193. Reactions of Tricyclic Vinylcyclopropanes with Metal Carbonyls

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Summary

Irradiation of the tricyclic vinylcyclopropane **3** and Fe(CO)$_5$ resulted in the formation of the σ,π-bonded iron complex **7** and the π,π-bonded iron complex **8** *(Scheme 2).* Complex **8** was easily degraded with silica gel to give hydrocarbon **9**, which reproduced **8** by photolysis in the presence of Fe(CO)$_5$. Photolysis of **7** afforded a mixture of **3** (23%), **9** (27,5%), and three other hydrocarbons. Oxidative degradation of **7** with ceric ammonium nitrate in methanol gave the dimethoxyhydrocarbon **10**. – The tricyclic hydrocarbon **3** isomerized thermally to the bicyclic hydrocarbon **11** (with CH$_3$–C(9) in an *exo* position) *via* a homosigmatropic [1,5]-H-shift. On the other hand, **3** was converted into the other isomer **14** (with CH$_3$–C(9) in an *endo* position) by action of Mo(CO)$_6$ or TsOH. Both isomers **11** and **14** reacted with 4-phenyl-1,2,4-triazoline-3,5-dione to give the isomeric *Diels-Alder* adducts **12** and **15**, respectively, which were photochemically converted into the cage compounds **13** and **16**, respectively *(Scheme 3).* – Photochemical reaction of the tricyclic vinylcyclopropane **6** with Fe(CO)$_5$ gave the σ,π-bonded iron complexes **17** and **18**. Heating of **17** at 80° resulted in a loss of one mol of carbon monoxide to give **18** in quantitative yield. Oxidative degradation of **17** with ceric ammonium nitrate in ethanol afforded the polycyclic lactones **19** and **20** by a novel type of reaction *(Scheme 4).* – The tricyclic ketone **21** was thermally converted into the α,β-unsaturated ketone **22** *via* a homosigmatropic [1,5]-H-shift. The configuration at C(7) of **22** was confirmed to be same as that of **11** (CH$_3$–C(9) in an *exo* position) by chemical conversions: **22** was reduced with NaBH$_4$ to alcohol **23** which, in turn, was dehydrated with POCl$_3$/pyridine to **11** *(Scheme 5).* Reaction of ketone **21** with Mo(CO)$_6$ gave the α,β-unsaturated ketone **25** and a cage compound **X**, whose structure was not fully elucidated. – Reaction of the polycyclic epoxide **26** with Fe$_2$(CO)$_9$ or Mo(CO)$_6$ yielded the allyl alcohol **27** in a novel type of reaction. The epoxides **29** and **32** were similarly converted into the corresponding allyl alcohols **30** and **33**, respectively *(Scheme 6).*

1. Introduction. – Vinylcyclopropanes are known to react with iron carbonyls to give iron complexes resulting from cleavage of a C–C bond of the cyclopropane ring [1] [2]. This type of complex formation was also observed in the reactions of

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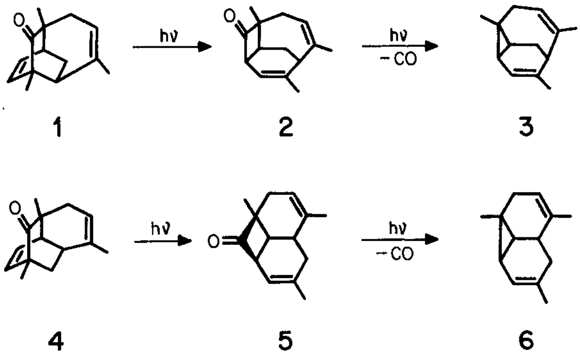
[1]) Deceased December 19, 1976.

bicyclic [3] [4] and polycyclic hydrocarbons containing vinylcyclopropane systems such as bullvalene [5a], isobullvalene [5c], semibullvalene [6], homosemibullvalene [7], tetracyclo[4.4.0.$0^{5,7}$.$0^{2,10}$]deca-3,8-diene [5b], azabullvalene [8], and barbaralone [9]. The reaction was extended to the hetero analogues (*e.g.*, vinyloxiranes [10] [11] and vinylaziridine [10a]), in which a C–X bond was cleaved to form iron complexes. These reactions have potentially a great synthetic utility. The iron unit of the complexes can easily be replaced by other species (*e.g.*, CO) to introduce a new functional group [12] [13], or can oxidatively be eliminated to form a new C,C bond [14].

We recently have reported the facile synthesis of the tricyclic vinylcyclopropanes **3** and **6**, starting from the ketones **1** and **4**, respectively, through photochemical [1,3]-acyl-shift (**2** and **5**) and decarbonylation [15] *(Scheme 1)*.

Scheme 1

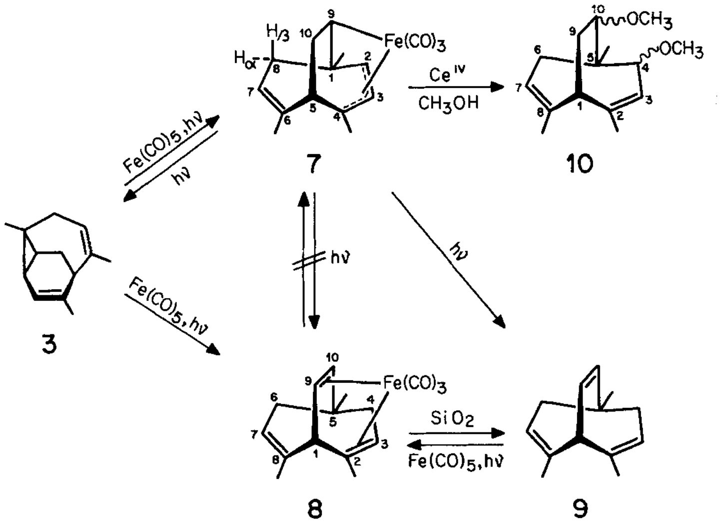


Thus, it was of interest to investigate the reaction of the vinylcyclopropanes **3**, **6** and some of their derivatives with iron carbonyls ($Fe(CO)_5$ and $Fe_2(CO)_9$) and molybdenum hexacarbonyl ($Mo(CO)_6$). The results are discussed in comparison with those of the pure thermal reaction.

2. Complex Formation of Hydrocarbon 3 with Fe(CO)$_5$ (*Scheme 2*). - Irradiation of a pentane solution of vinylcyclopropane **3** and an equivalent of iron pentacarbonyl ($Fe(CO)_5$) with a high-pressure mercury lamp (150 W, Pyrex filter) at room temperature under nitrogen resulted in the formation of a mixture of tricarbonyl[2-4-η-1,4,6-trimethyl-bicyclo[3.3.2]deca-3,6-diene-2,9-diyl]iron (**7**), tricarbonyl[2-3:9-10-η-2,5,8-trimethylbicyclo[3.3.2]deca-2,7,9-triene]iron (**8**) and starting material **3**. The yields were dependent on irradiation time (1 h: 46,5% of **3**, 22% of **7**, **8** not detectable; 3 h: 35% of **3**, 25% of **7**, and 11% of **8**). Although **7** was isolated by chromatography on silica gel, **8** was decomposed under this condition. Hence, isolation and purification of **8** was achieved by repeated bulb to bulb distillation (see exper. part).

The structure of **7** was deduced from elemental analysis and spectroscopic data. The mass spectrum displayed a molecular ion peak at *m/e* 314 and prominent frag-

Scheme 2



ments at m/e 286 (M^+ – CO, 7), 258 (M^+ – 2CO, 42) and 230 (M^+ – 3CO, 48)[2]). The IR. spectrum (KBr) showed absorptions for $\tilde{\nu}$(Fe–C≡O) at 2040, 1980 and 1970 cm^{-1}. The ^{1}H-NMR. spectrum (C_6D_6)[3]) exhibited signals of an olefinic proton at an uncomplexed double bond at δ 4,76 (*d*×*m*, *J*(7,8) = 8.0, H–C(7)), two protons of a π-allylic system bonded to iron at δ 3.98 (*d*, *J*(3,2) = 7.0, H–C(3)) and 3.40 (*d*×*d*, *J*(2,3) = 7.0, H–C(2)), three methyl groups at δ 1.85 (*s*, H_3C–C(4)), 1,64 (small *m*, H_3C–C(6)) and 1.08 (*s*, H_3C–C(1)), and a proton at a bridgehead carbon atom bonded to iron at δ 0.86 (*m*, H–C(9)). This high field chemical shift of H–C(9) is in agreement with other observations [3] [6]. The mass spectrum of complex **8** showed a molecular ion peak at m/e 314 and the characteristic fragmentation pattern (m/e 286 (M^+ – CO, 36), 258 (M^+ – 2CO, 59) and 230 (M^+ – 3CO, 100)). The IR. spectrum (film) showed absorptions for $\tilde{\nu}$(Fe–C≡O) at 2025 and 1955 (broad) cm^{-1}, and the ^{1}H-NMR. spectrum signals of a proton at an uncomplexed double bond at δ 5.60-5.44 (*m*, H–C(7)), three olefinic protons of a π-bonded system at δ 3.53 (*d*, *J*(10,9) = 8.0, H–C(10), 3.11 (*t*, *J*(9,10) = *J*(9,1) = 8.0, H–C(9)) and 2.74-2.59 (*m*, H–C(3)), and three methyl groups at δ 1.96 (*s*, H_3C–C(2)), 1.82 (br. *s*, H_3C–C(8)) and 1.31 (*s*, H_3C–C(5)).

No interconversion of **7** and **8** was observed under the above photochemical conditions, suggesting that these complexes were formed by competitive reactions (see discussion). While **8** was photochemically stable, irradiation of **7** gave a mixture (total yield 84%) of **3** (rel. yield by GC. 23%), **9** (27,5%) and three further hydro-

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[2] The numbers in brackets indicate relative intensities.

[3] Unless otherwise stated, NMR. spectra were measured, on a 100 MHz spectrometer in $CDCl_3$. The chemical shifts are expressed in δ values with tetramethylsilane as an internal standard (= 0 ppm). *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *m* = multiplet, br. = broad. The coupling constants *J* are given in Hz.

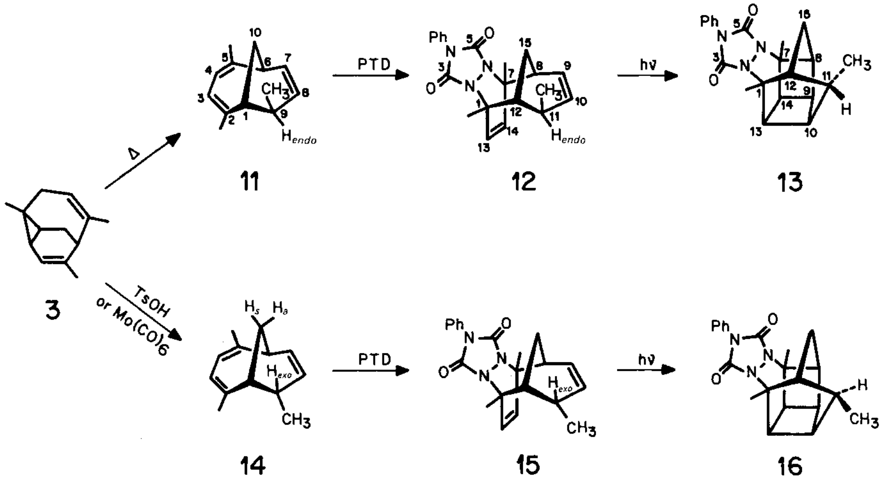
carbons (7,5%, 14% and 15,6%) which were not isolated. On the other hand, treatment of **8** with silica gel yielded 2,5,8-trimethyl-bicyclo[3.3.2]deca-2,7,9-triene (**9**) in 83% yield, which reproduced **8** as the sole product (61%) by photochemical reaction with Fe(CO)$_5$ *(Scheme 2)*.

The nature of **9** as an isomer of **3** was apparent from the elemental analysis and mass spectrum (M^+ at m/e 174). The ^{1}H-NMR. spectrum of **9** showed signals of two coupled olefinic protons at δ 6.17 ($d \times d$, $J(9,10) = 10$, $J(9,8) = 8$, H–C(9)) and 5.57 (d, $J(10,9) = 10$, H–C(10)), two equivalent olefinic protons at δ 5.39-5,23 (m, H–C(3) and H–C(7)), an allylic methine proton at δ 2,71 (d, $J(1,9) = 8$, H–C(1)), two equivalent groups of allylic methylene protons at δ 2.37-2.15 (m, 2 H–C(4) and 2 H–C(6)), two equivalent methyl groups at δ 1.84 (br. s, H_3C–C(2) and H_3C–C(8)) and a methyl group at δ 1.07 (s, H_3C–C(5)). This is only consistent with the presence of a plane of symmetry within the molecule.

Treatment of complex **7** with ceric ammonium nitrate in methanol yielded the methoxylated hydrocarbon **10** in 58% yield (*Scheme 2*). The mass spectrum of **10** showed the molecular ion peak at m/e 236 (15%) and the base peak at m/e 204 ($M^+ - CH_3OH$). Structural assignment to **10** followed from its ^{1}H-NMR. spectrum (see exper. part) which exhibited signals of two methoxy groups at δ 3.37 and 3.21 (each s), three methyl groups at δ 1.83 (small m), 1.71 (br. s) and 1,24 (s), and two methine protons adjacent to a methoxy group at δ 3.47 (br. d, H–C(4)) and 2.41 (br. d, H–C(10)). The configuration at C(4) and C(10) is not clear from these data, but the high field position of the H–C(10) signal may be attributed to the shielding effect of either the C(2), C(3)- or C(7), C(8)-double-bond.

3. Rearrangements of Hydrocarbon 3 (*Scheme 3*). - Heating of **3** in a sealed tube at 140° for 24 h resulted in quantitative isomerization to 2,5,9*exo*-trimethyl-bicyclo[4.3.1]deca-2,4,7-triene (**11**). On the other hand, treatment of **3** with Mo(CO)$_6$

Scheme 3



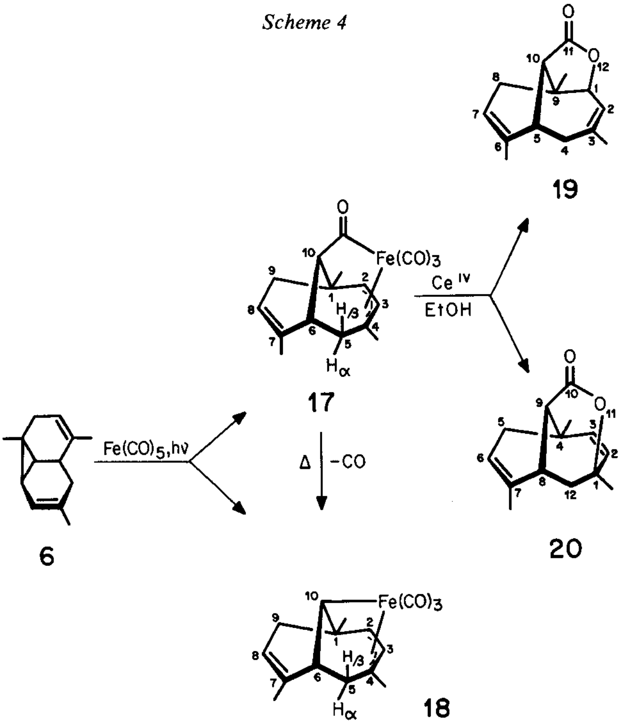
gave the *endo*-isomer **14** in 73% yield. This compound was also obtained by reaction of **3** with *p*-toluene sulfonic acid (TsOH) in 70% yield.

The structural resemblance of **11** and **14** was suggested by the similarity of their mass spectrum (M^{+} at *m/e* 174), IR., UV. and ^{1}H-NMR. spectra. In the NMR. spectra one of the three methyl groups ($H_3C-C(9)$) appeared as *d* ($J=7.0$) at δ 1.06 for **11** and 1.16 for **14**. In the case of **11** H-C(9) was observable at δ 2.37 as *qa*×*d* ($^3J(9,CH_3)=7.0$, $J(9,1)=4.0$) (*cf.*, the corresponding signal of **14** was overlapping with that of H-C(1)), suggesting the *exo* configuration of the methyl group at C(9) since molecular models show that the dihedral angle for H-C(8)-C(9)-H*endo* in the most stable conformation of **11** is near 90°.

The structural assignment was further confirmed by the following reactions. **11** and **14** reacted with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) at $-78°$ to give the *Diels-Alder* adducts **12** (m.p. 151-152.5°, 93%) and **15** (m.p. 131-133°, 32%), respectively, both resulting from the addition of PTD to the conjugated diene system from the *exo*-side. The structure was elucidated on the basis of mass spectrum (M^{+} at *m/e* 349), IR. (**12**: $\tilde{\nu}$(CO) = 1753 and 1698 cm^{-1}; **15**: $\tilde{\nu}$(CO) = 1760 and 1695 cm^{-1}) and ^{1}H-NMR. spectra (see exper. part). The more diagnostic spectral feature of **12** and **15** was the difference in the chemical shifts of their allylic protons. In the case of **15**, two allylic protons (H-C(8) and H-C(11)) appeared as *m* at δ 2.97-2.64, but in **12** only one proton, H-C(8), was observed in this region (δ 2.87-2.61, *m*). The shift of *endo* H-C(11) to higher field can be attributed to the shielding effect of the C(13),C(14) double bond. Furthermore, adducts **12** and **15** were converted into the cage compounds **13** (m.p. 158-159.5°, 54%) and **16** (m.p. 181-183°, 81%), respectively, on irradiation in ether/benzene solution through a quartz filter (*Scheme 3*). Their structures were determined on the basis of mass spectrum (M^{+} at *m/e* 349), IR. (**13**: $\tilde{\nu}$(CO) = 1750 and 1698 cm^{-1}; **16**: $\tilde{\nu}$(CO) = 1755 and 1705 cm^{-1}) and ^{1}H-NMR. spectra (see exper. part). This intramolecular [$\pi 2+\pi 2$]-cycloaddition is only possible for the assigned configurations of **12** and **15**.

4. Complex Formation of Hydrocarbon 6 with Fe(CO)$_5$ (*Scheme 4*). - Irradiation of **6** in the presence of a small molar excess of Fe(CO)$_5$ in pentane through a Pyrex filter afforded tricarbonyl[(2-4-η-1,4,7-trimethyl-bicyclo[4.3.1]deca-3,7-dien-2-yl-10-carbonyl]iron (**17**) and tricarbonyl[2-4-η-1,4,7-trimethyl-bicyclo[4.3.1]deca-3,7-diene-2,10-diyl]iron (**18**) in 34% and 25% yield, respectively. Isolation of these complexes was achieved without using chromatography since **17** decomposed under the conditions of chromatography (see exper. part). On heating at 80° **17** was quantitatively converted into **18** by loss of CO.

The IR. spectrum (KBr) of **17** showed absorptions for $\tilde{\nu}$(Fe-C≡O) at 2060, 2000, 1980 cm^{-1} and for $\tilde{\nu}$(Fe-C=O) at 1643 cm^{-1}. The mass spectrum exhibited no molecular ion peak, but a parent peak at *m/e* 314 ($M^{+}-CO$, 2) and fragments at *m/e* 286 ($M^{+}-2CO$, 15), 258 ($M^{+}-3CO$, 10) and 230 ($M^{+}-4CO$, 26). The ^{1}H-NMR. spectrum (C_6D_6) revealed signals of a proton at an uncomplexed double bond at δ 5,18-5,04 (*m*, H-C(8)), two olefinic protons of a π-bonded system at δ 4.08 (*d*×*d*, $J(3,2)=9.0$, $J(3,5\beta)=2.0$, H-C(3)) and 3.80 (*d*, $J(2,3)=9.0$, H-C(2)), *Scheme 4*



and three methyl groups at δ 1.50 (*s*, $H_3C-C(4)$), 1.44 (br. *s*, $H_3C-C(7)$) and 1.06 (*s*, $H_3C-C(1)$).

The structure of **18** was similarly determined on the basis of the IR. spectrum ($\tilde{\nu}$(Fe−C≡O)) = 2040 and 1965 (broad) cm^{-1}) and mass spectrum. The latter displayed a molecular ion peak at *m/e* 314 (4) and fragments at *m/e* 286 ($M^+ - CO$, 28), 258 ($M^+ - 2\,CO$, 17), and 230 ($M^+ - 3\,CO$, 38). The ^{1}H-NMR. spectrum of **18** was very similar to that of **17** except for the apparent high field shift of the signal for H−C(10) (δ 1.24–1.08) (see exper. part).

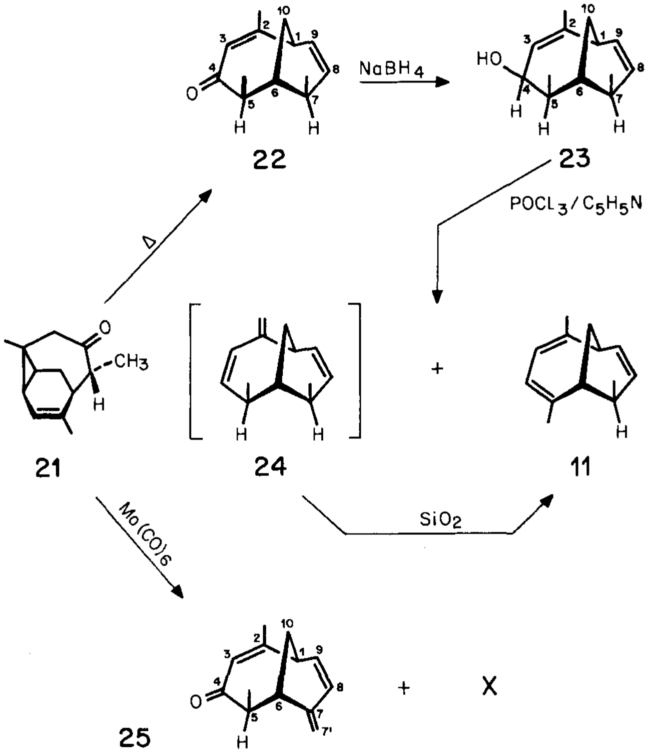
Oxidative degradation of complex **17** with ceric ammonium nitrate in ethanol gave 20% of 3,6,9-trimethyl-12-oxa-tricyclo[7.3.0.0^{5,10}]dodeca-2,6-dien-11-one (**19**) and 20% of 1,4,7-trimethyl-11-oxa-tricyclo[6.3.1.0^{4,9}]dodeca-2,6-dien-10-one (**20**) (*Scheme 4*), which were isolated by chromatography on silica gel. The lactone structure of **19** was indicated by the elemental analysis, MS. (M^+ at *m/e* 218) and IR. spectrum which exhibited the carbonyl absorption of a five-membered lactone at 1770 cm^{-1}. In the ^{1}H-NMR. spectrum, the characteristic absorption was a *d* at δ 4.41 which was assigned to H−C(1) on the basis of $J(1,2) = 7.0$ Hz. Two methyl groups attached to a double bond appeared at δ 1.75 and 1.66 (2 br. *s*, $H_3C-C(6)$ and $H_3C-C(3)$), and a third methyl group was observed at δ 1.19 (*s*, $H_3C-C(9)$).

The mass spectrum (M^+ at *m/e* 218) suggested that **20** was isomeric to **19**. In the IR. spectrum of **20** the intense absorption at 1740 cm^{-1} was characteristic of the six-membered lactone. In the ^{1}H-NMR. spectrum two signals coupled with each other at δ 5.60 (*d*, $J = 11.0$) and 5.21 (*d*×*d*, $J = 11.0$, $J = 1.5$) were assigned to

H–C(3) and H–C(2), and the *m* at δ 5.35-5.21 was attributed to the only other olefinic proton (H–C(6)). A methyl group bonded to a double bond appeared at δ 1.70 (br. *s*, H_3C–C(7)) and the signals of two other methyl groups were observed at δ 1.41 and 1.51 (2 *s*, H_3C–C(4) and H_3C–C(1)).

5. Reactions of the Tricyclic Ketone 21 (*Scheme 5*). - Ketone **21** was easily obtained on irradiation of the corresponding diketone derivative of **1** [15]. Heating of **21** in a sealed tube at 180° for 4 h resulted in a quantitative formation of 2,5,7-trimethyl-bicyclo[4.3.1]deca-2,8-dien-4-one (**22**).

Scheme 5



The nature of **22** as an isomer of **21** was apparent from the elemental analysis and the mass spectrum (M^+ at *m/e* 190). The presence of an α,β-unsaturated ketone system was suggested by IR. ($\tilde{\nu}$(CO) = 1675 cm^{-1}) and UV. spectra. The latter showed an intense absorption at 231 nm (ε 8660). In the ^{1}H-NMR. spectrum (C_6D_6) two methyl groups appeared as *d* (*J* = 7.5) at δ 1.17 and 0.89 (H_3C–C(5) and H_3C–C(7)), respectively, and a third methyl group bonded to a double bond at δ 1.56 (*d*, *J* = 1.5, H_3C–C(2)). H–C(5) was observed at δ 2.55 as a *qa* (*J* = 7.5) and H–C(7) at δ 2.00-1.77 as a *m*. The configuration at C(5) was retained during the reaction since the absence of coupling between H–C(5) and H–C(6) in **22** was understandable on the basis of model considerations only by an *endo*-H (*i.e. exo*-methyl) configuration at C(5). The *endo*-H configuration at C(7) was assumed from the reaction mechanism (thermally allowed homosigmatropic[1,5]-H-shift [16]) and confirmed by the chemical conversion of **22** into the hydrocarbon **11** (*Scheme 5*).

Reduction of **22** with $NaBH_4$ in methanol at 0° gave a nearly quantitative yield of a single crystalline alcohol **23**, m.p. 107.5-108.5° (MS.: M^+ at *m/e* 192; IR.: $\tilde{\nu}(OH) = 3410\ cm^{-1}$). The *exo*-OH configuration was assigned on the assumption that the reagent can attack the carbonyl function of **22** more favourably from the *endo* side, the *exo* side being heavily shielded by the methyl group at C(5) and the methylene bridge (C(10)). When alcohol **23** was treated with $POCl_3$ in pyridine and the product mixture directly analysed by GC., two compounds (**11** and **24**) were observed in the ratio 1.2:1. However, chromatography of the mixture on silica gel gave only the former (80%) as a colourless oil which was identical with **11** from **3** in all aspects. The minor product which was converted to **11** by silica gel can plausibly be considered to be the 1,4-dehydration product **24** (*Scheme 5*).

On the other hand, reaction of ketone **21** with $Mo(CO)_6$ in benzene at 75° resulted in the formation of 26% of 2,5-dimethyl-7-methylidene-bicyclo[4.3.1]deca-2,8-dien-4-one (**25**) and 18% of the cage compound **X**[4]) whose structure was not fully elucidated (*Scheme 5*).

The structure determination of **25** was achieved on the basis of the mass spectrum (M^+ at *m/e* 188), IR. ($\tilde{\nu}(CO) = 1675\ cm^{-1}$) and UV. spectra ($\lambda_{max} = 226$ nm (ε 20680)) which indicated an α,β-unsaturated ketone structure. In the ^1H-NMR. spectrum (C_6D_6) only two methyl signals were observed at δ 1.49 (*d*, $J = 2.0$, $H_3C-C(2)$) and 1.20 (*d*, $J = 6.6$, $H_3C-C(5)$), and characteristically two methylidene protons as *s* at δ 4.70 (2 H−C(7′)). Two olefinic protons, coupled with each other, appeared at δ 5.98 (*d*, $J(8,9) = 9.5$, H−C(8)) and 5.50 ($d \times d$, $J(9,8) = 9.5$, $J(9,1) = 5.6$, H−C(9)), and an olefinic proton α to the carbonyl at δ 5.79 (small *m*, H−C(3)). The *exo*-methyl configuration at C(5) was again assigned on account of the absence of a coupling between H−C(5) (δ 2.61 (*qa*, $J = 6.6$)) and H−C(6) (*cf.* compound **22**). The possibility that **22** is an intermediate in the formation of **25** could be ruled out, because **22** was not affected by $Mo(CO)_6$ under the reaction conditions.

6. Reactions of Epoxides 26, 29 and 32 (*Scheme 6*). - The polycyclic epoxides **26** and **29** were synthesized by irradiation of the corresponding epoxides of ketones **1** and **4**, respectively [15]. Reaction of **26** and diiron enneacarbonyl ($Fe_2(CO)_9$) in hexane for 20 h at 50° resulted in the formation of a mixture of 25% of unreacted **26** and 55% of 2,7-dimethyl-5-methylidene-tricyclo[4.3.1.0^{2,9}] dec-7-en-4-ol (**27**). A similar result was obtained when $Mo(CO)_6$ was taken instead of $Fe_2(CO)_9$: 18% of **26** and 23% of **27**. The product isolation was achieved by chromatography on silica gel. Furthermore, the secondary alcohol **27** (IR.: $\tilde{\nu}(OH) = 3390\ cm^{-1}$) was easily converted to the acetate **28**, m.p. 70-71° (IR.: $\tilde{\nu}(CO) = 1735\ cm^{-1}$). The isomeric nature of **27** and **26** was apparent from the elemental analysis and its mass spectrum

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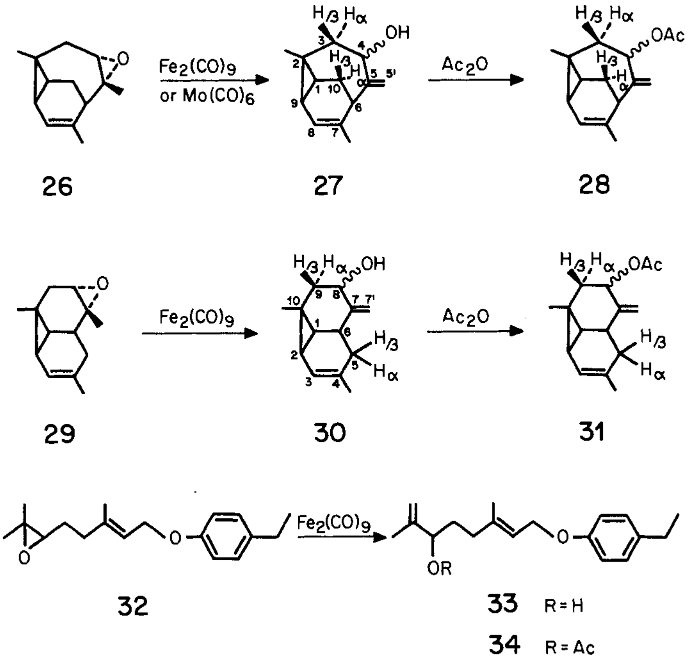
[4]) Compound **X** is isomeric with the starting material (MS. evidence) and shows no signals for olefinic protons in the NMR. spectrum (see exper. part).

Scheme 6

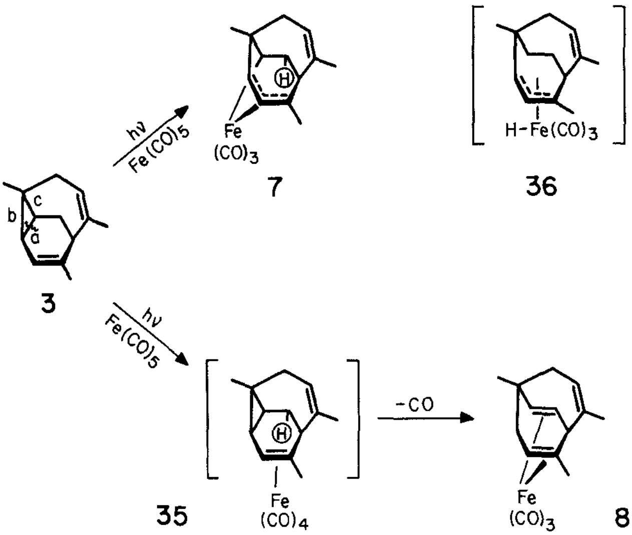


(M^+ at m/e 190). In the ^{1}H-NMR. spectrum of **27**, two signals at δ 4.98 ($d\times d$, $J=2.0$ and $J=1.0$) and 4.90 (d, $J=2.0$) were characteristic for methylidene protons (2 H–C(5′)). Two methyl groups were seen at δ 1.71 (small m, H_3C–C(7)) and 1.25 (s, H_3C–C(2)), and a $d\times d\times d$ ($J=5.5$, $J=4.5$ and $J=1.0$) at δ 4.30 was assigned to H–C(4). A s at δ 1.89 (HO) disappeared after shaking with D_2O. In the case of the acetate **28** the spectral pattern was very similar except for the appearance of the signal of the acetyl group at δ 2.11 (s) instead of the HO-signal, and the characteristic low field shift of the H–C(4) signal (δ 5.38). However, these spectral data are not sufficient to assign the configuration at C(4) of **27** and **28**.

Similarly, epoxides **29** and **32** were converted into the corresponding allyl alcohols **30** (IR.: $\tilde{\nu}$(OH) = 3350 cm^{-1}) and **33** (IR.: $\tilde{\nu}$(OH) = 3410 cm^{-1}), respectively, in moderate yields by treating with $Fe_2(CO)_9$ (*Scheme 6*). Their structures were determined on the basis of spectroscopic data (see exper. part) and the conversion into the acetates **31** (IR.: $\tilde{\nu}$(CO) = 1740 cm^{-1}) and **34** (IR.: $\tilde{\nu}$(CO) = 1745 cm^{-1}), respectively. The configuration at C(8) in **30** and **31** was not elucidated.

7. Discussion. - Both complexes **7** and **8** result from cleavage of a bond of the cyclopropyl group in **3** (*Scheme 7*). However, they must be formed by independent reactions since no interconversion between **7** and **8** was observed. While a lot of analogous reactions to form σ, π-bonded complexes like **7** are reported [2–9] [17a] (see also [17b]), such a type of reaction to form **8** from **3** is rarely known. The reaction might be initiated by an *exo*-attack of iron carbonyl on the double bond

Scheme 7



conjugated with the cyclopropyl group to form the irontetracarbonyl complex **35** as an intermediate, followed by the rearrangement to the π, π-bonded complex **8** with loss of CO.

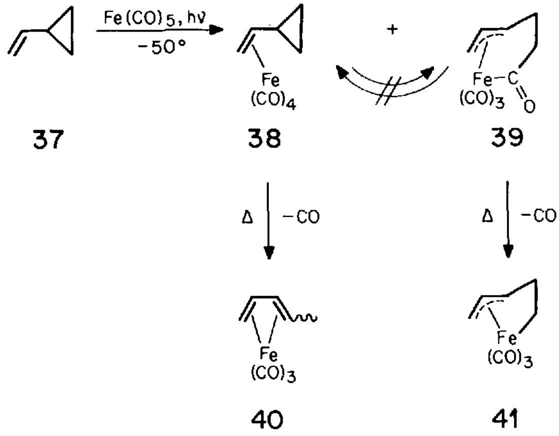
Aumann [2] has recently reported interesting observations on the reaction of vinylcyclopropane (**37**) and Fe(CO)$_5$ (*Scheme 8*) [2]. A low temperature irradiation resulted in the competitive formation of π-bonded complex **38** and σ, π-bonded complex **39**, and on warming these were converted to **40** and **41**, respectively. Our results are essentially in agreement with *Aumann*'s observation. The only difference is the formation of the non-conjugated diene complex **8** instead of a conjugated diene complex of type **40**, the formation of which is sterically hindered. Photochemical degradation of **7** into **9** (*cf. Scheme 2*) is understandable by considering the initial formation of **36** through abstraction of the vicinal hydrogen atom by the iron (*Scheme 7*). Analogous intermediates were often considered for the isomerization of mono-olefins induced by iron carbonyls [18].

In the case of **6** two σ, π-bonded complexes **17** and **18** were obtained, but no π, π-bonded complex. Complexes **17** and **18** were photochemically inactive perhaps since the vicinal hydrogen atom at C(6) (bridgehead carbon atom) is not available for the migration to the iron centre. Although the mechanism of oxidative degradation of **17** to lactones **19** and **20** is not yet clear, this method may provide a new route for lactone synthesis.

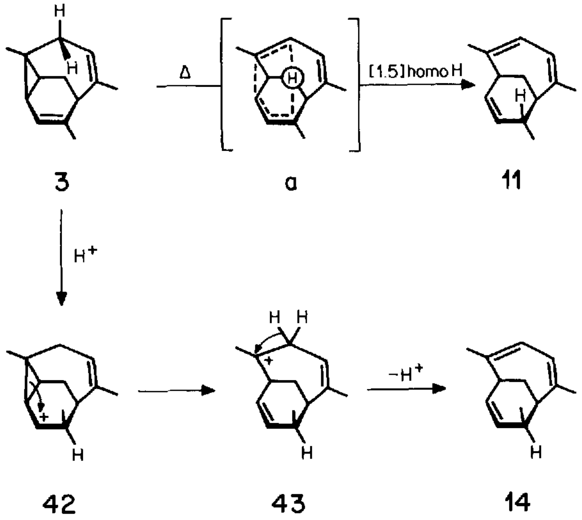
Thermal rearrangement of **3** (or **21**) to **11** (or **23**) can be considered as the result of a homosigmatropic[1,5]-H-shift [16]; *endo*-H at C(4) in **3** migrates, by passing transition state **a**, to C(9) from the *endo*-side to yield **11** (*Scheme 9*).

On the other hand, in the reaction with TsOH **3** is initially protonated at C(9) from the sterically favourable *exo*-side to give the cyclopropylmethyl cation **42**. A cyclopropylmethyl-homoallyl cation rearrangement in **42** provides the tertiary carbocation **43**, deprotonation of which yields **14** (*Scheme 9*). In the case of **6** no

Scheme 8

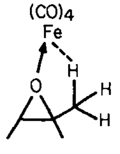


Scheme 9

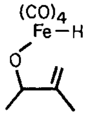


such clear-cut reaction was observed, but a rather complicated mixture was obtained in both thermal and acid-catalysed reactions. This may be attributed to the fact that an efficient orbital overlap necessary for such reactions is not available on the corresponding reaction paths for **6**.

It should be noted that the epoxides **26**, **29** and **32** were *mildly* converted to the allyl alcohols **27**, **30** and **33** by $Fe_2(CO)_9$. Such transformations are usually carried out under much more energetic conditions with a strong base such as lithium diethylamide [19-21], although a relative mild method was also developed [22]. The reaction is regioselective, *i.e.*, the H-atom at the primary C-Atom (CH_3) is more readily eliminated than the H at the secondary C-Atom (CH_2). A possible mechan-



44



45

ism for this new type of reaction is the initial complexation of the oxide with the $Fe(CO)_4$ moiety (*e.g.* **44**) and hydrogen shift from the methyl group to the ironcarbonyl unit with concomitant opening of the epoxy ring to yield intermediate **45** which will expel the ironcarbonyl unit to form the allyl alcohol.

The support of this work by *the Swiss National Science Foundation* is gratefully acknowledged. We are grateful to Professor *H.-J. Hansen* for his useful discussion and encouragement. We thank also the analytical department of our institute and Dr. *Gy. Fráter* for the supply of ketones **1** and **4**, and epoxide **32**.

Experimental Part

General. - M.p.'s were taken on a *Mettler* FP-2 apparatus. Mass spectra (MS.) were taken on a *CEC*-21-110B mass spectrometer at an ionising voltage of 70 eV and data are expressed in *m/e* (rel. %). Infrared (IR.) data are given in cm^{-1}. UV. spectra were performed, unless otherwise stated, in hexane and λ_{max} (sh = shoulder, min. = λ_{min}) are expressed in nm (ε). ^{1}H-NMR. spectra: see footnote 3). Analytical gas-liquid phase chromatography (GC.) was performed on a *C. Erba* apparatus, using a glass capillary column coated with XE-60 [23]. Preparative GC. was done on a *C. Erba* apparatus with a XE-60 column, using nitrogen as a carrier gas. Analytical and preparative thin layer chromatography (TLC.) was carried out on *Polygram* silica gel and silica gel 60 F_{254} (*Merck*) 'Fertigplatten', respectively. For column chromatography silica gel 60 (*Merck*) was used. Distillations were done in a bulb-tube, using the *Büchi* GKR-50 distillation apparatus.

1. General Procedure for Photochemical Reactions of Iron Pentacarbonyl ($Fe(CO)_5$) with Olefins. - Photolysis was performed in a half-cylindric quartz vessel [24] at room temp. under N_2 using a 150W mercury high-pressure lamp (TQ-150, *Quarzlampengesellschaft mbH.*, Hanau) and pyrex filter. The pentane solutions containing olefins (0.01–0.02M) and 1.1–3.6 equivalents of $Fe(CO)_5$ were flushed with N_2 prior to photolysis. Under these conditions no dark reactions were observed. The photochemical reaction was monitored by TLC.

2. Photochemical Reaction of 2,5,9-Trimethyl-tricyclo[4.3.1.0^{5,7}]deca-2,8-diene (3) with $Fe(CO)_5$. - 2.1. *Short-time Irradiation.* A solution of 300 mg (1.72 mmol) of **3** and 340 mg (1.74 mmol) of $Fe(CO)_5$ in 80 ml of pentane was irradiated 1 h. During this time the solution became heterogeneous. After filtration[5]) the solvent was removed under reduced pressure. The brown residue was separated by prep. TLC.with hexane as an eluant to give, in order of elution, 120 mg (22%) of **7** and 140 mg (46.5%) of **3**.

Tricarbonyl[2-4-η-1,4,6-trimethyl-bicyclo[3.3.2]deca-3,6-diene-2,9-diyl]iron (**7**): pale yellow prisms, m.p. 88–89° (from ethanol). - UV.: 212 (20600), 263 sh (7850). - IR. (KBr): 2970, 2940, 2900, 2860, 2040 (Fe–C≡O), 1980 (Fe–C≡O), 1970 (Fe–C≡O), 1455, 1385, 1378, 1028, 778. - NMR. (C_6D_6): 4.76 (*d*× *m*, *J*(7,8*a*) = 8.0, H–C(7)), 3.98 (*d*, *J*(3,2) = 7.0, H–C(3)), 3.40 (*d*× *d*, *J*(2,3) = 7.0, *J*(2,9) = 1.0, H–C(2)), 2.47 (*d*× *m*, *J*(5,10) = 9.0, H–C(5)), 2.40–1.48 (*m*, superimposed by *s* and small *m*, 4 H), 1.85 (*s*, H_3C–C(4)), 1.64 (small *m*, H_3C–C(6)), 1.08 (*s*, H_3C–C(1)), 0.86 (*m*, H–C(9)). Decoupling exper-

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[5]) Care should be exercised in handling the deposit. It was reported that ignition had occurred during filtration (*cf.* [25]).

iments: 3.40→3.98 (*s*) and 0.86 (changed). NMR. ($CDCl_3$): 4.92 ($d \times m$, $J(7,8a) = 7.0$, H–C(7)), 4.42 (*d*, $J(3,2) = 7.5$, H–C(3)), 3.89 (*d*, $J(2,3) = 7.5$, H–C(2)), 2.83 ($d \times m$, $J(5,10) = 8.5$, H–C(5)), 2.58-1.66 (*m*, superimposed by *s* and br. *s*, 4 H), 2.21 (*s*, H_3C–C(4)), 1.89 (br. *s*, H_3C–C(6)), 1.30 (*s*, H_3C–C(1)), 1.04 (*m*, H–C(9)). - MS.: 314 (M^+, 3.5), 286 ($M^+ - CO$, 7), 258 ($M^+ - 2CO$, 42), 230 ($M^+ - 3CO$, 48), 228 (63), 174 (39), 162 (57), 159 (95), 157 (37), 145 (41), 131 (36), 129 (44), 128 (33), 119 (79), 106 (100), 105 (55), 91 (84), 81 (33), 79 (43), 77 (45).

$C_{16}H_{18}FeO_3$ (314.16) Calc. C 61.17 H 5.77% Found C 61.30 H 5.94%

2.2 *Prolonged Irradiation.* A solution of 300 mg (1.72 mmol) of **3** and 340 mg (1.74 mmol) of $Fe(CO)_5$ in 80 ml of pentane was irradiated under the same conditions as in 2.1., but for 3 h. The mixture was filtered and the solvent removed under vacuum to give a brown residue, from which 105 mg (35%) of **3** was recovered by distillation at 80-100°/10 Torr. The remaining residue was further distilled at 100-120°/0.008 Torr to afford a mixture which was shown by TLC. to contain the two iron complexes **7** (major) and **8** (minor). The mixture was dissolved in a minimum volume of ethanol. Upon cooling to −20°, 115 mg (21.2%) of **7** was precipitated from the solution. The filtrate containing mainly **8** was evaporated under vacuum, and the residue distilled carefully at 118-120°/0.008 Torr to give first 21 mg (4%) of **7** and then 60 mg (11%) of *tricarbonyl[2-3:9-10-η2,5,8-trimethyl-bicyclo[3.3.2]deca-2,7,9-triene]iron* (**8**), yellow oil, b.p. 118-120°/0.008 Torr. - UV.: 216 (21040), 228 sh (2200). - IR. (film): 2960, 2930, 2910, 2880, 2025 (Fe–C≡O), 1955 (br., Fe–C≡O), 1445, 1385, 1372, 1288, 1022. - NMR.: 5.60-5.44 (*m*, H–C(7)), 3.53 (*d*, $J(10,9) = 8.0$, H–C(10)), 3.11 (*t*, $J(9,10) = J(9,1) = 8.0$, H–C(9)), 2.74-2.59 (*m*, H–C(3)), 2.57 (*d*, $J(1,9) = 8.0$, H–C(1)), 2.36-2.07 (*m*, 4 H), 1.96 (*s*, H_3C–C(2)), 1.82 (br. *s*, H_3C–C(8)), 1.31 (*s*, H_3C–C(5)). - MS.: 314 (M^+, 27), 286 ($M^+ - CO$, 36), 258 ($M^+ - 2CO$, 59), 230 ($M^+ - 3CO$, 100), 228 (82), 174 (45), 162 (68), 160 (57), 119 (39), 106 (55), 91 (32).

$C_{16}H_{18}FeO_3$ (314.16) Calc. C 61.17 H 5.77% Found C 61.29 H 5.98%

3. Degradation of Iron Complex 8 with Silica Gel. - To a solution of 170 mg (0.54 mmol) of **8** in 30 ml of hexane 5 g of silica gel (mesh 70-230) were added, and the suspension was stirred vigorously for 24 h at room temp. The crude product was filtered and eluted further with 50 ml of benzene. The combined filtrate was evaporated under vacuum and distilled to give 78 mg (83%) of *2,5,8-trimethyl-bicyclo[3.3.2]deca-2,7,9-triene* (**9**), colourless oil, b.p. 98-100°/8 Torr. - UV.: 212 (2530), 246 sh (350). - IR. (film): 3020, 2960, 2930, 2910, 2880, 1460, 1450, 1375, 860, 790, 695. - NMR. 6.17 ($d \times d$, $J(9,10) = 10.0$, $J(9,1) = 8.0$, H–C(9)), 5.57 (*d*, $J(10,9) = 10.0$, H–C(10)), 5.39-5.23 (*m*, H–C(3), –C(7)), 2.71 (*d*, $J(1,9) = 8.0$, H–C(1)), 2.37-2.15 (*m*, 4 H), 1.84 (br. *s*, H_3C–C(2), –C(8)), 1.07 (*s*, H_3C–C(5)). Decoupling experiments: 2.71→6.17 (*d*, $J = 10.0$), 2.28→5.39-5.23 (changed), 1.84→5.32 (*t*, $J = 3.5$). - MS.: 174 (M^+, 11), 159 (71), 145 (24), 144 (24), 131 (40), 119 (47), 117 (35), 115 (24), 106 (100), 105 (41), 91 (77).

$C_{13}H_{18}$ (174.27) Calc. C 89.59 H 10.41% Found C 89.75 H 10.41%

4. Photolysis of Complex 7. - A solution of 60 mg (0.19 mmol) of **7** in 50 ml of pentane (0.004M) was irradiated for 4 h in the usual way. During this time the solution changed from homogeneous to heterogeneous. After filtration and evaporation of the solvent, the residue was distilled at 50-80°/0.008 Torr to afford 28 mg (84%) of a colourless oil. Its GC. analysis showed the presence of compounds **3** (23%), **9** (27.5%) and three new hydrocarbons (7.5%, 14%, 15.6%) which were not isolated.

5. Photochemical Reaction of Hydrocarbon 9 with $Fe(CO)_5$. - A solution of 100 mg (0.57 mmol) of **9** and 400 mg (2.04 mmol) of $Fe(CO)_5$ in 80 ml of pentane was irradiated for 5 h according to the general procedure. After the work-up the residue was distilled at 100-110°/8 Torr to recover 21 mg (21%) of **9**. Distillation of the remaining residue at 110-120°/0.006 Torr gave 110 mg (61%) of a yellow oil which was shown to be **8** by TLC., GC., and IR.

6. Oxidative Degradation of Complex 7. - A mixture of 100 mg (0.32 mmol) of **7** and 1.0 g (1.82 mmol) of ceric ammonium nitrate in 20 ml of methanol was stirred 4 h at room temp. under argon. The solvent was evaporated, and the residue shaken with water (15 ml) and methylene chloride (15 ml). The layers were separated and the aqueous phase was extracted further with methylene chloride (2 × 15 ml). The combined organic layers were washed with water, dried, and evaporated. The residue was purified by prep. TLC. with benzene/acetone 10:1 as an eluant to give 44 mg (58%) of *4,10-dimethoxy-2,5,8-*

trimethyl-bicyclo[3.3.2]deca-2,7-diene (**10**), colourless oil, b.p. 90–93°/0.008 Torr. - UV.: 208 (4540), 237 (590); min. 228 (410). - IR. (film): 2970, 2920, 2875, 2820, 1677, 1450, 1440, 1380, 1120, 1080 (C–O–C), 925, 820. - NMR.: 5.63 (*d*×*m*, *J*(3,4) = 5.0, H–C(3)), 5.33–5.17 (*m*, H–C(7)), 3.47 (br. *d*, *J*(4,3) = 5.0, H–C(4)), 3.37 and 3.21 (2 *s*, 2 CH_3O), 2.41 (br. *d*, *J*(10,9) = 6.0, H–C(10)), 2.27–1.60 (*m*, 5 H), 1.83 (small *m*, H_3C–C(8)), 1.71 (br. *s*, H_3C–C(2)), 1.24 (*s*, H_3C–C(5)). Decoupling experiments: 5.63 → 3.47 (br. *s*) and 1.71 (*s*); 5.25 → 2.27–1.60 (changed) and 1.83 (*d*, *J* = 2.0). - MS.: 236 (M^+, 15), 204 ($M^+ - CH_3OH$, 100), 189 (22), 151 (55), 119 (31), 105 (18), 91 (23), 89 (60), 85 (98).

$C_{15}H_{24}O_2$ (236.34) Calc. C 76.22 H 10.24% Found C 76.50 H 9.96%

7. Thermal Rearrangement of Hydrocarbon 3. - 1 g (5.75 mmol) of **3** was placed in an annealed pyrex ampoule. After de-aerating the ampoule by repeated evacuations it was sealed and heated at 140° for 24 h. The mixture was cooled to room temp. and chromatographed on a silica gel column with hexane to give in order of elution 30 mg (3%) of **3** and 950 mg (95%) of *2,5,9*exo-*trimethyl-bicyclo[4.3.1]deca-2,4,7-triene* (**11**), colourless oil, b.p. 110–113°/8 Torr. - UV.: 212 (5345), 254 sh (8450), 263 (9690), 273 sh (6140); min. 229 (1860). - IR. (film): 3020, 2960, 2925, 2870, 1450, 1440, 825, 745, 710. - NMR.: 5.81–5.36 (*m*, H–C(3), –C(4), –C(7), –C(8)), 2.88–2.70 (*m*, H–C(6)), 2.37 (*qa*×*d*, ^3J(9, CH_3) = 7.0, *J*(9,1) = 4.0, H–C(9)), 2.27–1.55 (*m*, 3 H), 1.88 and 1.84 (2 small *m*, H_3C–C(2), –C(5)), 1.06 (*d*, ^3J(CH_3,9) = 7.0, H_3C–C(9)). - MS.: 174 (M^+, 43), 159 (97), 145 (57), 131 (52), 119 (100), 117 (55), 106 (58), 105 (49), 91 (94).

$C_{13}H_{18}$ (174.27) Calc. C 89.59 H 10.41% Found C 89.40 H 10.55%

8. Reaction of 11 with 4-Phenyl-1,2,4-triazoline-3,5-dione. - A solution of 205 mg (1.18 mmol) of **11** and 192 mg (1.1 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 10 ml of methylene chloride was stirred for 3 h at –78°. The mixture was warmed up to room temp. and evaporated under vacuum. The residue was chromatographed on a silica gel column with chloroform to give 357 mg (93%) of *1,7,11*exo-*trimethyl-4-phenyl-2,4,6-triazatetracyclo[5.5.2.1^{8,12}.0^{2,6}]pentadeca-9,13-dien-3,5-dione* (**12**), colourless crystals, m.p. 151–152.5° (from hexane). - UV. (methanol): 219 (3490). - IR. (KBr): 1753 (CO), 1698 (CO), 1598, 1512, 1415, 1395, 1310, 1146, 760, 745, 700. - NMR. (60 MHz): 7.60–7.27 (*m*, 5 aromat. H), 5.94 and 5.69 (*AB*-system, *J*(*A*,*B*) = 10.0, H–C(13), –C(14)), 5.86–5.43 (*m*, superimposed by *AB*-system, H–C(9), –C(10)), 2.87–2.61 (*m*, H–C(8)), 2.26–1.87 (*m*, partially overlapped, H–C(11), –C(12)), 2.01 (*s*, H_3C–C(1), –C(7)), 1.84–1.65 (*m*, 2 H–C(15)), 1.04 (*d*, ^3J(CH_3, 11) = 6.5, H_3C–C(11)). - MS.: 349 (M^+, 33), 257 (23), 256 (100), 137 (65), 119 (35), 108 (59), 96 (95), 91 (27), 79 (36), 77 (22).

$C_{21}H_{23}N_3O_2$ (349.42) Calc. C 72.18 H 6.63 N 12.03% Found C 71.91 H 6.56 N 12.15%

9. Photochemical Intramolecular Cycloaddition of Adduct 12. - A solution of 210 mg (0.60 mmol) of **12** in 110 ml of ether/benzene 95:5 (volume) was irradiated for 16 h through a quartz filter under argon. The solvent was removed under vacuum and the residue chromatographed on a silica gel column with chloroform to afford 114 mg (54%) of *1,7,11-trimethyl-4-phenyl-2,4,6-triaza-hexacyclo[5.5.2.1^{8,12}.0^{2,6}.0^{9,14}.0^{10,13}]pentadeca-3,5-dione* (**13**), colourless prisms, m.p. 158–159.5° (from hexane). - UV. (methanol): 219 (5550). - IR. (KBr): 2962, 2940, 2902, 1750 (CO), 1698 (CO), 1603, 1508, 1460, 1410, 1305, 1140, 1305, 1140, 805, 760, 740, 695. - NMR. (60 MHz): 7.60–7.28 (*m*, 5 aromat. H), 3.00–2.09 (*m*, 7 H), 1.96 and 1.91 (2 *s*, H_3C–C(1), –C(7)), 1.60–1.20 (*m*, 2 H), 0.92 (*d*, ^3J(CH_3, 11) = 7.0, H_3C–C(11)). - MS.: 349 (M^+, 50), 256 (88), 137 (40), 119 (38), 108 (62), 96 (100), 91 (47), 79 (46), 77 (38).

$C_{21}H_{23}N_3O_2$ (349.42) Calc. C 72.18 H 6.63 N 12.03% Found C 71.88 H 6.92 N 12.10%

10. Reactions of Hydrocarbon 3 with *p*-Toluenesulfonic Acid and Molybdenum Hexacarbonyl. - 10.1. *With* p-*Toluenesulfonic Acid Monohydrate* (TsOH.H_2O). To a solution of 200 mg (1.15 mmol) of **3** in 15 ml of benzene 600 mg (3.16 mmol) of TsOH.H_2O were added and the suspension was vigorously stirred for 6 h at 60°. The mixture was cooled to room temp., the solvent removed under vacuum, and the residue directly chromatographed on a silica gel column with hexane to give 141 mg (70.5%) of *2,5,9*endo-*trimethyl-bicyclo[4.3.1]deca-2,4,7-triene* (**14**), colourless oil, b.p. 58–65°/0.008 Torr. - UV.: 208 (24600), 251 sh (9230). - IR. (film): 3020, 2960, 2925, 2870, 1450, 1442, 823, 747. - NMR.: 5.80–5.36 (*m*, H–C(3), –C(4), –C(7), –C(8)), 2.86 (*m*, H–C(6)), 2.77–2.43 (*m*, H–C(1), –C(9)), 2.10 (*d*×*d*×*d*, *J*(*gem*) = 13.6, *J*(10,1) = 6.0, *J*(10,6) = 3.0, H_a–C(10)), 1.93 and 1.85 (2 br. *s*, H_3C–C(2),

–C(5)), 1.98–1.65 (*m*, overlapped, H_s–C(10)), 1.16 (*d*, ^3J(CH_3, 9)=7.0, H_3C–C(9)). - MS.: 174 (M^+, 52), 159 (90), 145 (41), 131 (35), 119 (94), 106 (56), 91 (100), 77 (78), 65 (49), 53 (65), 51 (71).

$C_{13}H_{18}$ (174.27) Calc. C 89.59 H 10.41% Found C 89.66 H 10.34%

10.2. *With Molybdenum Hexacarbonyl (Mo(CO)$_6$).* A mixture of 500 mg (2.87 mmol) of **3** and 750 mg (2.84 mmol) of $Mo(CO)_6$ in 20 ml of benzene was stirred for 4 days at 80° in a closed bottle. After the vessel had been cooled to room temp. and unreacted $Mo(CO)_6$ removed by filtration, the filtrate was reduced under vacuum. Chromatography of the residue on a silica gel column with hexane followed by distillation (58–65°/0.008 Torr) gave 364 mg (73%) of a colourless oil which was identified with the above mentioned product **14** by TLC., GC., IR., and NMR.

11. Reaction of 14 with 4-Phenyl-1,2,4-triazoline-3,5-dione. - A solution of 190 mg (1.09 mmol) of **14** and 178 mg (1.02 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 20 ml of methylene chloride was stirred for 3 h at –78°. The mixture was warmed up to room temp. and evaporated. Chromatography of the residue on a silica gel column with chloroform gave 113 mg (32%) of *1,7,11*endo-*trimethyl-4-phenyl-2,4,6-triaza-tetracyclo[5.5.2.1^{8,12}.0^{2,6}]pentadeca-9,13-dien-3,5-dione* (**15**), colourless prisms, m.p. 131–133° (from hexane). - UV. (methanol): 220 (4690). - IR. (KBr): 1760 (CO), 1695 (CO), 1603, 1508, 1415, 1395, 1300, 1215, 1135, 770, 758, 745, 696. - NMR.: 7.65–7.27 (*m*, 5 aromat. H), 6.08 and 5.65 (*AB*-system, *J*(*A*,*B*)=9.5, H–C(13), –C(14)), 5.77–5.42 (*m*, superimposed by *AB*-system, H–C(9), –C(10)), 2.97–2.64 (*m*, H–C(8), –C(11)), 2.58–2.40 (*m*, H–C(12)), 2.26–1.81 (*m*, superimposed by 2 *s*, 2 H–C(15)), 2.06 and 2.01 (2 *s*, H_3C–C(1), –C(7)), 1.22 (*d*, ^3J(CH_3, 11)=7.5, H_3C–C(11)). Decoupling experiments: 2.78→1.22 (*s*); 1.22→2.97–2.64 (changed). - MS.: 349 (M^+, 74), 256 (28), 255 (34), 254 (28), 137 (29), 119 (30), 108 (100), 96 (41), 91 (35), 79 (54), 77 (36).

$C_{21}H_{23}N_3O_2$ (349.42) Calc. C 72.18 H 6.63 N 12.03% Found C 72.22 H 6.88 N 12.04%

12. Photochemical Intramolecular Cycloaddition of Adduct 15. - A solution of 150 mg (0.43 mmol) of **15** in 80 ml of ether/benzene 1:1 was irradiated for 10 h through a quartz filter. After work-up the residue was chromatographed on a silica gel column with chloroform to give 122 mg (81%) of *1,7,11-trimethyl-4-phenyl-2,4,6-triaza-hexacyclo[5.5.2.1^{8,12}.0^{2,6}.0^{9,14}.0^{10,13}]pentadeca-3,5-dione* (**16**), colourless prisms, m.p. 181–183° (from ethanol/hexane 1:3). - UV. (methanol): 218 (6450). - IR. (KBr): 2980, 2940, 2910, 2860, 1755 (CO), 1705 (CO), 1603, 1503, 1415, 1293, 1208, 1141, 760. - NMR. (60 MHz): 7.58–7.25 (*m*, 5 aromat. H), 3.02–2.46 (*m*, 6 H), 2.20–1.54 (*m*, partially overlapped with methyl signals, 3 H), 2.04 and 1.94 (2 *s*, H_3C–C(1), –C(7)), 1.03 (*d*, ^3J(CH_3, 11)=7.0, H_3C–C(11)). - MS.: 349 (M^+, 93), 257 (44), 256 (44), 255 (46), 242 (18), 230 (25), 173 (16), 172 (17), 157 (19), 137 (44), 119 (23), 108 (100), 96 (36), 91 (28), 79 (34), 77 (20).

$C_{21}H_{23}N_3O_2$ (349.42) Calc. C 72.18 H 6.63 N 12.03% Found C 72.39 H 6.71 N 12.10%

13. Photochemical Reaction of 2,5,9-Trimethyl-tricyclo[4.4.0.0^{5,7}]deca-2,8-diene (6) with Fe(CO)$_5$. - 13.1. *Formation of Iron Complexes* **17** *and* **18**. A solution of 200 mg (1.15 mmol) of **6** and 260 mg (1.33 mmol) of $Fe(CO)_5$ in 70 ml of pentane was irradiated for 3 h according to the general procedure. After filtration of the iron deposit the solvent was removed under vaccum. The precipitated yellow solid was filtered, washed with a minimum volume of cold ether, and dried to yield 136 mg (34.6%) of **17**. The combined filtrates were evaporated and distilled at 80–90°/10 Torr to recover 40 mg (20%) of **6** as a colourless oil. Further distillation of the remaining residue at 95–100°/0.04 Torr gave 90 mg (25%) of **18**. *Tricarbonyl[(2-4-η-1,4,7-trimethyl-bicyclo[4.3.1]deca-3,7-dien-2-yl)-10-carbonyl]iron* (**17**): yellow prisms, m.p. 75–77° (decomp.; from pentane). - UV.: 208 (24600), 251 sh (9230). - IR. (KBr): 2060 (Fe–C≡O), 2000, (Fe–C≡O), 1980 (Fe–C≡O), 1643 (Fe–C=O), 1455, 1445, 1375, 1050, 660. - NMR. (C_6D_6): 5.18–5.04 (*m*, H–C(8)), 4.08 (*d*×*d*, *J*(3,2)=9.0, *J*(3,5)=2.0, H–C(3)), 3.80 (*d*, *J*(2,3)=9.0, H–C(2)), 2.37 (*d*×*m*, *J*(*gem*)=18.0, H*a*–C(5)), 2.12–1.82 (*m*, 5 H), 1.50 (*s*, H_3C–C(4)), 1.44 (br. *s*, H_3C–C(7)), 1.06 (*s*, H_3C–C(1)). - MS.: 314 (M^+ –CO, 2), 286 (M^+ –2CO, 15), 258 (M^+ –3CO, 10), 230 (M^+ –4CO, 26), 162 (100), 105 (46), 91 (43), 56 (65).

$C_{17}H_{18}FeO_4$ (342.16) Calc. C 59.67 H 5.30% Found C 59.82 H 5.30%

Tricarbonyl[2-4-η-1,4,7-trimethyl-bicyclo[4.3.1]deca-3,7-diene-2,10-diyl]iron (**18**), pale yellow oil, b.p. 95–100°/0.04 Torr. - UV.: 210 (19300), 229 sh (17300), 273 sh (2930). - IR. (film): 2960, 2930, 2855, 2040 (Fe–C≡O), 1965 (br., Fe–C≡O), 1453, 1375, 1040, 1025, 768. - NMR. (C_6D_6): 5.15 (*d*×*m*, *J*(8,9)=8.0, H–C(8)), 4.06 (*d*×*d*, *J*(3,2)=7.0, *J*(3,5*β*)=2.0, H–C(3)), 3.74 (*d*, *J*(2,3)=7.0, H–C(2)), 2.86–1.40 (*m*, superimposed by br. *s* and *s*, 5 H), 1.79 (br. *s*, H_3C–C(4)), 1.64 (*s*, H_3C–C(7)), 1.24–1.08 (*m*, superimposed by *s*, H–C(10)), 1.20 (*s*, H_3C–C(1)). - MS.: 314 (M^+, 3.5), 286 (M^+ – CO, 28), 258 (M^+ – 2CO, 17), 230 (M^+ – 3CO, 38), 162 (100), 105 (19), 91 (11), 56 (36).

13.2. *Thermal Conversion of* **17** *into* **18**. 100 mg (0.29 mmol) of **17** were dissolved in 15 ml of benzene and the solution was heated under reflux for 30 min under N_2. After removal of the solvent, distillation of the residue at 90–100°/0.008 Torr gave 87 mg (95%) of a yellow oil which was identified with the complex **18** by IR. and NMR.

14. Oxidative Degradation of 17. - A mixture of 260 mg (0.76 mmol) of **17** and 1.5 g (2.74 mmol) of ceric ammonium nitrate in 50 ml of ethanol was stirred for 30 min at 0° under N_2. The mixture was warmed up to room temp. and stirred for additional 30 min. After the solvent was evaporated, the residue was dissolved in water (50 ml) and extracted with ether (3×20 ml). The combined organic layers were washed with water, dried, and evaporated. The crude product was separated by prep. TLC. with benzene/ethanol 100:1 to give 33 mg (20%) of **19** and 33 mg (20%) of **20** in order of elution. *3,6,9-Trimethyl-12-oxa-tricyclo[7.3.0.0^{5,10}]dodeca-2,6-dien-11-one* (**19**): colourless oil, b.p. 130–133°/0.004 Torr. - UV.: 211 (2325). - IR. (film): 2965, 2930, 2910, 2880, 2855, 1770 (CO), 1640, 1450, 1440, 1290, 1160, 965. - NMR.: 5.44 (*d*×*m*, *J*(2,1)=7.0, H–C(2)), 5.47–5.33 (*m*, H–C(7)), 4.41 (*d*, *J*(1,2)=7.0, H–C(1)), 2.78–1.92 (*m*, 6 H), 1.75 and 1.66 (2 br. *s*, H_3C–C(6), –C(3)), 1.19 (*s*, H_3C–C(9)). - MS.: 218 (M^+, 16), 159 (15), 119 (39), 112 (24), 108 (100), 107 (61), 106 (74), 91 (37).

$C_{14}H_{18}O_2$ (218.28) Calc. C 77.03 H 8.31% Found C 77.15 H 8.35%

1,4,7-Trimethyl-11-oxa-tricyclo[6.3.1.0^{4,9}]dodeca-2,6-dien-10-one (**20**): colourless oil, b.p. 135–138°/0.003 Torr. - UV. 203 (1515), 230 sh (785). - IR. (film): 3020, 2975, 2950, 2880, 1740 (CO), 1452, 1378, 1292, 1260, 1092, 1080. - NMR.: 5.60 (*d*, *J*(2,3)=11.0, H–C(2) or –C(3)), 5.35–5.21 (*m*, superimposed by *d*×*d*, H–C(6)), 5.21 (*d*×*d*, *J*(3,2)=11.0, *J*(long range)=1.5, H–C(3) or –C(2)), 2.74–2.44 (*m*, 2 H), 2.17–1.76 (*m*, 4 H), 1.70 (br. *s*, H_3C–C(7)), 1.41 and 1.15 (2 *s*, H_3C–C(4), –C(1)). Decoupling experiment: 2.62→5.21 (*d*, *J*=11.0). - MS.: 218 (M^+, 27), 190 (41), 149 (46), 137 (92), 119 (52), 112 (54), 107 (72), 106 (100), 91 (76).

$C_{14}H_{18}O_2$ (218.28) Calc. C 77.03 H 8.31% Found C 77.21 H 8.43%

15. Thermal Rearrangement of the Tricyclic Ketone 21. - 200 mg (1.05 mmol) of **21** were placed in an annealed pyrex ampoule. After de-aerating, the ampoule was sealed and heated at 180° for 4 h. Distillation of the mixture at 88–90°/0.004 Torr gave 196 mg (98%) of *2,5*exo*,7*exo*-trimethyl-bicyclo[4.3.1]deca-2,8-dien-4-one* (**22**), colourless oil, b.p. 88–90°/0.004 Torr. - UV.: 203 sh (3040), 231 (8660). - IR. (film): 3020, 2965, 2930, 2870, 1675 (CO), 1640, 1455, 1445, 1380, 1190, 735. - NMR. (C_6D_6): 5.83 (*qa*, ^4J(3, CH_3)=1.5, H–C(3)), 5.59–5.50 (*m*, H–C(9), –C(8)), 2.55 (*qa*, ^3J(5, CH_3)=7.5, H–C(5)), 2.48–2.30 (*m*, H–C(1)), 2.00–1.77 (*m*, H–C(7)), 1.53 (*d*×*d*, *J*(6,10)=6.0, *J*(6,7)=3.0, H–C(6)), 1.73–1.26 (*m*, 2 H–C(10)), 1.56 (*d*, ^4J(CH_3, 3)=1.5, H_3C–C(2)), 1.17 (*d*, *J*=7.5, H_3C–C(7) or –C(5)), 0.89 (*d*, *J*=7.5, H_3C–C(5) or –C(7)). - MS.: 190 (M^+, 22), 175 (21), 162 (47), 135 (42), 119 (43), 107 (44), 105 (46), 93 (57), 91 (100), 79 (50), 77 (67), 65 (35), 55 (37).

$C_{13}H_{18}O$ (190.27) Calc. C 82.06 H 9.54% Found C 81.94 H 9.35%

16. Reactions of Ketone 22. - 16.1. *Reaction of* **22** *with Mo(CO)$_6$*. A mixture of 100 mg (0.53 mmol) of **22** and 80 mg (0.30 mmol) of $Mo(CO)_6$ in 15 ml of benzene was stirred for 6 days under N_2. GC. analysis of the mixture showed the presence of **22** only (no quantitative analysis was done).

16.2. *Reduction of* **22** *with NaBH$_4$*. To a solution of 310 mg (1.63 mmol) of **22** in 25 ml of methanol 430 mg (11.4 mmol) of $NaBH_4$ were added in portions and the solution was stirred for 3 h at 0°. After excess $NaBH_4$ was destroyed with aqueous ether, the crude material was filtered and evaporated. Chromatography of the residue on a silica gel column with chloroform gave in order of elution 35 mg (11%) of **22** and 228 mg (73%) of *2,5*exo*,7*exo*-trimethyl-bicyclo[4.3.1]deca-2,8-dien-4*exo*-ol* (**23**), colourless needles, m.p. 107.5–108.5° (from hexane). - UV. (methanol): 212 (933). - IR. (KBr): 3410 (OH), 3020, 2970, 2890, 1452, 1440, 1400, 1380, 1150, 1045, 1015, 840, 740. - NMR. (60 MHz):

5.90–5.36 (*m*, H–C(9), –C(8)), 5.34–5.16 (*m*, H–C(3)), 4.86–4.60 (*m*, H–C(4)), 2.56–2.31 (*m*, H–C(1)), 2.23–1.47 (*m*, superimposed by small *m* and br. *s*, 5 H), 1.78 (small *m*, H_3C–C(2)), 1.54 (br. *s*, HO), 1.05 (*d*, *J* = 7.5, H_3C–C(5) or –C(7)), 1.02 (*d*, *J* = 6.8, H_3C–C(7) or –C(5)). – MS.: 192 (M^+, 96), 135 (75), 121 (58), 109 (100), 96 (62), 95 (51), 93 (75), 91 (81), 79 (72), 77 (87), 55 (81).

$C_{13}H_{20}$ (192.29) Calc. C 81.20 H 10.48% Found C 81.35 H 10.51%

16.3. *Dehydration Reaction of Alcohol* **23**. A solution of 195 mg (1.02 mmol) of **23** and 300 mg (1.96 mmol) of $POCl_3$ in 10 ml of benzene/pyridine 1:1 was heated at 60° for 1 h. The mixture was cooled and poured into ice water, and the organic layer separated. The aqueous layer was extracted with ether and the combined organic layers were washed with 1N hydrochloric acid, saturated sodium hydrogencarbonate solution, and water. TLC. and GC. analyses of this solution showed the presence of **11** and a product **24** in the ratio of 1.23:1. Chromatography of the mixture on a silica gel column with hexane gave 141 mg (80%) of **11** only, which was identified with the thermal product mentioned in 7. by IR. and NMR.

17. Reaction of the Tricyclic Ketone 21 with $Mo(CO)_6$. – A mixture of 500 mg (2.63 mmol) of **21** and 400 mg (1.52 mmol) of $Mo(CO)_6$ in 30 ml of benzene was stirred for 6 days at 75°. After cooling to room temp. unreacted $Mo(CO)_6$ was removed by filtration. GC. analysis of the filtrate showed the presence of **21**, **25**, and **X** in the ratio of 1:2.6:1.9 Isolation of the products was accomplished by prep. GC.: 130 mg (26%) of **25** and 90 mg (18%) of **X**. *2*exo,*5*exo*-Dimethyl-7-methylidene-bicyclo[4.3.1]deca-2,8-dien-4-one* (**25**), colourless oil, b.p. 87–89°/0.005 Torr. – UV.: 226 (20680). – IR.: 3080, 3023, 2970, 2930, 2870, 1675 (CO), 1640, 1450, 1375, 1183, 897. – NMR. (C_6D_6): 5.98 (*d*, *J*(8,9) = 9.5, H–C(8)), 5.79 (small *m*, H–C(3)), 5.50 (*d* × *d*, *J*(9,8) = 9.5, *J*(9,1) = 5.6, H–C(9)), 4.70 (*s*, 2 H–C(7′)), 2.61 (*qa*, ^3J(5, CH_3) = 6.6, H–C(5)), 2.50–2.34 (*m*, H–C(1)), 2.21–2.03 (*m*, H–C(6)), 1.94–1.52 (*m*, 2 H–C(10)), 1.49 (*d*, ^4J(CH_3,3) = 2.0, H_3C–C(2)), 1.20 (*d*, ^3J(CH_3,5) = 6.6, H_3C–C(5)). – MS.: 188 (M^+, 100), 173 (30), 159 (34), 145 (45), 131 (25), 105 (26), 97 (87), 96 (43), 92 (36), 91 (49).

$C_{13}H_{16}O$ (188.26) Calc. C 82.93 H 8.57% Found C 82.68 H 8.59%

Compound X. colourless oil, b.p. 44–46°/0.004 Torr. – UV.: 223 sh (360). – IR. (film): 3020, 2950, 2925, 2865, 1710 (CO), 1455, 1400, 1380, 1325, 1255, 1185, 1098, 1087, 1030, 960, 855. – NMR. (60 MHz, $CDCl_3$): 2.93–0.90 (*m*, partially overlapped with methyl signals, 9 H), 1.36 (*s*, H_3C), 1.24 (*s*, H_3C), 0.69 (*d*, *J* = 7.0, H_3C). – MS.: 190 (M^+, 37), 133 (49), 119 (14), 108 (23), 107 (100), 106 (23), 105 (31), 94 (29), 93 (27), 91 (68), 82 (15), 79 (29), 78 (27), 77 (37).

18. Reactions of Epoxide 26 [15]. – 18.1 *Reaction with Diiron Enneacarbonyl ($Fe_2(CO)_9$).* A mixture of 200 mg (1.05 mmol) of **26** and 920 mg (2.53 mmol) of $Fe_2(CO)_9$ in 20 ml of hexane was stirred for 20 h at 50° under N_2. The mixture was filtered and evaporated. Separation of the residue by prep. TLC. with benzene/acetone 20:1 gave in order of elution 50 mg (25%) of **26** and 110 mg (55%) of *2,7-Dimethyl-5-methylidene-tricyclo[4.3.1.0^{2,9}]dec-7-en-4-ol* (**27**), colourless oil, b.p. 72–75°/0.008 Torr. – UV.: 204 (9880), 227 (9630); min. 213 (7730). – IR. (film): 3390 (OH), 2950, 2910, 2880, 2860, 1450, 1435, 1070, 1040, 905, 895. – NMR.: 5.90–5.78 (*m*, H–C(8)), 4.98 (*d* × *d*, *J*(*gem*) = 2.0, *J*(5′,4) = 1.0, H–C(5′)), 4.90 (*d*, *J*(*gem*) = 2.0, 2 H–C(5′)), 4.30 (*d* × *d* × *d*, *J*(4,3*a*) = 5.5, *J*(4,3*β*)4.5, *J*(4,5′) = 1.0, H–C(4)), 2.87 (br. *d*, *J*(6,10*a*) = 6.0, H–C(6)), 2.31 (*d* × *m*, *J*(*gem*) = 13.5, H*β*–C(10)), 2.10–1.98 (*m*, 2 H), 1.96–1.64 (*m*, superimposed by *s* and small *m*, 1 H), 1.89 (*s*, HO), 1.71 (small *m*, H_3C–C(7)), 1.43–1.13 (*m*, superimposed by *s*, 2 H), 1.25 (*s*, H_3C–C(2)). Decoupling experiments: 5.84 → 1.71 (changed); 4.30 → 4.98 (*d*, *J* = 2.0). – MS.: 190 (M^+, 4.5), 175 (12), 172 (13), 157 (39), 143 (23), 142 (30), 134 (30), 129 (48), 119 (47), 117 (30), 115 (35), 107 (42), 105 (59), 91 (100), 79 (50), 77 (54).

18.2. *Reaction with $Mo(CO)_6$).* A mixture of 120 mg (0.63 mmol) of **26** and 85 mg (0.32 mmol) of $Mo(CO)_6$ in 15 ml of benzene was stirred for 4 days at 60°. Working-up and separation of the mixture by prep. TLC. with benzene/ethanol 80:1 gave 22 mg (18%) of **26** and 27 mg (23%) of **27**.

18.3. *Acetylation of Alcohol* **27**. A solution of 35 mg (0.18 mmol) of **27** and 400 mg (3.92 mmol) of acetic anhydride in 2 ml of pyridine was stirred for 20 h at 40°. The mixture was poured into water and extracted with ether (3 × 10 ml). The combined organic layers were washed with 1percentic HCl-solution and water, and evaporated to yield 34 mg (79%) of *2,7-dimethyl-5-methylidene-tricyclo[4.3.1.0^{2,9}]dec-7-en-4-yl acetate* (**28**), colourless prisms, m.p. 70–71° (from hexane). – UV.: 208

(4480), 228 (5810); min. 212 (4325). - IR. (KBr): 3000, 2960, 2880, 1735 ($OCOCH_3$), 1375, 1245, 1230, 920. - NMR.: 5.84-5.72 (*m*, H–C(8)), 5.38 (*d*×*d*, *J*(4,3*a*) = 7.0, *J*(4,3β) = 2.5, H–C(4)), 4.98 and 4.91 (2 br. *s*, 2 H–C(5')), 2.82 (br. *d*, *J*(6,10*a*) = 6.0, H–C(6)), 2.28 (*d*×*m*, *J*(*gem*) = 13.5, Hβ–C(10)), 2.29-1.92 (*m*, superimposed by *s*, 2 H), 2.11 (*s*, CH_3CO), 1.84-1.60 (*m*, 1 H), 1.73 (br. *s*, H_3C–C(7)), 1.38-1.12 (*m*, 2 H), 1.18 (*s*, H_3C–C(2)). - MS.: 232 (M^+, 22), 190 (13), 171 (35), 157 (100), 143 (39), 105 (38), 91 (39), 77 (31).

$C_{15}H_{20}O_2$ (232.31) Calc. C 77.55 H 8.68% Found C 77.78 H 8.49%

19. Reactions of epoxide 29 [15]. - 19.1. *Reaction with* $Fe_2(CO)_9$. A mixture of 500 mg (2.63 mmol) of **29** and 500 mg (1.37 mmol) of $Fe_2(CO)_9$ in 30 ml of hexane was stirred for 6 days at 60° under nitrogen. After work-up, chromatography of the mixture on a silica gel column with benzene/acetone 30:1 afforded 397 mg (79.4%) of unreacted **29** and 52 mg (10.4%) of **30** in order of elution.

4,10-Dimethyl-7-methylidene-tricyclo$[4.4.0.0^{2,10}]$*deca-3-en-8-ol* (**30**). Colourless oil, b.p. 85-88°/0.008 Torr. - UV.: $\lambda_{max} = 211$ (3780). - IR. (film): 3350 (OH), 2960, 2925, 2860, 1450, 1375, 1070, 1030, 895. - NMR.: 5.55 (br. *s*, H–C(3)); 4.88 (*t*, *J* = 1.5; H–C(7')); 4.82 (br. *s*, H–C(7')); 4.41-4.20 (*m*, H–C(8)); 3.27 (*d*×*d*×*m*, *J*(6,1) = 7.5, *J*($6,5_a$) = 7.0; H–C(6)); 2.43 (*d*×*m*, *J*(gem) = 15.0; H*a*–C(5)); 2.23 (*d*×*d*, *J*(gem) = 13.5, *J*(9_a, 8) = 6.0; H*a*–C(9)); 1.87-0.88 (*m*, superimposed by 3*s*, 4 H); 1.79 (br. *s*, OH), 1.65 (small *m*, H_3C–C(10)). Decoupling experiments: 4.30 → 2.23 (*d*, *J* = 8.0); 3.28 → 2.43 (changed). - MS.: 190 (M^+, 5), 172 (50), 157 (100), 143 (27), 119 (57), 107 (27), 91 (31), 79 (17), 77 (24).

$C_{13}H_{18}O$ (190.27) Calc. C 82.06 H 9.54% Found C 82.35 H 9.77%

19.2. *Acetylation of Alcohol* **30**. A solution of 25 mg (0.13 mmol) of **30** and 250 mg (2.45 mmol) of acetic anhydride in 1 ml of pyridine was stirred for 20 h at 50°. The usual work-up gave 26 mg (85%) of *4,10-dimethyl-7-methylidene-tricyclo*$[4.4.0.0^{2,10}]$*dec-3-en-8-yl acetate* (**31**), colourless oil, b.p. 93-95°/0.008 Torr. - UV.: 211 (4820). - IR. (film): 2960, 2930, 2910, 2860, 1740 ($OCOCH_3$), 1655, 1445, 1370, 1240, 1030, 895. - NMR.: 5.60 (br. *s*, H–C(3)), 5.45 (*d*×*d*×*m*, *J*(8,9β) = 8.0, *J*(8,9*a*) = 6.0, H–C(8)), 4.84 (*d*, *J* = 1.5, H–C(7')), 4.80 (*t*, *J* = 1.5, 2 H–C(7')), 3.27 (*d*×*d*×*m*, *J*(*gem*) = 8.0, *J*(6,5*a*) = 6.5, H–C(6)), 2.45 (*d*×*m*, *J*(*gem*) = 16.0, H*a*–C(5)), 2.13 (*d*×*d*, *J*(*gem*) = 13.5, *J*(9*a*,8) = 6.0, H*a*–C(9)), 2.08 (*s*, CH_3CO), 1.87-0.90 (*m*, superimposed by small *m* and *s*, 4 H), 1.72 (small *m*, H_3C–C(4)), 1.13 (*s*, H_3C–C(10)). - MS.: 232 (M^+, 7), 172 (28), 157 (100), 142 (38), 129 (21), 119 (49), 91 (33), 79 (20), 77 (29).

$C_{15}H_{20}O_2$ (232.31) Calc. C 77.55 H 8.68% Found C 77.54 H 8.68%

20. Reaction of Epoxide 32. - 20.1. *Reaction with* $Fe_2(CO)_9$. A mixture of 300 mg (1.09 mmol) of **32** and 800 mg (2.2 mmol) of $Fe_2(CO)_9$ in 20 ml of hexane was stirred for 40 h at 45° under N_2. After work-up, chromatography of the residue on a silica gel column with benzene/acetone 40:1 gave in order of elution 180 mg (60%) of **32** and 79 mg (26%) of **33** *8-(4-ethylphenoxy)-2,6-dimethyl-octa-1,6-dien-3-ol* (**33**), colourless oil, b.p. 140-145°/0.006 Torr. - UV.: 202 (14870), 225 (12520), 277 (1960), 284 (1769); min. 214 (8220), 247 (587), 281 (1370). - NMR.: 7.06 and 6.79 (*AA'BB'*-system, *J*(*A*,*B*) = 8.0, 4 aromat. H), 5.52 (*t*×*m*, *J*(7,8) = 7.0, H–C(7)), 4.93 (br. *s*, H–C(1)), 4.84 (*qa*, *J* = 2.0, H–C(1)), 4.51 (*d*, *J*(8,7) = 7.0, 2 H–C(8)), 4.06 (*t*, *J*(3,4) = 6.0, H–C(3)), 2.61 (*qa*, *J* = 7.3, CH_2CH_3), 2.32-1.61 (*m*, 2 H–C(4), –C(5), HO), 1.77 (small *m*, H_3C–C(2), –C(6)), 1.24 (*t*, *J* = 7.3, CH_2CH_3). - MS.: 274 (M^+, 1), 122 (86), 107 (100), 93 (13), 91 (10), 82 (13), 81 (16), 77 (17), 67 (29).

$C_{18}H_{26}O_2$ (274.39) Calc. C 78.79 H 9.55% Found C 78.72 H 9.44%

20.2. *Acetylation of Alcohol* **33**. A mixture of 79 mg (0.29 mmol) of **33** and 700 mg (6.9 mmol) of acetic anhydride in 5 ml of pyridine was stirred for 20 h at 450°. After the work-up chromatography of the residue on a silica gel column with benzene gave 74 mg (81%) of *8-(4-ethylphenoxy)-2,6-dimethyl-octa-1,6-dien-3-yl acetate* (**34**), colourless oil, b.p. 148-152°/0.006 Torr. - UV.: 202 (15200), 225 (11060), 277 (1980), 284 (1580); min. 214 (7500), 247 (789), 281 (1180). - NMR.: 7.09 and 6.81 (*AA'BB'*-system, *J*(*A*,*B*) = 8.5, 4 aromat. H), 5.50 (*t*×*m*, *J*(7,8) = 7.0, H–C(7)), 5.17 (*t*, *J*(3,4) = 6.0, H–C(3)), 4.95 (br. *s*, H–C(1)), 4.90 (*qa*, *J* = 2.0, H–C(1)), 4.52 (*d*, *J*(8,7) = 7.0, 2 H–C(8)), 2.63 (*qa*, *J* = 7.3, CH_2CH_3), 2.27-1.62 (*m*, superimposed by *s* and small *m*, 4 H), 2.09 (*s*, CH_3CO), 1.78 (small *m*, H_3C–C(2), –C(6)), 1.26 (*t*, *J* = 7.3, CH_2CH_3). Decoupling experiment: 4.52 → 5.50 (br. *s*). - MS.: 316 (M^+, 7), 194 (4), 175 (5), 153 (5), 135 (26), 134 (19), 122 (100), 107 (59), 93 (43), 81 (15), 79 (16), 77 (17), 67 (15), 54 (21).

$C_{20}H_{28}O_3$ (316.42) Calc. C 75.91 H 8.92% Found C 75.69 H 8.96%

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