Reaction of 3-Methylindole and 2,3-Dimethylindole with Dimethyl Acetylenedicarboxylate Using Boron Trifluoride-Diethyl Ether Catalysis

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Reactions of dimethyl acetylenedicarboxylate with 3-methylindole and 2,3-dimethylindole under boron trifluoride-diethyl ether catalysis were carried out at low temperature (0-25°). Thermally unstable cyclobutenes were isolated, mainly in apolar solvents, which isomerized to benzazepines. The other compounds isolated were Michael adducts and dihydro-2-oxocarbazoles.

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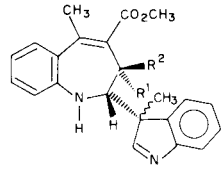
The products obtainable from the reaction of indoles and dimethyl acetylenedicarboxylate (DMAD) depend greatly on the conditions of the reaction and have been investigated extensively by Acheson [1]. Treatment of indole with DMAD gives many products arising either from initial electrophilic attack at the 3-position to give maleate or fumarate [2], or from cyclisation to a cyclobutene intermediate followed by ring opening to a benzazepine [3] and subsequent reactions. As indicated in a preliminary report [4], from the reaction of 1,2,3-trimethylindole and 1,3-dimethylindole with DMAD using boron trifluoride-diethyl ether (BTE) catalysis we have isolated, for the first time, cyclobutenes in good yields under thermal conditions. In order to obtain more information concerning the structural features, reactivity and mechanism we have now extended the study of this reaction to 3-methylindole and 2,3-dimethylindole.

Results and Discussion.

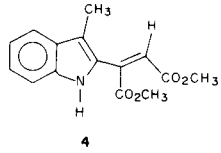
The reaction of 3-methylindole (skatole) with DMAD in benzene with BTE at 0-4° for 19 hours gave four compounds. Three are 2:1 adducts (skatole:DMAD). The ^{1}H nmr of the first showed only one NH proton. The 5-methyl doublet at δ 2.08 with J = 1 Hz is due the homoallylic coupling [5] since it was simplified by double irradiation of the double quartet (J = 8 and 1 Hz) at 4.28. The ir spectrum gave absorptions at 3420 (NH), 1745 (CO) and 1665 cm^{-1} (C=N). These data are consistent with **1**. The second compound was the epimer **2** with the protons at C-2 and C-3 at δ 4.28 and 3.38, respectively, with J = 12 Hz. These two substances were eluted together from the column and isolated by preparative thick layer chromatography. The yield was 21% for **1** and 10% for **2**. When this mixture was left 24 hours in a dichloromethane solution, the ^{1}H nmr gave a 1:1 proportion. These two compounds have never been isolated before in reactions of indoles with DMAD. The third substance isolated in 44% yield gave a ^{1}H nmr spectrum characteristic of a symmetric structure consistent with **3**. The last compound, isolated in 17% yield, was the maleate **4**. When the reaction was carried out with an excess of skatole the maleate **4** was not isolated but the yield of **1**, **2** and **3** increased.

Reaction of 2,3-dimethylindole with DMAD in 40 ml of benzene with 1 ml of BTE for 6 days at room temperature gave three compounds. The ^{1}H nmr spectrum of an orange solid **5** isolated from the chromatographic column in 48% yield, showed an upfield (δ 1.45 and 1.48) chemical shift of the methyl groups when compared with 2,3-dimethylindole (δ 2.19). The reaction of the orange solid with acetyl chloride-sodium carbonate gave the acetyl derivative **6**, which



1 R^1 = H, R^2 = CO_2CH_3

2 R^1 = CO_2CH_3, R^2 = H



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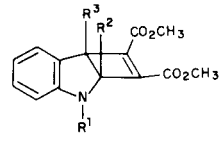
upon heating was converted to benzazepine **7**. The formation of **7** may be interpreted as a ring expansion from **6** by thermal decomposition. The structures of **5** and **6** were confirmed by ^{13}C nmr (Table). The absence of a deshielding of H-7 of the aromatic ring as well as strong steric effects from MeCO-N expected in the endo of **6** as shown by models, allow us to predict the *exo* conformer for **6**. It's not surprising that we were unable to isolate the thermolysis product of **5** since it's well known that 1-non-substituted benzazepines are unstable [6,7]. Structural analysis of the second product indicated that it was a 1:2 adduct of 2,3-dimethylindole with DMAD. The ^{1}H nmr and ir data suggested that it was a mixture of maleate and fumarate isomers. During separation by thick layer chromatography, one isomer transformed into the other and only one product was isolated as yellow crystals in 11% yield. The ^{1}H nmr spectrum showed an upfield chemical shift of the methyl group (δ 1.70) when compared with 2,3-dimethylindole. The singlet at δ 6.30 (1H) was assigned to a vinylic maleate hydrogen [8]. Under reflux in carbon tetrachloride, this product was converted into colourless crystals

Table
^{13}C NMR Values an Multiplicities of cyclobutenes Measured in Deuteriochloroform

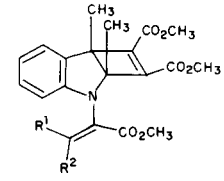
Carbon	Compound 5	6	14 [b]	15	9
1	68.4 s	73.3 s	71.9 s	70.1 d	73.0 s
3	148.6 s	142.9 s	149.8 s	150.3 s	143.5 s [c]
4	129.8 s	131.6 s	129.3 s	128.6 s	131.1 s
5	57.6 s	56.0 s	56.5 s	53.8 s	57.6
6	144.2 s	143.7 s	143.8 s	145.6 s	146.8 s
7	138.7 s	139.1 s	137.1 s	134.6 s	137.7 s
8	124.7 d	125.1 d	123.9 d	123.2 d	124.4 d
9	118.4 d	123.5 d	116.7 d	116.0 d	121.5 d
10	128.5 d	128.7 d	128.8 d	128.3 d	128.5 d
11	110.1 d	115.8 d	106.3 d	106.1 d	111.5 d
12	160.8 s	162.1 s	160.4 s	160.0 s	160.5 s
13	51.6 1	52.1 q	51.1 q	50.8 q	51.5 q
14	160.8 s	160.7 s	160.8 s	160.3 s	160.0 s
15	51.6 q	51.9 q	51.1 q	50.8 q	50.8 q
16	15.0 1	16.2 q	15.1 q	18.1 q	13.9 q
17	17.6 q	16.6 q	15.1 q		15.7 q
18		169.7 s	29.1 q	31.9 q	143.1 s [c]
19		25.8 q			107.4 d
20					164.7 s
21					51.5 q
22					165.5 s
23					52.1 q

[a] The δ values are in ppm downfield from TMSI (Chloroform) + 77.2 ppm. [b] Solvent carbon tetrachloride, (TMSI = δ (carbon tetrachloride) + 96.0 ppm. [c] These assignments could be interchanged.

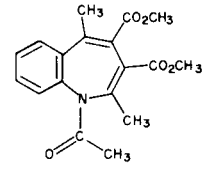
whose structure was assigned to be **8**. Thus, the thermolabil yellow crystal should be **9**. Under reflux in carbon tetrachloride the mixture of **9** and **10** was isomerized to benzazepine **8** in 83% yield. The third compound was a orange solid isolated in 28% yield whose mass spectrum and chemical analysis showed a loss of methanol relative to the starting materials. The ir showed an ester absorption in 1715 cm^{-1} and an unsaturated carbonyl at 1630 cm^{-1}, which is compatible with dihydro-2-oxocarbazole **11**. This compound was methylated to give 98% yield of the known dienone **12** [4]. When the reaction was carried out in benzene at 0-4° for 40 hours, 25% of the starting material was recovered. We isolated **5** in 6% yield, and **11** in 12% yield as well as a orange solid (48%) **10**. To verify the



5 R^1 = H , R^2 = R^3 = CH_3
6 R^1 = $COCH_3$, R^2 = R^3 = CH_3
14 R^1 = R^2 = R^3 = CH_3
15 R^1 = R^3 = CH_3 , R^2 = H



9 R^1 = H , R^2 = CO_2CH_3
10 R^1 = CO_2CH_3 , R^2 = H



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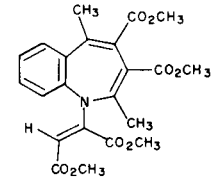

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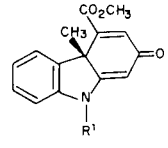
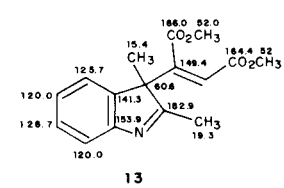


11 R^1 = H
12 R^2 = CH_3

influence of the solvent, the reaction was run in acetonitrile at room temperature for 5 days. The products isolated were the cyclobutene **5** (10%), the maleate **9** (6%), the fumarate **10** (7%), the dienone **11** (36%) and a pale yellow solid, mp 90-92° (25%). The molecular ion, M^+ 287 of its mass spectrum revealed a 1:1 adduct. The ir showed a signal at 1730 cm^{-1} (C=O) and at 1640 cm^{-1} (C=N), while the ^{1}H nmr spectra had a singlet at δ 5.79 with integration for 1H, suggesting a vinylic fumarate or maleate hydrogen. The stereochemistry was determined by ^{13}C nmr which revealed a $^3J_{CO,H}$ coupling of 12 Hz characteristic of maleate derivatives [9,10]. These data are consistent with **13**.



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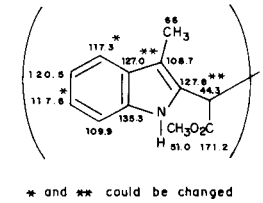

* and ** could be changed

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In order to collect more information about the structures of the cyclobutenes, we obtained the ^{13}C nmr spectra (Table). Also included are two compounds that we have described previously, **14** and **15** [4]. We started the assignments at C-1 in **15** that presented a doublet at δ 70.1. By comparison we assigned the signals for C-1 of the other

structures. The sp^2 aromatic carbons were compared with indolines, indolenines and indole [11]. The chemical shifts of C-6 and C-7 were determined by analogy with cyclobutene derivatives [12] and 1,4-dicarbonyl compounds [13]. The models for C-18 and C-19 are well known in the literature [14].

Both reaction of skatole and 2,3-dimethylindole with DMAD only occur in the presence of BTE. In its absence, even under refluxed conditions for long periods, there was no reaction. The influence of the Lewis acid catalyst on the formation of the cyclobutenes has been attributed to a lowering of the energy of the frontier orbitals because of complexation to the Lewis acid [15]. The affirmation of Acheson *et al.* [16] that DMAD does not need BFE catalysis to induce reaction with indoles is not absolutely correct since at the temperature of refluxing acetic acid the (2 + 2) cycloadducts are not stable. Under the conditions used by Acheson, the temperature and the reaction medium favors the two step process which becomes the predominant pathway over the (2 + 2) cycloaddition. This explains how the different products are formed, even using similar reagents and solvents, and only varying the reaction conditions.

EXPERIMENTAL

Boron trifluoride etherate, DMAD, 3-methylindole and 2,3-dimethylindole were purchased from Aldrich Chemical Co. All melting points were obtained on a Mettler FP 52 melting point apparatus and are uncorrected. Infrared spectra were taken on a Jasco A-202 spectrophotometer. The ^{1}H-nmr and ^{13}C-nmr spectra were recorded with a Varian XL-100 spectrometer using tetramethylsilane as an internal standard. Uv spectra were recorded using a Bauch & Lomb 2000 spectrophotometer. Mass spectra were obtained on a Varian Mat 311 A instrument at 70 eV using a direct insertion probe. Preparative thick layer chromatography (plc) was carried out on plates coated with silica gel PF 254 (Merck) and column chromatography was run on silica gel 60 (Merck).

Reaction of 3-Methylindole with Dimethyl Acetylenedicarboxylate.

To a solution of DMAD (0.750 g, 5.28 mmoles) and 3-methylindole (0.642 g, 4.90 mmoles) in dry benzene (5 ml), purged with nitrogen and cooled to 0° was added BTE (0.6 ml). The solution was kept 19 hours at 0°. The solvent was removed and the residue chromatographed on a column (silica, 40 g).

a. *trans*-2,3-Dihydro-3,4-bis(methoxycarbonyl)-5-methyl-2-(3'-methylindol-3'-yl)-1*H*-1-benzazepine (**1**).

Elution with ether-hexane (1:4) gave a mixture of two components which was subject to plc (silica, 7 consecutive elutions with benzene). The first component (at R_f 0.6) was **1** (0.102 g, 10%) and was obtained as colourless crystals mp 195-196° (cyclohexane-carbon tetrachloride); ir (potassium bromide): 3440 (NH), 1740 (C=O), and 1610 cm^{-1} (C=N); ^{1}H nmr (deuteriochloroform): δ 1.73 (s, 3H, 3'-CH_3), 2.12 (d, 3H, J = 1 Hz, 5-CH_3, 3.38 (d, 1H, J = 12 Hz, 2-H), 3.83 (s, 6H, OCH_3), 4.28 (dq, 1H, J = 12 and 1 Hz, 3-H), 4.50 (br, 1H, NH, removed by deuterium oxide shake), 5.96 (s, 1H, 2'-H), 6.45-7.72 (m, 8H, aromatic H) (irradiation at 2.12 caused the double quartet at 4.28 to collapse to a doublet); uv-vis (chloroform): λ max (log ϵ) 228 (4.51), 284 (4.06), 294 nm (4.05); ms: m/e 404 (M$^+$, 22), 254 (100), 241 (13), 202 (16), 170 (28), 131 (20), 130 (18).

Anal. Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found: C, 70.98; H, 6.01; N, 6.86.

b. *cis*-2,3-Dihydro-3,4-bis(methoxycarbonyl)-5-methyl-2-(3'-methylindol-3'-yl)-1*H*-1-benzazepine (**2**).

A second component (at R_f 0.5) gave **2** as colourless crystals mp 211-213° (dichloromethane-ether); ir (potassium bromide): 3420 (NH), 1745 (C=O) and 1665 cm^{-1} (C=N); ^{1} nmr (deuteriochloroform): δ 1.57 (s, 3H, 3'-CH_3), 2.08 (d, 3H, J = 1 Hz, 5-CH_3), 3.62 (d, 1H, J = 8 Hz, 2-H), 3.67 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.28 (dq, 1H, J = 8 and 1 Hz, 3-H), 4.78 (br, 1H, NH, removed by deuterium oxide shake), 5.92 (s, 1H, 2'-H), 6.50-7.63 (m, 8H, aromatic H) (irradiation at 4.28 cause the doublet at 2.08 to collapse to a singlet); uv-vis (ethanol): λ max (log ϵ) 226 (4.31), 286 (3.90), 294 nm (3.87); ms: m/e 404 (M$^+$, 100), 273 (56), 214 (32), 213 (21), 192 (57), 170 (51), 144 (20), 131 (47), 130 (24).

Anal. Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.03. Found: C, 71.27; H, 5.98; N, 6.93.

c. 1,2-Bis(methoxycarbonyl)-1,2-bis-(3'-methylindol-2'-yl)ethane (**3**).

Elution with ether-hexane (1:1) gave **3** (0.435 g, 44%) as colourless crystals mp 233-236° dec (dichloromethane-hexane); ir (potassium bromide): 3395 (NH), 1710 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ϵ) 224 (4.73), 285 (4.25), 293 nm (4.20); ^{1}H nmr (deuteriochloroform): δ 1.73 (s, 6H, 3'-CH_3), 3.73 (s, 6H, OCH_3), 4.64 (s, 2H, 1-H), 6.85-7.54 (m, 8H, aromatic H), 8.37 (br, 2H, removed by deuterium oxide shake); ms: m/e 404 (M$^+$, 23), 202 (100), 160 (80), 144 (9), 143 (10), 142 (8), 125 (9).

Anal. Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found: C, 70.97; H, 6.01; N, 6.77.

d. Dimethyl 2'-(3-Methylindol-2-yl)maleate (**4**).

Elution with ether gave **4** (0.227 g, 17%) as pale yellow crystals mp 142-143° (dichloromethane-cyclohexane); ir (potassium bromide): 3385 (NH), 1700 cm^{-1} (C=O); uv-vis (ethanol); λ max (log ϵ) 212 (4.39), 253 (3.90), 352 nm (4.37); ^{1}H nmr (deuteriochloroform): δ 2.35 (s, 3H, 3-CH_3), 3.73 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 6.18 (s, 1H, olefinic H), 6.92-7.67 (m, 4H, aromatic H), 8.43 (br, 1H, NH, removed by deuterium oxide shake); ms: m/e 273 (M$^+$, 86), 241 (15), 214 (28), 213 (20), 181 (15), 155 (100), 128 (15).

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53. Found: C, 66.11; H, 5.56; N, 5.04.

Reaction of 2,3-Dimethylindole with Dimethyl Acetylenedicarboxylate.

Procedure A.

A solution of DMAD (0.525 g, 3.7 mmoles) and 2,3-dimethylindole (0.507 g, 3.5 mmoles) in dry benzene (40 ml) was purged with nitrogen and after addition of BTE (0.9 ml) was kept 6 days at room temperature. The solvent was removed and the residue chromatographed on a column (silica).

a. 6,7-Bis(methoxycarbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (**5**).

Elution with ether-light petroleum (1:5) gave **5** (0.482 g, 48%) as orange crystals mp 101-103° (hexane); ir (potassium bromide):

3265 (NH), 1725, 1700 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 234 (3.94), 400 nm (3.01); ^1H nmr (deuteriochloroform): δ 1.45 (s, 3H, 1-CH_3), 1.48 (s, 3H, 5-CH_3), 3.71 (s, 6H, OCH_3), 4.34 (br, 1H, NH, removed by deuterium oxide shake), 6.28-7.23 (m, 4H, aromatic H); ms: m/e 287 (M^+, 54), 214 (90), 145 (100).

Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found: C, 66.94; H, 6.04; N, 4.78.

b. Dimethyl 2'-[6,7-Bis(methoxycarbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-dien-2-yl]maleate (**9**).

Elution with ether-light petroleum (1:4) gave a solid mixture. Plc of this mixture (hexane-ether, 1:3, 5 consecutives elutions) gave **9** (0.087 g, 11%) as yellow crystals mp 94-96° (hexane-ether 1:1) ir (potassium bromide): 1745, 1705 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 234 (4.15), 335 nm (4.09); ^1H nmr (deuteriochloroform): δ 1.56 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.84 (s, 6H, OCH_3), 6.30 (s, 1H, olefinic H), 6.65-7.46 (m, 4H, aromatic H); ms: m/e 429 (M^+, 15), 287 (20), 184 (100), 156 (24).

Anal. Calcd. for $C_{22}H_{23}NO_8$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.54; H, 5.43; N, 3.01.

c. 2,4a-Dihydro-4-methoxycarbonyl-4a-methyl-2-oxocarbazole (**11**).

Elution with ether-ethyl acetate (1:5) gave **11** (0.250 g, 28%) as orange crystals mp 168° dec (benzene); ir (potassium bromide): 3425 (NH), 1715 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 238 (3.98), 272 (3.82), 406 nm (3.82); ^1H nmr (deuteriochloroform): δ 1.90 (s, 3H, 4a-CH_3), 3.91 (s, 3H, OCH_3), 5.84 (d, 1H, J = 1.6 Hz, 1-H), 6.90 (d, 1H, J = 1.6 Hz, 3-H), 6.75-8.10 (m, 4H, aromatic H), 8.50 (br, 1H, NH, removed by deuterium oxide shake); ms: m/e 255 (M^+, 100), 240 (15), 239 (86), 212 (17), 168 (37), 167 (15).

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 71.01; H, 5.14; N, 5.34.

Reaction of 2,3-Dimethylindole with Dimethyl Acetylenedicarboxylate.

Procedure B.

A solution of DMAD (0.897 g, 6.32 mmoles) and 2,3-dimethylindole (0.896 g, 6.18 mmoles) in dry benzene (2 ml) was purged with nitrogen and after BTE (0.3 ml) was added, kept 40 hours at 0-4°. The solvent was removed and the residue chromatographed on a column (silica). a. Elution with ether-light petroleum (1:20) furnished the starting material (25%). b. Elution with ether-petroleum (1:5) gave **5** (0.106 g, 6%). c. Elution with ether-ethyl acetate (1:5) gave (**11**) (0.190 g, 12%).

d. Dimethyl 2'-[6,7-Bis(methoxycarbonyl)-1,5-dimethyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-dien-2-yl]fumarate (**10**).

Elution with ether-light petroleum (1:4) gave **10** (0.651 g, 48%) as orange crystals mp 99-101° (ether-petroleum); ir (potassium bromide): 1725, 1705 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 328 (3.33), 390 nm (3.35); ^1H nmr (deuteriochloroform): δ 1.50 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.72 (s, 6H, OCH_3), 3.75 (s, 3H, OCH_3), 6.62 (s, 1H, olefinic H), 6.10-7.40 (m, 4H, aromatic H); ms: m/e 429 (M^+, 13), 287 (17), 184 (100), 156 (24).

Anal. Calcd. for $C_{22}H_{23}NO_8$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.68; H, 5.37; N, 3.17.

Procedure C.

Reaction of 2,3-Dimethylindole with Dimethyl Acetylenedicarboxylate.

A solution of DMAD (0.577 g, 4.06 mmoles) and 2,3-dimethylindole (0.576 g, 3.97 mmoles) in dry acetonitrile (3 ml) was purged with nitrogen and BTE (0.8 ml) was added, kept 5 days at room temperature. The solvent was removed and the residue was chromatographed on a column (silica). a. Elution with ether-light petroleum (1:5) gave **5** (0.144 g, 10%). b. Elution with ether-light petroleum (1:4) gave a mixture of **9** and **10** (0.113 g, 13%).

c. Dimethyl 2'-(2,3-Dimethyl-3*H*-indol-3-yl)maleate (**13**).

Elution with ether-ethyl acetate (1:4) gave **13** (0.285 g, 25%) as pale yellow crystals mp 90-92° (ether-hexane); ir (potassium bromide): 1730 (C=O), 1640 cm^{-1} (C=N); uv-vis (ethanol): λ max (log ε) 214 nm (4.43); ^1H nmr (carbon tetrachloride): δ 1.37 (s, 3H, 3-CH_3), 2.22 (s, 3H, 2-CH_3), 3.45 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 5.79 (s, 1H, olefinic H), 6.99-7.56 (m, 4H, aromatic H); ms: m/e 287 (M^+, 65), 228 (100), 212 (21), 196 (21), 168 (100), 155 (26), 144 (25), 129 (34), 128 (33), 115 (25).

Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found: C, 67.04; H, 5.93; N, 4.76.

6,7-Bis(methoxycarbonyl)-1,5-dimethyl-2-acetyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (**6**).

To a solution of the cyclobutene (**5**) (0.112 g, 0.4 mmole) in dry benzene (2 ml) was added anhydrous sodium carbonate (0.1 g) and the mixture was stirred at 0-4. A solution of acetylchloride (1.1 g, 14 mmoles) in dry benzene (2 ml) was added dropwise and two new portions of sodium carbonate were added at intervals of 30 minutes. The temperature was raised to room temperature and at the end of 2 hours the reaction mixture was filtered and the residue washed with benzene (25 ml). Evaporation of the combined solution left an oil which was eluted through a short column of silica (5 g) with dichloromethane to give **6** (0.105 g, 82%) as colourless crystals mp 130-131° (dichloromethane-light petroleum); ir (potassium bromide): 1735, 1720, 1650 cm^{-1} (C=O); ^1H nmr (deuteriochloroform); δ 1.57 (s, 3H, 5-CH_3), 1.83 (s, 3H, 1-CH_3), 2.43 (s, 3H, $COCH_3$), 3.77 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.87-7.73 (m, 4H, aromatic H); ms: m/e 329 (M^+, 36), 298 (15), 214 (100), 145 (54), 144 (30).

Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.78; H, 5.76; N, 4.16.

1-Acetyl-2,5-dimethyl-3,4-bis(methoxycarbonyl)-1*H*-1-benzazepine (**7**).

The cyclobutene **6** (0.107 g, 0.33 mmole) was heated at 245° for 3 minutes. The dark residue was chromatographed on a column (silica; dichloromethane) and gave **7** (0.095 g, 89%) as colorless crystals mp 117-119° (ether-light petroleum); ir (potassium bromide): 1725, 1670 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 227 (4.22), 265 nm (3.87); ^1H nmr (deuteriochloroform): δ 1.86, 2.20 (2 x s, total 3H, 2-CH_3), 2.51, 2.54 (2 x s, total 3H, 1-$COCH_3$), 2.62 (s, 3H, 5-CH_3), 3.72 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 7.20-7.80 (m, 4H, aromatic H); ms: m/e 329 (M^+, 12), 298 (30), 297 (70), 255 (20), 254 (25), 214 (100), 168 (20), 145 (16).

Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.64; H, 5.74; N, 4.09.

Dimethyl 2'-[2,5-Dimethyl-3,4-bis(methoxycarbonyl)-1*H*-1-benzazepin-1-yl]maleate (**8**).

A mixture of **9** and **10** (0.232 g, 0.54 mmole) was refluxed in

carbon tetrachloride for 2 days. The solvent was removed and the residue recrystallized from dichloromethane-light petroleum to give **8** (0.193 g, 83%) as colorless crystals mp 133-134°; ir (potassium bromide): 1730, 1705 cm^{-1} (C=O); uv-vis (ethanol): λ max (log ε) 235 (4.15), 263 nm (4.19); ^1H nmr (deuteriochloroform): δ 2.47 (s, 3H, 5-CH_3), 2.62 (s, 3H, 2-CH_3), 3.65 (s, 6H, OCH_3), 3.72 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 4.89 (s, 1H, olefinic H), 7.16-7.79 (m, 4H, aromatic H); ms: m/e 429 (M^+, 10), 184 (100), 156 (56), 115 (28).

Anal. Calcd. for $C_{12}H_{23}NO_6$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.17; H, 5.32; N, 3.20.

2,4a-Dihydro-4-methoxycarbonyl-4a,9-dimethyl-2-oxocarbazole (**12**).

To a cold solution of **11** (0.117 g, 0.46 mmole) in dry acetonitrile (10 ml) was added potassium carbonate (0.600 g). The suspension was stirred and methyl iodide (2.3 g, 16 mmoles) was added. After 1 day at 25 the reaction was filtered and washed with acetonitrile. The solvent was removed and the residue was purified by column chromatography (silica, 8 g). Elution with ether-ethyl acetate (4:1) gave the dienone **12** (0.121 g, 98%) as orange crystals mp 147-148° (ether-hexane) [4].

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