 cm$^3$), dried ($Na_2SO_4$) and filtered, and the ether was removed under reduced pressure. The resulting orange residue was crystallised from light petroleum to give the hydrate **49** as crystals (3.1 g, 74%), m.p. 95 °C (lit.,[17c] 95 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3450–3160, 1780, 1730, 1250, 1100 and 1020; $\delta_H$ 5.27 (br s, exchanged with $D_2O$, 2 × OH), 1.20 (2 × Me) and 1.08 (2 × Me).

4,4,5,5-*Tetramethylcyclopentane*-1,2,3-*trione* **44**.—The *freshly prepared* trione hydrate **49** (0.56 g, 3.0 mmol) was placed in a small kugelrohr apparatus fitted with B.10 joints together with an equal quantity of phosphorus(v) oxide. The mixture was heated at 150 °C for 30 min at atmospheric pressure. The pressure was then reduced to 10 Torr* to allow the blue, crystalline trione **44**[17c] (0.48 g, 97%) to pass over to the next bulb. Argon was admitted into the apparatus, and the bulb containing trione **44** was immediately transferred into a dry-bag under argon.

*Ene Reactions with* 4,4,5,5-*Tetramethylcyclopentane*-1,2,3-*trione*.—The trione **44**, prepared as above, was immediately dissolved in dry methylene dichloride (5 cm$^3$) and the solution was placed in the reaction vessel (Method B) contained in the dry-bag. The olefin (1.5 mol equiv.) and a small magnetic follower were added and the vessel was sealed. The reactions were conducted in the usual way at 25 or 80 °C (depending upon the reactivity of the ene—see *Physical Data*, below) and monitored by the disappearance of the blue colour of the triketone. Products were isolated as in Method B.

*Preparation of* 4,4,6,6-*Tetramethylcyclohexane*-1,2,3-*trione Hydrate* **53**.—This compound was prepared by the route shown in Scheme 2 and according to published procedures:[18] 3,3,5,5-tetramethylcyclohexanone (84.5%), b.p. 84 °C/20 Torr (lit.,[18a,b] 59–61 °C/5.5 Torr); $\nu_{max}$(film)/cm$^{-1}$ 1710; $\delta_H$ 2.06 ($CH_2COCH_2$), 1.56 (4-$H_2$) and 1.06 (4 × Me); 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone, crystals from methanol (84.6%), m.p. 175–176 °C (lit.,[18c] 174.5–175.5 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 1730; $\delta_H$ 4.72 (CHCOCH), 2.20 (d, *J* 14, 4-H$^a$), 1.98 (d, *J* 14, 4-H$^b$), 1.26 (2 × Me) and 1.08 (2 × Me); 2-hydroxy-4,4,6,6-tetramethylcyclohex-2-enone **50**, crystals from methanol (84%), m.p. 84–85 °C (lit.,[18c] 87–88 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3400, 1680, 1650, 1250 and 1050; $\delta_H$ 5.95 (br s, exchanged with $D_2O$, OH), 5.80 (=CH), 1.76 ($CH_2$) and 1.22 (4 × Me); 3-bromo-2-hydroxy-4,4,6,6-tetramethylcyclohex-2-enone **51** [procedure (b)][18d] and recrystallisation from light petroleum afforded crystals (70%), m.p. 64–65 °C (lit.,[18d] 64–66 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3400, 1650, 1550, 1240, 1150, 1060 and 1010; $\delta_H$ 6.50 (br s, exchanged with $D_2O$, OH), 1.92 ($CH_2$), 1.32 (2 × Me) and 1.26 (2 × Me); 2,3-dihydroxy-4,4,6,6-tetramethylcyclohex-2-enone **52**, needles (62%), m.p. 119–121 °C (lit.,[18d] 119.5–121 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3350, 1680, 1600, 1280, 1220, 1180 and 1050; $\delta_H$ 7.76 (br s, exchanged with $D_2O$, 2 × OH), 1.76 ($CH_2$) and 1.28 (4 × Me); 4,4,6,6-tetramethylcyclohexane-1,2,3-trione hydrate **53**, needles (57%), m.p. 50–52 °C (lit.,[18d] 51–53 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3470, 1740, 1250 and 1100; $\delta_H$ 4.96 (br s, exchanged with $D_2O$, 2 × OH), 2.04 ($CH_2$) and 1.32 (4 × Me).

*Preparation of* 4,4,6,6-*Tetramethylcyclohexane*-1,2,3-*trione* **45**.—The *freshly prepared* triketone hydrate **53** (0.4 g, 2 mmol) was mixed thoroughly with an equal quantity of phosphorus(v) oxide in the kugelrohr apparatus described in the preparation of the cyclopentanetrione **44**. The mixture was heated at 38 °C/10 Torr to allow the deep red crystalline triketone (0.32 g, 90%) to pass over to the next bulb. Argon was admitted into the apparatus and the bulb containing the triketone was immediately transferred into a dry-bag under argon.

*Attempted Ene Reaction of* 4,4,6,6-*Tetramethylcyclohexane*-1,2,3-*trione with* β-*Pinene*.—The trione **45**, prepared as above, was immediately dissolved in dry methylene dichloride (5 cm$^3$) and the solution was placed in the reaction vessel (Method B) contained in the dry-bag. β-Pinene (0.5 g, 3.7 mmol) and a small magnetic follower were added and the vessel was sealed. The reaction was conducted at 25 °C. The usual pronounced colour change failed to occur. Isolation of the products in the usual way for Method B afforded an orange liquid. Since TLC analysis

* 1 Torr = 133.322 Pa.

revealed the presence of at least six components (even for reactions conducted at various temperatures in the range 0–60 °C), further work was abandoned.

*Ene Reactions of* 2,2-*Dimethyl*-1,3-*dioxane*-4,5,6-*trione* **46**.—A methylene dichloride solution of compound **46**, prepared by Schank and Lick's procedure[19] from the phenyliodonium ylide (0.5 g, 1.44 mmol), was freed of ozone by out-gassing with dry oxygen. The ene (2 mol equiv.) was added, and the mixture was boiled under gentle reflux (nitrogen atmosphere) overnight. The product was isolated and purified as for the other ene reactions, above.

*Physical and Spectroscopic Data for the Reaction Products Derived from Triones* **1**, **44** and **46** (*see also Table 1*).

*Physical data.* **3b** [Method B (25 °C/24 h), 89%], b.p. 94 °C/0.05 Torr; m.p. 50.5 °C (Found: C, 74.8; H, 9.5. $C_{19}H_{28}O_3$ requires C, 75.0; H, 9.3%); **3c** [Method A (40 °C/12 h), 40%], m.p. 92.5 °C (Found: C, 65.0; H, 7.7. $C_{16}H_{22}O_5$ requires C, 65.3; H, 7.5%); **16a** [Method A2 (110 °C/0.25 h), 58%], m.p. 157–159 °C (Found: C, 73.4; H, 6.1%; $M^+$, 310.1185. $C_{19}H_{18}O_4$ requires C, 73.5; H, 5.9%; M, 310.1205). Compound **18** [Method B1 (80 °C/2 h), 97%], m.p. 108.5–109.5 °C (lit.,[15] 88–90 °C) (Found: C, 73.5; H, 5.4%; $M^+$, 228.0782; $C_{14}H_{12}O_3$ requires C, 73.7; H, 5.3%; *M*, 228.0786); **20** [Method A2 (110 °C/2 h), 94%], m.p. 78–79 °C (Found: C, 75.2; H, 6.6%; $M^+$, 256.1062. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%; M, 256.1099); **22b** [Method B (80 °C/5 h), 60%], b.p. 119 °C/10 Torr (Found: C, 70.9; H, 9.9. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%).

*IR Spectra.—General features.* Owing to the presence of the 2-hydroxyindane-1,3-dione moiety in all of the series **a** ene adducts, all gave absorptions within the following ranges: $\nu_{max}$(KBr—unless stated otherwise)/cm$^{-1}$ 3475–3350, 3100–3020, 2980–2900, 1760–1730, 1720–1700, 1610–1580, 1280–1240, 1180–1140, 980–900 and 760–730.

*Other absorptions*: $\nu_{max}$/cm$^{-1}$ **3a** 1220 and 800; **3b** (film) 3450, 3050, 1760, 1720 and 1640; **3c** ($CH_2Cl_2$) 3550, 3255, 1790, 1755 and 1100; **4a** 1210, 1200, 780 and 700; **5a** 1100; **6a** 1660 and 1080; **7a** 1640; **8a** 1220 and 1050; **9a** + **12a** 1090; **10a** ($CHCl_3$) 1660; **11a** + **13a** 1040; **13a** 1050 and 890; **16a** 1620; **18** 2850, 1760, 1720, 1600, 1290, 1250, 1130, 1060 and 920; **20** 2925, 1760, 1720, 1610, 1300, 1250, 1200, 1140, 1040 and 980; **21a**—; **22a** 2810, 1640 and 1135; **22b** (film) 3450, 2950, 2910, 2850, 1760, 1720, 1660, 1260 and 970; **23a** (film) 2860; **24a** (film) 2875; **25a** (film) 1650 and 1050; **26a** (film) 2840; **27a** (film) 1660, 1640, 1200 and 1040; **28a** 1500, 1100 and 790; **29a** 1060; **30a** 2250, 1220 and 1100; **31a** 1680, 1190 and 990; **32a** 1220, 1100 and 1040; **33a** (film)—; **34a** (film) 1650 and 1080; **36a** ($CHCl_3$) 3650; **37a** 1660 and 1220; **38a** (film) 1070; **39a** 1010 and 780; **40a** 1950, 1120 and 885; **41a** 3300, 2140, 1970, 1190 and 1050; **42a** (film) 1980, 1500 and 1080; **43a** (film) 1960, 1520, 1020 and 920.

$^1$H *NMR Spectra.—General features.* Owing to the presence of the 2-hydroxyindane-1,3-dione moiety in all of the series **a** ene adducts, all gave signals within the following ranges: $\delta_H$ 8.10–7.85 (2 m, 4 × ArH) and 3.90–3.05 (br s, OH); notable exceptions for the position of the OH resonance are listed below.

*Other signals.* $\delta_H$ **3a** 5.38 (br m, 3-H), 2.77 (d, *H* 12.8, 10-H$^a$), 2.54 (d, *J* 12.8, 10-H$^b$), 2.06 (1 H, m), 1.95 (1 H, m), 1.85 (1 H, br m), 1.78 (1 H, dt, *J* 1.3, 5.5), 1.14 (*anti*-Me), 0.85 (1 H, m), 0.66 (*syn*-Me) and 0.13 (d, *J* 8.7, *syn*-7-H); **3b** (90 MHz) 5.57 (br m, 3-H), 3.00 (br s, OH), 2.60 (d, *J* 9, 10-H$^a$), 2.46 (2 H, m), 2.34 (2 H, m), 2.15 (1 H, m), 1.95 (1 H, m), 1.37 (1 H, m), 1.30 (*anti*-Me), 1.17 (2 × Me), 1.11 (2 × Me) and 0.90 (*syn*-Me); **3c** 5.50 (m, 3-H), 3.85 (OH), 2.82 (d, *J* 14.9, 10-H$^a$), 2.72 (d, *J* 14.9, 10-H$^b$), 2.35 (1 H, m), 2.23 (2 H, m), 2.13 (1 H, m), 2.04 (1 H, m), 1.79 (2 × Me), 1.25 (*anti*-Me), 1.10 (d, *J* 8.6, *syn*-7-H) and 0.81 (*syn*-Me); **4a** 7.15 (m, ArH), 7.06 (m, 2 × ArH), 6.83 (m, 2 × ArH), 5.14 (=C*H*H), 5.11 (=CH*H*) and 3.25 ($CH_2$); **5a** (90 MHz) 5.50 (br m, =CH), 2.61 (HOCC$H_2$), 1.90–1.60 (4 H, br m, C$H_2$C=CHC$H_2$) and 1.35–1.10 (4 H, br m, 2 × $CH_2$); **6a** (90 MHz) 6.85 (br m, =CH), 5.08 (br s, =C*H*H), 4.88 (m, =CH*H*), 4.72 (br s, OH), 3.62 (m, HOCC$H_2$), 2.60–2.30 (m, $CH_2$CO), 1.90 (Me) and 1.73–1.65 (3 H, m, $CH_2$CH); **7a** 4.84 (=C*H*H), 4.77 (=CH*H*), 2.65 ($CH_2$) and 1.60 (Me); **8a** + ? (90 MHz) 5.55 (0.5 H, br s, unknown), 4.96 (=C*H*H), 4.84 (=CH*H*), 2.83 (br s, unknown), 2.77 ($CH_2$), 1.20 (2 H, s, unknown) and 0.94 (3 × Me); **9a** + **12a** (~20:80; 90 MHz) 5.34 (0.75 H, ~q, *J* 7.5, =C*H*Me), 4.80 (0.5 H, br s, =$CH_2$), 2.74 (0.5 H, HOCC$H_2$), 2.68 (1.5 H, HOCC$H_2$), 1.87 (0.5 H, q, *J* 7.5, C$H_2$Me), 1.60–1.30 (3 H, m, MeC= and *Me*CH=) and 0.84 (0.75 H, t, *J* 7.5, $CH_2$*Me*); **10a** (90 MHz) 4.89 (d, *J* 2, =C*H*H), 4.76 (d, *J* 2, =CH*H*), 2.92 ($CH_2$) and 2.00 (Me); **13a** (90 MHz) 5.32 (q, *J* 7.5, =CH), 2.83 (q, *J* 7.5, HOCC*H*), 1.42 (d, *J* 7.5, *Me*CH=), 1.36 (=CMe) and 1.16 (d, *J* 7.5, *Me*CH); **11a** + **13a** (~70:30; 90 MHz) 5.35 (0.3 H, m, =CH), 4.90 and 4.83 (1.4 H, 2 s, =$CH_2$), 2.85 (1 H, q, *J* 7.5, HOCC*H*), 1.85 (1.4 H, q, *J* 8, C$H_2$Me), 1.45–1.07 (4.8 H, overlapping 2 d and s, 2 × *Me*CH + MeC= + *Me*CH=) and 0.82 (2.1 H, t, *J* 8, $CH_2$*Me*); **16a** (90 MHz) 6.60 (br s, OH), 4.28–4.08 (br m, HOCC*H*), 2.90–2.61 (m, $COCH_2$), 2.48 (~t, *J* 8, 2 × =$CCH_2$), 2.05 (~q, *J* 8, $COCH_2CH_2$) and 1.70–1.30 (m, $CHCH_2CH_2$); **18** 8.00 (m, 2 × ArH), 7.90 (m, 2 × ArH), 5.66 (m approx. to octet, reduces to q on irradiation of $OCH_2$ signal at $\delta$ 4.55, *J* 1.5, =CH), 4.55 (m approx. to septet, reduces to q on irradiation of =CH signal at $\delta$ 5.66, *J* 2.1, $OCH_2$), 2.23 (br m, $OCCH_2$) and 1.78 (br m, reduces to m approx. to pentet on irradiation of =CH signal at $\delta$ 5.66, =CMe); **19** (as impurity in uncrystallised **18**) detected by satellite m signals at $\delta$ 5.58, 4.43, 2.35 and 1.73; **20** (90 MHz) 8.05–7.95 (m, 4 × ArH), 5.70 (m, =CH), 2.23 (br s, $CCH_2$), 1.82 (br s, =CMe) and 1.38 ($CMe_2$); **21a** (90 MHz) 4.95 (t, *J* 8, =CH), 2.65 (d, *J* 8, $CH_2$) and 1.58 (br s, 2 × Me); *E*-**22a** 5.57 (m ~dt, *J* 6.9 and 15.0, =CH), 5.21 (m ~dt, *J* 7.6 and 15.0, =CH), 2.58 (d, *J* 7.6, HOCC$H_2$), 1.89 (m ~q, *J* 6.9, =CHC$H_2$), 1.24 (m, C$H_2$Me) and 0.77 (t, *J* 7.4, Me); *Z*-**22a** (as minor component in **22a**) detected by satellite signals at $\delta$ 2.68 (d, *J* 7.9), 1.98 (m) and 0.86 (t, *J* 7.4); **22b** (90 MHz) 5.57 (m, HC=CH), 3.01 (br s, OH), 2.40 (m, HOCC$H_2$), 2.02 (m, =CHC$H_2$), 1.40 (C$H_2$Me), 1.10 (2 × $CMe_2$) and 0.87 (t, *J* 7.5, $CH_2$*Me*); **23a** (90 MHz) 5.56 (~dt, *J* 15 and 7.5, *H*C=CH), 5.26 (~dt, *J* 15 and 7.5, HC=C*H*), 2.61 (d, *J* 8, HOC$H_2$) [minor, *Z*-isomer $\delta$ 2.71 (d, *J* 8, HOC$H_2$)], 2.05–1.70 (br m, =CHC$H_2$), 1.35–1.00 (br m, C$H_2$C$H_2$Me) and 0.80 (t, *J* 7.5, Me); **24a** 5.58 (~dt, *J* 15.2 and 6.9, HOCC$H_2$HC=C*H*), 5.20 (~dt, *J* 15.2 and 7.6, HOCC$H_2$*H*C=CH), 2.58 (dd, *J* 7.6 and 0.7, HOCC$H_2$) [minor, *Z*-isomer 2.68 (d, *J* 7.9, HOC$H_2$)], 1.88 (m, =CHC$H_2$) [minor, *Z*-isomer 1.98 (m, =CHC$H_2$)], 1.30–1.05 (br m, C$H_2$C$H_2$Me) and 0.83 (t, *J* 6.9, Me); **25a** (90 MHz) 5.95–5.15 (m, CH=CH), 5.00 (m, =C*H*H), 4.85 (m, =CH*H*), 2.65 (d, *J* 8, HOCC$H_2$) [minor, *Z*-isomer 2.72 (d, *J* 8, HOCC$H_2$)], 2.10–1.70 (m, 2 × C$H_2$CH=) and 1.55–1.10 (m, $CH_2CH_2CH_2$); **26a** (90 MHz) 5.70–4.90 (m, CH=CH), 4.30 (br s, OH), 3.69 (OMe), 2.64 (d, *J* 7, HOCC$H_2$) [minor, *Z*-isomer 2.72 (d, *J* 7, HOCC$H_2$)], 2.28 (t, *J* 7.5, $CH_2$COO), 2.00–1.70 (m, C$H_2$CH=), 1.70–1.45 (m, C$H_2CH_2$COO) and 1.40–1.00 (m, 4 × $CH_2$); **27a** (90 MHz) 5.80–5.10 (2 × CH=CH), 4.13 (q, *J* 7.5, $OCH_2$), 3.00 (m, $CH_2$CO), 2.63 (d, *J* 7, HOCC$H_2$) [minor, *Z*-isomer 2.73 (d, *J* 7, HOCC$H_2$)], 1.80–2.15 (m, $CH_2CH_2$) and 1.21 (t, *J* 7.5, Me); *E*-**28a** ($CD_3COCD_3$) 7.28–7.15 (m, Ph), 6.42 (d, *J* 15.8, PhC*H*=CH), 6.06 (~dt, *J* 15.8 and 7.5, PhCH=C*H*), 2.98 (br s, OH) and 2.81 (d, *J* 7.5 and 1.1, $CH_2$); *E*- + *Z*-**29a** (no TMS added) 6.15 (~dt, *J* 14.5 and 7.2, *E*-$Me_3$SiCH=C*H*), 5.80–5.60 (m, *Z*-$Me_3$SiC*H*=C*H* and *E*-$Me_3$SiC*H*=CH), 2.69 and 2.68 (2 d, *J* 7.0, *E*- + *Z*-$CH_2$), 0.06 (*E*-$Me_3$Si) and −0.16 (*Z*-$Me_3$Si); *E*-

**30a** 6.66 (dt, *J* 16.3 and 7.5, NCCH=C*H*), 5.40 (dt, *J* 16.3 and 1.4, NCC*H*=CH) and 2.65 (dd, *J* 7.5 and 1.4, $CH_2$); *Z*-**30a** 6.75 (dt, *J* 11.0 and 7.4, NCCH=C*H*), 5.25 (dt, *J* 11.0 and 1.4, NCC*H*=CH) and 2.80 (dd, *J* 7.4 and 1.4, $CH_2$); *E*-**31a** (90 MHz) 6.95 (dt, *J* 16 and 7.5, =C*H*$CH_2$), 5.90 (dd, *J* 16 and 1.5, =CHCOO), 4.21 (br s, OH), 3.70 (OMe) and 2,78 (dd, *J* 7.5 and 1.5, $CH_2$); *E*-**32a** ($CD_3COCD_3$) 7.35–6.81 (m, Ph), 6.56 (dt, *J* 12.0 and 1.2, =C*H*OPh), 5.00 (dt, *J* 12.0 and 8.1, $CH_2CH$=), 2.92 (br s, OH) and 2.64 (dd, *J* 8.1 and 1.2, $CH_2$); *Z*-**32a** ($CD_3COCD_3$) 7.35–6.81 (m, Ph), 6.46 (dt, *J* 6.1 and 1.4, =C*H*OPh), 4.74 (dt, *J* 6.1 and 7.6, $CH_2CH$=), 2.92 (br s, OH) and 2.81 (dd, *J* 7.6 and 1.4, $CH_2$); **33a** (90 MHz) 5.86–5.28 (m, CH=CH), 4.60 (br s, OH), 3.07 (d, *J* 7, $CH_2CO$), 2.66 (d, *J* 7, HOCC$H_2$) and 2.06 (Me); **34a** (90 MHz) 6.00–5.52 (m, C*H*=$CH_2$), 5.15–4.85 (m, CH=C$H_2$), 4.23 (br s, OH), 3.36 (HOCC$H_2$), 2.75–2.45 (m, $CH_2CH_2CO$) and 2.35–2.15 (m, C$H_2CH_2CO$); **36a** (90 MHz) 5.95–5.55 (m, CH=CH), 2.35 (m, C*H*CH=) and 2.00–1.70 (m, $CH_2CH_2$); **37a** (90 MHz) 6.00–5.65 (m, CH=CH), 2.86–2.66 (m, C*H*CH=), 2.05–1.86 (m, =CHC$H_2$) and 1.70–1.27 (m, CHC$H_2CH_2$); **38a** (90 MHz) 6.10–5.85 (m, CH=CH), 3.00–2.80 (m, C*H*CH=), 2.20–1.95 (m, =CHC$H_2$) and 1.85–1.00 (m, 3 × $CH_2$); **39a** (90 MHz) 5.97–5.53 (m, CH=CH), 3.33–3.02 (m, C*H*CH=), 2.89 (br s, OH), 2.30–2.00 (m, =CHC$H_2$) and 1.85–1.00 (m, 4 × $CH_2$); **40a** 5.39–5.30 (m, CH=C=CH), 1.89–1.81 (m, =CHC$H_2$), 1.27–1.15 (m, C$H_2$Me) and 0.80 (t, *J* 7.3, Me); **41a** (90 MHz) 5.57–5.22 (m, CH=C=CH), 4.22 (br s, OH), 2.25–1.82 (m, C$H_2$CH= + $CH_2C{\equiv}$ + ≡CH) and 1.53–1.22 (m, $CH_2CH_2CH_2$); **42a** 7.40 (m, Ph), 5.60–5.45 (m, CH=C=CH), 5.13 (OC$H_2$Ph), 4.41 (br s, OH) and 2.98 (d, *J* 7, COC$H_2$CH=); **43a** 8.40–8.28 (m, 4 × ArH), 5.65–5.40 (m, CH=C=CH), 4.60 (br s, OH), 4.35 (t, *J* 7, $CH_2O$) and 2.60–2.30 (m, =CHC$H_2$).

$^{13}$C *NMR Spectra*.—For clarity, assignments for resonances of the 2-hydroxyindane-1,3-dione moiety are enclosed within square brackets. $\delta_C$ **3a** 200.3 [C-1], 200.2 [C-3], 140.8 [C-3a], 140.6 [C-7a], 140.3 (C-2), 136.5 [=CH], 136.3 [=CH], 124.6 (C-3), 123.9 [=CH], 123.7 [=CH], 77.6 [C-2], 46.5 (C-1), 44.8 (C-10), 39.9 (C-5), 38.0 (C-6), 31.5 (C-4/-7), 31.3 (C-7/-4), 26.1 (*anti*-Me) and 20.8 (*syn*-Me); **3b** 216.7 (CO), 215.6 (CO), 141.6 (C-2), 125.6 (C-3), 75.4 (COH), 53.0 (CO*C*$Me_2$), 52.2 (CO*C*$Me_2$), 47.7 (C-1), 42.9 (C-10), 40.2 (C-5), 37.9 (C-6), 32.3 (C-4/-7), 31.9 (C-7/-4), 26.2 (*anti*-Me), 21.1 (Me), 20.9 (*syn*-Me), 20.7 (Me), 19.4 (Me) and 19.1 (Me); **4a** 199.5 [C-1 + -3], 141.7 (quat. -C=), 140.7 [C-3a + −7a], 139.1 (quat. -C=), 136.1 [2 × =CH], 128.1 (2 × =CH), 127.9 (=CH), 126.4 (2 × =CH), 123.3 [2 × =CH], 119.3 (=$CH_2$) 78.4 [C-2] and 43.1 ($CH_2$); **7a** 199.6 [C-1 + -3], 140.4 [C-3a + -7a], 138.3 (quat. =C–), 136.5 [2 × =CH], 123.8 [2 × =CH], 117.6 (=$CH_2$), 77.7 [C-2], 44.4 ($CH_2$) and 23.6 (Me); **16a** 209.7 (*C*O$CH_2$), 200.0 [C-1], 199.5 [C-3], 156.1 (quat. =C), 141.1 [C-3a], 140.8 [C-7a], 136.2 [=CH], 135.9 [=CH], 133.1 (quat. =C–), 123.1 [=CH], 123.0 [=CH], 80.1 [C-2], 46.7 (HOC*C*H), 39.1 ($CH_2$), 33.2 ($CH_2$), 29.9 ($CH_2$), 28.2 ($CH_2$), 21.6 ($CH_2$) and 18.9 ($CH_2$); *E*-**22a** 199.6 [C-1 + -3], 140.3 [C-3a + -7a], 138.3 (=CH), 136.4 [2 × =CH], 123.8 [2 × =CH], 120.4 (=CH), 77.1 [C-2], 39.5 (HOC*C*$H_2$), 34.4 (=CH*C*$H_2$), 22.1 (*C*$H_2$Me) and 13.4 (Me); *Z*-**22a** (a minor component in **22a**) detected by satellite signals at $\delta_C$ 199.5, 123.6, 119.6, 77.3, 34.3, 29.0, 22.5 and 13.6; **22b** 216.3 (2 × CO), 138.7 (=CH), 120.6 (=CH), 72.2 (COH), **52.6** (2 × *C*$Me_2$), 38.9 (HOC*C*$H_2$), 34.7 (=CH*C*$H_2$), 22.3 (*C*$H_2$Me), 20.2 (C*Me*$_2$), 19.9 (C*Me*$_2$) and 13.6 ($CH_2$*Me*); *E*-**24a** 200.3 [C-1 + -3], 140.5 [C-3a + -7a], 137.3 (=CH), 136.5 [2 × =CH], 123.6 [2 × =CH], 120.8 (=CH), 77.7 [C-2], 39.4 (HOC*C*$H_2$), 34.2 (=CH*C*$H_2$), 31.0 (=CHC$H_2$*C*$H_2$), 28.5 (*C*$H_2$C$H_2$Me), 22.3 (*C*$H_2$Me) and 13.8 (Me); *Z*-**24a** (a minor component in **24a**) detected by satellite signals at $\delta_C$ 200.2, 140.4, 136.3, 135.5, 120.2, 77.5, 34.2, 31.3, 28.9, 22.4 and 13.9; *E*-**28a** ($CD_3COCD_3$) 200.0 [C-1 + -3], 140.3 [C-3a + -7a], 137.1 (quat. =C–), 136.6 [2 × =CH], 134.4 (=CH), 128.4 (2 × aryl =CH), 127.4 (aryl =CH), 126.1 (2 × aryl =CH), 123.4 [2 × =CH], 122.2 (=CH), 77.5 [C-2] and 39.1 ($CH_2$); *E*-**29a** (no TMS added) 199.7 [C-1 + -3], 140.2 [C-3a + -7a], 138.5 (=CH), 136.7 [2 × =CH], 136.6 (=CH), 123.9 [2 × =CH], 77.7 [C-2], 39.7 ($CH_2$) and 0.15 ($SiMe_3$); *Z*-**29a** 200.2 [C-1 + -3], 140.6 [C-3a + -7a], 138.0 (=CH), 137.2 [2 × =CH], 135.5 (=CH), 123.6 [2 × =CH], 77.7 [C-2], 43.7 ($CH_2$) and −1.56 ($SiMe_3$); *E*-**30a** 198.5 [C-1 + -3], 147.2 (*C*H=CHCN), 139.7 [C-3a + -7a], 137.2 [2 × =CH], 124.3 [2 × =CH], 119.8 (CN), 104.5 (CH=*C*HCN), 76.2 [C-2] and 38.7 ($CH_2$); *Z*-**30a** 198.3 [C-1 + -3], 147.0 (*C*H=CHCN), 139.5 [C-3a + -7a], 137.1 [2 × =CH], 124.7 [2 × =CH], 116.6 (CN), 103.3 (CH=*C*HCN), 76.5 [C-2] and 37.3 ($CH_2$); **40a** 204.3 (=C=), 197.0 [C-1], 196.9 [C-3], 140.3 [C-3a], 140.2 [C-7a], 136.4 [2 × =CH], 124.2 [=CH], 124.1 [=CH], 96.9 (HOC*C*H=C=), 91.0 (=C=*C*HC$H_2$), 77.8 [C-2], 30.1 (=CH*C*$H_2$), 21.8 (*C*$H_2$Me) and 13.5 (Me); **42a** 205.1 (CH=*C*=CH), 197.3 [C-1], 197.1 [C-3], 170.4 (COO), 139.9 [C-3a], 139.8 [C-7a], 136.5 [2 × =CH], 135.5 (=*C*$CH_2O$), 128.5 (2 × aryl =CH), 128.25 (aryl =CH), 128.19 (2 × aryl =CH), 124.0 [2 × =CH], 92.1 (HOC*C*H=), 89.6 (=*C*HC$H_2$), 77.4 [C-2], 66.7 ($OCH_2$) and 33.4 (=CH*C*$H_2$CO); **43a** 204.9 (CH=*C*=CH), 197.4 [C-1], 197.2 [C-3], 164.7 (COO), 150.5 (=C$NO_2$), 139.9 [C-3a + -7a], 136.7 [2 × =CH], 135.4 (=*C*COO), 130.8 (2 × aryl =CH), 124.1 (2 × aryl =CH), 123.5 [2 × =CH], 92.4 (HOC*C*H=), 91.9 (=*C*HC$H_2$), 77.5 [C-2], 64.3 ($CH_2O$) and 27.4 (=CH*C*$H_2$).

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## References

1 H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 556.
2 B. B. Snider, *Acc. Chem. Res.*, 1980, **13**, 426.
3 H. H. Wasserman and J. L. Ives, *Tetrahedron*, 1981, **37**, 1825; L. M. Stephenson, M. J. Grdina and M. Orfanopoulos, *Acc. Chem. Res.*, 1980, **13**, 419.
4 G. E. Keck, R. R. Webb and J. B. Yates, *Tetrahedron*, 1981, **37**, 4007; G. E. Keck and R. R. Webb, *J. Org. Chem.*, 1982, **47**, 1302; G. E. Keck and J. B. Yates, *J. Org. Chem.*, 1982, **47**, 3590.
5 G. Wittig and H. Durr, *Justus Liebigs Ann. Chem.*, 1964, **672**, 55; G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 1962, **95**, 2718; H. E. Simmons, *J. Am. Chem. Soc.*, 1961, **83**, 1657.
6 D. C. England, *J. Am. Chem. Soc.*, 1961, **83**, 2205.
7 J. P. Benner, G. B. Gill, S. J. Parrott and B. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 1984, 291; J. P. Benner, G. B. Gill, S. J. Parrott, B. Wallace and M. J. Begley, *J. Chem. Soc., Perkin Trans. 1*, 1984, 315.
8 B. B. Snider, *J. Org. Chem.*, 1974, **39**, 255; B. B. Snider and J. V. Duncia, *J. Am. Chem. Soc.*, 1980, **102**, 5926; J. V. Duncia, P. T. Lansbury, T. Miller and B. B. Snider, *J. Am. Chem. Soc.*, 1982, **104**, 1930.
9 G. B. Gill and K. S. Kirollos, *Tetrahedron Lett.*, 1982, **23**, 1399.
10 M. E. Salomon, S. N. Pardo and R. G. Salomon, *J. Am. Chem. Soc.*, 1980, **102**, 2473; see also O. Achmatowicz and O. Achmatowicz, Jr., *Rocz. Chem.*, 1962, **36**, 1791 (*Chem. Abstr.*, 1963, **59**, 8610b).
11 A. Schonberg and R. Moubacher, *J. Chem. Soc.*, 1943, 71.
12 A. R. Lepley and J. P. Thelman, *Tetrahedron*, 1966, **22**, 101.
13 A. Schonberg and E. Singer, *Chem. Ber.*, 1970, **103**, 3871.
14 G. B. Gill and D. A. Whiting, *Aldrichimica Acta*, 1986, **19**, 31.
15 A. Schonberg and E. Singer, *Chem. Ber.*, 1971, **104**, 160.
16 M. Rubin, *Chem. Rev.*, 1975, **75**, 177.

17 (*a*) cited in *Beilstein's Handbuch der Organischen Chemie*, 1918, **1**, 710; (*b*) F. Francis and F. G. Willson, *J. Chem. Soc.*, 1913, **103**, 2238; (*c*) C. W. Shoppee, *J. Chem. Soc.*, 1936, 269.
18 (*a*) M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, 1941, **63**, 2308; (*b*) P. R. Thornburrow, Ph.D. Thesis, University of Nottingham, 1969; (*c*) C. Sandris and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1956, 958; (*d*) G. Hesse and P. Beyer, *Justus Liebigs Ann. Chem.*, 1971, **747**, 84.
19 K. Schank and C. Lick, *Synthesis*, 1983, 392.

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