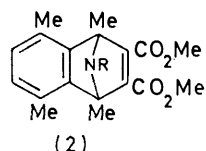
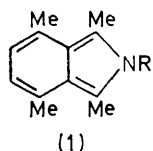


## Reactions of Some Isoindoles with Acetylenic Esters

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*N*-*n*-Butyl- and *N*-ethyl-isoindole react with dimethyl acetylenedicarboxylate to give rearranged 1:2 adducts, whereas with ethyl propiolate diethyl 3,3'-oxydiacrylate is obtained. Several 1,2,3,4,7-pentasubstituted isoindoles give 1:1 adducts with dimethyl acetylenedicarboxylate, and their failure to form 1:2 adducts is ascribed to steric effects.

DIELS-ALDER adducts have been obtained from a number of isoindoles and maleic anhydride;<sup>1,2</sup> some of them are formed reversibly.<sup>2,3</sup> Treatment of 1-benzyl-2-methyl- and 1-phenyl-isoindole with maleic anhydride gives Michael adducts instead, by substitution at the 3-position.<sup>3,4</sup> 1,3-Diphenylisoindole gives the expected Diels-Alder adduct<sup>5</sup> with diethyl acetylenedicarboxylate, and the analogous adducts (2a and b) from isoindoles (1a and b) are the only other examples of this type hitherto described.<sup>2</sup> The reaction of *N*-methylisoindole with dimethyl acetylenedicarboxylate (DMAC) appears to be exceptional in giving an oily 2:1 adduct.<sup>6</sup>

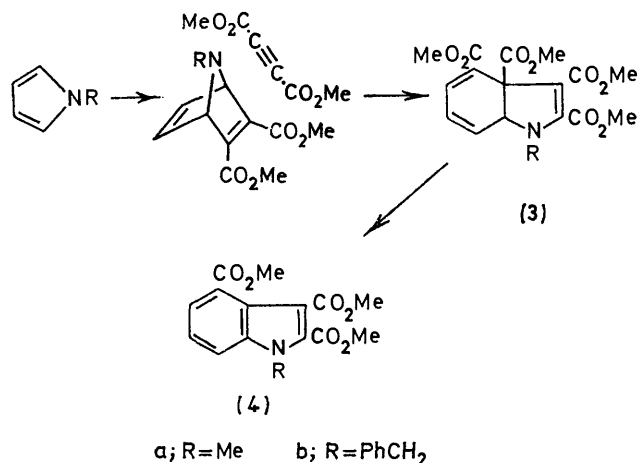


a; R=H    b; R=PhCH<sub>2</sub>    c; R=Me    d; R=Ph

The 1:1 adduct (2a) reacts further with DMAC in refluxing benzene, giving a 1:2 adduct, to which a structure was assigned<sup>2</sup> by analogy with those of the dihydroindoles (3a and b) obtained from *N*-methyl- and *N*-benzyl-pyrrole and the acetylenic ester.<sup>7</sup> In the latter case the stepwise nature of the addition (Scheme) had not been proved, but the structure of the 1:2 adducts (3a and b) was established by aromatisation to the corresponding indoletricarboxylic esters (4a and b), and in the case of adduct (3a) by further reaction with DMAC to give trimethyl *N*-methylpyrrole-2,3,4-tricarboxylate and benzene-1,2,3-tricarboxylate.<sup>7</sup> Our intention to confirm the proposed mechanism of addition of DMAC by examining reactions of some isoindoles with acetylenic esters was partly anticipated by publication of work<sup>2</sup> relating to the isoindole (1a). We now describe addition reactions of some other isoindoles, as well as the preparation of some new 1,3-diarylisindoles.

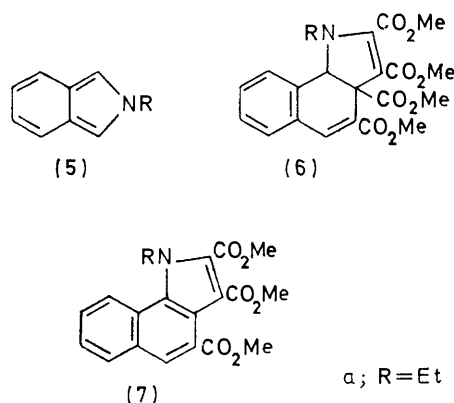
*N*-Ethyl- and *N*-*n*-butyl-isoindole (5a and b) reacted exothermically with DMAC to give directly the corresponding 1:2 adducts (6a and b). Even at 0° no intermediate 1:1 adduct was isolable. In the n.m.r. spectra of both adducts (6a and b) the bridgehead hydrogen atom absorbed as a singlet ( $\tau$  4.81). Other n.m.r. absorptions, as well as i.r. and mass spectra and elemental

composition, are in accord with the assignment of structures (6a and b). *N*-Ethylphthalimide, which was isolated after prolonged interaction of (5a) and DMAC, is believed to have arisen by autoxidation of unchanged



SCHEME

isoindole (5a); the analogous autoxidation of *N*-*n*-butylisoindole (5b) to *N*-*n*-butylphthalimide and other products has been described elsewhere.<sup>8</sup>



The *N*-ethylisoindole adduct (6a) on treatment with bromine in chloroform was incompletely converted, by

<sup>1</sup> J. D. White and M. E. Mann, *Adv. Heterocyclic Chem.*, 1969, **10**, 113, and references cited therein.

<sup>2</sup> C. O. Bender, R. Bonnett, and R. G. Smith, *J. Chem. Soc. (C)*, 1970, 1251.

<sup>3</sup> D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.*, 1964, **86**, 4152.

<sup>4</sup> G. Wittig and H. Streib, *Annalen*, 1953, **584**, 1.

<sup>5</sup> J. C. Emmett and W. Lwowski, *Tetrahedron*, 1966, **22**, 1011.

<sup>6</sup> G. Wittig and H. Ludwig, *Annalen*, 1955, **589**, 55.

<sup>7</sup> R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1962, 1148.

<sup>8</sup> J. K. Kochi and E. A. Singleton, *Tetrahedron*, 1968, **24**, 4649.



groups is very large (e.g. phenyl), the resulting 1:2 adduct would be severely strained. Insofar as this strain is reflected in the transition state for addition of DMAC to structure (2) or (12), the failure to form adducts in these cases compared with the easy formation of adducts (6a and b) and the similar 1:2 adduct from isoindole (1a) is understandable. However, under more forcing conditions adducts (2c) and (12a and b) reacted further with DMAC in a different sense to give deaminated products:<sup>14</sup> results of this work will be the subject of a subsequent paper.

#### EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene. <sup>1</sup>H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Low resolution mass spectra were recorded with an A.E.I. MS 12 instrument operating at 70 eV, with a direct insertion probe and with facility for rapid scanning of g.l.c. peaks. High resolution mass spectra were obtained through the Physico-Chemical Measurements Unit, Aldermaston. G.l.c. analyses were performed on a column (1.6 m × 4 mm) containing silicone gum rubber SE 30 as stationary phase. Alumina for chromatography was Laporte type H, in some cases deactivated prior to use by being intimately mixed with 10% w/w of aqueous 5% acetic acid. Light petroleum was the fraction of b.p. 60–80°, unless otherwise stated.

1,2-Dibenzoylthane was obtained by reduction of 1,2-dibenzoyl ethylene with zinc and acetic acid; satisfactory results were achieved only if the zinc dust was cleaned and activated as recommended by Tsuda.<sup>15</sup> 1-Methyl-2,5-diphenylpyrrole (65%), m.p. 206–207° (lit.,<sup>16</sup> 204°), was prepared by heating 1,2-dibenzoyl ethane with methylamine in refluxing acetic acid. 1-Ethyl-2,5-diphenylpyrrole (37%), m.p. 83–85° (lit.,<sup>16</sup> 88–89°), 1-benzyl-2,5-diphenylpyrrole (62%), m.p. 142–144° (lit.,<sup>17</sup> 142°), and 1,2,5-triphenylpyrrole (66%), m.p. 239–240° (lit.,<sup>18</sup> 228–229°), were similarly prepared from 1,2-dibenzoyl ethane with ethylamine, benzylamine, and aniline, respectively. This simple procedure is based on one described elsewhere for the preparation of 2,5-diphenylpyrrole<sup>19</sup> and other 1,2,5-trisubstituted pyrroles;<sup>20</sup> for its convenience and generally high yields this synthesis of *N*-substituted 2,5-diphenylpyrroles is preferable to other methods (e.g. refs. 16 and 18).

*Preparation of Isoindoles.*—2-Ethyl- and 2-*n*-butylisoindoles (5a and b) were prepared via the corresponding isoindolines and their *N*-oxides.<sup>21</sup> 1,2,3,4,7-Pentamethylisoindole (1c) resulted from the condensation of hexane-2,5-dione with methylamine as described;<sup>13</sup> isoindoles (1b and d) were prepared by the method of Bender and Bonnett<sup>13</sup> from hexane-2,5-dione and the appropriate 1,2,5-trisubstituted pyrroles.<sup>20</sup> Attempted condensation of hexane-2,5-dione with 1,2,5-triphenylpyrrole in refluxing aqueous acetic acid (cf. ref. 13) was unsuccessful for formation of 4,7-dimethyl-1,2,3-triphenylisoindole (11d). Instead the

isoindoles (11a–d) were prepared following Fletcher's procedure for 4,7-dimethyl-1,3-diphenylisoindole<sup>11</sup> by the acid-catalysed condensation of hexane-2,5-dione with the appropriate 1,2,5-trisubstituted pyrroles in refluxing toluene, using a Dean–Stark trap for separation of water. 2,4,7-Trimethyl-1,3-diphenylisoindole (11a) (38%) was thereby obtained as needles, m.p. 214–215° (from ethanol–benzene) (lit.,<sup>12</sup> 210–213°), (Found: C, 88.8; H, 6.9; N, 4.4. Calc. for C<sub>23</sub>H<sub>21</sub>N: C, 88.7; H, 6.8; N, 4.5%).  $\tau$  2.53 (10H, s, ArH), 3.42 (2H, s, 5- and 6-H), 6.63 (3H, s, NMe), and 7.99 (6H, s, ArMe), *m/e* 311 (*M*<sup>+</sup>, 100%), 145 (49), 100 (56), and 99 (67). 2-Ethyl-4,7-dimethyl-1,3-diphenylisoindole (11b) (22%) formed pale yellow needles, m.p. 143–144° (from ethanol–benzene) (Found: C, 88.3; H, 7.0; N, 4.4. C<sub>24</sub>H<sub>23</sub>N requires C, 88.6; H, 7.1; N, 4.3%).  $\nu_{\max}$  1600, 1120, 1040, 830, 820, 760, and 710 cm<sup>-1</sup>,  $\tau$  2.3–2.8 (10 H, m, ArH), 3.39 (2H, s, 5- and 6-H), 6.08 (2H, q, *J* 7 Hz, N·CH<sub>2</sub>), 7.97 (6H, s, ArMe), and 9.08 (3H, t, CH<sub>3</sub>·CH<sub>2</sub>), *m/e* 325 (*M*<sup>+</sup>, 100%), 91 (25), and 78 (37). 2-Benzyl-4,7-dimethyl-1,3-diphenylisoindole (11c) (37%) was obtained as needles, m.p. 177–178° (from ethanol–benzene) (Found: C, 89.9; H, 6.6; N, 3.5. C<sub>29</sub>H<sub>25</sub>N requires C, 89.9; H, 6.5; N, 3.6%).  $\nu_{\max}$  1600, 1500, 815, 765, and 705 cm<sup>-1</sup>,  $\tau$  2.6–3.0 (15H, m, ArH), 3.41 (2H, s, 5- and 6-H), 4.95 (2H, s, N·CH<sub>2</sub>), and 8.00 (6H, s, ArMe), *m/e* 387 (*M*<sup>+</sup>, 68%), 296 (*M* – PhCH<sub>2</sub>, 100), 294 (36), 291 (86), 280 (32), and 91 (PhCH<sub>2</sub><sup>+</sup>, 54) *m*<sup>\*</sup> 226 (387 → 296). 4,7-Dimethyl-1,2,3-triphenylisoindole (11d) (47%) was similarly obtained as pale yellow needles, m.p. 212–213° (from benzene) (Found: C, 89.6; H, 6.2; N, 3.6. C<sub>28</sub>H<sub>23</sub>N requires C, 90.0; H, 6.2; N, 3.8%).  $\nu_{\max}$  1603, 1510, 835, 750, and 705 cm<sup>-1</sup>,  $\tau$  2.5–3.1 (15H, m, ArH), 3.41 (2H, s, 5- and 6-H), and 7.94 (6H, s, ArMe), *m/e* 373 (*M*<sup>+</sup>, 100%).

1:2 Adducts of the Isoindoles (5a and b) with Dimethyl Acetylenedicarboxylate.—The acetylenic ester (10 g) was added dropwise during 1 h to 2-ethylisoindole (5a) (6.0 g) in carbon tetrachloride (10 ml), under nitrogen, cooled in ice-water. The mixture was set aside at room temperature for 3 weeks, and then divided into two equal parts. One half of the brown tar was extracted with hot benzene, and the extract was filtered and cooled to yield tetramethyl 1-ethyl-3a,9b-dihydro-1H-benz[*g*]indole-2,3,3a,4-tetracarboxylate (6a) (2.0 g, 23% based on all the isoindole used) as prisms, m.p. 181–182° (from benzene) (Found: C, 61.3; H, 5.6; N, 3.2. C<sub>22</sub>H<sub>23</sub>NO<sub>8</sub> requires C, 61.5; H, 5.4; N, 3.3%).  $\nu_{\max}$  1721s and 1718s (C=O stretch), 1619, 1260br (C–O stretch), 1140s, 1083, 1062, 950, and 795 cm<sup>-1</sup> (Ar–H bend),  $\tau$  2.5–2.8 (5H, m, ArH and 5-H), 4.81 (1H, s, CH), 6.13 (3H, s, OMe), 6.26 (3H, s, OMe), 6.30 (6H, s, OMe), 7.15 (2H, q, *J* 7 Hz, N·CH<sub>2</sub>), and 8.99 (3H, t, CH<sub>3</sub>·CH<sub>2</sub>), *m/e* 429 (*M*<sup>+</sup>, 7%), 398 (*M* – OMe, 4), 339 (22), 338 (100), 311 (6), 278 (8), and 208 (6), *m*<sup>\*</sup> 287 (398 → 338), 266 (429 → 338), and 229 (338 → 278). Two months later the second half of the tarry reaction mixture was chromatographed on a column of deactivated alumina, from which mixtures of light petroleum–benzene eluted *N*-ethylphthalimide (0.6 g), m.p. 77–78° (lit.,<sup>22</sup> 78–79°), (Found: C, 68.5; H, 5.2; N, 7.7. Calc.

<sup>14</sup> Preliminary communication, L. J. Kricka and J. M. Vernon, *Chem. Comm.*, 1971, 942.

<sup>15</sup> K. Tsuda, *J. Org. Chem.*, 1963, **28**, 783.

<sup>16</sup> K. E. Schulte, J. Reisch, and H. Walker, *Chem. Ber.*, 1965, **98**, 98.

<sup>17</sup> V. Spiro and I. Fabra, *Ann. Chim. (Italy)*, 1956, **46**, 263.

<sup>18</sup> P. L. Southwick, D. I. Sapper, and L. A. Pursglove, *J. Amer. Chem. Soc.*, 1950, **72**, 4940.

<sup>19</sup> J. M. Tedder and B. Webster, *J. Chem. Soc.*, 1960, 3270.

<sup>20</sup> S. J. Hazlewood, G. K. Hughes, F. Lions, K. J. Baldick, J. W. Cornforth, J. N. Graves, J. J. Maunsell, T. Wilkinson, A. J. Birch, R. H. Harradence, S. S. Gilchrist, F. H. Monaghan, and L. E. A. Wright, *J. Proc. Roy. Soc. New South Wales*, 1937, **71**, 92 (*Chem. Abs.*, 1938, **32**, 1695).

<sup>21</sup> J. Thesing, W. Schäfer, and D. Melchior, *Annalen*, 1964, **671**, 119.

<sup>22</sup> G. Vanags, *Acta Univ. Latviensis, Kim. Fakultat*, 1939, [4], 405 (*Chem. Abs.*, 1940, **34**, 1982<sup>b</sup>).

for  $C_{10}H_9NO_2$ : C, 68.5; H, 5.2; N, 8.0%),  $\nu_{\max}$ . 1760 and 1710 (C=O stretch), 1610, 1400, 1200, 1180, 1085, 1038, 900, 880, and 720s  $cm^{-1}$ ,  $\tau$  2.0–2.3 (4H, m, ArH), 6.23 (2H, q,  $J$  8 Hz, N-CH<sub>2</sub>), and 8.73 (3H, t, CH<sub>3</sub>·CH<sub>2</sub>).

Dimethyl acetylenedicarboxylate (2.0 g) was added dropwise to 2-*n*-butylisindole (5b) (2.0 g) in chloroform (10 ml) under nitrogen, cooled in ice-water. The mixture was left at room temperature for 17 days; it was then evaporated and the residue was redissolved in benzene and chromatographed on deactivated alumina (300 g). Elution with light petroleum-benzene gave first brown oils which were discarded, then the adduct (6b) (1.0 g), m.p. 118–119° [from light petroleum (b.p. 40–60°)-ether] (Found: C, 62.7; H, 6.0; N, 2.9.  $C_{24}H_{27}NO_8$  requires C, 63.0; H, 6.0; N, 3.1%),  $\nu_{\max}$ . 1720br (C=O stretch), 1605, 1320br, 1250br (C–O stretch), 1155s, 1070, 943, and 785  $cm^{-1}$  (Ar–H bend),  $\tau$  2.34 (1H, s, vinylic 5-H), 2.67 (4H, s, ArH), 4.83 (1H, s, CH), 6.14 (3H, s, OMe), 6.26 (3H, s, OMe), 6.32 (6H, s, OMe), 7.15br (2H, N-CH<sub>2</sub>), and 8.6–9.3 (7H, Pr<sup>n</sup>),  $m/e$  457 ( $M^+$ , 7%), 426 ( $M$  – OMe, 4), 367 (24), 366 (100), 278 (13), and 208 (5),  $m^*$  314 (426 → 366), 293 (457 → 366), and 211 (366 → 278). Further elution of the column with benzene and ether gave brown oils, which were combined and rechromatographed to give a further quantity of the adduct (6b) (0.8 g; total yield (33%).

*Aromatisation of the 1:2 Adduct (6a).*—A solution of bromine (0.2 g) in chloroform (5 ml) was added dropwise to the adduct (6a) (1.0 g) dissolved in chloroform (12 ml). After 3 days the mixture was evaporated to a yellow oil, which was chromatographed on silica gel. Elution with ether and ether-chloroform (1:1 v/v) afforded trimethyl 1-ethyl-1H-benz[*g*]indole-2,3,4-tricarboxylate (7a) (0.3 g, 35%), m.p. 121–123° (from light petroleum-benzene) [Found: C, 63.1; H, 5.2; N, 3.7%;  $M^+$  (mass spectrum), 369.12,  $C_{20}H_{19}NO_6$  requires C, 65.1; H, 5.2; N, 3.8%);  $M$ , 369.1212. The unsatisfactory microanalytical value for carbon is due to persistent contamination of this product with the starting material (6a) (peak at  $m/e$  429 in the mass spectrum). Repeated treatment of the product with bromine rechromatography, and recrystallisation failed to give a sample of (7a) analytically pure],  $\tau$  1.4–2.5 (5H, m, ArH), 5.13 (2H, m, N-CH<sub>2</sub>), 5.99 (3H, s, OMe), 6.05 (6H, s, OMe), and 8.35 (3H, m, CH<sub>2</sub>·CH<sub>3</sub>)  $m/e$  370 (15%), 369 ( $M^+$ , 64), 339 (20), 338 ( $M$  – OMe, 100), 278 (34), 117 (46), 116 (51), 115 (59), 93 (46), and 91 (56).

*Reaction of the 1:2 Adduct (6b) with Bromine.*—An excess of bromine was added to a solution of the adduct (6b) (0.4 g) in chloroform, and the mixture was left in the dark for 5 days. Unused bromine was removed by shaking with aqueous sodium hydrogen sulphite, and the chloroform layer was separated, dried (MgSO<sub>4</sub>), and evaporated to a yellow oil which was chromatographed on deactivated alumina. Light petroleum-benzene (7:3 v/v) eluted a product (30 mg), m.p. 162–163° which is provisionally identified as trimethyl 1-*n*-butyl-6,9(?)-dibromo-1H-benz[*g*]indole-2,3,4-tricarboxylate [Found:  $M^+$ , 552.9741 (mass spectrum).  $C_{22}H_{21}Br_2NO_6$  requires  $M$ , 552.9737],  $m/e$  557, 555, and 553 ( $M^+$ , 56, 100, and 51%), 526, 524, and 522 ( $M$  – OMe, 9, 23, and 9), 438, 436, and 434 (11, 23, and 11), and 366 (28). The n.m.r. spectrum was poorly resolved except for three lines of equal intensity,  $\tau$  5.67, 5.74, and 5.81 (3 × OMe).

*Reactions with Ethyl Propiolate.*—The isoindole (5a) (1.7 g) and ethyl propiolate (2.5 g) in chloroform (10 ml) were stirred at room temperature for 9 days. The solvent was

evaporated off, and the residue was dissolved in chloroform-benzene and chromatographed on deactivated alumina (200 g). Elution with light petroleum-benzene (9:1 v/v) afforded diethyl trans,trans-3,3'-oxydiacrylate (9a) (1.5 g, 56%), m.p. 110–111° (from benzene) (Found: C, 56.1; H, 6.6.  $C_{10}H_{14}O_5$  requires C, 56.1; H, 6.6%),  $\nu_{\max}$ . 1710, 1695 and 1660 (C=O stretch), 1610br, 1339s, 1205, 1150br (C–O stretch), 980s (trans-CH=CH), 862s, and 743s  $cm^{-1}$ ,  $\tau$  2.30 (2H) and 4.30 (2H, two d,  $J$  12 Hz, trans-CH=CH), 5.75 (4H, q,  $J$  7 Hz, O-CH<sub>2</sub>), and 8.70 (6H, t, CH<sub>3</sub>·CH<sub>2</sub>),  $m/e$  214 ( $M^+$ , 39%), 169 ( $M$  – OEt, 50), 144 ( $M$  – C<sub>3</sub>H<sub>2</sub>O<sub>2</sub>, 28), 141 ( $M$  – CO<sub>2</sub>Et, 22), 140 (11), 139 (17), 101 (12), 99 (41), 97 (45), and 71 (100),  $m^*$  133 (214 → 169), 97 (214 → 144), 93 (169 → 141), and 55 (169 → 97).

The isoindole (5b) (2.0 g) and ethyl propiolate (2.0 g) in chloroform (10 ml) were left at room temperature for 3 months. Evaporation and column chromatography as before afforded the same diester (9a) (0.5 g, 23%), m.p. and mixed m.p. 109–110°.

Ethyl propiolate (1.0 ml) was added to triethylamine (1.0 ml) containing water (0.2 ml). A violent, exothermic reaction occurred and the mixture darkened. After 4 days the mixture was dissolved in chloroform, and this solution was washed repeatedly with water and dried (MgSO<sub>4</sub>). Evaporation gave a brown oil containing the diester (9a), which was identified by comparison of g.l.c. retention time and g.l.c.-mass spectrum with those of authentic material. The g.l.c.-mass spectrum of another volatile component of the brown oil was consistent with its being a mixture of ethyl β-diethylaminoacrylate [ $m/e$  171 ( $M^+$ ), 142 ( $M$  – Et), 126 ( $M$  – OEt), and 98 ( $M$  – CO<sub>2</sub>Et)] and diethyl but-1-en-3-yne-1,4-dicarboxylate [ $m/e$  196 ( $M^+$ ), 151 ( $M$  – OEt), and 123 ( $M$  – CO<sub>2</sub>Et)].

Ethyl propiolate was added to a stirred suspension of the sodium enolate of ethyl formylacetate<sup>23</sup> in ether, causing a violent, exothermic reaction. Acetic acid (1.7 g) in ether (50 ml) was added; the mixture was stirred for 60 h, then poured into water and extracted with ether. The extract was dried (MgSO<sub>4</sub>) and evaporated to afford triethyl benzene-1,3,5-tricarboxylate (10a) (1.2 g), m.p. 133–135° (lit.<sup>24</sup> 133–134°) (from ethanol),  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>CO] 1.22 (3H, s, ArH), 5.46 (6H, q, O-CH<sub>2</sub>), and 8.60 (9H, t, CH<sub>3</sub>·CH<sub>2</sub>). The reaction was repeated, except that the sequence of addition of ethyl propiolate and acetic acid to the sodium enolate was reversed. Work-up as before again afforded the triester (10a).

*1:1 Adducts of the Isoindoles (1) and (11) with Dimethyl Acetylenedicarboxylate.*—The isoindole (1b) (6.0 g) was added in portions to the acetylenic ester (5.0 g) in carbon tetrachloride (10 ml) at 0°. The mixture was refluxed for 6 h, and then left for 3 weeks. The solid product (0.4 g) was separated; the mother liquor was evaporated and the residual oil was chromatographed on alumina (200 g), from which light petroleum-benzene eluted a further quantity (0.4 g) of the same product. The two batches were combined and recrystallised to give the adduct (2b) (8%), m.p. 107–108° (lit.<sup>2</sup> 110–112°), i.r. and n.m.r. spectra in agreement with those reported,<sup>2</sup>  $m/e$  405 ( $M^+$ , 5%), 346 ( $M$  – CO<sub>2</sub>Me, 5), 263 ( $M$  – DMAC, 26), 241 (16), 172 ( $M$  – DMAC – PhCH<sub>2</sub>, 22), 132 (MeC≡N<sup>+</sup>·CH<sub>2</sub>Ph, 11), and 91 (PhCH<sub>2</sub><sup>+</sup>, 100),  $m^*$  296 (405 → 346) and 112.5 (263 → 172).

<sup>23</sup> W. Wislicenus, *Ber.*, 1887, **20**, 2930.

<sup>24</sup> W. Wislicenus and M. von Wrangrell, *Annalen*, 1911, **381**, 367.

The isoindole (1c) (20.0 g) was added in portions to the acetylenic ester (17.0 g) in carbon tetrachloride (20 ml) with stirring, under nitrogen, and stirring was continued for 5 days. The solvent was evaporated off and the remaining brown tar was extracted with boiling light petroleum. This extract deposited crystals on cooling. The brown tar which remained was redissolved in benzene (5 ml) and chromatographed on alumina (250 g), from which light petroleum-benzene (1:1 v/v) eluted more of the same solid product. The two batches were combined and further recrystallised to give *dimethyl 1,4-dihydro-1,4,5,8,9-pentamethyl-1,4-epiminonaphthalene-2,3-dicarboxylate* (2c) (13.0 g, 30%), m.p. 79° (from light petroleum) (Found: C, 69.4; H, 7.0; N, 4.4.  $C_{19}H_{26}NO_4$  requires C, 69.3; H, 7.0; N, 4.3%),  $\nu_{\max}$  1730s and 1708s (C=O stretch), 1230 (C-O stretch), 1200s, 1039 (benzene ring), 839, and 814  $cm^{-1}$  (Ar-H bend),  $\tau$  3.34 (2H, s, 6- and 7-H), 6.25 (6H, s, OMe), 7.65 (6H, s, ArMe), 7.85 (3H, s, NMe), and 8.12 (6H, s, CMe),  $m/e$  329 ( $M^+$ , 9%), 270 ( $M - CO_2Me$ , 12), 188 (16), 187 ( $M - DMAC$ , 87), 186 (27), and 56 ( $MeC\equiv NMe$ , 100). A subsequent preparation by stirring the same reactants in dimethyl sulphoxide at room temperature [*cf.* preparation of (1a)] gave the adduct (2c) but in reduced yield.

The isoindole (1d) (1.5 g) was added in portions to dimethyl acetylenedicarboxylate (1.0 g) in acetone (8 ml) and light petroleum (b.p. 40–60°; 3 ml) with cooling in ice-water. The solution was warmed on a steam-bath, then left at room temperature for 2 days. The solid product was separated and recrystallised to give the *adduct* (2d) (0.9 g, 36%), m.p. 124° (from light petroleum) (Found: C, 73.6; H, 6.6; N, 3.7.  $C_{24}H_{26}NO_4$  requires C, 73.8; H, 6.4; N, 3.6%),  $\nu_{\max}$  1730s and 1703s (C=O stretch), 1650, 1595, 1494s, 1300br, 1250br (C-O stretch), 1195, 1071s (benzene ring), 1040, 814, and 708  $cm^{-1}$  (Ar-H bend),  $\tau$  2.6–3.1 (5H, m, ArH), 3.30 (2H, s, 6- and 7-H), 6.23 (6H, s, OMe), 7.83 (6H, s, ArMe), and 8.13 (6H, s, CMe),  $m/e$  391 ( $M^+$ , 6%), 332 ( $M - CO_2Me$ , 3), 250 (8), 249 ( $M - DMAC$ , 39), 248 (8), 119 (9), 118 ( $MeC\equiv NPh$ , 100), and 77 (21),  $m^*$  50 (118  $\rightarrow$  77).

The isoindole (11a) (1.5 g) and dimethyl acetylenedicarboxylate (4 ml) in ether (10 ml) were stirred at room temperature for 5 days. The resulting solid was collected, washed with light petroleum, and recrystallised to give the *adduct* (12a) (2.0 g, 90%) as needles, m.p. 157–158° [from light petroleum (b.p. 40–60°)-benzene (1:1 v/v)] (Found: C, 76.4; H, 6.1; N, 3.4.  $C_{29}H_{27}NO_4$  requires C, 76.8; H, 6.0; N, 3.1%),  $\nu_{\max}$  1740 (C=O stretch), 1618, 1280br, 1250br

(C-O stretch), 1160, 1003 (benzene ring), 820, 765, and 715  $cm^{-1}$  (Ar-H bend),  $\tau$  2.63 (10H, s, ArH), 3.33 (2H, s, 6- and 7-H), 6.30 (6H, s, OMe), 8.20 (6H, s, ArMe), and 8.41 (3H, s, NMe),  $m/e$  454 (24%), 453 ( $M^+$ , 41), 395 ( $M - CO_2Me$ , 11), 394 (35), 312 (9), 311 ( $M - DMAC$ , 41), 293 (12), 143 (12), 118 ( $PhC\equiv NMe$ , 100), 77 (15), and 69 (18).

The same procedure with the isoindoles (11b–d) gave the following 1:1 adducts: *dimethyl 9-ethyl-1,4-dihydro-5,8-dimethyl-1,4-diphenyl-1,4-epiminonaphthalene-2,3-dicarboxylate* (12b) (41%), m.p. 176–177° (from benzene) (Found: C, 77.1; H, 6.3; N, 3.0.  $C_{30}H_{29}NO_4$  requires C, 77.1; H, 6.3; N, 3.0%),  $\nu_{\max}$  1740s and 1720s (C=O stretch), 1290br, 1245br (C-O stretch), 1138, 819w, 775, and 720  $cm^{-1}$  (Ar-H bend),  $\tau$  2.3–2.7 (10H, m, ArH), 3.30 (2H, s, 6- and 7-H), 6.27 (6H, s, OMe), 7.71 (2H, q,  $J$  7 Hz,  $N\cdot CH_2$ ), 8.20 (6H, s, ArMe), and 9.99 (3H, t,  $CH_3\cdot CH_2$ ),  $m/e$  467 ( $M^+$ , 27%), 325 ( $M - DMAC$ , 39), 298 (19), 248 (11), 247 (73), 220 (19), 219 (100), 218 (13), 217 (23), 216 (12), 191 (15), 165 (10), 132 ( $PhC\equiv NEt$ , 89), 115 (39), 111 (19), 105 (31), 104 (62), and 77 (39); *dimethyl 9-benzyl-1,4-dihydro-5,8-dimethyl-1,4-diphenyl-1,4-epiminonaphthalene-2,3-dicarboxylate* (12c) (82%), m.p. 205–206° (from benzene) (Found: C, 79.4; H, 6.1; N, 2.9.  $C_{35}H_{31}NO_4$  requires C, 79.4; H, 5.9; N, 2.6%),  $\nu_{\max}$  1720s and 1703s (C=O stretch), 1605, 1503, 1440, 1280 (C-O stretch), 820w, 765s, and 705  $cm^{-1}$  (Ar-H bend),  $\tau$  2.5–2.9 (15H, m, ArH), 3.23 (2H, s, 6- and 7-H), 6.20 (6H, s, OMe), 6.58 (2H, s,  $N\cdot CH_2$ ), and 8.18 (6H, s, ArMe),  $m/e$  529 ( $M^+$ , 14%), 470 ( $M - CO_2Me$ , 22), 387 ( $M - DMAC$ , 26), 296 (30), 194, ( $PhC\equiv N\cdot CH_2Ph$ , 9), and 91 ( $PhCH_2^+$ , 100),  $m^*$  420 (529  $\rightarrow$  470) and 226 (387  $\rightarrow$  296); *dimethyl 1,4-dihydro-5,8-dimethyl-1,4,9-triphenyl-1,4-epiminonaphthalene-2,3-dicarboxylate* (12d) (68%), m.p. 217–218° (from benzene) (Found: C, 78.9; H, 5.7; N, 2.8.  $C_{34}H_{29}NO_4$  requires C, 79.2; H, 5.7; N, 2.7%),  $\nu_{\max}$  1732s, and 1703s (C=O stretch), 1600br, 1482s, 1453s, 1414s, 1290, 1250 (C-O stretch), 1233s, 1135s, 833s, 755s, 723s, and 713  $cm^{-1}$  (Ar-H bend),  $\tau$  2.4–2.9 (15H, m, ArH), 3.22 (2H, s, 6- and 7-H), 6.20 (6H, s, OMe), and 8.13 (6H, s, ArMe),  $m/e$  515 ( $M^+$ , 15%), 456 ( $M - CO_2Me$ , 16), 373 ( $M - DMAC$ , 24), 295 (11), 181 (12), 180 ( $PhC\equiv NPh$ , 100), and 77 (19),  $m^*$  406 (515  $\rightarrow$  456). Crystals of this adduct (12d) developed a purple colouration on exposure to light.

We thank the S.R.C. for a Studentship (to L. J. K.) and Dr. C. B. Thomas for discussion of mass spectra.

[1/1711 Received, 20th September, 1971]