Synthesis, Electronic Spectra, and Thermal Behavior of Bis(heptaphenylcycloheptatrienes)

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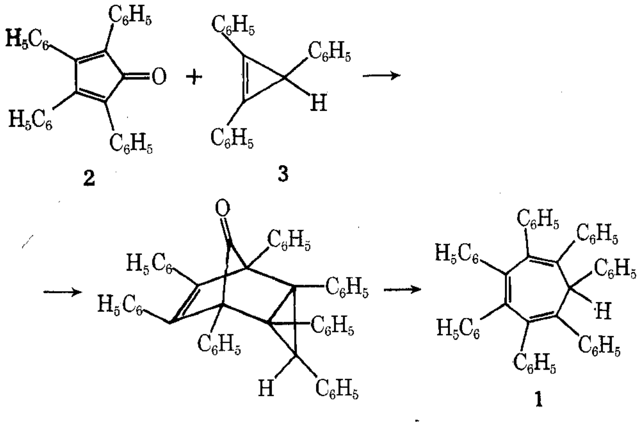
The synthesis of several members of a new class of compounds, the bis(heptaphenylcycloheptatrienes), is reported where the linking groups connecting the two hexaphenylcycloheptatriene moieties include phenyl, diphenyl, diphenylmethane, and diphenyl ether. The electronic spectral behavior of the bis(heptaphenylcycloheptatrienes) shows that the major chromophore of these compounds is an individual heptaphenylcycloheptatriene moiety. Differential thermal analysis shows two or more endotherms for each bis(heptaphenylcycloheptatriene) in the range 430–656 °C with indications of liquid crystal behavior. Comparison of the thermal behavior of these compounds with that of the parent heptaphenylcycloheptatriene is also discussed.

The synthesis of a wide variety of polyphenylated hydrocarbons has been made feasible by the Diels–Alder reaction followed by the decarboxylation reaction of the Diels–Alder adducts.[1] To date the heptaphenylcycloheptatrienes reported have been made via this approach and include the parent 1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-triene (**1**),[2] 1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-trien-7-ol,[3] 7-methoxy-1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-triene,[3] the monobromide,[3] tribromide,[3] triiodide,[4] fluoroborate,[3] and potassium[4] salts of the 1,2,3,4,5,6,7-heptaphenyltropylium ion, and several 7,8,9,10,11-pentaphenylcyclohept[*a*]acenaphthylenes and their covalent derivatives.[5] The parent compound **1** was synthesized by Battiste[2] in 1961 via the Diels–Alder reaction of 2,3,4,5-tetraphenylcyclo-2,4-pentadien-1-one (tetracyclone, **2**) and 1,2,3-triphenylcyclopropene (**3**) with the subsequent loss of carbon monoxide from the initially formed Diels–Alder adduct. By varying[2] the reaction conditions (temperature and solvent) the product **1** could be obtained directly. The only report[4] of a bis(heptaphenylcycloheptatriene) as a possible product was in the zinc reduction of the heptaphenyltropylium salts, but none of the bis analogue was isolated.

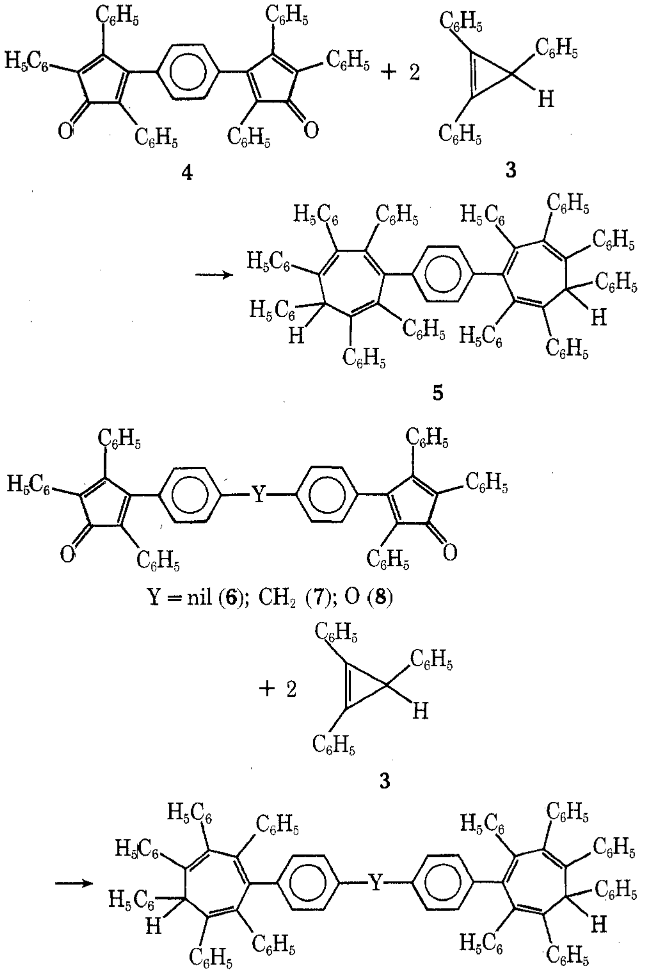


We now wish to report the successful synthesis of several bis(heptaphenylcycloheptatrienes) and their electronic and unique thermal behavior.

Synthesis. The route chosen to prepare the bis(heptaphenylcycloheptatrienes) was via the Diels–Alder reaction of the dienophile **3** with several bistetracyclone[6,7] dienes (Chart I). Reaction of a 1:2 ratio of diene to dienophile in refluxing diglyme for periods ranging from 14 to 19 days afforded the bis(heptaphenylcycloheptatrienes) in yields ranging from 51 to 87% (Table I).

Electronic Spectra. The spectra features for the bis(heptaphenylcycloheptatrienes) in 1,2-dichloroethane are shown in Table II and consist of a major band in the region 2600–2680 Å and a shoulder in the region 2750–3200 Å. The molar extinction coefficients at the wavelength of maximum absorption for compounds **5**, **9**, **10**, and **11** are all approximately double that for the parent molecule **1**, which indicates that the major chromophore in the bis(heptaphenylcycloheptatrienes) is an individual heptaphenylcycloheptatriene unit.

Chart I



Y = nil (**6**); CH$_2$ (**7**); O (**8**)

Y = nil (**9**); CH$_2$ (**10**); O (**11**)

Thermal Behavior. In obtaining the melting point for the parent 1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-triene (**1**), it is clearly observed that the solid becomes a liquid in the range 289–290 °C. However, when the same technique was used to obtain the melting points for compounds **5**, **9**, **10**, and **11**, no true melting points were observed; instead, at the temperatures reported in Table III, the solids gave the appearance of softening (sintering) but no liquefaction occurred.

Table I. Physical Data for Bis(heptaphenylcycloheptatrienes)

Compd	Reaction time, days	Yield, %	Formula[a]
1,4-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)benzene (**5**)	14	77	$C_{92}H_{66}$
4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)biphenyl (**9**)	16	51	$C_{98}H_{70}$
4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenylmethane (**10**)	14	79	$C_{99}H_{72}$
4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenyl ether (**11**)	19	87	$C_{98}H_{70}O$

[a] Satisfactory analytical data (±0.3% for C, H) for all compounds were submitted for review.

To further investigate this observation differential thermal analysis (DTA) was performed on the bis(heptaphenylcycloheptatrienes) and, although no endotherm or exotherm was observed in the thermograms which would correspond to the visually observed point of softening, each of the thermograms did show two or three endotherms (Table III). This particular type of thermal behavior could be attributed to several phenomena: decomposition, different crystal forms, thermal cleavage followed by recombination, liquid crystal behavior, or thermal rearrangement. In order to eliminate several of the possibilities proposed above the following experiments were conducted. Samples of compounds **5**, **9**, **10**, and **11** were all subjected to repetitive DTA determinations on the same samples. After each endotherm was observed, the respective samples were cooled to 25 °C below the temperature of that particular endotherm and the sample was again heated to 25 °C above the temperature of the observed endotherm. This procedure was repeated five times at each endotherm observed for each compound and neither the position of the endotherms nor the ratio of the areas under the endotherms changed for any of the samples. These experiments eliminated the possibility of either decomposition or the presence of different crystals forms, since if either were true, a loss of one or more endotherms or a change in the ratio of the areas under the endotherms should have been observed. A DTA was also performed on a 1:1 mixture of 4,4′-bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenylmethane (**10**) and 4,4′-bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenyl ether (**11**) to establish if the thermal behavior of the original samples was due to thermal cleavage followed by recombination. If this process was indeed occurring then the thermogram of the original mixture should reveal the original five endotherms at 431, 435, 563, 570, and 656 °C corresponding to the original two compounds, whereas subsequent thermograms should reveal other endotherms corresponding to the newly formed recombination products. Again five repetitive DTA's on the same sample mixture over the entire temperature range did not show any new endotherms or any change in the ratio of the areas under the originally observed endotherms.

The remaining possibility to explain the thermal behavior of the bis(heptaphenylcycloheptatrienes) is liquid crystal behavior which can be determined by observing the birefringence of compounds **5**, **9**, **10**, and **11** with the aid of a polarizing microscope fitted with a hot stage. Owing to the specialized nature of the equipment required for these determinations it was not possible for us to establish this possibility; however, the liquid crystal explanation is the most viable explanation available to explain the observed thermal behavior of these compounds.

Thermal Behavior of 1,2,3,4,5,6,7-Heptaphenylcyclohepta-1,3,5-triene (1). Although compound **1** does show a true melting point in the range 289–290 °C, repetitive DTA's were performed on a single sample of this compound in order to use the results obtained as a model for the thermal behavior of the bis(heptaphenylcycloheptatrienes). Surprisingly the first five repetitive DTA's performed showed the position of the observed endotherm to be lower than the preceding DTA, while the endotherms obtained from runs 5 and 6 were constant (Table IV). At this point a new sample of **1** was placed in a Carius tube, sealed under an inert atmosphere of nitrogen, and placed in a Wood's metal bath at 300 °C for 45 min. After this time the sample was removed and its melting point taken and compared with the melting point of an unheated sample. The melting point of the heated sample was 238–240 °C, while the melting point of the unheated sample was 289–290 °C. Both the infrared and the NMR spectra of the heated sample were taken and compared to the corresponding spectra taken

Table II. Spectral Features of Heptaphenylcycloheptatriene and Bis(heptaphenylcycloheptatrienes)

Registry no.	Compd[a]	λ_1, Å	$\epsilon_1 \times 10^{-3}$	Point of inflection, Å	λ_{sh}, Å	$\epsilon_2 \times 10^{-3}$
1835-56-9	1,2,3,4,5,6,7-Heptaphenylcyclohepta-1,3,5-triene (**1**)[b]	2675	27.8	3000	3120	14.8
59907-73-2	1,4-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)benzene (**5**)	2680	57.5	2680	2755	50.2
59907-74-3	4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)biphenyl (**9**)	2680	60.9	2845	3200	37.2
59907-75-4	4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenylmethane (**10**)	2650	60.3	2990	3190	28.6
59907-76-5	4,4′-Bis(2,3,4,5,6,7-hexaphenylcycloheptatri-1,3,6-enyl)diphenyl ether (**11**)	2680	61.6	2980	3190	31.9

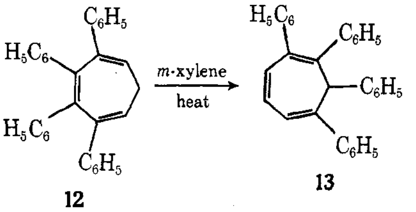
[a] 1,2-Dichloroethane used as solvent. [b] Reported[2] $\lambda_{max}(CH_3CN)$ (log ϵ) 2660 (4.46), 3060 (sh) (4.19).

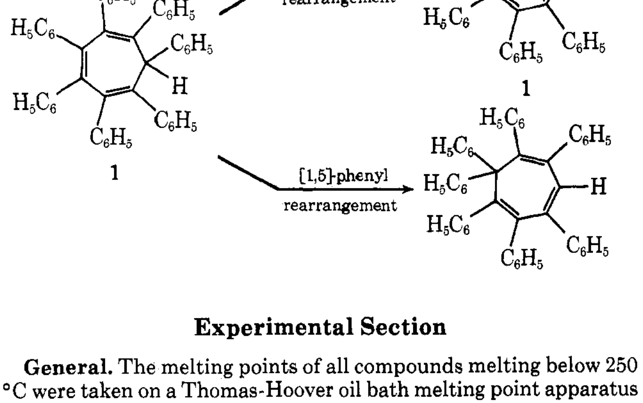
Table III. Differential Thermal Analysis of Bis(heptaphenylcycloheptatrienes)

Compd	Observed sintering point, °C	Endotherms, °C
5	190	445 and 662
9	218–220	440 and 644
10	185	431, 563, and 656
11	302–305	435 and 570

on an unheated sample and several differences were observed. The infrared spectrum of the heated sample was similar to the infrared spectrum of the unheated sample except for the disappearance of four peaks at 1574 (saturated C–H out-of-plane bending or wagging in a cycloalkane), 1328, 1308, and 730 cm^{-1}. The NMR spectrum of the heated sample lacked the singlet at τ 4.73 which was present in the sample before heating and which has been attributed to the cyclic proton on C_7,[8] while the mass spectrum of the sample after heating showed the same molecular weight as the mass spectrum for the unheated sample.

The above results strongly indicate that the sample after heating differs from an unheated sample only to the extent of the positioning of one proton, which appears to be explainable in terms of a thermally allowed[9] [1,5]-phenyl rearrangement. It has been reported[10] that heating 2,3,4,5-tetraphenylcyclohepta-1,3,5-triene (**12**) in *m*-xylene affords 1,2,6,7-tetraphenylcyclohepta-1,3,5-triene (**13**) via a thermal [1,5]-hydrogen rearrangement. However, if 1,2,3,4,5,6,7-heptaphenylcyclohepta-1,3,5-triene (**1**) underwent a similar thermal [1,5]-hydrogen rearrangement the product formed would be identical in structure with the starting material and no change in the spectra or melting point should be observed. The observed spectral and melting point changes can be explained, however, if compound **1** undergoes a thermal [1,5]-phenyl rearrangement upon heating.





Experimental Section

General. The melting points of all compounds melting below 250 °C were taken on a Thomas-Hoover oil bath melting point apparatus and are corrected; melting points above 250 °C were taken on a Mel-Temp capillary melting point apparatus and are also corrected. A Stone thermal analyzer was used to obtain the differential thermal analysis (DTA) information. Infrared spectra were taken on solid potassium bromide pellets using a Perkin-Elmer IR-621 grating spectrophotometer and the ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer using a set of matched 1.0-cm quartz cells. Duplicate samples were run for each ultraviolet spectrum reported and all spectral values obtained agreed to within ±0.01% for the wavelength determinations and ±1.00% for the molar extinction coefficient determinations. Ultraviolet spectra were taken in freshly distilled 1,2-dichloroethane with the samples being weighed on a microbalance. No solubility problems were encountered. Mass spectra were obtained on a Hitachi Perkin-Elmer RMV-6E mass spectrometer at 50 eV.

Table IV. Repetitive Differential Thermal Analysis of a Single Sample of Heptaphenylcycloheptatriene

Run no.	Endotherm, °C	Run no.	Endotherm, °C
1	289	4	259
2	284	5	240
3	264	6	240

1,2,3-Triphenylcyclopropene (3). This compound was prepared in an overall yield of 45% via the 1,2,3-triphenylcyclopropenyl *tert*-butyl ether[11] followed immediately by reduction using triethylsilane.[12]

Bistetracyclones (4, 6, 7, and 8). The bistetracyclones were all prepared via literature procedures.[6,7]

Bis(heptaphenylcycloheptatrienes) (5, 9, 10, and 11). The following general procedure was used for the preparation of all the bis(heptaphenylcycloheptatrienes). Into a 500-ml, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer were placed 10 mmol of the appropriate bistetracyclone and 30 mmol of 1,2,3-triphenylcyclopropene (**3**) in 250 ml of diglyme. The reaction mixture was refluxed for the appropriate number of days reported in Table I, then the diglyme was removed by vacuum distillation. To the remaining solution was added 500 ml of 95% ethanol and the solid which separated was collected and dried. Recrystallization from a 1:5 benzene–ethanol solution afforded analytically pure samples in the yields reported in Table I. Other solvents used for this reaction included benzene, toluene, *p*-xylene, and methyl isobutyl ketone, but these solvents all gave lower yields than those obtained with diglyme.

Thermal Analysis of Bis(heptaphenylcycloheptatrienes). Differential thermal analyses (DTA) were performed on analytical samples of all the bis(heptaphenylcycloheptatrienes) under an inert atmosphere of dry nitrogen. After each endotherm was obtained the instrument was cooled to 25 °C below the temperature of that particular endotherm and the sample was again heated to 25 °C above the temperature of the observed endotherm. This procedure was repeated five times for each endotherm observed and for each compound. No change in position or ratio of areas of the endotherms was observed in any experiment.

A 1:1 mixture of **10** and **11** was prepared by grinding the samples together in a mortar and pestle and subjected to the above procedure and no change in positions or ratio of areas of the endotherms was observed.

Thermal Analysis of Heptaphenylcycloheptatriene (1). A differential thermal analysis was performed on an analytical sample of **1** under an inert atmosphere of nitrogen. After the entire thermogram was obtained the instrument was cooled to room temperature and the same sample was rescanned from room temperature to 500 °C. This procedure was repeated six times and the results are shown in Table IV.

A 0.5-g sample of **1**, mp 289–290 °C, was placed in a Carius tube, and the tube sealed under nitrogen and placed in a Wood's metal bath at 300 °C for 45 min. After this time the tube was removed, cooled, and opened, and the yellow solid removed and recrystallized from a 1:4 mixture of benzene–ethanol. The melting point of the sample obtained was 238–240 °C.

Unheated **1**: ir (KBr) 3082, 3060, 3023, 1945, 1875, 1800, 1743, 1598, 1574, 1493, 1488, 1442, 1438 (sh), 1328, 1308, 1156, 1090, 1080 (sh), 1070, 1040, 1028, 1023 (sh), 1002, 917 (sh), 910, 845, 804, 788, 768, 734, 730, 703, 588, 580 (sh), 578, and 540 cm^{-1}; NMR ($CDCl_3$) τ 2.03–3.70 (m, 35, ArH) and 4.73 (s, 1, cyclic proton) [lit.[8] 2.10–3.85 (m, ArH) and 4.73 (s)].

Heated **1**: the ir (KBr) spectrum of **1** after heating was the same as the spectrum of **1** obtained before heating except for peaks at 1574, 1328, 1308, and 730 cm^{-1}, which were absent; NMR ($CDCl_3$) τ 2.10–3.85 (m, ArH), no signal observed at 4.73.

The mass spectra of both the heated and the unheated samples were essentially identical. The sample after heating was scanned to m/e 1600 and no peak corresponding to a dimer of 1 was observed. The C and H analyses for both the heated and unheated samples were satisfactory.

Registry No.—2, 479-33-4; 3, 16510-49-9; 4, 3432-73-3; 6, 16325-29-4; 7, 59907-77-6; 8, 13092-45-0.

References and Notes

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On the Photochemistry of Hexamethyl-2,4-cyclohexadienone 4,5-Epoxide and on Subsequent Rearrangements of Its Photoisomer, *endo*-5-Acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]pentan-2-one

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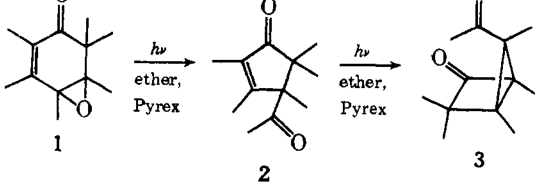
Irradiation (Pyrex) of hexamethyl-2,4-cyclohexadienone 4,5-epoxide (1) gives 2,3,4,5,5-pentamethyl-4-acetyl-2-cyclopentenone (2), which then photoisomerizes to *endo*-5-acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]pentan-2-one (3). This bicyclic diketone is photochemically and thermally labile. On irradiation in ether through Corex, 3 is converted to lactones 4 and 5. The thermal rearrangements of 3, which probably proceed via ketene 7, show a remarkable solvent effect. In carbon tetrachloride the products are 2 and lactone 8, whereas in methanol the products are lactones 9 and 10. Mechanisms for all these transformations are proposed and supported by deuterium labeling experiments.

Although the photochemistry of α,β-epoxy ketones has been extensively studied,[1] only recently have the vinylogous α,β-unsaturated γ,δ-epoxy ketones received attention.[2-6] The few results reported thus far suggest that this class of epoxy ketones undergoes a wide range of fascinating photochemical rearrangements.

One class of easily accessible[7] α,β-unsaturated γ,δ-epoxy ketones whose photochemistry has not been studied are the 2,4-cyclohexadienone 4,5-epoxides. In this paper we describe the irradiation of hexamethyl-2,4-cyclohexadienone 4,5-epoxide (1).[8] The initial photoproduct undergoes further photoisomerization to a second product which itself is both photo- and thermolabile, resulting in an interesting array of molecular rearrangements.

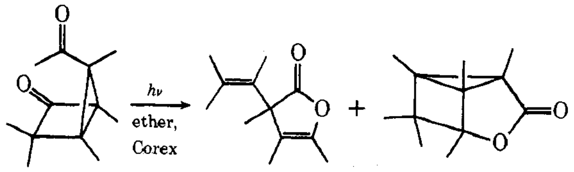
Results and Discussion

Photochemistry of 1. Irradiation of 1 (0.01 M in ether, 0 °C) through Pyrex was followed by NMR. As peaks due to 1 decreased in intensity, a new set of peaks which could be ascribed to the known 2[8] appeared. At 50% conversion both sets of peaks began to diminish in area in favor of a third set of peaks. After 16 h only the third set was present, and a crystalline product to which we assign structure 3 was isolated in 90% yield.[9] The structural assignment is based on spectra and on chemical transformations. Ir bands at 1760 and 1710 cm^{-1} are attributed to the cyclobutanone and acetyl absorptions, respectively. The absence of ir bands in the 1500–1680-cm^{-1} region together with the fact that all the methyl signals in the NMR spectrum (except the acetyl methyl, at δ 2.15) appeared as singlets above δ 1.3 indicated the absence of C=C bonds. The mass spectrum showed that 3 was an isomer of 1 and 2 (M$^+$ 194, 20%); the base peak at m/e 152 corresponded to loss of ketene (presumably from the acetyl group). The endo configuration for the acetyl group is required by subsequent reactions of 3 (vide infra).



1 2 3

Photochemistry of 3. The bicyclic diketone 3 had a λ_{max} (MeOH) at 225 nm (ϵ 2590) and was photolabile when irradiated through a Corex filter (0.017 M in ether, 0 °C). The major photoproduct was assigned structure 4, and the minor product is tentatively assigned structure 5. The $\nu_{C=O}$ at 1790 cm^{-1} in 4 is consistent with the five-membered enol lactone moiety. The NMR spectrum of 4 showed two homoallylically coupled methyl signals at δ 1.50 and 1.87 assigned (from labeling experiments; vide infra) to the allylic methyls of the lactone ring. Other allylic methyl signals appeared at δ 1.70 (6 H) and 1.37 (3 H),[10] and the aliphatic methyl was a sharp singlet at δ 1.30.



3 4 (79.6%) 5 (20.4%)

The minor product 5 had a $\nu_{C=O}$ at 1760 cm^{-1} consistent with a strained five-membered lactone. The absence of ir bands in the 1500–1680-cm^{-1} region and the location of all methyl singlets in the NMR spectrum at or above δ 1.20 showed the absence of C=C bonds. The mass spectrum of 5