Double Diels-Alder Reactions of Coumalic Acid with 1,3-Dienes

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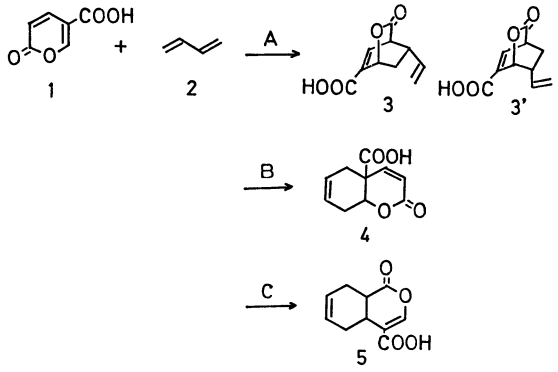
Thermal reaction of coumalic acid with 1,3-butadienes gave after diazomethane treatment dimethyl tricyclo[3.2.1.$0^{2,7}$]oct-3-ene-2,4-dicarboxylate *via* double Diels-Alder reaction. This represents the simplest synthesis of such a tricyclic system. The reaction with cyclopentadiene was also studied.

Diels-Alder reaction of 2-pyrone and esters of some 2-pyronecarboxylic acids are well documented.[1] With acetylenes as dienophile the reaction provided the benzene derivatives by loss of carbon dioxide from the intermediary adduct. With olefinic dienophiles, a decarboxylative double diene synthesis occurred to afford a bicyclo[2.2.2]oct-2-ene system, and with electron-rich dienophiles the so-called Diels-Alder reaction with inverse electron-demand[2] was effected with high regiospecificity.

In view of these facts, the reaction in the combination of coumalic acid (**1**) and 1,3-butadienes (**2**) seems most probably to follow the path A (Scheme 1).



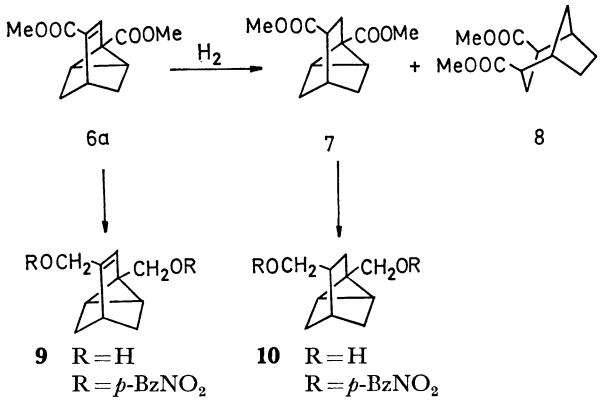
Scheme 1.

Meanwhile, taking the properties of 1,3-butadienes as a good diene part in Diels-Alder reaction as well as the lesser electron-withdrawing nature of the carboxylic acid **1** than that of the ester in consideration, we are intrigued by the possibility of the reaction path B[3] or C, the product **5** in the latter reaction path being a potential intermediate for the synthesis of natural products.[4]

Evidences to be presented gave the precedence to the reaction path A and the structural investigation and the fate of the adduct **3** will be described in detail in this report.[5]

Results and Discussion

The reaction of **1** with excess of butadiene (**2a**) in anhydrous methanolic solution at 100 °C for 6 h in a pressure bottle gave after treatment with ethereal diazomethane colorless needles **6a**, mp 101—102 °C, in 70% yield. This product was analyzed for C_8H_8-$(COOMe)_2$ by elemental analysis and mass spectrometry. The presence of a saturated ester function and an α,β-unsaturated ester moiety was apparent from the intense IR absorptions at 1735, 1710, and 1620 cm^{-1}. In UV spectrum a maximum at 243 nm (log ε 4.08) was interpreted to show the presence of a

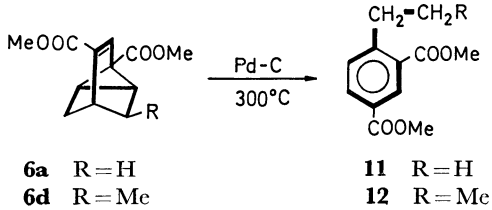


Scheme 2.

β-cyclopropylacrylic ester chromophore[6] where the arrangement of the cyclopropane ring attains the maximum conjugation with the double bond, *i.e.*, the "bisected" conformation. Catalytic hydrogenation over Raney-Ni resulted in the uptake of one equivalent of hydrogen to yield the saturated ester **7**, but the hydrogenation over Pd–C gave a mixture of **7** and another product **8** resulting from the uptake of two equivalents; this fact clearly suggests the coexistence of a cyclopropane ring and a double bond. The structure of **8** was later deduced from the consideration of the reaction path and the symmetry confirmed by seven signals in its ^{13}C-NMR spectrum.

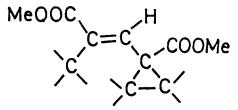
Lithium aluminum hydride reduction of **6a** and **7**, followed by treatment with *p*-nitrobenzoyl chloride gave the di-*p*-nitrobenzoates **9** and **10**, respectively. Although the NMR spectrum of **9** showed two singlets in the region of acyloxymethyl protons, **10** showed a singlet and a doublet of 6.6 Hz spacing. These facts indicate that **6a** has a carboxyl group on a tertiary carbon atom and an α,β-unsaturated ester group having no hydrogen at the α-position.

The fact that thermal treatment of **6a** over Pd–C at 300 °C gave an aromatic isomer, dimethyl 4-ethylisophthalate (**11**), especially combined with the fact that similar treatment of the 1,3-pentadiene adduct **6d** gave dimethyl 4-propylisophthalate (**12**), implicates the retention of a 1,3-dicarboxylate moiety and a butadiene moiety in **6a** without rearrangement or



Scheme 3.

cleavage as shown by bold lines in Scheme 3. These results, taken together, require the partial structure i in **6a**.



i

Formula 1.

Further structural evidences were obtained from its NMR spectrum which showed five well-separated multiplets for eight ring-protons as well as the two singlets due to the ester methyl protons, indicating the inherent symmetry of the molecule (Fig. 1); its ^{13}C-NMR spectrum confirmed this symmetry. The large coupling constant between H_a and H_b (12.3 Hz) may be ascribed to the geminal coupling of the methylene protons. In view of the observed spin-spin couplings between H_a (2H) and H_b (2H), and H_c (2H) and H_d (1H) (4.8 Hz), these five protons must constitute the partial structure ii, in which the coupling J_{ad} is nearly

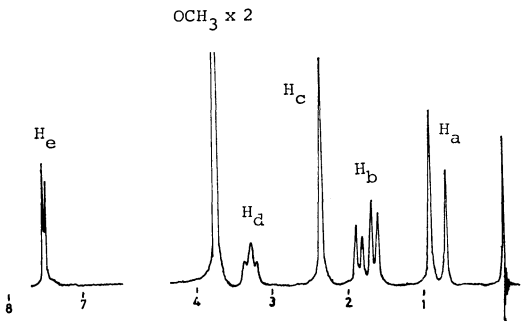
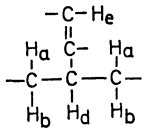


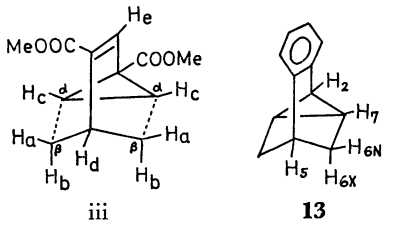
Fig. 1. ^{1}H-NMR spectrum of **6a** (60 MHz).



ii

Formula 2.

0 Hz. The triplet signals of H_d are further spin-splitted by the long-range coupling (1.7 Hz) with the olefinic proton H_e; this fact allows us to link the partial structures i and ii. Taking the total number of carbons and hydrogens into account, the other two protons (H_c) causing the 2H singlet may be divided into a cyclopropane ring as shown in the structure iii from consideration of the molecular symmetry. The bonding of C_α and C_β leads to a structure iii.



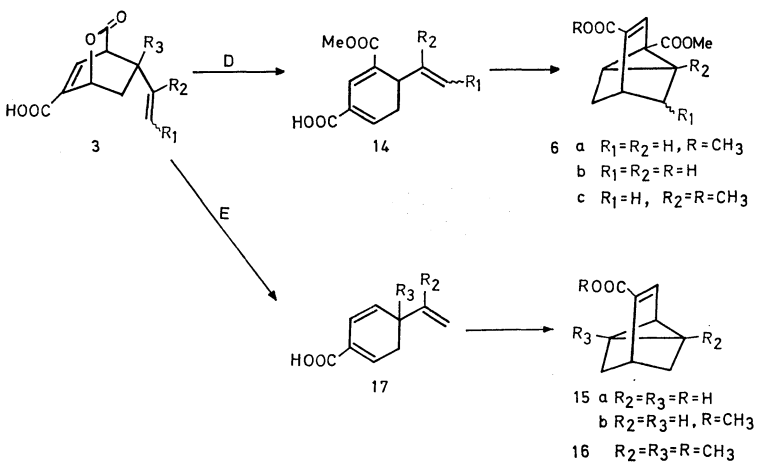
iii **13**

Formula 3.

At this stage, it was helpful to consider the NMR spectral features of the reported tricyclo[3.2.1.0^{2,7}]oct-3-ene system,[7] particularly of benzo[3,4]tricyclo[3.2.1.0^{2,7}]oct-3-ene (**13**).[7a] The cyclopropyl protons of **13** form a doublet due to the coupling with the other cyclopropyl proton H_2, but that of **6a** a singlet. The other coupling feature of the methylene protons is very similar in both compounds. It is well established[7] that, since the dihedral angles of *endo*-H_6–C_6–C_5–H_5 and *endo*-H_6–C_6–C_7–H_7 are close to 80°, little, if any, splitting is expected for these protons.

The reaction of **1** and butadiene **2a** under the same conditions described above gave, without diazomethane treatment, a half-ester **6b**. The structure of **6b** follows from the NMR spectrum which showed a similar pattern of the ring protons to that of **6a** except one ester methyl group. Its IR spectrum displayed strong carbonyl absorptions at 1740 and 1680 cm^{-1}: these bands are characteristic for a saturated ester and an α,β-unsaturated carboxylic acid. Therefore, to the half-ester **6b** is assigned the structure shown. Treatment of **6b** with diazomethane gave **6a** quantitatively.

These findings lead to the conclusion that **6b** is best explained as a result of two sequential Diels-Alder reactions. That is, the thermal [4+2]cycloaddition



Scheme 4.

reaction between the diene moiety of **1** and the ene part of **2** as the dienophile with inverse electron-demand would generate the bicyclic lactone **3**, which could then undergo methanolysis-dehydration to produce the half-ester of vinylcyclohexadienedicarboxylic acid **14**. The succeeding intramolecular Diels-Alder reaction also takes place with inverse electron-demand, giving the product **6b**. This [4+2]cycloaddition step leading to the cyclopropane ring formation has rather ample analogy.[8] Since the reaction step D in Scheme 4 without added acid-catalyst is unprecedent, the intermediate **3** was trapped to disclose the reaction mechanism. The reaction at lower temperature (80 °C) and in aprotic solvent (benzene) gave the lactone **3**. Thus obtained **3** reacted in anhydrous methanol only very sluggishly at 100 °C and gave at 150 °C **6b** and **15a** in a ratio of 1 : 3. The reaction temperature and course are different from those of the reaction of **1** and **2a**. This difference may be ascribed to the absence or presence of acid catalysis of **1** itself.[9]

The reaction of **1** with isoprene at 100 °C for 20 h gave after diazomethane treatment **6c** in 23% yield. The location of the methyl substitution is clearly demonstrated by consideration of the coupling pattern in the NMR spectrum. In this case, the coupling constant between the cyclopropyl proton H_7 and *endo*-methylene proton H_{6N} was observed as 2.3 Hz.

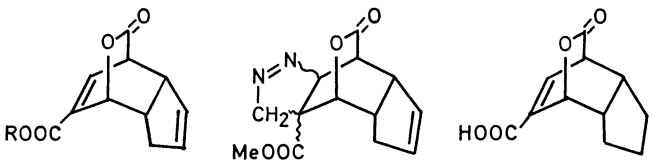
The reaction of **1** with 1,3-pentadiene at 100 °C for 20 h gave **6d** in 20% yield after diazomethane treatment.

In sharp contrast to the aforementioned case, the reaction of **1** with 2,3-dimethylbutadiene at 100 °C for 30 h gave chiefly a crystalline decarboxylated adduct **15b**. The structure of **15b** follows from its spectral characteristics. Treatment with diazomethane gave an oily ester **16**, which was identical with the tricyclic adduct obtained by the reaction of methyl coumalate with 2,3-dimethylbutadiene.[3]

This fact implies that with the change of the substituent(s) on the butadiene component, the construction of the ene-diene moiety necessary for the posterior Diels-Alder reaction of the primary cycloadduct was achieved by an alternative route E, *i.e.*, a simple decarboxylative step into **17**. Although the concurrent route E is supposed to be the reason for the low yield of **6c** and **6d**, inspection of the fore-run of distillation was fruitless since so many components were included.

We believe that the reaction presented herewith represents the simplest synthesis of the tricyclo[3.2.1.$0^{2,7}$]oct-3-ene system yet reported.[10]

The reaction of **1** with cyclopentadiene in boiling methanol for 3 h gave **18** in 48% yield. Elemental analysis showed it to be an undecarboxylated 1 : 1 adduct and its NMR spectrum revealed a marked similarity to that of the product **19** obtained by the reaction of methyl coumalate with cyclopentadiene. The identity of the skeletal structures of **18** and **19** was established by the fact that both gave the same 1,3-dipolar cycloadduct of the methyl ester **20** by the treatment with excess of ethereal diazomethane. Half hydrogenated product **21** of the adduct **18** showed in its NMR spectrum three well separated, mutually coupled pairs of doublet of doublets in the lower field region (δ 3.97, 5.73, and 7.57): this reinforces the assignment of the signals in the spectrum of **18**.



18 R=H
19 R=CH_3

20 **21**

Formula 4.

It should be emphasized that even cyclopentadiene can behave mainly as a dienophile in this type of reaction.

Experimental

All the melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR 27-G spectrometer, and UV spectra on a Hitachi EPS-2 spectrophotometer. Mass spectra (MS) were obtained with a Hitachi RMS-4 spectrometer (70 eV). NMR spectra were measured on a JEOL C-60HL spectrometer using TMS as an internal standard. We are grateful to Dr. S. Kojima for the courtesy that made possible the use of this instrument. ^{13}C-NMR spectra were obtained with a Varian CFT-20 spectrometer at 20 MHz in $CDCl_3$ solution using TMS as an internal standard. Microanalyses were performed by Mrs. K. Fujimoto using a Yanagimoto C.H.N. Corder MT-1. GLC was performed with a Shimadzu GC-4AIT with a 3 mm×3 m column packed with 10% High Vacuum Silicone Grease on Chromosorb W (80—100 mesh).

Reaction of ***1*** *with Butadiene.* (a) A suspension of **1**[9] (7.0 g) and excess of butadiene (20 ml) in methanol (35 ml) was heated in a pressure bottle at 100—110 °C for 5 h. After removal of the solvent, treatment with ethereal diazomethane, concentration, and distillation gave with a small amount of fore-run, a fraction of bp 172 °C/15 Torr, which crystallized immediately (mp 97—98 °C). Recrystallization from diisopropyl ether or methanol gave **6a** (2.2 g; 70%) as colorless needles: mp 101—102 °C; IR and UV (EtOH): see text; MS, *m/e*(rel intensity) 222(M^+, 44), 207 (16), 191(25), 190(20), 163(100), 131(44), 119(20), 103 (37), 91(26), 77(22), 59(45); NMR (CCl_4): δ 0.84 (2H, d, 12.3 Hz, H_{6N} and H_{8N}), 1.74(2H, dd, 4.9 and 12.3 Hz, H_{6X} and H_{8X}), 2.28(2H, bs, H_1 and H_7), 3.27 (1H, bt, 4.9 and 1.8 Hz, H_5), 7.36(1H, d, 1.8 Hz, H_3), and 3.70 and 3.73(3H each, s, COOMe); ^{13}C-NMR: δ 28.3(t, C_6 and C_8), 29.4(d, C_1 and C_7), 29.7(s, C_2), 31.1(d, C_5), 51.4 and 52.0 (q, OMe), 131.1(s, C_4), 132.4(d, C_3), 164.9 (C=C-C=O), 171.5(s, C=O). Found: C, 65.05; H, 6.38%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

(b) A similar reaction using 2.00 g of **1** afforded without diazomethane treatment 0.89 g (30%) of **6b**, on standing for many days after removal of the solvent: mp 178—178.5 °C (MeOH); IR(Nujol): see text; NMR ($CDCl_3$): δ 0.88 (2H, d, 12.3 Hz, H_{6N} and H_{8N}), 1.82(2H, dd, 12.3 and 4.8 Hz, H_{6X} and H_{8X}), 2.43(2H, bs, H_1 and H_7), 3.32(1H, bt, 4.8 Hz, H_5), 7.70(1H, d, 1.8 Hz, H_3), 3.76 (3H, s, COOMe). Found: C, 63.18; H, 5.65%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

(c) A suspension of **1** (500 mg) and excess of butadiene (1 ml) in benzene (20 ml) with a trace amount of hydroquinone was heated in a pressure bottle at 150 °C for 20 h.

After removal of the solvent, distillation gave a fraction of bp 160—180 °C/25 Torr (381 mg; 71%), which crystallized soon (mp 107—110 °C). Recrystallization from ether gave an analytically pure **15a**: mp 117—118 °C; IR(Nujol): 1660, 1600 cm^{-1}; NMR ($CDCl_3$), δ 0.75(2H, d, 12.0 Hz, H_{6N} and H_{8N}), 1.5—2.0(3H, cm, H_1, H_2, and H_7), 3.23(1H, bt, H_5), 7.24(1H, dd, 5.4 and 2.0 Hz, H_3). Found: C, 71.97; H, 6.65%. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71%.

(d) A similar mixture from 310 mg of **1** was heated at 80 °C for 6 days. After removal of the solvent, preparative TLC separation gave 109 mg of **3a** as thermally very labile oil; NMR($CDCl_3$): δ 1.53 (1H, ddd, 14, 4, and 2 Hz, H_{5N}), 2.52(1H, ddd, 14, 10, and 4 Hz, H_{5X}), 2.90(1H, m, H_4), 3.80(1H, dd, 6.4 and 2.8 Hz, H_3), 5.0—6.0(4H, complex m, H_6 and vinyl H), 7.48(1H, dd, 6.4 and 2.4 Hz, H_2).

The adduct **3a** (72 mg) in anhydrous methanol was heated at 100 °C for 6 h to result in only small conversion. Heating further at 150 °C for 4 h gave a mixture of **6b** and **15a** in a ratio of 1 : 3 (by NMR analysis).

*Catalytic Hydrogenation of **6a**.* A solution of **6a** (111 mg) in methanol (30 ml) was hydrogenated over Raney-Ni, resulting in one equivalent H_2 uptake. Filtration and solvent removal gave oily **7** (110 mg) which showed only one peak on GLC analysis. Analytical sample of **7** had bp 142—143.5 °C/5 Torr: $n_D^{24.8}$ 1.4924; IR(neat): 1750, 1720, 1625 cm^{-1}; MS: *m/e* 224(M^+, 20), 193(35), 192(100), 164 (76), 137(28), 132(49), 105(77), 79(23), 77(22), 59(26): NMR($CDCl_3$): δ 1.4—2.7(10H, m), 3.67 and 3.72(3H each, s, $COOCH_3$); ^{13}C-NMR: δ 19.3(t), 23.1(s), 27.0(t), 27.7(d), 27.6(d), 32.4(t), 32.7(d), 41.8(d), 51.6(q), 51.7(q), 174.7(s), 175.1(s). Found: C, 64.39; H, 7.17%. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%.

A solution of **6a** (444 mg) in ethanol (30 ml) was hydrogenated over 5% Pd–C (400 mg), resulting in 74 ml (1.65 eq) of H_2 uptake. Removal of the catalyst and the solvent gave an oily mixture, which was shown by GLC analysis to consist of two components **7** and **8** in the ratio of 5.9 : 1. After preparative GLC separation, the major component was identified to be **7** by spectral comparison. The minor component **8** had bp 140—145 °C(bath)/5 Torr; NMR ($CDCl_3$): δ 1.4—2.7 (12H, m), 3.78(6H, s, $COOCH_3$); ^{13}C-NMR: δ 21.9(t), 28.8(t×2), 32.5(t), 36.4(d×2), 44.8 (d×2), 51.6(q×2), 175.3(s×2); MS: *m/e* 226 (M^+, 5), 195(23), 194(59), 167(30), 166(100), 162(20), 160(20), 135(31), 134(31), 107(61), 80(31), 79(55), 67(23). Found: C, 63.98; H, 8.06%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

*Di-p-nitrobenzoate **9**.* A solution of **6a** (222 mg) in ether (30 ml) was added dropwise to $LiAlH_4$ (100 mg) suspended in dry ether (30 ml). The mixture was stirred for 2 h and excess of hydride was decomposed by addition of ethyl acetate and then satd. Rochelle salt solution (50 ml). The ethereal solution was dried (Na_2SO_4) and evaporated to give diol (227 mg). The diol without purification was dissolved in pyridine–CH_2Cl_2, and *p*-nitrobenzoyl chloride (371 mg) was added. After standing overnight at room temperature the mixture was poured onto ice water, and extracted with CH_2Cl_2. The organic solution was washed successively with dil HCl, satd. $NaHCO_3$, and water. The solution was dried and evaporated, and digestion of the residue with ethanol and several recrystallizations gave **9**: mp 91—92 °C; IR(Nujol): 1720, 1528, and 1350 cm^{-1}; NMR ($CDCl_3$): δ 0.95 (2H, d, 14 Hz, H_{6N} and H_{8N}), 1.66(2H, bs, H_1 and H_7), 1.7(2H, m, H_{6X} and H_{8X}), 2.76(1H, bt, H_5), 6.17(1H, bs, H_3), 4.47(2H, s, $-OCH_2$), 4.88(2H, s, $-OCH_2$), 8.28(8H, s, Ar-H). Found: C, 61.88; H, 4.23; N, 5.75%. Calcd for $C_{24}H_{20}N_2O_8$: C, 62.06; H, 4.34; N, 6.03%.

*Di-p-nitrobenzoate **10**.* Similarly to the above, the dihydro ester **7** (254 mg) was reduced by $LiAlH_4$ (110 mg). After usual work-up, the resulting diol without purification was treated with 400 mg of *p*-nitrobenzoyl chloride, giving **10**, mp 143—144 °C (EtOH); IR(Nujol): 1722(with shoulder), 1528, 1355 cm^{-1}; NMR($CDCl_3$): δ 1.4—2.3(10H, m), 5.88 (2H, s, $-O-CH_2$), 5.76(2H, d, 6.6 Hz, $-OCH_2$), 8.25(8H, s, Ar-H). Found: C, 61.56; H, 4.78; N, 5.75%. Calcd for $C_{24}H_{22}N_2O_8$: C, 61.80; H, 4.75; N, 6.01%.

*Isomerization of **6a** with Pd–C.* A suspension of 10% Pd–C (500 mg) in **6a** (1.0 g) was heated in a test tube at 300—310 °C for 2 h. Ethereal extract of the reaction mixture was evaporated to give crude oil (802 mg), which showed a single peak on GLC analysis. Distillation gave diemthyl 4-ethylisophthalate[12] (**11**) (591 mg): bp 142—146 °C/5 Torr; $n_D^{26.0}$ 1.5202; IR(neat): 1738(with shoulder), 1614 cm^{-1}; NMR(CCl_4): δ 1.24(3H, t, 7.5 Hz, $CH_2\underline{CH_3}$), 3.04 (2H, q, 7.5 Hz, $\underline{CH_2}CH_3$), 7.27(1H, d, 8.6 Hz, H_5), 8.01 (1H, dd, 8.6 and 2.0 Hz, H_6), 8.44(1H, d, 2.0 Hz, H_2), 3.93(6H, s, $COOCH_3$). (Found: C, 64.94; H, 6.38%).

For comparison, when **6a** (500 mg) was heated without addition of Pd-C at 300—310 °C for 3 h, **6a** (200 mg) was recovered after distillation: mp 98—110 °C.

*Reaction of **1** with Isoprene.* A suspension of **1** (2.0 g) and isoprene (6 ml) in methanol (50 ml) was heated at 100—110 °C for 24 h in a pressure bottle. Removal of the solvent, treatment with ethereal diazomethane and subsequent evaporation gave an oily mixture. Fractional distillation with a Vigreux column gave a fore-run (bp 120—160 °C/15 Torr: 1.01 g) and **6c** (761 mg: 23%); bp 160—165 °C/15 Torr. The fore-run showed on GLC analysis at least six peaks and the structures were not further investigated. Analytically pure **6c** had bp 132—136 °C/5 Torr; IR(neat): 1740 (with shoulder), 1620 cm^{-1}; NMR(CCl_4): δ 0.85(2H, d, 12.3 Hz, H_{6N} and H_{8N}), 1.43 (3H, s, C_1-CH_3), 1.65 (1H, dd, 12.3 and 5.0 Hz, H_{8X}), 1.82(1H, ddd, 12.3, 5.0, and 2.3 Hz, H_{6X}), 2.26(1H, bd, 2 Hz, H_7), 3.22(1H, bt, H_5), 7.32(1H, d, 1.7 Hz, H_3), 3.67 and 3.73(3H each, s, $COOCH_3$). Found: C, 65.91; H, 7.06%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

*Reaction of **1** with 1,3-Pentadiene.* A suspension of **1** (2.0 g) and 1,3-pentadiene (*cis/trans* mixture: 4 ml) in methanol (50 ml) was heated at 110 °C for 9 h. After diazomethane treatment and solvent removal, the residue was fractionally distilled at 4 Torr with a 10 cm Vigreux column, giving four fractions; A: 85—95 °C (470 mg); B: 95—118 °C (837 mg); C: 128—140 °C (725 mg); D: 140—155 °C (249 mg). From the fractions B, C, and D, crystalline **6d** (286 mg) was obtained: mp 98.5—99.5 °C. Column chromatography (Al_2O_3: PhH) of the mother liquid (B,C,D) gave further crop of crystals (415 mg: total 21%); IR(Nujol): 1740 (with shoulder), 1620 cm^{-1}; MS: *m/e* 326(M^+, 77), 221(29), 205(44), 204(60), 177(100), 163(33), 145(61), 117(40), 105(36), 91(31), 59(37); NMR(CCl_4): δ 0.61(3H, d, 7.2 Hz, *endo*-CH_3-C_6), 0.90(1H, d, 12.2 Hz, H_{8N}), 1.87 (1H, ddd, 12.2, 2.0, and 4.8 Hz, H_{8X}), 2.1(1H, ddd lower half was obscured by overlapping, 7.3, 3.7, and 2 Hz, H_{6X}), 2.18 and 2.28 (1H each, AB q with further splitting, 5.4 and 2 Hz, H_1 and H_7), 3.16(1H, bt, H_5), 7.67(1H, d, 2.0 Hz, H_3), 3.76(6H, s, 2×$COOCH_3$). Found: C, 65.96; H, 6.75%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

*Pd–C Treatment of **6d**.* A sample of **6d** (200 mg) was heated with Pd-C at 300—310 °C as described before. Work-up and distillation gave a single substance **12**: bp 150 °C (bath)/5 Torr; IR(neat): 1735 (with shoulder), 1610 cm^{-1}; MS: *m/e* 236 (M^+, 37), 205(100), 189(57); NMR(CCl_4):

δ 1.02(3H, t, 7.0 Hz, CH_3), 1.57(2H, m, $CH_2\underline{CH_2}CH_3$), 2.99 (2H, t, 8.2 Hz, $\underline{CH_2}CH_2CH_3$), 7.31(1H, d, 8.2 Hz, H_6), 8.07 (1H, dd, 8.2 and 1.8 Hz, H_5), 8.53(1H, d, 1.8 Hz, H_2), 3.92(6H, s, $2\times COOCH_3$). Found: C, 66.12; H, 6.91%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

*Reaction of **1** with 2,3-Dimethylbutadiene.* A suspension of **1** (2.0 g) and 2,3-dimethylbutadiene (2 ml) in methanol (50 ml) was heated at 100—110 °C for 30 h. Removal of the solvent and distillation gave an oily mixture (2.156 g): bp 150—180 °C/20 Torr. Upon standing **15b** crystallized (378 mg): mp 191—192 °C(CH_2Cl_2); IR(Nujol): 3400—2400, 1670, 1608 cm^{-1}; MS: *m/e* 178(M^+, 82), 163(29), 133(100), 119(26), 117(27), 105(70), 93(33), 91(71), 79(34); NMR ($CDCl_3$): δ 0.82(2H, d, H_{6N} and H_{8N}), 1.63(2H, dd, 12.3 and 3.4 Hz, H_{6X} and H_{8X}), 3.11(1H, bt, H_5), 7.40(1H, dd, 7 and 2 Hz, H_3), 1.28(6H, s, CH_3-C_1 and CH_3-C_7), 1.3 (1H, d, H_2). Found: C, 74.30; H, 7.99%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

The acid **15b** was esterified with CH_2N_2 giving in a quantitative yield the ester **16** which was identical in all respects with an authentic sample.[3]

*Reaction of **1** with Cyclopentadiene.* A solution of **1** (2.0 g) and freshly prepared cyclopentadiene (2.5 g) in methanol (80 ml) was heated under reflux for 3 h. Removal of the solvent and dicyclopentadiene gave a crystalline residue. Recrystallization from ethanol gave **17** (1.397 g: 47.5%): mp 198—199 °C(dec); IR($CHCl_3$): 3400—2400, 1738, 1688, 1630 cm^{-1}; NMR($CDCl_3+CF_3COOH$): δ 1.90(1H, d with further splittings, 17.2 Hz, H_{1N}), 2.57(1H, dd, with further splittings, 17.2 and 9.2 Hz, H_{1X}), 3.2(1H, m, H_{7a}), 3.4(1H, m, H_{3a}), 3.93(1H, dd, 6.3 and 2.9 Hz, H_4), 5.38 and 5.58(1H each, AB q with further splittings, 6.8 Hz, H_3 and H_2), 5.67 (1H, dd, H_7), 7.32(1H, dd, 6.3 and 2.3 Hz, H_5). Found: C, 63.82; H, 4.87%. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%.

*Partial Hydrogenation of **18**.* A solution of **18** (1.0 g) in ethanol (100 ml) was hydrogenated over 5% Pd-C (0.5 g) until about one equivalent (120 ml) of H_2-uptake resulted. Immediate removal of the catalyst and the solvent, followed by several recrystallizations from ethanol gave **21** (525 mg): mp 160—161 °C (dec with frothing); IR(Nujol): 1716, 1760(shoulder), 1628 cm^{-1}; NMR ($CDCl_3+CF_3COOH$): δ 0.8—2.2(6H, m, $3\times CH_2$), 2.4—3.2(2H, m, $2\times CH$), 3.97(1H, dd, 6.9 and 3.0 Hz, H_4), 5.73(1H, dd, 4.2 and 2.6 Hz, H_7), 7.57(1H, dd, 6.9 and 2.6 Hz, H_5). Found: C, 63.40; H, 5.69%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

1,3-Dipolar Cycloaddition of Diazomethane. A solution of **19** (650 mg) in CH_2Cl_2 was treated with excess of CH_2N_2. After standing for 4 h, AcOH was added until the faint yellow color of CH_2N_2 was disappeared. Solvent removal followed by recrystallization (MeOH) gave **20** (694 mg): mp[12] 146—147 °C(dec with frothing); IR ($CHCl_3$): 1765, 1746 cm^{-1}; MS: *m/e* 234(M^+, small), 190(20), 175(61), 169(50), 131(100), 129(27), 116(27), 115(30), 91(45), 66(41), 44(93); NMR($CDCl_3$): δ 2.3—2.8(2H, m, CH_2), 2.7—3.5 (4H, m, CH), 4.82 and 4.92(1H each, AB q, NCH_2), 5.6—5.8(2H, m, olefinic H), 3.85(3H, s, $COOCH_3$). Found: C, 59.29; H, 5.32; N, 10.77%. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68%.

A solution of **18** (500 mg) in methanol was treated with CH_2N_2 as described above. The obtained crystals had mp[12] 146—147 °C. The spectral characteristics were consistent with those of the product described above.

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