bromo-2-butene, 3017-71-8; methyl (*E*)-3-bromo-2-methyl-2-propenoate, 40053-01-8; (*Z*)-1-bromo-1-hexene, 13154-12-6; (*E*)-3-iodo-3-hexene, 16403-09-1; (*E*)-3-bromo-2-methyl-1,1-dimethoxy-2-propene, 76232-48-9; 1-bromocyclohexene, 2044-08-8; 1-bromo-3-(tetrahydropyranyloxy)-1-propene, 76232-49-0; (*Z*)-3-iodo-3-hexene, 16403-13-7; (*Z*)-3-bromo-3-hexene, 16645-01-5; (*Z*)-1-bromo-1-hexene, 13154-12-6; (*E*)-3-bromo-2-methyl-2-propenoic acid, 24557-13-9; methyl (*E*)-3-bromo-2-methyl-2-propenoic acid, 40053-01-8; 1-bromo-2-methyl-1-propene, 3017-69-4; 1-iodo-1-hexene, 16644-98-7; (*Z*)-3-iodo-3-hexene, 16403-13-7; 2-bromo-1-propene, 557-93-7; (*Z*)-4,5-dimethyl-2,4-hexadienoic acid, 76232-50-3; dimethyl (*E,E*)-2-methyl-2,4-hexadienedioate, 39995-94-3; (*E,Z*)-2,4-nonadienamide, 76232-51-4; (*E*)-2,5-dimethyl-2,4-hexadienamide, 76232-52-5; dimethyl 2-(2-methylenepropylidenyl)butanedioic acid, 76232-53-6; dimethyl 2-(2-hexenylidenyl)butanedioic acid, 76232-54-7; $Pd(OAc)_2$, 3375-31-3.

Supplementary Material Available: Table II listing the physical properties, NMR spectral data, and molecular weights (high-resolution mass spectroscopy) for the new compounds prepared (7 pages). Ordering information is given on any current masthead page.

Thermal Rearrangement of a 2-Methylenebicyclo[2.1.1]hexane

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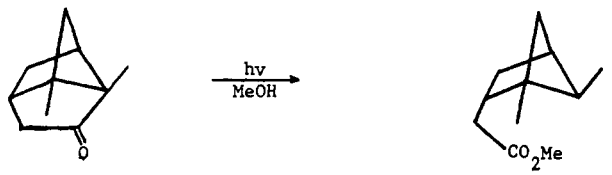
Received July 7, 1980

Pyrolysis of 1,*exo*-5-dimethyl-2-[(carbomethoxy)methylene]bicyclo[2.1.1]hexane results in isomerization of the 5-methyl group to the endo configuration. A homolytic cleavage mechanism of the vinylcyclobutane system is proposed to explain this unexpected result.

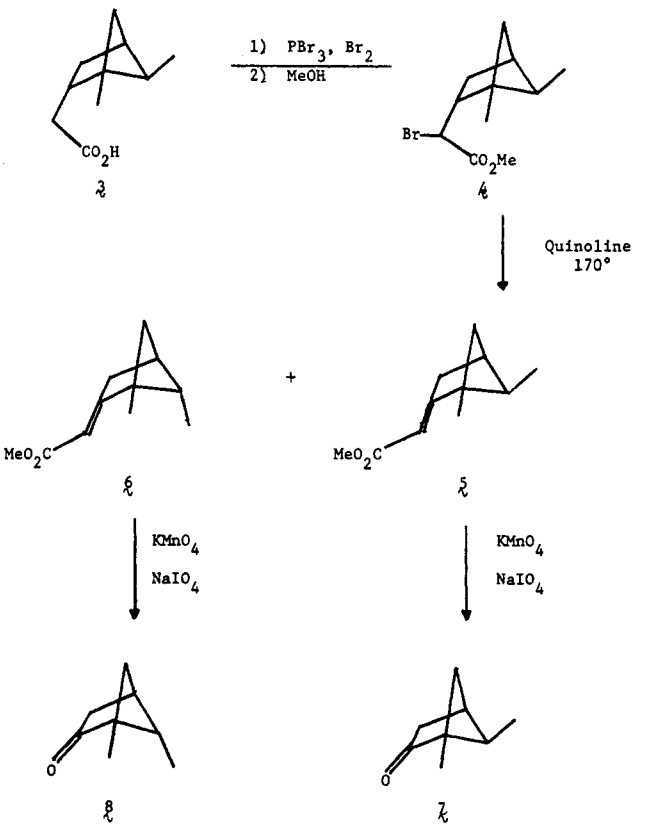
During work on the photochemical behavior of carvone camphor[1] **1**, we devoted extensive effort to development of a degradation method to prove unambiguously the structure and stereochemistry of the photolysis product **2**. This work ultimately showed that **2** is the exclusive



1 **2**

product of the photolytic process, in accord with results obtained by others.[2] In one degradation attempt (Scheme I) bromination of the acid **3** with Br_2/PBr_3 followed by methanolysis gave a 1:1 mixture of bromo esters **4**. Dehydrobromination of **4** by quinoline at 170 °C resulted in the formation, in variable amounts, of two unsaturated esters which could not be isolated in good purity because of their instability during preparative gas chromatography. Data obtained on impure samples strongly suggested the structures **5** and **6** in which one product apparently resulted from rearrangement during one of the steps of the degradation sequence. Confirmation of the structure of the ring portion of ester **5** was obtained by oxidation of a partially purified sample to the known ketone **7**, which was identical with the sole product obtained by an alternate degradation sequence of **3**.[1] Oxidation of **6** gave a different ketone, establishing that **5** and **6** did not differ simply in the configuration of the double bond. The ketone showed properties in excellent agreement with those predicted for **8** [e.g., ν 1754 cm^{-1}; δ 0.79 (3 H, d, 5-endo CH_3)], but an unambiguous structure proof was lacking. In subsequent work, presented in this paper, we have confirmed the structure of ketone **8** by an unambiguous synthesis, established the complete structures of esters **5**

Scheme I



3 **4** **6** **5** **8** **7**

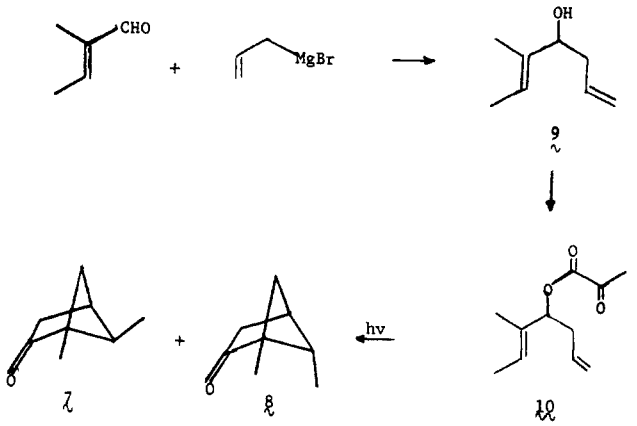
and **6**, and determined that the ester **6** is the result of a thermal rearrangement of **5**.

Synthesis of 8. The method developed for preparation of **8** is shown in Scheme II. The original intent was to generate the bicyclic ketones by photocyclization of the ketone corresponding to alcohol **9**,[3] but all attempts to oxidize **9** failed. This problem was overcome by using a

(1) T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966).
(2) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965).
(3) T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **37**, 1148 (1972).

0022-3263/81/1946-1073$01.25/0

Scheme II



recently developed method for conversion of alcohols to ketones via the pyruvate esters.[4] Irradiation of pyruvate **10** in benzene through Pyrex generated **7** and **8** directly in low yield in a ratio of 71:29. Evidence for the transient existence of the dienone was obtained by gas chromatography by comparison with a sample obtained in small amount by Jones oxidation of **9**. No other volatile products were observed, and the bicyclic ketones proved to be identical in all respects with those obtained from degradation of **3**. Precedent for the formation of bicyclo[2.1.1]hexanones as the exclusive bicyclic photoproducts of dienones such as this exists (see, for example, ref 3). This, in conjunction with the spectral data obtained, serves to exclude the alternative bicyclo[2.2.0]hexanone structure for **8**. While we made no attempts to optimize this process, the pyruvate method would appear to be potentially very useful for carrying out this photocycloaddition reaction, since it avoids the need to isolate the unstable dienones.

Source of the Rearrangement Product. That the rearrangement does not occur in the bromination step was established by reduction of the mixture of bromo esters **4** with tributyltin hydride. The sole product of this reduction was the ester **2**, formed in 61% yield, showing that **4** is a mixture of α-bromo diasteroisomers. Dehydrobromination of **4** with hot quinoline could conceivably lead to rearrangement by thermal or acid-catalyzed processes. In fact, dehydrobromination with sodium methoxide in methanol at 60 °C gave only ester **5** in high yield, with no evidence for **6**. Pyrolysis of **5** in a sealed, base-washed tube at 170 °C led to the formation of a mixture of **6** and **5** in a ratio of 84:16, respectively.[5] Pyrolysis in dodecane solution gave good first-order kinetics for the disappearance of **5** with a rate constant at 180 °C of 2.3×10^{-2} min^{-1} ($t_{1/2}$ = 5 h). Purification of **6** was accomplished by preparative gas chromatography. This material, when submitted to pyrolysis, regenerated the same mixture of **6** and **5** as was previously obtained from **5**, showing that the 84:16 mixture is a true thermal equilibrium.

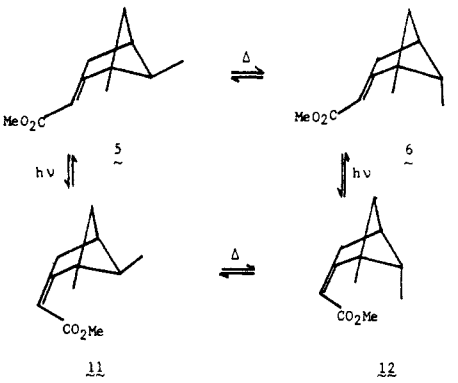
The stereochemistry about the double bond of esters **5** and **6** presented a problem which was solved in the following way. Irradiation of a pentane solution of **5** with a low-pressure mercury resonance lamp gave rise to a single product, isolated in a pure state by high-pressure LC and assigned structure **11** on the basis of ^{1}HMR and mass spectra. In particular, the ^{1}HMR spectrum of **11** is fully consistent with retention of the bicyclo[2.1.1]hexane system, as well as the exo stereochemistry of the 5-methyl group. The signal at δ 2.71 in **5** (Table I) can confidently be assigned to the C_3 methylene group on the basis of its lower field position and symmetrical quartet structure. In the photoisomer **11**, this signal is shifted upfield to δ 2.40, in good agreement with effects in acyclic unsaturated esters, e.g., *cis*- and *trans*-methyl geranate.[6] In **6**, this signal appears at δ 2.64, shifted upfield slightly with respect to that in **5** by the anisotropic effect of the *endo*-5-methyl group. The change in configuration at C_5 also introduces some dissymmetry into the environment of C_3, causing the quartet to become somewhat distorted. Similar effects on the bridgehead methyl group (C_7) support these stereochemical assignments. The bathochromic shift of 6 nm for the ultraviolet absorption maximum for **11** with respect to **5** and **6** is compatible with the expected increased ground-state energy of the more sterically encumbered photoisomer.

Table I. NMR Data[a]

compd	5	6	11	12
C_3	2.71	2.64	2.40	2.32
C_7	1.07	1.13	1.36	1.45
C_8	1.16	0.59	1.14	0.70

[a] δ values for chemical shifts of protons on the indicated carbon in $CDCl_3$. C_7 = bridgehead methyl and C_8 = 5-methyl.

Scheme III



Further support for these assignments was sought by examination of the properties of the still-missing member of the series, **12** (Scheme III). This compound was prepared by pyrolysis of **5**, followed by irradiation of the mixture of **5** and **6** formed. This resulted in a mixture of the four compounds **5**, **6**, **11**, and **12** in proportions of 9:56:6:28, respectively. Isolation of pure **12** was accomplished by preparative high-pressure LC. The ^{1}H NMR spectral data (cf. Table I and Experimental Section) are in full accord with the data obtained from the other compounds and nicely confirm the stereochemical assignments to the entire series.

Finally, pyrolysis of **12** was carried out to determine whether the sterically crowded environment at the ester group in this compound would result in double bond isomerization. Under conditions in which **5** and **6** equilibrate to a 16:84 mixture (180 °C, 24 h, sealed tube), **12** was converted to a mixture of **12** and **11** in an approximate ratio of 90:10. Small amounts, ca. 2% and 3%, respectively, of peaks corresponding in high-pressure LC retention volume to **6** and **5** were also observed. These were not positively identified but show that double bond isomerization cannot be occurring to an extent greater than about 5% under these conditions.

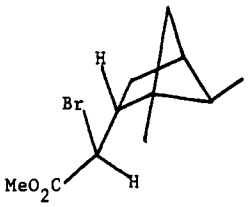
(4) R. W. Binkley, *J. Org. Chem.*, 41, 3030 (1976).

(5) Attempts to carry out this reaction in solvents usually lead to the formation of new and as yet unidentified compounds in addition to **5** and **6**. This presumably acid-catalyzed process is under active investigation.

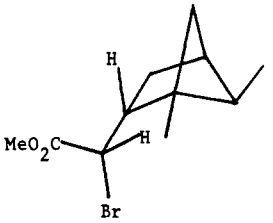
(6) J. W. K. Burrell, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc., London*, 263 (1959).

Discussion

The formation of a single compound by low-temperature, sodium methoxide promoted dehydrohalogenation of the mixture of bromo esters **4** could be due to isomerization of the olefin mixture after elimination to give exclusively **5** or to elimination of the two diastereoisomers by different mechanisms. The former possibility can be eliminated by the observation that **11** was recovered unchanged after treatment with sodium methoxide under the conditions of the dehydrobromination. Conformational control in the elimination, however, provides a ready rationalization for the formation of a single isomer. In **4a**,



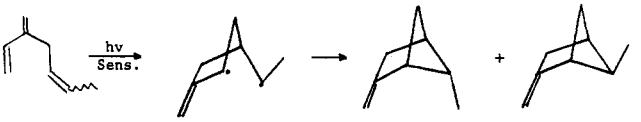
4b



4a

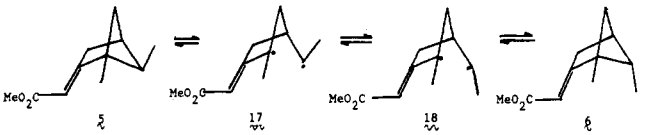
the anti conformation would appear to be favored on the basis of examination of the Dreiding model, while an anti conformation of **4b** would lead to strong nonbonded interaction between the ester and bridgehead methyl groups. On the reasonable assumption that these eliminations proceed via E2 mechanisms, this suggests that elimination in **4b** follows a syn pathway, providing **5** as the only product, as would **4a** by an anti elimination.

The 84:16 ratio of **6** to **5** and **12** to **11** obtained on thermal equilibration of the esters is in excellent agreement with the result obtained by sensitized photocycloaddition of dienes **13**.[7] Irradiation of either isomer of **13** gave rise to the same 85:15 mixture of **14** and **15**, attributed to the



13 **16** **14** **15**

intervention of a biradical (**16**) which retained sufficient triplet character to undergo rotational equilibration before closure to products. The isomers of **13** were not interconverted under these conditions. Indeed, direct irradiation of **13** gave rise, presumably by way of singlet diradical intermediates, to different ratios of products **14** and **15**. Thermal cleavage of vinyl cyclobutanes such as **5** and **6** is generally recognized to involve diradical intermediates, necessarily singlet in nature.[8] Cleavage of the 1,5-bond in **5** or **6** would lead to biradicals **17** and **18** initially, which



5 **17** **18** **6**

could equilibrate before reclosure to generate the observed mixture. This conclusion is strongly supported by the observation of the formation of identical mixtures of stereoisomers **5** and **6** and **11** and **12** as previously seen with **13**.

It is probable that the diradicals **17** and **18** are stabilized relative to **16** by the presence of the conjugated ester. A comparison of the rates of isomerization of **14** and **15** with those of **5** and **6** would be interesting in determining the influence of the ester group. The potentially available 1,3 shift is thwarted in this case by the highly strained nature of the product, which would possess a bicyclo[2.2.1]heptene framework with a bridgehead double bond. The absence of fragmentation products, which are generally observed from pyrolysis of vinyl cyclobutanes at high temperature,[8] may simply be a result of the moderate temperatures employed in this work. Higher temperature pyrolysis of these compounds should eventually result in regeneration of acyclic trienes.

Experimental Section[9]

Bromination of 1,5-Dimethylbicyclo[2.1.1]hexane-2-acetic Acid (3). To 2.92 g (17.4 mmol) of the acid (obtained from the irradiation of *d*-carvone in methanol followed by hydrolysis) was added 7.94 g (29.3 mmol) of PBr_3. After about 1 h at ambient temperature under Argon, Br_2 (9.15 g, 57 mmol) was added in two batches. The reaction mixture was heated on a steam bath for 3 h, cooled, and quenched with excess dry methanol. After dilution with ether, extraction with saturated aqueous $NaHCO_3$ and water followed by drying over $MgSO_4$ gave 6.3 g of crude product. Distillation in a short-path still gave 4.00 g (88%) of bromo ester **4**, bp 58–59 °C (0.35 mm). Gas chromatography showed the presence of a single major product and about 1% of the methyl ester of the starting acid. A pure sample of the major product, isolated by preparative gas chromatography, showed the following: ν_{max} 1745 cm^{-1}; NMR δ 4.18 (0.5 H, d, J = 6.0 Hz), 4.07 (0.5 H, d, J = 7.5 Hz), 3.74 (3 H, s), 2.63 (1 H, m), 2.0 (3 H, m), 1.55 (2 H, m), 1.19 (1 H, d, J = 7.5 Hz), 1.2 (1 H, m), 1.14 (~2 H, d, J = 7.2 Hz), 1.07 (~1 H, d, J = 7.2 Hz), 0.85 (~2 H, s). The mass spectrum (isobutane chemical ionization) gave $(M + H)^+$ ions at m/z 261.0471 and 263.0419 (calcd 261.0489 and 263.0469).

Anal. Calcd for $C_{11}H_{17}BrO_2$: C, 50.58; H, 6.56; Br, 30.60. Found: C, 51.87; H, 6.84; Br, 31.70.

Dehydrobromination of Bromo Esters 4. A. Aromatic Amines. A 10.0-g sample of bromo esters **4** was dissolved in 25 mL of synthetic quinoline (previously distilled from BaO) and the solution heated at 170 °C in an oil bath for 3.5 h. The cooled solution was diluted with ether, and the ether solution was extracted twice with H_2O, twice with 3% HCl, and once with saturated $NaHCO_3$, boiled with charcoal, and dried over $MgSO_4$. Evaporation of the solvent gave 7.5 g of an oil showing two peaks in a 58:42 ratio on gas chromatography. Distillation in an 18-in., spinning-band column gave a series of fractions of varying composition and allowed isolation of both components in greater than 95% purity. The minor component showed properties in accord with the expected product **5**: ν_{max} 1718, 1698 cm^{-1}; λ_{max} (EtOH) 224 nm (ϵ 19 000); $[\alpha]_{5461}$ −44.6° (*c* 1.95, EtOH); NMR δ 1.07 (3 H, s), 1.16 (3 H, d, J = 6.5 Hz), 1.26 (1 H, t, J = 6.5 Hz), 1.65 (1 H, quintet, J = 6.5 Hz), 2.21 (2 H, m), 2.71 (2 H, q, J = 2 Hz), 3.68 (3 H, s), 5.64 (1 H, t, J = 2 Hz).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.21; H, 8.84.

The major component (**6**) showed the following: ν_{max} 1720 cm^{-1}; λ_{max} (EtOH) 224 nm (ϵ 28 900); $[\alpha]_{5461}$ −23.9° (*c* 2.09, EtOH); NMR δ 0.59 (3 H, d, J = 6.5 Hz), 1.13 (3 H, s), 1.25 (1 H, d, J = 6.5 Hz), 1.50 (1 H, m), 1.9 (1 H, m), 2.35 (1 H, m), 2.64 (2 H, m), 3.71 (3 H, s), 5.64 (1 H, t, J = 2 Hz).

Anal. Found: C, 73.11; H, 8.96.

A similar result was obtained when the dehydrobromination was carried out in refluxing 2,6-lutidine, except that 4 days were required for complete disappearance of bromo ester.

B. NaOMe. The bromo ester **4** (2.35 g) was added to 30 mL of dry MeOH in which 0.5 g of sodium had been dissolved. The solution was maintained at 60 °C in an oil bath for 5 days, after

(7) R. S. H. Liu and G. Hammond, *J. Am. Chem. Soc.*, 89, 4936 (1967).
(8) For an excellent discussion of vinylcyclobutane pyrolysis, see L. Jordan, Ph.D. Dissertation, Yale University, 1974.

(9) Infrared spectra were determined on a Perkin-Elmer Model 257 spectrometer, ^{1}HMR spectra on a Varian HA-100 instrument, mass spectra on a Kratos MS-30, and UV spectra on a Cary Model 14 spectrometer. Gas chromatographic analyses were obtained on a Varian 202B instrument using 5 ft × $^1/_4$ in. packed columns with either butanediol succinate or SE-30. Microanalyses were performed by Spang Microanalytical Laboratory.

which no 4 remained. The solution was diluted with ether, washed twice with water, and dried over $MgSO_4$, and the solvent was removed by distillation. Distillation in a Kugelrohr apparatus gave 1.36 g (84%) of product, bp 80–90 °C (0.2 mm). NMR and high-pressure LC analyses showed the presence of unrearranged ester **5**, with no evidence for the presence of **6**.

Oxidation of 6. A 1.73-g sample of an ~1:10 mixture of esters **5** and **6** was treated with 0.22 g of $KMnO_4$, 6.0 g of $NaIO_4$, and 2.2 g of K_2CO_3 in 150 mL of water with vigorous stirring overnight. Extraction with ether gave an ~1:10 mixture of ketones, isolated by preparative gas chromatography. The minor ketone proved to be identical with **7**, as obtained previously.[1] The major product showed the following: ν_{max} 1754 cm^{-1}; mass spectrum, identical with that of **7**; NMR δ 0.79 (3 H, d, J = 7.0 Hz), 1.07 (3 H, s), 1.57 (1 H, d, J = 7.0 Hz), 1.77 (1 H, m), 2.08 (3 H, m), 2.60 (1 H, m).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.39; H, 9.82.

Preparation of 3-Methyl-2,6-heptadien-4-ol (9). Tiglic aldehyde (53 g) was added over 0.5 h to the Grignard reagent made from 63 g of allyl chloride and 110 g of Mg turnings in 1 L of ether. After 0.5 h at ambient temperature, the product was hydrolyzed with saturated Na_2SO_4 solution, dried over anhydrous Na_2SO_4, filtered, and stripped on a rotary evaporator to give 89 g of crude product. Distillation in an 18-in., spinning-band column gave 63.4 g (79%) of the alcohol **9**, showing >98% purity by gas chromatographic analysis. Material purified by preparative gas chromatography showed the following: ν_{max} 3030, 1639, 990, 914 cm^{-1}; NMR, δ 5.4–6.0 (2 H, m), 5.11 (1 H, dq, J = 17, 1 Hz), 5.07 (1 H, dt, J = 11, 1 Hz), 4.04 (1 H, t, J = 6.8 Hz), 2.32 (1 H, t, J = 6.8 Hz), 2.18 (1 H, s, OH), 1.63 (3 H, s), 1.62 (3 H, d, J = 5 Hz).

Irradiation of Pyruvate Ester. The pyruvate ester **10** was prepared by the method of Binkley.[4] The crude product, which was not purified further, showed about 10% unreacted alcohol. Irradiation of 10.3 g of the ester in 450 mL of dry benzene was carried out with a 450-W, medium-pressure Hg lamp through Pyrex for 94 h, at which time only a small amount of pyruvate ester could be detected by gas chromatographic analysis. Distillation of the solvent followed by vacuum distillation of the residue through an 18-in., spinning-band column gave 1.48 g (23%) of a 29:71 mixture of ketones, bp 41–50 °C (20 mm). The major and minor ketones proved to be identical (gas chromatography and IR) with **7** and **8**, respectively.

Tributyltin Hydride Reduction of Bromo Ester 4. To a solution of 0.560 g of bromo ester in 15 mL of benzene was added 0.65 g of Bu_3SnH. After 4 h of refluxing, the reaction mixture was allowed to cool to room temperature and stand over 3 days. The solvent was removed on a rotary evaporator, 60 mL of 1 N NaOH was added, and the resulting mixture was heated to 50 °C overnight. After the mixture was cooled and the neutral products were extracted with ether, acidification followed by CH_2Cl_2 extraction gave 0.45 g of acid. Esterification with methyl-*p*-tolyltriazine gave 0.45 g of crude ester. Distillation in a modified Hickman still gave 0.240 g (61%) of ester **2**, uncontaminated with other materials.

Pyrolysis of 5. A 41.0-mg sample of **5** was sealed under argon into a small ampule which had been washed with ammonium hydroxide and dried at 110 °C for 1 week. The ampule was immersed in an oil bath and heated to 170 ± 2 °C for 24 h, cooled rapidly, and opened. Gas chromatographic analysis showed the esters **5** and **6** in a ratio of 14:86, identical with that observed on high-pressure LC analysis. Isolation of the major peak by preparative gas chromatography gave ester **6** (13.0 mg) which showed no **5** in the ^1H NMR spectrum.

Pyrolysis of 5 in Dodecane. A solution of 4.2 mg of **5** and 2.1 mg of methyl palmitate (internal standard) in 0.50 mL of dodecane was heated at 180 ● 1 °C in a base-washed, 5 mL, round-bottomed flask. The system was kept under argon throughout. Aliquots were removed at intervals and analyzed by high-pressure LC on a Whatman 10/50 Magnum PAC column eluted with 95:5 hexane/ether at 4.5 mL/min. A first-order plot gave a straight line through 5.5 h, with $k = 2.3 \times 10^{-2}$ min^{-1} and a half-life of 301 min for disappearance of **5**. Further heating generated new products of unknown structures.

Irradiation of 5. A solution of 118.5 mg of **5** in mL of pentane was irradiated with a mercury resonance immersion lamp (254 nm) for 150 min. Distillation of solvent at atmospheric pressure followed by Kugelrohr distillation at 100 °C (4 mm) gave 113.8 mg (96%) of a 7:3 mixture of **5** and **11**. Attempts to separate the mixture by gas chromatography were hampered by rearrangement to **6** and what is presumably the thermal rearrangement product of **11**. However, high-pressure LC proved convenient for isolation of pure **11**, under the conditions described for the analysis of the pyrolysis followed by Kugelrohr distillation. This material showed the following: ν_{max} 1724, 1656, 1165 cm^{-1}; λ_{max} (EtOH) 230 nm (ϵ 10 000); ^1H NMR δ 1.14 (3 H, d, J = 6.5 Hz), 1.36 (3 H, s), 1.43 (1 H, m), 1.76 (1 H, quintet, J = 7 Hz), 2.16 (2 H, m), 2.40 (2 H, q, J = 2 Hz), 3.68 (3 H, s), 5.66 (1 H, t, J = 2 Hz). The high-resolution mass spectrum showed a parent ion at m/e 180.1175 (calcd for $C_{11}H_{16}O_2$, 180.1150).

Preparation of 12. A 250-mg sample of **5** was sealed in an ammonia-washed vial and heated to 180 °C for 23 h, generating a mixture of **5** and **6** in a ratio of 16:84. The entire product was dissolved in 80 mL of high-pressure LC grade hexane, flushed with argon for 30 min, and irradiated with a low-pressure mercury resonance immersion lamp for 2 h, generating a mixture of **5**, **6**, **11**, and **12** in proportions of 9:56:6:28. Isolation of products by preparative high-pressure LC, under the same conditions as previously used for **11**, gave 38 mg of **12**, 104 mg of **6**, and 74 mg of a mixture of all four compounds (86% recovery). Pure **12**, freed from solvent by Kugelrohr distillation, showed the following: ν_{max} 1728, 1662, 1168 cm^{-1}; λ_{max} (EtOH) 230 nm (ϵ 9300); ^1H NMR δ 0.70 (3 H, d, J = 6.5 Hz), 1.41 (2 H, d, $J \simeq 7$ Hz), 1.45 (3 H, s), 1.92 (1 H, d, J = 7 Hz), 2.32 (3 H, m), 3.67 (3 H, s), 5.83 (1 H, t, $J \simeq 1.5$ Hz). The high-resolution mass spectrum showed a parent ion at m/e 180.1110.

Pyrolysis of 12. Pyrolysis of 4.1 mg of **12** was carried out in a sealed tube at 180 °C for 24 h. High-pressure LC analysis of the product showed four peaks in proportions of 85:10:2:3, corresponding in retention volumes to **12**, **11**, **6**, and **5**, respectively. The ratio of **12** to **11** could not be determined accurately due to overlap of peaks.

Base Treatment of 11. A small piece of sodium was added to 150 μL of methanol in a dry vial capped with a septum. After all the sodium was dissolved, 9.1 mg of **11** was added via syringe and the vial heated to 60 °C for 25 h. High-pressure LC analysis of the reaction mixture showed only **11**, with no ester **5** present.

Acknowledgment. The author expresses his gratitude to A. DeStefano and R. Neal for obtaining the mass spectra and to J. Wendel for the NMR spectra.

Registry No. **2**, 4583-28-2; **3**, 4583-27-1; **4a**, 76282-50-3; **4b**, 76332-80-4; **5**, 76282-51-4; **6**, 76332-81-5; **7**, 76332-82-6; **8**, 76332-83-7; **9**, 76282-52-5; **10**, 76282-53-6; **11**, 76332-84-8; **12**, 76332-85-9; tiglic aldehyde, 497-03-0; allyl chloride, 106-95-6.