(C-6), 177.10 (OCN), 195.10 (C=O); mass spectrum, *m/e* (relative intensity) 365 (3), 363 (3), 285 (21), 284 (100), 266 (3), 264 (3), 202 (36), 201 (10), 186 (10). Anal. Calcd for M$^+$: *m/e* 365.0085 and 363.0106. Found: *m/e* 365.0082 and 363.0081. Anal. Calcd for $C_{16}H_{14}NO_4Br$: C, 52.77; H, 3.87. Found: C, 53.19; H, 4.11. The ^{1}H and ^{13}C absorptions for the CH_2Br group of 4.43 and 21.37 ppm, compared to 4.50 and 21.54 ppm for the indenone **8a**, indicate that also in this case the CH_2Br must be located on C-3.

3-(2,2-Dicarbethoxyethyl)-6-methoxy-2-methyl-1-indenone (10a). A solution of 4 mmol of diethyl sodiomalonate in 10 mL of dry glyme is prepared from equivalent amounts of NaH and diethyl malonate. To this solution is added 4 mmol of indenone **8c** dissolved in 40 mL of dry glyme in one portion. The mixture is heated for 5 min at 40 °C. After filtration, the reaction mixture is concentrated, and the residue is purified by preparative TLC on silica gel with benzene–ethyl acetate (90/10). Recrystallization from hexane affords 3.86 mmol of indenone **10a** as red crystals: mp 71 °C; yield 96%; IR ($CHCl_3$) 1730, 1710 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.24 (6, t, 2 $OCHCH_3$), 1.81 (3, s, 2-CH_3), 3.13 (2, d, J = 7 Hz, 3-$\mathbf{CH_2}$–CH), 3.69 (1, t, J = 7 Hz, $CH_2\mathbf{CH}$), 3.83 (3, s, 6-OCH_3), 4.22 (4, q, 2 $O\mathbf{CH_2}CH_3$), 6.74 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 6.96 (1, d, J_o = 8 Hz, 4-H), 7.01 (1, d, J_m = 2 Hz, 7-H); mass spectrum, *m/e* (relative intensity) 346 (35), 301 (5), 272 (4), 254 (4), 227 (6), 187 (55), 186 (100). Anal. Calcd for M$^+$: *m/e* 346.1416. Found: *m/e* 346.1410.

2,3-Bis(2-benzyl-2,2-dicarbethoxyethyl)-6-methoxy-1-indenone (10b). Eight millimoles of diethyl benzylmalonate is stirred with 8 mmol of NaH in 10 mL of dry glyme until all the NaH has disappeared. A 4-mmol sample of indenone 1 dissolved in 50 mL of dry glyme is added in one portion. The mixture is stirred for 3 h at room temperature and then filtered, and the filtrate is evaporated. The residue is purified by a chromatography on silica gel with benzene–ethyl acetate (90/10), affording 2.7 mmol of **10b** as a red oil which could not be crystallized: yield 67%; IR ($CHCl_3$) 1760 and 1730 cm^{-1} ($\nu_{C=O}$); NMR δ 0.98–1.36 (12, m, 4 $OCH_2\mathbf{CH_3}$), 3.12 (2, s, 3-CH_2), 3.22 (2, s, 2-CH_2), 3.48 and 3.50 (2 s, 2 H each, 2 $\mathbf{CH_2}Ph$), 4.14–4.56 (8, m, 4 $O\mathbf{CH_2}CH_3$), 7.16 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 7.44 (1, d, J_m = 2 Hz, 7-H), 7.56 (1, d, J_o = 8 Hz, 4-H), 7.56–7.72 (10, m, 2 Ph); mass spectrum, *m/e* (relative intensity) 684 (17), 593 (15), 91 (100). Anal. Calcd for M$^+$: *m/e* 684.2934. Found: *m/e* 684.2929.

2-(2,2-Dicarbethoxyethyl)-4-(dicarbethoxymethylene)-7-methoxy-1-tetralone (11). A solution of 12 mmol of diethyl sodiomalonate in 10 mL of dry glyme is prepared by reacting equivalent amounts of sodium hydride and diethyl malonate for 1 h. To this mixture is added 4 mmol of indenone 1 dissolved in 50 mL of dry glyme in one portion, and the mixture is stirred for an additional hour at room temperature, after which it is filtrated. The filtrate is concentrated in vacuo, and the residue is purified by a preparative TLC on silica gel with benzene–ethyl acetate (85/15), yielding 3.55 mmol of **11** as a slightly yellow oil: yield 89%; IR ($CHCl_3$) 1730 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$) δ 1.12–1.41 (12, m, 4 $OCH_2\mathbf{CH_3}$), 1.90–3.02 (4, m, 2 CH–$\mathbf{CH_2}$), 3.42–3.80 (2, m, 2 $\mathbf{CH}$–CH_2), 3.86 (3, s, 7-OCH_3), 4.09–4.22 (8, m, 4 $O\mathbf{CH_2}CH_3$), 7.05 (1, dd, J_o = 9 Hz, J_m = 3 Hz, 6-H), 7.42 (1, d, J_o = 9 Hz, 5-H), 7.52 (1, d, J_m = 3 Hz, 8-H); ^{13}C NMR ($CDCl_3$) 13.5 and 13.7 (4 $OCH_2\mathbf{CH_3}$), 29.3 (2-$\mathbf{CH_2}$–CH), 35.5 (C-3), 45.7 (C-2), 49.5 (-CH), 55.4 (OCH_3), 61.3 and 61.5 (4 $O\mathbf{CH_2}CH_3$), 110.4 (C-8), 120.7 (C-6), 124.8 (C-5), 128.9 (4 =C), 131.1 (C-4a), 133.6 (C-8a), 149.2 (C-4), 161.8 (C-7), 164.8 and 166.9 (2 =$C(\mathbf{COOEt})_2$), 169.1 and 169.3 (2 $CH(\mathbf{COOEt})_2$), 197.8 (C-1); mass spectrum, *m/e* (relative intensity) 504 (4), 459 (35), 458 (100), 413 (16), 412 (42), 385 (5), 367 (10), 366 (20), 298 (33). Anal. Calcd for M$^+$: *m/e* 504.1995. Found: *m/e* 504.1999.

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Registry No. 1, 55288-51-2; **2**, 73636-05-2; **3a**, 73636-06-3; **3b**, 73651-38-4; **3c**, 73636-07-4; **3c** acetate, 73636-08-5; **3d**, 73636-09-6; **3d** acetate, 73636-10-9; **3e**, 73636-11-0; **3e** acetate, 73636-12-1; **3f**, 73636-13-2; **3f** acetate, 73636-14-3; **3g**, 73651-39-5; **3j**, 73636-15-4; **3j** acetate, 73636-16-5; **5a**, 73636-17-6; **5b**, 73636-18-7; **6**, 73636-19-8; **8a**, 73636-20-1; **8c**, 55288-50-1; **8d**, 73636-21-2; **10a**, 73636-22-3; **10b**, 73636-23-4; **11**, 73636-24-5; diethyl malonate, 105-53-3; succinimide, 123-56-8; diethyl benzylmalonate, 607-81-8.

Cycloaddition Reactions of Indenes. 1. Adducts of 1*H*-Indene-3-carboxylic Acid with Ethylenic Dienophiles

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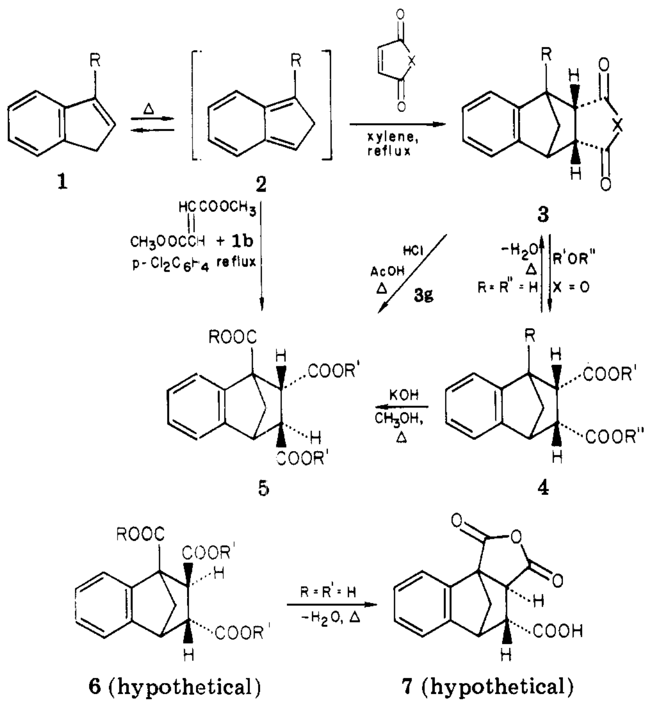
1*H*-Indene-3-carboxylic acid (**1b**) and its methyl ester (**1c**) react when heated via intermediate 2*H*-indenes (isoindenes) with the more reactive ethylenic dienophiles, giving the corresponding 1:1 Diels–Alder adducts as 1,2,3,4-tetrahydro-1,4-methanonaphthalene-1-carboxylic acid 2,3-derivatives **3**. Thus, 1:1 adducts were obtained with **1b** in refluxing xylene with maleic anhydride (**3b**, 71%) and *N*-phenylmaleimide (**3g**, 46%) and in refluxing 1,2-dichlorobenzene (but not in xylene) with dimethyl fumarate (**5c**, 19%). The less reactive **1c** gave a 1:1 adduct (**3c**, 43%) in refluxing xylene with maleic anhydride but not with *N*-phenylmaleimide. That the reaction is quite sensitive to steric hindrance is shown by the facts that **1b** failed to give 1:1 adducts in refluxing xylene with citraconic (methylmaleic) anhydride, dichloromaleic anhydride, β-nitrostyrene, tetracyanoethylene, and diethyldiazenedicarboxylate, neat at 130 °C with phenylmaleic anhydride, or in refluxing 1,2-dichlorobenzene with cinnamic acid. The transformations which were carried out include hydrolysis of adduct **3b** to the 2-endo,3-endo triacid **4b** (64%), Fischer esterification to the trimethyl ester **4d** (69% from **3b**, 66% from **4b**), thermal dehydration of **4b** back to **3b**, and methanolysis of **3b** to a monomethyl 3-ester (**4e**, 83%) which underwent simple hydrolysis in 5% NaOH to **4b** (22%) but epimerized during hydrolysis in methanolic 5% KOH to the 2-endo,3-exo triacid **5a** (83%; similarly from **4d**, 60%), which at 300 °C was reepimerized and dehydrated to **3b** (22%). Hydrolysis of the 2,3-diester adduct **5c** with both 5% NaOH (68%) and methanolic 5% KOH (60%) also gave **5a**, showing that **5c** has the same stereochemistry as **5a**. With diazomethane, **5a** gave its trimethyl ester (**5b**, 59%). Hydrolysis of adduct **3c** with 5% NaOH gave **4b** (68%), while neutral hydrolysis gave the 1-methyl ester **4c** (78% as a hydrate), which at 150–160 °C was reconverted to **3c** (99%). Epimerization also occurred during the acidic hydrolysis of adduct **3g**, giving **5a** (11%). With diazomethane, **3g** gave the 1-methyl ester **3h** (72%), which was not obtained directly by reaction of **1c** with *N*-phenylmaleimide.

The thermal addition (at 250 °C in benzene) of 1*H*-indene (**1a**) to maleic anhydride to give a 1:1 adduct (**3a**, 30%) was first reported by Alder, Pascher, and Vagt,[2] who postulated a mechanism involving prior isomerization to

0022-3263/80/1945-3456$01.00/0

Scheme I

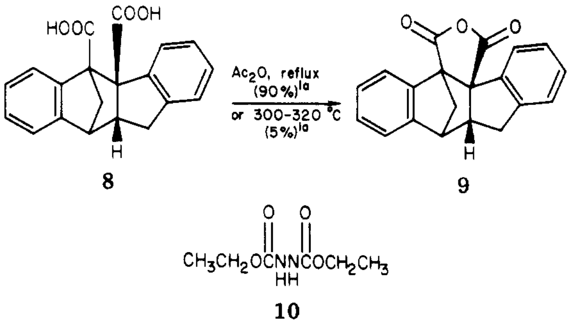


	R	X	R'	R''
1-3a	H	O		
1-4b	COOH	O	H	H
1-4c	$COOCH_3$	O	H	H
4d	$COOCH_3$		CH_3	CH_3
4e	COOH		H	CH_3
4f	COOH		CH_3	H
3g	COOH	NC_6H_5		
3h	$COOCH_3$	NC_6H_5		
5a, 6a	H		H	
5b	CH_3		CH_3	
5c	H		CH_3	

2*H*-indene (isoindene, **2a**). More recently, the isomerization of **1a** to **2a** has been demonstrated by deuterium-labeling studies,[3] which support this mechanism. In the course of our determination of the structure of the dimer (**8**)[1a,4] produced by heating of 1*H*-indene-3-carboxylic acid (**1b**), we have studied the Diels–Alder reaction of **1b** with various ethylenic dienophiles.

Addition of **1b** to maleic anhydride in refluxing xylene for 22 h gave a 1:1 adduct (**3b**, 71%; Scheme I). Hydrolysis of **3b** gave a triacid (**4b**, 64%). When heated to the melting point, 180–195 °C (on a hot stage preheated to ~150 °C), the crystals of the triacid **4b** dehydrated with steam evolution, resolidified at ~200 °C, and remelted at 227–228 °C, the melting point of the anhydride **3b**, which they were shown then to be by mixture melting point comparison. Fischer methyl esterification of **3b** or **4b** gave the trimethyl ester **4d** (69% from **3b**, 66% from **4b**). The NMR spectrum of **4d** in $CDCl_3$ shows three methyl ester singlets at δ 3.42, 3.47, and 3.82. A Fieser model of **4d** suggests that the two *endo*-methyl ester groups should be

Scheme II



shielded by the benzene ring, thus explaining their unusually high chemical shift. Methanolysis of the anhydride ring of **3b** in refluxing methanol gave a monomethyl ester diacid (**4e**, 83%). Hydrolysis of this diacid in refluxing aqueous 5% sodium hydroxide for 1 h gave (after acidification) the corresponding triacid **4b** (22%), but hydrolysis in refluxing methanolic 5% potassium hydroxide for 62 h was accompanied by epimerization, giving the 2-endo,3-exo triacid **5a** (83%), which was converted by re-epimerization and dehydration to the original anhydride acid **3b** (22%) by heating to 300 °C. Hydrolysis of the triester **4d** in refluxing methanolic 5% potassium hydroxide was also accompanied by epimerization, giving (after acidification) the same epimeric triacid **5a** (60%). Of the two possible structures, **5a** or **6a**, for the epimeric triacid, structure **6a** can be eliminated, since its configuration should permit formation of a new anhydride (**7**) between the cis 1- and 2-carboxyl groups. Analogy for this assumption is the formation of the anhydride **9** from the dimer of 1*H*-indene-3-carboxylic acid (**8**) either by heating at 300–320 °C (5%) or by refluxing in acetic anhydride (90%)[1a] (Scheme II). In the formation of triacid **5a** from the monomethyl ester **4e** (or **4f**), if it is assumed that a proton α to an ester carbonyl group is more readily epimerizable than a proton α to a carboxylate ion and that epimerization occurs prior to ester hydrolysis, then it follows that the 3-ester structure **4e** (rather than the 2-ester structure **4f**) is the structure of the monomethyl ester. This is also consistent with nucleophilic attack of methanol at what should be the less sterically hindered carbonyl group of the anhydride. Methyl esterification of **5a** with diazomethane gave the trimethyl ester **5b** (59%) as an oil. In the NMR spectrum of **5b** in $CDCl_3$, the 2-*endo*-methyl ester protons appear as an upfield singlet at δ 3.48, shielded by the benzene ring, while the 1-bridgehead and 3-*exo*-methyl ester protons appear as downfield singlets at δ 3.75 and 3.84. The 3-endo proton appears at δ 2.91 as a doublet of doublets ($J_{3,2}$ = 5 Hz, $J_{3,9a}$ = 2 Hz). The long-range coupling observed here between the syn and endo protons has been observed previously in norbornenes.[5]

The methyl ester (**1c**) of **1b** also added to maleic anhydride in refluxing xylene, giving the ester anhydride **3c** (43%). The base peak in the mass spectrum of **3c** appeared at *m*/*e* 174, corresponding to the **1c** cation, probably formed via the retrodiene **2c** by a retro-Diels–Alder reaction. Alkaline hydrolysis of **3c** gave the triacid **4b** (68%), while neutral hydrolysis gave the 1-methyl ester diacid **4c** as a hydrate (78%), which gave the anhydrous form after crystallization from acetonitrile. Heating of **4c**

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(1) (a) Taken from, in large part, the Ph.D. Thesis of Lawrence L. Landucci, University of Minnesota, Minneapolis, MN, Mar 1967; *Diss. Abstr. B.* **1968**, *28*, 3223–3224. (b) Taken in part from the Ph.D. Thesis of Venkataraman Kameswaran, University of Minnesota, Minneapolis, MN, June 1971; *Diss. Abstr. Int. B.* **1972**, *32*, 6918–6919. For a previous paper in this series, see: Noland, W. E.; Landucci L. L.; Darling, J. D. *J. Org. Chem.* **1979**, *44*, 1358–1359, 5007.

(2) Alder, K.; Pascher, F.; Vagt, H. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 1501–1514.

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(4) Weissgerber, R. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1436–1448.

(5) (a) Meinwald, J.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1963**, *85*, 2514–2515. (b) Laszlo, P.; Schleyer, P. v. R. *Ibid.* **1964**, *86*, 1171–1179. (c) Davis, J. C., Jr.; Van Auken, T. V. *Ibid.* **1965**, *87*, 3900–3905. (d) Noland, W. E.; Langager, B. A.; Manthey, J. W.; Zacchei, A. G.; Petrak, D. L.; Eian, G. L. *Can. J. Chem.* **1967**, *45*, 2969–2978.

hydrate at 150–160 °C regenerated the ester anhydride **3c** (99%).

Addition of **1b** to dimethyl fumarate in refluxing 1,2-dichlorobenzene for 44 h gave the *trans*-2,3-diester **5c** (19%). The 2-endo,3-exo configuration of the two ester groups was established by alkaline hydrolysis of **5c** to the triacid **5a** with either aqueous 5% sodium hydroxide (68%) or methanolic 5% potassium hydroxide (60%). Addition of **1b** to *N*-phenylmaleimide in refluxing xylene for 9 h gave the corresponding 1:1 adduct **3g** (46%). Acidic hydrolysis of **3g** (recovered in 35% yield) in refluxing 1:1 hydrochloric acid–acetic acid was also accompanied by epimerization, giving **5a** (11%). Methyl esterification of **3g** with diazomethane gave the corresponding 1-methyl ester **3h** (72%). An attempt to prepare **3h** by the Diels–Alder reaction of the methyl ester (**1c**) of **1b** with *N*-phenylmaleimide in refluxing xylene did not give **3h**, suggesting that **1c** is less reactive than **1b**.

The sensitivity of the Diels–Alder reaction to steric hindrance is shown by the fact that **1b** failed to give 1:1 adducts in refluxing xylene with citraconic (methylmaleic) anhydride, dichloromaleic anhydride, β-nitrostyrene, tetracyanoethylene, and diethyl diazenedicarboxylate, neat at 130 °C with phenylmaleic anhydride, or in refluxing 1,2-dichlorobenzene with cinnamic acid. In most cases at least some starting materials were recovered. β-Nitrostyrene also gave a polymeric product, probably poly-β-nitrostyrene, and tetracyanoethylene also gave an insoluble black complex. Diethyl diazenedicarboxylate produced dehydrogenation, giving diethyl 1,2-hydrazinedicarboxylate (**10**) as the only crystalline product.

The mechanism of the formation of the adducts was also investigated. In order to test for the possible intermediacy of 2*H*-indenes (**2**) in the formation of the 1:1 adducts (**3**, **5c**) from **1b** and **1c**, we deuterated **1c** at C_1 by reaction with 1-butyllithium followed by D_2O (69% yield). The deuterium content was found by NMR to be completely at C_1 and to be 0.97 D atom per molecule by NMR and 0.95 D atom per molecule by mass spectrometric analysis. The deuterated ester was allowed to react with maleic anhydride in refluxing xylene for 12 h, giving deuterated adduct **3c**. The NMR spectrum in acetone-d_6 was similar to that of undeuterated **3c**, except that the number of protons at C_9 was 1.63 (0.37 D) and at C_4 was 0.51 (0.49 D), corresponding to a total deuterium content of 0.86 D atom per molecule. This agrees well with the mass spectrometric value of 0.83 D atom per molecule. A decrease in deuterium content from that of the indene **1a** was also observed in the formation of the indene–maleic anhydride adduct **3a**.[3] The scrambling of the deuterium label is consistent with the presence of an isoindene intermediate (**2c**) in the reaction of **1c** with maleic anhydride and, by analogy, also in the other reactions of indenes with ethylenic dienophiles.

Experimental Section

Melting points were determined on calibrated Fisher-Johns hot stages. Ultraviolet spectra (UV) were determined on either a Bausch and Lomb Spectronic Model 505 or a Cary Model 11 recording spectrophotometer. Infrared spectra (IR) were determined on a Perkin-Elmer 21, a Beckman IR-5, or a Unicam SP-200 spectrophotometer. Nuclear magnetic resonance spectra (NMR) were determined on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. The low-resolution electron-impact mass spectrum was determined on a Hitachi Perkin-Elmer RMU-6D spectrometer at 70 eV and 200 °C by Roger A. Upham and his associates. Elemental microanalyses were performed at the University of Minnesota by Mrs. Olga Hamerston and her assistants, Robert E. Johnson, James E. Johnson, Mrs. Kathleen Nelson Juneau, Mrs. Fay M. Thompson, Brian H. Chollar, and Lawrence L. Landucci.

1*H*-Indene-3-carboxylic Acid (1b).[6] 1*H*-Indene (**1a**; 128 g, 1.07 mol, 97.5% minimum purity, Neville Chemical Co.) was added to a hexane solution of 1-butyllithium (containing 64 g, 1.00 mol, Foote Mineral Co.) in anhydrous diethyl ether (1000 mL) at a rate sufficiently slow (~3 mL/min) that gentle refluxing was maintained. After the addition, the yellow-orange solution was refluxed for 1 h and then poured slowly with stirring onto a large excess of crushed dry ice. The mixture was allowed to warm to room temperature, and then water (600 mL) was added with stirring. The aqueous layer was separated, warmed on a steam bath to remove dissolved ether, cooled, and acidified to pH <2 with concentrated hydrochloric acid. The resulting yellow solid was collected on a filter, washed with cold water, and dried at 50 °C in a vacuum oven to give a yellow solid: 142 g, (89%); mp 161–162 °C (lit.[7] mp 159.5–161 °C). The ether layer was extracted with water (3 × 50 mL), and the aqueous extracts were treated as above and acidified, giving more yellow solid: 16.6 g (10%; total 99%); mp 155–157 °C.

Methyl 1*H*-Indene-3-carboxylate (1c). A solution of **1b** (19.5 g, 122 mmol) in methanol (200 mL) was saturated with dry HCl gas and kept at room temperature for 24 h. The solution was evaporated under vacuum on a steam bath. The resulting orange oil was dissolved in diethyl ether (200 mL) and washed with aqueous saturated sodium bicarbonate (2 × 25 mL) and water (2 × 25 mL). The ether extract was dried (Na_2SO_4), concentrated by evaporation, and vacuum distilled, giving a colorless liquid: 15.4 g (72%); bp 76 °C (0.1 mm) [lit.[4] bp 153–154 °C (23 mm)]; IR (neat) 1700 (s, C═O), 1625 (w), 1575 (m), 1555 (m, C═C) cm^{-1}.

Diels–Alder Reactions (General Workup Procedure). In the Diels–Alder reactions and attempted reactions, after reflux, the usual workup consisted of keeping the solutions at room temperature in an open container to allow slow evaporation. In the successful reactions the products separated after anywhere from a few minutes to 12 h. If the starting material was the first to separate, the reaction was assumed to be unsuccessful (since the adducts were assumed to be considerably less soluble), and no further attempt was made to recover additional starting material.

Reaction of 1b with Maleic Anhydride: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid Cyclic 2,3-Anhydride (3b). A solution of **1b** (3.20 g, 20.0 mmol) and maleic anhydride (3.92 g, 40.0 mmol) in xylene (25 mL) was refluxed for 22 h. Workup gave white flakes: 3.67 g (71%); mp 226–228 °C. Recrystallization from xylene gave white flakes: mp 227–228 °C; IR (Nujol) 2700 (mw), 2630 (mw, br, OH), 1860 (m), 1835 (sh, mw), 1780 (s), 1710 (s, C═O) cm^{-1}.

Anal. Calcd for $C_{14}H_{10}O_5$ (mol wt 258.22): C, 65.12; H, 3.90. Found: C, 64.83; H, 3.91.

Hydrolysis of 3b: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid (4b). Adduct **3b** (440 mg, 1.70 mmol) was refluxed with water (10 mL) for 15 min, and the resulting solution was concentrated on a hot plate to 3 mL and allowed to cool, causing separation of white crystals: 300 mg (64%); mp 177.5–178.5 °C. Four recrystallizations from water gave white crystals: mp 180–195 °C dec, with gas evolution on a hot stage preheated to ~150 °C, resolidifies at ~200 °C, melting point and mixture melting point with starting **3b** 227–228 °C; IR of **4b** (Nujol) 3440 (ms), 2620 (m, br, OH), 1750 (ms), 1700 (s, C═O) cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_6$ (mol wt 276.24): C, 60.87; H, 4.38. Found: C. 60.75; H, 4.42.

Trimethyl Ester of 4b: Trimethyl 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylate (4d). A. By Methyl Esterification of 4b. A solution of **4b** (1.52 g, 5.50 mmol) in methanol (25 mL) was saturated with dry HCl gas

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(6) We are indebted to Leonard J. Czuba for suggesting this procedure. The procedure was carried out under the author's supervision by Dennis P. Landucci in the Advanced Organic Chemistry Laboratory course at the University of Minnesota, Feb 1966.

(7) Knowles, W. S.; Kuck, J. A.; Elderfield, R. C. *J. Org. Chem.* **1942**, *7*, 374–382. These authors described their product as "indene-1-carboxylic acid" but later evidence proved that it was 1*H*-indene-3-carboxylic acid: Melera, A.; Claesen, M.; Vanderhaeghe, H. *J. Org. Chem.* **1964**, *29*, 3705–3706.

and kept at room temperature for 24 h. The solvent was evaporated under vacuum on a steam bath. The resulting colorless oil was dissolved in diethyl ether (50 mL), washed with aqueous saturated sodium bicarbonate (5 mL) and water (2 × 5 mL), dried (Na_2SO_4), and evaporated, giving a white crystalline solid: 1.15 g (66%); mp 95–95.5 °C; IR (Nujol) 3380 (vw, overtone), 1725 (s, C=O) cm^{-1}; NMR (30% w/v in $CDCl_3$) δ 2.10 (br s, $w_{1/2}$ = 3 Hz, 1.9 H, 9-CH_2), 3.47 and 3.42 (2 s, 5.9 H, 2- and 3-$COOCH_3$), 3.82 (s, 1-$COOCH_3$) overlapping 3.80 (complex m with major peak at 3.73, $w_{1/2}$ = 28 Hz, total 6.0 H, 4-, 3-, and 2-H), 7.19 (complex m, $w_{1/2}$ = 9 Hz, 5-, 6-, and 7-H), 7.57 (complex m, $w_{1/2}$ = 13 Hz, 1.2 H, 8-H).

Anal. Calcd for $C_{17}H_{18}O_6$ (mol wt 318.31): C, 64.14; H, 5.70. Found: C, 63.82; H, 5.67.

B. By Methyl Esterification of 3b. By the procedure of part A, **3b** was esterified to **4d** in 69% yield; mp 94–95.5 °C. The IR spectrum in Nujol was identical with that from part A.

Methanolysis of 3b: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid 3-Methyl Ester (4e). A solution of **3b** (3.66 g, 14.1 mmol) in methanol (25 mL) was refluxed for 1 h. Most of the methanol was replaced by water by boiling the solution but keeping the volume constant by addition of water. The resulting aqueous solution was allowed to cool, causing separation of white flakes: 3.14 g (83%); mp 183–184 °C. Recrystallization from water gave white flakes: mp 183.5–184 °C; UV (95% C_2H_5OH) λ_{max} 245 nm (sh, log ϵ 2.19), 251 (sh, 2.27), 256 (2.45), 263 (2.60), 270 (2.57); IR (Nujol) 2700 (m, br), 2600 (m, br, OH), 3440 (w, overtone), 1740 (s), 1715 (sh, s), 1695 (s, C=O) cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_6$ (mol wt 290.26): C, 62.06; H, 4.86. Found: C, 61.80; H, 4.81.

Alkaline Hydrolysis of 4e to 4b. A solution of **4e** (273 mg, 0.941 mmol) in aqueous 5% sodium hydroxide (6 mL) was refluxed for 1 h. The solution was concentrated to 4 mL, acidified to pH <2 with concentrated hydrochloric acid, and filtered. The filtrate was concentrated to 2 mL and allowed to cool, causing separation of white crystals: 56 mg (22%); mp 163–166 °C. Recrystallization from water gave white crystals, mp 176–178 °C dec with gas evolution on a hot stage preheated to ~150 °C. There was no depression in the mixture melting point (176–178 °C dec) with the sample of **4b** from hydrolysis of **3b**, and the two samples showed the same resolidification and remelting behavior.

Alkaline Hydrolysis and Epimerization of 4e: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*exo*-tricarboxylic Acid (5a). A solution of **4e** (480 mg, 1.65 mmol) in methanolic 5% potassium hydroxide (10 mL) was refluxed for 62 h. The solution was concentrated on a hot plate to 2 mL, during which the methanol was gradually replaced with water. The solution was acidified to pH <2 with concentrated hydrochloric acid and allowed to cool, causing separation of white crystals: 378 mg (83%); mp 232–236 °C. Four recrystallizations from water gave white needles: mp 272–274 °C; UV (95% C_2H_2OH) λ_{max} 246 nm (sh, log ϵ 2.12), 251 (sh, 2.31), 256 (2.54), 263 (2.71), 270 (2.71); IR (Nujol) 2700 (m), 2630 (m, OH), 1705 (s), 1665 (sh, ms) cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_6$ (mol wt 276.24): C, 60.87; H, 4.38. Found: C, 61.08; H, 4.47.

Alkaline Hydrolysis and Epimerization of 4d to 5a. The triester **4d** (395 mg, 1.24 mmol) was treated as above (for **4e** to **5a**), giving white crystals: 204 mg (60%); mp 264–267 °C. There was no depression in the mixture melting point with the sample of **5a** from **4e**, and the IR spectra in Nujol were identical.

Methyl Esterification of 5a: Trimethyl 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*exo*-tricarboxylate (5b). A solution of **5a** (213 mg, 0.769 mmol) in methanol (10 mL) was cooled to 0 °C and added to a solution of diazomethane[8] (~6 mmol) in diethyl ether (25 mL) at 0 °C. The resulting solution was kept in an ice bath for 5 min and then at room temperature overnight in a hood until the yellow color, due to excess diazomethane, disappeared. The solution was concentrated to 5 mL, diluted with water (25 mL), and extracted with ether (2 × 25 mL). The ether extract was washed with aqueous saturated sodium bicarbonate (5 mL) and water (3 × 5 mL), dried (Na_2SO_4), and evaporated, leaving a pale yellow oil: 144 mg (59%); IR (Nujol) 3400 (w, overtone), 1735 (s, C=O) cm^{-1}; NMR (36% w/v in $CDCl_3$) AB pattern (J_{AB} = 9 Hz) at δ 2.07 (dt, $J_{9a,4} = J_{9a,3}$ = 1.5 Hz, 1.0 H, 9a-H) and 2.35 (dd, $J_{9b,4}$ = 1.5 Hz, 1.0 H, 9b-H), 2.91 (dd, $J_{3,2}$ = 5 Hz, $J_{3,9a}$ = 2 Hz, 1.0 H, 3-H), 3.48 (s, 3.1 H, 2-$COOCH_3$), 3.68 (br s, 4-H) overlapping 3.75 and 3.84 (2 s, total 6.8 H, 1- and 3-$COOCH_3$), 4.18 (d, $J_{2,3}$ = 5 Hz, 1.1 H, 2-H), 7.19 (complex m with major peak at 7.21, $w_{1/2}$ = 17 Hz, 3.0 H, 5-, 6-, and 7-H), 7.55 (complex m, $w_{1/2}$ = 11 Hz, 1.0 H, 8-H).

Dehydration and Epimerization of 5a to 3b. Triacid **5a** (1.95 g, 7.06 mmol) was heated at 300 °C under nitrogen for 15 min. The resulting dark brown residue was crystallized from xylene, giving a yellow solid: 400 mg (22%); mp 177–192 °C; IR spectrum in Nujol identical with that of **3b**.

Reaction of 1c with Maleic Anhydride: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid 1-Methyl Ester Cyclic 2,3-Anhydride (3c). A solution of **1c** (2.61 g, 15 mmol) and maleic anhydride (2.94 g, 30.0 mmol) in xylene (12 mL) was refluxed for 15 h. Workup gave large colorless crystals: 1.75 g (43%); mp 164.5–166.5 °C. Recrystallization from xylene gave white crystals: mp 168–169 °C; IR (Nujol) 1860 (m), 1775 (s), 1730 (s, C=O) cm^{-1}; NMR (16% w/v in $CDCl_3$) AB pattern (J_{AB} = 10 Hz) at δ 2.26 (d, J = 1 Hz, 1.0 H, 9a-H) and 2.38 (d, J = 1 Hz, 1.1 H, 9b-H), 3.91 (s, 1-$COOCH_3$) overlapping 4.11 (complex m, $w_{1/2}$ = 34 Hz, total 5.8 H, 4-, 3-, and 2-H), 7.37 (complex m with strongest peak at 7.27, $w_{1/2}$ = 20 Hz, 4.1 H, 5–8-H); mass spectrum (50 eV, 125 °C; for relative intensity > 12), *m/e* (relative intensity) 272 (21, M), 174 (100, M – $C_4H_2O_3$, retro-Diels–Alder diene, **1c** cation), 142 (19, M – $C_4H_2O_3$ – OCH_3 – H or M – C_2O_3 – $COOCH_2$), 141 (37, M – $C_4H_2O_3$ – OCH_3 – H_2 or M – C_2O_3 – $COOCH_3$), 139 (M – C_2O_3 – $HCOOCH_3$ – H), 129 (22, $C_{10}H_9$, dihydronaphthalene cation), 115 (88, C_9H_7, 1*H*-indenyl cation).

Anal. Calcd for $C_{15}H_{12}O_5$ (mol wt 272.25): C, 66.17; H, 4.44. Found: C, 66.05; H, 4.65.

Alkaline Hydrolysis of 3c to 4b. A mixture of **3c** (254 mg, 0.934 mmol) and aqueous 5% sodium hydroxide (6 mL) was refluxed for 1 h and worked up as described for the alkaline hydrolysis of **4e** to **4b**, giving white crystals: 174 mg (68%); mp 176–180 °C dec with gas evolution on a hot stage preheated to ~150 °C. There was no depression in the mixture melting point (183–186 °C dec) with the sample of **4b** from the hydrolysis of **3b**, the two samples showed the same resolidification and remelting behavior, and the IR spectra in Nujol were very similar.

Hydrolysis of 3c under Neutral Conditions: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid 1-Methyl Ester (4c) and Hydrate. A mixture of **3c** (1.15 g, 4.23 mmol) and water (50 mL) was refluxed for 30 min, and the resulting solution was concentrated on a hot plate to 15 mL and allowed to cool overnight, causing separation of the hydrate as white crystals: 1.02 g (78%); mp 95–105 °C; IR (Nujol) 3360 (m), 3120 (m), 2700 (mw), 2590 (mw, br, OH), 1705 (s), 1655 (sh, m) cm^{-1}.

The hydrate (919 mg, 2.98 mmol, calculated as the monohydrate) was dried by being boiled with benzene (35 mL, volume kept constant by adding more benzene as needed) to azeotrope off the water. The supernatant benzene solution was decanted from the residual undissolved solid and allowed to cool, causing separation of a fluffy white solid: 155 mg (16%); mp 123–128 °C, resolidifies at ~160 °C, remelts at 165–167 °C. The elemental analyses show that the crystals contained occluded benzene.

Anal. Calcd for $C_{15}H_{14}O_6 \cdot 0.35C_6H_6$ (mol wt 317.60): C, 64.66; H, 5.11. Found: C, 64.86, 64.63; H, 5.27, 4.75.

The sample which had been crystallized from benzene (127 mg, 0.400 mmol) was crystallized from acetonitrile, giving white crystals: 41 mg (35%); mp 174–176 °C dec with gas evolution. Recrystallization from acetonitrile gave white crystals: mp 174–176 °C dec with gas evolution; IR (Nujol) 3130 (ms), 2690 (mw), 2600 (mw, br, OH), 1730 (s), 1710 (s, C=O) cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_6$ (mol wt 290.26): C, 62.06; H, 4.86. Found: C, 61.95; H, 5.01.

Dehydration of 4c Hydrate to 3c. The hydrate of **4c** (19.24 mg, 0.0625 mmol) was heated at 150–160 °C in a platinum boat for 10 min, giving a white solid (16.89 mg, 99%) having an IR spectrum in Nujol identical with that of **3c** from the reaction of **1c** with maleic anhydride.

Reaction of 1b with Dimethyl Fumarate: 1,2,3,4-Tetrahydro-1,4-methanonaphthalane-1,2-*endo*,3-*exo*-tricarboxylic Acid 2,3-Dimethyl Ester (5c). A solution of **1b** (1.60 g, 10.0 mmol) and dimethyl fumarate (2.88 g, 20.0 mmol) in 1,2-dichlorobenzene (20 mL) was refluxed for 44 h. The yellow solution was allowed to cool to room temperature overnight, causing separation of two types of crystals, which were filtered and separated by hand. The large colorless crystals were dimethyl fumarate: 400 mg (14% recovery); mp 108–111 °C; mmp with starting material 103–110 °C. The smaller, yellow crystals [590 mg (19%), mp 187.5–190.5 °C] were recrystallized twice from methanol–water, giving white crystals: mp 192.5–193.5 °C; IR (Nujol) 2700 (mw), 2600 (mw, br, OH), 1730 (s), 1720 (s), 1695 (ms, C=O) cm^{-1}; NMR (7% w/v in $CDCl_3$) AB pattern (J_{AB} = 9 Hz) at δ 2.19 (d, poorly resolved with much hyperfine splitting, 0.9 H, 9a-H) and 2.41 (dd, J = 1.5 Hz, 1.0 H, 9b-H), 2.94 (dd, J = 4 and 1.5 Hz, 1.2 H, 4-H), 3.53 (s, 2.7 H, 2-$COOCH_3$), 3.72 (br s, $w_{1/2}$ = 4 Hz, 3-*endo*-H) overlapping 3.80 (s, total 3.8 H, 3-$COOCH_3$), 4.21 (d, J = 5 Hz, 1.2 H, 2-*exo*-H), 7.15 (complex m, with principal peak at 7.21, $w_{1/2}$ = 11.5 Hz, 3.0 H, 5–7-H), 7.54 (complex m, $w_{1/2}$ = 14 Hz, 1.2 H, 8-H), 10.82 (br hump, $w_{1/2}$ = 10 Hz, 1.0 H, 1-COOH).

Anal. Calcd for $C_{16}H_{16}O_6$ (mol wt 304.29): C, 63.15; H, 5.30. Found: C, 63.07; H, 5.60.

When the above reaction was attempted in refluxing xylene for 20 h, only unchanged starting materials were recovered.

Alkaline Hydrolysis of 5c to 5a. A solution of **5c** (96.0 mg, 0.315 mmol) in aqueous 5% sodium hydroxide (5 mL) was refluxed for 1 h. Workup as described for the alkaline hydrolysis of **4e** to **4b** gave white crystals: 58.8 mg (68%); mp 264–267 °C. Recrystallization from water gave white crystals, mp 272–274 °C. There was no depression in the mixture melting point (272–274 °C) with the sample of **5a** from the alkaline hydrolysis and epimerization of **4e** and the IR spectra in Nujol were identical.

Hydrolysis of **5c** in refluxing methanolic 5% potassium hydroxide for 95 h and workup as described for the conversion of **4e** to **5a** also gave **5a** in 60% yield.

Reaction of 1b with *N*-Phenylmaleimide: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid *N*-Phenyl-2,3-dicarboximide (3g). A solution of **1b** (800 mg, 5.0 mmol) and *N*-phenylmaleimide (3.46 g, 20.0 mmol) in xylene (12 mL) was refluxed for 9 h. Workup gave a yellow powder: 760 mg (46%); mp 256–264 °C. Sublimation at 260 °C (0.2 mm) and two crystallizations from methanol–water gave white crystals: mp 263–265 °C; UV (95% C_2H_2OH) λ_{max} 255 nm (log ϵ 2.86), 261 (2.82), 269 (2.64); IR (Nujol) 2700 (mw), 2620 (mw), 2550 (mw, br, OH), 1775 (mw), 1710 (s), 1695 (sh, s, C=O), 1590 (mw, C=C) cm^{-1}.

Anal. Calcd for $C_{20}H_{15}NO_4$ (mol wt 333.33): C, 72.06; H, 4.54; N, 4.20. Found: C, 71.78; H, 4.59; N, 3.99.

Acidic Hydrolysis of 3g to 5a. A solution of **3g** (376 mg, 1.13 mmol) in 1:1 v/v concentrated hydrochloric acid–acetic acid (8 mL) was refluxed for 30 h. The solution was concentrated to 4 mL and boiled for 30 min while most of the acetic acid was replaced by keeping the volume constant by the addition of water. The concentrate was allowed to cool to room temperature, causing separation of unchanged **3g** as white crystals: 132 mg (35% recovery); mp and mmp with the starting material 260–264 °C. The colorless filtrate was concentrated to 2 mL and kept overnight, causing separation of white globular crystals: 33 mg (11%); mp 228–238 °C. Recrystallization from water gave white crystals, mp 268–273 °C. There was no depression in the mixture melting point (268–273 °C) with the sample of **5a** from the alkaline hydrolysis and epimerization of **4e**, and the IR spectra in Nujol were very similar.

Methyl Esterification of 3g: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic Acid 1-Methyl Ester *N*-Phenyl-2,3-dicarboximide (3h). A solution of **3g** (172 mg, 0.516 mmol) in methanol (10 mL) was cooled to 0° C and added to a solution of diazomethane[8] (~6 mmol) in diethyl ether (25 mL) at 0 °C. The resulting solution was kept in an ice bath for 5 min and then warmed gently to ~50 °C in a hood until the yellow color, due to excess diazomethane, disappeared. The solution was concentrated to 3 mL, water was added to the point of turbidity, and the solution was allowed to cool, causing separation of white crystals: 129 mg (72%); mp 163–165 °C. Two recrystallizations from methanol–water gave white needles: mp 165.5–166.5 °C; IR (Nujol) 1765 (mw), 1730 (s), 1705 (s, C=O), 1590 (w, C=C) cm^{-1}; NMR (29% w/v in $CDCl_3$) δ 2.32 (br s, $w_{1/2}$ = 4 Hz, 1.9 H, 9-CH_2), 3.33–4.15 (complex m, 4-, 3-, and 2-H), overlapping 3.88 (s, total 6.2 H, 1-$COOCH_3$), 6.39 (complex m, $w_{1/2}$ = 12 Hz, 1.8 H, *N*-phenyl 2- and 6-H), 7.33 (complex m, with major peaks at 7.20 and 7.25, $w_{1/2}$ = 32 Hz, 7.1 H, 7 aromatic H).

Anal. Calcd for $C_{21}H_{17}NO_4$ (mol wt 347.35): C, 72.61; H, 4.93; N, 4.03. Found: C, 72.55; H, 5.07; N, 3.59.

Attempted Reaction of 1c with *N*-Phenylmaleimide. A solution of **1c** (1.74 g, 10.0 mmol) and *N*-phenylmaleimide (3.44 g, 20.0 mmol) in xylene (10 mL) was refluxed for 10 h. Workup gave a tan powder: 3.30 g (95% based on *N*-phenylmaleimide); mp 152–162 °C. Precipitation from boiling xylene gave a tan powder: 1.74 g (50% based on *N*-phenylmaleimide); mp 242–247 °C. Three more precipitations from boiling xylene gave what appears to be a polymer of *N*-phenylmaleimide as a tan powder: mp 278–281 °C; IR (Nujol) 1775 (w), 1705 (s, C=O), 1590 (w, C=C) cm^{-1}. The powder was too insoluble in ethanol to permit determination of the UV spectrum.

Anal. Calcd for $(C_{10}H_7NO_2)_n$ (mol wt 173.16n): C, 69.83; H, 4.07; N, 8.09. Found: C, 69.87; H, 4.59; N, 6.87, 7.29, 6.85.

Attempted Reaction of 1b with Citraconic (Methylmaleic) Anhydride. A solution of **1b** (800 mg, 5.00 mmol) and citraconic anhydride (2.24 g, 20.0 mmol) in xylene (8 mL) was refluxed for 21 h. Workup gave unchanged **1b** as orange crystals: 190 mg (24% recovery); mp and mmp with the starting material 156–159 °C.

Attempted Reaction of 1b with Phenylmaleic Anhydride. Acid **1b** (400 mg, 2.50 mmol) and phenylmaleic anhydride (870 mg, 5.00 mmol) were mixed and heated at 130 °C in an oil bath for 6 h. The resulting dark red oil was dissolved in ether and allowed to evaporate slowly, causing separation of unchanged phenylmaleic anhydride as an orange solid [60 mg (7% recovery), mp 118–123 °C] having an IR spectrum in Nujol essentially identical with that of the starting material.

Attempted Reaction of 1b with Dichloromaleic Anhydride. A solution of **1b** (800 mg, 5.00 mmol) and dichloromaleic anhydride (1.67 g, 10.0 mmol) in xylene (10 mL) was refluxed for 14 h. Workup gave unchanged **1b** as orange crystals in two crops [300 mg (38% recovery), mp 159–162 °C, and 180 mg (22% recovery; total 60%), mp 153–158 °C] which gave no depression in the mixture melting point with the starting material.

Attempted Reaction of 1b with Cinnamic Acid. A solution of **1b** (800 mg, 5.00 mmol) and cinnamic acid (1.48 g, 10.0 mmol) in 1,2-dichlorobenzene (10 mL) was refluxed for 8 h. Workup gave unchanged cinnamic acid as yellow crystals: 669 mg (45% recovery); mp and mmp with the starting material 132–134 °C. A second crop of yellow crystals [338 mg (23% recovery calculated as cinnamic acid), mp 115–125 °C] was shown to be a mixture of cinnamic acid and **1b** by TLC on silica gel.

Attempted Reaction of 1b with β-Nitrostyrene. A solution of **1b** (800 mg, 5.00 mmol) and β-nitrostyrene (3.00 g, 20.1 mmol) in xylene (6 mL) was refluxed for 3 h. The black solution was extracted with aqueous saturated sodium bicarbonate (2 × 10 mL). The alkaline extract was acidified to pH <2 with concentrated hydrochloric acid, giving unchanged **1b**: 100 mg (12% recovery); mp 150–160 °C. From the xylene solution, a brown solid, probably poly-β-nitrostyrene, separated: mp 220–225 °C dec; IR (Nujol) no OH or C=O bands, 1565 (s), 1380 (s, NO_2) cm^{-1}.

Attempted Reaction of 1b with Tetracyanoethylene. A mixture of **1b** (160 g, 10.0 mmol) and tetracyanoethylene (640 mg, 5.00 mmol) in xylene (10 mL) was refluxed for 14 h. The insoluble black precipitate (1.42 g, probably a 1:1 complex), which was present throughout the reflux, was filtered off. Workup of the xylene filtrate as described in the previous experiment gave unchanged **1b** as a yellow solid: 280 mg (17% recovery); mp and mmp with the starting material 160–161 °C.

Reaction of 1b with Diethyl Diazenedicarboxylate: Diethyl 1,2-Hydrazinedicarboxylate (10). A solution of **1b** (800 mg, 5.00 mmol) and diethyl diazenedicarboxylate (diethyl azodicarboxylate; 1.74 g, 10.0 mmol) in xylene (6 mL) was refluxed for 3 h. Workup gave an orange solid: 160 mg; mp 128–132 °C. Crystallization from ethanol–water gave yellow crystals: mp 130–132 °C (lit. mp 130 °C,[9a] 131–132 °C,[9b] 132.5–133.5 °C[9c]); IR

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[8] Arndt, F "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. 2, pp 165–167, footnote 3.

(Nujol) 3200 (s, NH), 1735 (ms), 1685 (s), 1660 (sh, m, C=O), 1525 (s) cm^{-1}. The IR spectrum in Nujol was identical with that of a sample of **10**.[9c]

Methyl 1*H*-Indene-3-carboxylate-*1-d* (1c-*1-d*). Ester **1c** (8.70 g, 49.9 mmol) was added to a hexane solution (2.35 M, 21.3 mL) of 1-butyllithium (50.0 mmol) in anhydrous diethyl ether (50 mL) at -60 °C, causing the formation of a yellow solid. The mixture was stirred at -60 °C for 1 h and then slowly warmed to -10 °C. Deuterium oxide (10 mL, 500 mmol) was added. The ether layer was separated, washed with water (3 × 20 mL), dried (Na_2SO_4), and evaporated. The red-brown liquid was distilled, giving a colorless liquid [6.00 g (69%), bp 153-154 °C (23 mm)] which was redistilled for deuterium analysis, again giving a colorless liquid, bp 153-154 °C (23 mm). The hydrogen content at the C_1 methylene was obtained by statistical analysis of the integrated intensities in the NMR spectrum in CCl_4. The areas of the methylene, methoxycarbonyl, vinylene, and aromatic protons were each obtained from ten integrations. On the basis of these values the average area of the methylene protons was calculated, and the deuterium content, which was found to be completely at C_1, was found to be 0.97 ± 0.03 D atom per molecule. By mass spectrometric analysis the total deuterium content was found to be 0.95 ± 0.05 D atom per molecule, in good agreement with the NMR data.

Reaction of 1c-*1-d* with Maleic Anhydride: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic-*4,9-d*$_2$ Acid 1-Methyl Ester Cyclic 2,3-Anhydride (3c-*4,9-d*$_2$). The deuterated ester **1c**-*1-d* described above was allowed to react with maleic anhydride in refluxing xylene for 12 h according to the procedure described above for conversion of **1c** to **3c**, giving deuterated **3c** in 40% yield as white crystals, mp 168-169 °C. Recrystallization from benzene gave white crystals, mp 168-169 °C. The NMR spectrum (20% w/v in acetone-d_6) was similar to that observed for nondeuterated **3c**. Since the C_4 bridgehead proton and the C_2 and C_3 methine protons appear very close to the methyl ester protons in the NMR spectrum, the total area was calculated for all of these protons together. All the proton areas were calculated by statistical analysis from ten integrations. With the assumption that the number of aromatic protons is equal to 4.00, the ratio to the C_9 bridge methylene protons and to the remaining protons was found to be 4.00:1.63 ± 0.04:5.51 ± 0.04, respectively. This gives, by difference, deuterium contents at the C_9 bridge and C_4 bridgehead of 0.37 ± 0.04 and 0.49 ± 0.04 D atom per molecule, or a total of 0.86 ± 0.08 D atom per molecule. By mass spectrometric analysis the total deuterium content was found to be 0.83 ± 0.05 D atom per molecule, in good agreement with the NMR data.

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Intramolecular Diels-Alder and Ene Reactions of 2,6-Dimethyl-2,7-octadienal

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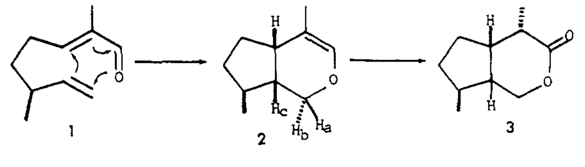
2,6-Dimethyl-2,7-octadienal (**1**) undergoes a BF_3-catalyzed reaction to give *exo*-4,8-dimethyl-2-oxabicyclo[3.3.1]non-3-ene (**4**) in 49% yield. Adduct **4** is probably formed by a Lewis acid catalyzed inverse-electron-demand Diels-Alder reaction in which the α,β-unsaturated aldehyde functions as the diene. Upon pyrolysis of **1** at moderate temperatures (~370 °C), a 1:4:1 kinetically controlled mixture of Diels-Alder adduct **2** and cis substituted ene adducts **14** and **15** are formed. At higher temperatures (405 °C), complex mixtures of Diels-Alder adducts **2**, **4**, and **9** and ene adducts **14-18** are formed.

The thermal and Lewis acid catalyzed reactions of 2,6-dimethyl-2,7-octadienal (**1**) were examined. An intramolecular Diels-Alder reaction of **1** should give **2**, a potential intermediate for the synthesis of iridomyrmecin (**3**) (see Scheme I), an insecticidal iridoid isolated from the Argentinian ant *Iridomyrmex humilis*.[2] This approach is particularly attractive since both enantiomers of **1** are readily available from pyrolysis of the appropriate pinane.[3]

Scheme I



Although Diels-Alder reactions of α,β-unsaturated carbonyl compounds are well-known,[4] there are very few examples of intramolecular reactions of this type.[5]

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[1] Fellow of the Alfred P. Sloan Foundation, 1979-1981.

[2] Cavill, G. W. K. In "Cyclopentanoid Terpenoid Derivatives"; Taylor, W. I.; Battersby, A. R., Eds.; Marcel Dekker: New York, 1969; pp 214-219.

[3] Reinäcker, R.; Ohloff, G. *Angew, Chem.* **1961**, *73*, 240.

[4] Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

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