62747-73-3; **15**, 62747-66-4; **16**, 51310-26-0; **17**, 50902-99-3; **18**, 74272-43-8; **19**, 42842-58-0; **20**, 58310-20-6; **24**, 65103-92-6; **25**, 72292-07-0; **26**, 75032-42-7; **27**, 75032-43-8; **28**, 75032-44-9; **29**, 65086-13-7; **30**, 65086-15-9; **31**, 31367-60-9; **36**, 67177-29-1; **37**, 67177-31-5; **39**, 75032-45-0; **40**, 75032-46-1; 9,10-dicyanoanthracene, 1217-45-4; triphenylallylphosphonium bromide, 1560-54-9; 3,4-diphenyl-3-buten-2-one, 1722-69-6; 1-allyl-2-methyl-3-phenyl-1-indanol, 75032-47-2; 2-methyl-3-phenylindanone, 52957-74-1; 4-bromo-1-butene, 5162-44-7; 1-(4-butenyl)-2-methyl-3-phenyl-1-indanol, 75032-48-3; 1-methyl-2,3-diphenylcyclopropenylium ClO_4^-, 75032-50-7; 2-phenyl-3-methylindanone, 62907-55-5; phenylacetic acid, 103-82-2; 2-bromo-1-phenylpropane, 2114-39-8; *cis*-2-phenyl-3-methylindanone, 54444-11-0; 1,2-diphenyl-3-methyl-1-indanol, 75032-51-8; 1-methyl-1-ethyl-2,3-diphenylindene, 75032-52-9.

Cycloaddition Reactions of Indenes. 2. Reactions with Dimethyl Acetylenedicarboxylate and Maleic Anhydride[1]

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1*H*-Indenes (**1**) react with dimethyl acetylenedicarboxylate (DMAD), unlike maleic anhydride and other ethylenic dienophiles, without prior isomerization to 2*H*-indenes (**2**), giving a 1:1 Diels–Alder adduct (**6**) formed with destruction of the aromaticity of the benzene ring. This intermediate, not isolated in the present work, appears to serve as the precursor for all further adducts. Thus, 1*H*-indene (**1a**) and 1-methyl-1*H*-indene (**1b**), but not the more sterically hindered 1-ethyl-1*H*-indene, react with DMAD in refluxing benzene (with **1a**) or toluene (with **1b**) via a 1,2-cycloaddition to **6** to give solid 1:2 adducts (**7a**, 34%; **7b**, 30%). In refluxing xylene the reaction goes further to give a 1:3 adduct (**11a**; 40% from **1a**, 71% from **7a**) formed by a Diels–Alder addition of a third molecule of DMAD across the remaining diene system of **7a**. Reaction of 2-methyl-1*H*-indene (**1c**) with DMAD in refluxing xylene gave the corresponding 1:3 adduct (**11c**, 5–6%), but an attempt in refluxing toluene to isolate a solid 1:2 adduct (**7c**) was unsuccessful. A 3-substituent in the 1*H*-indene, which becomes a 4-substituent in **6**, blocks the 1,2-cycloaddition (to give **7**) and diverts the DMAD to the cyclohexadiene system of **6**, where a Diels–Alder reaction occurs in refluxing xylene to give another type of 1:2 adduct (**8**). The following 3-substituted 1*H*-indenes (**1**) gave 1:2 adducts of type **8**: 3-methyl- (**8d**, 41%), 3-ethyl- (**8e**, 40%), 1,3-dimethyl- (**8f**, 31%), 2,3-dimethyl- (**8g**, 19%), 3-carboxy- (**8l**, 74%), 3-(methoxycarbonyl)- (**8m**, 66%), and 3-cyano-1*H*-indene (**8n**, 63%). Alkaline hydrolysis of **8l** and acidification to pH <2 gave the monosodium salt (91%) of the corresponding pentacarboxylic acid (**13l**). Hydrogenation of **8l** over PtO_2 gave a tetrahydro derivative (**14l**, 100%). That maleic anhydride can take the place of the second (but not the first) molecule of DMAD in **8** is shown by the formation of a 1:1:1 mixed adduct (**10l**, 17%) along with the 1:2 adduct (**8l**, 18%) from reaction of **1l**, DMAD, and maleic anhydride in a 1:2:2 molar ratio in refluxing xylene. A similar 1:1:1 mixed adduct (**10n**, 59%), but no 1:2 adduct (**8n**), was isolated from the corresponding reaction of **1n**, DMAD, and maleic anhydride in a 1:1:1 molar ratio. Similarly, maleic anhydride can take the place of the third molecule of DMAD in the 1:3 adduct **11**. Thus, reaction of **7a** and **7b** with maleic anhydride in refluxing xylene gave the corresponding 1:2:1 mixed adducts (**12a**, 69%; **12b**, 32%), formed by Diels–Alder addition across the cyclohexadiene system of **7a** and **7b**. Reaction of 1-methyl-1*H*-indene (**1b**), DMAD, and maleic anhydride in a 1:2:1 molar ratio in refluxing xylene also gave **12b** (31%) but no 1:3 adduct (**11b**). Methyl esterification of **12a** gave the corresponding hexamethyl ester (**15a**, 52%). On the basis of the shielding effects of neighboring ethylene groups on the methylene bridge protons, an NMR rationale has been developed for assignment of stereochemistry to the adducts **8**–**12**.

The previous paper[1] reports that 1*H*-indene-3-carboxylic acid (**1l**) and its less reactive methyl ester (**1m**) react upon heating (in refluxing xylene or, when necessary, in 1,2-dichlorobenzene), via intermediate 2*H*-indenes (isoindenes, **2**), with the more reactive ethylenic dienophiles, such as maleic anhydride or *N*-phenylmaleimide, or the less reactive dimethyl fumarate, to give 1:1 Diels–Alder adducts (**3** and **4**, 1,2,3,4-tetrahydro-1,4-methanonaphthalene-1-carboxylic acid 2,3-derivatives). 1*H*-Indene (**1a**) itself reacts with maleic anhydride at 250[3] or 180 °C[4] in benzene or at 198 °C in tetralin[3b] solution to give the corresponding 1:1 adduct (**3a**)[3a] by the same mechanism.[3a,4] The dimer[5] formed by heating **1l** at 180 °C has been shown[2b] to have the corresponding structure **5**,[1,2b] formed by one molecule of **1l** isomerizing to 2*H*-indene-3-carboxylic acid (**2l**) and another molecule of **1l**, acting as an ethylenic dienophile, adding to it in a head-to-head Diels–Alder fashion (Scheme I).

With the more reactive acetylenic dienophile dimethyl acetylenedicarboxylate (DMAD, dimethyl 2-butynedioate),[6] however, the reactions with indenes take a different course. 1*H*-Indene (**1a**) with DMAD gave a 1:2 adduct[3,7] in refluxing benzene,[3a] or more slowly at room temperature[7] or even at 0–5 °C,[8] the structure of which was shown to be **7a** by X-ray analysis of its 6,9-dibromide.[7] The four vinylene protons of **7a** were shown to come from

(1) Paper 1: Noland, W. E.; Landucci, L. L.; Kameswaran, V. *J. Org. Chem.* **1980**, *45*, 3456–3461. For an earlier indene paper in this series, see Noland, W. E.; Landucci, L. L.; Darling, J. D. *Ibid.* **1979**, *44*, 1358–1359.

(2) Taken from (a) in large part the Ph.D Thesis of Venkataraman Kameswaran, University of Minnesota, Minneapolis, MN, June 1971 [*Diss. Abstr. Int. B.* **1972**, *32*, 6918–6919; *Chem. Abstr.* **1972**, *77*, 151725], and (b) the Ph.D. Thesis of Lawrence L. Landucci, University of Minnesota, Minneapolis, MN, March 1967 [*Diss. Abstr. B* **1968**, *28*, 3223–3224; *Chem. Abstr.* **1968**, *69*, 27071].

(3) (a) Alder, K.; Pascher, F.; Vagt, H. *Ber. Dtsch. Chem. Ges. B* **1942**, *75*, 1501–1514. (b) Huebner, C. F.; Strachan, P. L.; Donoghue, E. M.; Cahoon, N.; Dorfman, L.; Margerison, R.; Wenkert, E. *J. Org. Chem.* **1967**, *32*, 1126–1130.

(4) Berson, J. A.; Aspelin, G. B. *Tetrahedron* **1964**, *20*, 2697–2700.

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

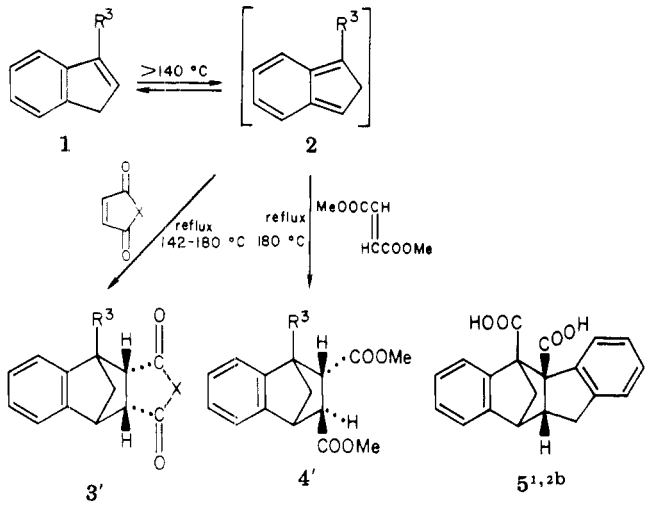
(6) Clearly the greater reactivity of DMAD over maleic anhydride toward indenes found here in the first addition step (though not necessarily in the second or third) is quite different from that toward cyclopentadiene and 9,10-dimethylanthracene reported: Sauer, J.; Wiest, H.; Mielert, A. *Z. Naturforsch. B* **1962**, *17*, 203–204.

(7) Muir, K. W.; Sim, G. A.; Strachan, P.; Huebner, C. F. *Chem. Ind. (London)* **1964**, 1581–1582.

(8) Jones, D. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 673–676.

0022-3263/80/1945-4564$01.00/0

Scheme I



	R^3	X
1, 2, 3, 4 l	COOH	O
3 o	COOH	NC_6H_5
1, 2, 3 m	COOMe	O

the benzene ring of 1*H*-indene (**1a**) since they were still present in the 1:2 adduct prepared from 1*H*-indene-*1,1,3-d*$_3$.[7] Similar 1:2 adducts were obtained at 100 °C from 5- and 6-methyl-1*H*-indene (**7i** and **7j**) and 5-fluoro-1*H*-indene (**7k**) while 1-methyl- (**1b**), 2-methyl- (**1c**), 5-methoxy-, and 6-nitro-1*H*-indene were reported to be unreactive under these conditions.[3b] Reaction of 3-methyl-1*H*-indene (**1d**) with DMAD at 100 °C gave a different type of 1:2 adduct, for which structure **8d** was proposed, based on the NMR spectrum.[3b] Recently, by lowering the temperature to 20 °C and using the reactants in a 1:1 molar ratio, Jones[8] isolated a 1:1 adduct (**6d**, 47%), along with the 1:2 adduct (**8d**, 39%, mp 122–124 °C). Similar reactions with DMAD at room temperature gave 1:1 adducts with 1-methyl-1*H*-indene (**6b**, 9-*anti*[9]-methyl, 6%), 1,3-dimethyl-1*H*-indene (**6f**, a 3:1 mixture of 9-*anti*- and 9-*syn*[9]-methyl adducts, 35%), and 3,4,7-trimethyl-1*H*-indene (**6h**, 88%) which gave a more stable, recrystallizable adduct.[8] At 100 °C, with a 1:2 molar ratio of the latter indene to DMAD, both the 1:1 adduct (**6h**, 20%) and a 1:2 adduct (**8h**, 46%, mp 130–133 °C) were isolated.[8] The 1:1 adduct (**6h**) reacted with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione at 20 °C in benzene to give a 1:1:1 mixed adduct (**9**, 31%) similar in structure to **8h**[8] (Scheme II).

In the present work we have carried out deuterium substitution studies and have extended the preparation of 1:2 adducts to determine the influence of other substituents in the 3-position and of substituents in the 1- and 2-positions of the 1*H*-indene nucleus. In addition, we have prepared and characterized two 1:1:1 mixed adducts, two 1:3 adducts, and two 1:2:1 mixed adducts, thus broadening the scope of the reaction. All of the adducts have NMR (Table 3), UV (Table 1), and IR (Table 2) and in many cases mass spectra (Table 4), as well as elemental analyses (Table 5), which are consistent with the structures assigned (see Supplementary Material).

1:2 Adducts of 1*H*-Indenes and DMAD. Reaction of 1*H*-indene-*1-d*, containing 1.12 atoms of D at C_1 and 1.16 total atoms of D per molecule, with DMAD gave **7a**-*10-d* (34%) containing 1.08 atoms of D at the C_{10} bridge and 1.15 total atoms of D per molecule. Reaction of 1*H*-indene-*1,1,3-d*$_3$,[5] fully deuterated at C_1 and C_3 and containing 0.11 atom of D at C_2, with DMAD gave **7a**-*2a,10,10-d*$_3$ (34%) fully deuterated at the C_{2a} bridgehead and C_{10} bridge and containing 0.07 atom of D at the C_3 bridgehead. These results show that there is no scrambling of hydrogens in the 1-, 2-, and 3-positions of the 1*H*-indene nucleus. This rules out the possibility of a 2*H*-indene intermediate (**2a**) during the formation of **7a** and shows that addition of DMAD to 1*H*-indene is faster than isomerization to 2*H*-indene. These results are consistent with a mechanism involving no hydrogen shifts and a rate-determining addition of DMAD to form a 1:1 Diels–Alder adduct (**6a**), which retains the maximum possible amount of conjugation in its conjugated triene system. This is followed by a relatively fast (though thermally forbidden) [$2_\pi + 2_\pi$] cycloaddition of a second molecule of DMAD to **6a** to give **7a**, which again retains the maximum possible amount of conjugation in its still-present conjugated diene system. In contrast to the reaction of 1-methyl-1*H*-indene (**1b**), where a 1:1 adduct (**6b**) has been isolated, the relatively unhindered **6a** reacts so rapidly with DMAD that it has not been possible to isolate it.[8]

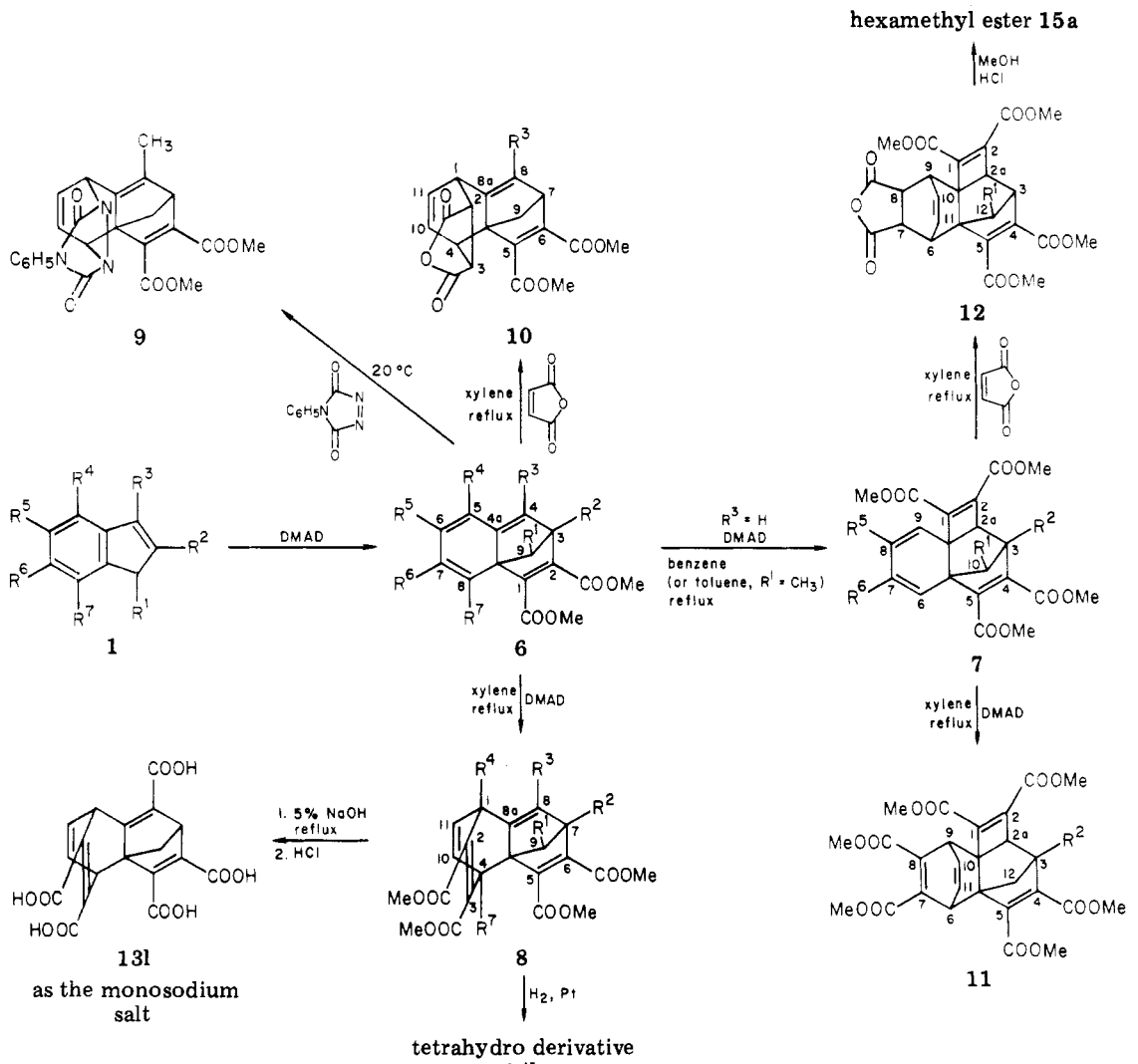
When the temperature was raised from room temperature, which gave only the 1:1 adduct **6b** in 6% yield,[8] past 100 °C (which was reported to give no reaction[3b]) to refluxing toluene for 24 h, the reaction of 1-methyl-1*H*-indene (**1b**) with DMAD gave a 1:2 adduct (**7b**) in 30% yield. If it is assumed that the first molecule of DMAD adds anti[9] to the methyl group, as has been reported for the 1:1 adduct isolated (**6b**, 9-*anti*[9]-methyl),[8] then the second molecule of DMAD, which is assumed to approach from the exo side of the norbornadiene ring system, will encounter considerable steric hindrance from the methyl group, which will be syn to it. With an ethyl group in the corresponding position, with 1-ethyl-1*H*-indene, the steric hindrance to approach of the second DMAD molecule should be considerably greater and probably accounts for the fact that no solid 1:2 adduct was isolated from the reaction with DMAD under comparable conditions.

The presence of a 3-substituent in the original 1*H*-indene (**1**), which becomes a 4-substituent in the 1:1 adduct **6** (which is the proposed common intermediate to **7** and **8**), stabilizes its end of the conjugated triene system electronically and shields it sterically, causing attack to occur by a Diels–Alder-type addition at the remaining cyclohexadiene end of the system, giving 1:2 adducts of type **8**. It has been suggested[3b] that, if the addition is free radical in character, initial addition at C_8 (of **6d**) will be favored since it will give a tertiary radical at the C_4 end of the pentadienyl system, whereas addition at C_4 would give a less stable, secondary radical at the C_8 end of the pentadienyl system. A summary of the 1:2 adducts of variously 3-substituted 1*H*-indenes and DMAD is included in Table 5 (see Supplementary Material). Consistently higher yields were obtained with the electron-withdrawing substituents in **1l–n** than in the methyl- or ethyl-substituted cases (**1d–h**).

An attempt to reverse the Diels–Alder formation of **8l** by refluxing at a higher temperature, in 1,2-dichlorobenzene for 44 h, gave unchanged **8l** in 64% recovery. Alkaline hydrolysis of **8l** followed by acidification to pH <2 gave a monosodium salt (91%) of the corresponding pentacarboxylic acid (**13l**). Catalytic hydrogenation of **8l** over platinum(IV) oxide gave what appears to be a tetrahydro derivative (**14l**, 100%) formed by selective hydrogenation of the least deactivated double bonds, those at C_{10}–C_{11} and C_8–C_{8a}. Diphenylethyne was not sufficiently reactive to give an adduct with **1l**. Thus, attempted re-

(9) Syn and anti refer here to the methyl groups toward or away from the 1,2 double bond of **6**, 5,6 double bond of **8** and **10**, or 4,5 double bond of **7**, **11**, and **12**.

Scheme II



		R¹	R²	R³	R⁴	R⁵	R⁶	R⁷
1, 6, 7, 11, 12	a	H	H	H	H	H	H	H
1, 6, 7, 12	b	Me	H	H	H	H	H	H
1, 6, 11	c	H	Me	H	H	H	H	H
1, 6, 8	d	H	H	Me	H	H	H	H
1, 6, 8	e	H	H	Et	H	H	H	H
1, 6, 8	f	Me	H	Me	H	H	H	H
1, 6, 8	g	H	Me	Me	H	H	H	H
1, 6, 8	h	H	H	Me	Me	H	H	Me
1, 6, 7	i	H	H	H	H	Me	H	H
1, 6, 7	j	H	H	H	H	H	Me	H
1, 6, 7	k	H	H	H	H	F	H	H
1, 6, 8, 10	l	H	H	COOH	H	H	H	H
1, 6, 8	m	H	H	COOMe	H	H	H	H
1, 6, 8, 10	n	H	H	CN	H	H	H	H

action of 1*H*-indene-3-carboxylic acid (**11**, 1 mol) with diphenylethyne (3 mol) in refluxing xylene for 6 h gave unchanged **11** in 50% recovery as the first crystals to separate.

Attempted further reaction of the isolated 1:2 adduct **8m** with DMAD in refluxing xylene or, at higher temperature, in 1,2-dichlorobenzene gave unchanged **8m** in 74–75% recoveries. Reaction of methyl 1*H*-indene-*1-d*-3-carboxylate (**1m**-*1-d*) containing 0.97 atom of D at C_1 with DMAD gave the corresponding 1:2 adduct **8m**-*9-d* (66%) containing 0.92 atom of D at the C_9 bridge and none at the C_7 bridgehead. This again shows that there is no scrambling of hydrogen from the 1-position to the 2-position of the 1*H*-indene nucleus and rules out the possibility of a 2*H*-indene intermediate during the formation of **8m**. Thus, addition of DMAD is faster than isomerization to a 2*H*-indene. As in the formation of **7a**, this result is consistent with a mechanism involving no hydrogen shifts and a stepwise addition of DMAD, first to form the intermediate 1:1 adduct **6m** and then the 1:2 adduct **8m**.

1:1:1 Mixed Adducts of 1*H*-Indenes, DMAD, and Maleic Anhydride. Maleic anhydride is apparently unreactive with 1*H*-indenes and requires temperatures at least as high as refluxing xylene (142 °C)[1] to isomerize the indene to the much more reactive 2*H*-indene before a Diels–Alder reaction occurs. Reaction of 1*H*-indene-3-carboxylic acid (**11**), DMAD, and maleic anhydride in a 1:2:2 molar ratio in refluxing xylene for 8 h, however, gave

a mixed 1:1:1 adduct (**10l**) in 17% yield along with the 1:2 adduct with DMAD (**8l**, 18%) already described. This indicates that maleic anhydride is able to compete with DMAD as a dienophile. On the basis of the relative reactivities already observed, however, it would be anticipated that the indene reacts first with DMAD, which is sufficiently reactive to break up the aromatic stability of the indene and give a reactive 1:1 adduct (**6l**) having a diene system which can then undergo a Diels–Alder addition with a second molecule of DMAD or with maleic anhydride to give the 1:2 (**8l**) and 1:1:1 mixed (**10l**) adducts observed. More evidence in support of this conclusion is the fact that maleic anhydride did not react further with its 1:1 adduct (**3l**,[1,2b] 55% recovery) from the same indene (formed via a 2*H*-indene intermediate, **2l**) under comparable conditions, in refluxing xylene for 12 h. 1*H*-Indene-3-carbonitrile (**1n**) also formed a 1:1:1 mixed adduct (**10n**, 59%) with a mixture of DMAD and maleic anhydride in a 1:1:1 molar ratio in refluxing xylene for 22 h. In this case, none of the 1:2 adduct (**8n**) with DMAD was isolated (though it could have been present), and the yield alone suggests that maleic anhydride is able to compete quite effectively with DMAD in the second step of the addition reaction. The 1:1:1 mixed adduct (**9**)[8] prepared, in this case, from the 1:1 adduct (**6h**) of 3,4,7-trimethyl-1*H*-indene (**1h**) and DMAD by reaction with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione is structurally similar to **10**.

1:3 Adducts of 1*H*-Indenes and DMAD. When the temperature of the reaction between 1*H*-indene (**1a**) and DMAD was raised from that of refluxing benzene to refluxing xylene (for 7.5 h) and a 1:3 molar ratio was used, a 1:3 adduct (**11a**) was isolated in 40% yield. That the 1:2 adduct (**7a**) is a likely intermediate was shown by its reaction with DMAD in refluxing xylene under the same conditions to give the 1:3 adduct (**11a**) in 71% yield. Reaction of 1*H*-indene-*1,1,3-d*$_3$[4] fully deuterated at C_1 and C_3 (and containing 0.11 atom of D at C_2) with DMAD in a 1:3 molar ratio in refluxing xylene gave the corresponding 1:3 adduct **11a**-*2a,12,12-d*$_3$ in 36% yield. The NMR spectrum does not show either of the C_{12} bridge protons and the multiplet assumed to contain the C_{2a} bridgehead proton in **11a** appears to contain one less proton. These results show that there has been no loss of deuterium from the original 1,1- and 3-positions of the 1*H*-indene nucleus. As with **7a**, this rules out the possibility of a 2*H*-indene intermediate during the formation of **11a** from **1a** and again shows that the addition of DMAD to 1*H*-indene is faster than isomerization to 2*H*-indene. The formation of **11a** from **7a** and the NMR spectrum of **11a** are consistent with the postulate that **11a** contains the structure of **7a** to which a third molecule of DMAD has added across the still available diene system of **7a** at its 6- and 9-positions. In this respect, then, addition of the third molecule of DMAD to 1*H*-indene (or really to **7a**) resembles the addition of the second molecule of DMAD to 3-substituted-1*H*-indenes (or really to **6**) where a 3-substituent has blocked the mode of addition of the second molecule of DMAD observed with 3-unsubstituted-1*H*-indenes.

Reaction of 2-methyl-1*H*-indene (**1c**) and DMAD in a 1:2 molar ratio in refluxing xylene for 18 h gave only a 1:3 adduct (**11c**) in 5–6% yield as the only solid product. An attempted reaction at lower temperature, in refluxing toluene, gave no solid product. Failure here to isolate a 1:2 adduct (**7c**) in refluxing toluene under conditions which gave a 1:2 adduct (**7b**, 30%) with 1-methyl-1*H*-indene (**1b**) suggests that steric hindrance by the 2-methyl group may raise the activation energy of the first addition of DMAD to the point where the usually rapid second addition (perhaps here slightly also sterically retarded) is followed by an even faster third addition. The steric hindrance by the 2-methyl group may also account for the low yield of 1:3 adduct in the reaction, since it might permit successful competition by other reactions, leading to nonsolid products. A similar explanation might also account for the relatively low yield (19%) of 1:2 adduct (**8g**) from 2,3-dimethyl-1*H*-indene (**1g**) and DMAD and for the fact that 2-bromo-1*H*-indene (which would be subject to electronic as well as steric deactivation) and DMAD in refluxing xylene or toluene gave no solid products.

1:2:1 Mixed Adducts of 1*H*-Indenes, DMAD, and Maleic Anhydride. The 1:2 adduct (**7a**) of 1*H*-indene and DMAD reacted with maleic anhydride in refluxing xylene during 7 h to give a 1:2:1 mixed adduct (**12a**) in 69% yield, in which maleic anhydride has replaced the third molecule of DMAD in the 1:3 adduct **11a**. Because of its low solubility in the common NMR solvents, **12a** was converted to the corresponding hexamethyl ester (**15a**, 52%). Its NMR spectrum is consistent with the expectation that, in its precursor **12a**, maleic anhydride has added across the 6- and 9-positions of the 1:2 adduct (**7a**) just as DMAD did in forming the 1:3 adduct (**11a**). The trideuterated 1:2 adduct, **7a**-*2a,10,10-d*$_3$, was allowed to react with maleic anhydride in refluxing xylene in a manner analogus to the preparation of **12a**, giving **12a**-*2a,12,12-d*$_3$ (50%), which was similarly converted to its hexamethyl ester, **15a**-*2a,12,12-d*$_3$ (50%), to facilitate NMR analysis. The NMR spectrum does not show either of the C_{12} bridge protons and the multiplet assumed to contain the C_{2a} bridgehead proton in **9a** appears to contain one less proton. These results show that there has been no loss of deuterium from the corresponding positions of **7a** during the addition of a molecule of maleic anhydride.

Reaction of 1-methyl-1*H*-indene (**1b**), DMAD, and maleic anhydride in a 1:2:1 molar ratio in refluxing xylene for 24 h also gave a 1:2:1 mixed adduct (**12b**, 31%). Failure to isolate a 1:3 adduct (**11b**) derived exclusively from DMAD in this reaction suggests that maleic anhydride is quite effective in competing with DMAD as a dienophile in the third addition step, adding across the 6- and 9-positions of the diene in the intermediate 1:2 adduct **7b**, but, as would be expected from the preceding observations, it does not compete effectively in the first and second addition steps. That the 1:2 adduct (**7b**) of **1b** and DMAD is a likely intermediate was shown by its reaction with maleic anhydride in refluxing xylene for 18 h to give the 1:2:1 adduct (**12b**) in 32% yield.

Stereochemical Considerations. In the NMR spectrum (in $CDCl_3$) of the 1:2 adduct **7a**, the C_{10} methylene bridge protons appear as a degenerate AB pattern at δ 2.10, indicating relatively little chemical shift difference. This is also true with the corresponding C_9 methylene bridge protons in the 1:1:1 mixed adducts **10l** (δ 2.41) and **10n** (δ 2.52), but in none of the other adducts. In **7b** the C_{10} methine bridge proton (10b-H) appears downfield at δ 2.66. The C_{10} bridge methyl group is believed for steric reasons (see earlier) to be anti to the maleate group derived from the first DMAD molecule to add, as has also been argued for the corresponding C_9 bridge methyl group in the 1:1 adduct **6b**.[8] This would place the C_{10} proton (10b-H) of **7b** [and the corresponding C_9 proton (9b-H) of **6b**] in the syn configuration with respect to the maleate group. In all the 1:1 adducts **6**, the chemical shifts of the 9a and 9b protons are different, as reported by Jones:[8] **6b**, δ 3.21 (9b); **6d**, δ 1.8 (9a), 2.55 (9b); **6f** δ 2.4 (9a, *syn*-methyl isomer), 3.06 (9b, *anti*-methyl isomer); **6h**, δ 1.94 (9a), 2.85 (9b). The greater shielding of the 9a protons in **6** can be at-

tributed to the presence of the 4,4a double bond, which is a part of a conjugated triene system.[8] Since this is absent from the corresponding position in **7** and no longer conjugated in **10**, this could account for the relative absence of shielding in the 10a and 9a protons in **7a** and **10**, respectively. In addition, the two maleate groups in **7a**, while in different steric environments, apparently exert similar shielding effects on the 10a and 10b protons. In the NMR spectra of our 1:2 adducts (**8d,e,g,l,m,n**) from 3-substituted indenes, the 9a (δ 1.74–2.08, average δ 1.93) and 9b (δ 2.22–2.48, average δ 2.37) bridge methylene protons, which appear as an AB pattern, have widely different chemical shifts (average $\Delta\delta$ = 0.43). In **8f** the C_9 methine bridge proton (9b-H) appears downfield at δ 2.44. Since in **8f** the C_9 bridge methyl group is likely, for steric reasons, to be anti to the maleate group derived from the first DMAD molecule to add (and was found in the 1:1 adduct **6f**[8] to be anti to the corresponding maleate group, in a 3:1 ratio), the 9b proton is expected to be in the corresponding syn configuration. After allowance is made for the fact that this is a methine instead of a methylene proton, this can serve as a chemical shift model for the 9b protons in the remaining 1:2 adducts **8**. It follows, then, that the upfield 9a protons are in the anti configuration and are also shielded relative to the corresponding 10a (and 10b) proton in the 1:2 adduct **7a**. It seems likely that this shielding may be due in part to shielding by the 8,8a double bond in **8**, which, having at most one electronegative substituent, should be more effective in shielding than the maleate group, which constitutes the other part of the norbornadiene system. Since such a double bond is also present in **10**, another explanation is necessary to account for the difference between the chemical shifts of the bridge methylene protons in **8** and **10**. It is more likely that the additional shielding of the 9a protons in **8** is due to the proximity of a third ethylene bridge (2,3 double bond), which is absent in **10**. As would be expected, the relative shielding of the 9a protons in **8** by the 2,3-maleate ethylene bridge is less than the corresponding shielding of the 9a protons in **6** by the 4,4a conjugated double bond. This is also consistent with the observed chemical shifts of the bridge methyl groups in the adducts **6b** [δ 0.6 (9a-methyl)],[8] **6f** [δ 0.58 (9a-methyl, anti isomer)],[8] **8f** [δ 0.90 (9a-methyl)], and **7b** [δ 1.06 (10a-methyl)]. A similar shielding effect, leading to chemical shift differences, is also observed in the 1:3 adducts **11a** [δ 1.47 (12a), 2.37 (12b)] and **11c** [δ 1.57 (12a), 2.18 (12b)] and in the 1:2:1 mixed adducts **12a** [δ 1.75 (12a), 2.30–2.77 (12b)] and in the hexamethyl ester **15a** [δ 1.94 (12a), 2.33 (12b)] and **12b** [δ 1.90–2.40 (12a,b)]. This suggests that an important element of shielding present in **12** is absent in **10**: that the 10,11-ethylene bridge is syn to the 12-methylene bridge in **12** and anti to the 9-methylene bridge in **10** (with probably similar stereochemistry for **9** for the same reason). This must mean that maleic anhydride has added on opposite sides of the diene-containing ring in the two cases. This appears reasonable, since in the formation of **12** the 1,2-maleate ethylene bridge in **7** should strongly hinder the approach of maleic anhydride, causing it to approach from the endo side of the norbornene ring system, anti to the 12-methylene bridge (of **12**). In the formation of **10** there is no such steric constraint, because in **6** there is no corresponding maleate ethylene bridge, only a planar 4,4a double bond, which should permit the approach of maleic anhydride from the exo side of the norbornadiene ring system syn to the 9-methylene bridge, which would probably be sterically favored. Extending this argument to the formation of **11**, it would follow by analogy that the third molecule of DMAD should approach **7** from the endo side of the norbornene ring system, thus placing the shielding 10,11-ethylene bridge syn to the 12-methylene bridge of **11**.

By the same reasoning as for the formation of **10**, it can be argued (though perhaps with less conviction) that in the formation of **8** the second molecule of DMAD should approach from the exo side of the norbornadiene ring system syn to the 9-methylene bridge. This would place the 2,3-maleate ethylene bridge derived from the DMAD (not the 10,11-ethylene bridge) in a position to shield the 9a proton. As has been noted above, the maleate ethylene bridge should be less effective in shielding than the unsubstituted ethylene bridge. Thus, if all other things were equal (which they are not) one might expect less shielding of the 9a proton in **8** (δ 1.93, average of seven compounds) than of the 12a proton in **12** (**12a**, δ 1.75; **12b**, δ >1.90) and **11** (**11a**, δ 1.50; **11c**, δ 1.57). Since in **8** this does appear to be the case, the 2,3-maleate bridge is assigned the configuration syn to the 9-methylene bridge.

Mass Spectral Fragmentations. Most of the mass spectral fragmentations of the adducts involve loss of fragments from their ester groups. Among the most important or commonest fragmentations (Table 4, Supplementary Material) were M – CH_3OH – $COOCH_3$, M – $2CH_3OH$, M – $COOCH_3$ – $HCOOCH_3$, M – CH_3OH – $HCOOCH_3$, M – $2CH_3OH$ – $COOCH_3$, and M – OCH_3; M – $COOCH_3$ was the base peak in **8f**. The molecular ion was the base peak in **12a**, second in **12b**, and fourth in **8d**. Loss of CH_2 was the base peak in **12b** and also occurred in **12b** in conjunction with four ester fragmentations. Retro-Diels–Alder fragmentations of DMAD were of no significance, but in **12a** and especially in **12b** loss of the elements of maleic anhydride was observed in conjunction with ester fragmentations in numerous peaks of relative intensity ≤30%.

Experimental Section

Melting points were determined largely on a calibrated Mel-Temp melting point apparatus. Ultraviolet spectra (UV) were determined on a Beckman DK-2A recording spectrophotometer. Infrared spectra (IR) were determined on a Perkin-Elmer Model 257 spectrophotometer. Nuclear magnetic resonance spectra (NMR) were determined on a Varian Associates Model A-60, A-60D, or T-60 spectrometer, using tetramethylsilane as an internal standard, unless otherwise specified. Low-resolution electron-impact mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6D spectrometer by Mr. Adrian S. Swanson and his associates. Elemental microanalyses were performed by M-H-W Laboratories, Garden City, MI (now Phoenix, AZ) or by Fay M. Thompson, Henry V. Isaacson, and Luke Lam under the supervision of Professor C. F. Koelsch at the University of Minnesota. In the deuterium analyses, uncertainties in the number of atoms of D are expressed as standard deviations.

Reaction of 1*H*-Indene (1a) with DMAD. Tetramethyl 2a,3-Dihydro-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate (7a). 1*H*-Indene (**1a**) was allowed to react with DMAD as described by Alder, Pascher, and Vagt,[3a] giving the 1:2 adduct as white crystals, mp 118–119 °C. Two recrystallizations, one from chloroform–petroleum ether (bp 60–68 °C) and one from ethyl acetate–petroleum ether, gave white crystals, mp 117–118 °C (apparently a dimorphic form) (lit.[3a] mp 130–131 °C).

Reaction of 1*H*-Indene with DMAD. Deuterium Labeling Studies. A. Preparation of 1*H*-Indene-*1-d* (1a-*1-d*). 1*H*-Indene (**1a**, 5.8 g, 49.9 mmol) was added over 15 min under nitrogen to a hexane solution (21.3 mL of 2.35 M) of 1-butyllithium (50.0 mmol) in anhydrous diethyl ether (20 mL). The solution was refluxed for 45 min and then cooled to 0 °C in an ice bath. Deuterium oxide (5 mL) was added slowly at a rate which held the temperature below 5 °C. The mixture was stirred for 10 min

and the ether layer was separated, washed with water (3 × 20 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual pale yellow oil was distilled in a vacuum, giving a colorless liquid (3.9 g, 67%), bp 76 °C (20 mm) [lit.[4] bp 76 °C (20 mm)]. The ratios of the protons in the NMR spectrum in CCl_4 were calculated by statistical methods from the average of 10 integrations and 4 planimetric measurements of peak areas. With the number of aromatic protons (δ ~7.3) set at 4.00, the ratios of protons were found to be at C_1 (δ ~3.2), 0.88 ± 0.03, at C_2 (δ ~6.3), 0.99 ± 0.04, and at C_3 (δ ~6.8), 0.97 ± 0.06, which corresponds to a total deuterium content of 1.16 ± 0.13 atoms of D per molecule. By mass spectrometric analysis the deuterium content was found to be 1.15 atoms of D per molecule, in good agreement. From the mass spectrum, the percentage distribution of deuterated molecules was found to be d_0, 0.0 ± 10.3, d_1, 84.8 ± 4.4, d_2, 15.2 ± 3.4, d_3, 0.0 ± 3.2.

B. Reaction of 1*H*-Indene-*1-d* (1a-*1-d*) with DMAD. Tetramethyl 2a,3-Dihydro-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate-*10-d* (7a-*10-d*). 1*H*-Indene-*1-d* (1a-*1-d*) was allowed to react with DMAD as described by Alder, Pascher, and Vagt,[3a] giving the 1:2 adduct in 34% yield as white crystals, mp 130–131 °C (lit.[3a] (34% crude) mp 130–131 °C). The ratios of the protons in the NMR spectrum in $CDCl_3$ were calculated as described in part A above. With the number of vinylene protons (δ ~6.0) set at 4.00, the ratios of protons were found to be at the C_{10} bridge (δ ~2.1), 0.92 ± 0.06, at the C_{2a} bridgehead (δ ~3.1), 1.01 ± 0.06, and at the C_3 bridgehead (δ ~3.2), 0.92 ± 0.03, which corresponds to a total deuterium content of 1.15 ± 0.14 atoms of D per molecule.

C. Preparation of 1*H*-indene-*1,1,3-d*$_3$ (1a-*1,1,3-d*$_3$) was carried out as described by Berson and Aspelin,[4] giving in 52% yield a colorless liquid, bp 76 °C (20 mm) [lit.[4] bp 76 °C (20 mm)]. The ratios of the protons in the NMR spectrum in CCl_4 were calculated by statistical methods from the average of 10 integrations. With the number of aromatic protons (δ ~7.3) set at 4.00, the ratio of protons at C_2 was found to be 0.89 ± 0.04. There was practically complete incorporation of deuterium at C_1 and C_3. Thus, the total deuterium content was found to be 3.11 atoms of D per molecule.

D. Reaction of 1*H*-Indene-*1,1,3-d*$_3$ (1a-*1,1,3-d*$_3$) with DMAD. Tetramethyl 2a,3-Dihydro-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate-*2a,10,10-d*$_3$ (7a-*2a,10,10-d*$_3$). 1*H*-Indene-*1,1,3-d*$_3$ (1a-*1,1,3-d*$_3$) was allowed to react with DMAD as described by Alder, Pascher, and Vagt,[3a] giving the 1:2 adduct in 34% yield as white crystals, mp 130–131 °C [lit.[3a] (34% crude) mp 130–131 °C]. The ratios of the protons in the NMR spectrum in $CDCl_3$ were calculated by statistical methods from the average of 10 integrations. With the number of vinylene protons (δ ~6.0) set at 4.00, the ratio of protons at the C_3 bridgehead was found to be 0.93 ± 0.04. There was practically complete incorporation of deuterium at the C_{2a} bridgehead and the C_{10} bridge. Thus, the total deuterium content was found to be 3.07 atoms of D per molecule.

1-Methyl-1*H*-indene (1b). A. From 3-Phenylbutanoic Acid. 1. 2,3-Dihydro-3-methyl-1*H*-inden-1-one. The procedure is similar to that of Koelsch and LeClaire[10] for the preparation of 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-one. Phosphorus pentachloride (24.20 g, 115 mmol) was added slowly, with stirring, to a solution of 3-phenylbutanoic acid (Aldrich Chemical Co.; 16.40 g, 99.9 mmol) in benzene (50 mL). The solution was refluxed for 0.5 h and then cooled to room temperature. Benzene (25 mL) and then aluminum chloride (13.35 g, 100 mmol) were added. The mixture was refluxed for 20 min, cooled, and poured into a mixture of ice (~200 g) and concentrated hydrochloric acid (10 mL). The benzene layer was separated and the aqueous layer was extracted with benzene (2 × 25 mL). The benzene layer and extracts were combined and washed with water (3 × 25 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual red-brown oil was distilled in vacuo, giving a pale yellow liquid (8.10 g, 55%), bp 110–113 °C (9 mm) [lit.[11] 81%, bp 112–113.5 °C (9 mm)].

2. 2,3-Dihydro-3-methyl-1*H*-inden-1-ol. 2,3-Dihydro-3-methyl-1*H*-inden-1-one was reduced with lithium aluminum hydride as described by Christol and Plenat,[12] giving in 94% yield a white solid, mp 86.5–87 °C [lit. 94%, mp 86.5–87 °C,[11] 90%, mp 69 °C[12]].

3. 1-Methyl-1*H*-indene (1b). 2,3-Dihydro-3-methyl-1*H*-inden-1-ol was dehydrated by distillation over potassium hydrogen sulfate as described by Christol and Plenat,[12] giving in 35% yield a pale yellow liquid, bp 75–78 °C (17 mm) [lit. 89%, bp 82 °C (15 mm), n^{20}_D 1.5630;[12] 48%, bp 67.0–67.5 °C (pressure not stated),[11] bp 55–56 °C (3.75 mm), n^{20}_D 1.5565[13]].

Cedheim and Eberson[14] have since reported the methylation of 1*H*-indene to **1b** in 74% yield by inverse addition of 1*H*-inden-1-yllithium in an ether–hexane solution to a vigorously stirred solution of dimethyl sulfate (1 mol) in ether at room temperature, a process which apparently prevents the base-catalyzed partial isomerization of **1b** to **1d** commonly observed.

B. From 1*H*-Indene (1a). 1*H*-Indene (**1a**, n^{28}_D 1.5704, 11.60 g, 99.9 mmol) was added over 15 min to a hexane solution (42.6 mL of 2.35 M) of 1-butyllithium (Ventron Alfa Inorganics; 99.9 mmol) in anhydrous diethyl ether (50 mL). The solution was stirred for 15 min and then cooled to 0 °C. Methyl iodide (14.19 g, 100 mmol) was added over 20 min at 5–10 °C. The solution was allowed to warm to room temperature and then water (30 mL) was added. The ether layer was separated, washed with water (3 × 25 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual red-brown oil was distilled in vacuo, giving a pale yellow liquid (10.40 g, 80%): bp 75–77 °C (17 mm); n^{28}_D 1.5566 [lit. see part A.3]. This sample was used in all the experiments reported in this paper.

Reaction of 1-Methyl-1*H*-indene (1b) with DMAD. Tetramethyl 2a,3-Dihydro-10-methyl-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate (7b). A solution of **1b** (1.30 g, 10.0 mmol) and DMAD (4.26 g, 30.0 mmol) in toluene (5 mL) was refluxed for 24 h. The toluene was removed in a rotating evaporator and the residual dark red brown oil was dissolved in diethyl ether. After the solution was allowed to evaporate for 0.5 h, a pale yellow solid separated (1.25 g, 30%), mp 146–148 °C. Crystallization from benzene–petroleum ether (bp 60–68 °C) gave white crystals, mp 148–148.5 °C.

1-Ethyl-1*H*-indene. 1*H*-Indene (**1a**, 5.8 g, 49.9 mmol) was added over 15 min to a hexane solution (21.3 mL of 2.35 M) of 1-butyllithium (50.0 mmol) in anhydrous diethyl ether (25 mL). The solution was stirred for 15 min and then cooled to 0 °C. Ethyl iodide (7.8 g, 50.0 mmol) was added over 20 min at <5 °C. The solution was allowed to warm to room temperature and then water (15 mL) was added. The ether layer was separated, washed with water (3 × 25 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual red-brown oil was distilled in vacuo, giving a colorless liquid (5.52 g, 76%): bp 84–87 °C (13 mm); n^{28}_D 1.5638 [lit.[15] bp 76–77 °C (9 mm), n^{20}_D 1.5509].

Cedheim and Eberson[14] have since reported the ethylation of 1*H*-indene to 1-ethyl-1*H*-indene in 80% yield by inverse addition over 0.5 h of 1*H*-inden-1-yllithium in an ether–hexane solution to a vigorously stirred solution of ethyl bromide (4 mol) in ether at room temperature. Our experience suggests that this procedure is not necessary when ethyl iodide is used.

Attempted Reaction of 1-Ethyl-1*H*-indene with DMAD. A solution of 1-ethyl-1*H*-indene (1.45 g, 10.1 mmol) and DMAD (4.26 g, 30.0 mmol) in toluene (5 mL) was refluxed for 24 h. The toluene was removed in a rotating evaporator. The residual thick dark brown oil could not be crystallized, so it was chromatographed on silica gel and eluted successively with petroleum ether (bp 60–68 °C), benzene, chloroform, and diethyl ether. The chloroform–ether and ether fractions removed the only products as oils, which gave more than one spot on TLC and could not be induced by attempted crystallization to give solid products.

3-Methyl-1*H*-indene (1d). 1-Methyl-1*H*-indene (**1b**, 4.0 g, 307 mmol) was stirred with a solution of sodium methoxide (100 mg) in absolute methanol (30 mL) at room temperature for 18 h, and the solution slowly turned yellow. The methanol was distilled, using an oil bath kept at 80–85 °C, leaving a residual

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dark red liquid. Water (10 mL) was added and the mixture was extracted with diethyl ether (3 × 20 mL). The ether extracts were combined, washed with water (3 × 20 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual red-brown oil was distilled in vacuo, giving a colorless liquid (2.32 g, 58%): bp 76–78 °C (15 mm); n^{28}_D 1.5605 [lit.[12] bp 90 °C (17 mm), n^{20}_D 1.5630].

Reaction of 3-Methyl-1*H*-indene (1d) with DMAD. Tetramethyl 1,7-Dihydro-8-methyl-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylate (8d). A solution of **1d** (1.30 g, 10.0 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 22 h. The xylene was removed in a rotating evaporator. The residual dark red-brown oil was shaken with diethyl ether and petroleum ether (bp 60–68 °C) and the extract layer was decanted quickly from the oil. After the extracts had been allowed to evaporate for about 15 min, white solid separated (1.70 g, 41%), mp 121–122.5 °C. No more solid was obtained by attempted crystallization of the oily residue remaining after the extraction. Crystallization of the solid from benzene–petroleum ether gave white crystals, mp 122–122.5 °C [lit. mp 106–107.5 °C from aqueous methanol;[3b] 39%, mp 122–124 °C[8]].

1,3-Dimethyl-1*H*-indene (1f) was prepared from 2,3-dihydro-3-methyl-1*H*-inden-1-one, as described by Ohlsson, Wallmark, and Bergson,[16] in 70% overall yield as a pale yellow liquid, bp 81–82 °C (10 mm) [lit. 72%, bp 78–80 °C (9 mm);[16] 82%, bp 98 °C (16 mm),[12] bp 66 °C (3 mm), n^{20}_D 1.5477[13]].

Reaction of 1,3-Dimethyl-1*H*-indene (1f) with DMAD. Tetramethyl 1,7-Dihydro-8,9-dimethyl-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylate (8f). A solution of **1f** (0.72 g, 5.0 mmol) and DMAD (1.42 g, 10.0 mmol) in xylene (10 mL) was refluxed for 15 h. The xylene was removed in a rotating evaporator and the residual dark red-brown oil was chromatographed on a column of silica gel (Matheson, Coleman and Bell SX144-6, W. R. Grace no. 923). Elution with petroleum ether (bp 60–68 °C) removed traces of unchanged **1f** identified by TLC. Elution with mixtures of chloroform (increasing in 20% increments) removed traces of unidentified oils, and elution with chloroform removed a white solid (0.67 g, 31%), mp 136–138 °C. Crystallization from chloroform–petroleum ether gave white crystals, mp 139.5–140 °C.

2,3-Dimethyl-1*H*-indene (1g) was prepared from 2,3-dihydro-2-methyl-1*H*-inden-1-one, as described by Colonge and Weinstein[17a] and modified by Rinehart,[17b] as a pale yellow liquid: bp 92 °C (8 mm); n^{28}_D 1.5550 [lit. bp 99.5–100 °C (11 mm),[17a] bp 92 °C (7.6 mm),[17b] bp 77 °C (3 mm), n^{20}_D 1.5612[13]].

Reaction of 2,3-Dimethyl-1*H*-indene (1g) with DMAD. Tetramethyl 1,7-Dihydro-7,8-dimethyl-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylate (8g). A solution of **1g** (1.45 g, 10.1 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 24 h. Workup as described for **8d** gave a pale yellow solid (0.80 g, 19%), mp 128–130 °C. Crystallization from benzene–petroleum ether (bp 60–68 °C) gave white crystals, mp 132–132.5 °C.

3-Ethyl-1*H*-indene (1e). 1-Ethyl-1*H*-indene (2.9 g, 20.1 mmol) was stirred with a solution of sodium methoxide (100 mg) in absolute methanol (50 mL) at room temperature for 24 h. The methanol was distilled, using a short-path condenser and an oil bath kept at 80–85 °C, leaving a dark brown liquid. Water (25 mL) was added and the mixture was extracted with diethyl ether (3 × 20 mL). The ether extracts were combined, washed with water (3 × 20 mL), dried (Na_2SO_4), and evaporated in a rotating evaporator. The residual dark brown liquid was fractionally distilled in a vacuum, giving first unchanged 1-ethyl-1*H*-indene as a pale yellow liquid (0.370 g, 13% recovery), bp 84–87 °C (13 mm), and then **1e** as a colorless liquid (1.54 g, 61% conversion): bp 103–104 °C (13 mm); n^{28}_D 1.5558 [lit.[13] bp 61–61.5 °C (1.4 mm), n^{20}_D 1.5572].

Reaction of 3-Ethyl-1*H*-indene (1e) with DMAD. Tetramethyl 8-Ethyl-1,7-dihydro-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylate (8e). A solution of **1e** (1.45 g, 10.1 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 24 h. The xylene was removed in a rotating evaporator. The residual dark brown oil was dissolved in diethyl ether–petroleum ether (bp 60–68 °C) and the solution was allowed to evaporate slowly, causing separation of a cream-colored solid (1.73 g, 40%), mp 114–116 °C. Crystallization from benzene–petroleum ether gave white crystals, mp 116–116.5 °C.

Reaction of 1*H*-Indene-3-carboxylic Acid (1l) with DMAD. 1,7-Dihydro-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6,8-pentacarboxylic Acid 2,3,5,6-Tetramethyl Ester (8l). A solution of **1l**[1,2b] (2.40 g, 15.0 mmol) and DMAD (5.68 g, 40.0 mmol) in xylene (10 mL) was refluxed for 12 h. The orange solution was allowed to cool, causing separation of yellow crystals (4.94 g, 74%), mp 233–236 °C. Recrystallization from methanol–water gave white crystals, mp 236–239 °C. The product did not decolorize a solution of bromine in chloroform.

Refluxing the reactants in a 1:1 molar ratio in xylene for only 5 h gave an 11% yield of **8l**, with 75% recovery of **1l**.

Attempted Retro-Diels–Alder Reaction of 8l. A solution of **8l** (544 mg) in 1,2-dichlorobenzene (6 mL) was refluxed (at 180 °C) for 44 h. The solution was allowed to cool, causing separation of unchanged **8l** as a white solid (350 mg, 64% recovery), mp 234–236 °C, which gave no depression in mixture melting point, 234–236 °C, with the starting material.

Alkaline Hydrolysis of 8l. 1,7-Dihydro-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6,8-pentacarboxylic Acid Monosodium Salt (Monosodium Salt of 13l). A solution of **8l** (1.02 g, 2.30 mmol) in aqueous 5% sodium hydroxide (10 mL, 12 mmol) was refluxed for 4 h. The dark red solution was decolorized with Norit activated carbon, acidified to pH <2 with concentrated hydrochloric acid and concentrated to 4 mL on a hot plate. Cooling caused precipitation of a white solid (860 mg, 91%), chars >270 °C.

Tetrahydro Derivative of 8l. 1,7,8,8a-Tetrahydro-4*H*-1,4-ethano-4a,7-methanonaphthalene-2,3,5,6,8-pentacarboxylic Acid 2,3,5,6-Tetramethyl Ester (14l). A solution of **8l** (1.00 g, 2.25 mmol) in methanol (150 mL) containing platinum(IV) oxide (100 mg) was hydrogenated at 2 atm for 24 h. The platinum black was filtered off and the filtrate was evaporated, leaving a yellow solid (1.02 g, 100%), mp 102–106 °C. Two digestions in carbon tetrachloride gave white microcrystals, mp 123–128 °C. Recrystallization from chloroform–petroleum ether (bp 60–68 °C) gave fluffy, white needles, mp 195–196 °C.

An attempt to carry out the hydrogenation under the same conditions, but with 10% palladium-on-carbon as the catalyst, gave only a 97% recovery of unchanged **8l**.

Attempted Reaction of 1*H*-Indene-3-carboxylic Acid (1l) with Diphenylethyne. A solution of **1l** (800 mg, 5.00 mmol) and diphenylethyne (2.67 g, 15.0 mmol) in xylene (8 mL) was refluxed for 6 h. The yellow solution was allowed to cool and evaporate slowly overnight, causing separation of unchanged **1l** as yellow crystals (403 mg, 50% recovery), mp and mmp 161–162 °C.

Reaction of Methyl 1*H*-Indene-3-carboxylate (1m) with DMAD. Pentamethyl 1,7-Dihydro-4*H*-1,4-ethano-4a,7-methanonaphthalene-2,3,5,6,8-pentacarboxylate (8m). A solution of **1m**[1,2b,5] (1.74 g, 10.0 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (6 mL) was refluxed for 12 h. The dark red solution was allowed to cool, causing separation of colorless crystals (3.05 g, 66%), mp 146–147.5 °C. Recrystallization from xylene gave white crystals, mp 148.5–149.5 °C. In contrast to **7a**, which does so readily, the product did not decolorize a solution of bromine in chloroform.

Carrying out the same reaction in refluxing xylene for only 9 h gave a 52% yield of **5j**. Attempted further reactions of **5j** (2.29 g, 5.00 mmol) with DMAD (0.71 g, 5.00 mmol) in refluxing xylene (5 mL) for 8 h or, at higher temperature, of **5j** (2.00 g, 4.37 mmol) and DMAD (1.24 g, 8.74 mmol) in refluxing 1,2-dichlorobenzene (5 mL) for 8 h gave unchanged **5j** in 74 and 75% recoveries.

Methyl 1*H*-indene-3-carboxylate-*1-d* (1m-*1-d*) was prepared by the procedure of Noland, Landucci, and Kameswaran.[1,2a] The deuterium content, which was found to be completely at C_1, was found by NMR analysis to be 0.97 ± 0.03 atom of D per molecule, in good agreement with the total deuterium content found by mass spectrometric analysis to be 0.95 ± 0.05 atom of D per molecule.

(16) Ohlsson, L.; Wallmark, I.; Bergson, G. *Acta Chem. Scand.* **1966**, *20*, 750–753.

(17) (a) Colonge, J.; Weinstein, G. *Bull. Soc. Chim. Fr.* **1952**, 462–465. (b) Rinehart, J. Kent Ph.D. Thesis (with William E. Parham), University of Minnesota, Minneapolis, MN, Feb 1967, pp 108–111; *Diss. Abstr. B* **1968**, *28*, 3656–3657.

Reaction of 1m-*1-d* with DMAD. Preparation of 8m-*9-d*. The deuterated 1:2 adduct 8m-*9-d* was obtained from 1m-*1-d* and DMAD by the procedure described above for preparation of 8m from 1m and DMAD in 66% yield as a white solid, mp 148.5–149 °C [lit.[2] 66%, mp 148.5–149 °C]. Two crystallizations from benzene gave white crystals, mp 148.5–149 °C. The NMR spectrum (20% w/v in $CDCl_3$) was similar to that reported above for nondeuterated 8m. The proton areas were calculated by statistical analysis from ten integrations. With the number of vinylene protons (10- and 11-H) set equal to 2.00, the ratio of the vinylene to the C_7 bridgehead and to the C_9 bridge methylene protons was found to be 2.00:1.10:1.08 ± 0.07, respectively. This gives, by difference, a deuterium content of the C_9 bridge of 0.92 ± 0.07 atom of D per molecule. By mass spectrometric analysis the total deuterium content was found to be 0.95 ± 0.05 atom of D per molecule, in good agreement with the NMR data.

1*H*-Indene-3-carboxamide. 1*H*-Indene-3-carboxylic acid[1,2b] (11, 8.0 g, 50 mmol) was added slowly, over 15 min, to a solution of thionyl chloride (11.9 g, 100 mmol) in benzene (10 mL). The solution was refluxed for 2 h. The benzene and excess thionyl chloride were removed in a rotating evaporator, leaving a dark red solid, which was added immediately, with stirring, to concentrated ammonia (28.5%, 50 mL) at −10 to −20 °C. The mixture was stirred at −10 °C for 1 h and then allowed to warm to room temperature. The solid was filtered, washed with small amounts of cold 95% ethanol, and dried under vacuum, giving a yellow solid (7.55 g, 95%), mp 195–212 °C dec; IR (Nujol) 3328 (m), 3154 (m, NH_2), 1667 (s), 1634 (s, C=O) cm^{-1}.

1*H*-Indene-3-carbonitrile (1n). The crude 1*H*-indene-3-carboxamide (3.18 g, 20.0 mmol) was mixed thoroughly with P_2O_5 (5.68 g, 40.0 mmol) and sand (10 g) and distilled in vacuo, using a short-path condenser and a gentle flame, giving a pale yellow liquid (1.27 g, 45%), bp 135–137 °C (7 mm). Redistillation gave a colorless liquid: bp 133.5 °C (7 mm); n^{28}_D 1.5758; IR (neat) 2218 (C≡N) cm^{-1}.

Anal. Calcd for $C_{10}H_9N$ (141.18): C, 85.09; H, 4.99; N, 9.92. Found: C, 84.79; H, 5.22; N, 9.61.

Reaction of 1*H*-Indene-3-carbonitrile (1n) with DMAD. Tetramethyl 8-Cyano-1,4,4a,7-tetrahydro-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylate (8n). A solution of 1n (1.27 g, 9.00 mmol) and DMAD (2.55 g, 17.9 mmol) in xylene (5 mL) was refluxed for 22 h. The red-orange solution was allowed to cool, causing separation of a pale yellow solid (2.42 g, 63%), mp 151–152 °C. Crystallization from benzene–petroleum ether (bp 60–68 °C) gave white crystals, mp 151–152 °C.

When carried out in refluxing benzene (10 mL) for 24 h, the reaction gave a lower yield (11%), mp 152–152.5 °C.

Reaction of 1*H*-Indene-3-carboxylic Acid (11) with Maleic Anhydride and DMAD. 1,2,3,7-Tetrahydro-4*H*-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6,8-pentacarboxylic Acid Cyclic 2,3-Anhydride 5,6-Dimethyl Ester (10l) and 8l. A solution of 11 (800 mg, 5.00 mmol), maleic anhydride (980 mg, 10.0 mmol), and DMAD (1.42 g, 10.0 mmol) in xylene (8 mL) was refluxed for 8 h. The orange solution was allowed to cool, causing separation of pale yellow crystals (346 mg, 17%, in two crops), mp 259–269 °C dec with gas evolution. Two recrystallizations from boiling xylene gave colorless flakes, mp 279–285 °C dec with gas evolution.

The original filtrate was allowed to evaporate slowly for 3 days, causing separation of 8l as a white powder (393 mg, 18%), mp and mmp 220–229 °C.

Attempted Reaction of 3l with DMAD. A solution of 3l[1,2b] (1.50 g, 5.81 mmol) and DMAD (2.13 g, 15.0 mmol) in xylene (6 mL) was refluxed for 12 h. The yellow solution was allowed to cool, causing separation of unchanged 3l as pale yellow crystals (818 mg, 55% recovery), mp and mmp 226–227 °C. The IR spectrum in Nujol was identical with that of the starting material 3l.

Reaction of 1*H*-Indene-3-carbonitrile (1n) with Maleic Anhydride and DMAD. 8-Cyano-1,2,3,7-tetrahydro-1,4-etheno-4a,7-methanonaphthalene-2,3,5,6-tetracarboxylic Acid Cyclic 2,3-Anhydride Dimethyl Ester (10n). A solution of 1n (1.41 g, 10.0 mmol), maleic anhydride (0.98 g, 10.0 mmol), and DMAD (1.42 g, 10.0 mmol) in xylene (5 mL) was refluxed for 22 h. The solution was allowed to cool, causing separation of a white solid (2.25 g, 59%, in two crops), mp 258–262 °C. Crystallization from chloroform gave white crystals, mp 263–263.5 °C dec. The compound was nearly insoluble in common NMR solvents, especially in the crystalline form, so that the first crop of crude white solid was examined for NMR.

Hexamethyl 2a,3,6,9-Tetrahydro-6,9-etheno-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5,7,8-hexacarboxylate (11a). A. From Reaction of 1*H*-Indene (1a) with 3 Equiv of DMAD. A solution of 1a (1.16 g, 10.0 mmol) and DMAD (4.26 g, 30.0 mmol) in xylene (10 mL) was refluxed for 7.5 h. The solution was allowed to cool and evaporate overnight, causing separation of a pale yellow solid (2.16 g, 40%), mp 175–176 °C. Crystallization from benzene gave white crystals, mp 179.5–180 °C.

B. From Reaction of 7a with DMAD. A solution of 7a[3a] (2.00 g, 5.00 mmol) and DMAD (0.71 g, 5.00 mmol) in xylene (10 mL) was refluxed for 7.5 h. The solution was allowed to cool and evaporate overnight, causing separation of a white solid (1.90 g, 71%), mp 177–179 °C. Crystallization from benzene gave white crystals, mp 179.5–180 °C. There was no depression in mixture melting point, 179.5–180 °C, with the sample prepared from 1*H*-indene as described in part A above, and the IR spectra in Nujol were essentially identical.

Reaction of 7a-*10-d* with DMAD. 11a-*12-d*. By the procedure for 11a described in part B, 7a-*10-d* and DMAD gave 11a-*12-d* in 70% yield as a white solid: mp 179.5–180 °C; NMR (22% w/v in $CDCl_3$) δ 1.47 (s, $w_{1/2}$ = 2 Hz, 0.3 H, 12a-H), 2.37 (d, J = 6 Hz, $w_{1/2}$ = 2.5 Hz, 0.2 H, 12b-H), 3.52 and down (m, 2a-, 3-H) overlapping 3.70, 3.75, 3.78 (3 s, 6 $COOCH_3$, total 20.2 H), 4.05–4.19 (m, 1.4 H, 6-H), 5.20–5.33 (m, 1.0 H, 9-H), 6.47–6.62 (m, 1.9 H, 10-, 11-H). The NMR spectrum is very similar to that of nondeuterated 11a except that the AB pattern at the C_{12} bridge has collapsed to a doublet and a singlet. The deuterium content is (by difference) at C_{12a} 0.7 atom of D and at C_{12b} 0.8 atom of D.

Reaction of 1*H*-Indene-*1,1,3-d*$_3$ (1a-*1,1,3-d*$_3$) with DMAD. 11a-*2a,12,12-d*$_3$. By the procedure for 11a described above in part A, 1a-*1,1,3-d*$_3$[4] and DMAD gave 11a-*2a,12,12-d*$_3$ in 36% yield as white crystals: mp 179.5–180 °C; NMR (20% w/v in $CDCl_3$) δ 3.72–4.00 (m, 3-H) overlapping 3.75, 3.77, 3.80 (3 s, 6 $COOCH_3$, total 19.1 H), 4.00–4.30 (m, 1.0 H, 6-H), 5.17–5.40 (m, 1.0 H, 9-H), 6.40–6.70 (m, 1.9 H, 11-, 10-H). The NMR spectrum is very similar to that of the nondeuterated 11a and 11a-*12-d* described above except that it does not show either of the C_{12} bridge protons, and the complex pattern from 3.52 and down containing a multiplet and the methyl ester singlets appears to contain one less proton (which is assumed to be replaced by deuterium at C_{2a}).

2-Methyl-1*H*-indene (1c) was prepared by the general method of Colonge and Weinstein,[17a] by dehydration of 2,3-dihydro-2-methyl-1*H*-inden-1-one with oxalic acid, as a pale yellow liquid: bp 64–66 °C (3 mm); n^{28}_D 1.5587 [lit.[13] bp 64–65 °C (2.7 mm), n^{20}_D 1.5645].

Reaction of 2-Methyl-1*H*-indene (1c) with DMAD. Hexamethyl 2a,3,6,9-Tetrahydro-3-methyl-6,9-etheno-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5,7,8-hexacarboxylate (11c). A solution of 1c (1.30 g, 10.0 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 18 h. The xylene was removed in a rotating evaporator. The residual dark red brown oil was dissolved in diethyl ether (5 mL) and petroleum ether (bp 60–68 °C, 5 mL) and allowed to evaporate for 2 h, causing separation of a white solid (250 mg, 6%), mp 196–198 °C. Preparative TLC of the mother liquor on silica gel PF-254 with chloroform as eluant gave no more solid products. Crystallization of the white solid from benzene–petroleum ether gave white crystals, mp 198–198.5 °C.

Repetition of the reaction and workup by chromatography on silica gel gave 11c in 5% yield, mp 198–198.5 °C, as the only solid product. An attempted reaction at lower temperature, in refluxing toluene, and workup by chromatography on silica gel gave no solid products.

2-Bromo-1*H*-indene was prepared as described by Porter and Suter[18] by dehydration of 2-bromo-2,3-dihydro-1*H*-inden-1-ol (Aldrich Chemical Co.) with P_2O_5 in 46% yield, mp 38–39 °C [lit.[18] 55%, mp 38–39 °C].

(18) Porter, H. D.; Suter, C. M. *J. Am. Chem. Soc.* **1935**, *57*, 2022–2026.

Attempted Reaction of 2-Bromo-1*H*-indene with DMAD. A solution of 2-bromo-1*H*-indene (1.95 g, 10.0 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 24 h. The xylene was removed in a rotating evaporator. Chromatography of the residual dark brown oil on silica gel gave no solid products. Repetition of the reaction at lower temperature, in refluxing toluene, also gave no solid products.

Reaction of 7a with Maleic Anhydride. 2a,3,6,7,8,9-Hexahydro-6,9-etheno-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5,7,8-hexacarboxylic Acid Cyclic 7,8-Anhydride Tetramethyl Ester (12a). A solution of **7a**[3a] (4.00 g, 10.0 mmol) and maleic anhydride (0.98 g, 10.0 mmol) in xylene (10 mL) was refluxed for 7 h. The solution was allowed to cool and evaporate for 2 days, causing separation of a pale yellow solid (3.43 g, 69%), mp 245–248.5 °C. Crystallization from benzene gave white crystals, mp 248–249.5 °C. The compound was quite insoluble in common NMR solvents, especially in the crystalline form, so that the crude pale yellow solid was examined for NMR.

Methyl Esterification of 12a. Hexamethyl 2a,3,6,7,8,9-Hexahydro-6,9-etheno-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5,7,8-hexacarboxylate (15a). A solution of **12a** (2.49 g, 5.00 mmol) in methanol (20 mL) was saturated with dry HCl gas and then stirred at room temperature for 24 h. The solvent and HCl were removed in a rotating evaporator, leaving a waxy white solid. Crystallization from benzene gave white crystals (1.40 g, 52%), mp 191–192 °C. Two recrystallizations from benzene gave white crystals, mp 191.5–192 °C.

Reaction of 7a-*2a,10,10-d*$_3$ with Maleic Anhydride. 12a-*2a,12,12-d*$_3$. By the procedure for **12a** described above, **7a**-*2a,10,10-d*$_3$ and maleic anhydride gave **12a**-*2a,12,12-d*$_3$ in 50% yield as white crystals, mp 248–248.5 °C. The product was methyl esterified as described below to enhance the solubility for determination of the NMR spectrum.

Methyl Esterification of 12a-*2a,12,12-d*$_3$. 15a-*2a,12,12-d*$_3$. By the procedure for **5a** described above, **12a**-*2a,12,12-d*$_3$ was methyl esterified to **15a**-*2a,12,12-d*$_3$ in 50% yield as white crystals: mp 191.5–192 °C; NMR (14% w/v in $CDCl_3$) δ 2.73–3.37 (complex m with a major peak at 3.25, $w_{1/2}$ of major peak = 3 Hz, 3.8 H, 3-, 6-, 7-, 8-H), 3.37–4.03 (complex m, 9-H) overlapping 3.62, 3.70, 3.72, 3.73, 3.75, 3.78 (6 s, 6 $COOCH_3$, total 19.2 H), 6.30-6.44 (m, 2.0 H, 11-, 10-H). The NMR spectrum is very similar to that of nondeuterated **15a** except that it does not show either of the C_{12} bridge protons, and the complex multiplet at δ 3.37–4.03 overlapping the methyl ester singlets appears to contain one less proton (which is assumed to be replaced by deuterium at C_{2a}).

2a,3,6,7,8,9-Hexahydro-12-methyl-6,9-etheno-3,5a-methano-5a*H*-cyclobuta[*d*]naphthalene-1,2,4,5,7,8-hexacarboxylic Acid Cyclic 7,8-Anhydride Tetramethyl Ester (12b). A. From Reaction of 1-Methyl-1*H*-indene (1b) with DMAD and Maleic Anhydride. A solution of **1b** (1.30 g, 10.0 mmol), DMAD (2.84 g, 20.0 mmol), and maleic anhydride (0.98 g, 10.0 mmol) in xylene (10 mL) was refluxed for 24 h. The solution was cooled and allowed to evaporate for 2 days, causing separation of a white solid (1.60 g, 31%), mp 240–244 °C. Crystallization from benzene gave white crystals, mp 249.5–251.5 °C. The compound was nearly insoluble in common NMR solvents, especially in the crystalline form, so that the crude white solid was used, but it crystallized in the NMR tube while the spectrum was being taken.

B. From Reaction of 7b with Maleic Anhydride. A solution of **7b** (700 mg, 1.69 mmol) and maleic anhydride (180 mg, 1.84 mmol) in xylene (3 mL) was refluxed for 18 h. The solution was cooled and allowed to evaporate overnight, causing separation of a white solid (0.28 g, 32%), mp 244–248 °C. Crystallization from benzene gave white crystals, mp 249.5–252 °C. There was no depression in mixture melting point, 249–251 °C, with the sample prepared from **1b**, DMAD, and maleic anhydride as described in part A, and the IR spectra in Nujol were identical.

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Registry No. **1a**, 95-13-6; **1a**-*1-d*, 933-61-9; **1a**-*1,1,3-d*$_3$, 770-96-7; **1b**, 767-59-9; **1c**, 2177-47-1; **1d**, 767-60-2; **1e**, 2294-91-9; **1f**, 2177-48-2; **1g**, 4773-82-4; **1l**, 14209-41-7; **1m**, 39891-79-7; **1m**-*1-d*, 74143-68-3; **1n**, 29872-81-9; **7a**, 7695-31-0; **7a**-*10-d*, 74843-80-4; **7a**-*2a,10,10-d*$_3$, 74843-81-5; **7b**, 74843-82-6; **8d**, 74868-02-3; **8e**, 74843-83-7; **8f**, 74843-84-8; **8g**, 74843-85-9; **8l**, 74843-86-0; **8m**, 74843-87-1; **8m**-*9-d*, 74843-88-2; **8n**, 74868-60-3; **10l**, 74843-89-3; **10n**, 74843-90-6; **11a**, 74843-91-7; **11a**-*12-d*, 74843-92-8; **11a**-*2a,12,12-d*$_3$, 74843-93-9; **11c**, 74843-94-0; **12a**, 74843-95-1; **12a**-*2a,12,12-d*$_3$, 74868-61-4; **12b**, 74843-96-2; **13l** monosodium salt, 74843-97-3; **14l**, 74843-98-4; **15a**, 74843-99-5; **15a**-*2a,12,12-d*$_3$, 74844-00-1; 2,3-dihydro-3-methyl-1*H*-inden-1-one, 6072-57-7; 3-phenylbutanoic acid, 4593-90-2; 2,3-dihydro-3-methyl-1*H*-inden-1-ol, 22339-44-2; DMAD, 762-42-5; 1-ethyl-1*H*-indene, 6953-66-8; 1*H*-indene-3-carboxamide, 74844-01-2; maleic anhydride, 108-31-6; 2-bromo-1*H*-indene, 10485-09-3.

Supplementary Material Available: Spectral data on indenes and their adducts [Tables 1 (UV), 2 (IR), 3 (NMR), and 4 (mass spectra)] and melting points, yields, and elemental analyses for all new indene adducts and their derivatives (Table 5) (19 pages). Ordering information is given on any current masthead page.