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DIELS–ALDER REACTION OF METHYL COUMALATE WITH 1,3-DIENES

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Abstract—Reaction of methyl coumalate (**1b**) with 1,3-butadienes at 100° afforded the tetrahydrocoumarins (**6**) and the 4-methoxycarbonyltricyclo[3.2.1.$0^{2,7}$]octenes (**7**). The similar reaction of **1b** with cyclohexadiene gave exclusively tetrahydronaphthalene-2-carboxylate. With cyclopentadiene, **1b** afforded a product (**10**) resulting from the addition reaction in which cyclopentadiene acted as a dienophile. The reaction giving **6** is the first example of the reaction of a 2-pyrone as a dienophile.

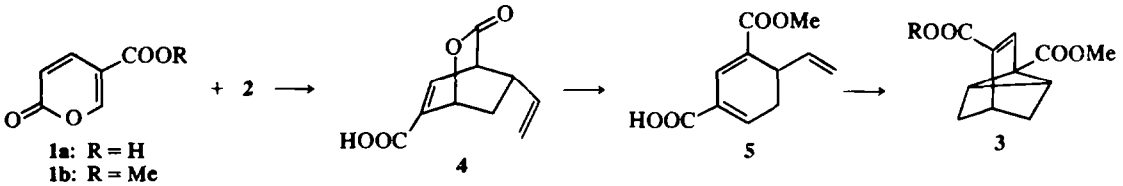
Recently we reported[1] the thermal cycloaddition reaction of coumalic acid (2-pyrone-5-carboxylic acid; **1a**) with 1,3-butadienes (**2**) in methanol solution to afford the 1,3-dimethoxycarbonyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene derivatives (**3**). We rationalized the reaction pathway as follows: the reaction starts from the first Diels–Alder (D–A) reaction between the diene moiety of **1a** and the ene part of butadienes (**2**) as a dienophile in the mode of inverse electron demand[2] to give a strained lactone (**4**) followed by the formation of a half-ester (**5**), and comes to an end by the second intramolecular D–A reaction leading to **3**.

In this report, we wish to describe the results of the thermal cycloaddition reaction of **1b** with several acyclic and cyclic 1,3-dienes.[3]

RESULTS

Reaction with acyclic 1,3-*dienes.* The reaction of methyl coumalate (**1b**) with 2,3-dimethylbutadiene (**2a**) in benzene solution at 100° for 17 h in a pressure bottle afforded two products (**6a** and **7a**) in a ratio of 10:1 as revealed by GLC.

The structure of the major product (**6a**), 6, 7 - dimethyl - 4a - methoxycarbonyl - 4a,5,8,8a - tetrahydrocoumarin, follows from its elemental composition, IR and NMR spectra. In the NMR spectrum, two olefinic protons constituting an AB quartet were observed, the chemical shifts of which were characteristic for the protons of an α,β-unsaturated carbonyl moiety. These results are consistent with the proposed structure (**6a**) and exclude an alternative structure (**8**), NMR spectrum of which should show only one olefinic proton. The *endo*-addition nature was evident from the values of $J_{8,8a}$ and $J_{8',8a}$ as shown in Table 1.

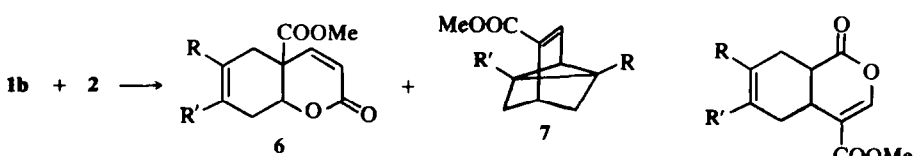


1a: R = H
1b: R = Me

4 **5** **3**

SCHEME 1.

In view of the involved double D–A reactions with inverse electron demand, the substitution of the carboxyl group on the 2-pyrone (**1a**) with a more electron-withdrawing alkoxycarbonyl group might accelerate the reaction. On the other hand, this substitution may cause the change of the reaction path, since these butadienes are well known to act as a good diene component of the D–A reaction with electron-deficient dienophiles.



6 **7** **8**

a: R = R' = Me
b: R = Me, R' = H
c: R = R' = H

SCHEME 2.

Table 1. NMR data for tetrahydrocoumarins **6**

	Chemical shifts, δ							Coupling constants, Hz		
	H_3	H_4	H_6, H_7	H_{8a}	$H_5, H_8(4H)$	$=C-CH_3$	$COOCH_3$	$J_{3,4}$	$J_{8,8a}$	$J_{8',8a}$
6a	5·80	6·65	—	4·76	1·7–2·8	1·58	3·58	9·8	5·4	2·4
6b	5·63	6·51	5·15	4·68	1·8–2·8	1·65	3·53	9·3	4·7	2·9
6c	6·03	6·90	5·69	5·00	1·8–3·0	—	3·75	9·6	5·0	3·0

Table 2. NMR data for tricyclic compounds **7**

	Chemical shifts, δ								Coupling constants, Hz		
	H_{8N}	H_{8X}	H_1	H_5	H_2	H_3	CH_3	$COOCH_3$	$J_{8N,8X}$	$J_{2,3}$	$J_{3,5}$
7a	0·79	1·57	—	3·08	1·2	6·99	1·28	3·64	11·7	6·3	2·1
7b	0·71	1·75	2·09	3·07	1·30	6·70	1·30	1·30	12·2	5·3	1·8
7c	0·72	1·59	1·57	3·12	1·6	6·93	—	3·64	11·7	5·6	1·8

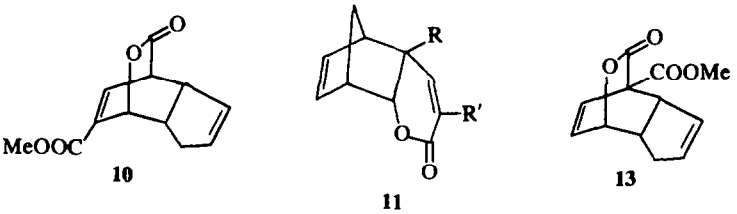
The minor product (**7a**) was a decarboxylated adduct as judged from its elemental analysis and mass spectrum. The structure of **7a**, methyl 1,7 - dimethyltricyclo[3.2.1.$0^{2,7}$]oct - 3 - ene - 4 - carboxylate, may be readily deduced by the comparison of the NMR spectrum with that of **3**. Although the lower-field half of the new ring proton (H_2) seems to be masked by the strong (6H) signals of the two methyl protons, the olefinic proton doublet splitted by the long range coupling is further splitted (6·3 Hz) by the vicinal cyclopropyl proton H_2.

The reaction of **1b** with an excess of isoprene (**2b**) at 100° for 17 h gave a mixture of a tetrahydrocoumarin (**6b**) and a tricyclic compound (**7b**) in a ratio of 4:3. The position of the Me substitution cannot be clarified to date.

The reaction of **1b** with butadiene (**2c**) at 100° for 17 h gave a mixture of **6c** and **7c** in a ratio of 3:4. The tetrahydrocoumarin (**6c**) is thermally labile and when heated above 150°, **6c** was transformed into a mixture of **7c** and methyl 4-vinylcyclohexa-2,6-dienecarboxylate (**9**), the structure of which was mainly based on the NMR spectrum (Experimental). The similar thermal treatment of **9** gave only **7c**, and under these conditions, **7c** was recovered unchanged. These facts may explain that the reaction between **1b** and **4c** at higher temperature (170°) resulted in the formation of only **7c**, and this mode of reaction can be of value for preparation of the tricyclic compound.

On the other hand, thermal treatment of **6a** and **6b** at 170° did not induce any change at all, but at 190°, **6b** changed gradually into **7b**.

Reaction with cyclic 1,3-*dienes.* The reaction of **1b** with cyclopentadiene in boiling benzene for 3 h yielded specifically 6-methoxycarbonyl-r-3a,4,c-7a-tetrahydroindene-c-4,c-7-carbolactone (**10**).* The NMR spectrum showed four-proton signals at δ 5·4–5·7, typical of normal olefinic proton region, in addition to 1-proton signal at δ 7·22. This fact may remind us of the structure **11a**, but this has several discrepancies in the coupling patterns. For example, the largest coupling constant (18 Hz) of two signals at the highest field is far from the reported values (8–10 Hz) of the geminal coupling of the methylene protons of the bicyclo[2.2.1]heptene systems[4] and is only explicable by those of allylic methylene protons with adjacent π-bond.[6] In order to elaborate the structural assignment further, the reaction of methyl 2-pyrone-3-carboxylate (**12**) with cyclopentadiene was undertaken to obtain the adduct (**13**). The coupling assignments for **10** and **13** are established by decoupling techniques and shown in Table 2. Since the close correspondence in all the coupling constants for **10** and **13** indicates the identity of the molecular frameworks and the



10 **11** **13**

a: R = COOMe, R' = H
b: R = H, R' = COOMe

Fig 1.

*The structure of **10** has been erroneously assigned in the preliminary communication.[3]

Table 3. NMR data for **10** and **13**

H	Chemical shifts, δ 10	13	J	Coupling constants, Hz 10	13
1N	2·53	2·54	1N, 1X	18·0	16·8
1X	1·86	1·85	1N, 7a	10·0	10·0
2	5·62	5·66	1X, 7a	3·8	4·0
3	5·47	5·40	1N, 2	2·2	2·2
3a	3·38	3·70	1X, 2		4
4	3·76		2, 3	6·0	5·8
5	7·22	6·64	3, 3a		2·2
6		6·41	3a, 7a	9	9
7	5·62	5·19	3a, 4	3·2	—
7a	3·16	3·18	4, 5	6·6	—
$COOCH_3$	3·78	3·88	5, 6	—	8·0
			5, 7	2·5	2·2
			6, 7	—	5·0
			7, 7a	4·5	5·0

spectra of **13** easily exclude the alternative structure **11b**, the structural assignment for **10** is established as shown.

The *endo* nature of the adduct is readily determined by the values of $J_{3a,4}$ and $J_{7,7a}$.[6] The position of the double bond in the cyclopentene ring (regiospecificity) is ascertained on the basis of the coupling assignement established by irradiation at the H_{7a} signal position.

The reaction of **1b** with cyclohexa-1,3-diene at 170° gave exclusively methyl *cis*-4a,7,8,8a-tetrahydronaphthalene-2-carboxylate (**14**), which was characterized by Pd-C dehydrogenation to give methyl naphthalene-2-carboxylate,[7] as well as by the D–A reaction with 4-phenyl-1,2,4-triazoline-3,5-dione[8] to give an adduct (**15**).

DISCUSSION

The observations shown in Table 4 clearly reveal the qualitative differences between the reactivities of the 1,3-dienes as a dienophile and as a diene in D–A reaction. Generally in D–A reaction,[10] introduction of Me group at 2- and 3-positions of a 1,3-diene is known to result in an increase of the reaction rate by stabilizing the transition state for adduct formation by electron donation as well as populating the s-*cis* conformation of the 1,3-diene. On the contrary, when a 1,3-diene behaves as a dienophile with inverse electron demand, the net effect of the Me substitution should reduce the dienophilicity owing to the difficulty of close approach of a diene, although the substitution should increase the electron density in the double bond by electron release. As expected, 2,3-dimethylbutadiene (**2a**) having no vinyl group reacted mainly as a diene component, and isoprene (**2b**) and butadiene (**2c**) in order decrease the potentiality as a diene function in the reaction.

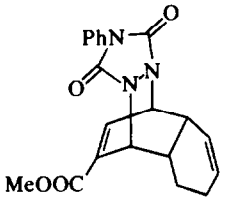
Although cyclopentadiene was found to be a very reactive dienophile in D–A reaction with inverse electron demand, for example, with hexachlorocyclopentadiene[2a] and 4a-azoniaanthracene ion,[2b] its reactivity as a diene component is also very well known. In view of these facts, it should be noted that cyclopentadiene

Table 4. Product ratios in the reaction with **1b**

Diene	6/7
2a	10
2b	1·3
2c	0·75
Cyclopentadiene	0[a]
Cyclohexadiene	0[b]

[a]The product in this case is **10**.

[b]The product is **14**.



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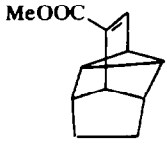

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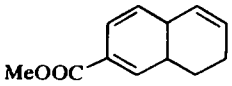

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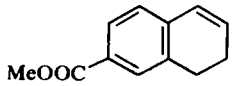

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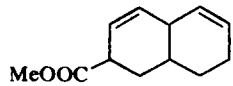


18

Fig 2.

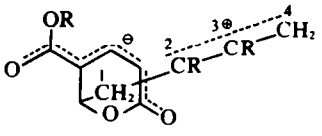
An attempted thermal cyclization of **14** into the tetracyclic compound (**16**) was unsuccessful, since it underwent disproportionation[9] into two compounds (**17** and **18**), the structure of the latter being tentatively assigned from the four olefinic protons in the NMR spectra and not further investigated.

reacted only as a dienophile in the case of the reaction with **1b**.

In the reaction with cyclohexadiene, the adduct **14** seems sterically too hindered to be constrained into a tetracyclic compound (**16**) by the second intramolecular D–A reaction.

The reaction to give the tetrahydrocoumarins (**6**) constitutes the first example of the D–A reaction in which a 2-pyrone derivative functions as a dienophile. In this reaction, the addition occurs only at its 5,6-double bond to give **6**. Tetrahydroisocoumarin (**8**), which might result from the addition to the 3,4-double bond of **1b**, was never detected. This fact does not contradict with the known selective nucleophilic attack[11] to the 6-position of **1b** and also with the net atomic charge of **1b** calculated by means of the extended Hückel method.[12]

It should be also noted that when **1b** behaves as a diene component, a 1,3-diene reacts always in such a manner as the residual ene part is situated remote from the initial 6-position of **1b**, as if the reaction would occur from the intermediate **19**. However, the intermediate with such a prominent charge separation cannot explain the product ratio in the case



19a: R = Me

Fig 3.

of **2a**, since the positive charge should be localized at the position 2 in **19a**, favourably leading to the product (**7a**). Analogous regiospecificity has been found and discussed in the reaction of **1b** with ketene acetals[6] or phenylacetylenes.[12]

The mechanistic details of the thermally induced conversion of **6** into **7** were not examined. But the [3,3]-sigmatropic reaction (Cope rearrangement) is thought to be a more favourable candidate than an alternative cycloreversion–cycloaddition process, because the decreased feasibility caused by the Me substitution is more lucidly interpreted by the large steric hindrance of the transition state in the case of [3,3]-sigmatropic reaction.

This reaction represents a one-step assemblage of a tricyclo[3.2.1.$0^{2,7}$]oct-3-ene ring system. From a practical point of view, we conclude that it is a better method of choice to use the ester of coumalic acid rather than the free acid since the former gives usually cleaner product.

EXPERIMENTAL

All m.ps were determined on a hot-stage microscope and are uncorrected as are b.p.s. IR spectra were recorded as neat film, unless otherwise specified, on a Shimadzu IR-27C spectrometer, and UV spectra were obtained in MeOH on a Hitachi EPS-2 spectrophotometer. Mass spectra (MS) were obtained with a Hitachi RMS-4 spectrometer at 70 eV. NMR spectra were measured on a JEOL C-60HL spectrometer in CCl_4, unless otherwise specified, using TMS as an internal standard. We are grateful to Dr. S. Kozima for the courtesy that made possible the use of this instrument. Decoupling experiments were achieved on a Varian HA-100 spectrometer (frequency sweep). 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).

Compound **1b** was prepared according to the reported method.[6] **12** was prepared by the modification of the method of Windholz[13] using 1,1,3,3-tetramethoxypropane and dimethyl malonate, m.p. 74–76° (lit.[14] m.p. 75–77°).

Reaction of **1b** *with* **2a**. A soln of **1b** (1·0 g) and **2a** (1·5 ml) in PhH (30 ml) was heated in a pressure bottle at 100° for 40 h. The solvent and excess of the diene were removed *in vacuo* to give the residue (1·695 g), which was shown on GLC analysis to be composed of **6a** and **7a** in a ratio of 10:1. Recrystallization from i-Pr_2O gave 795 mg of **6a**, m.p. 110–111·5°. Chromatographic separation of the mother liquor (SiO_2: PhH–AcOEt(9:1)) gave the first fraction **7a** (98 mg; 8%) and a further crop of **6a** (333 mg; total 75%).

Analytically pure sample of **6a** had m.p. 112·5–114·0°; IR (nujol): 1763, 1720, 1630 cm^{-1}; MS: *m/e* 236 (M^+, 23), 177 (18), 159(40), 91(20), 82(100), 67(68%). (Calc. for $C_{13}H_{16}O_4$: C, 66·08; H, 6·83. Found: C, 65·95; H, 6·94%).

After heating for 1 h in boiling *o*-Cl_2Ph, **6a** showed a single peak due to the starting material on GLC analysis.

7a had b.p.$_3$ 80–83°; IR: 1720, 1636 cm^{-1}; UV: λ_{max} 262 nm (log ϵ 3·99). (Calc. for $C_{12}H_{16}O_2$: C, 74·97; H, 8·39. Found: C, 75·06; H, 8·17%).

Reaction of **1b** *with* **2b**. A similar reaction of **1b** with **2b** gave **6b** and **7b** in a ratio of 4:3. Column chromatographic separation and distillation gave **6b** (34%), b.p.$_3$ 160–165°; IR: 1730, 1745(shoulder), 1635 cm^{-1}; MS: *m/e* 222(M^+, small), 163(28), 145(55), 68(100), (Calc. for $C_{12}H_{14}O_4$: C, 64·85; H, 6·35. Found: C, 65·06; H, 6·09%) and **7b** (28%), b.p.$_3$ 80–82°; IR: 1720, 1620 cm^{-1}; UV: λ_{max} 257 nm (log ϵ 4·08); MS: *m/e* 178(M^+, 65), 119(100), 91(83%). (Calc. for $C_{11}H_{14}O_2$: C, 74·13; H, 7·92. Found: C, 74·25; H, 7·74%).

A pure sample of **6b** showed a single peak due to the starting material on GLC column at 170°, but, when heated for 1 h in boiling *o*-Cl_2Ph a small amount of **7b** was detected in addition to unchanged **6b** on GLC analysis.

Reaction of **1b** *with* **2c**. (a) The reaction of **1b** with **2c** was effected at 100° for 30 h. Careful GLC analysis at a column temp of 120° showed **6c** and **7c** in a ratio of 3:4. Chromatographic separation and further purification by preparative GLC at 120° gave **6c** (16%); IR: 1770, 1730, 1635 cm^{-1}; MS: *m/e* 208(M^+, 55), 149(29), 126(55), 105(94), 54(100%), (Calc. for $C_{11}H_{12}O_4$: C, 63·45; H, 5·81. Found: C, 63·40; H, 5·71%), and **7c** (18%); IR: 1705, 1620 cm^{-1}; UV: λ_{max} 250 nm (log ϵ 4·01); MS: *m/e* 164(M^+, 55), 105(100), 77(28%). (Calc. for $C_{10}H_{12}O_2$: C, 73·14; H, 7·37. Found: C, 73·27; H, 7·37%).

When the reaction mixture was distilled at 4 mmHg (bath temp about 190°), the distillate showed on GLC analysis the peaks of **7c** and **9**, but the peak of **6c** disappeared. Methyl 4-vinylcyclohexa-2,6-diene-1-carboxylate (**9**) was obtained by preparative GLC; IR: 1730, 1640 cm^{-1}; UV: λ_{max} 267 nm (log ϵ 3·49); MS: *m/e* 164(M^+, 43), 105(100), 77(44%); NMR: δ 6·35(d × t, $J_{1,3}$ = 9·9 Hz, H_2), 5·7(m, H_3), 2·25(m, H_4), 2·43(m, 2 × H_5),

6·80(d × t, H_6), 5·8(m, H–C= in vinyl), 4·85 and 5·10 (m, $\begin{matrix} H \\ \diagdown \\ H \end{matrix}$>C= in vinyl). (Calc. for $C_{10}H_{12}O_2$: C, 73·14; H, 7·37. Found: C, 73·36; H, 7·16%).

When a sample of **6c**, the purity of which had been checked with GLC (120°), was injected into a GLC column at 170°, three peaks of **9**, **7c**, and **6c**, in order of elution, were detected. Similarly, **9** showed two peaks of **9** and **7c**, and **7c** showed no change.

(b) A soln of **1b** (2·0 g) and **2c** (5 ml) in PhH (20 ml) was heated at 170° for 40 h. Distillation gave only **7c** (1·06 g; 50%), b.p.$_3$ 88–90°.

Reaction of **1b** *with cyclopentadiene.* A soln of **1b** (700 mg) and cyclopentadiene (0·5 g) in PhH (10 ml) was heated under reflux for 3 h. After removal of the solvent and dicyclopentadiene, recrystallization from i-Pr_2O gave **10** (723 mg; 72%); m.p. 123–124°; IR (Nujol): 1770, 1720, 1625 cm^{-1}; UV: λ_{max} 235 nm (log ϵ 3·53); MS: *m/e* 220(M^+, small), 176(14), 155(58), 117(37), 66(100%). (Calc. for $C_{12}H_{12}O_4$: C, 65·44; H, 5·49. Found: C, 65·38; H, 5·56%).

Catalytic hydrogenation of **10** over Pd-C in MeOH resulted in the uptake of two moles of H_2, giving the tetrahydro product (65%); m.p. 85–86°; IR (Nujol): 1750, 1730(shoulder) cm^{-1}; NMR ($CDCl_3$): δ 4·98(d × d, O–CH, 3·6 Hz), 3·74(s, $COOCH_3$), 1·5–3·3(12 H, m, other protons). (Calc. for $C_{12}H_{16}O_4$: C, 64·27; H, 7·19. Found: C, 64·04; H, 7·25%).

Reaction of **11** *with cyclopentadiene.* A soln of **11** (500 mg) and cyclopentadiene (2 ml) in PhH (15 ml) was refluxed for 3 h. Evaporation of the solvent and dicyclopentadiene gave **13** (690 mg; 95%); m.p. 81–82°; IR (Nujol): 1740, 1720, 1615 cm^{-1}; MS: *m/e* 220(M^+, small), 176, 145, 117(100%), 66. (Calc. for $C_{12}H_{12}O_4$: C, 65·44; H, 5·49. Found: C, 65·62; H, 5·52%).

Reaction of **1b** *with cyclohexa-1,3-diene.* A soln of **1b** (4·2 g) and cyclohexa-1,3-diene (3·0 g) in PhH (10 ml) was heated at 100° for 21 h. GLC analysis showed a single product. Distillation gave **14** (2·75 g; 55%), b.p.$_4$ 130–135°; IR: 1725, 1645, 1595 cm^{-1}; UV: λ_{max} 288 nm (log ϵ 3·60); MS: *m/e* 190(M^+, 47), 131(100), 91(55%); NMR: δ 6·63(d, 5·1 Hz, H_1), 6·15(d × t, 9·3 Hz, H_3), 5·5(d × d, 4·2 Hz, H_4), 5·58(m, H_5 and H_6), 1·14–2·20(m, 2 × H_7 and 2 × H_8), 2·6(m, H_9), 2·9(m, H_{10}), 3·68(s, $COOCH_3$). (Calc. for $C_{12}H_{14}O_2$: C, 75·76; H, 7·42. Found: C, 75·88; H, 7·39%).

Pd–C *dehydrogenation of* **14**. The mixture of **14** (200 mg) and 5% Pd–C (50 mg) was heated at 200–220° for 3 h. Extraction with CH_2Cl_2, filtration, and evaporation of the solvent gave methyl naphthalene-2-carboxylate, m.p. 75–76° (lit.[7] m.p. 78–79°), which showed the spectroscopic data identical with those of the literature.[7]

Phenyltriazoline adduct (**15**). A soln of **14** (330 mg) and 4-phenyl-1,2,4-triazoline-3,5-dione (prepared from 660 mg of 4-phenylurazole[8]) in THF (10 ml) was allowed to react overnight at room temp. The resulting crystals (**15**), after recrystallization from THF, had m.p. 204–205°; IR (Nujol): 1780, 1710 (broad), 1620, 1595 cm^{-1}; NMR ($CDCl_3$): δ 5·20(d × d, $J_{1,9}$ = 2·4 Hz, H_1), 6·98(d × d, $J_{1,3}$ = 1·8 Hz, $J_{3,4}$ = 6·0 Hz, H_3), 2·8(m, H_9 and H_{10}), 5·40(H_5), 5·75(H_6; H_7 and H_8 constitute perturbed AB system (J_{AB} = 10 Hz)), 1·8 (m, 2 × H_7 and 2 × H_8), 3·62(s, $COOCH_3$), 7·13(m, 5 × Ar–H). (Calc. for $C_{20}H_{17}N_3O_4$: C, 65·74; H, 5·24; N, 11·50. Found: C, 65·62; H, 5·41; N, 11·24%).

Thermal treatment of **14**. A sample of **14** (100 mg) was heated in a small sealed tube at 200° for 1 h. GLC analysis showed a complete conversion into **16** and **17** in a ratio of about 1 : 1. These were fractionated by preparative GLC.

The first eluate (**16**); UV: end absorption only; MS: *m/e* 192(M^+), 160, 133, 132, 91(100%); NMR: δ 6·4(m, 4 × olefinic proton), 2·1–3·0(m, 9H), 3·70(s, $COOCH_3$).

The second eluate (**17**); m.p. 34–35°; UV: λ_{max} 226, 289 nm; MS: *m/e* 188(M^+), 157, 129(100%); NMR: δ 7·68(s, H_1), 7·8(d × d, 1·6 Hz, H_3), 6·95(d × d, 6·8 and 1 Hz, H_4), 6·42(d × t, 11·4, 1·5, and 1·5 Hz, H_5), 6·01(d × d, 11·4 and 4·5 Hz, H_6), 2·6–3·0(m, 2 × H_7), 2·1–2·5(m, 2 × H_8), 3·80(s, $COOCH_3$).

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