75-mL portions of brine and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by gravity chromatography of the residue on silica gel with 30% diethyl ether–hexane, afforded 0.52 g (83%) of acetal **25** as a pale yellow liquid: IR (neat) 1740 cm^{-1} (CO_2R); ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.20 (s, 9 H, $C(CH_3)_3$), 1.65 (m, 2 H, CH_2CH_3), 3.77–4.00 (m, 4 H, $(CH_2)_2$), 4.78–4.95 (m, 2 H, $HC(O(CH_2)_2O)$, $HC(C_2H_5)$). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.41; H, 9.30.

2-Hydroxybutanal Ethylene Acetal (26). A suspension of 0.07 g (1.8 mmol) of lithium aluminum hydride (95% dispersion in mineral oil) in 5 mL of anhydrous diethyl ether was stirred under nitrogen at 0 °C. A solution of 0.20 g (0.9 mmol) of acetal **24** in 2 mL of anhydrous diethyl ether was added slowly. The mixture was stirred for 30 min, the cooling bath was removed, and stirring was continued for an additional 1 h. After sequential treatment with 0.5 mL water, 0.5 mL of 15% aqueous sodium hydroxide, and 1 mL of water, the suspension was filtered, and the solid washed well with diethyl ether. The ether portions were combined and dried ($MgSO_4$). Evaporation of solvent at reduced pressure on a rotary evaporator and Kugelrohr distillation of the residue afforded 0.07 g (58%) of alcohol **25** as a colorless liquid: IR (neat) 3500 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7 Hz, CH_2CH_3), 1.33–1.80 (m, 2 H, CH_2CH_3), 2.00 (d, J = 4.5 Hz, 1 H, OH), 3.40–3.73 (m, 1 H, HCOH), 3.77–4.07 (m, 4 H, $(CH_2)_2$), 4.68 (d, 1 H, J = 4.5 Hz, $HC(O(CH_2)_2O)$. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.82; H, 8.98.

Acknowledgment. This research was supported in part by a Grant (No. CA20436) from the National Cancer Institute.

Registry No. **1a**, 72552-75-1; **1b**, 85664-55-7; **1c**, 85664-56-8; **1d**, 85664-57-9; **1e**, 85664-58-0; **2**, 72552-74-0; **2**·HCl, 72552-79-5; **3**, 58751-78-3; **3**·HCl, 72552-80-8; **5**, 85664-59-1; **6**, 80387-13-9; **8** (R = H; R′ = CH_2CH_3; R″ = $C(CH_3)_3$), 85664-60-4; **8** (R = R′ = CH_3; R″ = $C(CH_3)_3$), 85664-61-5; **8** (R = R′ = $(CH_2)_5$; R″ = $C(CH_3)_3$), 85664-62-6; **9a**, 5921-90-4; **9b**, 85664-63-7; **10a**, 22094-24-2; **10b**, 85664-64-8; **11a**, 56037-77-5; **11b**, 85664-65-9; **11c**, 85664-66-0; **11d**, 85664-67-1; **11e**, 85664-68-2; **12a**, 55638-24-9; **12b**, 85664-69-3; **13a**, 60860-35-7; **13b**, 85664-70-6; **14a**, 52789-75-0; **14b**, 85664-71-7; **15a**, 17472-04-7; **15b**, 85664-72-8; **16**, 55830-07-4; **17**, 85664-73-9; **18**, 85664-74-0; **19**, 82937-45-9; **20**, 85664-75-1; **21**, 85664-76-2; **22**, 2522-81-8; **23**, 65055-38-1; **24**, 15753-47-6; **25**, 85664-77-3; **26**, 85664-78-4; CH_3COCl, 75-36-5; CH_3CH_2COCl, 79-03-8; $(CH_3)_2CHCOCl$, 79-30-1; $(CH_3)_3CCOCl$, 3282-30-2; PhCOCl, 98-88-4; *N-tert*-butylhydroxylamine, 16649-50-6; *tert*-butylamine, 75-64-9; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2; cyclohexanecarboxaldehyde, 2043-61-0; 3-cyclohexene-carboxaldehyde, 100-50-5; 2-phenylpropionaldehyde, 93-53-8.

Electrophile-Initiated Ring-Opening Reactions of 2-Methylene-6,6-dimethylbicyclo[3.1.0]hexanes. New Methodology for the Synthesis of Highly Functionalized 1,2,3-Trisubstituted Cyclopentenes

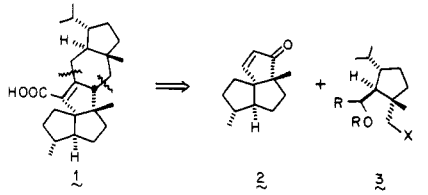
Richard A. Roberts,[1] Volker Schüll, and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received September 13, 1982

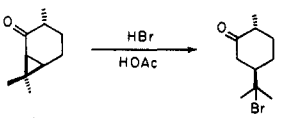
A pair of 1-substituted 2-methylene-6,6-dimethylbicyclo[3.1.0]hexanes has been determined to undergo smooth cyclopropane ring opening with formation of 1,2,3-trisubstituted cyclopentenes in the presence of electrophilic or free radical agents. High optical purity can be incorporated into these products, starting with the readily available *l*-menthyl 6,6-dimethyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate, the two diastereomers of which are chromatographically separable. Through suitable chemical correlation, the absolute configurations of the various enantiomers have been made known. Finally, a scheme for transforming the cyclopentenes to 1,1,2,3-tetrasubstituted cyclopentanes as a necessary prelude to a synthesis of retigeranic acid is detailed.

Retigeranic acid (**1**), a pentacyclic sesterterpene having eight chiral centers and five quaternary carbon atoms,[2] is a topologically most unique polyquinane system.[3] At the outset of our consideration of **1** as a synthetic target, we set as our goal the development of a strategy that would yield optically active material by penultimate installation of the two indicated C–C σ bonds. Consequently, the success of this protocol rests rather specifically upon our ability to construct segments **2** and **3** in proper enantiomeric form. This requirement has proven to be more vexacious than originally expected in the case of the highly functionalized 1,1,2,3-tetrasubstituted cyclopentane **3**, a little-studied class of compounds whose members are virtually unknown in optically active condition. Herein, we describe a general and efficient method for the synthesis of heavily substituted precursor cyclopentenes which can be used for the preparation of racemates or either enantiomer with full knowledge of the relevant absolute configuration.



1 **2** **3**

Whereas cyclopropylcarbinyl cations have garnered considerable attention from physical organic chemists,[4] these strained and reactive intermediates have been much less used in directed synthesis. From the response of caranone **4** and related ketones to hydrogen bromide in



4 **5**

(1) Continental Oil Company Fellow, 1982.
(2) (a) Kaneda, M.; Takabashi, R.; Itaka, Y.; Shibata, S. *Tetrahedron Lett.* **1972**, 4609. (b) Kaneda, M.; Iitaka, Y.; Shibata, S. *Acta Crystallogr., Sect. B* **1974**, *B30*, 358.
(3) Paquette, L. A. *Fortschr. Chem Forsch.* **1979**, *79*, 43.
(4) (a) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. (b) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, a. J., III. In "Carbonium Ions"; Vol. III, Olah, G. A. and Schleyer, P. von R., ed.; Wiley-Interscience: New York, 1972; Chapter 26. (c) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577.

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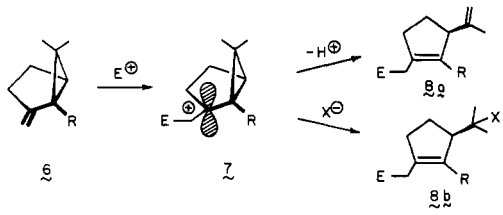
acetic acid,[5] it has become clear that steric and electronic factors combine to favor rupture of the proximal *external* bond, the *gem*-dimethyl functionality providing a low-energy carbonium ion pathway to **5**. Since the added rigidity of a bicyclo[3.1.0]hexane nucleus serves to align yet more favorably the π orbitals of the exocyclic double bond and bent σ orbitals of the three-membered ring, we considered that electrophilic addition to a vinylcyclopropane such as **6** might well trigger conversion via **7** to diene **8a** or 1,5-adduct **8b**.



Electrophilic Processes

For the reasons just described, the known keto ester **11** was prepared by suitable modification of the Trost–Vladuchick procedure.[6] Condensation of the dianion of methyl acetoacetate with 1 equiv of prenyl bromide (Scheme I) conveniently afforded **9** in 82% yield. Exposure of **9** to *p*-toluenesulfonyl azide and triethylamine in acetonitrile led quantitatively to diazo keto ester **10**, whose cyclization to **11** in the presence of copper bronze efficiently (89%) furnished **11**.

Although reaction of **11** with methylenetriphenylphosphorane in dimethyl sulfoxide solution[7] gave rise only to trace quantities of **12**, olefination proceeded very satisfactorily (80–85%) under those equilibrating conditions which make use of methyltriphenylphosphonium bromide and potassium *tert*-butoxide in refluxing diisopropyl ether solution.[8] Following arrival at **12**, the *tert*-butyldimethylsilyl ether **13** was synthesized conventionally.

The preparation of **12** has given evidence of being rather restricted in breadth. Thus, treatment of **11** with dimethylsulfonium methylide[9] afforded a large array of uncharacterized products. When the less reactive dimethylsulfoxonium methylide was screened, no appreciable reaction was seen at room temperature during 1 h. Heating

Scheme I

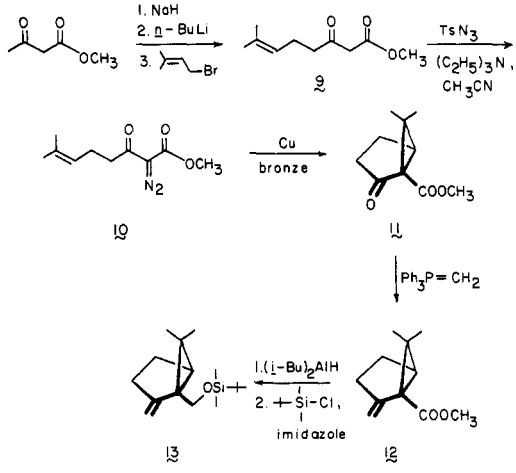
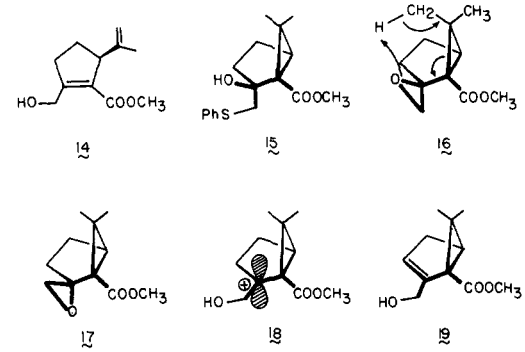


Chart I



to 55 °C for 4 h successfully induced reaction, but a product subsequently identified as hydroxy ester **14** (Chart I) was isolated in low yield. This rearrangement does not appear to materialize during the 1,2-addition step, since (phenylthio)methyllithium reacts chemo- and stereospecifically with **11** to provide **15**. However, subsequent exposure of **15** to methyl iodide and sodium in warm (70 °C) dimethylformamide[10] likewise afforded **14** as product (51%). These observations suggested that formation of syn epoxide **16** may be followed rapidly by an intramolecular six-electron reorganization (see arrows) involving proton transfer from the *endo*-methyl group to oxygen with concurrent cyclopropane and oxirane ring cleavage. Alternatively, the heightened reactivity of **16** may allow for facile intermolecular-catalyzed isomerization.

To shed further light on this question, we were next led to examine the peracid epoxidation of **12**. With *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at room temperature, no observable reaction was seen during several hours. In refluxing chloroform, reaction proceeded to completion overnight to deliver **14** once again in low yield. However, the product was contaminated with an inseparable compound which has been formulated as the isomeric hydroxy ester **19**, since its ^{1}H NMR spectrum gives evidence of a vinyl proton multiplet of area 1 at δ 5.32 and a pair of singlets characteristic of the *gem*-dimethylcyclopropane segment at δ 1.25 and 0.98. The byproduct may arise directly from ene reaction of **12** with the peracid. More likely, acid-catalyzed ring opening of the highly strained tricyclic epoxide **17** to give tertiary cyclopropylcarbinyl cation **18** may be followed by partitioning to **14** (major) and **19** (minor). Remarkably, however, reaction of **12** with 1 equiv of MCPBA in refluxing dichloromethane for 15 h leads to **14** with virtual elimination of the formation of **19**. However, an unimpressive yield (35%) was realized, probably because of overoxidation of the product.

The structural assignment to **14** is based chiefly upon its spectral properties. The IR spectrum clearly reveals the presence of hydroxyl (3450 cm^{-1}) and conjugated ester functionality (1700 and 1640 cm^{-1}). At 200 MHz, the exocyclic methylene protons appear together at δ 4.66, unmistakingly coupled to the neighboring methyl group (δ 1.17). Furthermore, the chemical shift of the pair of allylic carbinol protons (δ 4.48) is fully consistent with its local environment. The ^{13}C NMR data for **14** proved to be particularly revealing (see A).

It was clear from these early observations that **12** is highly susceptible to conversion to cyclic olefins of general formula **8a** under electrophilic conditions. This latent reactivity became more evident upon reaction of **12** with

(5) Fringuelli, F.; Taticchi, J. *J. Chem. Soc. C* **1971**, 297.
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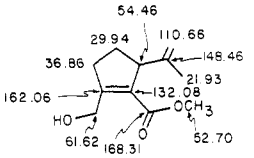
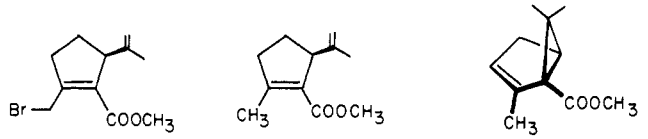
(8) (a) Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron Lett.* **1975**, 4053. (b) Schostarez, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 722.
(9) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(10) (a) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097. (b) Corey, E. J.; Jautelat, M. *Tetrahedron Lett.* **1968**, 5787.



A

ethereal *N*-bromosuccinimide. Clean consumption of the halogenating agent was complete during 1.5 h, and bromo ester **20** was isolated in 95% yield. To ensue was a comparative study of the response of **12** and **13** to various electrophilic agents. The results, which are summarized in Table I, indicate that access to polyfunctionalized cyclopentenes can be expediently realized in this manner.



20 **21** **22**

Two observations are worthy of specific comment. First, exposure of **12** to *p*-toluenesulfonic acid in chloroform at room temperature initially gives rise to a mixture of **21** (major) and **22** (minor); at longer reaction times, **21** becomes the exclusive product. The course of this isomerization can be conveniently monitored by ^{1}H NMR. After 16 h, the vinyl proton multiplet (δ 5.11) and methyl signals (δ 1.19 and 0.90) due to **22** have usually faded into the base line. Accordingly, close correlation exists with the course of the peroxidation reaction. Second, under the conditions of Friedel–Crafts acetylation, **12** gave rise to the 1,5-addition product **24**. During preparative VPC purification, dehydrochlorination was seen to occur spontaneously and furnish the propenyl derivative.

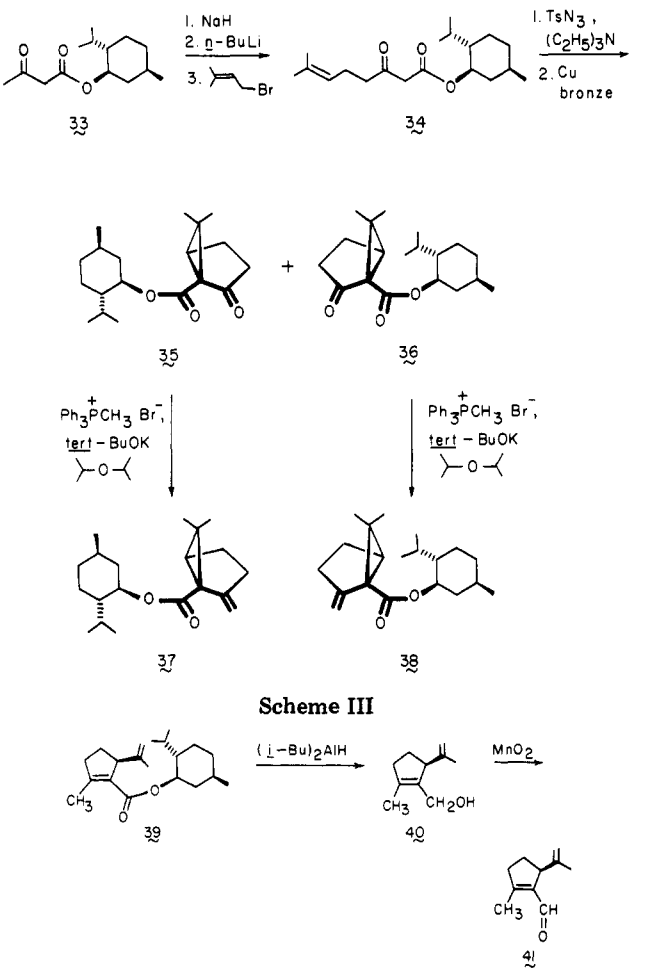
Free Radical Additions

Since cyclopropylcarbinyl free radicals are also prone to three-membered ring cleavage,[11] the present investigation was expanded to include several examples of such processes. As can be seen from the data compiled in Table II, **12** and **13** react readily with carbon tetrachloride and thiophenol to provide trisubstituted cyclopentenes in respectable yields after chromatography. The formation of **30** and **32** demonstrates the feasibility of generating an isopropyl group directly (see **3**). The ease of these rearrangements makes possible the utilization of reaction conditions sufficiently mild that the residual double bond in both **31** and **32** is not prone to further attack by the free radical agents.

Incorporation of Optical Activity

The presence of an ester function in **12** suggested that acquisition of a suitable bicyclo[3.1.0]hexanone of this type in high optical purity might be best achieved through formation and chromatographic separation of a diastereomeric mixture of esters derived from a readily chiral alcohol. Following removal of the chiral auxiliary, incorporation of the desired enantiomeric enrichment would have materialized, although the task of establishing absolute stereochemistry would remain. Accordingly, *l*-menthol was acylated with diketene to give **33**,[12] the dianion of which[13,14] was alkylated with prenyl bromide as

Scheme II



33 **34** **35** **36** **37** **38**

Scheme III

39 **40** **41**

before to give **34** (Scheme II). In accordance with the behavior of **9**, **34** underwent efficient diazo transfer and carbenoid cyclization. The resulting 1:1 mixture of keto esters **35** and **36** could be conveniently separated by preparative HPLC on a Waters Prep 500 instrument. Whereas the more rapidly eluted diastereomer **35** proved to be an oily substance, **36** was crystalline (the correct absolute configurations are given in the formulas; see below). Independent Wittig olefination of **35** and **36** as before furnished **37** and **38** without complication.

Elucidation of the absolute configuration of **38** began by acid-catalyzed isomerization to **39** (Scheme III). Rather unexpectedly, the rate of rearrangement of **38** proved qualitatively to be much faster than that of **12**. Diisobutylaluminum hydride reduction of **39** afforded allylic alcohol **40** which was readily separated from the isomeric menthol byproduct. At this point, chirality transfer to C-3 of the cyclopentenyl ring was completed. Although **40** is known in optically active form,[15] the authors failed to report relevant optical rotation data. Consequently, it was necessary to transform **40** by manganese dioxide oxidation to the more completely characterized aldehyde **41**.[16] The $[\alpha]_D$ of our sample (+56.1°) compared closely to the literature value (+61.5°) for (*S*)-**41**, thereby establishing the absolute stereostructures of **35**–**41**.

Adaptation to the Retigeranic Acid Synthesis

The availability of a wide range of 1,2,3-trisubstituted cyclopentene derivatives set the stage for an investigation

(11) Wilt, J. W. In "Free radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 8, pp 399–406.
(12) Mauz, O. *Justus Liebigs Ann. Chem.* **1974**, 345.
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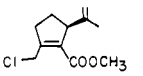
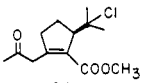
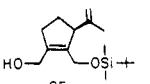
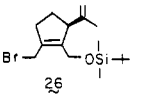
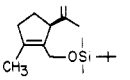
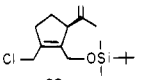
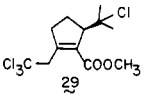
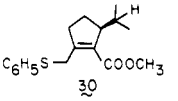
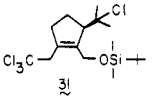
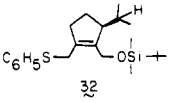
(14) Taber, D. F.; Saleh, S. A.; Korsmeyer, R. W. *J. Org. Chem.* **1980**, *45*, 4699.
(15) Wolinsky, J.; Nelson, D. *Tetrahedron* **1969**, *25*, 3767.
(16) Wolinsky, J.; Slabaugh, M. R.; Gibson, T. *J. Org. Chem.* **1964**, *29*, 3740.

Table I. Electrophilic Ring-Opening Reactions of 12 and 13

compd	electrophile	conditions[d]	product	yield, %
12	MCPBA	CH_2Cl_2/Δ/18 h	**14**	35[a]
	NBS	Et_2O/rt/90 min	**20**	95
	TsOH	$CHCl_3$/rt/17 h	**21**	80
	t-BuOCl	HCOOMe/rt/1 h/dark	 **23**	90
	$CH_3COCl/AlCl_3$	CH_2Cl_2/−30 °C/1 h	 **24**	34[b]
13	MCPBA	CH_2Cl_2/Δ/18 h	 **25**	40[c]
	NBS	Et_2O/rt/4 h	 **26**	99
	TsOH	$CHCl_3$/rt/17 h	 **27**	78
	t-BuOCl	HCOOMe/rt/15 h/dark	 **28**	89

[a] This compound may be efficiently prepared in >95% yield by mild hydrolysis of the readily available **43** with 0.2% K_2CO_3 in 20% aqueous methanol at room temperature for 12 h. [b] Hydrogen chloride was eliminated upon VPC purification of this substance. [c] This compound is readily available from **26** by using a sequence analogous to *a* and to that in the text. [d] rt = room temperature.

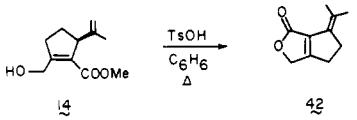
Table II. Ring-Opening Reactions of 12 and 13 under Free Radical Conditions

compd	reagent	conditions[b]	product	yield, %
12	CCl_4	AIBN/Δ/5 h	 **29**	68[a]
	C_6H_5SH	C_6H_6/rt/3 h	 **30**	58
13	CCl_4	AIBN/Δ/5 h	 **31**	64
	C_6H_5SH	C_6H_6/rt/14 h	 **32**	70

[a] Spontaneous elimination of HCl and formation of the isopropenyl derivative occurred upon gas chromatographic purification of this substance. [b] rt = room temperature.

of their conversion to chiral cyclopentanes of type **3** as a prelude to arriving at retigeranic acid (**1**). One stereocontrolled approach is detailed here.

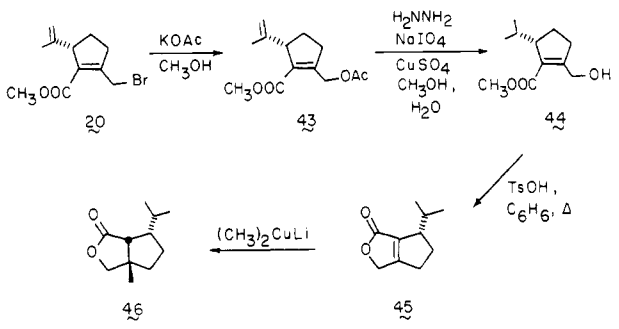
While hydroxy ester **14** gives indication of being a suitable precursor, two limitations seriously detract from its usefulness. Not only is **14** available in moderate yield at best but its lactonization under acidic conditions also leads to the conjugated isopropylidene system **42** which is devoid of chiral centers.



14 **42**

These complications were neatly circumvented by subjecting the readily available bromo ester **20** (95% from **12**) to the action of potassium acetate in methanol at room temperature. Under these conditions, S_N2 displacement of bromide ion proceeded efficiently to deliver **43** in quantitative yield (Scheme IV). Exposure of **43** to diimide, as generated by Cu(II)-catalyzed periodate oxidation of hydrazine *in the absence of oxygen*,[17] resulted in concurrent reduction of the isopropenyl side chain and hydrolysis of the acetoxy group.[18] Subsequent cyclization

(17) (a) Corey, E. J.; Mock, W. L.; Pasto, D. J. *Tetrahedron Lett.* **1961**, 347. (b) Hunig, S.; Muller, H. R.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271. (c) Miller, C. E. *J. Chem. Educ.* **1965**, *42*, 254.



provided lactone **45** in 70% overall yield from **12**.

Conjugate addition of lithium dimethylcuprate to **45** *in the absence of Lewis acid catalysts*[19,20] proceeded with complete stereocontrol to deliver **46**. Presently, it is assumed that the angular methyl group has entered exclusively from that surface of the π system which is opposite to that occupied by the isopropyl group, in line with precedent.[21] The somewhat reduced magnitude of the coupling constant for the angular α-carbonyl proton (J = 4.7 Hz)[22] is apparently a consequence of molecular deformations caused by the quasi-axial isopropyl group in its attempt to relieve nonbonded steric interactions. Embodied in **46** are all the structural elements necessary to arrive at **3**. It remains to epimerize the center α to the carbonyl group, a stereochemical inversion which might well be accomplished after lactone ring opening. Further details will appear elsewhere.

In summary, the preparation of cyclopentenes carrying functional groups at positions 1, 2, and 3 has been demonstrated to be feasible in few steps from readily available materials. The acquisition of these same intermediates in high optical purity and known absolute configuration can be achieved in parallel fashion. The high stereoselectivity realized in conjugate addition to **45** can now translate into a high degree of stereocontrol for formation of a tetrasubstituted cyclopentanes **3** for use in our planned construction of retigeranic acid.[23]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian T-60, Varian EM-390, Bruker WP-200, and Bruker WM-300 spectrometers. Carbon spectra were recorded with a Bruker WP-80 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Methyl 7-Methyl-3-oxo-6-octenoate (9). A slurry of sodium hydride (37.1 g of 50% dispersion, 0.77 mol) in anhydrous tetrahydrofuran (1750 mL) was prepared under nitrogen in a 5-L three-necked flask. Following the addition of methyl acetoacetate (81.2 g, 0.7 mol) the mixture was stirred at 0 °C for 15 min before *n*-butyllithium (477 mL of 1.54 M in hexane, 0.73 mol) was introduced. The resulting orange solution was stirred at 0 °C for 15 min, and prenyl bromide (109.2 g, 0.73 mol) in tetrahydrofuran (140 mL) was added dropwise. The reaction mixture was maintained at 5–10 °C during this period and for an additional 45 min prior to quenching with 10% hydrochloric acid until acidic. Ether was added, and washing with water was continued until neutral to litmus. Following drying and solvent evaporation, the residue was distilled to give 105.8 g (82%) of **9**: bp 85–90 °C (0.6 torr) [lit[6,24] bp 85–90 °C (0.6 torr); bp 129–131 °C (12 torr)]; homogeneous by TLC; ^{1}H NMR ($CDCl_3$) δ 5.18–4.90 (m, 1 H), 3.65 (s, 3 H), 3.30 (s, 2 H), 2.65–2.00 (m, 4 H), 1.64 (br s, 6 H).

Methyl 7-Methyl-3-oxo-2-diazo-6-octenoate (10). A solution of **9** (80.3 g, 0.44 mol) in anhydrous triethylamine (61 mL, 0.44 mol) and acetonitrile (570 mL) was treated with tosyl azide (85.9 g, 0.44 mol) in the same solvent (150 mL). The reaction mixture was stirred at room temperature for 10 h and added to a separatory funnel containing ether (2 L) and saturated ammonium chloride solution (2 L). The phases were separated, the aqueous layer was back-extracted with ether, and the combined organic solutions were washed with cold (0–5 °C) 4 N potassium hydroxide, saturated sodium bicarbonate solution, and brine prior to drying. Solvent evaporation furnished 91 g (98%) of **10** which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 5.20–4.95 (m, 1 H), 3.80 (s, 3 H), 2.85 (t, J = 6 Hz, 2 H), 2.50–2.10 (m, 2 H), 1.65 (br s, 6 H).

1-Carbomethoxy-6,6-dimethyl-2-oxobicyclo[3.1.0]hexane (11). A stirred slurry of **10** (91 g), copper bronze powder (39 g), and toluene (1500 mL) was heated at reflux for 3 h, cooled, filtered through Celite, and diluted with ether. This solution was washed with saturated ammonium chloride solution and brine, dried, and concentrated. Distillation of the residue afforded 70.8 g (89.8%) of **11** as colorless oil: bp 75–80 °C (0.5 torr) [lit[6] bp 74–78 °C (0.5 torr)]; ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 2.5–1.5 (series of m, 5 H), 1.12 (s, 3 H), 1.10 (s, 3 H).

1-Carbomethoxy-6,6-dimethyl-2-methylenebicyclo[3.1.0]hexane (12). An ice-cooled mixture of triphenylphosphonium bromide (4.32 g, 11.7 mmol) and potassium *tert*-butoxide (1.36 g, 12.3 mmol) in diisopropyl ether (60 mL) was stirred for 30 min before the addition of **11** (2.0 g, 11 mmol) in diisopropyl ether (5 mL). This mixture was heated at reflux for 15 h, cooled, treated with saturated aqueous oxalic acid solution, and extracted with ether. The organic solution was washed with brine, dried, and evaporated to leave an oil which was passed through a short silica gel column (elution with 50% ethyl acetate in petroleum ether) before purification on a Waters Prep 500 HPLC (silica gel; 2% ethyl acetate in petroleum ether). There was isolated 1.7 g (85%) of **12** as a homogeneous, colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.35 (m, 1 H), 5.00 (m, 1 H), 3.70 (s, 3 H), 2.5–1.5 (series of m, 5 H), 1.12 (s, 3 H), 0.98 (s, 3 H); mass spectrum, calcd (M^+) m/e 180.1150, obsd 180.1156. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.03; H, 8.96.

1-[(*tert*-Butyldimethylsiloxy)methyl]-6,6-dimethyl-2-methylenebicyclo[3.1.0]hexane (13). A cold (−78 °C), nitrogen-blanketed solution of **12** (2.0 g, 11.1 mmol) in ether (30 mL) was treated slowly with diisobutylaluminum hydride (30 mL of 1 M in hexane, 30 mmol). The reaction mixture was stirred at −78 °C for 2 h, quenched with saturated ammonium chloride solution, and allowed to warm to room temperature. Following an additional 2 h of stirring, the organic layer was decanted, and the aqueous layer was extracted with ether. The combined ethereal solutions were washed with water and brine prior to drying and solvent evaporation. Purification of the residue by HPLC on silica gel (elution with 12% ethyl acetate in petroleum ether) gave the pure alcohol (1.33 g, 80%); IR ($CDCl_3$) 3470, 1640, 990, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.1–5.0 (m, 1 H), 4.07 and 3.73 (AB q, J = 12 Hz, 2 H), 2.8–1.3 (series of m, 6 H), 1.18 (s, 3 H), 0.95 (s, 3 H); mass spectrum, calcd (M^+) m/e 152.1201, obsd 152.1205.

To a solution of the alcohol (850 mg, 5.59 mmol) and imidazole (400 mg) in dry dimethylformamide (30 mL) was added *tert*-butyldimethylsilyl chloride (880 mg, 5.87 mmol). This mixture was stirred under nitrogen at room temperature for 24 h, cooled

(18) Hoffman, J. M.; Schlessinger, R. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1245.

(19) Yamamoto, Y.; Yamamoto, S.; Yatagi, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem* **1982**, *47*, 119. In our hands, use of $(CH_3)_2CuLi$-BF_3·$(C_2H_5)_2O$ or CH_3CuBF_3 led to formation of dark resinous materials in this instance.

(20) Pernet, A. G.; Nakamoto, H.; Ishizuka, N.; Aburatani, M.; Nakahashi, K.; Sakamoto, K.; Takeuchi, T. *Tetrahedron Lett.* **1979**, 3933.

(21) Pesaro, M.; Bachmann, J. *J. Chem. Soc., Chem. Commun.* **1978**, 203.

(22) Compare: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733.

(23) The synthesis of triquinane portions of retigeranic acid (see **2**) has also been successfully pursued: (a) Hudlicky, T.; Short, R. P. *J. Org. Chem.* **1982**, *47*, 1522. (b) Roberts, R. A., unpublished results.

(24) Leyendecker, F. *Tetrahedron* **1976**, *32*, 349.

in ice, diluted with water, and transferred to a separatory funnel. The product was extracted into ether, and the ethereal solution was washed with water and brine before being dried. Removal of solvent and MPLC purification (silica gel; 1% ethyl acetate in petroleum ether) afforded 1.11 g (75%) of **13** as a clear, colorless oil: IR (neat) 3040, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.01 (m, 1 H), 4.74 (m, 1 H), 3.88 and 3.70 (AB q, J = 9 Hz, 2 H), 2.59–1.19 (series of m, 5 H), 1.09 (s, 3 H), 0.89 (s, 3 H), 0.79 (s, 9 H), –0.11 (s, 6 H). Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 72.05; H, 11.27.

Reaction of 11 with Dimethylsulfoxonium Methylide. A 50-mL flask charged with sodium hydride (150 mg of 50% dispersion, 3.1 mmol) and blanketed under nitrogen was flushed three times with pentane to remove the oil. Trimethyloxosulfonium iodide (660 mg, 3 mmol) was introduced followed by dry dimethyl sulfoxide (10 mL). Following vigorous evolution of hydrogen and formation of a milky white mixture, keto ester **11** (0.50 g, 2.75 mmol) dissolved in dimethyl sulfoxide (1 mL) was added. The reaction mixture was stirred at room temperature for 15 min and at 55 °C for 4 h. After the mixture was cooled and water (10 mL) added, the product was extracted into ether, and the combined ethereal layers were washed with water and brine. After the mixture was dried and the solvent removed, the resulting oil was purified by MPLC (silica gel; 22% ethyl acetate in petroleum ether). In addition to recovered **11** (90 mg, 18%) and an unidentified product (100 mg), there was isolated 100 mg (18.9%) of **14**, identical in all aspects with the material produced in a following experiment.

1-Carbomethoxy-6,6-dimethyl-2-[(phenylthio)methyl]bicyclo[3.1.0]hexan-2-ol (15). A cold (0 °C), magnetically stirred solution of Dabco (300 mg, 2.78 mmol) and thioanisole (0.32 mL, 2.73 mmol) in anhydrous tetrahydrofuran (5 mL) was treated under nitrogen with n-butyllithium in hexane (1.76 mL of 1.55 M, 2.73 mmol). The mixture was stirred at room temperature for 45 min and cooled to –78 °C, whereupon **11** (500 mg, 2.75 mmol) in tetrahydrofuran (2 mL) was rapidly added. After 5 min, saturated ammonium chloride solution was added, the mixture was allowed to warm to room temperature, and the product was extracted into ether. The combined ether layers were washed with saturated ammonium chloride solution and brine, dried, and evaporated to give after MPLC on silica gel 580 mg (69%) of **15** as a colorless oil: IR ($CDCl_3$) 3500, 1720, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65–7.00 (m, 5 H), 3.65 (s, 3 H), 3.25 (s, 2 H), 2.80 (s, 1 H), 2.4–1.6 (series of m, 5 H), 1.42 (s, 3 H), 1.15 (s, 3 H); mass spectrum, calcd (M^+) m/e 306.1290, obsd 306.1297.

Attempted Methylation–Cyclization of 15. To a solution of **15** (580 mg, 1.9 mmol) in dimethylformamide (10 mL) containing sodium iodide (1.5 g) was added methyl iodide (5 mL). The mixture was heated at reflux under nitrogen for 18 h, cooled, diluted with ether, washed with water and brine, and dried. Evaporation of the solvent and purification by MPLC (silica gel; 50% ethyl acetate in petroleum ether) afforded 190 mg (51%) of **14** whose spectra were superimposable upon those of an authentic sample (see below).

Peracid Treatment of 12. (A) Chloroform Solution. A solution of **12** (500 mg, 2.78 mmol) in chloroform (5 mL) was treated with a solution of m-chloroperbenzoic acid (600 mg, 3.5 mmol) in the same solvent (30 mL). The reaction mixture was heated at reflux for 15 h, cooled, washed with saturated sodium bicarbonate solution and water, dried, and concentrated. MPLC purification of the residue (silica gel; 50% ethyl acetate in petroleum ether) gave **14** (200 mg, 37%) which was contaminated with an isomer believed to be **19** on the basis of ^1H NMR signals (in $CDCl_3$) at δ 5.32 (m), 1.25 (s), and 0.99 (s).

(B) Dichloromethane Solution. A solution of **12** (200 mg, 1.11 mmol) and buffer-washed m-chloroperbenzoic acid (220 mg, 1.28 mmol) in dichloromethane (15 mL) was heated at reflux for 15 h and processed as described above to provide 77 mg (35%) of **14** as a colorless oil which was virtually devoid of the impurity: ($CDCl_3$) 3610, 3450, 3075, 1700, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69–4.63 (m, 2 H), 4.48 (m, 2 H), 3.71 (s, 3 H), 3.81–3.59 (m, 2 H), 2.71–2.54 (m, 2 H), 2.24–2.04 (m, 1 H), 1.78–1.63 (m, 1 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) 168.3 (s), 162.1 (s), 148.5 (s), 132.1 (s), 110.2 (t), 61.6 (t), 54.5 (d), 52.7 (q), 36.9 (t), 29.9 (t), 21.9 ppm (q); mass spectrum, calcd (M^+) m/e 196.1099, obsd 196.1107.

1-(Bromomethyl)-2-carbomethoxy-3-isopropenylcyclopentene (20). To a suspension of N-bromosuccinimide (5.0 g, 28.3 mmol) in ether (750 mL) was added **12** (5.0 g, 27.8 mmol) in ether (20 mL). The mixture was stirred at room temperature for 90 min during which time the solution became homogeneous. Washing with water and brine was followed by drying and solvent evaporation. Purification of the residue by HPLC (silica gel; elution with 5% ethyl acetate in petroleum ether) gave 6.84 g (95%) of **20** as a colorless oil: IR (neat) 3045, 1720, 1652, 1642, 1440, 1270, 1250, 1110, 1030, 890, 790, 730, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.71–4.63 (m, 2 H), 4.51 (s, 2 H), 3.73 (s, 3 H), 3.64–3.60 (m, 1 H), 2.78–2.74 (m, 1 H), 2.66–2.61 (m, 1 H), 2.20–2.12 (m, 1 H), 1.78–1.68 (m, 1 H), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) 165.4 (s), 152.9 (s), 147.1 (s), 133.7 (s), 109.9 (t), 53.4 (d), 51.4 (q), 35.5 (t), 28.4 (t), 27.0 (t), 20.8 ppm (q); mass spectrum, calcd (M^+ – OCH_3) m/e 277.0072, obsd 277.0079. Anal. Calcd for $C_{11}H_{15}BrO_2$: C, 50.98; H, 5.83. Found: C, 51.18; H, 5.90.

1-(Hydroxymethyl)-2-[(*tert*-butyldimethylsiloxy)methyl]-3-isopropenylcyclopentene (25). Treatment of **13** (200 mg, 0.75 mmol) with buffer-washed m-chloroperbenzoic acid (130 mg, 0.76 mmol) in dichloromethane (20 mL) at reflux for 18 h as before and MPLC purification (silica gel; 10% ethyl acetate in petroleum ether) gave 85 mg (40%) of **25** as a clear, homogeneous oil: IR (neat) 3360, 3060, 1640, 1290 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.67 (s, 2 H), 4.20–4.02 (m, 4 H), 3.35–3.25 (m, 2 H), 2.50–2.30 (m, 2 H), 2.10–1.98 (m, 1 H), 1.68–1.63 (m, 1 H), 1.59 (s, 3 H), 0.87 (s, 9 H), 0.05 (s, 6 H).

1-(Bromomethyl)-2-[(*tert*-butyldimethylsiloxy)methyl]-3-isopropenylcyclopentene (26). Reaction of N-bromosuccinimide (335 mg, 1.89 mmol) with **13** (500 mg, 1.88 mmol) in ether (50 mL) as before (room temperature, 4 h) gave pure **26** directly (640 mg, 99%) as a homogeneous colorless oil: IR (CCl_4) 3060, 1640, 1300, 1110 cm^{-1}; ^1H NMR (C_6D_6) δ 4.75–4.70 (m, 2 H), 4.15 and 4.01 (AB q, J = 13 Hz, 2 H), 4.07 and 3.91 (AB q, J = 10 Hz, 2 H), 3.98–3.89 (m, 1 H), 2.55–2.45 (m, 1 H), 2.29–2.19 (m, 1 H), 1.92–1.79 (m, 1 H), 1.62–1.51 (m, 1 H), 1.55 (s, 3 H), 0.94 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) 147.1, 142.4, 135.9, 111.1, 59.0, 55.0, 34.6, 28.7, 27.9, 25.9, 19.4, 18.3, –5.45 ppm; mass spectrum, calcd (M^+ – C_4H_9) m/e 287.0467, obsd 287.0474.

1-Methyl-2-carbomethoxy-3-isopropenylcyclopentene (21). A solution of **12** (300 mg, 1.66 mmol) in chloroform (5 mL) containing a crystal of p-toluenesulfonic acid was stirred at room temperature for 17 h during which time it became dark brown. Following washing with saturated sodium bicarbonate solution (2×) and water (2×), the reaction mixture was dried and evaporated to leave an oil which was purified by distillation at 70–80 °C (0.9 torr) in a Kugelrohr apparatus. There was obtained 240 mg (80%) of **21** as a colorless oil: IR (neat) 3070, 1720, 1645, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57 (br s, 2 H), 3.65 (s, 3 H), 3.55 (m, 1 H), 2.6–1.8 (series of m, 4 H), 2.15 (br s, 3 H), 1.7 (br s, 3 H); ^{13}C NMR ($CDCl_3$) 166.6 (s), 156.5 (s) 148.1 (s) 129.6 (s), 109.1 (t), 53.4 (d), 50.8 (q), 39.3 (t), 28.6 (t), 210.6 (q), 16.3 ppm (q); mass spectrum, calcd (M^+) m/e 180.1150, obsd 180.1155.

1-Methyl-2-[(*tert*-butyldimethylsiloxy)methyl]-3-isopropenylcyclopentene (27). A solution of **13** (300 mg, 1.06 mmol) in chloroform (5 mL) was treated with a crystal of p-toluenesulfonic acid and stirred at room temperature for 17 h. The usual workup gave 270 mg of a dark brown oil which was distilled in a Kugelrohr apparatus [80–100 °C (0.1 torr)] and purified further by MPLC (silica gel; 3% ethyl acetate in petroleum ether) to give 220 mg (78%) of **27**: IR (neat) 3060, 1630, 1050, 875, 825, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.62 (br s, 2 H), 4.17 and 3.89 (AB q, J = 12 Hz, 2 H), 3.4 (m, 1 H), 2.4–1.5 (series of m, 4 H), 1.70 (br s, 3 H), 1.59 (s, 3 H), 0.87 (s, 9 H), 0.01 (s, 6 H); ^{13}C NMR ($CDCl_3$) 148.3 (s), 136.7 (s), 135.8 (s), 110.2 (t), 58.3 (t), 54.3 (d), 38.0 (t), 28.2 (t), 26.1 (q), 19.4 (q), 18.5 (s), 14.1 (q), 5.3 ppm (q); mass spectrum, calcd (M^+ – CH_3) m/e 251.1831, obsd 251.1837. Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.18; H, 11.28. Found: C, 71.98, H, 11.28.

1-(Chloromethyl)-2-carbomethoxy-3-isopropenylcyclopentene (23). A solution of **12** (300 mg, 1.66 mmol) and *tert*-butyl hypochlorite (197 mg, 1.82 mmol) in methyl formate (10 mL, freshly distilled from P_2O_5) was stirred under nitrogen in the dark for 11 h. The solvent was evaporated, and the product was isolated by MPLC (silica gel; 2% ethyl acetate in petroleum ether). There was obtained 320 mg (90%) of **23** as a colorless, homogeneous oil:

IR (neat) 3060, 1715, 1640, 870, 770, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (m, 4 H), 3.72 (s, 3 H), 3.6 (m, 1 H), 2.9–1.8 (series of m, 4 H), 1.72 (t, J = 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 165.3 (s), 152.4 (s), 147.0 (s), 133.5 (s), 109.8 (t), 40.1 (t), 53.4 (d), 51.3 (q), 34.9 (t), 28.5 (t), 20.8 ppm (q); mass spectrum, calcd (M^+) m/e 214.0761, obsd 214.0766. Anal. Calcd for $C_{11}H_{15}ClO_2$: C, 61.65; H, 7.01. Found: C, 61.46; H, 7.02.

1-(Chloromethyl)-2-[(*tert*-butyldimethylsiloxy)methyl]-3-isopropenylcyclopentene (28). A solution of **13** (370 mg, 1.41 mmol) and *tert*-butyl hypochlorite (170 mg, 1.57 mmol) in methyl formate (10 mL, freshly distilled from P_2O_5) was stirred in the dark and under nitrogen at room temperature for 15 h. A workup in the predescribed manner afforded 380 mg (89%) of **28** after silica gel chromatography (5% ethyl acetate in petroleum ether): IR (neat) 3070, 1635, 1245, 870, 830, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (br s, 2 H), 4.28 (br s, 2 H), 4.08 and 3.91 (AB q, J = 13.5 Hz, 2 H), 3.34 (m, 1 H), 2.6–1.3 (series of m, 4 H), 1.48 (s, 3 H), 0.84 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) 147.0 (s), 141.9 (s), 135.8 (s), 111.0 (t), 58.8 (t), 54.9 (d), 40.5 (t), 34.1 (t), 27.4 (t), 25.9 (q), 25.7 (q), 19.3 (s), 5.5 ppm (q); mass spectrum, (M^+ – HCl) m/e 264.

Friedel–Crafts Acetylation of 12. To a cold (–30 °C), stirred slurry of anhydrous aluminum chloride (306 mg, 2.3 mmol) in dry dichloromethane (10 mL) was added **12** (380 mg, 2.1 mmol) in the same solvent (5 mL) during 15 min. The reaction mixture was stirred for 1 h at –15 to –25 °C, poured onto ice, and diluted with dichloromethane. Concentrated hydrochloric acid was added dropwise until the salts dissolved. The layers were separated, and the aqueous phase was extracted twice with dichloromethane. The combined organic layers were washed with saturated sodium bicarbonate solution and brine, dried, and evaporated. Purification of the product by MPLC (silica gel; 15% ethyl acetate in petroleum ether) afforded 185 mg (34%) of **24**: IR (neat) 1710, 1640, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 4.0–3.28 (m, 3 H), 2.8–1.8 (series of m, 4 H), 1.52 (s, 3 H), 1.50 (s, 3 H); ^{13}C NMR ($CDCl_3$) 204.5 (s), 166.7 (s), 152.7 (s), 131.8 (s), 75.4 (s), 58.2 (d), 51.1 (q, 45.3 (t), 38.1 (t), 31.5 (q), 29.8 (q), 28.4 (q), 27.0 ppm (t); mass spectrum, calcd (M^+) m/e 258.1023, obsd 258.1030.

Attempted VPC purification of **24** (10% SE-30, 150 °C) led to spontaneous loss of hydrogen chloride and formation of the isopropenyl derivative: IR (neat) 3070, 1720, 1645, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.66 (br s, 2 H), 3.76 (br s, 2 H), 3.68 (s, 3 H), 3.6 (m, 1 H), 2.6–1.8 (series of m, 4 H), 2.24 (s, 3 H), 1.72 (m, 3 H); ^{13}C NMR ($CDCl_3$) 204.6 (s), 165.7 (s), 152.5 (s), 147.6 (s), 132.7 (s), 109.5 (t), 52.9 (d), 51.0 (q), 45.2 (t), 37.8 (t), 30.0 (q), 28.8 (t), 20.7 ppm (q); mass spectrum, calcd (M^+) m/e 222.1256, obsd 222.1263.

1-(2,2,2-Trichloroethyl)-2-carbomethoxy-3-(1-chloro-1-methylethyl)cyclopentene (29). A solution of **12** (300 mg, 1.66 mmol) in carbon tetrachloride (20 mL) containing azobis(isobutyronitrile) (AIBN, 250 mg) was heated at reflux for 5 h. After cooling, the solvent was removed, and the product was purified by MPLC (silica gel, 3% ethyl acetate in petroleum ether). There was isolated 373 mg (68%) of **29** as a colorless homogeneous oil: IR (neat) 1720, 1635, 800, 775–695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03 (m, 2 H), 3.8 (s, 3 H), 3.51 (m, 1 H), 3.0–1.78 (series of m, 4 H), 1.53 (s, 3 H), 1.52 (s, 3 H); ^{13}C NMR ($CDCl_3$) 168.8 (s), 148.7 (s), 136.0 (s), 97.1 (s), 74.4 (s), 58.4 (d), 53.8 (t), 51.4 (q), 37.1 (t), 31.1 (q), 30.0 (q), 27.1 ppm (t); mass spectrum, m/e 332 (M^+).

Attempted VPC purification of **29** led to spontaneous loss of hydrogen chloride and formation of the isopropenyl derivative: IR (neat) 3080, 1720, 1635, 1200–1040, 895, 800, 775–695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.66 (m, 2 H), 4.19 (d, J = 4 Hz, 2 H), 3.70 (s, 3 H), 3.55 (m, 1 H), 3.1–1.8 (series of m, 4 H), 1.73 (m, 3 H); ^{13}C NMR ($CDCl_3$) 161.1 (s), 149.0 (s), 147.0 (s), 137.4 (s), 110.1 (t), 97.4 (s), 53.7 (t), 53.1 (t), 51.3 (q), 37.1 (t), 29.2 (t), 20.9 ppm (q). Anal. Calcd for $C_{12}H_{15}Cl_3O_2$: C, 48.64; H, 5.07. Found: C, 48.48; H, 5.16.

1-(2,2,2-Trichloroethyl)-2-[(*tert*-butyldimethylsiloxy)methyl]-3-(1-chloro-1-methylethyl)cyclopentene (31). Reaction of **13** (300 mg, 1.13 mmol) with AIBN (250 mg) and carbon tetrachloride (5 mL) in the predescribed manner (reflux, 5 h) afforded 300 mg (64%) of **31** as a colorless, homogeneous oil after MPLC on silca gel (elution with 3% ethyl acetate in petroleum ether): IR (neat) 1050, 820, 790, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (m, 2 H), 3.90 and 3.48 (AB q, J = 15 Hz, 2 H), 3.21 (m, 1 H), 2.5–1.8 (series of m, 4 H), 1.63 (br s, 6 H), 0.93 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR ($CDCl_3$) 144.1 (s), 136.5 (s), 99.0 (s), 60.5 (t), 59.3 (d), 54.5 (t), 37.0 (t), 31.2 (q), 30.5 (q), 28.0 (t), 26.0 (q), 18.3 (s), 5.3 ppm (q); mass spectrum, calcd (M^+ – C_4H_9) m/e 361.0116, obsd 361.0124.

1-[(Phenylthio)methyl]-2-carbomethoxy-3-isopropylcyclopentene (30). A solution of **12** (299 mg, 1.27 mmol) and thiophenol (140 mg, 1.27 mmol) in benzene (10 mL, freshly distilled from potassium carbonate) was stirred at room temperature for 3 h, washed with potassium carbonate solution, and dried. Solvent evaporation and MPLC purification of the product (silica gel; 7% ethyl acetate in petroleum ether) afforded **30** as a colorless, homogeneous oil: 213 7g (58%); IR (neat) 1705, 1625, 1575 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48–7.1 (7, 5 H), 4.03 (m, 2 H), 3.6 (s, 3 H), 3.11–2.84 (m, 1 H), 2.7–2.4 (m, 2 H), 2.2–1.45 (series of m, 3 H), 0.83 (d, J = 10.5 Hz, 3 H), 0.58 (d, J = 10.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 166.2 (s), 152.9 (s), 135.7 (s), 133.4 (d), 130.8 (d), 128.7 (d), 126.6 (s), 52.3 (d), 50.9 (q), 36.3 (t), 33.3 (t), 29.7 (d), 22.5 (t), 21.1 (q), 16.6 ppm (q); mass spectrum, calcd (M^+) m/e 290.1340, obsd 290.1345. Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.34; H, 7.59. Found: C, 70.13; H, 7.61.

1-[(Phenylthio)methyl]-2-[(*tert*-butyldimethylsiloxy)methyl]-3-isopropylcyclopentene (32). Reaction of **13** (483 mg, 1.82 mmol) with thiophenol (200 mg, 1.82 mmol) in benzene (5 mL) in the predescribed manner (room temperature, 14 h) followed by an identical workup gave 450 mg (70%) of **32**: IR (neat) 1060, 825, 760, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.14 (m, 5 H), 4.11 and 3.82 (AB q, J = 12.6 Hz, 2 H), 3.86 and 3.54 (AB q, J = 13.9 Hz, 2 H), 2.81 (m, 1 H), 2.49–2.32 (m, 2 H), 2.0–1.5 (m, 3 H), 0.89 (s, 9 H), 0.87 (d, J = 10.5 Hz, 3 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) 141.2 (s), 136.8 (s), 134.0 (d), 130.5 (d), 128.7 (d), 126.3 (s), 58.3 (t), 52.6 (d), 35.1 (t), 33.1 (t), 28.6 (d), 25.9 (q), 21.7 (q), 21.4 (t), 18.3 (s), 15.9 (q), 5.3 ppm (q); mass spectrum, calcd (M^+ – C_4H_9) m/e 319.1552, obsd 319.1557.

***l*-Menthyl 7-Methyl-3-oxo-6-octenoate (34).** Treatment of **33**[12,14] (55.97 g, 0.23 mol) with sodium hydride (12.82 g of 50% dispersion, 0.267 mol), *n*-butyllithium (156 mL of 1.6 *M*, 0.256 mol), and prenyl bromide (42.98 g, 0.29 mol) as with the methyl ester furnished 73.77 g (90%) of **34** as a colorless, homogeneous oil: IR (CCl_4) 1740, 1720, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.10–5.05 (m, 1 H), 4.79–4.67 (dt, J = 11, 4 Hz, 1 H), 3.41 (s, 2 H), 2.60–2.52 (t, J = 7 Hz, 2 H), 2.33–2.22 (m, 2 H), 2.06–1.71 (m, 2 H), 1.68 (s, 3 H), 1.62 (s, 3 H), 1.58–0.95 (m, 7 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.89 (d, J = 6.5 Hz, 3 H), 0.77 (d, J = 7 Hz, 3 H); mass spectrum, calcd (M^+) m/e 308.2351, obsd 308.2359.

***l*-Menthyl 6,6-Dimethyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (35 and 36).** A solution of **34** (10.0 g, 32.5 mmol) and triethylamine (6.5 mL) in acetonitrile (40 mL) was treated with tosyl azide (8.20 g, 35.8 mmol) in acetonitrile (10 mL), stirred at room temperature for 24 h, diluted with ether (330 mL), and poured into a separatory funnel. The reaction mixture was washed with saturated ammonium chloride solution (3×) and cold (5 °C) 4 N potassium hydroxide (3×). Further washing with saturated sodium bicarbonate solution and brine, followed by drying and solvent evaporation, gave 10.7 g (99%) of the diazo derivative which was used directly.

A slurry of the diazo keto ester (10.7 g, 32.0 mmol) and copper bronze powder (4.3 g) in dry toluene (250 mL) was heated at reflux for 3 h, cooled, filtered through Celite, and diluted with ether. The filtrate was washed with saturated ammonium chloride solution and brine, dried, and evaporated. HPLC purification of the residual oil (silica gel; 10% ethyl acetate in petroleum ether) gave pure **35** (1.84 g, 19%) as the least polar component, pure **36** (2.3 g, 23%), and an overlapping mixture of the two diastereomers (1.0 g; total yield 52.4%).

For **35**: colorless, viscous oil; $[\alpha]^{20}_D$ –5.76° (c 1.9, $CHCl_3$); IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (dt, J = 11, 4 Hz, 1 H), 2.47–1.44 (series of m, 10 H), 1.17 (s, 6 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.86 (d, J = 6.5 Hz, 3 H), 0.70 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 207.7, 166.9, 50.3, 46.9, 41.0, 39.2, 38.8, 34.4, 32.6, 31.6, 25.6, 23.3, 23.1, 22.1, 21.0, 17.8, 16.9, 15.8 ppm; mass spectrum, calcd (M^+) m/e 306.2195, obsd 306.2205.

For **36**: colorless, viscous oil which solidified in the cold; mp 50–54 °C; $[\alpha]^{20}_D$ –80.9° (*c* 2.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.70 (dt, *J* = 11, 4 Hz, 1 H), 2.49–1.40 (series of m, 10 H), 1.19 (s, 3 H), 1.16 (s, 3 H), 1.13–0.90 (m, 4 H), 0.86 (d, *J* = 6.5 Hz, 3 H), 0.85 (d, *J* = 6.5 Hz, 3 H), 0.71 (d, *J* = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 207.7, 166.98 76.6, 50.0, 46.7, 40.9, 39.3, 34.3, 33.0, 31.6, 26.2, 23.4, 22.0, 20.8, 17.7, 17.1, 16.2 ppm; mass spectrum, calcd (M^+) *m/e* 306.2195, obsd 306.2203.

***l*-Menthyl 6,6-Dimethyl-2-methylenebicyclo[3.1.0]hexane-1-carboxylate (37).** An ice-cooled mixture of methyltriphenylphosphonium bromide (960 mg, 2.94 mmol) and potassium *tert*-butoxide (310 mg, 294 mmol) in diisopropyl ether (25 mL) was stirred for 30 min before the addition of **35** (500 mg, 1.63 mmol) in the same solvent (2 mL). The resulting mixture was heated at reflux for 18 h and worked up as previously described. Final MPLC purification of the product (silica gel; 2% ethyl acetate in petroleum ether) gave 211 mg (42.5%) of **37** as a colorless, viscous oil: $[\alpha]^{20}_D$ –16.67° (*c* 15.8, $CHCl_3$); IR (neat) 1705, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.34 (m, 1 H), 4.96 (m, 1 H), 4.72 (dt, *J* = 10, 4 Hz, 1 H), 2.75–1.30 (series of m, 15 H), 1.14 (s, 3 H), 1.01 (s, 3 H), 0.95–0.70 (m, 9 H); ^{13}C NMR ($CDCl_3$) 170.7, 148.4, 107.8, 74.5, 47.3, 47.1, 41.1, 39.2, 36.0, 34.4, 31.5, 30.5, 25.9, 23.2, 23.0, 22.2, 22.1, 21.0, 16.8, 15.8 ppm; mass spectrum, calcd (M^+) *m/e* 304.2402, obsd 304.2409.

***l*-Menthyl 6,6-Dimethyl-2-methylenebicyclo[3.1.0]hexane-1-carboxylate (38).** Reaction of **36** (500 mg, 1.63 mmol) with methylenetriphenylphosphorane in the analogous manner afforded 200 mg (40.3%) of **38** as a colorless, viscous oil; $[\alpha]^{20}_D$ –83.31° (*c* 18.6, $CHCl_3$); IR (neat) 1705, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20 (m, 1 H), 4.99 (m, 1 H), 4.75 (dt, *J* = 10, 4 Hz, 1 H), 2.90–1.40 (series of m, 14 H), 1.20–0.70 (series of m, 15 H); mass spectrum, calcd (M^+) *m/e* 304.2402, obsd 304.2409.

***l*-Menthyl (*S*)-1-Methyl-3-isopropenylcyclopentene-2-carboxylate (39).** Reaction of **38** (200 mg) with *p*-toluenesulfonic acid (10 mg) in chloroform (10 mL) at room temperature for 24 h and a workup as before afforded 150 mg (75%) of **39** as a colorless, homogeneous oil: IR (neat) 1690, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.8–4.4 (m, 3 H), 3.6–3.4 (m, 1 H), 2.9–1.3 (series of m, 19 H), 1.1–0.7 (series of m, 9 H); mass spectrum, calcd (M^+) *m/e* 304.2402, obsd 304.2409.

(*S*)-1-Methyl-2-(hydroxymethyl)-3-isopropenylcyclopentene (40). A cold (–78 °C) solution of **39** (150 mg, 0.49 mmol) in ether (20 mL) was treated with diisobutylaluminum hydride (1.5 mL of 1 M in hexane), and the reaction mixture was stirred at –78 °C for 90 min before the addition of 10% hydrochloric acid. The solution was allowed to warm to room temperature, the phases were separated, and the aqueous phase was extracted with ether. Washing of the combined organic layers with saturated sodium bicarbonate sodium and brine was followed by drying and solvent removal. Purification of the residue by MPLC (silica gel; 10% ethyl acetate in petroleum ether) gave **40** (30 mg, 40%) as a colorless oil: $[\alpha]^{20}_D$ +143.9° (*c* 1.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.7–4.5 (m, 2 H), 4.00 and 3.80 (AB q, *J* = 12 Hz, 2 H), 3.5–3.2 (m, 1 H), 2.40–1.30 (m, 11 H).[25]

(*S*)-1-Methyl-3-isopropenylcyclopentene-2-carboxaldehyde (41). A solution of **40** (18 mg, 0.12 mmol) in dichloromethane (5 mL) was stirred with activated manganese dioxide (0.2 g) at room temperature for 48 h, filtered through Celite, and evaporated. There was isolated 13 mg (73%) of **41** as a colorless oil: $[\alpha]^{20}_D$ +56.1° (*c* 0.98, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 9.90 (s, 1 H), 4.8–4.6 (m, 2 H), 3.8–3.5 (*m*, 1 H), 2.8–1.1 (series of m, 4 H), 2.18 (s, 3 H), 1.65 (br s, 3 H); mass spectrum, calcd (M^+) *m/e* 150.1045, obsd 150.1039.

Acid-Catalyzed Cyclization of 14. A solution of **14** (200 mg, 1.0 mmol) in benzene (30 mL) containing *p*-toluenesulfonic acid (10 mg) was heated at reflux for 18 h under a Dean–Stark trap. The reaction mixture was cooled, diluted with ether, washed with saturated sodium bicarbonate solution and brine, and dried. Following solvent evaporation, the residue was purified by MPLC on silica gel (elution with 13% ethyl acetate in petroleum ether), giving lactone **42** (120 mg, 72%) as a colorless oil: IR (neat) 1755, 1615, 900, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.79 (br s, 2 H), 3.3–2.8 (m, 2 H), 2.8–2.4 (m, 2 H), 2.18 (s, 3 H), 1.71 (s, 3 H); mass spectrum, calcd (M^+) *m/e* 164.0837, obsd 164.0841.

1-(Acetoxymethyl)-2-carbomethoxy-3-isopropenylcyclopentene (43). A solution of **20** (500 mg, 1.93 mmol) and potassium acetate (4.5 g, 20.4 mmol) in methanol (25 mL) was stirred at room temperature for 24 h during which time potassium bromide precipitated. The methanol was removed in vacuo, and the residue was partitioned between water and ether. The organic layer was removed, and the aqueous phase was twice extracted with ether. The combined ethereal solution was washed with water and brine, dried, and evaporated. MPLC purification of the residue (silica gel; 12% ethyl acetate in petroleum ether) afforded 440 mg (96%) of **43** as a colorless oil: IR (neat) 1750, 1720, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.05 (m, 2 H), 4.50 (m, 2 H), 3.60 (s, 3 H), 3.6–3.4 (m, 1 H), 2.8–2.0 (series of m, 4 H), 2.00 (s, 3 H), 1.80 (s, 3 H); mass spectrum, calcd (M^+) *m/e* 238.1205, obsd 238.1212.

1-(Hydroxymethyl)-2-carbomethoxy-3-isopropylcyclopentene (44). To a solution of **43** (440 mg, 1.85 mmol) in methanol (75 mL) under a nitrogen atmosphere was added hydrazine hydrate (9 mL), acetic acid (9 drops), and saturated copper sulfate solution (10 drops). This stirred mixture was maintained at 25 °C while a solution of sodium periodate (7.9 g, 20 eq) in water (60 mL) was added dropwise during 1 h. Upon completion of the addition, stirring was maintained for 36 h before removal of most of the methanol under reduced pressure. The product was taken up in ether, washed with water and brine, dried, and concentrated in vacuo. There was obtained 330 mg (90.1%) of **45** which was not further purified: ^1H NMR ($CDCl_3$) δ 4.4 (m, 2 H), 3.70 (s, 3 H), 3.1–1.4 (series of m, 7 H), 0.95 (d, *J* = 6 Hz, 3 H), 0.70 (d, *J* = 6 Hz, 3 H); mass spectrum, calcd (M^+) *m/e* 198.1256, obsd 198.1262.

Acid-Catalyzed Cyclization of 44. A solution of **44** (500 mg, 2.52 mmol) in benzene (50 mL) containing *p*-toluenesulfonic acid (50 mg) was heated at reflux under a Dean–Stark trap for 18 h. The usual workup and MPLC purification (silica gel; 10% ethyl acetate in petroleum ether) afforded 340 mg (81%) of **45** as a colorless, homogeneous oil: IR ($CDCl_3$) 1765, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80–4.71 (m, 2 H), 2.91–2.83 (m, 1 H), 2.65–2.44 (m, 3 H), 2.26–2.15 (m, 1 H), 2.03–1.92 (m, 1 H) 0.94 (d, *J* = 7 Hz, 3 H), 0.91 (d, *J* = 7 Hz, 3 H); mass spectrum, calcd (M^+) *m/e* 166.0994, obsd 166.0997. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 8.46.

5-Methyl-8-isopropyl-2-oxo-3-oxabicyclo[3.3.0]octene (46). A solution dimethylcopperlithium was prepared by addition of ethereal methyllithium (1.3 M) to a slurry of copper iodide (2.3 g, 12.1 mmol) in dry ether (40 mL) at 0 °C until the mixture became homogeneous and almost colorless. Approximately 18.6 mL of reagent was required. The resulting solution was cooled to –78 °C, and **45** (400 mg, 2.41 mmol) in ether (4 mL) was slowly added via syringe pump over a 4-h period. The dark solution was stirred at –78 °C for an additional 4 h, warmed to 0 °C, and quenched with basic ammonium chloride solution. The mixture was extracted with ether (2 × 50 mL), and the combined ether extracts were washed with ammonium chloride solution (30 mL) and brine (30 mL) before drying. Evaporation of the solvent and purification by MPLC (silica gel; 10% ethyl acetate in petroleum ether) gave **46**: 310 mg (70.7%); IR (neat) 1780, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.07 and 3.93 (AB q, *J* = 9 Hz, 2 H), 2.28 (d, *J* = 4.7 Hz, 1 H), 2.05–1.95 (m, 1 H), 1.89–1.82 (m, 1 H), 1.69–1.49 (m, 4 H), 1.19 (s, 3 H), 0.98 (d, *J* = 6.5 Hz, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 180.9, 77.2, 54.8, 51.8, 47.6, 38.6, 33.1, 30.2, 23.7, 21.4, 20.4 ppm; mass spectrum, calcd (M^+) *m/e* 182.1307, obsd 182.1314. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.25; H, 9.86.

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Registry No. **1**, 40184-98-3; **9**, 53067-23-5; **10**, 62344-23-4; **11**, 68151-47-3; **12**, 85719-84-2; **13**, 85719-85-3; **13**-ol, 85720-09-8; **14**, 85719-86-4; **15**, 85719-87-5; **19**, 85719-88-6; **20**, 85719-89-7; **21**, 73719-07-0; **23**, 85719-90-0; **24**, 85719-91-1; **24** (isopropylidene derivative), 85720-10-1; **25**, 85719-92-2; **26**, 85719-93-3; **27**, 85719-94-4; **28**, 85719-95-5; **29**, 85719-96-6; **29** (isopropenyl derivative), 85720-12-3; **30**, 85719-97-7; **31**, 85719-98-8; **32**, 85719-99-9; **33**, 59557-05-0; **34**, 85720-00-9; **34** (diazo derivative), 85720-11-2;

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35, 85720-01-0; 36, 85761-23-5; 37, 85720-02-1; 38, 85761-24-6; 39, 85720-03-2; 40, 85761-25-7; 41, 38231-11-7; 42, 85720-04-3; 43, 85720-05-4; 44, 85720-06-5; 45, 85720-07-6; 46, 85720-08-7; TsN_3, 941-55-9; *t*-BuOCl, 507-40-4; $(CH_3)_2CuLi$, 15681-48-8; CCl_4, 56-23-5; CH_3COCl, 75-36-5; MCPBA, 937-14-4; NBS, 128-08-5; TsOH, 104-15-4; methyl acetoacetate, 105-45-3; prenyl bromide, 870-63-3; *tert*-butyldimethylsilyl chloride, 18162-48-6; dimethylsulfoxonium methylide, 5367-24-8; thioanisole, 100-68-5.

Photochemistry of Alkyl Halides. 9. Geminal Dihalides[1]

Paul J. Kropp* and Norbert J. Pienta

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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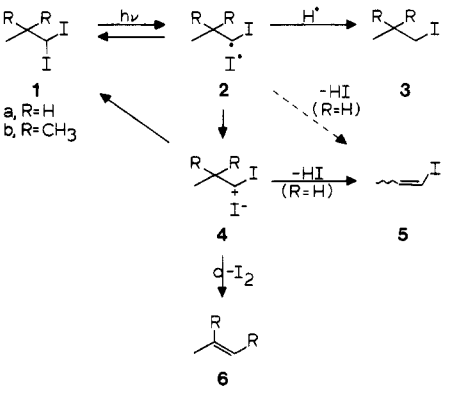
The photobehavior of the geminal dihalides (diiodomethyl)cyclohexane (**7**), (bromoiodomethyl)cyclohexane (**11**), (dibromomethyl)cyclohexane (**17**), (diiodomethyl)cyclopentane (**22**), 3,3-dimethyl(diiodomethyl)cyclobutane (**27**), and 8,8-diiodo-2,6-dimethyl-2-octene (**31**) has been studied and compared with that previously observed for diiodomethane. In all solvents the corresponding vinyl halides (iodomethylene)cyclohexane (**13**), (bromomethylene)cyclohexane (**21**), (iodomethylene)cyclopentane (**23**), 3,3-dimethyl(iodomethylene)cyclobutane (**28**), or *cis*- and *trans*-3,7-dimethyl-1-iodo-1,6-octadiene (**33**) were obtained, which are thought to arise from an α-halo cationic intermediate formed via initial light-induced homolytic cleavage of the carbon–iodine bond followed by electron transfer within the resulting caged radical pair, as shown in Schemes II and III. In the case of diiodide **31** competing intramolecular trapping of the α-iodo cation afforded in addition the cyclized isopulegyl iodide (**34**). In polar solvents the vinyl iodides were accompanied by the nonhalogenated products methylenecyclohexane (**15**), 1-methylcyclopentene (**25**), cyclohexene (**26**), 4,4-dimethylcyclopentene (**29**), and *cis*- and *trans*-carane (**35**), which are thought also to arise from the α-halo cationic intermediate. 1,1-Diiodo-2,2-dimethylpropane (**1b**) afforded 2-methyl-2-butene (**6b**). Except for carane (**35**) from diiodide **31** there was no detectable formation of cyclopropanes. In methanol the nucleophilic substitution products (dimethoxymethyl)cyclohexane (**14**), (dimethoxymethyl)-cyclopentane (**24**), and 1,1-dimethoxy-2,2-dimethylpropane (**30**) were obtained. It is concluded that geminal dihalides undergo predominant, if not exclusive, photoreaction via initial cleavage of a single carbon–halogen bond in analogy with monohalides and that carbene intermediates are not formed. A similar conclusion has been reached previously for diiodomethane in the photocyclopropanation of alkenes.

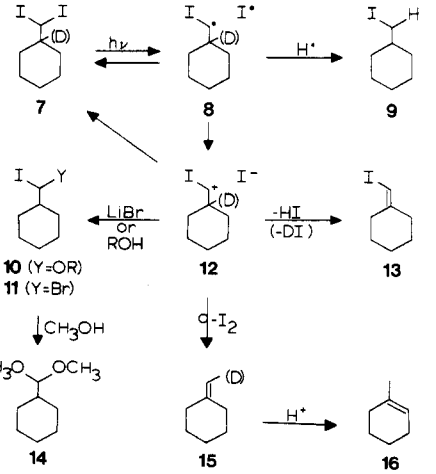
It has been known for some time that irradiation of polyhalomethanes in the presence of alkenes results in the formation of cyclopropanes.[2-4] Recent studies in these laboratories have shown that photocyclopropanation of alkenes with diiodomethane is a convenient procedure which has synthetic utility, being much less subject to steric inhibition than the traditional Simmons–Smith procedure.[5] Both carbene[2,4] and carbenoid[2,5] intermediates have been suggested for the photocyclopropanation process. In an effort to gain further mechanistic insight, Neuman studied the intramolecular photobehavior of iodides **1a,b** in hydrocarbon solvents.[3] It was concluded that the observed products (**3a** and **5a** from iodide **1a**; **3b** from iodide **1b**) arise from an initially formed radical pair **2** (Scheme I); the absence of cyclopropane and 1,1-dimethylcyclopropane was taken to indicate that no carbene intermediates are formed.[6] We report here a more detailed study of the photobehavior of geminal dihalides and relate the insights gained to the photocyclopropanation reaction.[7,8]

(Dihalomethyl)cycloalkanes. The results from irradiation of (diiodomethyl)cyclohexane (**7**) and its deuterated derivative **7-*d*** are summarized in Scheme II and Table I.

Scheme I



Scheme II



Irradiation of **7** at wavelengths >280 nm in a variety of solvents of low polarity afforded principally the vinyl iodide **13**, accompanied by small amounts of the reduction

(1) Part 8: Kropp, P. J.; Worsham, P. R.; Davidson, R. I.; Jones, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 3972–3980.
(2) Blomstrom, D. C.; Herbig, K.; Simmons, H. E. *J. Org. Chem.* **1965**, *30*, 959–964.
(3) Neuman, R. C.; Wolcott, R. G. *Tetrahedron Lett.* **1966**, 6267–6272.
(4) (a) Marolewski, T.; Yang, N. C. *J. Chem. Soc., Chem. Commun.* **1967**, 1225–1226. (b) Yang, N. C.; Marolewski, T. A. *J. Am. Chem. Soc.* **1968**, *90*, 5644–5646.
(5) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229–3236.
(6) Propene (**6a**) and 2-methyl-2-butene (**6b**) were also obtained in low yield, but their origin was described as "not clear".
(7) For a preliminary report of a portion of the present study, see: Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 655–657.
(8) For another recent report see: Moret, E.; Jones, C. R.; Grant, B. *J. Org. Chem.*, this issue. We are indebted to these authors for sharing their results prior to publication.

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