# 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'-tetra-methyl-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 reported ${ }^{1}$ that the bi-indene (1) reacts with two molecules of dimethyl acetylenedicarboxylate (dmad) $\left(20{ }^{\circ} \mathrm{C} ; 20 \mathrm{~d}\right)$ to give a yellow ( $\lambda_{\text {max }} 436 \mathrm{~nm}$ ) 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 $\mathrm{H}_{\mathrm{a}}, \mathrm{H}_{\mathrm{b}}$, and $\mathrm{H}_{\mathrm{c}}$ appear respectively at $\delta 4.17(\mathrm{t}, J 1.6 \mathrm{~Hz}), 2.71$ (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 $\delta 4.17$, and $\mathrm{H}_{3}$ would not be expected to couple with $\mathrm{H}_{\mathrm{c}}$. Excluding dramatic homo-conjugative effects the triene chromophore in (2) would show $\lambda_{\max }$. $c a .313 \mathrm{~nm}$ (Woodward's rules) rather than the observed value of 436 nm . Moreover it was suggested ${ }^{1}$ 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 $\mathrm{C}(4 \mathrm{a})$ and $C\left(4 a^{\prime}\right)$ and concomitant hydrogen shifts from C(1) to C(3) and from $\mathrm{C}\left(1^{\prime}\right)$ to $\mathrm{C}(3)$ appears unusual. The reported data are more consistent with structure ( 4 a or b) for the adduct which would then be simply derived by DielsAlder addition of dmad to each indene moiety in (1). In (4a or b), $\mathrm{H}_{\mathrm{a}}$ ( $\delta 4.17$ ) would be expected to couple with both $\mathrm{H}_{\mathrm{b}}$ and $\mathrm{H}_{\mathrm{c}}$ with the observed coupling constant (1.6 $\mathrm{Hz}) .^{.}$The long wavelength u.v. absorption of the adduct is also more consistent with structure ( 4 a 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 $6-\mathrm{H}$

(3)

(4a)

(4b)
singlets for the four $\mathrm{C}-\mathrm{Me}$ groups present, the n.m.r. spectrum of compound B shows two C-Me singlets and a broad $6-\mathrm{H}$ singlet for the other two $\mathrm{C}-\mathrm{Me}$ 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), $\mathrm{Me}_{\mathrm{A}}$ and $\mathrm{Me}_{\mathrm{A}}$, have identical environments. In contrast, in the other conformers derived from (4b), $\mathrm{Me}_{\mathrm{A}}$ and $\mathrm{Me}_{\mathrm{A}^{\prime}}$ have different environments. Thus $90^{\circ}$ rotation in the sense shown in (4b) places $\mathrm{Me}_{\mathrm{A}}$ above the endo-face of the bicycloheptadiene unit in the other half of the molecule, and $\mathrm{Me}_{\mathrm{A}}$. over the exo-face of the other bicycloheptadiene unit. The ${ }^{13} \mathrm{C}$ n.m.r. spectrum of compound A also agrees with the revised constitution (4) but not structure (2); $\delta\left(\mathrm{CDCl}_{3}\right.$ relative to $\left.\mathrm{SiMe}_{4}\right)$ $19.37,19.89(\mathrm{CMe}), 51.95(\mathrm{OMe}), 56.37(\mathrm{CH}), 68.72$ (quaternary C), $77.30\left(\mathrm{CDCl}_{3}\right.$ and $\left.\mathrm{CH}_{2}\right), 123.47(=\mathrm{CH})$, 125.55 (=СН), 130.62, 136.53, 143.43, 146.74, 148.69, 159.88 (olefinic C), $165.60,165.86$ p.p.m. ( $\mathrm{C}=\mathrm{O}$ ). In the off-resonance proton-decoupled spectrum these signals have the appropriate multiplicities; structure (2) with three different $=\mathrm{CH}$ units and no methylene group is
therefore ruled out. The $\delta$-value of the $\mathrm{CH}_{2}$ carbon ( 77.30 p.p.m.) is similar to that of C-7 in norbornadiene (75.1 p.p.m.). ${ }^{3}$

(5)

(7)

(6)

(8)

$$
\mathrm{E}=\mathrm{CO}_{2} \mathrm{Me}
$$

Diels-Alder addition of dmad to indene does not stop at the stage of the $1: 1$-adduct $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{R}^{3}=\right.$ $\mathrm{R}^{4}=\mathrm{H}$ ) ; rapid addition of a second molecule of dmad occurs at room temperature, ${ }^{4}$ and as we have observed even at $0-5{ }^{\circ} \mathrm{C}$, to give (6). ${ }^{5}$ For 3 -methylindene the 3-methyl substituent diverts addition of a second molecule of dmad to the cyclohexadiene system to give (7; $\mathrm{R}=\mathrm{H}) .{ }^{4} \quad$ The original authors attributed this result to increased stability of an intermediate biradical (8) when $R=M e$ rather than $R=H$. However it appears equally likely that the methyl substituent sterically inhibits addition to the exocyclic double bond of (5) and that concerted Diels-Alder addition to the six-membered ring diene system occurred because of the reaction temperature $\left(100^{\circ} \mathrm{C}\right)$, and the availability of a second molecule of dienophile. To test this point, equimolar quantities of dmad and 3-methylindene were set aside at $20^{\circ} \mathrm{C}$ for 20 d with exclusion of light. This gave a mixture of the known $2: 1$ adduct $(7 ; \mathrm{R}=\mathrm{H})$ and the $1: 1$ adduct $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{Me}\right.$ ) with the latter predominating. The physical properties of the $1: 1$ adduct agree with the assigned structure (see Experimental section). In particular the long wavelength u.v. absorption ( $\lambda_{\text {max }} 327 \mathrm{~nm}$ ) and the presence of only one olefinic proton resonance below $\delta 6.0$ in the n.m.r. spectrum provide strong evidence for the presence of a conjugated triene system. Thus addition of dmad to a 3 -substituted indene at $20{ }^{\circ} \mathrm{C}$ can be limited to addition of one molecule of the dienophile. Addition of dmad to 3,4,7-trimethylindene was investigated to provide closer precedent for the additions leading to (4a) and (4b). The reaction proceeded cleanly giving the mono-adduct $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{Me}, \mathrm{R}^{3}=\mathrm{R}^{4}=\right.$ H ) in $\mathbf{8 8} \%$ yield. This adduct could be crystallised to analytical purity whereas $\left(5 ; \quad \mathrm{R}^{1}=\mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}\right.$, $\mathrm{R}^{2}=\mathrm{Me}$ ) decomposed on attempted recrystallisation. With 1-phenyltriazoline-3,5-dione (5; $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{Me}$,
$\mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}$ ) gave the adduct (9), and reaction of 3,4,7-trimethylindene with two molecular equivalents of dmad at $100^{\circ} \mathrm{C}$ gave ( $7 ; \mathrm{R}=\mathrm{Me}$ ).

(9)
$E=\mathrm{CO}_{2} \mathrm{Me}$
The stereochemistry of the adduct (6) elucidated by $X$-ray analysis ${ }^{5}$ shows that attack of a second molecule of dmad on the exocyclic double bond of a mono-adduct of type (5) occurs on the side of the methylene bridge, and should therefore be inhibited when $\mathrm{R}^{3}$ is a methyl group. Since preferred attack of dmad on the less hindered face of 1 -methylindene should lead to the antiadduct (5; $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{R}^{4}=\mathrm{H}, \mathrm{R}^{3}=\mathrm{Me}$ ) this monoadduct might also be isolable. Reaction of 1 -methylindene with dmad did indeed give this mono-adduct. Reaction of 1,3 -dimethylindene with dmad gave a $c a .3: 1$ mixture of the anti-adduct (5; $\mathrm{R}^{1}=\mathrm{R}^{4}=\mathrm{H}$, $\mathrm{R}^{2}=\mathrm{R}^{3}=\mathrm{Me}$ ) and the syn-adduct $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{3}=\mathrm{H}\right.$, $\mathrm{R}^{2}=\mathrm{R}^{4}=\mathrm{Me}$ ). Presumably no adduct of the syntype was observed in the addition to 1 -methylindene because the exocyclic double bond lacks the protection afforded by an attached methyl group or a syn-methyl group at the methylene bridge, and consequently adds a further molecule of dmad.

It is remarkable that although dmad adds to indene at or below room temperature, addition of maleic anhydride to indene apparently fails to occur to a noticeable extent except at high temperatures when addition of the dienophile to an isoindene intermediate is observed. ${ }^{5}$

## EXPERIMENTAL

## For general details see ref. 6.

Addition of Dimethyl Acetylenedicarboxylate to 3,4,7-Tri-methylindene.-The indene ( 0.474 g ) and dienophile ( 0.426 g) were set aside in a $\mathrm{N}_{2}$-flushed sealed tube wrapped in aluminium foil ( 21 d ). The yellow crystalline product was chromatographed on silica in benzene-ether ( $95: 5$ ) to give the adduct $\left(5 ; R^{1}=R^{2}=\mathrm{Me}, \mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}\right)(0.79 \mathrm{~g})$, m.p. $81-84{ }^{\circ} \mathrm{C}$ (from light petroleum) (Found: C, 72.05 ; $\mathrm{H}, 6.6 . \quad \mathrm{C}_{18} \mathrm{H}_{20} \mathrm{O}_{4}$ requires $\mathrm{C}, 72.0 ; \mathrm{H}, 6.7 \%$ ); $\nu_{\max } 1706$, 1736 , and $1636 \mathrm{~cm}^{-1}$; $\delta(90 \mathrm{MHz}) 1.86(3 \mathrm{H}, \mathrm{br} \mathrm{s}), 1.94$ $(1 \mathrm{H}, \mathrm{dd}, J 8$ and $c a .2 \mathrm{~Hz}), 2.05(3 \mathrm{H}$, br s), $2.19(3 \mathrm{H}, \mathrm{s})$, $2.58(1 \mathrm{H}, \mathrm{dd}, J 8$ and 2 Hz$), 3.75(6 \mathrm{H}, \mathrm{d}), 3.90(1 \mathrm{H}, \mathrm{t}$, $J c a .2 \mathrm{~Hz}), 5.63(1 \mathrm{H}, \mathrm{brd}, J 7 \mathrm{~Hz})$, and $5.92(1 \mathrm{H}, \mathrm{br} \mathrm{d}$, $J 7 \mathrm{~Hz})$; $\lambda_{\text {max. }}(\mathrm{EtOH}) 325 \mathrm{~nm}(\varepsilon 6562) ; m / e 300.1359$ $\left(M^{+}\right.$requires 300.1361$)$, $268\left([M-\mathrm{MeOH}]^{+}\right)$, $240([M-$ $\mathrm{MeOH}-\mathrm{CO}]^{+}$), 158 (ionised 3,4,7-trimethylindene), and 143 (protonated dmad) (31.5, 49.5, 31.0, 100, and $87.3 \%$ respectively). When $3,4,7$-trimethylindene ( 78 mg ) was heated with dimethyl acetylenedicarboxylate ( 142 mg ) at $100^{\circ} \mathrm{C}(18 \mathrm{~h})$, chromatography on silica in benzene-ether
( $9: 1$ ) yielded the adduct (5; $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{Me}, \mathrm{R}^{3}=\mathrm{R}^{4}=$ H) ( 30 mg ) and the adduct ( 7 ; $\mathrm{R}=\mathrm{Me}$ ) ( 100 mg ), m.p. 130-133 ${ }^{\circ} \mathrm{C}$ (from methylene chloride-light petroleum) (Found: C, 65.1; H, 5.7. $\mathrm{C}_{24} \mathrm{H}_{26} \mathrm{O}_{8}$ requires $\mathrm{C}, 65.15 ; \mathrm{H}$, $5.9 \%)$; $\nu_{\text {max }} 1705,1720$, and $1732 \mathrm{~cm}^{-1} ; \delta 1.67(3 \mathrm{H}, \mathrm{s})$, $1.75(3 \mathrm{H}, \mathrm{s}), 1.90(3 \mathrm{H}, \mathrm{s}), 2.15(1 \mathrm{H}, \mathrm{br} \mathrm{d}, J 7 \mathrm{~Hz})$ (the other part of this AB system is hidden by the preceding signals), 3.5 ( 1 H , br s, $J c a .1 \mathrm{~Hz}$ ), 3.7 ( $12 \mathrm{H}, 2$ lines), 6.02 $(1 \mathrm{H}, \mathrm{d}, J 8 \mathrm{~Hz})$, and $6.25(1 \mathrm{H}, \mathrm{d}, J 8 \mathrm{~Hz})$.

Addition of Adduct $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{Me}, \mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}\right)$ to 1-Phenyltriazoline-2,5-dione. -The adduct (5; $\mathrm{R}^{\mathbf{1}}=$ $\mathrm{R}^{2}=\mathrm{Me}, \mathrm{R}^{3}=\mathrm{R}^{4}=\mathrm{H}$ ) ( 60 mg ) in benzene ( 2 ml ) was treated with l-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 ${ }^{\circ} \mathrm{C}$ (from ethanol) (Found: C, 65.5; H, 5.5; N, 8.65. $\mathrm{C}_{26} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{O}_{6}$ requires $\mathrm{C}, 65.7 ; \mathrm{H}, 5.3 ; \mathrm{N}, 8.8 \%)$; $\nu_{\text {max. }} 1710,1732$, and $1763 \mathrm{~cm}^{-1}$; $\delta(90 \mathrm{MHz}) 2.1(\mathrm{~s}, 3 \mathrm{H}), 2.2(\mathrm{~s}, 3 \mathrm{H}), 2.22(\mathrm{~s}$, $3 \mathrm{H}), 2.1-2.22(2 \mathrm{H}$, hidden multiplet), $3.78(6 \mathrm{H}, 2$ lines and 1 H , concealed), $6.25(1 \mathrm{H}, \mathrm{d}, J 8 \mathrm{~Hz}), 6.33(1 \mathrm{H}, \mathrm{d}$, $J 8 \mathrm{~Hz}$ ), and $7.4(5 \mathrm{H}, \mathrm{br} \mathrm{s})$.

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 $\left(5 ; \mathrm{R}^{1}=\mathrm{R}^{3}=\right.$ $\mathrm{R}^{4}=\mathrm{H}, \quad \mathrm{R}^{2}=\mathrm{Me}$ ) ( 238 mg ) (Found: $M^{+}, 272.1048$. $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{O}_{4}$ requires $M^{+}, 272.1048$ ); $\nu_{\text {max. }} 1715(\mathrm{br}) \mathrm{cm}^{-1}$; $\lambda_{\text {max. }} 327 \mathrm{~nm}(\varepsilon>3417) ; \delta 1.8(1 \mathrm{H}$, dd, $J 6.5$ and $c a .1 .5$ $\mathrm{Hz}), 2.01(3 \mathrm{H}, \mathrm{s}), 2.55(1 \mathrm{H}, \mathrm{dm}, J 6.5 \mathrm{~Hz}), 3.7(6 \mathrm{H}, \mathrm{s})$, $3.95(1 \mathrm{H}, \mathrm{t}, J c a .1 .5 \mathrm{~Hz})$, and $5.8-6.7(4 \mathrm{H}, \mathrm{m}) ; m / e 272$ $\left(M^{+}\right), 240\left([M-\mathrm{MeOH}]^{+}\right), 214,213\left(\left[M-\mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), 212$ ( $\left[M-\mathrm{HCO}_{2} \mathrm{Me}\right]^{+}$), 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; $\mathrm{R}=\mathrm{H}$ ) ${ }^{4}$ ( 160 mg ), m.p. 122-124 ${ }^{\circ} \mathrm{C}$ (from methanol); $\delta 1.86(3 \mathrm{H}, \mathrm{s}$ and concealed $1 \mathrm{H}, \mathrm{dd}$ ), $2.24(1 \mathrm{H}, \mathrm{br}$ d, $J 7 \mathrm{~Hz}), 3.55(1 \mathrm{H}, \mathrm{t}$, $J c a .1 \mathrm{~Hz}$ ), $3.7-3.8$ ( $12 \mathrm{H}, 2$ lines), $4.41(1 \mathrm{H}, \mathrm{dd}, J 6$ and $2 \mathrm{~Hz}), 4.68(1 \mathrm{H}, \mathrm{dd}, J 6$ and 2 Hz$)$, and $6.1-6.7(2 \mathrm{H}, \mathrm{m})$.
(ii) 1-Methylindene ( 260 mg ) and the dienophile ( 284 mg ) were set aside ( 22 d ); chromatography as above gave the adduct (5; $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{R}^{4}=\mathrm{H}, \mathrm{R}^{3}=\mathrm{Me}$ ) ( 35 mg ) (Found: $M^{+}, 272.1045$ ); $\nu_{\text {max }} 1720$ (br) $\mathrm{cm}^{-1} ; \lambda_{\text {max, }} 320 \mathrm{~nm}$ $(\varepsilon>3101) ; \delta 0.6(3 \mathrm{H}, \mathrm{d}, J 6.5 \mathrm{~Hz}), 3.21(1 \mathrm{H}, \mathrm{qm}, J 6.5$ $\mathrm{Hz}), 3.7(6 \mathrm{H}, \mathrm{OMe}), 3.85(1 \mathrm{H}, \mathrm{m})$, and $5.5-6.8(5 \mathrm{H}, \mathrm{m})$; $m / e 272\left(M^{+}\right), 257\left([M-\mathrm{Me}]^{+}\right), 241\left([M-\mathrm{OMe}]^{+}\right), 242$ $\left([M-\mathrm{MeOH}]^{+}\right), 225\left([M-\mathrm{MeOH}-\mathrm{Me}]^{+}\right), 213([M-$ $\left.\left.\mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), \quad 212\left(\left[M-\mathrm{HCO}_{2} \mathrm{Me}\right]^{+}\right), \quad 182 \quad([M-\mathrm{CO}-$ $\left.2 \mathrm{OMe}]^{+}\right), \quad 181\left([M-\mathrm{CO}-2 \mathrm{OMe}-\mathrm{H}]^{+}\right), \quad 154([M-$ $\left.\left.2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), \quad 153\left(\left[M-\mathrm{H}-2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), \quad 152 \quad([M-$ $\left.2 \mathrm{HCO}_{2} \mathrm{Me}\right]^{+}$), 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 $(142 \mathrm{mg})$ were set aside ( 14 d ); chromatography on silica as above gave a ca. $3: 1$ mixture of adducts $\left(5 ; R^{1}=R^{4}=H\right.$, $\mathrm{R}^{2}=\mathrm{R}^{3}=\mathrm{Me}$ ) and (5; $\mathrm{R}^{1}=\mathrm{R}^{3}=\mathrm{H}, \quad \mathrm{R}^{2}=\mathrm{R}^{4}=\mathrm{Me}$ ) ( 100 mg ) (Found: $M^{+}, 286.1193 . \mathrm{C}_{17} \mathrm{H}_{18} \mathrm{O}_{4}$ requires $M^{+}$, $286.1205)$; $\lambda_{\max } 330 \mathrm{~nm}(\varepsilon>3884)$; $\delta$ (anti-isomer) 0.58 $(3 \mathrm{H}, \mathrm{d}, J 6.5 \mathrm{~Hz}), 2.0(3 \mathrm{H}, \mathrm{s}), 3.06(1 \mathrm{H}, \mathrm{qm}, J 6.5 \mathrm{~Hz})$, 3.67 ( $6 \mathrm{H}, \mathrm{OMe}$ ), ca. 3.7 ( 1 H , hidden), and $5.6-6.7(4 \mathrm{H}$, $\mathrm{m})$; $\delta(s y n$-isomer) $1.2(3 \mathrm{H}, \mathrm{d}, J 6.5 \mathrm{~Hz}), 2.0(3 \mathrm{H}, \mathrm{s}), 2.4$ $(1 \mathrm{H}, \mathrm{q}, J 6.5 \mathrm{~Hz})$, ca. $3.7(1 \mathrm{H}$, hidden), $3.67(6 \mathrm{H}, \mathrm{OMe})$,
and 5.6-6.7 (4 H, m); m/e $286\left(M^{+}\right), 271\left([M-\mathrm{Me}]^{+}\right)$, $255\left([M-\mathrm{OMe}]^{+}\right), 254\left([M-\mathrm{MeOH}]^{+}\right), 239([M-\mathrm{Me}-$ $\left.\mathrm{MeOH}]^{+}\right), 227\left(\left[M-\mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), 226\left(\left[M-\mathrm{HCO}_{2} \mathrm{Me}\right]^{+}\right)$, $196 \quad\left(\left[M-\mathrm{CO}_{2} \mathrm{Me}-\mathrm{OMe}\right]^{+}\right), \quad 195 \quad\left(\left[M-\mathrm{CO}_{2} \mathrm{Me}-\right.\right.$ $\left.\mathrm{MeOH}]^{+}\right), \quad 168 \quad\left(\left[M-2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), \quad 167 \quad([M-\mathrm{H}-$ $\left.\left.2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), \quad 166\left(\left[M-2 \mathrm{HCO}_{2} \mathrm{Me}\right]^{+}\right), \quad 153 \quad([M-\mathrm{Me}-$ $\left.\left.2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), 152\left(\left[M-\mathrm{H}-\mathrm{Me}-2 \mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right), 144$ ( $1,3-$ 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, $3^{\prime}$-bi-indene.-The bi-indene ${ }^{1}\left(\begin{array}{ll}0.5 & \mathrm{~g})\end{array}\right.$ and dienophile ( 10 ml ) were stirred in the dark under $\mathrm{N}_{2}(18 \mathrm{~d})$. The yellow precipitate was filtered off and washed with light petroleum to give a solid ( 0.37 g ), m.p. $158-165^{\circ} \mathrm{C}$, purified by crystallisation from methanol to give yellow needles ( 200 mg ), m.p. $164-168{ }^{\circ} \mathrm{C}$ (lit., ${ }^{1}$ m.p. $165-$ $167^{\circ} \mathrm{C}$ ). The i.r., u.v., and n.m.r. spectra of this product agree with the reported data; $m / e 570.2254\left(M^{+}\right.$, $\mathrm{C}_{34} \mathrm{H}_{34} \mathrm{O}_{8}$, requires 570.2253 ), $539\left([M-\mathrm{OMe}]^{+}\right), 538$ $\left([M-\mathrm{MeOH}]^{+}\right), 523,511\left(\left[M-\mathrm{CO}_{2} \mathrm{Me}\right]^{+}\right)$, 506 ( $[M-$ $2 \mathrm{MeOH}]^{+}$), 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 ( $\left[M-2 \mathrm{CCO}_{2} \mathrm{Me}\right]^{+}$), 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 $70{ }^{\circ} \mathrm{C}$ 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. $158-161{ }^{\circ} \mathrm{C}$ (from methanol) (Found: $M^{+}, 570.2260 . \quad \mathrm{C}_{34} \mathrm{H}_{34} \mathrm{O}_{8}$ requires $M^{+}, 570.2253$ ); $\lambda_{\text {max. }} 430(\varepsilon 10585)$ and $390 \mathrm{~nm}(\mathrm{br})$ ( $\varepsilon 9907$ ) ; $\delta 1.3(3 \mathrm{H}, \mathrm{s}), 1.74(3 \mathrm{H}, \mathrm{s}), 1.90(6 \mathrm{H}, \mathrm{br} \mathrm{s}), 2.12$ ( $2 \mathrm{H}, \mathrm{m}$ ), $2.68(2 \mathrm{H}, \mathrm{m}), 3.49(3 \mathrm{H}, \mathrm{s}), 3.7(6 \mathrm{H}, \mathrm{s}), 3.79$ $(3 \mathrm{H}, \mathrm{s}), 4.18(2 \mathrm{H}, \mathrm{m})$, and $5.25-6.2(4 \mathrm{H}, \mathrm{m})$. 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. $148-155{ }^{\circ} \mathrm{C}$ (from methanol) (Found: C, 67.35; H, 5.85. $\quad \mathrm{C}_{40} \mathrm{H}_{40} \mathrm{O}_{12}$ requires $\left.\mathrm{C}, 67.4 ; \mathrm{H}, 5.7 \%\right) ; \lambda_{\text {max. }} 340 \mathrm{~nm}$ ( $\varepsilon 8352$ ) ; $\delta 1.4(3 \mathrm{H}, \mathrm{s}), 1.54(3 \mathrm{H}, \mathrm{s}), 1.73(3 \mathrm{H}$, s), 1.90 $(3 \mathrm{H}, \mathrm{s}), 1.9-2.5(3 \mathrm{H}, \mathrm{m}), 2.73(1 \mathrm{H}, \mathrm{br} \mathrm{d}, J 7 \mathrm{~Hz}), 3.5$ $(3 \mathrm{H}, \mathrm{s}, 3.6-3.8(15 \mathrm{H}, 3$ lines, OMe and hidden 1 H$), 4.09$ $(1 \mathrm{H}, \mathrm{t}, J c a .1 \mathrm{~Hz}), 5.65(1 \mathrm{H}$, br d, $J 6 \mathrm{~Hz}), 5.92(1 \mathrm{H}, \mathrm{br} \mathrm{d}$, $J 6 \mathrm{~Hz}), 6.05(1 \mathrm{H}, \mathrm{d}, J 7 \mathrm{~Hz})$, and $6.3(1 \mathrm{H}, \mathrm{d}, J 7 \mathrm{~Hz})$. 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 $100^{\circ} \mathrm{C}$ gave an intractable mixture
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