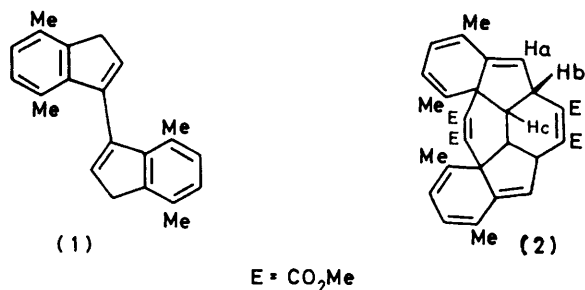


1 : 1 Adducts of Indenes with Dimethyl Acetylenedicarboxylate

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1-Methylindene, 3-methylindene, 1,3-dimethylindene, and 3,4,7-trimethylindene react with dimethyl acetylenedicarboxylate at room temperature (20 d) to give mainly the 1 : 1 adducts (5). The adduct from 4,4',7,7'-tetramethyl-3,3'-bi-indene (1) is reformulated as (4); it is accompanied by a stereoisomer and a product derived by addition of three molecules of the dienophile to (1).

It is reported¹ that the bi-indene (1) reacts with two molecules of dimethyl acetylenedicarboxylate (dmad) (20 °C; 20 d) to give a yellow (λ_{max} , 436 nm) adduct formulated as (2), mainly on the basis of the n.m.r. spectrum which requires a structure of this or related symmetry. Resonances attributed to H_a , H_b , and H_c appear respectively at δ 4.17 (t, J 1.6 Hz), 2.71 (dd, J 8 and 1.6 Hz), and 1.96 (dd, J 8 and 1.6 Hz). The proton H_a in (2) would be expected to resonate to lower field than δ 4.17, and H_a would not be expected to couple with H_c . Excluding dramatic homo-conjugative effects the triene chromophore in (2) would show λ_{max} , ca. 313 nm (Woodward's rules) rather than the observed value of 436 nm. Moreover it was suggested¹ that (2) arose *via* the Diels-Alder adduct (3) of (1) with dmad; such a reaction is unlikely as the required *cisoid* conformation of (1) would be strongly destabilised by

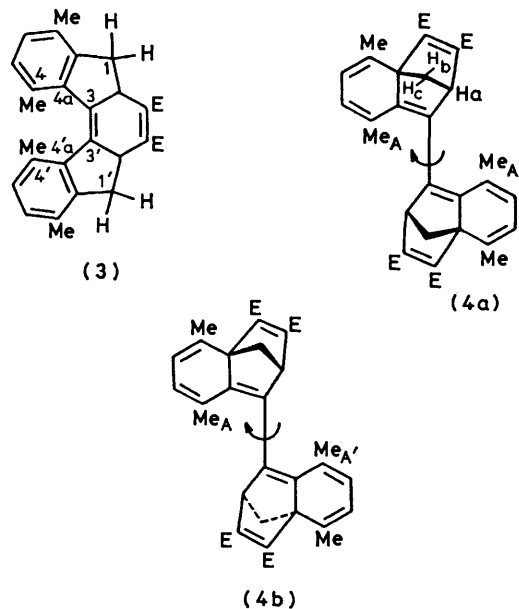


steric clash between the 4- and 4'-methyl groups. Additionally the reaction of (3) with dmad to give (2) involving attachment of the dienophile at C(4a) and C(4a') and concomitant hydrogen shifts from C(1) to C(3) and from C(1') to C(3) appears unusual. The reported data are more consistent with structure (4a or b) for the adduct which would then be simply derived by Diels-Alder addition of dmad to each indene moiety in (1). In (4a or b), H_a (δ 4.17) would be expected to couple with *both* H_b and H_c with the observed coupling constant (1.6 Hz).² The long wavelength u.v. absorption of the adduct is also more consistent with structure (4a or b), although it is not clear to what extent steric factors allow conjugation across the central single bond in the system.

RESULTS AND DISCUSSION

Repetition of the reaction of (1) with dmad in the manner described by Kemp and Spanswick,¹ but with exclusion of light, gave a yellow crystalline precipitate (compound A) which had properties in accord with those reported.¹ In addition, chromatographic work-up of the mother liquor obtained after filtering off compound A

gave an adduct derived by addition of three molecules of dmad to (1), and compound B, isomeric with compound A, and with very similar u.v. and mass spectra. Whilst the n.m.r. spectrum of compound A shows two 6-H



singlets for the four C-Me groups present, the n.m.r. spectrum of compound B shows two C-Me singlets and a broad 6-H singlet for the other two C-Me groups. This observation shows that compound A is the (\pm)-diastereoisomer (4a) and compound B is the *meso*-form (4b). It is likely that rotation about the central single bond will be slow in both (4a) and (4b). In the other conformational isomers derived by such rotation in (4a), Me_A and $Me_{A'}$ have identical environments. In contrast, in the other conformers derived from (4b), Me_A and $Me_{A'}$ have different environments. Thus 90° rotation in the sense shown in (4b) places Me_A above the *endo*-face of the bicycloheptadiene unit in the other half of the molecule, and $Me_{A'}$ over the *exo*-face of the other bicycloheptadiene unit. The ¹³C n.m.r. spectrum of compound A also agrees with the revised constitution (4) but not structure (2); δ (CDCl₃ relative to SiMe₄) 19.37, 19.89 (CMe), 51.95 (OMe), 56.37 (CH), 68.72 (quaternary C), 77.30 (CDCl₃ and CH₂), 123.47 (=CH), 125.55 (=CH), 130.62, 136.53, 143.43, 146.74, 148.69, 159.88 (olefinic C), 165.60, 165.86 p.p.m. (C=O). In the off-resonance proton-decoupled spectrum these signals have the appropriate multiplicities; structure (2) with *three* different =CH units and no methylene group is

(9 : 1) yielded the adduct (5; $R^1 = R^2 = \text{Me}$, $R^3 = R^4 = \text{H}$) (30 mg) and the adduct (7; $R = \text{Me}$) (100 mg), m.p. 130—133 °C (from methylene chloride–light petroleum) (Found: C, 65.1; H, 5.7. $\text{C}_{24}\text{H}_{26}\text{O}_8$ requires C, 65.15; H, 5.9%); ν_{max} 1705, 1720, and 1732 cm^{-1} ; δ 1.67 (3 H, s), 1.75 (3 H, s), 1.90 (3 H, s), 2.15 (1 H, br d, J 7 Hz) (the other part of this AB system is hidden by the preceding signals), 3.5 (1 H, br s, J ca. 1 Hz), 3.7 (12 H, 2 lines), 6.02 (1 H, d, J 8 Hz), and 6.25 (1 H, d, J 8 Hz).

Addition of Adduct (5; $R^1 = R^2 = \text{Me}$, $R^3 = R^4 = \text{H}$) to 1-Phenyltriazoline-2,5-dione.—The adduct (5; $R^1 = R^2 = \text{Me}$, $R^3 = R^4 = \text{H}$) (60 mg) in benzene (2 ml) was treated with 1-phenyltriazoline-2,5-dione (30 mg) in benzene (2 ml) to give a slightly pink solution. The product was chromatographed on silica in benzene–ether (4 : 1) to give the adduct (9) (25 mg), m.p. 130—133 °C (from ethanol) (Found: C, 65.5; H, 5.5; N, 8.65. $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_8$ requires C, 65.7; H, 5.3; N, 8.8%); ν_{max} 1710, 1732, and 1763 cm^{-1} ; δ (90 MHz) 2.1 (s, 3 H), 2.2 (s, 3 H), 2.22 (s, 3 H), 2.1—2.22 (2 H, hidden multiplet), 3.78 (6 H, 2 lines and 1 H, concealed), 6.25 (1 H, d, J 8 Hz), 6.33 (1 H, d, J 8 Hz), and 7.4 (5 H, br s).

Addition of Dimethyl Acetylenedicarboxylate to Other Indenes.—(i) 3-Methylindene (240 mg) and the dienophile (284 mg) were set aside (20 d); chromatography on silica in benzene–ether (9 : 1) gave the adduct (5; $R^1 = R^3 = R^4 = \text{H}$, $R^2 = \text{Me}$) (238 mg) (Found: M^+ , 272.104 8. $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires M^+ , 272.104 8); ν_{max} 1715 (br) cm^{-1} ; λ_{max} 327 nm ($\epsilon > 3$ 417); δ 1.8 (1 H, dd, J 6.5 and ca. 1.5 Hz), 2.01 (3 H, s), 2.55 (1 H, dm, J 6.5 Hz), 3.7 (6 H, s), 3.95 (1 H, t, J ca. 1.5 Hz), and 5.8—6.7 (4 H, m); m/e 272 (M^+), 240 ($[M - \text{MeOH}]^+$), 214, 213 ($[M - \text{CO}_2\text{Me}]^+$), 212 ($[M - \text{HCO}_2\text{Me}]^+$), 153, 152, 130 (ionised 3-methylindene), 129, and 115 (indenyl cation) (10.7, 14.4, 12.3, 16.5, 8.4, 14.0, 10.5, 100, 27.3, and 33.1% respectively). Continued elution of the column gave the adduct (7; $R = \text{H}$)⁴ (160 mg), m.p. 122—124 °C (from methanol); δ 1.86 (3 H, s and concealed 1 H, dd), 2.24 (1 H, br d, J 7 Hz), 3.55 (1 H, t, J ca. 1 Hz), 3.7—3.8 (12 H, 2 lines), 4.41 (1 H, dd, J 6 and 2 Hz), 4.68 (1 H, dd, J 6 and 2 Hz), and 6.1—6.7 (2 H, m).

(ii) 1-Methylindene (260 mg) and the dienophile (284 mg) were set aside (22 d); chromatography as above gave the adduct (5; $R^1 = R^2 = R^4 = \text{H}$, $R^3 = \text{Me}$) (35 mg) (Found: M^+ , 272.104 5); ν_{max} 1720 (br) cm^{-1} ; λ_{max} 320 nm ($\epsilon > 3$ 101); δ 0.6 (3 H, d, J 6.5 Hz), 3.21 (1 H, qm, J 6.5 Hz), 3.7 (6 H, OMe), 3.85 (1 H, m), and 5.5—6.8 (5 H, m); m/e 272 (M^+), 257 ($[M - \text{Me}]^+$), 241 ($[M - \text{OMe}]^+$), 242 ($[M - \text{MeOH}]^+$), 225 ($[M - \text{MeOH} - \text{Me}]^+$), 213 ($[M - \text{CO}_2\text{Me}]^+$), 212 ($[M - \text{HCO}_2\text{Me}]^+$), 182 ($[M - \text{CO} - 2\text{OMe}]^+$), 181 ($[M - \text{CO} - 2\text{OMe} - \text{H}]^+$), 154 ($[M - 2\text{CO}_2\text{Me}]^+$), 153 ($[M - \text{H} - 2\text{CO}_2\text{Me}]^+$), 152 ($[M - 2\text{HCO}_2\text{Me}]^+$), 130 (methylindenyl cation radical), 129, and 115 (indenyl cation), (39.5, 10.3, 50.4, 37.8, 23.4, 78.4, 23.8, 53.7, 54.6, 74.2, 100, 62.6, 99.1, 48.2, and 82.7% respectively).

(iii) 1,3-Dimethylindene (144 mg) and the dienophile (142 mg) were set aside (14 d); chromatography on silica as above gave a ca. 3 : 1 mixture of adducts (5; $R^1 = R^4 = \text{H}$, $R^2 = R^3 = \text{Me}$) and (5; $R^1 = R^3 = \text{H}$, $R^2 = R^4 = \text{Me}$) (100 mg) (Found: M^+ , 286.119 3. $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires M^+ , 286.120 5); λ_{max} 330 nm ($\epsilon > 3$ 884); δ (*anti*-isomer) 0.58 (3 H, d, J 6.5 Hz), 2.0 (3 H, s), 3.06 (1 H, qm, J 6.5 Hz), 3.67 (6 H, OMe), ca. 3.7 (1 H, hidden), and 5.6—6.7 (4 H, m); δ (*syn*-isomer) 1.2 (3 H, d, J 6.5 Hz), 2.0 (3 H, s), 2.4 (1 H, q, J 6.5 Hz), ca. 3.7 (1 H, hidden), 3.67 (6 H, OMe),

and 5.6—6.7 (4 H, m); m/e 286 (M^+), 271 ($[M - \text{Me}]^+$), 255 ($[M - \text{OMe}]^+$), 254 ($[M - \text{MeOH}]^+$), 239 ($[M - \text{Me} - \text{MeOH}]^+$), 227 ($[M - \text{CO}_2\text{Me}]^+$), 226 ($[M - \text{HCO}_2\text{Me}]^+$), 196 ($[M - \text{CO}_2\text{Me} - \text{OMe}]^+$), 195 ($[M - \text{CO}_2\text{Me} - \text{MeOH}]^+$), 168 ($[M - 2\text{CO}_2\text{Me}]^+$), 167 ($[M - \text{H} - 2\text{CO}_2\text{Me}]^+$), 166 ($[M - 2\text{HCO}_2\text{Me}]^+$), 153 ($[M - \text{Me} - 2\text{CO}_2\text{Me}]^+$), 152 ($[M - \text{H} - \text{Me} - 2\text{CO}_2\text{Me}]^+$), 144 (1,3-dimethylindene radical cation), 129 (methylindenyl cation), and 128 (25.8, 6.2, 9.2, 19.7, 27.8, 72.3, 20.3, 17.9, 34.5, 15.2, 30.1, 11.7, 22.8, 30.0, 100, 98.2, and 43.6% respectively).

Addition of Dimethyl Acetylenedicarboxylate to 4,4',7,7'-Tetramethyl-3,3'-bi-indene.—The bi-indene¹ (0.5 g) and dienophile (10 ml) were stirred in the dark under N_2 (18 d). The yellow precipitate was filtered off and washed with light petroleum to give a solid (0.37 g), m.p. 158—165 °C, purified by crystallisation from methanol to give yellow needles (200 mg), m.p. 164—168 °C (lit.¹ m.p. 165—167 °C). The i.r., u.v., and n.m.r. spectra of this product agree with the reported data; m/e 570.225 4 (M^+ , $\text{C}_{34}\text{H}_{34}\text{O}_8$ requires 570.225 3), 539 ($[M - \text{OMe}]^+$), 538 ($[M - \text{MeOH}]^+$), 523, 511 ($[M - \text{CO}_2\text{Me}]^+$), 506 ($[M - 2\text{MeOH}]^+$), 491, 480, 479, 478, 463, 452, 451, 447, 435, 431, 428, 419, 396, 391, 387, 381, 369, 364, 359, 353, 338, 337, 336, 310, 309, 295, 294, 293, 286 ($[M - 2\text{CCO}_2\text{Me}]^+$), 280, 279, 271, 265, 256, 253, 241, 239, 165, 152, 143 (protonated dmad), 128, 111, 59, 52, 44, and 39 (46.9, 6.0, 16.5, 21.7, 22.0, 21.7, 9.8, 10.2, 38.5, 31.6, 23.4, 12.0, 25.6, 25.2, 9.8, 9.0, 17.5, 30.7, 31.3, 16.9, 16.8, 10.1, 13.8, 10.7, 9.7, 12.8, 10.7, 38.1, 10.7, 22.6, 36.8, 17.5, 24.5, 12.0, 24.7, 14.9, 14.9, 26.1, 11.5, 10.5, 11.2, 10.9, 12.3, 15.4, 9.6, 100, 30.1, 82, 29.0, 10.5, 20.3, and 44.4% respectively).

The dmad solution left after filtering off the above yellow compound was evaporated to dryness at 70 °C in a high vacuum and a portion (330 mg) of the product (1.03 g) chromatographed on silica in benzene–ether (9 : 1). The adduct isolated above was eluted first (30 mg) followed by an *isomeric adduct* (60 mg), m.p. 158—161 °C (from methanol) (Found: M^+ , 570.226 0. $\text{C}_{34}\text{H}_{34}\text{O}_8$ requires M^+ , 570.225 3); λ_{max} 430 (ϵ 10 585) and 390 nm (br) (ϵ 9 907); δ 1.3 (3 H, s), 1.74 (3 H, s), 1.90 (6 H, br s), 2.12 (2 H, m), 2.68 (2 H, m), 3.49 (3 H, s), 3.7 (6 H, s), 3.79 (3 H, s), 4.18 (2 H, m), and 5.25—6.2 (4 H, m). The mass spectrum was closely similar to that of the preceding adduct, differing from it only in the intensity of some peaks.

Continued elution of the column gave an adduct (40 mg), m.p. 148—155 °C (from methanol) (Found: C, 67.35; H, 5.85. $\text{C}_{40}\text{H}_{40}\text{O}_{12}$ requires C, 67.4; H, 5.7%); λ_{max} 340 nm (ϵ 8 352); δ 1.4 (3 H, s), 1.54 (3 H, s), 1.73 (3 H, s), 1.90 (3 H, s), 1.9—2.5 (3 H, m), 2.73 (1 H, br d, J 7 Hz), 3.5 (3 H, s), 3.6—3.8 (15 H, 3 lines, OMe and hidden 1 H), 4.09 (1 H, t, J ca. 1 Hz), 5.65 (1 H, br d, J 6 Hz), 5.92 (1 H, br d, J 6 Hz), 6.05 (1 H, d, J 7 Hz), and 6.3 (1 H, d, J 7 Hz). This adduct is presumably related in structure to the adducts (7) derived by addition of two molecules of dmad to one indene moiety. The reaction of (4a) and (4b) with dmad was not investigated; reaction of (1) with dmad at 100 °C gave an intractable mixture.

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REFERENCES

- W. Kemp and J. Spanswick, *J. Chem. Soc. (C)*, 1967, 1456.
- L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1969, p. 289.

³ J. B. Grutgner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

⁴ C. F. Huebner, P. L. Strachan, E. M. Donoghue, N. Cahoon, L. Dorfman, R. Margerison, and E. Wenkert, *J. Org. Chem.*, 1967, **32**, 1126.

⁵ K. Alder, F. Pascher, and H. Vagt, *Ber.*, 1942, **75B**, 1501; G. A. Sim, P. Strachan, and C. F. Huebner, *Chem. and Ind. (London)*, 1964, 1581.

⁶ D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1977, 1313.