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An Abortive $(CH)_{12}$ Synthesis. Cis-Fused Divinyl Cyclopropanes Which Cannot Cope

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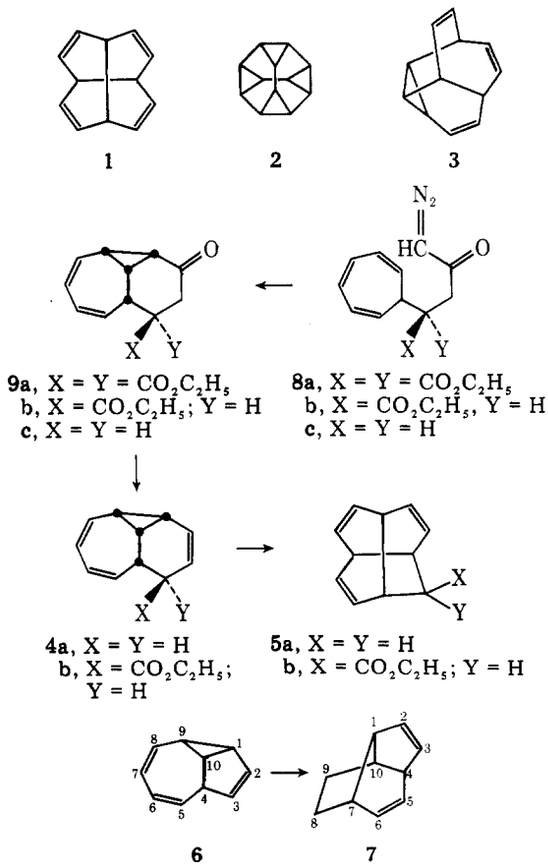
A synthetic approach to tricyclo[5.5.0.0^{4,10}]dodeca-2,5,8,11-tetraene (**1**) by Cope rearrangement of *cis*-divinylcyclopropane precursors failed. Several derivatives of tricyclo[5.4.0.0^{2,11}]undeca-3,5,9-triene (**4b, 21, 27, 28** and **29**) were prepared as potential substrates for Cope rearrangement. All of these compounds rearranged by thermal 1,3 shift; no evidence for the desired Cope products was found. The related substances **4b, 27,** and **29** rearrange to derivatives of tricyclo[6.3.0.0^{3,9}]undeca-4,6,10-triene. The related compounds **21** and **28,** having an additional sp^2 carbon in the six-membered ring, undergo a different 1,3 shift to give derivatives of tricyclo[6.3.0.0^{4,9}]undeca-2,6,10-triene. Synthesis of **4b** and **29** involves the cyclization of diazo ketone precursors as a key step. Cyclization of diazo ketone **8b** apparently gives both syn and anti fused products **9b** and **11b,c.** The geometry of **11b,c** allows facile 1,5-hydride shift to **10b,c.** Increased steric bulk in the diazo ketone side chain (as in **8a**) favors the pathway via **10a.** Conversion of **9b** to **4b** requires zinc–acetic acid induced reductive elimination of an intermediate bromohydrin **15.** This reaction gives 33% of **4b** and 64% of **16,** the product of transannular cyclization. The free radical derived from one-electron reduction of bromohydrin **15** appears to be the species responsible for transannular cyclization.

The chemistry of $(CH)_n$ hydrocarbons has been studied intensively over the past decade. As a result, many of the possible $(CH)_6$, $(CH)_8$, and $(CH)_{10}$ structures have been synthesized and much is known about the diverse and surprising rearrangements which occur thermally and photochemically.[1] Some of the possible $(CH)_{12}$ isomers have also been reported,[2] but numerous fascinating geometries await synthesis and study.

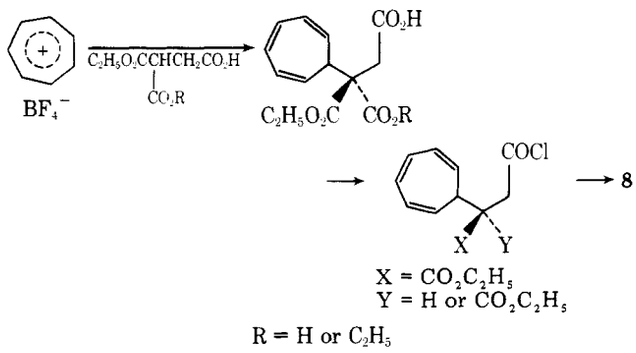
The tetraene **1** is among the more alluring target molecules in the $(CH)_{12}$ family. This substance has been proposed as a potential substrate for photochemical [2a + 2a + 2a + 2a] cycloaddition to the truncated tetrahedron **2.**[3] Whether this cyclization will compete with the more mundane (and far more precedented) di-π-methane rearrangement to **3** remains to be established.

We planned to synthesize **1** by an approach based on the Cope rearrangement of a *cis*-divinylcyclopropane such as **4.** Numerous related rearrangements are known,[4] including the closely analogous conversion of **6** to **7** at room temperature.[5] Molecular models indicate that overlap between C_4 and C_9 as required for the Cope rearrangement distorts the six-membered ring. Consequently we anticipated that **4** might be less reactive than **6.** On the other hand, the hypothetical product **5** appears less strained than **7,** a factor which would tend to lower the activation barrier.

After the Cope rearrangement, the functional groups X, Y must allow facile ring expansion. Also, these groups should be compatible with a sequence starting from the readily available tropylium fluoroborate. Suitable diazo ketones **8** are easily prepared according to Scheme I. Our plan was to convert these intermediates into **5a** (X = $CO_2C_2H_5$; Y = H), hydroxylate the



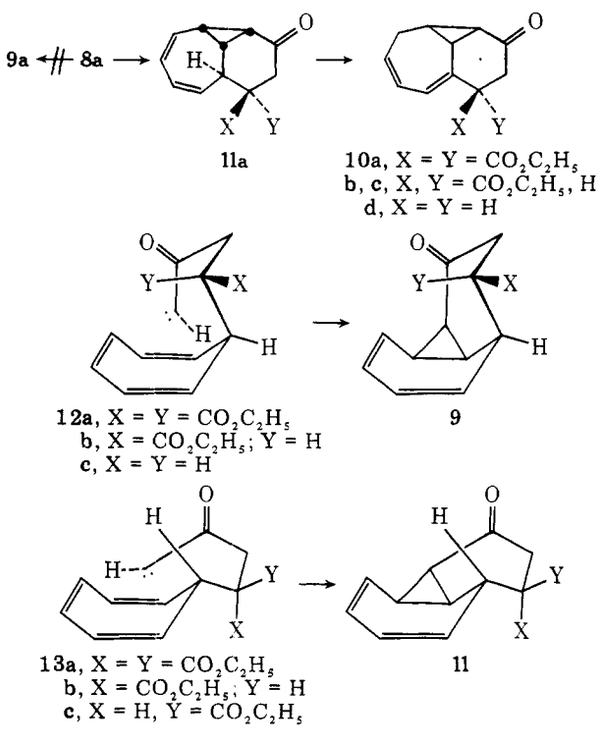
Scheme I



ester enolate (to **5**, X = $CO_2C_2H_5$; Y = OH), reduce and tosylate (to **5**, X = CH_2OTs; Y = OH), and perform a pinacol-type ring expansion. Simple enough in principle, these plans encountered unforseen difficulties at every turn.

The first major problem arose in the diazo ketone cyclization to **9**. Decomposition of **8a** in refluxing benzene/$CuSO_4$ gave a single major product in 44% yield. This material was obviously a cyclopropyl ketone (carbonyl at 1695 cm^{-1}), but only three vinyl protons could be found in the NMR spectrum. The absence of a signal for an allylic C_7 bridgehead proton indicated structure **10a** (Scheme II). No other product con-

Scheme II



taining a cyclopropyl ketone could be found, even when the diazoalkane decomposition was performed at room temperature using soluble copper catalysts.

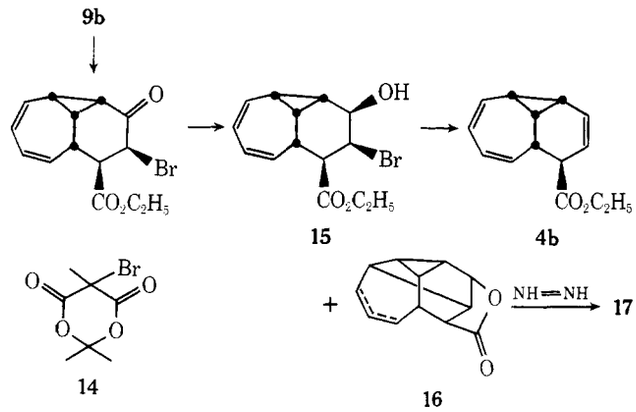
In contrast to the behavior of **8a**, decomposition of the unsubstituted model compound **8c**[6] gave the unrearranged cyclopropyl ketone **9c** (15%). In the case of **8b**, a complex mixture containing unrearranged product **9b** and the rearranged isomers **10b,c** was obtained. Reexposure of **9b** to the reaction conditinons (80°C, benzene + $CuSO_4$) did not cause any discernible rearrangement to **10b,c**. Since **9b** is not the precursor of **10b,c**, we conclude that the latter products must be formed from an anti-fused cyclopropyl ketone **11** (X or Y = $CO_2C_2H_5$ or H).

Molecular models indicate that **11** has ideal geometry for a 1,5 H shift to **10b,c**. Furthermore, the syn transition state **12b** leading to syn-fused **9b** suffers significant transannular interactions within the endo cavity of the developing tricyclic skeleton, while the anti geometry **13b,c** is relatively unstrained. Apparently, the transition state geometries similar to **12** are feasible only if Y = H. This hypothesis would explain the apparent failure of **8a** to cyclize to **9a**.

The optimum yield of **9b** (23%, ratio of **9b:10b,c** ca. 1:1) was obtained by diazo ketone decomposition in refluxing toluene (110 °C, $CuSO_4$). Relatively more **10b,c** was formed at 80 °C (**9b:10b,c** 0.75), while photosensitized diazo ketone decomposition[8] at 25 °C gave **10b,c** (22%) but no **9b**. Qualitatively, these results suggest that higher reaction temperatures allow a higher population of the pseudoaxial conformer **12b** required for cyclization to cis-fused **9b**.

With **9b** in hand, we turned to the problem of converting the sensitive cyclopropyl ketone into a vinyl cyclopropane **4b**. Treatment of **9b** with lithium bis(trimethylsilyl)amide at −70 °C followed by the selective brominating agent **14**[9] gave an α-bromo ketone in yields as high as 89% (Scheme III). Re-

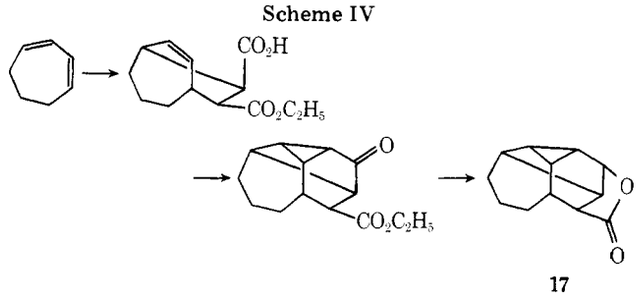
Scheme III



duction with sodium borohydride converted the bromo ketone into *all-cis*-bromohydrin **15**. The exo,cis stereochemistry of ester and bromine substituents in **15** follows from $J_{7,8}$ = 10.5 Hz, and $J_{8,9}$ = 2.0 Hz and is consistent with bromination from the less hindered exo face. Inspection of molecular models does not allow unambiguous assignment of hydroxyl stereochemistry from $J_{9,10}$ = 2.0 Hz and $J_{10,11}$ = 10.0 Hz, but the all-cis relationship is strongly indicated by subsequent reactions of **15**.

Reductive elimination of **15** to **4b** with a variety of electron donors was examined in detail. Under the best conditions (Zn/HOAc) the desired vinyl cyclopropane **4b** was obtained in 33% yield, but the major product of the reaction proved to be a crystalline mixture of two inseparable isomers **16**. Reduction of the isomer mixture **16** with diimide gave a single saturated lactone **17** which is identical with material synthesized by an independent route (Scheme IV). It is perhaps

Scheme IV

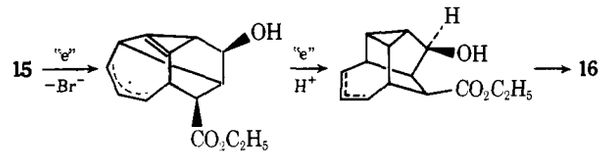


reassuring at this point that synthesis of **17** confirms the structure of **15** and its precursors as well as the structure of

16. In particular, only an all-cis fused tricyclo[5.4.0.0^{2,11}]-undecane can possibly be related to 17, and facile lactonization seems reasonable only if hydroxyl and ester stereochemistry in 15 is cis.

The undesired cyclization of 15 to 16 becomes the sole reaction when one-electron reducing agents such as Cr(II) are used. In all probability, the transannular cyclization occurs by a free-radical mechanism[10] as shown in Scheme V.

Scheme V



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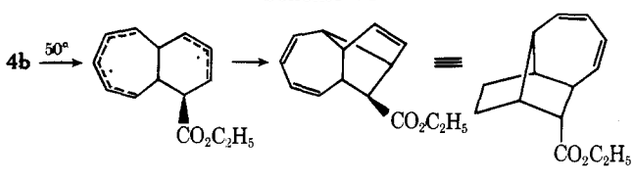
The accumulation of disastrous side reactions and isomer separation problems reduces the optimum overall yield of 4b from tropylyium ion to 3%. Nevertheless, sufficient material was available to investigate the crucial Cope rearrangement of 4b and related structures. The thermal stability of 4b proved surprisingly high, and temperatures above 50 °C were required to induce rearrangement. After 40 h at 55 °C, 4b was converted cleanly into a new isomer. Although the NMR spectrum of this substance can be reconciled with the desired Cope product 5a, the thermolysis product retains a conjugated 1,3-diene chromophore (λ_{max} 258 nm, ϵ 3600 in ethanol) and therefore cannot be a derivative of 5. On the basis of extensive decoupling studies in the presence of Eu(fod)$_3$ and the striking similarities in chemical shift data and coupling constants between analogous protons of *endo*-2-carbomethoxynorborn-5-ene[11] and the thermolysis product, the latter must be assigned structure 19 as shown in Scheme VI. This isomer is

Scheme VI



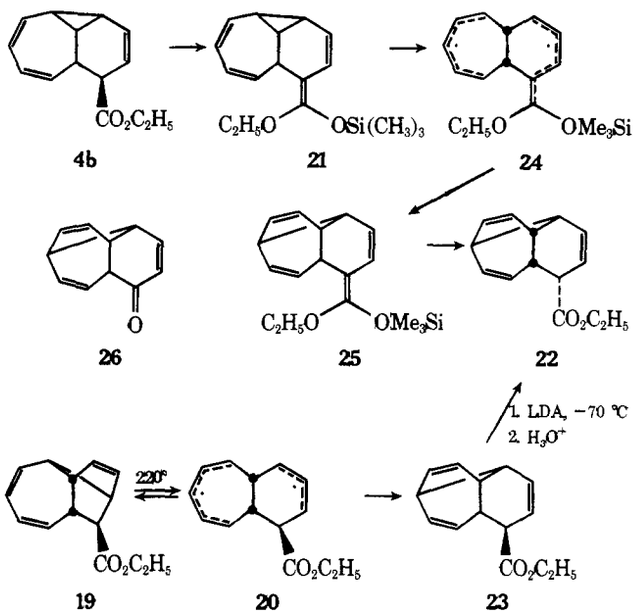
20 19

formally the result of a vinylcyclopropane → cyclopentene rearrangement, presumably via diradical 20.

Several attempts were made to convert the strained norbornene derivative 19 into the relatively unstrained isomer 5a by thermolysis. Indeed, rearrangement of 19 occurred in the injection port of a gas chromatograph (220 °C) resulting in partial conversion into an isomer. Complete separation of the new product from starting 19 could not be achieved but the incomplete spectral evidence was very encouraging. The thermolysis product of 19 did not have a conjugated chromophore, and retained the proper ratio of vinyl and aliphatic protons required for structure 5b. However, the high-temperature rearrangement was too inefficient to qualify as a potential step in the synthetic sequence.

If rearrangement of 19 involves thermodynamically controlled cyclization of diradical 20, then it should be possible to lower the reaction temperature by providing additional diradical stabilization. Accordingly, we examined the thermal behavior of ketene acetals derived from the ester function of 4b. Treatment of 4b with lithium diisopropylamide (LDA) at −70 °C followed by trimethylchlorosilane gave 21 without complications (Scheme VII). Surprisingly, thermolysis of 21 at the lower temperature used to convert 4b into 19 did not give an analogous product having a conjugated 1,3-diene chromophore after hydrolytic cleavage of the trimethylsilyl

Scheme VII



group. Instead, a single isomer 22 was formed which at first appeared to be the same as the product obtained from 19 at 220 °C. The NMR spectra of 22 and the thermolysis product from 19 were identical in the olefinic region, but the carboxylate α-methine protons of the two isomeric esters did not coincide. Since other physical and spectral characteristics of the isomers are indistinguishable, we suspected that high-temperature pyrolysis of 19 must give a diastereomer of 22. Treatment of the pyrolysate from 19 with LDA at −70 °C followed by quenching with aqueous acid (−70 °C) results in formation of 22. Thus 22 and the pyrolysis product of 19 differ only in the stereochemistry of the ester group (barring some remarkable anionic rearrangement), a finding which shatters any realistic hope that *either* isomer might be 5b. The latter can only exist as one diastereomer because the parent hydrocarbon 5a has a C_2 axis of symmetry.

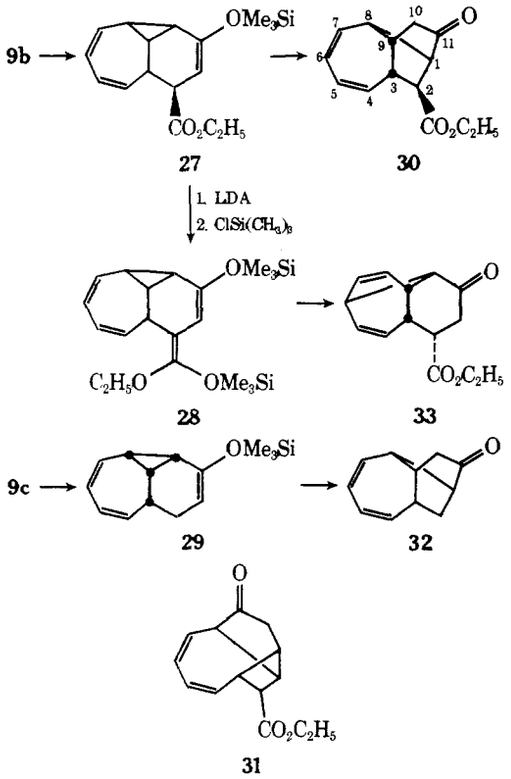
The only reasonable alternative structure which might result from reclosure of diradical 20 is the ester 23. Deprotonation of 23 with LDA followed by enolate protonation from the least hindered side would give diastereomer 22. Apparently, the thermolysis of 21 at 55 °C involves a diradical 24 which for some conformational reason prefers to close directly to 25. Hydrolysis of 25 by protonation from the least hindered face of the ketene acetal leads to 22.[12]

The structures assigned to 22 and 23 are consistent with extensive spectral data, but the methine region in the NMR spectra is not sufficiently resolved for conclusive structure assignment. On the other hand, the NMR features of 25 compare favorably with those of the model compound 26[14] which has the same carbon skeleton and a closely analogous substitution pattern.

In desperation, we examined thermolysis of enol ether derivatives 27, 28, and 29. Treatment of 9b with lithium bis(trimethylsily)amide followed by trimethylchlorosilane afforded 27, and repetition of the process gave 28. Similarly, 9c was converted into 29 via the enolate.

A single keto ester 30 was obtained from rearrangement of 27 at 55 °C with subsequent hydrolysis. The product 30 has the same chromophore as 18, an appropriately similar NMR spectrum, and a norbornanone carbonyl absorption at 1750 cm^{-1}. A conclusive assignment of structure follows from NMR decoupling studies which establish a continuous chain including C_2–C_9, and also demonstrate the connection between C_9, C_{10}, and C_{11}. The only alternative structure 31 which meets the connectivity requirements is ruled out by chemical shift

Scheme VIII



and Eu(fod)$_3$ evidence. The analogous rearrangement of **29** gave **32** after hydrolysis. Comparisons of UV and NMR data leave no doubt that **19**, **30**, and **32** have the same carbon skeleton and differ only in the substitution pattern of the norbornane subunit.

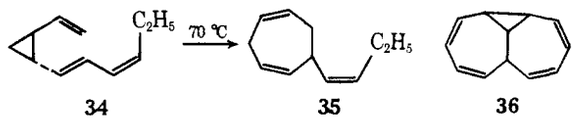
Finally, pyrolysis of **28** was examined. The only significant product other than recovered **9b** obtained after hydrolysis was the keto ester **33**. A combination of Eu(dpm)$_3$ and NMR decoupling techniques allows unequivocal assignment of all protons and all vicinal and geminal coupling constants in the molecule. The connectivity requirements are uniquely satisfied, and no alternative structures are possible. This evidence taken together with data presented earlier provides strong support for the view that **22**, **23**, and **33** have the same carbon skeleton.

Conclusions

The thermal behavior of **4b**, **21**, **27**, **28**, and **29** shows convincingly that the tricyclo[5.4.0.0^{2,11}]undeca-3,5,9-triene derivatives are among the very rare cis-fused divinylcyclopropane systems which fail to undergo Cope rearrangement.[4m,15] The related structures **4b**, **27**, and **29**, all having a double bond and an sp^3-hybridized carbon in the six-membered ring, rearrange by homolytic cleavage at C_2–C_{11} with rebonding at C_2–C_9. The structures **21** and **28**, having a double bond and an sp^2-hybridized carbon in the six-membered ring, form a bond between C_4 and C_{11} at the expense of the C_2–C_{11} bond. Differing kinetic preferences for rebonding in the diradical intermediates are probably determined by conformational changes depending on the hybridization at C_8. Conversion of **19** into **23** at 220 °C is due to strain energy associated with the norbornene moiety of **19**, and presumably reflects a kinetic preference for C_4–C_{11} bonding rather than C_4–C_9 bonding which would convert diradical **20** into **5**.

The failure of any of the cis-fused divinylcyclopropanes **4b**, **21**, **27**, **28**, and **29** to undergo Cope rearrangement may be due to geometric factors. The preferred conformation of **4b** and derivatives juxtaposes C_3 and C_9 rather than C_4 and C_9 as required for the six-center Cope transition state. A reasonable bonding distance between C_4 and C_9 can be achieved in a molecular model by flattening the six-membered ring. Apparently, this distortion introduces sufficient strain to raise the activation barrier for Cope rearrangement relative to model compounds such as **6**. Diradical cleavage of the C_2–C_{11} bond becomes the lowest energy pathway and formation of products by 1,3 shift is the result.

Given a sufficiently high barrier for Cope rearrangement, it is not surprising that a diradical process would compete. Diradical rearrangement of a *trans*-1-vinyl-2-dienyl cyclopropane **34** has been observed previously with E_a = 28.5



34 **35** **36**

kcal/mol at 70–90 °C.[16] The activation parameters for rearrangement of **4b** to **19** at 55–65 °C are in reasonable agreement (E_a = 31.7 ± 1.3 kcal/mol, $\Delta H^{\ddagger}$ = 31 ± 1.2 kcal/mol, $\Delta S^{\ddagger}$ = 13 ± 5 eu). We can only envy the smooth formation of Cope product **35** from **34** in spite of the intervention of a diradical. In our system, diradical intermediates rearrange exclusively by 1,3 shift with catastrophic consequences for the synthetic approach to **1**. Along more speculative lines, we suspect that potential thermal routes to **1** (such as by rearrangement of the hypothetical hydrocarbon **36**) will encounter disaster for similar reasons.

Experimental Section

General. Spectra were recorded using the following: NMR, Jeolco MH 100 or Varian XL-100 instruments; IR, Beckman IR-8; UV, Cary 15. Melting points were determined on a hot stage microscope apparatus and are uncorrected. Tetrahydrofuran was dried by distillation from lithium aluminum hydride.

Preparation of Intermediates in Scheme I. 3,3-Dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic Acid. To diethyl malonate (120 g, 0.75 mol) in 2 l. of dry tetrahydrofuran is added sodium hydride (24.0 g of a 50% dispersion in mineral oil, 0.50 m) at such a rate as to maintain gentle reflux. To the resulting clear solution is added over 0.5 h *tert*-butyl chloroacetate (82.9 g, 0.44 mol), and the reaction is stirred at reflux for 18 h. Commercial hexane (2 l.) is added, the reaction mixture is filtered, the solvent is evaporated, and the residual oil is distilled. After a forerun of starting materials, the monoalkylation product (116.2 g, 0.425 mol, 85%) distills at 112–118 °C (1.4 mm): n^{24}D 1.4298; NMR (CCl_4) δ 4.15 (2 H, q, J = 7.2 Hz), 3.65 (1 H, dd, J = 7.0, 8.0 Hz), 2.70 (2 H, d, J = 7.5 Hz), 1.40 (9 H, s), 1.25 (3 H, t, J = 7.2 Hz), IR (neat) 1725, 1420 cm^{-1}.

The distillate from above (31 g) is added dropwise to concentrated H_2SO_4 (70 g) at a rate such that the temperature is maintained at 0–5 °C (salt–ice bath). Three minutes after addition (total reaction time ca. 15 min) the solution is poured over ice (ca. 200 g), the aqueous layer is saturated with Na_2SO_4, and the product extracted with ether (4 × 100 ml). The organic phase is extracted with saturated Na_2CO_3 (4 × 50 ml), each carbonate extract is immediately added to a rapidly stirred mixture of 20% HCl–saturated NaCl–ether, and the ether layers are separated and dried over anhydrous $MgSO_4$. After evaporation, monoethyl(2-carboethoxy)succinate (27 g) is obtained as a pale yellow oil which solidifies in the freezer.

The crude monoethyl(2-carboethoxy) succinate (22 g) from above is added to a solution of cycloheptatrienyl fluoroborate[17] (19.8 g) in pyridine (50 ml). After 18 h at 25 °C, the solution is adjusted to pH 1 with 20% HCl and extracted with ether (3 × 100 ml). After drying over $MgSO_4$ and evaporation of ether, 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid crystallizes from hexane (27 g, two crops): NMR ($CDCl_3$) δ 1.24 (6 H, t, J = 7 Hz), 2.03 (1 H, t, J = 6 Hz), 3.08 (2 H, s), 4.25 (4 H, q, J = 7 Hz), 5.38 (2 H, dd, J = 9, 6 Hz), 6.25 (2 H, m), 6.70 (2 H, m), 11.42 (1 H, s).

3-Carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic Acid. The distillate obtained from alkylation of diethyl malonate and *tert*-butyl chloroacetate as described above (164 g, 0.6 mol) is dissolved in absolute ethanol (300 ml) and combined with a solution of potassium hydroxide (39.6 g of 85% commercial grade, 0.6 mol) in 300 ml of absolute ethanol. The reaction mixture is swirled in a 1-l. flask over a steam bath, and swirling is continued while the reaction is kept at reflux for 10 min by intermittent heating. After cooling and reaction

at room temperature (12 h) the solvent is removed by rotary evaporation (aspirator) and the residual oil is dried overnight under oil pump vacuum. The crude intermediate is partitioned between 1500 ml of ether and 30% aqueous hydrochloric acid. The ether is removed on a rotary evaporator (aspirator vacuum), and the residual oil is diluted with 200 ml of ether and cooled to 0 °C. Concentrated sulfuric acid (30 ml) is dripped into the solution with vigorous swirling in a 0 °C bath. After addition is complete, the reaction mixture is stirred for 1 h at 0°. Ice (200 g) is added, and the reaction is partitioned between 1 l. of ether and 250 ml of saturated brine. The aqueous phase is extracted with two 500-ml portions of ether. The ether layers are combined, dried over anhydrous magnesium sulfate, and concentrated. The residual oil is freed of ether under high vacuum, and slowly solidifies. The waxy solid is purified by trituration with carbon tetrachloride to give 2-carboethoxysuccinic acid (90.0 g, 0.474 mol, 79%) as a white solid, mp 76–70 °C, sufficiently pure for further reactions.

3-Carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic Acid. 2-Carboethoxysuccinic acid (90 g) dissolved in 400 ml of commercial pyridine and coolled to 0 °C is added to a cold solution of tropylium fluoroborate[17] (90 g) in 400 ml of commercial pyridine, and the reaction mixture is stirred for 13 h at room temperature. The clear tan solution is warmed to 85–90 °C, and stirred at that temperature for 7 h, after which time carbon dioxide evolution has ceased. After cooling, the reaction mixture is washed into a separatory funnel with 1 l. of ether; 2 l. of 30% sulfuric acid is poured through the ether layer, recovered, and poured through several times more. This must be done carefully to avoid local overheating and consequent loss of product out the top of the funnel. Ether is added from time to time, replacing that lost by the heat of the neutralization reaction, keeping the volume at approximately 1.5 l. After back-extraction of the acidic wash with two 500-ml portions of ether, the ether phases are combined and washed with two 500-ml portions of 10% HCl, then with acidic saturated brine, dried over sodium sulfate, and evaporated to give crude 3-carboethoxy-3-(7-cycloheptatrienyl)propionic acid as a dark oil after removal of residual solvent by oil pump vacuum (10 g): IR (neat) 3570–2380, 1710 cm^{-1}; NMR ($DCCl_3$) δ 11.2 (1 H, s) 6.6 (2 H, t, J = 3 Hz), 6.2 (2 H, dt, J = 10, 3, 3 Hz), 5.3 (2 H, dd, J = 10, 7 Hz), 4.2 (2 H, q, J = 7.0 Hz), 3.2–2.6 (3 H, m), 1.98 (1 H, q, J = 7 Hz), 1.25 (3 H, t, J = 7.0 Hz). This product is sufficiently pure for subsequent steps.

Diazo Ketone 8a. Piperidine (distilled from BaO) is added to a saturated solution of 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid (2 g) in ether until the odor of excess piperidine is apparent. Additional ether is added to a total volume of 25 ml and the piperidinium salt is allowed to crystallize in the freezer (2.3 g, two crops).

A solution of the salt (2 g) in dry chloroform (2 ml, distilled from P_2O_5) is added dropwise to thionyl chloride (2 g) in anhydrous ether (20 ml) over 20 min at 0 °C. The mixture is allowed to warm to 20° and is stirred for 1 h (SO_2 evolution!). Dry hexane (50 ml) is added, and the solution is decolorized with Norit, filtered, and evaporated to yield the crude acid chloride as a pale yellow oil.

The acid chloride is dissolved in ehter (20 ml) and added dropwise to a solution of diazomethane (ca. 0.8 g) in ether (35 ml) at 0 °C over 20 min. After 1 h at 0 °C and 2 h at 20 °C, the solvents are evaporated under a nitrogen stream. Rapid filtration chromatography of the residue over silica gel using chloroform–hexane gives a small forerun of colorless side products followed by a yellow diazo ketone fraction. Evaporation of the solvent (aspirator) gives **8a** as a yellow oil (1.5 g): NMR (CCl_4) δ 1.25 (6 H, t, J = 7 Hz), 1.93 (1 H, t, J = 6 Hz), 2.96 (2 H, s), 4.16 (4 H, q, J = 7 Hz), 5.29 (2 H, dd, J = 9, 6 Hz), 5.33 (1 H, s), 6.1 (2 H, m), 6.6 (2 H, m); IR (neat) 2100, 1725, 1640 cm^{-1}.

Diazo Ketone 8b. A solution of 3-carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid (130 g, 0.55 mol) in anhydrous ether (400 ml) is treated dropwise with dry (distilled from barium oxide) dicyclohexylamine (100 g, 0.552 mol) while cooling and swirling in an ice bath. Commercial hexane (600 ml) is then added, and the solution cooled to 4 °C overnight. After filtration, the solid is washed with hexane, and the mother liquors are concentrated for a second crop of the dicyclohexylammonium salt (186 g, 0.445 mol, 81%) as pale tan needles in pellets and clumps (mp 105–107 °C). The mother liquors of the second crop are evaporated to give a dark brown oil (45 g) which can be used in subsequent steps, although the products are more difficult to purify.

The crystalline salt (33.8 g, 0.081 mol) is dissolved in dry benzene (125 ml, distilled from CaH_2) and the solution is added dropwise to thionyl chloride (16.6 g, 0.14 mol) at room temperature. After 2 h of stirring, hexane (250 ml) is added, the slurry is filtered, and the cake of dicyclohexylamine hydrochloride washed with 200 ml of 30% benzene/hexane. Evaporation of the solvent, followed by several evaporative distillations of benzene–thionyl chloride azeotrope, yields crude acid chloride as a dark oil.

A solution of diazomethane generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (107 g, 0.5 mol)[18] is cooled to 0 °C. The crude acid chloride from above (ca. 21 g) in ether (50 ml) is added over 20 min. The solution is stirred at 0 °C for 1 h and stored overnight (10 h) at 4 °C. The solvent is blown off with dry nitrogen in a good hood. The crude yellow oil remaining is taken up in ether and deposited on an approximately equal weight of silica gel by drying in a rotary evaporator. This is deposited on top of a 6 by 2 in. column of silica gel under hexane. The column is eluted with hexane until the yellow band of diazo ketone is ready to elute, at which time the eluent is changed to 10% ether in hexane. The column is further eluted until there is no diazo absorption in the IR spectrum of the eluent. The diazo ketone containing fractions (ca. 2 l.) are cooled to −15 °C overnight, while pale yellow crystals separate from the solution. After filtration, diazo ketone **8b** (6.0–8.4 g, 0.023–0.032 mol, 46–64%) is isolated as yellow crystals, mp 56.0–57.0 °C. The mother liquors can be evaporated to give another 4–6 g of yellow oil, essentially pure **8b** by IR, NMR, and TLC; this can be used for further reactions, although yields are lower than for the crystalline material. IR (neat) 2120, 1730, 1640 cm^{-1}; NMR ($CDCl_3$) δ 6.8 (2 H, m), 6.4 (2 H, dt, J = 10, 3 Hz), 5.4 (3 H, m), 4.3 (2 H, q, J = 7 Hz), 2.6–3.5 (3 H, m), 1.9 (1 H, m), 1.3 (3 H, t, J = 7 Hz).

Diazo Ketone Decomposition. Decomposition of 8a. Preparation of 10a. A solution of **8a** (0.2 g) in dry benzene (5 ml, distilled from CaH_2) is added over 30 min to a vigorously stirred suspension of anhydrous $CuSO_4$ in refluxing benzene (10 ml). The mixture is refluxed for 30 min after addition is complete, filtered, and evaporated to give a dark oil. Preparative layer chromatography over silica gel (Brinkman PF 254) with 20% hexane in chloroform gives a single major zone, R_f 0.3. After extraction with ether and evaporation, crude **10a** is obtained as a crystalline solid (0.08 g, 44%). Colorless crystals of **10a** (mp 102–103 °C) are obtained from ether [Anal. ($C_{17}H_{20}O_5$) C, H]: UV (ethanol) λ_{max} 252 nm (ϵ 8520); IR ($CHCl_3$) 1725, 1695 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (3 H, t, J = 7 Hz), 1.29 (3 H, t, J = 7 Hz), 1.32 (1 H, m), 1.8–2.2 (4 H, m), 2.63 (1 H, d, J = 18 Hz), 3.32 (1 H, d, J = 18 Hz), 4.22 (4 H, q, J = 7 Hz), 5.9–6.3 (3 H, m).

Minor chromatography zones at R_f 0.4–0.6 and R_f 0.1–0.2 do not give characterizable products. None of these zones has significant carbonyl absorption at 1695 cm^{-1} characteristic of cyclopropyl ketones.

Thermal ($CuSO_4$) Decomposition of 8b. Isolation of 10b,c and 9b. A solution of **8b** (0.2 g) in dry toluene (5 ml, distilled from CaH_2) is added to a vigorously stirred suspension of anhydrous $CuSO_4$ (0.5 g, dried under vacuum at 300 °C) over 1 h. The mixture is refluxed for 1 h after addition is complete, cooled, filtered, and evaporated (aspirator) to give a dark brown residue.

Preparative layer chromatography over silica gel (Brinkman PF 254) using 15% ether/hexane, five developments, allows separation of three main zones: R_f >0.5, unidentified mixture of cycloheptatrienyl-containing products, no cyclopropyl ketone carbonyl absorption; R_f 0.4, 0.039 g (21%) of **10b,c**; and R_f 0.3, 0.041 g (23%).

Crystallization of the R_f 0.3 zone from CCl_4 gives colorless prisms of **9b** (mp 56–57.5 °C): UV (hexane) λ_{max} 253 nm (ϵ 4900); IR ($CHCl_3$) 1725, 1695 cm^{-1}; NMR (CCl_4) δ 5.65–6.05 (4 H, m), 4.1 (2 H, q, J = 7 Hz), 3.4 (1 H, m), 2.8 (1 H, m), 1.9–2.3 (4 H, m), 1.66 (1 H, dd, J = 8, 11 Hz), 1.2 (3 H, t, J = 7 Hz); exact mass 232.10769 found for $C_{14}H_{16}O_3$ (calcd, 232.10993).

Repeated preparative layer chromatography of the R_f 0.4 zone (four developments) results in partial separation of the **10b,c** mixture. The leading edge of the major zone gives the exo ester as a viscous oil: UV (ethanol) λ_{max} 251 nm (ϵ 4500); IR (neat) 1730, 1690 cm^{-1}; NMR (CCl_4) δ 6.3 (1 H, m), 6.0 (1 H, m), 5.7 (1 H, br d, J = 3 Hz), 4.15 (2 H, q, J = 7 Hz), 3.73 (1 H, dd, J = 12, 5 Hz), 2.8 (1 H, dd, J = 18, 5 Hz), 2.45 (1 H, dd, J = 18, 12 Hz), 1.8–2.4 (4 H, m), 1.2–1.35 (3 H, t, overlapping 1 H, m).

Crystallization of the trailing zone from CCl_4–hexane gives colorless needles of the endo ester (mp 89.5–93.5 °C); UV (ethanol) λ_{max} 252 nm (ϵ 7000); IR ($CHCl_3$) 1725, 1685 cm^{-1}; NMR (CCl_4) δ 6.3 (1 H, m), 5.95 (2 H, m), 4.1 (2 H, q, J = 7 Hz), 3.50 (1 H, d, J = 6 Hz), 3.05 (1 H, d, J = 18 Hz), 1.5–2.4 (5 H, m), 1.2–1.4 (3 H triplet overlapping 1 H multiplet); exact mass 232.11292 found for $C_{14}H_{16}O_3$. The exo and endo ester isomers are present in comparable amounts in the initial R_f 0.4 chromatography fraction.

Photosensitized Decomposition of 8b. A solution of **8b** (1.877 g, 0.00723 mol) and Michler's ketone (404 mg) in 2 l. of benzene deoxygenated by a dry nitrogen stream is exposed to a Hanovia lamp in a Pyrex well for 15 h, after which time the diazo IR absorption disap-

pears. The solvent is evaporated and the residue subjected to preparative layer chromatography on silica gel PF-254 (five developments by 15% ether/hexane) as before.

The area at R_f 0.3 contains no discernible **9b**. The R_f 0.4 zone gives **10b,c** (0.386 g, 22.4%) as a 1:9 mixture of endo:exo carboethoxy isomers.

Preparation of 8c. Cycloheptatrienylacetic acid[7,19] is converted into the acid chloride and the derived diazo ketone as described in the literature.[4g] To achieve Arndt–Eistert homologation, a solution of the diazo ketone (3.85 g) in THF (50 ml) is added dropwise over 30 min to a vigorously stirred solution of $AgNO_3$ (4 g), $Na_2S_2O_3$ (4.2 g), and water (170 ml) at 65 °C. After 1 h the mixture is cooled, acidified to pH 2 with 5% nitric acid, and extracted with ether (2 × 100 ml). The organic phase is extracted with 5% NaOH (3 × 50 ml), the base extract neutralized with 20% HCl, and extracted with ether (2 × 100 ml). The ether layer is dried ($MgSO_4$) and evaporated (aspirator) to give 3-(7-cyclohepta-1,3,5-trienyl)propionic acid as a pale yellow oil (3.3 g). Without further purification, the crude product is dissolved in ether (15 ml) and treated with dicyclohexylamine (3.9 ml). The colorless crystals of dicyclohexylammonium 3-(7-cyclohepta-1,3,5-trienyl)propionate are collected in two crops from ether (5.6 g). Conversion of the salt to 3-(7-cycloheptatrienyl)propionyl chloride and the derived diazo ketone is accomplished by the same method used to prepare **8b**. Starting with 8.56 g of dicyclohexylammonium salt and 8.25 g of $SOCl_2$, 4.47 g of crude acid chloride is obtained. Reaction with diazomethane generated in the usual way from 40 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide followed by filtration chromatography on silica gel (10 × 3 cm column) with hexane gives diazo ketone **8c** (3.4 g) as a yellow oil: IR (neat) 2120, 1630 cm^{-1}; NMR (CCl_4) δ 6.62 (2 H, m), 6.0–6.3 (2 H, m), 5.36 (1 H, s), 5.13 (2 H, dd, J = 9, 6 Hz), 1.5–2.6 (5 H, m).

Decomposition of 8c. Isolation of 9c. A solution of **8c** (2 g) is added to a vigorously stirred solution of anhydrous $CuSO_4$ (2 g) in refluxing benzene as described for preparation of **9b**. Separation of the crude product by preparative layer chromatography over silica gel with 15% acetone/hexane (three developments) gives two major zones (R_f 0.3 and 0.4) and four minor zones (R_f 0.15, 0.45, 0.55, and 0.7). No characterizable products can be isolated from the minor zones. The zone at R_f 0.4 (0.64 g) cannot be separated into individual components by TLC. Separation by GLC on 10 ft × 0.375 in. 10% Carbowax/Chromosorb P (170 °C) results in extensive thermal degradation, but the shortest retention time component corresponds by NMR to a component of the R_f 0.4 preparative TLC fraction. This noncrystalline product is spiro[6.4]undeca-6,8,10-trien-2-one based on spectral data: IR (neat) 1740 cm^{-1}; NMR (CCl_4) δ 6.5–6.7 (2 H, m), 6.0–6.3 (2 H, m), 5.28 (2 H, d, J = 10 Hz), 1.98 (2 H, s), 1.9–2.5 (4 H, m).

The NMR spectrum of the R_f 0.4 zones contains a doublet of doublets at δ 4.93, characteristic of a monosubstituted cycloheptatrienyl ring, other complex olefinic signals between δ 5.8 and 6.7, and a complex aliphatic region, δ 1.9–3. The combined integral ratio of olefinic:aliphatic protons is 7:9 (structure **10d** requires a ratio of 3:9).

The R_f 0.3 zone (0.27 g, 15%) gives a colorless oil consisting of **9c** (ca. 90% pure) and traces of side products: IR (neat) 1690 cm^{-1}; NMR (CCl_4) δ 5.7–6.3 (3 H, m), 3.15 (1 H, m), 1.7–2.3 (7 H); *m/e* 160 for $C_{11}H_{12}O$.

Conversion of 9b to 4b. Bromination of 9b. To the base from hexamethyldisilazane (4.00 g, 0.025 mol) and buthylithium (18.1 ml of a 2.19 M solution in hexane, 0.020 mol), prepared at −78 °C in dry tetrahydrofuran (20 ml) in a 100-ml oven-dried flask, is added keto ester **9b** (3.78 g, 0.0163 mol) dissolved in dry tetrahydrofuran (10 ml), and the reaction mixture stirred for 2 h at −78 °C. A solution of norbornene (3.8 g, 0.040 mol) and 5-bromo-2,2,5-trimethyl-1,3-dioxane-4,6-dione **14**[13] (4.74 g, 0.020 mol) in dry tetrahydrofuran (15 ml) is added, the cooling bath is removed, and the reaction mixture is allowed to warm to room temperature while stirring. (Omission of the norbornene lowers the yield by 15–30%; we assume that norbornene acts as a positive bromine trap.) After 20 min, the reaction is quenched with a mixture of 10% HCl (10 ml) and saturated brine (10 ml). The aqueous phase is separated and extracted with ether (20 ml), which is combined with the organic phase; the solvents are then removed (aspirator). The residue is deposited on silica gel (5 g) and placed on top of a 6 by 2 in. diameter column of silica gel under hexane. Elution with hexane (500 ml) removes the silyl compounds. Elution with 25% ether/hexane (500 ml) affords the bromo ketone (4.52 g, 0.0145 mol, 89%) as a pale yellow oil which slowly solidifies (mp 74.5–78 °C). This material is used without recrystallization: IR (neat) 1727, 1700 cm^{-1}; NMR (CCl_4) δ 5.7–6.4 (4 H, m), 4.46 (1 H, d, J = 3 Hz), 4.0–4.3 (2 H, m), 3.2–3.4 (2 H, m), 1.6–2.2 (3 H, m), 1.25 (3 H, t, J = 7 Hz). NMR shift decoupling studies, see Table I; exact mass observed 310.02168 for $C_{14}H_{15}O_3Br$ (calcd, 310.02050).

Table I. NMR Data for Ethyl 9β-Bromotricyclo[5.4.0.0^{2,11}]-undeca-3,5-dien-10-one-8β-carboxylate

		Shift europium added (arbitrary increments)			
Proton	Multiplicity	0	1st	2d	3d
1	q	2.18	2.42	2.56	2.80
2	t	1.96	2.10	2.22	2.40
3	dd	6.10	6.23	6.38	6.58
4	dd	5.84	5.84	5.86	5.86
5	dd	5.84	5.84	5.90	6.00
6	dd	6.40	6.54	6.64	6.84
7	m	3.34	4.26	4.56	5.20
8	dd	3.20	4.26	4.64	5.34
9	d	4.45	5.86	6.30	7.14
11	dd	1.66	2.68	3.00	3.60

Coupling constants (Hz): $J_{1,2}$ = 7.5; $J_{1,7}$ = 7.5; $J_{1,11}$ = 7.5; $J_{2,3}$ = 3; $J_{3,4}$ = 10; $J_{4,5}$ = 5; $J_{5,6}$ = 10; $J_{6,7}$ = 7.0; $J_{7,8}$ = 10; $J_{8,9}$ = 3 Hz.

Ethyl 9β-Bromo-1β,7β-tricyclo[5.4.0.0^{2,11}]undeca-3,5-dien-10β-ol-8β-carboxylate (15). In a 500-ml round-bottom flask the bromo ketone from above (4.52 g, 0.0145 mol) is dissolved in dry tetrahydrofuran (100 ml); commercial absolute ethanol (60 ml) is added, and the solution cooled with stirring to −78 °C. Sodium borohydride (1.52 g, 0.040 mol) is added, the cooling bath is removed, and the reaction mixture is stirred vigorously while slowly warming to room temperature. After 1 h, the reaction is quenched with Rochelle salts (10 g) dissolved in distilled water (40 ml). Sodium chloride (20 g) and 10% HCl (30 ml) are added, the phases separated, and the aqueous phase washed with ether (50 ml). The combined organic phases are evaporated; the residue is taken up in ether (400 ml), which is then washed with 10% HCl (150 ml) and saturated brine (150 ml), dried over magnesium sulfate, and evaporated, leaving **15** (4.32 g, 0.0138 mol, 95%) as a colorless oil which solidifies. Recrystallization from ether/chloroform/hexane yields pure **15**: mp 92.0–93.0 °C; IR (neat) 3450, 1730 cm^{-1}; NMR (CCl_4) δ 6.44 (1 H, dd, J = 11, 8 Hz), 6.15 (1 H, br d, J = 10 Hz), 5.93 (1 H, dd, J = 10, 5 Hz), 5.72 (1 H, dd, J = 11, 5 Hz), 4.75 (1 H, t, J = 2 Hz), 4.15 (2 H, m), 3.5 (1 H, br d, J = 10 Hz), 3.20 (1 H, dt, J = 8, 7 Hz), 2.5 (1 H, br d, J = 10 Hz), 2.45 (1 H, dd, J = 10, 2 Hz), 1.75 (1 H, q, J = 8 Hz), 1.6 (1 H, m), 1.3 (3 H, t, J = 7 Hz), 0.8 (1 H, ddd, J = 9, 8, 2 Hz); exact mass observed 312.03803 for $C_{14}H_{17}O_3Br$ (calcd, 312.03615).

Zinc Reduction of 15. Preparation of 4b. A solution of **15** (4.32 g, 0.0138 mol) in glacial acetic acid (180 ml) is cooled to 15 °C with a cold water bath while zinc dust (200 g) is added with vigorous mechanical stirring at such a rate that the internal temperature remains below 25 °C. The suspension is vigorously stirred for 13 h at room temperature; ether (150 ml) is added, and the stirring continued for 10 min more. The reaction mixture is filtered, and the cake of zinc and zinc salts is well washed with ether (300 ml). The filtrate is washed with 10% KOH (3 × 350 ml), which washings are back extracted with ether (100 ml). The ether phases are combined and evaporated; the residual oil is placed on a column of silica gel (50 g) in hexane. Elution with 3% ether/hexane (700 ml) yields ethyl 1β,7β-tricyclo[5.4.0.0^{2,11}]-undeca-3,5,9-triene-8β-carboxylate (**4b**) as a colorless, pleasant-smelling oil (0.998 g, 0.00462 mol, 33.5%): UV (ethanol) λ_{max} 257 nm (ϵ 2800); IR (neat) 1725 cm^{-1}; NMR (CCl_4) δ 6.4 (1 H, ddd, J = 9, 8, 2 Hz), 5.5–6.0 (5 H, complex), 4.03 (2 H, q, J = 7 Hz), 3.1 (1 H, q, J = 7 Hz), 2.8 (1 H, pentet, J = 3 Hz), 1.9 (1 H, q, J = 8 Hz), 1.6 (1 H, br t, J = 8 Hz), 1.2 (4 H, 7 Hz triplet, 3 H, overlapping 1 H multiplet); exact mass observed for $C_{14}H_{16}O_2$ 216.11589 (calcd, 216.11502).

Elution of the column with ether (700 ml) yields a mixture of the lactones 4-oxapentacyclo[6.5.0.0^{2,13}.0^{3,7}.0^{6,12}]tridec-9-en-5-one and -10-en-5-one (**16**) as a colorless oil which slowly solidifies (1.655 g, 0.00880 mol, 63.7%). Recrystallization from ether/hexane gives colorless needles of the mixture, mp 60.5–62.0 °C. Repeated recrystallizations do not change the isomer ratio: IR (neat) 1765 cm^{-1}; NMR (CCl_4) δ 5.4–6.2 (2 H, complex), 5.0 (1 H, m), 1.2–2.9 (9 H, complex); exact mass observed 188.08525 for $C_{12}H_{12}O_2$ (calcd, 188.08372).

Structure Proof of 16. Synthesis of 17 (Scheme IV). 8-Carboethoxybicyclo[3.2.2]non-6-ene-9-carboxylate Dicyclohexylammonium Salts. To a solution of sodium (1.960 g, 0.085 mol) in

absolute ethanol (50 ml) is added bicyclo[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic anhydride[20] (11.60 g, 0.0605 mol), and the solution warmed to 67 °C for 2 h. The solvent is removed on a rotary evaporator (aspirator) and the product partitioned between ether (200 ml) and 10% HCl (200 ml). The ether is separated, dried over magnesium sulfate, and evaporated. The product is extracted from the residual oil into hot hexane which is evaporated to yield the half ester carboxylic acid as a viscous oil. The oil is dissolved in ether (30 ml) and treated with dicyclohexylamine. Crystallization at −4 °C overnight gives colorless crystals (19.2 g, two crops), mp 93.5–99.5 °C.

Ethyl Tetracyclo[5.4.0.0^{2,11}.0^{3,9}]undecan-10-one-8-carboxylate. The crystalline salt from above (12.6 g, 0.03 mol) is dissolved in chloroform (40 ml) and treated with thionyl chloride (5 ml) at 20 °C for 2.5 h. Hexane (60 ml) is added, the suspension is filtered, and the cake of dicyclohexylammonium chloride is washed with hexane (100 ml). After solvent removal (aspirator), any residual thionyl chloride is removed by azeotropic distillation (aspirator) with dry (distilled from calcium hydride) benzene (50 ml). The resulting acid chloride is dissolved in ether (50 ml) and added to diazomethane prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (30 g)[24] in ether solution at 0 °C as described for preparation of **8b.** Filtration chromatography over silica gel (2 × 10 cm column) with hexane gives a yellow fraction which yields diazo ketone upon evaporation (7.34 g). A solution of the diazo ketone (4.37 g 0.0167 mol) in dry benzene (30 ml, distilled from CaH_2) is dripped over 1 h into a refluxing suspension of copper sulfate (4.0 g, predried at 350 °C and stored in a desiccator) in dry benzene (40 ml). After stirring for an additional 1 h, the suspension is filtered and the solvent removed (aspirator). The residual oil is taken into warm pentane (leaving a small amount of a brown, tarry substance) and the pentane evaporated to yield a colorless oil (3.7 g). The NMR spectrum lacks distinctive features other than to show the presence of ester and the absence of vinyl hydrogens; exact mass, observed 234.12498 for $C_{14}H_{18}O_3$ (calcd 243.12558).

Ethyl Tetracyclo[5.4.0.0^{2,11}.0^{3,9}]undecan-10-ol-8-carboxylate. The crude tetracyclic keto ester from above (12.9 g, 0.0055 mol) in ethanol (20 ml) is stirred at −20 °C with sodium borohydride (0.25 g, 0.0066 mol) for 1 h and then allowed to warm to 20 °C. The reaction is quenched with Rochell salts (3 g) in water (15 ml) and partitioned between ether (100 ml) and 10% HCl (30 ml). The ethereal phase is washed with 10% HCl (20 ml) and saturated brine (20 ml), dried over magnesium sulfate, and evaporated (aspirator). The residual colorless oil crystallizes from ether/hexane, giving the tetracyclic hydroxy ester (0.275 g, 0.00115 mol, 21%) as colorless crystals (mp 74.5–77.0 °C). The mother liquors can be evaporated to yield more product as an oil (overall 1.27 g, 0.00536 mol, 97%) which is suitable for use in the next reaction: IR ($HCCl_3$) 3510, 1720 cm^{-1}; NMR ($CDCl_3$) δ 4.4 (1 H, dd, J = 5, 2 Hz), 4.13 (2 H, q, J = 7 Hz), 3.4 (1 H, d, J = 9 Hz), 2.95 (1 H, s), 2.6 (1 H, br), 2.22 (2 H, m), 1.2–2.0 (8 H, m), 1.25 (3 H, t, J = 7 Hz), 0.95 (1 H, q, J = 6 Hz); exact mass observed 236.14099 for $C_{14}H_{20}O_3$ (calcd, 236.14123).

Lactonization to 17. The crude (not crystallized) hydroxy ester from above (1 g, 0.004 mol) is refluxed with sodium ethoxide from sodium (2.3 g) and ethanol (100 ml) overnight. The solution is cooled and treated with 20% HCl (20 ml) and the solvents are evaporated (aspirator). The residue is partitioned between ether (50 ml) and water (20 ml), and the ether layer is separated and washed with saturated brine (20 ml), dried over magnesium sulfate, and evaporated to give a brown oil (0.661 g). Preparative layer chromatography over silica gel using 20% ether/hexane affords **17** (0.38 g, 48%) as a colorless oil which slowly solidifies. Recrystallization from ether gives colorless prisms of **17** (mp 84.5–86.5 °C): IR ($CHCl_3$) 1765 cm^{-1}; NMR ($CDCl_3$) δ 5.0 (1 H, dd, J = 6, 4 Hz), 1.6–2.7 (12 H, complex), 1.25 (1 H, q, J = 7 Hz); exact mass observed 190.09882 for $C_{12}H_{14}O_2$ (calcd, 190.09937).

Attempted lactonization of the hydroxy ester under milder conditions gives recovered starting material. This may be due to unfavorable ester stereochemistry caused by epimerization during cleavage of the starting maleic anhydride adduct with sodium ethoxide.

Diimide Reduction of the Lactones 16. To a solution of lactones **16** (0.104 g, 0.000553 mol) in commercial pyridine (50 ml) is added potassium azodicarboxylate (10.4 g, 0.0553 mol), and the suspension mechanically stirred at room temperature while glacial acetic acid is dripped in over a 2-h period. After stirring for an additional 1 h, ether (200 ml) is added, and the reaction mixture is washed with 10% KOH (100 ml), 10% HCl (3 × 100 ml), and saturated brine (100 ml), dried over magnesium sulfate, and evaporated. The NMR spectrum indicates incomplete reduction, and the product is resubjected to the reaction. After three treatments, ca. 30% starting **16** still remains. To allow separation of product from starting material, the crude product is treated with bromine (0.05 g, 0.0003 mol) in CCl_4 (1 ml) at 0 °C, the solvent evaporated, and the crude product separated by preparative layer chromatography over silica gel. The zone corresponding to **17** is collected (0.06 g, 60%) which solidifies. Recrystallization from ether affords colorless prisms)mp 84.5–86.5 °C) identical by mixture melting point, NMR, IR, and TLC with **17** prepared independently.

Table II. NMR Europium Shift Decoupling Experiments on Ethyl Tricyclo[6.3.0.0^{3,9}]undeca-4,6,10-triene-2-*endo*-carboxylate

Chemical shifts, δ (CCl_4)		Eu(dpm)$_3$ added (arbitrary increments)		
Proton	Mult	0	1	2
9	s	2.37	2.62	2.90
8	br d	2.23	2.50	2.78
7	*a*	*a*	*a*	*a*
6	*a*	*a*	*a*	*a*
5	*a*	*a*	*a*	*a*
4	dd	6.22	6.38	6.52
3	cx m	2.50	3.58	4.66
2	t	2.90	3.94	5.06
1	br s	3.46	4.10	4.80
11	dd	6.10	6.68	7.28
10	dd	6.50	6.75	7.02

[a] Broad complex multiplet at δ 5.5–6.0, unseparated by europium. $J_{8,9}$ = ?, $J_{9,10}$ = 3, $J_{7,8}$ = 5.5, $J_{3,8}$ = 2, $J_{1,8}$ = 1.5, $J_{4,5}$ = 10, $J_{3,4}$ = 8, $J_{2,3}$ = 4, $J_{1,2}$ = 4, $J_{1,11}$ = 3, $J_{10,11}$ = 6 Hz.

Thermolysis of Divinylcyclopropane Derivatives. Ethyl Tricyclo[6.3.0.0^{3,9}]undeca-4,6,10-triene-2-*endo*-carboxylate (19). Triene ester **4b** (0.108 g, 0.00050 mol) dissolved in carbon tetrachloride (0.3 ml) in an NMR tube is placed in a 55.00 °C thermostated bath, and the NMR spectrum is monitored from time to time. Ester **4b** disappears with first-order kinetics (k_1 = 1.56 × 10^{-5} s^{-1}, ρ = 0.995 for six points). After 8 half-lives (88 h), there is only one product visible in the NMR. Rinsing the reaction into a tared flask with ether and evaporation yields ester **19** (0.108 g, 0.00050 mol, 100%) as a pale yellow oil: IR (neat) 1725 cm^{-1}; NMR (CCl_4) δ 6.50 (1 H, dd, J = 6, 3 Hz), 5.6–6.2 (5 H, m), 4.0 (2 H, q, J = 7 Hz), 3.46 (1 H, br s), 2.90 (1 H, t, J = 4 Hz), 2.2–2.5 (3 H, m), 1.1 (3 H, t, J = 7 Hz); exact mass observed 216.11370 for $C_{14}H_{16}O_2$ (calcd, 216.11502); UV (EtOH) λ_{max} 258 nm (ε 3650). GLC: retention time 52.5 min on 20% SE-30 on 60/80 Chromosorb P 20 ft × 0.125 in. at 150 °C, He flow 60 ml/min. NMR shift/decoupling studies: see Table II. Rearrangement at 65.00 °C proceeds with k_1 = 6.53 × 10^{-5} s^{-1} (ρ = 0.985, six points). This gives an Arrhenius ΔE_{act} = 31.7 (± 1.2) kcal mol^{-1} and log A = 16.19. An Eyring treatment gives $\Delta H^{\ddagger}$ = 31.0 (± 1.2) kcal/mol, $\Delta S^{\ddagger}$ = +13 (± 5) cal deg^{-1} mol^{-1}.

Pyrolysis of 19 under GLC Conditions. A solution of **4b** (50% in acetone) is injected (injection block temperature 220 °C) onto a 20 ft × 0.125 in. 20% SE-30 on Chromosorb P column at 150 °C with helium flow of 60 ml/min. The peak corresponding in retention time to **19** (52.5 min) is collected; it accounts for over 95% of the volatile materials, and contains (by NMR) approximately 30% **23** and 70% **19.** Preparative scale pyrolysis of **4b** (0.03 g) at 170 °C in a solution consisting of biphenyl (0.1 g), *o*-terphenyl (0.1 g), and naphthalene (0.05 g) in an NMR tube gives a mixture of **19** and **23.** After 15 h, the NMR signals due to **19** are no longer visible. Preparative layer chromatography of the mixture (six developments, hexane) over silica gel affords a zone corresponding to **19** in R_f. Extraction of the product with ether gives an oil (0.01 g, 34%) consisting of **23** contaminated with ca. 15% of **19:** NMR ($CDCl_3$) δ 6.5 (1 H, dd, J = 6, 3 Hz), 5.7–6.1 (4 H, complex), 5.1 (1 H, dd, J = 10, 4 Hz), 4.15 (2 H, q, J = 7 Hz), 2.94 (1 H, br s), 2.3–2.6 (4 H, complex), 1.25 (3 H, t, J = 7 Hz).

Preparation of 21 and Rearrangement to 25. Isolation of 22. Triene ester **4b** (0.0291 g, 0.000134 mol) is added to the base from diisopropylamine (0.200 g, 0.00198 mol) and butyllithium (0.80 ml of 1.01 M solution, 0.000808 mol) in dry tetrahydrofuran (10 ml) stirring under nitrogen at −78 °C, and the resultant orange solution is stirred for 45 min at −78 °C. Chlorotrimethylsilane (0.500 g, 0.0046 mol) is added, and the colorless solution is brought to room temperature with stirring. After 20 min, the solvent is removed on a rotary evaporator (aspirator); carbon tetrachloride (5 ml) is added to the residual slurry, and again the solvents are evaporated. Carbon tetrachloride (2 ml) is added, and the slurry is filtered through a tight

Table III. Europium Shift/Decoupling NMR Experiments on Ethyl Tricyclo[6.3.0.0^{4,9}]undeca-2,6,10-triene-5-*exo*-carboxylate (22)

Proton	Mult	Chemical shift, δ	Normalized $\Delta\delta$ (Eu)
4	br s	2.64	12.1
3	dddd	5.10	13.4
2	dd	6.10	3.5
1	br s	2.50	2.5
11	dd	6.50	1.4
10	dd	5.77	1.0
9	br s	2.50	3.7
8	br s	2.50	3.0
7	ddd	5.85	3.6
6	dd	6.05	12.3
5	br s	3.34	17.5

$J_{3,4} = 4, J_{4,9} = ?, J_{4,5} = 4, J_{2,3} = 9, J_{1,2} = 6, J_{1,11} = 3, J_{1,8} = 4, J_{10,11} = 5.5, J_{9,10} = 2, J_{8,9} = ?, J_{7,8} = 4, J_{6,7} = 10, J_{5,7} = 2, J_{5,6} = 1$ Hz.

Table IV. Europium Shift/Decoupling NMR Experiments on Ethyl Tricyclo[6.3.0.0^{4,9}]undeca-2,10-dien-7-one-5-*exo*-carboxylate (33)

Proton	Mult	Shift, δ	Normalized $\Delta\delta$ [Eu(dpm)$_3$]
4	ddd	2.8	4.6
3	dddd	5.14	4.3
2	dd	6.16	2.6
1	ddd	2.8	4.1
11	dd	6.49	1.2
10	dd	5.74	1.00
9	ddd	2.8	3.7
8	dd	2.6	10.3
6α	dd	2.5	14.1
6β	dd	2.6	12.2
5	ddd	2.9	5.6

$J_{3,4} = 6, J_{4,9} = 3, J_{4,5} = 3, J_{2,3} = 10, J_{1,2} = 5.5, J_{1,11} = 3, J_{1,8} = 5.5, J_{11,10} = 6, J_{10,9} = 3, J_{9,8} = 5.5, J_{6\alpha,6\beta} = 18, J_{6\alpha,5} = 10, J_{6\beta,5} = 7$ Hz.

plug of fiberglass in a disposable pipet (this having been assembled and dried at 100 °C for 2 h) with the aid of a carbon tetrachloride rinse (1 ml). This filtrate contains almost pure enol silane **21:** NMR (CCl_4) δ 6.5 (1 H, dd, J = 8, 11 Hz), 6.0 (1 H, d, J = 12 Hz), 5.5–5.7 (3 H, m), 5.34 (1 H, dd, J = 4, 10 Hz), 3.8 (2 H, q, J = 7 Hz), 3.4 (1 H, m), 1.8 (2 H, m), 1.2 (4 H, m), 0.2 (9 H, s).

Heating **21** to 70 °C for 15 h results in clean rearrangement to enol silane **25:** NMR (CCl_4) δ 6.5 (1 H, dd, J = 6, 3 Hz), 6.15 (1 H, d, J = 10 Hz), 5.7 (2 H, m), 5.5 (1 H, dd, J = 10, 5 Hz), 4.90 (1 H, dddd, J = 10, 4, 0.8, 0.8 Hz), 3.8 (2 H, q, J = 7 Hz), 3.0 (1 H, m), 2.2–2.6 (3 H, m), 1.2 (3 H, t, J = 7 Hz), 0.2 (9 H, s).

Aqueous hydrolysis (2:1 THF–H_2O, 2 h, 20 °C) yields almost pure ethyl tricyclo[6.3.0.0^{4,9}]undeca-2,6,10-triene-5-*exo*-carboxylate (**22**), which is purified by preparative gas chromatography. Retention time on a 20 ft × 0.125 in. 20% SE-30 on Chromosorb P column at 150 °C with a helium flow of 60 ml/min: 58.0 min. IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 6.50 (1 H, dd, J = 6, 3 Hz), 5.7–6.1 (4 H, m), 5.1 (1 H, dddd, J = 9, 4, 0.8, 0.8 Hz), 4.15 (2 H, q, J = 7 Hz), 3.3 (1 H, br s), 2.4–2.6 (4 H, m), 1.25 (3 H, t, J = 7 Hz). NMR europium-shift/decoupling experiments: see Table III.

Epimerization of 23 to 22. A mixture of **19** and **23** (0.216 g, 0.001 mol) obtained by pyrolysis (ratio of **19:23** ca. 10:1) is dissolved in dry THF at −78 °C and treated with lithium diisopropylamide (1.5 ml of 0.7 M solution in hexane–THF) under nitrogen flow. After 45 min at −78 °C, water (2 ml) is added to the stirred mixture. Partition between ether–water followed by drying ($MgSO_4$) and evaporation gives an oil (0.16 g). Preparative GLC (20 ft × 0.125 in. 20% SE-30/Chromosorb P, 150 °C) gives two peaks in the ratio 9:1. The major (lower retention time) peak is pure **19** while the minor peak is identical with **22** in all respects.

Preparation of Ethyl Tricyclo[6.3.0.0^{3,9}]undeca-4,6-dien-11-one-2-carboxylate (30). Keto ester **9b** (0.085 g, 0.000366 mol) in dry tetrahydrofuran (1 ml) is added to the base from hexamethyldisilazane (0.400 g, 0.00330 mol) and butyllithium (0.80 ml of 1.05 M solution, 0.00084 mol) stirring under nitrogen at −78 °C in dry tetrahydrofuran (10 ml). After stirring for 15 min at −78 °C, the reaction is quenched with chlorotrimethylsilane (0.80 g, 0.0073 mol) and stirred for 5 min while being warmed to room temperature. After the solvent is removed on a rotary evaporator (aspirator), carbon tetrachloride (2 ml) is added to the residual slurry, and the solvents are once again evaporated. The residual brown oily solid is suspended in carbon tetrachloride and filtered through an oven-dried plug of tightly packed glass wool in a disposable pipet. Evaporation yields enol silane **27:** NMR (CCl_4) δ 5.6–6.2 (4 H, m), 4.6 (1 H, d, J = 5 Hz), 4.1 (2 H, q, J = 7 Hz), 3.5 (1 H, m), 2.9 (1 H, m), 1.9 (1 H, q, J = 8 Hz), 1.4 (1 H, m), 1.25 (3, H, t, J = 7 Hz), 0.9 (1 H, m), 0.1 (9 H, s).

Heating **27** in CCl_4 for 18 h results in rearrangement. Hydrolysis in 2:1 THF–H_2O for 2 h at 25 °C followed by preparative layer chromatography over silica gel (20% ether/hexane, three developments) gives recovered **9b** in the slower zone (0.016 g, 23%), and **30** (0.034 g, 40%) in a faster zone: UV (ethanol) λ_{max} 259 nm (ϵ 4010), 268 (3640); IR 1755, 1725 cm^{-1}; NMR (CCl_4) δ 5.6–6.1 (4 H, m), 4.1 (2 H, m), 3.24 (1 H, t, J = 4 Hz), 3.0 (1 H, br d, J = 4 Hz), 2.85 (1 H, m), 2.6 (1 H, m) 2.45 (1 H, br s), 2.1 (2 H, ABX, J_{AB} = 19, J_{AX} = 4, J_{BX} ~0 Hz), 1.2 (3 H, t, J = 7 Hz). Decoupling studies in the presence of Eu(fod)$_3$ allow assignment of the folowing coupling constants (Hz): $J_{9,10} = 4, J_{7,8} = 6, J_{6,7} = 10, J_{5,6} = 6, J_{4,5} = 10, J_{3,4} = 8, J_{2,3} = 4, J_{1,2} = 4$.

Preparation of Ethyl Tricyclo[6.3.0.0^{4,9}]undeca-2,10-dien-7-one-5-carboxylate (33). In an oven-dried three-neck flask, one of whose necks is equipped with a short-path distillation setup, hexamethyldisilazane (1.21 g, 0.0075 mol) is added to dry tetrahydrofuran (20 ml), and butyllithium (2.0 ml of a 2.18 M solution in hexane, 0.00434 mol) is added under nitrogen flow. The solution is cooled with stirring to −78 °C, and keto ester **9b** (0.612 g, 0.00244 mol) dissolved in dry THF (30 ml) is added, and the solution stirred 90 min at −78 °C, at which time chlorotrimethylsilane (1.3 ml) is added. The solution is now heated to distill off the excess chlorotrimethylsilane. Dry THF (20 ml) is added, and the reaction cooled once again to −78 °C, at which time the base from hexamethyldisilazane (1.21 g, 0.0075 mol) and butyllithium (2.0 ml of a 2.18 M solution in hexane, 0.00434 mol) in dry THF (20 ml) is added by syringe. After 90 min, chlorotrimethylsilane (1.3 ml) is added, the dry ice bath is removed, and the reaction mixture is stirred for 20 h at room temperature. After quenching with 10% HCl (5 ml) 30 min, the volatiles are removed on a rotary evaporator (ASPIRATOR(/ Partition of the crude product between ether and water, followed by drying and solvent removal, yields the crude product as a brown oil (0.534 g). Preparative layer chromatography on silica gel PF-254 (four developments with 20% ether/pentane) affords pure **33** (0.102 g, 0.00044 mol, 16%) as a pale yellow oil, from the UV-inactive band behind **30** but ahead of starting material (both of which are UV active): IR (neat) 1730 cm^{-1}; NMR (CCl_4) δ 6.49 (1 H, dd, J = 6, 3 Hz), 6.16 (1 H, dd, J = 10, 6 Hz), 5.74 (1 H, dd, J = 6, 3 Hz), 5.14 (1 H, m), 4.1 (2 H, q, J = 7 Hz), 2.4–3.0 (7 H, m), 1.2 (3 H, t, J = 7 Hz); europium shift/decoupling NMR experiments, see Table IV. Exact mass observed 232.10894 for $C_{14}H_{16}O_3$ (calcd, 232.10993).

Rearrangement of 29. Isolation of Tricyclo[6.3.0.0^{3,9}]undeca-4,6-dien-11-one (32). A solution of **9c** (0.28 g, 0.00175 mol) in dry THF (10 ml) is added over 5 min to the base from hexamethyldisilazane (0.515 g, distilled) and *n*-butyllithium (1.2 ml of 2.33 M hexane solution, 0.0029 mol) in dry THF (15 ml) at −78 °C under nitrogen flow. After 90 min at −78 °C, chlorotrimethylsilane (0.6 ml) is added and the solution is stirred for 1 h at −78 °C and then allowed to reach room temperature. The THF solution of **29** is then warmed for 2 h each to 43 and 54 °C. Aliquots are withdrawn and hydrolyzed with methanol (2 h, room temperature). Analysis by TLC (15% acetone/hexane) on silica gel shows only recovered **9c.** The THF solution is then refluxed for 18 h, cooled to 45 °C, and treated with methanol (40 ml). After 2 h at 45 °C, the product is partitioned between ether and water, the ether layer is dried ($MgSO_4$) and evaporated, and the residual oil is separated by preparative TLC (15% acetone/hexane, silica gel PF 254). The main zone (R_f 0.3–0.4) is collected to yield **32** as a colorless oil (0.16 g, 58%), contaminated by ca. 10% of an unknown side product. Preparative GLC on 10 ft × 0.25 in. 10% Carbowax/Chromosorb P at 180 °C gives two minor peaks (retention times 9 and 14 min) and a peak at 16.5 min, identical by NMR with the major component in the major TLC fraction. Collection of the main GLC peak gives **32** as a colorless oil: UV (methanol) λ_{max} 269 nm (ϵ 4440), 259 (4905); IR (neat) 1740 cm^{-1}; NMR (CCl_4) δ 5.5–6.1 (4 H, complex), 2.8 (1 H, d, J = 4 Hz), 2.0–2.6 (6 H, complex), 1.86 (1 H, d, J = 18 Hz),

1.66 (1 H, dd, J = 13, 9 Hz). Decoupling experiments in the presence of Eu(fod)$_3$ indicate the following coupling constant assignments: $J_{1,2\text{-exo}} = 4$, $J_{9,10\text{-exo}} = 4$, $J_{9,10\text{-endo}} < 1$, $J_{10\text{-exo},10\text{-endo}} = 19$ Hz.

Registry No.—**4b,** 61063-63-6; **8a,** 61063-55-6; **8b,** 61063-56-7; **8c,** 61063-57-8; **9b,** 61063-58-9; **9c,** 61063-59-0; **10a,** 61063-60-3; **10b,** 61063-61-4; **10c,** 61116-91-4; **14,** 34817-42-0; **15,** 61063-62-5; **15** ketone derivative, 57261-23-1; **16** 9-ene, 61063-64-7; **16** 10-ene, 61092-33-9; **17,** 61092-34-0; **19,** 61063-65-8; **21,** 61063-66-9; **22,** 61063-67-0; **23,** 61116-92-5; **25,** 61063-68-1; **27,** 61063-69-2; **29,** 61063-70-5; **30,** 61063-71-6; **32,** 61063-72-7; **33,** 61063-73-8; *tert*-butyl chloroacetate, 107-59-5; diethyl malonate, 105-53-3; *tert*-butyl ethyl 2-carboethoxysuccinate, 61063-74-7; monoethyl(2-carboethoxy) succinate, 61063-75-0; cycloheptatrienyl fluoroborate, 61063-76-1; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid, 61063-77-2; 2-carboethoxysuccinic acid, 61063-78-3; 3-carboethoxy-3-(7-cycloheptatrienyl)propionic acid, 61063-79-4; piperidine, 110-89-4; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid piperidine, 61063-80-7; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionyl chloride, 61063-81-8; dicyclohexylamine, 101-83-7; 3-carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid dicyclohexylamine salt, 61063-82-9; diazomethane, 334-88-3; 3-carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionyl chloride, 61063-83-0; cycloheptatrienylacetic acid diazo ketone, 61063-84-1; 3-(7-cyclohepta-1,3,5-trienyl)propionic acid, 61063-85-2; dicyclohexylammonium 3-(7-cyclohepta-1,3,5-trienyl)propionate, 61063-86-3; 3-(7-cycloheptatrienyl)propionyl chloride, 61063-87-4; spiro[6,4]-undeca-6,8,10-trien-2-one, 61063-88-5; bicyclo[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic anhydride, 29577-71-7; ethyl bicyclo-[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic acid, 61063-89-6; dicyclohexylammonium ethyl bicyclo[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic acid, 61116-93-6; bicyclo[3.2.2]non-6-ene-8-*syn*-carboxylic acid 9-*syn*-carbonyl chloride, 61063-91-0; ethyl tetracyclo-[5.4.0.0^{2,11}.0^{3,9}]undecan-10-one-8-carboxylate, 61063-90-9; ethyl tetracyclo[5.4.0.0^{2,11}.0^{3,9}]undecan-10-ol-8-carboxylate, 61092-35-1.

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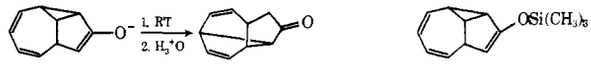

ii iii iv

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Protolytic and Pyrolytic Rearrangements of Polycyclic Methyl Cyclopropyl Ketones

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Certain methyl cyclopropyl ketones containing methylated tricyclo[3.2.1.0^{2,4}] nuclei undergo rapid rearrangement in dilute trifluoroacetic acid to give α,β-unsaturated ketones and cyclic enol ethers. The mechanism is discussed in terms of the cyclopropyl carbinyl to homoallylic rearrangement. Release of strain and stability of the cationic intermediates are thought to contribute to the ease of the rearrangement. Methyl migration appears to be slower than hydride transfer to the initial cationic center. When migration cannot readily occur, internal enol capture results leading to enol ethers. The related thermal rearrangement of these ketones at temperatures greater than 200 °C provides a route to certain γ,δ-unsaturated ketones.

As part of a study of mechanistic pathways by which cyclopropyl systems undergo substitution reactions, we had use for a variety of cyclopropyl containing substrates. As precursors for the preparation of compounds that would undergo substitution reactions, we have developed methods for the formation of certain methyl substituted cyclopropyl ketones.