# Oxidative Cleavage of Indane-1,2,3-trione-Ene Adducts; a Convenient Synthesis of Allyl and Allenyl Carboxylic Acids

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The ene adducts formed by the thermal reaction of indane-1,2,3-trione with olefins or terminal alkynes are cleaved in good yield by reaction with periodic acid in dry diethyl ether. Thereby the 2-hydroxyindane-1,2-dione moiety in the adduct is replaced by a CO_2H group; hence indane-1,2,3-trione is a masked equivalent of carbon dioxide in the ene reaction. The allyl or allenyl carboxylic acid may be separated from the co-products (phthalic acid and anhydride) by extraction into hexane.

The preceding paper summarises a detailed study of the thermal ene additions of indane-1,2,3-trione with a variety of olefins and terminal acetylenes (Type 1–5 enes).[1] The adducts possess the general structure 1 and as α-hydroxy ketones should be capable, in principle, of undergoing oxidative cleavage to give the allyl or allenyl carboxylic acid 2 and phthalic acid. The acid 2 is the hypothetical ene adduct of the original olefin or terminal alkyne with carbon dioxide. Hence indane-1,2,3-trione may function as a convenient (reactive) enophile equivalent of CO_2.
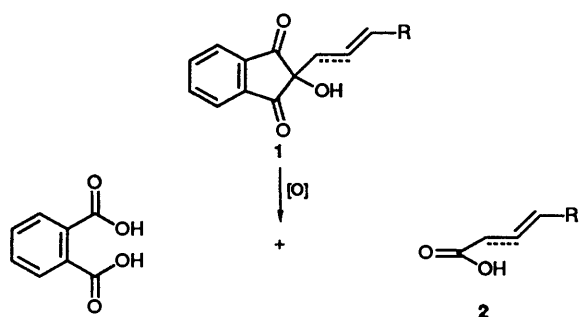
Periodic acid in dry diethyl ether is known[2] to promote the clean and efficient oxidative cleavage of tartrate esters to the corresponding glyoxylate esters. The reagent also cleaves α-hydroxy aldehydes, α-hydroxy ketones, α-diketones and (slowly) α-hydroxy acids. The aqueous acid is employed frequently, and for oxidations performed within the pH range 3–5 sodium metaperiodate has found use.[3]

We have found that the addition of periodic acid to a stirred, dry, ethereal solution of the indanetrione–ene adduct effected the desired cleavage reaction in 2–6 h at room temperature. Filtration, removal of the ether and extraction of the residue with hexane or (40–60 °C) light petroleum afforded the allyl or allenyl carboxylic acids in fair to excellent yield. The co-products (phthalic acid and anhydride) have a very low solubility in these solvents, and any remaining traces are readily removed in the final purification. The results for a cross-section of ene adduct structural types are summarised in Table 1.

The adducts 7a, 8a and 10a were mixtures of geometric isomers. Cleavage by periodic acid to give acids 7b, 8b and 10b (entries 5, 6 and 8) appeared not to have changed the isomer ratio significantly as judged from the ¹H NMR spectra of the crude products. Insignificant alteration in the E:Z ratio occurred on purification of products 7b and 8b, whereas the Z-isomer was removed on recrystallisation of compound 10b. Hence, the apparent absence of geometric isomerisation, or the formation of γ-lactones (from protonation of the C=C bond followed by nucleophilic attack by the CO_2H group), or of the Δ²-isomers of the product acids (e.g., of 4b, 6b, 7b, 11b and 14b–

Table 1 Allyl and allenyl carboxylic acids prepared by the oxidative cleavage of indane-1,2,3-trione–ene adducts

| Entry	Reactant[a]	Product[a]	Time (t/h)	Yield (%)[b]
1	3a	3b	2	96
2	4a	4b	5	72
3	5a	5b	6	70
4	6a	6b	2	95
5	7a	7b	2	95
6	8a	8b	4	85
7	9a	9b	5	93
8	10a	10b	4	60
9	11a	11b	4	65
10	12a	12b	5	58
11	13a	13b	6	63
12	14a	14b	5	65
13	15a	15b	5	66
14	16a	16b	5	87

[a] Isomer ratios (E:Z) for reactants and crude, *unpartitioned* products: 7a 81:19; 7b 85:15; 8a 65.5:34.5; 8b 66:34; 10a 64.5:35.5; 10b ~70:30. See Experimental for isomer ratios of purified products. [b] Yields are for purified compounds.

16b) resulting from double-bond migration, and especially the survival of the enol ether 10b, testifies to the mildness of the oxidative procedure.
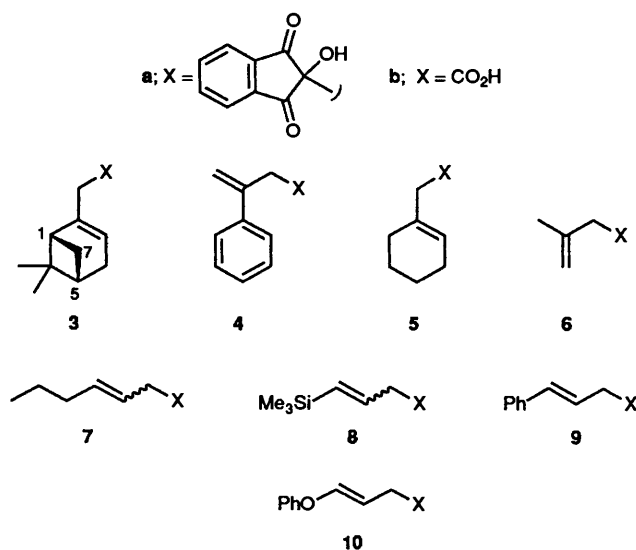

The procedure is best suited to the relatively small-scale preparation of allyl and allenyl carboxylic acids. Phthalic acid is the expected co-product, but in a number of reactions

appreciable quantities of phthalic anhydride were formed. This may be linked to variations in the dryness of the periodic acid employed, but the length of time the reaction is allowed to proceed may also be important. When oxidations were left to run overnight an increase in anhydride production usually resulted.

11   **12**

13

14   **15**   **16**
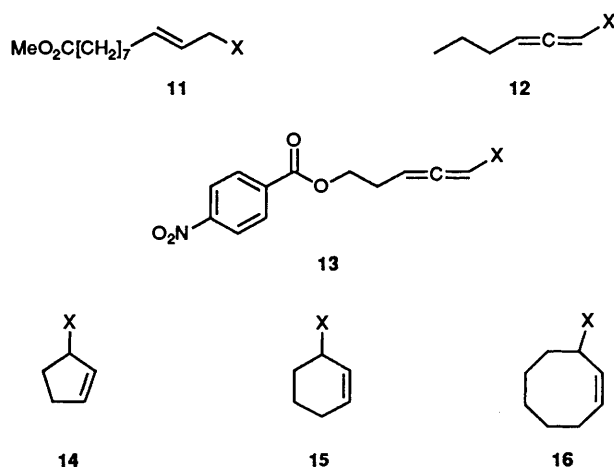
When the carboxylic acid was relatively non-polar (as in the case of products **3b**, **5b–8b**, **11b** or **16b**—which all have H:C ratios >1.5:1) the simple extraction into hexane was both an effective and efficient means for preliminary purification. The more polar carboxylic acids are much less soluble in hexane, larger quantities of the solvent become necessary, and appreciable amounts of phthalic acid and anhydride are co-extracted. For the crystalline acids (especially **9b**, **10b** and **13b**) this was not a problem since phthalic acid and anhydride were removed in the final crystallisation. However, with acids **4b**, **12b** and **14b** the removal of these co-products to an acceptable level before the final distillation proved to be more problematical (the oily carboxylic acid presumably acts as a solvent), and appreciable losses therefore occurred. Various other methods for the isolation of the required carboxylic acids were therefore investigated. Alternative extraction solvents such as diethyl ether or chloroform offered no advantage, attempted separation by relying on pK_a differences always afforded mixtures, and attempts to form specific lead(II) or calcium ion chelates of phthalic acid proved to be fruitless. Finally, an inherently different method for releasing the carboxylic acid from the adducts 1 was attempted following literature precedent.[4] Thus, treatment of adduct **3a** (or **4a**) with 4-methylaniline in boiling acetic acid afforded a dark oil (presumably **17**),[4] which was then treated with aqueous sodium hydroxide. Work-up afforded an oil which contained the desired carboxylic acid **3b** or **4b** (^{1}H NMR assay) among a number of other unidentified compounds. Hence, this approach was also abandoned.

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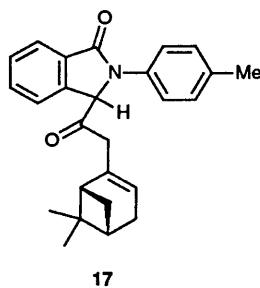
Experimental

The general methods, procedures and data abbreviations are

given in the preceding paper;[1] purified ene adducts **3a–16a** were employed as reactants. Diethyl ether was dried over sodium wire. Periodic acid (>99.0%) was purchased from Fluka Chemie AG.

General Procedure for the Oxidation of the Indane-1,2,3-*trione–Ene Adducts* **3a–16a** *with Periodic Acid.*—To a cooled and stirred solution of the ene adduct[1] (2 mmol) in dry diethyl ether (20 cm^3) in a 50 cm^3 round-bottomed flask was added periodic acid (4.1 mmol) in small portions at a rate as to maintain the temperature at 10 °C. After the addition was complete the flask was stoppered and the mixture was stirred at room temperature for 2–6 h. The reaction mixture was then filtered and the ether was removed at reduced pressure. The residue obtained (usually a white solid plus an oil) was extracted with warm hexane or (40–60 °C) light petroluem (usually 2 × 20 cm^3; 5 × 20 cm^3 was necessary for less soluble carboxylic acids **2**). Spectroscopic examination of the undissolved solid residue indicated that it was phthalic acid containing variable amounts of phthalic anhydride. The combined hexane extracts were evaporated under reduced pressure and the residue was refrigerated overnight. Solid products were recrystallised; oily products were examined for the deposition of phthalic acid crystals. In cases where a small impurity of phthalic acid remained, the oil was extracted with *a minimum* of hexane, and the product was then recovered by evaporation of the solvent. The oily carboxylic acid product was then distilled under reduced pressure in a kugelrohr apparatus.

(6,6-*Dimethylbicyclo*[3.1.1]*hept-2-en-2-yl*)*acetic acid* **3b**. B.p. 95 °C/0.05 Torr;* n_D^{23} 1.4937 (lit.,[5] b.p. 95 °C/0.05 Torr; n_D^{25} 1.4941); S-benzylisothiuronium salt, m.p. 154–155 °C; ν_{max}-(film)/cm^{-1} 3300–2500, 1700, 1645, 1410, 1360, 1300, 1230, 1160 and 910; δ_H 11.76 (br s, CO$_2$H), 5.44 (~ sept., J 1.5, =CH), 3.03 (~ qdd, J 15.2 and 1.5, CH$_2$CO$_2$H), 2.40 (dt, J 8.7 and 5.6, *anti*-7-H), 2.26 (br dd, J 17.7, 4-H$_2$), 2.14 (dt, J 5.6 and 1.5, 1-H), 2.09 (br m, 5-H), 1.28 (*anti*-Me), 1.24 (d, J 8.7, *syn*-7-H) and 0.84 (*syn*-Me).

3-*Phenylbut*-3-*enoic acid* **4b**. M.p. 47–48 °C (from hexane) (lit.,[6] 48–49.5 °C) (Found: C, 74.0; H, 6.4%; M$^+$, 162.0656. Calc. for C$_{10}$H$_{10}$O$_2$: C, 74.1; H, 6.2; M, 162.0681); ν_{max}(KBr)/cm^{-1} 3300–2800, 1710, 1680, 1580, 1510, 1420, 1280, 1240, 1200 and 920; δ_H 11.00 (br s, CO$_2$H), 7.45–7.42 (m, 2 × Ar H), 7.36–7.26 (m, 3 × ArH), 5.58 (=CHH), 5.27 (=CHH) and 3.55 (CH$_2$).

(*Cyclohexen*-1-*yl*)*acetic acid* **5b**. M.p. 34–35 °C (from hexane) (lit.,[7] 33–34 °C); ν_{max}(film)/cm^{-1} 3500–2800, 1720, 1680, 1450, 1420, 1300, 1250 and 930; δ_H (90 MHz) 10.80 (br s, CO$_2$H), 5.70 (br s, =CH), 3.00 (CH$_2$CO$_2$), 2.20–1.85 (m, CH$_2$C=CCH$_2$) and 1.85–1.50 (m, CH$_2$CH$_2$).

3-*Methylbut*-3-*enoic acid* **6b**. B.p. 87–88 °C/15 Torr; n_D^{23} 1.4309 (lit.,[8] b.p. 80–81/12 Torr; n_D^{23} 1.4310); amide had m.p. 117 °C (lit.,[9] 117 °C); ν_{max}(film)/cm^{-1} 3600–2500, 1700, 1640, 1400, 1280, 1210, 1160 and 900; δ_H (90 MHz) 11.28 (br s, CO$_2$H), 4.95 (m, =CHH), 4.90 (m, =CHH), 3.07 (br s, CH$_2$CO$_2$) and 1.83 (br s, Me).

(E)- *and* (Z)-*Hept*-3-*enoic acid* **7b**. Ratio E:Z ~85:15 (in **7a** E:Z, 81:19),[1] b.p. 89 °C/10 Torr; n_D^{23} 1.4401 (lit.,[10] b.p. 69.9 °C/1 Torr; n_D^{25} 1.4402); *p*-bromophenacyl ester had m.p. 77–78 °C (lit.,[10] 77.5–78.5 °C); ν_{max}(film)/cm^{-1} 3450–3000, 1710, 1600, 1460, 1400, 1250, 1160, 1100, 960 and 900; E-**7b**: δ_H 10.68 (br s, CO$_2$H), 5.58–5.37 (m, CH=CH), 2.99 (d, J 5.7, CH$_2$CO$_2$), 1.98–1.90 (m, =CHCH$_2$), 1.39–1.25 (m, =CHCH$_2$CH$_2$) and 0.82 (t, J 7.3, Me); Z-**7b**: δ_H 10.68 (br s, CO$_2$H), 5.58–5.37 (m, CH=CH), 3.06 (d, J 6, CH$_2$CO$_2$), 1.98–1.90 (m, CHCH$_2$), 1.39–1.25 (m, =CHCH$_2$CH$_2$) and 0.83 (t, J 7.3, Me).

* 1 Torr = 133.322 Pa.

(E)- and (Z)-4-Trimethylsilylbut-3-enoic acid **8b**. Ratio $E:Z$ 66:34 (in **8a** $E:Z$ 65.5:34.5),[1] b.p. 110–112 °C/8 Torr (Found: C, 53.1; H, 9.1. $C_7H_{14}O_2Si$ requires C, 53.1; H, 8.9%); v_{max}(film)/cm^{-1} 3400–2800, 1710, 1610, 1420, 1300, 1250, 1220, 1160, 990 and 940; δ_H (90 MHz; no TMS added) 10.70 (br s, CO_2H), 6.60–5.95 (m, E- + Z-CH=CHSi), 5.80 (d, J 19, E-CH=CHSi), 5.77 (d, J 13, Z-CH=CHSi), 3.20 (d, J 6, E-CH_2CO_2), 3.17 (d, J 6, Z-CH_2CO_2), 0.10 (E-SiMe$_3$) and 0.00 (Z-SiMe$_3$).

(E)-4-Phenylbut-3-enoic acid **9b**. M.p. 87 °C (from water) (lit.,[11] 87 °C); v_{max}(KBr)/cm^{-1} 3500–2500, 1700, 1600, 1455, 1400, 1255, 1160, 970 and 905; δ_H (90 MHz) 10.85 (br s, CO_2H), 7.40 (m, Ph), 6.59 (d, J 15, =CHPh), 6.31 (dt, J 15 and 6, =CHCH$_2$) and 3.31 (d, J 6, CH_2CO_2).

(E)-4-Phenoxybut-3-enoic acid **10b**. Z-Isomer detected in crude product, but removed in the purification (in **10a** $E:Z$ 64.5:32.5),[1] m.p. 59–60 °C (from hexane) (lit.,[12] 32 °C) (Found: C, 67.65; H, 5.7%; M$^+$, 178.0635. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.7%; M, 178.0630); v_{max}(KBr)/cm^{-1} 3300–2800, 1700, 1670, 1590, 1490, 1420, 1320, 1220, 1170, 1100 and 900; δ_H (90 MHz) 11.45 (br s, CO_2H), 7.42–7.00 (m, Ph), 6.65 (dt, J 12 and 1.5, =CHOPh), 5.48 (dt, J 12 and 7, =CHCH$_2$) and 3.12 (dd, J 7 and 1.5, CH_2CO_2).

ω-Methyl Hydrogen Dodec-3-enediolate **11b**. M.p. 35–36 °C (from hexane) (Found: C, 64.3; H, 9.5. $C_{13}H_{22}O_4$ requires C, 64.4; H, 9.15%); v_{max}(KBr)/cm^{-1} 3300–2800, 1730, 1680, 1430, 1340, 1280, 1240, 1160 and 960; δ_H (90 MHz) 10.50 (br s, CO_2H), 5.68–5.52 (m, CH=CH), 3.70 (OMe), 3.08 ($\sim$ d, J 5, =CHCH$_2CO_2H$), 2.33 (t, J 7, CH_2CO_2Me), 2.17–1.88 (m, =CHCH$_2$), 1.82–1.48 (m, $CH_2CH_2CO_2Me$) and 1.45–1.20 (m, 4 × CH$_2$).

(±)-Hepta-2,3-dienoic acid **12b**. B.p. 84–88 °C/0.6 Torr (lit.,[13] 86–90 °C/0.2 Torr) (Found: M$^+$, 126.0653. Calc. for $C_7H_{10}O_2$: M, 126.0681); v_{max}(film)/cm^{-1} 3400–2800, 1960, 1700, 1450, 1300, 1220 and 900; δ_H (90 MHz) 11.85 (br s, CO_2H), 5.80–5.58 (m, CH=C=CH), 2.30–2.00 (m, =CHCH$_2$), 1.72–1.30 (m, CH_2Me) and 0.96 (t, J 7, Me).

(±)-6-(4-Nitrobenzoyloxy)hexa-2,3-dienoic acid **13b**. M.p. 152–153 °C (from chloroform) (Found: C, 56.25; H, 4.1; N, 4.7%; M$^+$, 277.0583. $C_{13}H_{11}NO_6$ requires C, 56.3; H, 4.0; N, 5.05%; M, 277.0586); v_{max}(KBr)/cm^{-1} 3200–2300, 1950, 1720, 1670, 1600, 1510, 1450, 1350, 1300, 1220, 1120 and 920; δ_H (90 MHz) 9.00 (br s, CO_2H), 8.45–8.25 (m, 4 × ArH), 6.00–5.65 (m, CH=C=CH), 4.57 (t, J 7, CH$_2$OCO), and 2.90–2.50 (m, =CHCH$_2$).

(±)-Cyclopent-2-enecarboxylic acid **14b**. B.p. 105–106 °C/12 Torr (lit.,[14,15] 65 °C/4 Torr, 103–104 °C/11 Torr); v_{max}(film)/cm^{-1} 3400–2800, 1710, 1420 and 910; δ_H (90 MHz) 10.90 (br s,

CO_2H), 6.10–5.75 (m, CH=CH), 3.85–3.45 (m, CHCO$_2$) and 2.70–1.90 (m, CH_2CH_2).

(±)-Cyclohex-2-enecarboxylic acid **15b**. B.p. 124–125 °C/12 Torr [lit.,[16,17] 120 °C/10 Torr, 130 °C (bath)/14 Torr]; v_{max}(film)/cm^{-1} 3400–2800, 1705, 1420 and 910; δ_H (90 MHz) 10.80 br s, CO_2H), 6.00–5.70 (m, CH=CH), 3.30–3.05 (m, CHCO$_2$) and 2.15–1.45 (m, 3 × CH$_2$).

(±)-Cyclooct-2-enecarboxylic acid **16b**. B.p. 95–100 °C/0.05 Torr (Found: M$^+$, 154.0958. $C_9H_{14}O_2$ requires M, 154.0994); v_{max}(film)/cm^{-1} 3300–2800, 1710, 1450, 1420, 1290, 1240 and 940; δ_H (90 MHz) 11.35 (br s, CO_2H), 6.03–5.62 (m, CH=CH), 3.68–3.38 (m, CHCO$_2$), 2.30–1.90 (m, =CHCH$_2$) and 1.80–1.20 (m, 4 × CH$_2$).

Acknowledgements

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