case; on electron impact an independently synthesized sample of **12**[19] gave an ion at *m/e* 98 as its base peak.

Conclusion

The arguments presented above lead to the conclusion that at least part of the mass 84 ions from compound **2** arise through a double McLafferty rearrangement. The evidence from deuterium labeling supports a mechanism for the formation of these ions which has the specificity associated with the McLafferty rearrangement and excludes any simple mechanism involving prior ring opening of the bicyclic system. The structure of the mass 84 ion has not been established unambiguously, but it clearly is not a keto structure and may most probably be assigned as an enol. We thus find that the rearrangement process to form the mass 84 ion from compound **2** meets all the tests for the McLafferty rearrangement, and it seems safe to conclude that it is in fact a McLafferty rearrangement.

In the case of compound **4** the evidence for the formation of the mass 98 ion by a double McLafferty rearrangement is less clear-cut. However, the limited deuterium labeling evidence available does exclude the most obvious ring-opening pathway to this ion, and the evidence from metastable peaks is consistent with an enolic structure for it. We thus conclude that the evidence for compound **4** is consistent with (but does not demand) formation of the mass 84 ion by a double McLafferty rearrangement.

The observation that McLafferty rearrangement can and does occur in at least one compound where the angle τ between the plane of the carbonyl group and the γ-hydrogen atom is as high as 50° indicates that this particular steric effect is of less importance than had previously been calculated[7] in determining occurrence of rearrangement. Clearly further theoretical investigations are needed before we can be said fully to understand this remarkable reaction.

(19) J. M. Conia and F. Leyendecker, *Bull. Soc. Chim. Fr.*, 830 (1967).

Experimental Section

All mass spectra were recorded with an AEI-MS-902 double focusing mass spectrometer (heated inlet 225°, ion source temperature 50°). Metastable transitions in the first field-free region were observed with the aid of the metastable defocusing technique.[20] All spectral measurements were performed on substances which were purified by vapor phase chromatography (vpc) (8 ft × 0.25 in. SE-30, 20% on 60–80 mesh Chromosorb P or 8 ft × 0.25 in. Apiezon L, 10% on 5% H_3PO_4 washed 60–80 mesh Chromosorb W).

Deuterated Compounds. Deuterated compounds were prepared by suitable modifications of published procedures.[9-11] The α-deuterated compounds **8** and **11** were prepared by deuterium exchange of the parent compound. The β-deuterated compound **9** was prepared by diazo insertion[9] into cyclohexanone-*2,2,6,6-d*$_4$, and the γ-deuterated compound **10** was similarly prepared by diazo insertion into cyclohexanone-*3,3,5,5-d*$_4$.[8a]

Acknowledgment. We thank Dr. R. D. Sands for a gift of 1-carboxybicyclo[4.3.1]nonan-9-one, Dr. E. Warnhoff for a gift of bicyclo[5.3.1]undecan-11-one, and Dr. A. W. Herriott for assistance with a deuterium exchange experiment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(20) M. Barber and R. Elliott, 12th Annual Conference on Mass Spectrometry, Montreal, Canada, 1964, ASTM E-14; K. R. Jennings, *J. Chem. Phys.*, 43, 4176 (1965).

Molecular Design by Cycloaddition Reactions. IV.[1] Cycloaddition Reactions of Cycloheptatriene with 2-Pyrone Derivatives

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Abstract: Cycloaddition reactions of cycloheptatriene with coumalic acid and its ester afforded two bridged tetracycloundecadiene derivatives **3** and **4** together with [6 + 4] cycloadduct **5**, respectively. Similar reactions with 4,6-dimethylcoumalic acid and its ethyl ester gave only compounds **11**, and **12**, respectively. The structures of these cage adducts were deduced from spectral evidence.

Among Diels–Alder reactions of 2-pyrone derivatives with a variety of dienophiles, those with acetylenic compounds have been reported to give benzene derivatives by loss of carbon dioxide from the intermediate adducts.[2] In the case of alkyl coumalate, the reactions of electron-rich dienophiles (*i.e.*, dienophiles with inverse electron demand) give readily cycloadducts as suggested by extended Hückel MO calculation of the net charge distribution on methyl coumalate.[3] Recently, double Diels–Alder reactions of coumalic acid with 1,3-dienes have been documented.[4] However, similar reactions with conjugated trienes

(1) Part III of this series, "Studies of Bridged Heterocycles:" T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, *J. Chem. Soc., Perkin Trans. 1*, 2750 (1973).
(2) H. Behringer and P. Heckmaier, *Chem. Ber.*, 102, 2835 (1969).
(3) J. A. Reed, C. L. Schilling, Jr., R. F. Tarcin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, 34, 2188 (1969).
(4) (a) T. Imagawa, M. Kawanishi, and K. Sisido, *Chem. Commun.*, 1292 (1971); (b) *ibid.*, 288 (1972).

seem not to have been scrutinized. In addition, a considerable interest has been drawn in the cycloaddition reactions of conjugated polyenes with versatile diene components based on orbital symmetry consideration, and some competitive reactions have been observed.[5]

As a continuation of our previous works,[1,6] we have investigated the Diels–Alder reactions of coumalic acid derivatives as a diene component with cycloheptatriene as a conjugated triene from a standpoint of a molecular design for constructing a new carbon skeleton.

Results and Discussion

Coumalic acid (**2a**) was heated with excess amounts of cycloheptatriene (**1**) in xylene at 180° in a sealed tube affording decarboxylated 1:1 adducts (**3a** and **4a**) together with a 1:1 adduct (**5a**) in total yields of 12–15% (the ratio of 5:5:1) after recovery of a considerable amount of cycloheptatriene. Glpc monitoring of the reaction mixture obtained from similar reaction of excess amounts of **1** and methyl coumlate (**2b**) revealed the decrease in the formation of **5b** in proportion to the increase in the reaction times as shown in Table I.

Scheme I

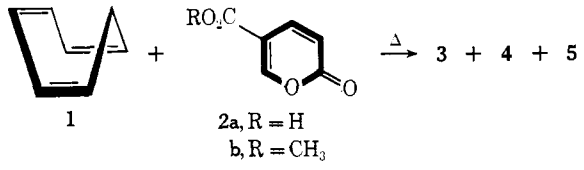


Table I. The Product Distribution (%) for the Reaction of Cycloheptatriene with Methyl Coumalate at 170° at Various Reaction Times

Compd no.[a]	Hours 3	4	5	6.5	9
3b	21	23	25	27	31
4b	56	57	57	57	58
5b	23	20	19	16	11

[a] Compounds **3b–5b** were identical with samples prepared by treatments of compounds **3a–5a** with diazomethane, respectively.

Compound **3a** showed a strong carbonyl absorption at 1670 cm^{-1} in the ir spectrum suggesting the presence of a cyclopropanecarboxylic acid group.[7] The laser–Raman spectrum of **3a** showed a carbon–carbon double bond absorption at 1634 cm^{-1}.

Compound **4a** showed absorptions at 1650 (C=O) cm^{-1} in the ir spectrum and at 1640 and 1624 cm^{-1} (C=C) in the laser–Raman spectrum indicating the presence of an α,β-unsaturated carbonyl group. The uv spectra showed clearly differences between **3a** (208 nm, log ϵ 3.71) and **4a** (255 nm, log ϵ 3.82). The uv maximum in **4a** indicates the presence of an α,β-cyclopropylacrylic ester chromophore.[4] The nmr spectrum consisted of four olefinic protons centered at τ 4.05 (3 H) and 4.68 (1 H), seven protons centered at

(5) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143 (1970).
(6) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc. C*, 2142 (1971); 783 (1972).
(7) The carbonyl absorption such as cyclopropane carboxylic acid is reported to appear at 1683 cm^{-1}: L. Crombic, L. Crossley, Jr., and D. A. Mitchard, *J. Chem. Soc.*, 4957 (1963).

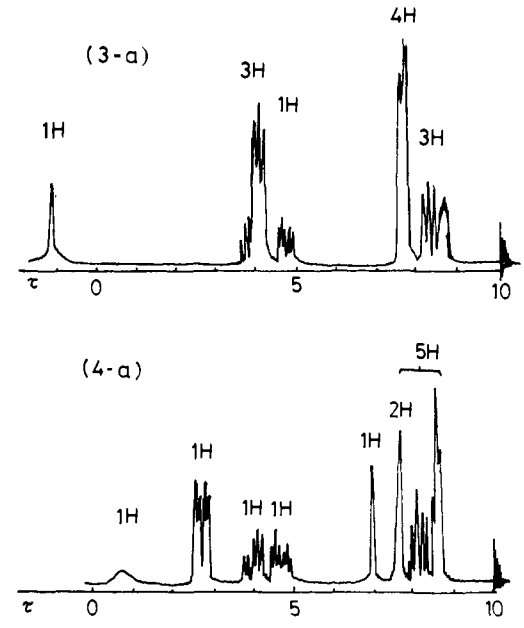
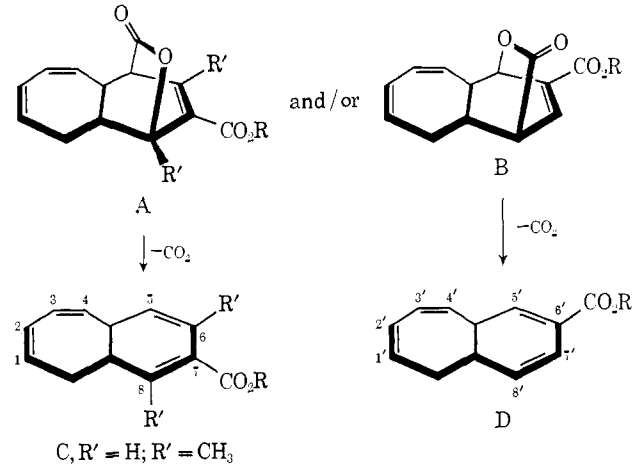


Figure 1. Nmr of **3a** and **4a**.

τ 7.70 (4 H) and 8.30 (3 H), and one proton of a carboxylic acid (exchanged by D_2O) at τ −1.6 in compound **3a** and of two olefinic protons centered at τ 4.00 (1 H) and 4.60 (1 H) due to a disubstituted double bond, one olefinic proton at τ 2.69 attributable to an α,β-unsaturated double bond, eight protons in the range of τ 6.95–8.65, and one proton of a carboxylic acid (exchanged by D_2O) at τ 0.80 in compound **4a** as shown in Figure 1. The fragmentations of mass spectra of **3a** and **4a** were very similar to each other: *m/e* 188 (M^+), 143 (M − COOH, base peak).

These data and elemental analyses indicated the presence of two disubstituted double bonds, five ring protons, one methylene group, and one carboxylic acid group attached to a cyclopropane moiety in **3a** and of one disubstituted double bond, one α,β-unsaturated carboxylic acid attached to a cyclopropane moiety, six ring protons, and one methylene group in **4a**. On the other hand, the mechanistic speculation leads to the consideration on the intermediacy of C and/or D by the [4 + 2] cycloaddition of **1** and **2** followed by decarboxylation.

Scheme II



Among the possible cage structures E–I constructed

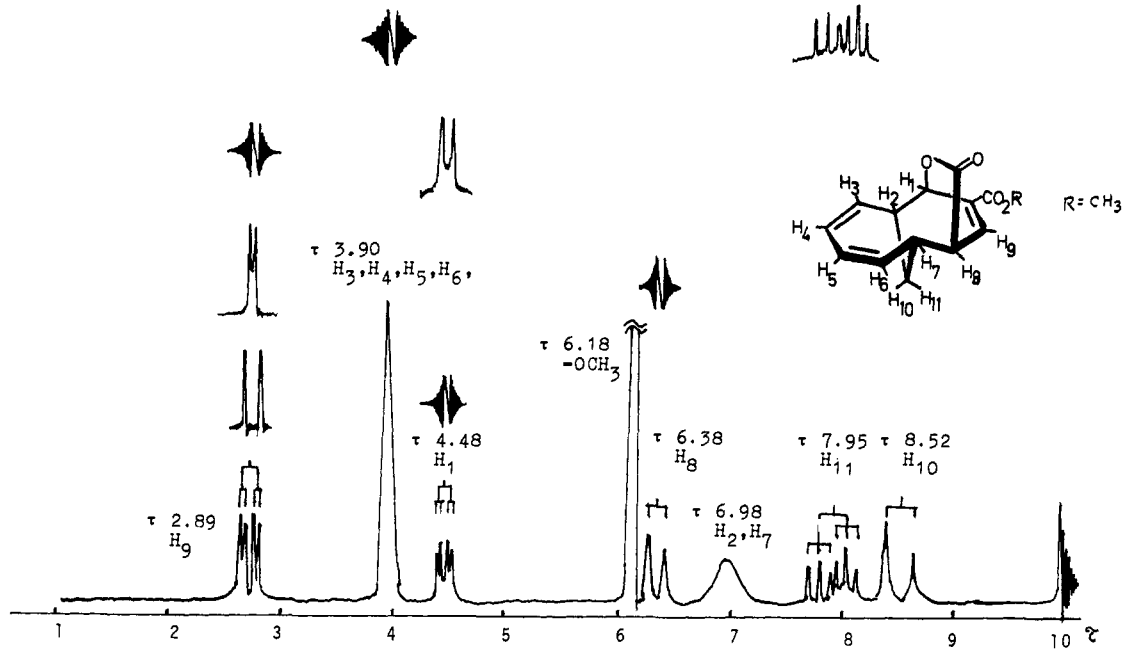
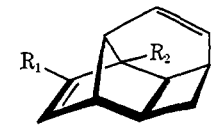


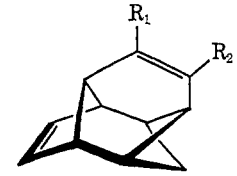
Figure 2. Nmr spectrum of **5b**.

by the second intramolecular [4 + 2] cyclization of the intermediacy of C and/or D, only structure I was satisfactory for **4** on the above mentioned spectral inspections.

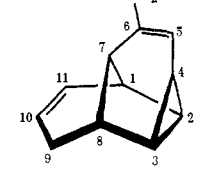
Scheme III



E, $R_1 = CO_2R$; $R_2 = H$(1′-8′, 4′-7′ bonding)
F, $R_2 = CO_2R$; $R_1 = H$(1-8, 4-7 bonding)



G, $R_1 = CO_2R$; $R_2 = H$(1′-8′, 2′-5′ bonding)
H, $R_2 = CO_2R$; $R_1 = H$(1-8, 2-5 bonding)



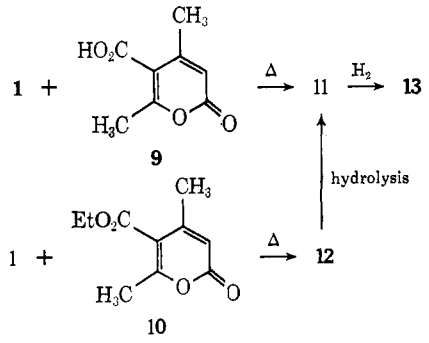
I, **4a**, R = H
b, R = CH_3(4-5, 3-8 bonding)

The structure of a minor product **5a** was readily assigned to be the [6 + 4] adduct from the ir (two carbonyl absorptions at 1680 and 1735 cm^{-1}) and the nmr of the methyl ester **5b**, which was obtained on treatment of **5a** with diazomethane: τ 2.89 (1 H, dd, J = 7.0 and 2.0 Hz), 3.90 (4 H, s), 4.48 (1 H, dd, J = 5.0 and 2.0 Hz), 6.18 (3 H, s, OCH_3), 6.38 (1 H, d, J = 7.0 Hz), 6.98 (2 H, br s), 7.95 (1 H, dt, J = −15.0 and 5.0 Hz), and 8.52 (1 H, d, J = −15.0 Hz). Spin decoupling experiments (see Figure 2) verified the presence of the 1,3-diene, α,β-unsaturated carbonyl, and δ-lactone moieties in compound **5**. The mass spectrum of **5a** was quite different from those of **3a** and **4a**; the most abundant ion (100%) is due to the C_7H_8 (m/e 92). The pyrolysis of adduct **5a** at 230° under reduced pressure afforded cycloheptatriene which was detected by glpc. This thermal behavior suggested the retro-type reactivity of **5a** and was in good accordance with the fragmentations in the mass spectrum (*i.e.*, **5** was a kinetically controlled product), and no Cope-type rearrangement products were observed in the cycloaddition reactions. Under these thermal conditions, **3a** and **4a** showed no interconversion with each other.

For further confirmation of the structures of **3a** and **3b**, similar reaction of 4,6-dimethylcoumalic acid (isodehydroacetic acid, **9**) with cycloheptatriene (**1**) in a sealed tube at 200° was carried out and only one decarboxylated 1:1 adduct (**11**) was obtained in 16% yield. Compound **11** showed a strong carbonyl absorption at 1665 cm^{-1} in the ir spectrum. This absorption is very similar to that of compound **3a**. The nmr spectrum consisted of four olefinic protons centered at τ 4.05 (3 H, m) and 4.75 (1 H, m), eight protons centered at τ 7.65 (4 H, m) and 8.65 (4 H, s), three protons due to a methyl group at τ 9.10 (s), and one proton of a carboxylic acid (exchanged by D_2O) at τ − 1.50 (br s). The uv spectrum of compound **11** (215 nm, log ε 3.80) is very similar to that of compound **3a** indicating the skeletal resemblance to each other. Similar reaction of ethyl 4,6-dimethylcoumalate (ethyl isodehydroacetate, **10**) with **1** give also only one decarboxylated 1:1 adduct (**12**) in 25% yield. Hydrolysis of **12** afforded **11**. Hydrogenation of **11** gave **13** in quantitative yield. The nmr spectrum of **13** showed no olefinic protons but two methyl signals at τ 8.70 and 8.83 both as a singlet.

Finally, the complete structures of compounds **3a**, **3b**, **11**, and **12** were established by X-ray diffraction

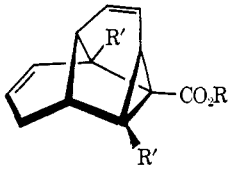
Scheme IV



analysis[8] of compound **14** which was prepared by lithium aluminum hydride reduction of **11** followed by *p*-bromobenzoylation. The structure of **14** is depicted in Figure 3.[8]

Thus, structure **13** was assigned as the 2-substituted 1,3-dimethyltetracyclo[5.4.0.0^{2,4}.0^{3,8}]undeca-5,10-diene derivative. Based on the above spectral and X-ray data, the cage compounds **3a**, **3b**, **11**, and **12** are determined as 2-carboxy-, 2-carbomethoxy-, 1,3-dimethyl-2-carboxy-, and 1,3-dimethyl-2-carboethoxytetracyclo-[5.4.0.0^{2,4}.0^{3,8}]undeca-5,10-dienes, respectively.

Scheme V



3a, R′ = H; R = H
b, R′ = H, R = CH_3
11, R′ = CH_3; R = H
12, R′ = CH_3; R = C_2H_5

From the above results, the formation of these cage compounds might be explained by the second intramolecular [4 + 2] cyclization after isomerization of intermediacy of C and D in the most stereochemically favorable manner. A possible pathway for the formation of **11** and **12** has been suggested by Kawanishi, *et al.*:[9] cycloreversion of C (R′ = Me) might proceed *via* *all-cis*-3-alkoxycarbonylcycloundecapentaene followed by 1, 5 hydrogen shift to give 4-alkoxycarbonylcycloundecapentaene which cyclizes into a bicyclic tetraene and then subjects to the second intramolecular cycloaddition. Unprecedented formation of these cage compounds is also another possibility, but we are further investigating the chemistry of cycloundecapentaene derivatives and a role played by the substituent.[10]

Experimental Section[11]

Cycloaddition Reaction of Coumalic Acid (2a) with Cycloheptatriene. A solution of coumalic acid (**2a**) (5 g, 0.036 mol) and cycloheptatriene (6.6 g, 0.072 mol) in xylene (30 ml) was heated in a sealed tube at 180° for 5 hr. The solvent was removed under reduced pressure and the residue was separated by column chromatography (silica gel with benzene as an eluent) to give three products **3a**, **4a**, and **5a** in total yields of 12–15% with the ratio of 5:5:1.

3a: mp 172–173° (from chloroform–*n*-hexane); ir (KBr) 1670 (C=O) cm^{-1}; Raman 1634 (C=C) cm^{-1}; uv (EtOH) 208 nm (log ϵ 3.71); nmr ($CDCl_3$) τ −1.60 (s, 1 H), 4.05 (m, 3 H), 4.68 (m, 1 H), 7.70 (m, 4 H), 8.30 (m, 3 H).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.59.

4a: mp 278–281° (from chloroform–*n*-hexane); ir (KBr) 1650 (C=O) cm^{-1}, Raman 1640 and 1624 (C=C) cm^{-1}; uv (EtOH) 255 (log ϵ 3.82) nm, nmr ($CDCl_3$) τ 0.80 (br s, 1 H), 2.69 (dd, 1 H, J = 6.0 and 2.0 Hz), 4.00 (m, 1 H), 4.60 (m, 1 H), 6.95–8.65 (m, 8 H).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.52; H, 6.43. Found: C, 76.55; H, 6.45.

5a: mp 226–229° (from chloroform); ir (KBr) 1735 and 1680 (C=O) cm^{-1}; uv (EtOH) 215 (log ϵ 4.01), 230 (4.01), 250 (3.83), 260 (3.65) nm.

Anal. Calcd for $C_{13}H_{13}O_4$: C, 67.23; H, 5.21. Found: C, 67.17; H, 5.26.

Methyl Ester of Adducts 3a, 4a, and 5a. To a solution of a mixture of **3a–5a** (1 mmol) in chloroform (15 ml) was added an ethereal diazomethane (1 mmol) at 0°. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using *n*-hexane as an eluent to give the methyl esters **3b**, **4b**, and **5b**, respectively, in quantitative yields.

3b: n^{22}D 1.5389; ir (neat) 1720 (C=O), 1625 (C=C) cm^{-1}; nmr (CCl_4) τ 3.70–4.20 (m, 3 H), 4.50–4.90 (m, 1 H), 6.42 (s, 3 H), 7.30–8.90 (m, 7 H).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.22; H, 6.98. Found: C, 77.44; H, 6.80.

4b: n^{22}D 1.5526; ir (neat) 1710 (C=O), 1625 (C=C) cm^{-1}; nmr (CCl_4) τ 3.00 (dd, 1 H, J = 6.0 and 2.0 Hz), 3.80–4.20 (m, 1 H), 4.50–4.80 (m, 1 H), 6.35 (s, 3 H), 7.00 (br s, 1 H), 7.50–8.80 (m, 7 H.)

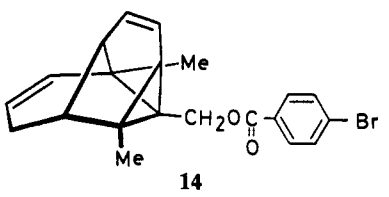
Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.22; H, 6.98. Found: C, 77.41; H, 6.83.

5b: mp 149–151° (fom *n*-hexane); ir (KBr) 1750, 1720 (C=O), 1635 (C=C) cm^{-1}; nmr ($CDCl_3$) τ 2.89 (dd, 1 H, J = 7.0 and 2.0 Hz), 3.90 (s, 4 H), 4.48 (dd, 1 H, J = 5.0 and 2.0 Hz), 6.18 (s, 3 H), 6.38 (d, 1 H, J = 7.0 Hz), 6.98 (s, 2 H), 7.95 (dt, 1 H, J = −15.0 and 5.0 Hz), 8.52 (d, 1 H, J = −15.0 Hz).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.48; H, 5.60.

Hydrogenation of Compound 3a. A solution of **3a** (0.5 g) in methanol (20 ml) was hydrogenated over PtO_2 (50 mg) for 1 day at room temperature. The catalyst was then separated by filtration and solvent was removed under reduced pressure. The residue was recrystallized from chloroform–*n*-hexane to give colorless needles in quantitative yield: mp 192–193°, ir (KBr) 1680 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.97; H, 8.52.



14

Figure 3.

(8) We are very grateful to Dr. H. Koyama of Shionogi Research Laboratory, Osaka, for determining structure **14** by X-ray analysis. Full analytical details will be presented elsewhere.

(9) We are grateful to Professor M. Kawanishi of Kyoto University for communicating these results prior to publication. While this paper was submitted, a report of the cycloaddition reaction of **1** with **9** has been reported independently by T. Imagawa, N. Sueda, and M. Kawanishi, *Chem. Lett.*, 417 (1973). It is to be noted that the structural elucidation of the tetracycloundecadiene skeleton has been confirmed by the europium shift reagent and decoupling technique of the nmr.

(10) It is surprising that there is little study on the thermal behavior and interconversions of the compound of the formula $(CH)_nCH_2$ ($n > 10$): L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972).

(11) Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 elemental analyser. The uv spectra were determined with a Jasco Model ORD/UV-5 recorder. The nmr spectra were taken with a JE-Model C-60-XL nmr spectrometer with TMS as an internal standard, and chemical shifts are expressed in τ values. The ir spectra were taken with a Jasco Model IR-S spectrophotometer. The laser-Raman spectra were taken with a Jasco Model R-300 spectrophotometer. The glpc was done isothermally on a Hitachi K-23 gas chromatograph with a 3 ft, 5 wt % SE-30 (Chromosorb G-NAW) column (flame-isomerization detector). A Varian aerograph Model 700 hydrogen flame ionization detector, nitrogen carrier gas, fitted with a 5 ft × 1/8 in. column (containing 12% Dow Corning Silicone oil 550 in 80–100 Chromosorb W), was used for preparative separations.

Hydrogenation of Compound 4a. A solution of **4a** (0.5 g) in methanol (20 ml) was hydrogenated over PtO_2 (50 mg) for 8 hr at room temperature. The catalyst was separated by filtration and the solvent was removed under reduced pressure. The residue was recrystallized from chloroform–*n*-hexane to give colorless prisms in quantitative yield: mp 239–241°; ir (KBr) 1675 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.03; H, 8.45.

Cycloaddition of Methyl Coumalate (2b) with Cycloheptatriene. A solution of methyl coumalate (**2b**) (5.6 g, 0.036 mol) and cycloheptatriene (6.6 g, 0.072 mol) in xylene (30 ml) was heated at 170° at various reaction times. The reaction mixture was evaporated under reduced pressure and analyzed by preparative glpc. The results are listed in Table I.

Pyrolysis of Adduct 5a. In the reaction flask connected with a trap immersed into Dry Ice–acetone, adduct **5a** (0.1 g) was heated under reduced pressure (1 mm) at 230° for 2 hr. The volatile material was collected on a cold finger at −30°, in which cycloheptatriene was detected by glpc inspection and much polymeric material remained in the pot.

Cycloaddition of 4,6-Dimethylcoumalic Acid (9) with Cycloheptatriene. A solution of **9** (5 g, 0.03 mol) and cycloheptatriene (5.4 g, 0.06 mol) in xylene (30 ml) was heated in a sealed tube at 200° for 2 days. Then the mixture was evaporated under reduced pressure and purified by silica gel chromatography using benzene to give **11** in 16% yield: mp 235–237° (in a sealed tube); ir (KBr) 1665 (C=O), 1623 (C=C) cm^{-1}; nmr ($CDCl_3$) τ −1.50 (br s, 1 H), 4.05 (m, 3 H), 4.75 (m, 1 H), 7.50–7.80 (m, 4 H), 8.65 (s, 4 H), 9.10 (s, 3 H, CH_3); Raman 1645, 1630 (C=C) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.46.

Cycloaddition of Ethyl 4,6-Dimethylcoumalate (10) with Cycloheptatriene. A solution of ethyl 4,6-dimethylcoumalate (**10**) (4.9 g, 0.025 mol) and cycloheptatriene (4.6 g, 0.05 mol) in xylene (25 ml) was heated in a sealed tube at 200° for 2 days. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using benzene to give **12** as a colorless oil in 25% yield.

A mixture of **12** (900 mg), 20% aqueous KOH (15 ml), and 20% methanolic KOH (15 ml) was refluxed for 20 hr. The solvent was removed under reduced pressure and then the residue was added with water (10 ml) and with 10% HCl (10 ml). Then pale yellow precipitate was filtered and recrystallized from chloroform to give colorless needles (**11**) in 40% yield, mp 235° (in a sealed tube), which was identified by mixture melting points with an authentic sample (**11**).

Hydrogenation of 11. A solution of **11** (108 mg, 0.5 mmol) in 20 ml of methanol was hydrogenated over 5% Pd-C (50 mg) for 0.5 hr at room temperature. The catalyst was then separated by filtration and solvent was removed under reduced pressure. The residue was recrystallized from chloroform–*n*-hexane to give colorless needles (**13**) in quantitative yield: mp 272–274° (in a sealed tube); ir (KBr) 1660 (C=O) cm^{-1}; nmr ($CDCl_3$) τ 0.00 (br s, 1 H), 8.70 (s, 3 H, CH_3), 8.83 (s, 3 H, CH_3), 7.50–9.00 (m, 13 H).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.61; H, 9.01.

Preparation of Compound 14. A mixture of **12** (2 mmol) and lithium aluminum hydride (4 mmol) in dry ether (20 ml) was stirred for 1 day. After addition of water, the solution was extracted with ether and the solvent was evaporated to dryness. The crude compound was used in the following reaction without further purification. A solution of the crude compound and *p*-bromobenzoyl chloride (2 mmol) and a drop of dry pyridine was stirred for 1 day at room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using *n*-hexane to give *p*-bromobenzoate (**14**) in 50% yield: colorless prisms; mp 60–61° (from *n*-hexane); ir (KBr) 1705 (C=O), 1620 (C=C) cm^{-1}; nmr ($CDCl_3$) τ 2.25 (d, 2 H, J = 9.0 Hz), 2.55 (d, 2 H, J = 9.0 Hz), 4.25 (m, 3 H), 4.75 (m, 1 H), 5.60 (s, 3 H), 7.70 (m, 3 H), 8.52 (dd, 1 H, J = 6.0 and 3.0 Hz), 8.76 (s, 4 H), 9.20 (s, 3 H).

Anal. Calcd for $C_{21}H_{21}O_2Br$: C, 65.46; H, 5.49. Found: C 65.44; H, 5.51.

Cyclization of 4-(*trans*-3,7-Octadienyl)-3-methyl-2-cyclohexen-1-ol and 4-(*trans,trans*-7-Methyl-3,7,11-dodecatrienyl)-3-methyl-2-cyclohexen-1-ol[1]

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Abstract: The trienol **3** has been synthesized from the substituted acetylene **9** (prepared as outlined in Scheme I) according to Scheme II, *i.e.*, **9** → **10** → **11a** → **3**. Similarly, the tetraenol **4** has been synthesized as depicted in Scheme III. Cyclization of trienol **3** with formic acid, followed by cleavage of the resulting formate esters, gave the tricyclic alcohol **14** as the major product, along with some of the epimer **15**. The cis,anti,trans configuration was established by reductive conversion to the hydrocarbon **18** which was compared with authentic material produced by reduction of the known diketone **26** *via* the bisthioketal **27**. Cyclization of the tetraenol **4** with formic acid (1 min) led to the tetracyclic substance **19** along with tricyclic material **23**. The latter material on further treatment with formic acid (20 min) was converted mainly into the C/D cis tetracyclic substance **22**. The structures and configurations of these tetracyclic products were proved by comparison of their derivatives with authentic materials produced by partial synthesis from natural steroids.

In 1966 the use of nonenzymatic cyclizations of allylic alcohol functionalized polyenes was extended to the stereospecific production of tricyclic systems, as exemplified by the synthesis of fichtelite.[2] This achievement, as well as a significant improvement in the ease and stereoselectivity of introducing trans trisubstituted olefinic bonds into cyclization substrates,[3] led imme-

(1) This represents part of a general study of nonenzymic biogenetic like olefinic cyclizations. For the previous paper of this series, see D. R. Morton and W. S. Johnson, *J. Amer. Chem. Soc.*, **96**, in press.

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