action, the assumption being supported by an upfield shift of C-20 in **5c** by 1.3 ppm.

This initial effort in ^{13}C NMR analysis of complex lactone systems has supplied some rather interesting data; more basic information, particularly that pertaining to electric field effects in α-oxygenated carbonyl compounds, is needed before any generalizations can be drawn.

Experimental Section

Carbon-13 spectra were determined at 25.03 MHz in the Fourier mode using a JEOL-PFT-100 spectrometer in conjunction with an EC-100 20K memory computer. The spectrometer features a deuterium lock system, a JNM-SD-HC random noise (2500-Hz bandwidth) proton decoupler, and JNM-DP-1 digital pulse programmer. Spectra of the compounds were determined in ~0.5 M deuteriochloroform solution (which also provided the lock signal) with 5% Me_4Si added as internal reference. All samples were contained in precision ground 10 mm o.d. tubes. The spectrometer was used in the crosscoil configuration. On the average, a 12-μs pulse, corresponding to an approximate tilt angle of 45°, was employed. For the average spectral width of 5000 Hz the delay between pulses was 3 s.

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Registry No.—**1**, 963-74-6; **2a**, 2466-25-3; **2b**, 42516-17-6; **2c**, 42516-18-7; **2d**, 42516-15-4; **2e**, 42516-16-5; **3**, 42516-19-8; **4**, 57901-22-1; **5a**, 468-84-8; **5b**, 54632-03-0; **5c**, 54656-75-6; **6**, 52811-58-2.

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Synthesis and Characterization of Some Polycyclic Cyclobutanones

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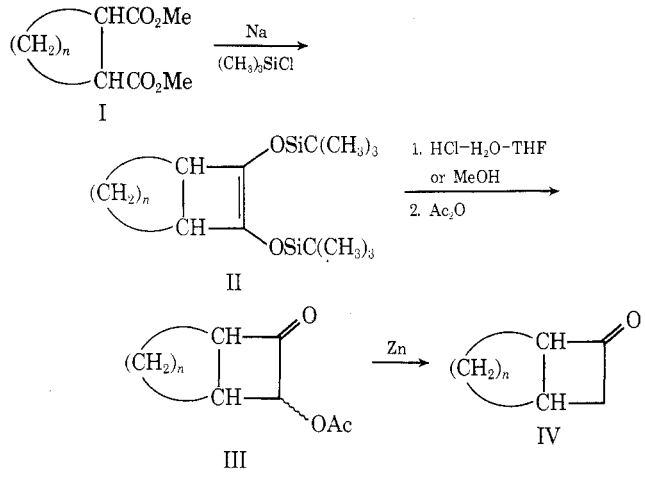
A new stereospecific synthesis of 2,3-cis fused polycyclic cyclobutanone derivatives from readily available starting materials is described. The technique provides a valuable compliment to the use of dichloroketene in that it can be run on a large scale, makes efficient use of reagents, and in a number of cases (e.g., **16** and **22**) gives much higher yields of the ketone than the former technique. In addition, the complimentary endo isomers **18**, **20**, **24**, and **26** are formed in cases where dichloroketene has been demonstrated or predicted to occur stereospecifically to produce the exo isomers. The ultraviolet spectra of the ketones have been examined for evidence of nonconjugated chromophore interaction. The exo unsaturated derivative **22** shows a strong intensification of the $n \rightarrow \pi^*$ transition most reasonably described in terms of a geometric dependent interaction between the π orbitals of the double bond and those of the carbonyl group via the exo σ bond α to the carbonyl group.

The synthesis of fused ring and polycyclic cyclobutanones in preparatively useful yields has been a difficult problem. The most commonly used techniques have involved the thermal cycloaddition of ketene and alkyl and aryl substituted derivatives to olefins and dienes to yield cyclobutanones directly.[1] This technique has suffered from a lack of generality, and difficulty in large-scale preparations. The latter has been particularly obvious in cycloadditions involving ketene itself. The discovery that the highly reactive intermediate, dichloroketene, could be generated in situ and trapped by olefins and dienes has surmounted some of these difficulties.[2] This novel reagent allows the preparation of many cyclobutanone derivatives in good yield and exhibits high regio- and stereospecificity. Still some difficulties remain even with this reagent. For example, certain olefins and dienes give rather low yields of cycloaddition products[3] and with unreactive reagents, a relatively large excess of the ketenophile is generally necessary to produce useful quantities of product. Ironically, even the regio- and stereospecificity of the reagent can be a disadvantage if the isomeric derivative is the one desired. We have sought a reaction sequence which (1) makes efficient use of scarce reagents, (2) produces cyclobutanones in good yields where the dichloroketene method does not, and (3) is stereospecific but in a complimentary sense to dichloroketene. This paper describes a technique for the large-scale, stereospecific, and high-yield preparation of a number of fused ring and polycyclic cyclobutanones from readily available starting materials. The overall synthetic sequence is described in Scheme I.

Results and Discussion

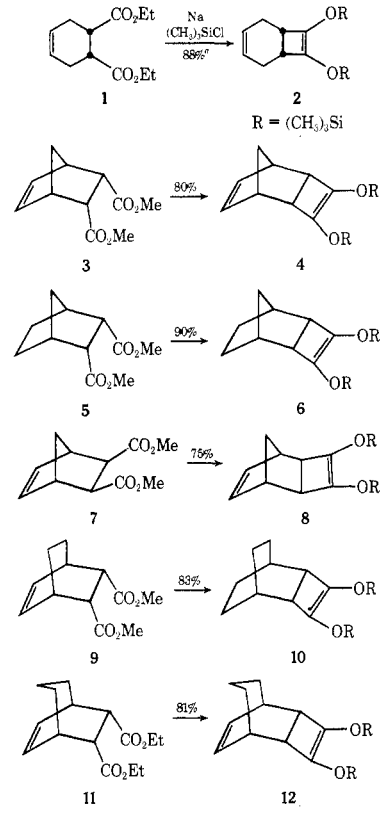
The first step in the sequence involves the acyloin condensation of the corresponding diesters using the basic technique described by Bloomfield.[4] All of the acyloin condensations went smoothly and in good yield in spite of a potential complicating factor of having a strained double bond in close proximity to the reactive centers in **3**, **9**, and

Scheme I



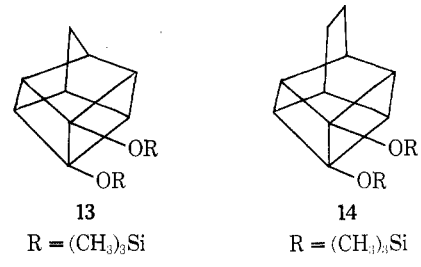
11 (see Table I). The bistrimethylsiloxy derivatives are all fluid, high-boiling liquids, colorless when pure, which are thermally stable but hydrolytically labile. Their infrared spectra are characterized by a vinyl ether band at ca. 1710 cm^{-1} and additional strong bands between 830–1000 and 1250–1430 cm^{-1}. The mass spectra of these compounds showed strong parent peaks and an intense fragment at *m/e* 73 [loss of $(CH_3)_3Si$]. The symmetry of the disiloxene derivatives is apparent from their NMR spectral data. For example, the NMR spectrum of **2** (see Table I) shows only four resonances at τ 4.40 (m, 2 H), vinyls, 7.40 (m, 2 H), cyclobutylmethines, 7.96 (m, 4 H), allylic, and 9.83 (s, 18 H), trimethylsiloxy protons. Since the ultimate usefulness of the synthesis depended on the retention of the ester geometry upon condensation, the stereochemistry of the bis(trimethylsiloxy)cyclobutene derivatives was further investigated. Molecular symmetry and geometric flexibility allowed no facile assignment of the relative stereochemical relationship of the cyclobutene methine protons in **2** by NMR. However, it seems extremely unlikely that the ring juncture is trans fused, since Bloomfield has shown that this is unstable with respect to the ring-opened product under the reaction conditions.[4] Consistently, when a neat sample of **2** was heated in a sealed tube to 190 °C for 12 h no significant isomerization could be detected by ir, NMR, or GLC. It was similarly anticipated that the stereochemistry of the bicyclic esters would be maintained under the cyclization conditions and this was confirmed by spectral and chemical means. The spectrum of **4** (see Table I) shows five main absorptions at τ 4.2 (t, J = 1.5 Hz, 2 H), 7.38 (d, J = 3 Hz broadened by additional splitting, 2 H), 7.51 (complex m, 2 H), 8.37 (AB q, J = 8.5 Hz, 2 H), and 9.90 (s, 18 H). The separation between central peaks of the AB quartet was δ 0.29. The considerable chemical nonequivalence of the bridge methylene protons is most consistent with the endo geometry.[5] Furthermore, double resonance experiments showed that the vinyl protons were coupled to the multiplet at τ 7.51 but not to the broad two-proton doublet at τ 7.38. From the models, the dihedral angle between the cyclobutane methine and the bridgehead protons in the endo derivative is ca. 40–45°. Simple extrapolation from a Karplus plot[6] predicts a coupling constant of 2.8–4.5 Hz, which is consistent with the observed valve of 3 Hz. Direct chemical evidence of the endo geometry was obtained by photolysis of **4**. Irradiation of **4** (0.15 M, 254 nm) in cyclohexane or ether produced 4,5-bis(trimethylsiloxy)homocubane (**13**) in almost quantitative yield.[7] The geometry of the saturated derivative **6** was verified as endo by its NMR spectrum, which again showed the cyclobutene methine

Table I



[a] Yields of purified material.

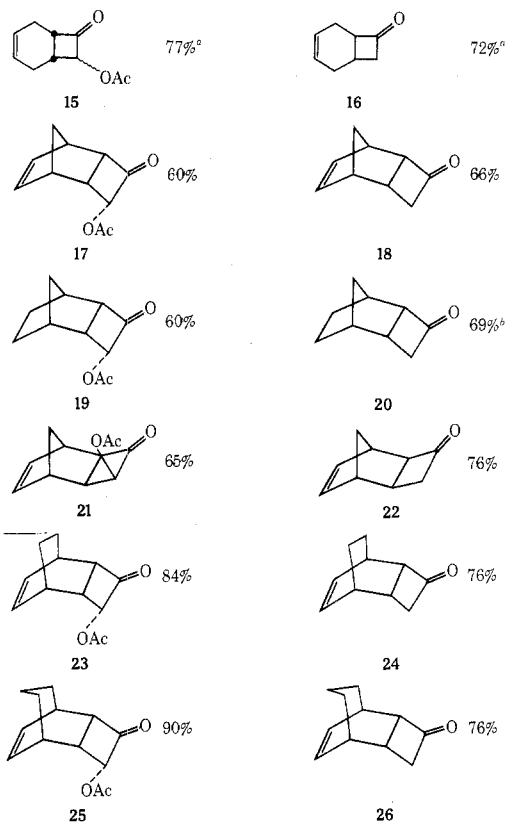
protons as a broad doublet (J = 3 Hz) complicated by further small splittings. The assignment of the exo geometry to derivative **8** followed logically again from consideration of its spectral data. The NMR spectrum of **8** shows the following absorptions: ($CDCl_3$) τ 3.90 (t, J = 2 Hz, 2 H), 7.51 (m, 2 H) bridgehead, 7.82 (s, $W_{1/2}$ = 2 Hz, 2 H), cyclobutene methines, and 8.48 (AB q, J = 9 Hz, 2 H). The upfield shift of the cyclobutene methine protons by ca. δ 0.44 relative to **4** is consistent with the expected increased shielding by the double bond of the norbornene moiety. Consistently, they appear as a slightly broadened singlet due to the small bridgehead coupling constant.[5] The separation between the central peaks of the AB quartet is only δ 0.18 compared to δ 0.29 in **4** reflecting the increasing similarity of chemical environment of the bridge methylene protons caused by the presence of the additional double bond in the exo position. Although NMR could not be conclusively used to confirm the stereochemistry of **10** as endo, it was again found that irradiation of a 0.15 M solution of **10** in cyclohexane produced the cage product **14** in ca. 6% yield.[7] The endo geometry of compound **12** was assumed by analogy, since analysis of the NMR spectrum was inconclusive and **12** failed to undergo photochemical cycloaddition under the conditions described above.



13 R = $(CH_3)_3Si$ **14** R = $(CH_3)_3Si$

It has been reported[4,8] that disiloxene derivatives can be hydrolyzed to the corresponding acyloins in neutral solu-

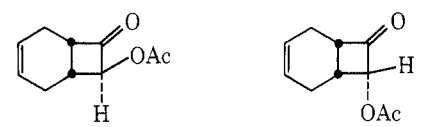
Table II



[a] Yields of purified material. [b] Based on reacted starting material.

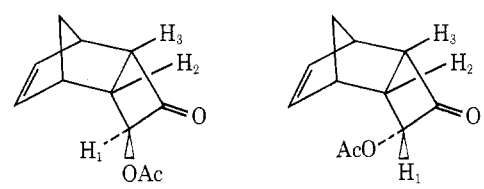
tion by refluxing methanol or by the use of dilute hydrochloric acid in tetrahydrofuran. During the course of our work, we have investigated both techniques. The alcoholysis reaction usually generated the acyloin in good yield and was experimentally a more convenient overall procedure. However, it was observed that occasionally, for no obvious reason, a mixture of ketals would be formed instead of or in addition to the desired acyloin. This occurred even though the glassware had been previously base treated and the methanol distilled from sodium methoxide. While this anomalous alcoholysis occurred rather infrequently, its unpredictability led us to favor the use of aqueous acid which produced the acyloins in yields comparable to the alcoholysis technique.[9] Owing to the potential instability of the acyloins, they were not further purified, but converted directly to the corresponding keto acetates with acetic anhydride. This was accomplished using refluxing acetic anhydride (2–3 h) or acetic anhydride–pyridine at room temperature (12–15 h). In those systems where the procedures were compared, the yields were similar and the acetic anhydride–pyridine method was favored owing to the simplified work-up procedure. The results of hydrolysis and acetylation are shown in Table II. All of the keto acetates were characterized by strong ir bands at 1780 (cyclobutanone), 1745 (acetate carbonyl), and 1230 cm^{-1} (acetate carbon–oxygen stretching).

While the hydrolysis and acetylation sequence might be expected to generate a epimeric mixture of keto acetates depending on the mechanism and steric environment, this was positively demonstrated in only one case. The hydrolysis of **2** using either methanol or aqueous acid and subsequent acetylation produced a mixture of two keto acetates, **15a** and **15b**, in approximately 1/4 ratio. The crude mixture could be converted directly to the ketone **16** in good yield upon subsequent treatment with zinc dust and acetic acid. The major isomer was collected with difficulty by GLC and had the following NMR spectrum: τ (CCl_4) 4.22–4.45 (m, 3 H), 6.57–7.36 (complex multiplet, 2 H), and 7.48–8.06 (multiplet containing superimposed acetate singlet, 7 H). The minor isomer, which was enriched during collection, showed very similar spectral data to the major with the most significant differences in its NMR spectrum. In the vinyl region a two-proton multiplet appeared at τ 4.03 and the cyclobutyl methine proton α to the acetate group appeared upfield as a doublet of doublets (J = 7, 3 Hz) at τ 5.05. The acetate resonance of the minor isomer was at only slightly higher field than the major isomer (7.99 vs. 7.96). Although conformational mobility of the basic carbon skeleton makes assignment of the geometry of the acetate group difficult, it seems reasonable that the upfield shift of the acetate methine proton in the minor isomer relative to the major ($\Delta\delta$ 0.70) is a result of increased shielding by the internal double bond. This led to a tentative assignment of geometry **15a** to the minor and **15b** to the major isomer.



15a **15b**

This assignment is also attractive from a mechanistic point of view, since the formation of predominantly **15b** can be rationalized on the basis of kinetic protonation from the least hindered side during hydrolysis. The other keto acetates **17, 19, 21, 23,** and **25** (see Table II) were formed predominantly as one stereoisomer as determined by NMR and GLC analysis. Assuming again protonation from the least hindered side, one would predict in each case that the acetate group should appear trans to the cyclobutane ring juncture protons. Since the tricyclic systems are considerably more rigid, assignment of the acetate configuration by the magnitude of the coupling constants can be made with more confidence.[10] This assignment is facilitated by the fact that in each of the tricyclic cases the tertiary proton α to the acetate group appears downfield as a doublet of doublets in the region τ 4.3–4.7. For the keto acetate **17**, which represents the most rigid of the materials prepared, models indicate that the cyclobutanone ring is nearly planar. The acetate methine proton of **17** appears at τ 4.68 as a doublet of doublets (J = 8.5, 3.5 Hz). Since the larger coupling is most probably due to the vicinal protons H_1 and H_2 rather than the long-range $H_{1,3}$ interaction,[10c] a stereochemical assignment is made based on the respective dihedral angles. The dihedral angle between H_1 and H_2 in **17b** is ca. 0°, while in **17a** it is ca. 117°. On this basis, consideration of



17a **17b**

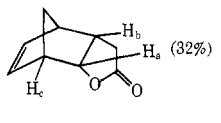
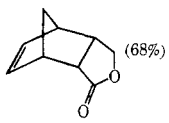
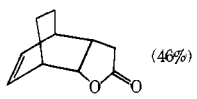
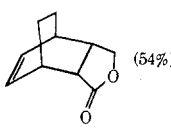
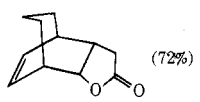
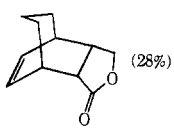
the relatively large vicinal coupling constant (J = 8.5 Hz) of the product leads to the most probable structural assignment of **17b** as the keto acetate formed upon hydrolysis and subsequent acetylation of **4.** Similarly in each of the additional keto acetates **19, 21, 23,** and **25** the acetate methine proton appeared as a doublet of doublets ($J_{1,2}$ = 8.5–9.0, $J_{1,3}$ = 3.0–4.0 Hz) and was tentatively assigned the same stereochemistry. It is interesting to note that the steric interaction of the methylene bridge protons in **21** is still

apparently great enough to dictate the formation of predominantly one acetate.

The subsequent reductive elimination from the keto acetates was accomplished without complications using zinc in refluxing acetic acid (see Table II). Under these conditions the production of **20** was quite slow, and even after heating for 39 h, 30% of the starting material remained. The slow rate of elimination may arise from steric hindrance to the loss of acetate caused by the presence of the endo hydrogens. The ketones were produced as colorless volatile liquids (**16, 22, 26**) or as waxy semisolids (**18, 20, 24**). All materials were characterized by analytical and spectral data supported by unambiguous synthesis or chemical transformation where necessary. Each of the ketones showed a strong band between 1775 and 1780 cm^{-1} (cyclobutanone) in the infrared and an intense parent ion in their mass spectra (70 eV). The NMR spectra, which are generally quite complex, are reported in detail in the Experimental Section and for this reason only a few pertinent points will be discussed here. For all of the endo tricyclic ketones (**18, 20, 24,** and **26**) a complex single-proton resonance appears downfield from the rest of the absorptions. This low-field signal is most reasonably assigned to the exo methine proton α to the carbonyl group. In the case of **22** and its saturated derivative **33,** this proton is upfield and merged with other resonances. Another feature which bears on the geometry of the cyclobutanone moiety in **18** and **22** is the separation between the two central peaks of the AB quartet due to the bridge methylene protons. As previously observed for **4** and **8,** the separation in **18** is δ 0.24, while in **22,** where the protons are more nearly equivalent owing to the additional shielding effect of the carbonyl group, it is only δ 0.18.

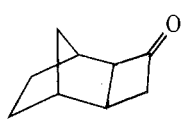
The NMR spectra of the cyclobutanones were rather complex, and chemical methods were used to further verify structures and stereochemistry. Since the photochemical cycloelimination of ketene from simple 2,3-disubstituted cyclobutanones shows high steroselectivity often described in terms of the most stable acyl-alkyl biradical,[11] this was used to confirm the structure of **16.** Accordingly, irradiation of **16** in pentane produced 1,4-cyclohexadiene and 3-norcarene in 58 and 13% yields, respectively. Additional confirmation was obtained by hydrogenation of **16** (hexane, PtO_2) with 1 equiv of hydrogen to produce bicyclo[4.2.0]octan-7-one, whose spectral properties were identical with those reported by Blomquist and co-workers.[12] The structure and stereochemistry of the endo ketones **18, 24,** and **26** were probed via Baeyer–Villiger oxidation (see Table III). Treatment of **18** with basic hydrogen peroxide generated the corresponding lactones **27** and **28** (60%).[13] The lactone **28** was synthesized in an unambiguous manner by reduction of *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride at −60 °C with lithium aluminum hydride using the method described by Bloomfield and Lee.[14] The endo geometry of **27** was assured by NMR analysis. The methine proton H_a (see Table III) appeared downfield at τ 5.06 as a doublet of doublets (J = 7, 4 Hz) due to splitting by H_b and H_c. The relatively large coupling with the bridgehead proton H_c (J_{ac} = 4 Hz) is indicative of an exo position for this proton.[5] Since the Baeyer–Villiger reaction is known to proceed with retention of configuration of the migrating group,[15] this assures the expected endo geometry for the ketone **18.** Similar applicaton of the oxidation procedure to **24** and **26** produced the results shown in Table III. Catalytic hydrogenation of **18** (PtO_2, hexane) produced the saturated derivative **20** identical in every way with the sample produced from the application of the described reaction sequence to the saturated endo ester **5.** The exo ketone, **22,** could be similarly hydrogenated to the saturated derivative

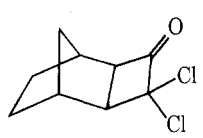
Table III. Results of Baeyer–Villiger Oxidation

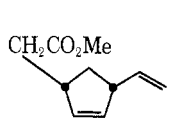
Ketone	Lactones	
	[60%][a]	
18	 (32%) **27**	 (68%) **28**
	[76%]	
24	 (46%) **29**	 (54%) **30**
	[85%]	
26	 (72%) **31**	 (28%) **32**

[a] Total lactone yield.

33 whose spectral properties were identical with those described by Sauers and co-workers.[16] In addition, the spectral properties of **22** were identical with those of a sample prepared in low yield by the addition of dichloroketene to norbornadiene to yield **34** and subsequent dechlorination.[2d,e] Since we had both isomers **18** and **22** in hand, we

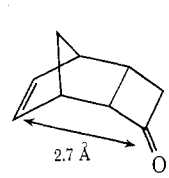

33

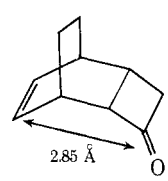

34

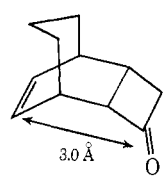

35

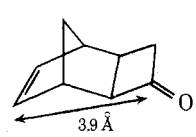
were able to verify by GLC analysis that the cycloaddition to norbornadiene and subsequent dechlorination produces >98% of the exo isomer which agrees with the results obtained by other workers by indirect analysis.[2e] The ketones **18** and **22** were further related to each other by photochemical transformation (300 nm) to the same ester, **35,** upon quenching with methanol after irradiation.[17]

Spectral Interaction. Spectral interaction between formally nonconjugated chromophores has been widely studied and found to be strongly geometry dependent.[18] The series of cyclobutanones **18, 22, 24,** and **26** by virtue of their structural rigidity provided an interesting series for a study of nonconjugated interaction as a function of geometry and distance between interacting centers (see below).


2.7 Å
18


2.85 Å
24


3.0 Å
26


3.9 Å
22

The shape and intensity of the n–π^* transition is remarkably similar for all of the polycyclic cyclobutanones with the exception of **22**, which is anomalous in that the extinction coefficient of the major vibrational component is ca. three times that of the other ketones and slightly red shifted (see paragraph at end of paper regarding supplementary material). That this striking intensification is caused by the presence of the double bond is clear from the spectrum of the saturated compound **33** which closely resembles the other derivatives. The distance between the chromophores in **22** is ca. 3.9 Å from models, which seems excessive for a simple through-space interaction. The n–π^* enhancement therefore seems best explained by chromophore interaction via the exo σ bond. Similar geometry dependent n–π^* enhancements of some polycyclic ketones have been reported recently by Hudec and co-workers.[19] These workers, however, also reported the presence of a short-wavelength σ coupled transition in the examples showing n–π^* intensification. We were unable to see any evidence of another maximum above 210 nm which could be ascribed to a σ coupled transition. The question of ground-state nonconjugated interactions in these and related systems is under investigation by photoelectron spectroscopy.

Summary

We have described a simple procedure for preparing 2,3-cis fused polycyclic cyclobutanones[20] on a preparative scale from available precursors which has provided a valuable complement to the use of dichloroketene in cyclobutanone synthesis. It has not only provided a high-yield synthesis of a number of ketones where the yield via dichloroketene was low but in addition has provided the complimentary endo isomers, **18, 20, 25,** and **26,** in cases where dichloroketone addition has been demonstrated or predicted to occur stereospecifically to produce the exo isomers. Further work on the chemistry of these and other related polycyclic cyclobutanones is proceeding.

Experimental Section[21]

***cis*-1,2-Dicarboethoxycyclohex-4-ene (1).** A 2-l. one-necked flask was charged with 100 g (0.66 mol) of *cis*-1,2,3,6-tetrahydrophthalic anhydride, 200 ml of anhydrous ethanol, 500 ml of dry benzene, and 2 ml of concentrated sulfuric acid. The mixture was refluxed for 16 h employing a Soxhlet extraction apparatus where the cup of the extractor was filled with activated 4 Å molecular sieves. The mixture was cooled and the solvent removed on a rotary evaporator. The residue was poured into a mixture of 200 ml of 10% salt solution and 400 ml of 5% sodium bicarbonate and extracted with ether. The organic layer was washed with water and dried over Na_2SO_4. Removal of the solvent and vacuum distillation yielded 1 as a main fraction [bp 112–114 °C (1 mm), 140 g, 95%].

7,8-Bis(trimethylsiloxy)bicyclo[4.2.0]octa-3,7-diene (2). This general procedure was followed for all acyloin condensations. Into a flamed 2-l. four-necked flask equipped with a Hershberg stirrer, addition funnel, argon gas inlet, and condenser with drying tube were placed 9.2 g (0.4 mol) of sodium and 200 ml of dry toluene. The mixture was heated to reflux and stirred rapidly for 0.5 h to disperse the sodium before cooling to room temperature. A mixture of 20.0 g (0.089 mol) of *cis*-1,2 dicarboethoxycyclohex-4-ene (1) and 45.6 g (0.42 mol) of distilled trimethylsilyl chloride in 50 ml of toluene was added dropwise over 3 h. After the addition, the mixture was *carefully*[22] heated to reflux for an additional 12 h. A blue-violet color developed soon after the heating was begun. After the reaction mixture was cooled to room temperature, the precipitate was removed by filtration through Celite. The toluene was removed under reduced pressure (45 mm) and the residue was pumped to 0.2 mm for 10 min at 0 °C to remove the last remnants of the solvent. The residue was distilled through a 6-in. Vigreux column to yield the disiloxene, **2,** as the major fraction [bp 80–81°C (0.35 mm), 21.9 g 88%]: NMR ($CDCl_3$) τ 4.40 (m, 2 H), 7.40 (m, 2 H), 7.96 (m, 4 H), and 9.83 (s, 18 H); ir (neat 3050, 2950, 2900, 2850, 1720, 1310, 1280, 1250, 1220, 1120, 1050, 970, 915, 890, 850, 760, and 680 cm^{-1}; mass spectroscopic molecular weight 282.

7-Acetoxybicyclo[4.2.0]oct-3-en-8-one (15). A. The following general procedure for hydrolysis and acetylation was used except where noted. A 1-l. three-necked flask equipped with a stirrer, N_2 inlet, and condenser was charged with 66.7 g (0.24 mol) of **2,** 220 ml of THF, and 17.3 g of 1 N HCl. The mixture was refluxed under N_2 for 1 h. After cooling to room temperature, 17.3 g (0.17 mol) of $CaCO_3$ was added and the mixture stirred at room temperature for an additional 1 h. After filtration the THF was removed on the rotary evaporator and the crude product was dissolved in 175 ml of ether which was washed with water and dried over Na_2SO_4. Removal of the ether yielded 24.5 g (0.2 mol) of the yellowish oily acyloin.

B. The above acyloin was placed in a 250-ml flask immersed in a water bath (25 °C) and 55.8 ml (0.60 mol) of acetic anhydride and 16 ml (0.20 mol) of dry pyridine were added. The reaction was stirred at room temperature for 16 h. After the addition of 100 ml of water, the initial two-phase system was stirred for 1 h and the aqueous layer extracted repeatedly with ether. The organic phase was carefully washed with saturated $NaHCO_3$ and water and dried over Na_2SO_4. The product was isolated by distillation through a 6-in. Vigreux column to yield 27.4 g [bp 80–85 °C (0.04 mm), 77%] of the desired keto acetate, **15.** GLC analysis on column 1 operated at 120 °C with flow of 35 ml/min showed the presence of two isomeric acetates in the ratio of 1/4: NMR (CCl_4) τ 4.04–4.48 (m, 2.8 H), 5.05 (dd, J = 6, 2 Hz, 0.2 H), 6.51–7.06 (m, with two sharp singlets at 7.95 and 7.98, 9 H); ir (neat 3030, 2930, 2840, 1775, 1740, 1650, 1370, 1225, and 665 cm^{-1}.

The major keto acetate could be separated by GLC using column 2 at 130 °C and a flow rate of 60 ml/min: NMR (CCl_4) τ 4.22–4.46 (m, 3 H), 6.56–7.14 (m with sharp singlet at 7.95, 9 H); ir (neat) 3030, 2930, 2840, 1775, 1740, 1650, 1370, 1225, and 665 cm^{-1}. The minor acetate which was enriched to ca. 50/50 during collection showed similar spectral properties. The low-field portion of its NMR spectrum was, however, somewhat different from that of the major isomer in that the vinyl protons appeared as a multiplet at τ 4.03 while the cyclobutyl methine proton adjacent to the acetate group appeared upfield as a doublet of doublets (J = 6, 2 Hz) at τ 5.05.

Bicyclo[4.2.0]oct-3-en-7-one (16). The following general procedure was followed for all reductive deacetylations. A 2-l. three-necked flask equipped with a mechanical stirrer and nitrogen inlet was charged with 14.3 g (0.08 mol) of the keto acetate mixture **15,** 350 ml of glacial acetic acid, and 155 g (2.38 mol) of Zn dust. The reaction mixture was heated at reflux with vigorous stirring for 30 h. After this time >95% of the starting material had disappeared by GLC analysis (column 1, 150 °C, 35 ml/min). The reaction mixture was cooled and filtered, and the solid was washed with ether and poured into 350 ml of H_2O. The aqueous layer was extracted with ether which was washed with saturated $NaHCO_3$ and water and dried over Na_2SO_4. The ether was removed by distillation at 1 atm and the residue distilled under vacuum through a 6-in. Vigreux column. The main fraction [bp 94–96 °C (27 mm), 7.0 g, 72%] was >97% pure by GLC analysis (column 1, 86 °C, 35 ml/min): NMR (CCl_4) τ 4.23 (m, 2 H), 6.5–7.12 (m, 2 H), 7.14–8.22 (m, 6 H); ir (neat) 3035, 2920, 2840, 1775, 1640, 1435, 1385, 1265, 1225, 1105, 1085, 1010, and 680 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_8H_{10}O$, 122.073; found, 122.074.

Hydrogenation of 16. The hydrogenation of **16** (182 mg, 1.49 mmol, PtO_2) in 10 ml of hexane was interrupted after an uptake of 97% of 1 equiv. The solvent was removed by distillation and the material collected by GLC (column 2, 110 °C, 80 ml/min). The spectral properties of the bicyclo[4.2.0]octan-7-one prepared in this manner were identical with those reported by Blomquist and Kwiatek:[12] NMR (CCl_4) τ 6.30–6.91 (m, 2 H) and 7.10–8.91 (m, 10 H); ir (neat) 2900, 2800, 1770, 1420, 1090, 1060, and 1040 cm^{-1}; mass spectroscopic molecular weight 124.

Irradiation of 16 to 1,4-Cyclohexadiene and 3-Norcarene. Into a Pyrex tube was placed 251 mg of **16** in 30 ml pf pentane and the solution was degassed for 10 min with nitrogen. The sample was irradiated for 5 h at 300 nm. GLC (column 1, 85 °C, 30 ml/min) and spectral analysis showed that the starting material had been consumed and 1,4-cyclohexadiene and 3-norcarene had been formed in 58 and 13% yields, respectively.

***endo*-2,3-Dicarbomethoxybicyclo[2.2.1]hept-5-ene (3).** This material was prepared in 88% yield by the method described by Morgan and co-workers:[23] NMR (CCl_4) τ 3.92 (m, 2 H), 6.53 (s, 6 H), 6.8–7.05 (m, 4 H), and 8.78 (AB q, J = 9 Hz, 2 H); ir (neat) 2980, 2950, 1740, 1440, 1340, 1250, 1195, and 1165 cm^{-1}.

***endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (4).** Following the general procedure, 4 was obtained in 80%

yield, bp 78–81 °C (0.05 mm). A small higher boiling fraction, bp 100–105 °C (0.045 mm), proved to be a complex mixture and was discarded. GLC analysis of the major fraction (column 1, 155 °C, 35 ml/min) showed that it was >98% pure: NMR ($CDCl_3$) τ 4.2 (t, J = 1.5 Hz, 2 H), 7.38 (br d, J = 3 Hz, 2 H), 7.51 (m, 2 H), 8.37 (AB q, J = 8.5 Hz, 2 H), and 9.90 (s, 18 H); ir (neat) 3060, 2960, 1705, 1300, 1250, 1210, 1170, 1085, 966, 900, 840, and 730 cm^{-1}; mass spectroscopic molecular weight 294.

Irradiation of 4 to 4,5-Bis(trimethylsiloxy)homocubane (13). A Vycor tube (33 × 3.8 cm) was charged with 11.05 g (0.038 mol) of freshly distilled **4** dissolved in 250 ml of dry spectrograde cyclohexane (0.15 M). The tube was sealed with a syringe stopper and degassed with a stream of dry nitrogen. The solution was irradiated at 254 nm (Southern New England Ultraviolet Co., RPR-208) for 48 h. After removal of the solvent, the mobile yellowish residue was distilled through a 6-in. vacuum-jacketed Vigreux column to yield 9.24 g [bp 85–88 °C (0.12 mm), 84%] of the cage compound **13:** NMR (CCl_4) τ 6.85 (s, $W_{1/2}$ = 2.3 Hz, 6 H), 8.22 (s, $W_{1/2}$ = 2.7 Hz, 2 H), and 9.75 (s, 18 H); ir (neat) 2980, 1355, 1305, 1255, 930, 095, 875, and 840 cm^{-1}; mass spectroscopic molecular weight 294.

***endo*-3-Acetoxytricyclo[4.2.1.$0^{2,5}$]non-7-en-4-one (17).** The generalized procedure for hydrolysis and acetylization of the disiloxenes was followed and the keto acetate **17** was obtained in 60% yield (>98% pure, GLC analysis, column 1, 170 °C, 35 ml/min): bp 88–93 °C (0.04 mm); NMR (CCl_4) τ 3.97 (m, 2 H), 4.68 (dd, J = 8.5, 3.5 Hz, 1 H), 6.25–7.0 (m, 4 H), 7.97 (s, 3 H), 8.37 (AB q, J = 9 Hz, 2 H); ir (neat) 3060, 2975, 2860, 1780, 1740, 1370, 1225, 1025, 910, and 725 cm^{-1}.

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.59; H, 6.44.

***endo*-Tricyclo[4.2.1.$0^{2,5}$]non-7-en-3-one (18).** Following the general procedure, the ketone **18** was generated as a waxy semisolid [bp 104–106 °C (33 mm), 66%]. The material was >95% pure by GLC analysis (column 1, 105 °C, 35 ml/min): NMR (CCl_4) τ 3.92 (t, J = 2.0 Hz, 2 H), 6.37 (m, 1 H), 6.97 (m, 2 H), 7.10–7.54 (m, 2 H), 7.76–8.1 (m, 1 H), and 8.43 (AB q, J = 9 Hz, 2 H); ir (CCl_4) 3060, 1985, 2870, 1775, 1640, 1280, 1335, 1250, 1170, 1085, and 715 cm^{-1}; mass spectroscopic molecular weight 134.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.73; H, 7.63.

***endo*-2,3-Dicarbomethoxybicyclo[2.2.1]heptane (5).** *endo*-Bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (67 g) was dissolved in 150 ml of dry methanol containing 1 g of *p*-toluenesulfonic acid monohydrate. The homogeneous mixture was refluxed under nitrogen for 12 h. After cooling, the solvent was removed on the rotary evaporator and the residue dissolved in ether. The ether was washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. After removal of the solvent the residue was vacuum distilled to yield 78.2 g of ester **5** [bp 112–115 °C (2.5 mm), 91%]: mp 52.5–53.5 °C; NMR ($CDCl_3$) τ 6.33 (s, 6 H), 7.0 (m, 2 H), 7.42 (m, 2 H), 7.91–8.78 (m, 6 H).

***endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.1.$0^{2,5}$]non-3-ene (6).** Following the general procedure, **6** was obtained in 90% yield: bp 84–85 °C (0.06 mm); NMR ($CDCl_3$) τ 7.4 (m, 2 H), 7.95 (m, 2 H), 8.45 (m, 2 H), 8.6 (m, 4 H), and 9.88 (s, 18 H); ir (neat) 2920, 2850, 1710, 1300, 1250, 1280, 1180, 1090, 985, 960, 890, 850, and 755 cm^{-1}; mass spectroscopic molecular weight 296.

***endo*-3-Acetoxytricyclo[4.2.1.$0^{2,5}$]nonan-3-one (19).** According to the usual procedure, the keto acetate **19** was obtained as a slightly pink liquid in 60% yield: bp 85–90 °C (0.08 mm); NMR ($CDCl_3$) τ 4.3 (dd, J = 9, 3 Hz, 1 H), 6.36–7.15 (m, 2 H), 7.45 (m, 2 H), 7.90 (s, 3 H), and 8.4 (m, 6 H); ir (neat) 2910, 2860, 1775, 1740, 1370, 1220, 1120, 1030, and 930 cm^{-1}.

***endo*-Tricyclo[4.2.1.$0^{2,5}$]nonan-3-one (20). A.** The ketone **20** was prepared using the general procedure for reductive deacetylation. GLC analysis (column 1, 151 °C, 35 ml/min) indicated olly 50% conversion after 23 h. The heating was continued for an additional 16 h after which the reaction was terminated despite the presence of ca. 30% starting material by GLC analysis. Work-up in the usual fashion and vacuum distillation yielded the ketone **20** as a waxy semisolid (bp 110–112 °C, 33 mm) and recovered starting material (bp 85–90 °C, 0.08 mm). The yield of **20** based on reacted starting material was 69%: NMR (CCl_4) τ 6.48 (m, 1 H), 7.0–7.3 (m, 5 H), and 8.41 (m, 6 H); ir (CCl_4) 2960, 2890, 1775, and 1090 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_9H_{12}O$, 136.089; found, 136.091.

B. Hydrogenation of 18. The ketone **18** (2.0 g, 14.9 mol) was hydrogenated at 1 atm in hexane containing 100 mg of PtO_2. The hydrogenation was interrupted after the uptake of 97% of the theoretical amount of hydrogen. The catalyst was removed and the hexane distilled at 1 atm. The product distilled under vacuum to yield 1.8 g of the desired ketone **20.** The physical and spectral properties were identical with those prepared by procedure A.

***exo*-2,3-Dicarbomethoxybicyclo[2.2.1]hept-5-ene (7).** This material was prepared from *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride[24] according to the procedure described for the preparation of **3:** mp 50–52 °C; NMR ($CDCl_3$) τ 4.79 (t, J = 2 Hz, 2 H), 6.34 (s, 6 H), 6.90 (m, 2 H), 7.36 (d, J = 2 Hz, 2 H), 8.15 (AB q, J = 8.5 Hz, 2 H); ir 3050, 1740, 1430, 1360, 1330, 1250, 1140, 1160, 1050, and 740 cm^{-1}.

***exo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (8).** Using the generalized procedure, the disiloxene derivative **8** was obtained in 75% yield: bp 78–85 °C (0.05 mm); NMR ($CDCl_3$) τ 3.90 (t, J = 2 Hz, 2 H), 5.51 (m, 2 H), 7.82 (s, 2 H), 8.48 (AB q, J = 9 Hz, 2 H), and 9.8 (s, 18 H); ir 3060, 1710, 1310, 1300, 1270, 1250, 1200, 1180, 1095, 945, 910, 880, 850, 760, and 710 cm^{-1}; mass spectroscopic molecular weight 294.

***exo*-3-Acetoxytricyclo[4.2.1.$0^{2,5}$]non-7-en-3-one (21).** Into a 250-ml flask equipped with a condenser and positive pressure N_2 bubbler was placed 19.0 g (0.065 mol) of **8** and 100 ml of methanol distilled from magnesium. The mixture was heated to reflux for 3 h and the solvent was removed on the rotary evaporator at 50 °C. The residue (9.0 g) solidified upon standing. The crude acyloin was treated with 17 ml (0.18 mol) of acetic anhydride and 4.84 ml (0.06 mol) of dry pyridine while maintaining ambient temperature with an external water bath. The dark solution was stirred at room temperature for 16 h and worked up according to the procedure described for the preparation of **13.** Vacuum distillation yielded 8.0 g of the keto acetate **21** [bp 93–96 °C (0.05 mm), 65%]. The pinkish distillate partially solidified in the freezer at −10 °C overnight: mp 42.5–43 °C (hexane); NMR ($CDCl_3$) τ 3.75 (m, 2 H), 4.43 (dd, J = 9, 3.5 Hz, 1 H), 6.64–7.32 (m, 2 H), 7.90 (s, 3 H), and 8.46 (AB q, J = 9.5 Hz, 2 H); ir (neat) 3050, 3000, 2990, 1780, 1740, 1280, 1230, 1100, 903, and 708 cm^{-1}.

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.84; H, 6.37.

***exo*-Tricyclo[4.2.1.$0^{2,5}$]non-7-en-3-one (22).** Application of the usual procedure for reductive elimination yielded the ketone **22** in 76% isolated yield: bp 105–106° (30 mm); NMR ($CDCl_3$) τ 3.80 (m, 2 H), 6.76–7.08 (m, 3 H), (m, 3 H), and 8.48 (m, 2 H); ir (neat) 3070, 3000, 2900, 1775, 1090, 732, and 690 cm^{-1}; mass spectroscopic molecular weight 134.

3,3-Dichlorotricyclo[4.2.1.$0^{2,5}$]non-7-en-4-one (34). A dry 1-l. three-necked flask equipped with a mechanical stirrer, N_2 inlet, and condenser was charged with 30.0 g (0.20 mol) of freshly distilled dichloroacetyl chloride, 181.1 g (2.05 mol) of norbornadiene, and 250 ml of pentane (distilled from CaH_2). A solution of dry triethylamine (21.39 g, 0.21 mol) in 50 ml of pentane was slowly added. The reaction mixture was stirred for 15 h at room temperature after the addition. After filtering, the low boilers were removed on the rotary evaporator at 45 °C and the residue vacuum distilled. The product which distilled as the major fraction [bp 60–61 °C (0.14 mm), 6.77 g, 17.5%] was slightly yellow. Owing to the limited stability of the dichlorocyclobutanone it was always used soon after preparation: NMR ($CDCl_3$) τ 3.82 (m, 2 H), 6.45 (doublet split into triplets, J = 6.5, 1.5 Hz, respectively), 6.77 (m, 1 H), 7.13 (dd, J = 6.5, 1.0 Hz, 1 H), and 8.47 (m, 2 H); ir (neat) 3070, 2970, 2860, 1785, 1656, 1310, 1010, 970, 822, 743, and 710 cm^{-1}.

Alternate Preparation of 22. A 500-ml flask was charged with 8.40 g (0.041 mol) of dichlorocyclobutanone **34,** 54.3 (0.83 mol) of Zn dust, and 250 ml of acetic acid. The mixture was heated to reflux with vigorous stirring for 2 h. The reaction mixture was worked up in the same manner as described for the preparation of **14.** Vacuum distillation yielded the product **22** (bp 85–88 °C, 15 mm) in 76% yield. The spectral data were identical with those previously described.

Hydrogenation of 22. The ketone **22** (235.5 mg, 1.76 mmol) was hydrogenated in hexane over 50 mg of PtO_2 at 1 atm. The reduction was interrupted after the consumption of 1.05 equiv of hydrogen. The catalyst was filtered and the hexane removed using a 6-in. glass helice packed column. The product, **33,** was isolated (85%) by gas chromatography (column 2, 145 °C, 60 ml/min). The spectral data of this material were identical with those reported by Sauers and co-workers:[16] NMR (CCl_4) τ 6.82–7.20 (m, 2 H), 7.39–7.97 (m, 4 H), and 8.22–9.06 (m, 6 H); ir (CCl_4) 2920, 2840, 1775, and 1093 cm^{-1}; mass spectroscopic molecular weight 136.

***endo*-2,3-Dicarbomethoxybicyclo[2.2.2]oct-5-ene (9).** The ester **9** was prepared from *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicar-

boxylic anhydride[25] using the procedure previously described for the preparation of **3**. The crude ester was recrystallized from ether to yield the pure dimethyl ester **9**, mp 68–69 °C (lit.[26] 69–71 °C).

***endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.2.0^{2,5}]deca-3,7-diene (10).** Using the generalized procedure described for the preparation of the disiloxenes, **10** was generated in 83% yield (bp 85–89 °C, 0.012 mm). The product after one distillation was >98% pure by GLC analysis (column 1, 170 °C, 35 ml/min): NMR ($CDCl_3$) τ 4.10 (m, 2 H), 7.25–7.9 (m, 4 H), 8.6 (m, 4 H), 9.8 (s, 18 H); ir (neat) 3040, 2940, 2840, 1710, 1310, 1250, 915, 875, and 840 cm^{-1}; mass spectroscopic molecular weight 306.

Irradiation of 10 to Yield 14. The disiloxene derivative **10** (1.0 g, 3.24 mmol) was dissolved in 30 ml of spectrograde cyclohexane and placed in a Vycor tube. The tube was degassed, sealed, and irradiated at 254 nm (as described for **13**) for 48 h. The solvent was removed at reduced pressure and the residue distilled through a molecular still (bath 150 °C, 0.017 mm) to yield 60 mg of a colorless liquid. The cage compound **14** was collected (column 2, 160 °C, 60 ml/min) to yield 40 mg of **14**: NMR (CCl_4) τ 7.17–7.55 (m, 6 H), 8.70 (m, $W_{1/2}$ = 4 Hz, 4 H), and 9.8 (s, 18 H); ir (neat) 2950, 2920, 1355, 1340, 1290, 1250, 900, 860, and 830 cm^{-1}; mass spectroscopic molecular weight 306.

***endo*-3-Acetoxytricyclo[4.2.2.0^{2,5}]dec-7-en-4-one (23).** The keto acetate **23** was prepared from **10** by the usual procedure. Vacuum distillation yielded 25.6 g (84% from **10**) of **23** [slightly pink, bp 108–112 °C (0.17 mm)]. The distilled material was 98% pure by GLC analysis (column 1, 180 °C, 35 ml/mm). A sample was crystallized from hexane to yield white crystals: mp 49–51 °C; NMR ($CDCl_3$) τ 3.90 (m, 2 H), 4.54 (dd, J = 9, 4 Hz, 1 H), 6.40–7.46 (m, 4 H), 7.96 (s, 3 H), and 8.97 (m, 4 H); ir (neat) 3050, 2940, 2870, 1780, 1735, 1370, 1220, 1025, and 700 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.74; H, 6.80.

***endo*-Tricyclo[4.2.2.0^{2,5}]dec-7-en-3-one (24).** The tricyclic ketone was produced by the general procedure in 77% yield: bp 116–120 °C (16 mm); NMR (CCl_4) τ 3.82 (m, 2 H), 6.74 (m, 1 H), 6.93–7.81 (m, 5 H), and 8.39–8.87 (m, 4 H); ir (CCl_4) 3050, 2910, 2820, 1775, 2380, 1220, 1100, 850, and 722 cm^{-1}; mass spectroscopic molecular weight 148.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04, H, 8.16. Found: C, 80.81; H, 8.31.

***endo*-2,3-Dicarboethoxybicyclo[3.2.2]non-5-ene (11).** *endo*-Bicyclo[3.2.2]non-5-ene-2,3-dicarboxylic anhydride (15.0 g, 0.078 mol)[27] was placed in a 1-l. flask with 100 ml of anhydrous ethanol, 300 ml of benzene, and 1 ml of concentrated sulfuric acid. The flask was attached to a Soxhlet extractor containing 4 Å molecular sieves in the cup and refluxed for 3 days. The clear reaction mixture was cooled and poured into a mixture of 100 ml of 10% NaCl and 300 ml of 5% $NaHCO_3$ solution. The layers were separated and the organic layer washed several times with water. After drying over Na_2SO_4 the solvent was removed on the rotary evaporator. Vacuum distillation of the residue yielded 19.43 g of the desired ester, **11** [bp 108–110 °C (0.04 mm), 93%]: NMR (CCl_4) τ 4.0 (m, 2 H), 6.02 (q, J = 7 Hz, 4 H), 6.94 (s, 2 H), 7.0–7.32 (m, 2 H), 8.1–8.6 (m, 6 H), and 8.8 (t, J = 7 Hz, 6 H); ir (neat) 3040, 2980, 2940, 2860, 1745, 1180, 1155, 1055, and 705 cm^{-1}.

***endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.3.2.0^{2,5}]undeca-3,10-diene (12).** Application of the usual procedure produced **12** in 81% yield: bp 100–104 °C (0.06 mm); NMR (CCl_4) τ 4.26 (m, 2 H), 7.44 (s, 2 H), 7.56–7.88 (m, 2 H), 8.15–8.92 (m, 6 H), and 9.80 (s, 18 H); ir (neat) 3040, 2960, 2910, 2850, 1715, 1310, 1285, 1250, 1200, 910, 880, and 840 cm^{-1}; mass spectroscopic molecular weight 322.

***endo*-4-Acetoxytricyclo[4.3.2.0^{2,5}]undec-10-en-3-one (25).** Following the general procedure, **25** was generated in 90% yield: bp 124–130 °C (0.09 mm); NMR (CCl_4) τ 4.04 (m, 2 H), 4.47 (dd, J = 9, 3.5 Hz, 1 H), 6.53–7.00 (m, 2 H), 7.3 (br m, 1 H), 7.6 (br m, 1 H), 8.02 (s, 3 H), and 8.28–8.67 (m, 6 H); ir (neat) 3043, 2935, 2860, 1786, 1740, 1240, 1233, and 708 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.47; H, 7.29.

***endo*-Tricyclo[4.3.2.0^{2,5}]undec-10-en-3-one (26).** The ketone **26** was prepared from **25**, using the general procedure described previously. After 22.5 h, GLC analysis (column 1, 177 °C, 35 ml/min) showed no more starting material present. Work-up in the usual manner and vacuum distillation yielded **26** [bp 85–86 °C (1.0 mm), 76.4%]: NMR (CCl_4) τ 4.92 (m, 2 H), 6.54 (m, 1 H), 6.80–7.63 (m, 5 H), and 8.0–8.62 (m, 6 H); ir (neat) 3030, 2929, 2850, 1775, 1380, 1090, and 708 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_{11}H_{14}O$, 162.104; found, 162.104.

Baeyer–Villiger Oxidation of 18. A 50-ml flask was charged with 134 mg (1 mmol) of **18**, 7 ml of MeOH, and 306 mg (30%) of H_2O_2 at ambient temperature. Then 0.14 ml of 9.3 N sodium hydroxide solution was added while maintaining room temperature with a water bath. The reaction mixture was stirred for 2.5 h at room temperature and diluted with 17 ml of 10% HCl solution. The aqueous solution was extracted four times with 20 ml of ether. After drying (Na_2SO_4) the solvent was removed to yield 90 mg (60%) of a crude lactone mixture. A single peak was observed by GLC (column 1, 125 °C, 35 ml/min). However, on column 3, 160 °C, 60 ml/min, the lactones were separated (32% **27**, 68% **28**). The lactones were collected from column 4 at 175 °C, 60 ml/min.

Lactone **27**: NMR (CCl_4) τ 3.81 (m, 2 H), 5.03 (dd, J = 8, 4 Hz, 1 H), 6.87 (br m, 1 H), and 6.9–8.78 (complex multiplet containing an AB q centered at τ 8.5, J = 9 Hz, 6 H); ir (CCl_4) 3065, 2900, 2880, 1770, 1355, 1160, 1070, 1055, and 1010 cm^{-1}; mass spectroscopic molecular weight 150.

Lactone **28**: NMR (CCl_4) τ 3.80 (br s, 2 H), 5.67–5.92 (m, 1 H), 6.20–6.43 (m, 1 H), 6.67–7.65 (m, 4 H), and 8.44 (AB q, J = 9 Hz, 2 H); ir (CCl_4) 3070, 2980, 2920, 2880, 1770, 1385, 1300, 1175, 1090, 1060, 1100, and 925 cm^{-1}; mass spectroscopic molecular weight 150.

Baeyer–Villiger Oxidation of 24. The same procedure run on a 1-mmol scale was used as described for the oxidation of **18**. After the usual work-up, 125 mg (76%) of the lactone mixture was obtained. GLC analysis (column 1, 140 °C, 35 ml/min) showed two lactones present in the ratio 1.3/1. The lactones were collected from column 4, 175 °C, 60 ml/min. The major lactone (54%) was identified as **30** and the minor (46%) as **29**.

Lactone **29**: NMR ($CDCl_3$) τ 3.70 (m, 2 H), 5.30 (dd, J = 8.3, 3 Hz, 1 H), 7.0 (m, 2 H), and 7.16–8.9 (complex multiplet, 7 H); ir (KBr) 2900, 1770, 1190, 1040, 1030, 1010, 880, 730, and 690 cm^{-1}; mass spectroscopic molecular weight 164.

Lactone **30**: NMR ($CDCl_3$) τ 3.72 (m, 2 H), 5.4–5.87 (m, 1 H), 6.00–6.35 (m, 1 H), 6.77–7.50 (m, 4 H), and 8.3–9.0 (m, 4 H); ir (CCl_4) 2900, 1770, 1180, 1050, and 1010 cm^{-1}; mass spectroscopic molecular weight 164.

Baeyer–Villiger Oxidation of 26. The procedure for preparation and collection was that described above. From 1 mmol of **26** was obtained 152 mg of a 1/2.8 mixture (column 1, 140 °C, 35 ml/min) of lactones **32** and **31**, respectively.

Lactone **31**: NMR (CCl_4) τ 3.88 (m, 2 H), 5.2 (m, 1 H), 7.0–8.0 (m, 5 H), and 8.42 (m, 6 H); ir (CCl_4) 3040, 2930, 2860, 1780, 1020, and 710 cm^{-1}; mass spectroscopic molecular weight 178.

Lactone **32**: NMR (CCl_4) τ 3.83 (m, 2 H), 5.62 (t, J = 9 Hz, 1 H), 6.28 (dd, J = 9, 4 Hz, 1 H), 6.85–7.29 (m, 3 H), 7.62 (m, 1 H), 8.05–8.58 (m, 6 H); ir (CCl_4) 3040, 2930, 2920, 2860, 1773, 1185, 1170, 1050, 1030, and 710 cm^{-1}; mass spectroscopic molecular weight 178.

Preparation of Lactone 28. The procedure followed was essentially that described by Bloomfield and Lee[14] using the following quantities: 16.4 g (0.1 mol) of *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, 2.2 g (0.05 mol) of lithium aluminum hydride in 150 ml of THF at −55 °C. Work-up as described yielded 12.1 g of a viscous oil. This was dissolved in 30 ml of ether and cooled to −78 °C to force crystallization. In this way 10.3 g (69%, mp 125–130 °C) of a white, crystalline material was obtained. The spectral data of this lactone were identical with those of **28** produced by the Baeyer–Villiger oxidation of the ketone **18**.

Preparation of Lactone 30. The procedure followed was that described by Nystrom and Brown[28] using the following quantities: 4.8 g of *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (0.03 mol) and 1.14 g (0.33 mol) of $LiAlH_4$ in 125 ml of ether. Work-up in the described fashion yielded 1.19 g (26%) of crystalline lactone from the reacidified basic extracts. This material was recrystallized from ether–pentane to yield a white, crystalline material, mp 86–88.5 °C, whose spectral data were identical in every way with those of **30** produced by Baeyer–Villiger oxidation of **24**.

Preparation of Lactone 32. The same procedure was followed as described for the preparation of **28** starting with *endo*-bicyclo-[3.2.2]non-8-ene-6,7-dicarboxylic anhydride. The crude product was distilled (bp 130–150 °C, 0.04 mm) using a 6-in. Vigreux column. The distillate was a mixture of the lactone **32** and the starting anhydride. The mixture was chromatographed on silica gel using 2% EtOAc–benzene to yield pure lactone **32**, whose spectral properties were identical with those produced by Baeyer–Villiger oxidation of **26**.

Irradiation of 18. Generation of 35. A solution of 200 mg of **18** in 40 ml of pentane (0.04 M) was placed in a Pyrex tube and degassed using N_2 for 15 min at room temperature. The tube was irradiated using a Southern New England Ultraviolet Rayonet reac-

tor and 300 nm lamps for 10 h. GLC analysis (column 1, 150 °C, 30 ml/min) showed that the starting material was gone. The solution was quenched with 1 ml of dry methanol and allowed to stand for 3 h at room temperature. The pentane was removed on the rotary evaporator after filtering to yield 162 mg (65%) of the ester **35** as a oil. This was further purified by GLC collection (column 2, 110 °C, 60 ml/min): NMR ($CDCl_3$) τ 3.93–4.43 (m, 3 H), 4.70–5.14 (m, 2 H), 6.24 (s, 3 H), 6.43–7.06 (m, 2 H), and 7.19–9.0 (m, 4 H); ir (neat) 3000, 2900, 2800, 1740, 1635, 1260, 1190, 1160, 1020, 995, 920, and 750 cm^{-1}; mass spectroscopic molecular weight 166.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26, H, 8.49. Found: C, 72.43; H, 8.26.

Irradiation of 22. The ketone **22** (32.9 mg) was dissolved in 12 ml of spectrograde pentane (0.02 M) and placed in a Pyrex tube. After degassing at 0 °C for 15 min the sample was irradiated as described above for 75 min. GLC analysis (column 1, 105 °C, 30 ml/min) indicated >95% consumption of starting material. The reaction was quenched with 0.5 ml of methanol added at room temperature. The major product (11%) was shown by GLC comparison and its spectral data to be the ester **35.**

Registry No.—**1,** 2305-26-2; **2,** 18014-24-9; **3,** 39589-98-5; **4,** 39762-43-1; **5,** 4098-47-9; **6,** 56514-07-9; **7,** 7184-07-8; **8,** 57819-09-7; **9,** 4545-84-0; **10,** 39762-44-2; **11,** 57774-80-8; **12,** 39762-45-3; **13,** 39873-35-3; **14,** 39762-46-4; **15a,** 57774-81-9; **15b,** 57819-10-0; **16,** 57774-82-0; **17,** 57819-11-1; **18,** 35150-63-1; **19,** 57774-83-1; **20,** 35150-65-3; **21,** 57819-12-2; **22,** 32166-31-7; **23,** 57774-84-2; **24,** 35237-74-2; **25,** 57774-85-3; **26,** 54566-00-6; **27,** 54566-21-1; **28,** 14315-51-6; **29;** 54566-22-2; **30,** 54595-30-1; **31,** 54566-24-4; **32,** 54566-25-5; **33,** 16529-77-4; **34,** 57774-86-4; **35,** 35150-66-4; *cis*-1,2,3,6-tetrahydrophthalic anhydride, 935-79-5; ethanol, 64-17-5; trimethylsilyl chloride, 75-77-4; *endo*-bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride 17812-27-0; methanol, 67-56-1; *exo*-bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, 2746-19-2; dichloroacetyl chloride, 79-36-7; norbornadiene, 121-46-0; *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride, 24327-08-0; *endo*-bicyclo[3.2.2]non-5-ene-2,3-dicarboxylic anhydride, 29577-71-7; lithium aluminum hydride, 16853-85-3.

Supplementary Material Available. The detailed ultraviolet spectra in the n–π^* region for compounds **16, 18, 20, 22, 26,** and **33** (1 page). Ordering information is given on any current masthead page.

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(20) This technique has also been used for preparing monocyclic cyclobutanones; e.g., a mixture of 2,2- and 3,3-dimethylcyclobutanone has been prepared in good yield from dimethyl 2,2-dimethylsuccinate in this manner (unpublished results).

(21) All melting and boiling points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. NMR spectra were recorded on a Joelco Minimar, Varian HA-60-IL, or HA-100 instrument with Me_4Si as an internal standard. Infrared spectra were run on a Beckman 521 grating instrument or a Perkin-Elmer Infracord. The ultraviolet spectra were taken on a Cary 14 instrument. We thank Dr. S. Rottschaeffer of the University of Oregon for the high-resolution mass spectra. The analytical and preparative gas chromatography were done using a Hewlett-Packard Model 5750 instrument employing the following columns: column 1, 6 ft × 0.125 in., 10% UCW 98 on Chromosorb W (HMDCS); column 2, 6 ft × 0.25 in., 20% SE-30 on Chromosorb W (HMDCS); column 3, 10 ft × 0.125 in., 10% Carbowax 20M on Chromosorb P; column 4, 6 ft × 0.25 in., 10% Carbowax 20M on Chromosorb P.

(22) If all of the ester and trimethylsilyl chloride were added prior to heating, a strong exotherm was observed upon warming once the internal temperature reached ca. 70 °C. The exotherm is accompanied by the appearance of the blue-violet color. An alternative proceudre which can be employed involves adding the ester–trimethylsilyl chloride mixture slowly to the well-stirred sodium dispersion at 70 °C. Similar results were obtained for both procedures and the latter is more convenient for large runs.

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