Total Synthesis of (±)-Isocomene and Related Studies

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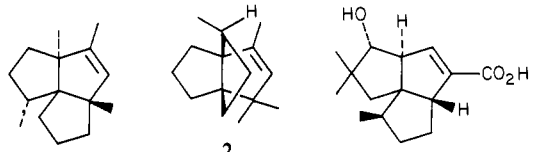
Abstract: The total synthesis of the tricyclic sesquiterpene isocomene is described. The key bond forming reaction involves an intramolecular [2 + 2] photocycloaddition to give tricyclo[6.3.0.0^{1,6}]undecanone **6**. Two routes are described from **6** to isocomene. The first involves acid-catalyzed rearrangement to tricyclo[5.3.1.0^{1,5}]undecanone **7**, addition of MeLi, and solvolysis, while the second uses a Wittig reaction followed by acid-catalyzed rearrangement. The question of maximum continuous orbital overlap in cyclobutyl carbinyl cation rearrangements is discussed, and certain stereochemical effects are found.

We recently described[1] an efficient total synthesis of the sesquiterpene isocomene. Other workers have also reported syntheses.[2] Ours is noted for its high stereoselection, high yield, and, with an intramolecular photocycloaddition, production of three contiguous, quaternary chiral centers with exactly the stereochemistry necessary for isocomene. This intramolecular version of the well-known [2 + 2] cycloaddition is rare in natural product synthesis. It has appeared only recently in Oppolzer's longifolene synthesis[3] and in an attempt at the synthesis of cedrene.[4]

In this paper, we would like to fully discuss our synthetic efforts. These include an alternative synthesis of the natural product via a cyclobutyl carbinyl ketone rearrangement and some experiments designed to answer questions of stereochemistry in the intramolecular cycloaddition and subsequent molecular rearrangements.

Synthetic Strategy

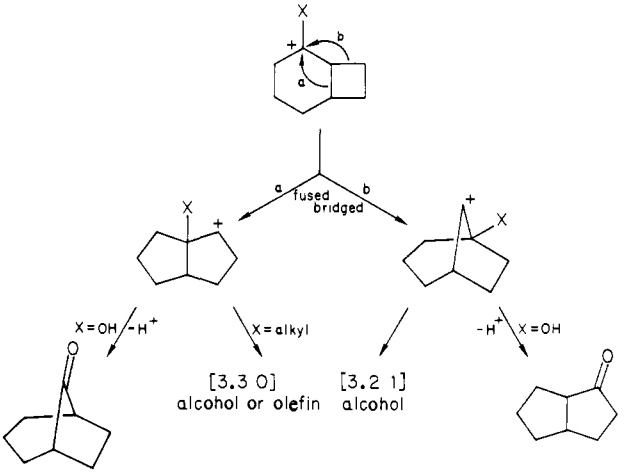
Isocomene (**1**) is one of a number of sesquiterpenes recently isolated[5] [cf. modhephene (**2**) and pentalenic acid (**3**)] whose



1 **2** **3**

structures are formed from three angularly fused cyclopentane rings. It occurred to us that a particularly attractive route to this class of molecules would be one in which a bicyclo [3.3.0] unit was generated by solvolytic rearrangement of a bicyclo [4.2.0] system, itself available by [2 + 2] photocycloaddition of a cyclohexenone. In evaluating this approach, we first considered how the rearrangement would occur. There are two alkyl shifts available which possess the driving force of relief of the cyclobutane strain. They are illustrated in a general way in Scheme I. One would anticipate that the principle of maximum continuous orbital overlap would predict the favored pathway: "bridged" migration (path b) allows perfect overlap of the migrating bond with the p orbital at the carbinyl center, while "fused" migration (path a) would seem to be constrained to occur in the nodal plane of this orbital. Yet, examples of both modes exist for the cyclobutyl carbinyl systems,[6] and exclusive fused migration occurs for cyclopropyl carbinyl systems.[7] In a reaction which follows essentially the same path, the acid-catalyzed rearrangement of cyclobutyl carbinyl ketones developed by Cargill,[8] both migratory modes are also found.[6b,8] However, this reaction consists of two 1,2-alkyl shifts. First, a [3.3.0] (or [3.2.1]) system is obtained with an OH at a bridgehead position, and this undergoes a second shift to a [3.2.1] (or [3.3.0]) system, regenerating the ketone (see Scheme I). In principle, it is complementary to the carbocationic rearrangement. If the Cargill reaction favors one bicyclooctane system, the carbocationic rearrangement should favor the other.

Scheme I



When this approach is applied to isocomene, it becomes apparent that the cycloaddition would necessarily be an intramolecular one (cf. to give **6**). We felt this plan would be viable, as Becker had achieved cycloaddition with a very similar system.[9] However, stereoselection was one point which we would have to address. Weisner[10a] has considered this problem, and he has proposed the following predictive tool: one assumes the β-carbon of the enone to be pyramidalized and allows this to select its most stable conformation. The stereochemistry of the product may be

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(1) M. C. Pirrung, *J. Am. Chem. Soc.*, **101**, 7130 (1979). M. C. Pirrung, Abstracts, 179th National Meeting of the American Chemical Society, Houston, Tex., March 25, 1980, ORGN 64.

(2) (a) W. Oppolzer, K. Battig, and T. Hudlicky, *Helv. Chim. Acta*, **62**, 1493 (1979); (b) S. Chatterjee, *J. Chem. Soc., Chem. Commun.*, 620 (1979); (c) L. Paquette and Y. K. Han, *J. Org. Chem.*, **44**, 4015 (1979).

(3) W. Oppolzer and T. Godel, *J. Am. Chem. Soc.*, **100**, 2583 (1978).

(4) M. Fetizon, S. Lazare, C. Pascard, and T. Prange, *J. Chem. Soc., Perkin Trans. 1*, 1407 (1979).

(5) (a) Isocomene: L. Zalkow, D. Harris, D. Van derVeer, and J. Bertrand, *J. Chem. Soc., Chem. Commun.*, 456 (1977); L. Zalkow, R. Harris III, and N. I. Burke, *J. Nat. Prod.*, **42**, 96 (1979). This material was also isolated by other workers, who gave it the name berkheyaradulene: F. Bohlmann, N. LeVan, and J. Pickardt, *Chem. Ber.*, **110**, 3777 (1977). (b) Modhephene: L. Zalkow, D. Harris, and D. Van derVeer, *J. Chem. Soc., Chem. Commun.*, 420 (1978); (c) Pentalenic acid: H. Seto, T. Sasaki, J. Uzawa, and S. Takeuchi, *Tetrahedron Lett.*, 4411 (1978).

(6) (a) K. Hayano, Y. Ohfune, H. Shirahama, and T. Matsumoto, *Chem. Lett.*, 1301 (1978). (b) K. Duc., M. Fetizon, and M. Kone, *Tetrahedron*, **34**, 3513 (1978).

(7) E. Wenkert, N. Golob, R. Hatch, and D. Wenkert, *Helv. Chim. Acta*, **60**, 1 (1977).

(8) (a) R. Cargill, T. Jackson, N. Peet, and D. Pond, *Acc. Chem. Res.*, **7**, 106 (1974). (b) D. Duc, M. Fetizon, and S. Lazare, *J. Chem. Soc., Chem. Commun.*, 282 (1975). (c) M. Yanigaya, K. Kaneko, K. Takashi, and T. Matsumoto, *Tetrahedron Lett.*, 1761 (1979).

(9) D. Becker, Z. Harel, and D. Birnbaum, *J. Chem. Soc., Chem. Commun.*, 377 (1975).

(10) (a) K. Weisner, *Tetrahedron*, **31**, 1655 (1975); (b) K. Weisner, G. Bettolo, S. Sahoo, and G. Poulton, *ibid.*, **36**, 719 (1980).

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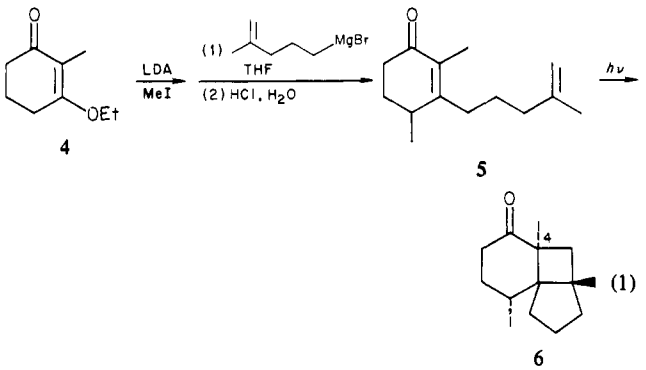
accounted for by attack of the olefin on this pyramidalized species. We note the similarity between this mnemonic device and that most commonly used to predict the stereochemistry of dissolving metal reductions of cyclohexenones. In fact, Weisner has recently described experiments which compare the stereoselection in allene photoadditions and Li/NH_3 reductions of cyclohexenones.[10b] A remarkable consonance is observed. Examination of some literature examples[11] of Li/NH_3 reductions of 3,4-dialkylcyclohexenones indicates that trans products are favored except when steric interaction between the alkyl groups becomes great; then cis product is favored. Alternatively, we felt that steric interactions between the vinyl methyl on the side chain and the secondary methyl group would be important, forcing cycloaddition to occur from the face of the enone opposite this methyl group. These arguments suggest that the precursor necessary for isocomene would be obtained.

Results

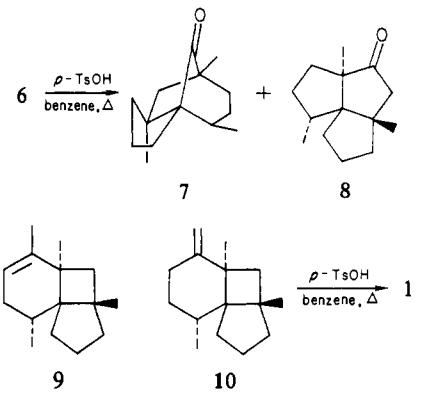
Our starting point was keto ether **4**, readily available from dihydroresorcinol in ca. 70% yield.[12] When the method of Stork and Danheiser is utilized,[13] **4** is methylated in 91% yield and subsequently converted to **5** by the following method: 1-bromo-4-methyl-4-pentene[14] is converted quantitatively into its Grignard derivative and added to the methylated keto ether. Acidic hydrolysis gives **5** (90%) after a simple chromatographic purification (eq 1).



We were now prepared to test the crucial cycloaddition step. Thus, irradiation of a solution of **5** in hexane (10^{-2} M) with 350-nm lamps in a Rayonet reactor provides **6** as a waxy solid in 77% yield after chromatography. Our structural assignment for the cycloadduct rests on its carbonyl stretching frequency of 1705 cm^{-1}, in addition to a methyl doublet and two methyl singlets in the ^1H NMR spectrum. It also exhibits an AX pattern (J = 12 Hz) for the cyclobutyl methylene protons with chemical shift values of 1.33 and 2.30 ppm. The wide disparity of chemical shift for these protons is consonant with widely different environments as caused by proximity to the carbonyl function.

The most important aspect of the photocycloaddition from a synthetic viewpoint is the fact that the reaction product is a single stereoisomer as judged by ^1H NMR, ^{13}C NMR, VPC, and TLC. The vinyl methyl group in the side chain is important in this regard, as a closely related cycloaddition apparently produces a stereoisomeric mixture.[9] That the stereochemistry of the cycloadduct corresponds to **6** follows from our previous mechanistic arguments and its conversion to isocomene (vide infra). The stereochemistry of the C-4 methyl group will be discussed later. *In this single reaction, we have produced three contiguous, quaternary chiral centers stereospecifically and effectively determined all the stereochemistry of the natural product.*

Scheme II



With **6** in hand, we anticipated that isocomene could be gained by simply adding MeLi and treating with acid. However, a number of nucleophilic methyl derivatives (MeLi, MeMgBr, and Me_4AlLi) fail to add to **6** under a variety of conditions. This was shown by a deuterium incorporation experiment to be due to enolization in the case of MeLi.

Since it seemed we would not be able to add nucleophiles to **6**, we turned to the Cargill rearrangement. Treatment of **6** with an equal weight of *p*-TsOH in refluxing benzene provides **7** and **8** in 75 and 15% yields, respectively, after chromatography (Scheme II). These were shown to be kinetic and not thermodynamic products by isolation and resubmission of each pure ketone to the reaction conditions. No change was observed even at prolonged reaction times. The following data allow the assignment of the structures below. Ketone **7** has an IR frequency of 1740 cm^{-1}, while that for **8** occurs at 1730 cm^{-1}. Both show two methyl singlets and a doublet in ^1H NMR, but **8** has an additional AB pattern (δ 2.28 (J = 17 Hz)) for the methylene adjacent to the ketone. Each pure ketone was treated with $LiAlH_4$. The secondary alcohol from **7** shows two singlets in a ca. 2:1 ratio in the carbinol region of its ^1H NMR spectrum, while that from **8** shows a much more complex pattern.

Interestingly, ketone **8** is claimed to have been an intermediate in the first reported synthesis of isocomene.[2b] However, the properties of the material we have prepared do not agree with those published for **8**. The melting point for a highly purified (preparative VPC) sample of our material is fully 100 °C higher than that claimed. We also had difficulty in adding organometallics to **8**, a problem not reported in the original work. We have been unable to contact the author to obtain comparison spectra to prove their difference. Nevertheless, our findings cast serious doubt on the stereostructure of the material claimed to be **8** and therefore the derived synthetic isocomene, reported as an oil (vide infra).[16]

The mixture obtained in the Cargill rearrangement proved disappointing as the more obvious precursor to isocomene was the minor product. Yet, the interconversion of [3.2.1] and [3.3.0] cations in the Cargill reaction led us to examine the analogous rearrangement with a carbocation, rather than an oxacarbonium ion. Consequently, **7** was treated with excess MeLi in refluxing THF to give a mixture of tertiary alcohols in quantitative yield. Enolization, a problem which plagued us with both **6** and **8**, is not possible with **7**. Upon treatment with formic acid at room temperature, the crude mixture of alcohols is transformed into isocomene (mp 57–59 °C) which crystallizes from the reaction mixture in 50% yield. Aqueous workup of the mother liquors

(11) D. Caine, *Org. React. (N.Y.)*, **23**, 1 (1976).

(12) J. McCullough, J. Kelly, and P. Rasmussen, *J. Org. Chem.*, **34**, 2733, (1969). We were able to improve the yield in the formation of the enol ether to 84% by the addition of a step in which the reaction mixture was refluxed through a Soxhlet extractor containing 3-Å molecular sieves.

(13) G. Stork and R. Danheiser, *J. Org. Chem.*, **38**, 1775 (1973).

(14) The bromide was prepared by the Johnson procedure from the alcohol.[15] No detailed procedure for its preparation is found in the literature, so we present one here (see Experimental Section) which routinely gave 90% distilled yields. We note that the Johnson synthesis of the bromide must be used, as attempts to apply more "modern" methods (PBr_3; NBS, Ph_3P) for the conversion of alcohols to bromides led to substantial olefin isomerization.

(15) A. Gen, K. Wiedhaup, J. Swoboda, H. Dunathan, and W. Johnson, *J. Am. Chem. Soc.*, **95**, 2656 (1973).

(16) Paquette[2c] has reached the same conclusion. Notably, our synthetic isocomene is the only material to be originally reported as a solid. Professor Paquette has spectrally compared our two materials and finds them identical. His sample has also crystallized (private communication).

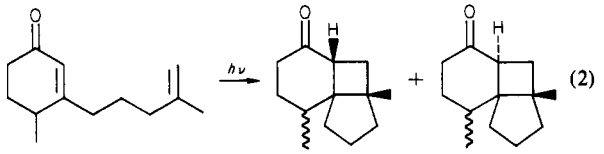
provides an additional 20%. Both are >95% pure by TLC, VPC, and NMR. Final purification by distillation or preparative VPC gives a transparent, crystalline solid, mp 60–62 °C, spectrally identical (^{1}H NMR, ^{13}C NMR, IR, MS) with the natural product.[17] This synthesis provides isocomene in six steps from **4** in 33% overall yield.

Although we had completed the synthesis, we continued to search for more efficient routes and were able to find two nucleophiles which would add to **6**. Treatment with Me_3Al (toluene, reflux, 8 h) leads to a ca. 45:35:20 mixture of starting material and two diasteromeric alcohols. Two more cycles consume virtually all of the ketone (yield 85%), but a new product begins to appear at shorter retention time (VPC) which we hypothesize to have structure **9** (MS, NMR). It originated by some unknown mechanism which is probably not cationic, since we assume that would result in rearrangement. When this mixture of materials is treated with formic acid at room temperature for 4 h, the product contains no **9** or alcohol but consists principally of isocomene along with other unidentified products. In view of the inelegance of this approach, it was abandoned.

We were finally able to find a nucleophile which would add effectively to **6**. Upon treatment with methylenetriphenylphosphorane in Me_2SO at 70 °C for 72 h, a 77% yield of **10** is realized. Treatment with formic acid leads to a mixture of products, evidently due to solubility problems. But when **10** is refluxed in benzene with *p*-TsOH, isocomene is obtained in 98% yield. This synthesis proceeds in five steps from **4** in 48% overall yield.

On the Stereostructure of 6

Though we were certain of the relative configuration at three centers of **6**, we attempted to determine the fourth. We had originally hypothesized[1] that it possessed a trans-fused bicyclo [4.2.0] ring system. Our approach was as follows: **11** was synthesized in a manner analogous to **5** and irradiated under the same conditions as **5** (eq 2). Two products were obtained in the yields



(2)

11 **12** (64%) 13 (33%)

indicated. The trans-fused products **12** (3:1 ratio, α:β) were separated from the cis-fused products **13** (3:1 ratio, β:α) by preparative high-pressure LC, but each homogeneous fraction proved to be a mixture of methyl epimers (NMR). The trans material could be equilibrated completely to the cis in base, establishing their stereochemical relationship.

The predominant stereochemistry at the secondary methyl group is opposite in the cis and trans isomers. This is best analyzed after the trans has been converted to the cis, when both methyl groups are well separated in the ^{1}H NMR spectrum. The stereochemistry can be inferred from chemical shift trends. The methyl signals in the minor cis cycloadduct occur downfield in ^{1}H NMR, while they occur upfield in ^{13}C NMR, as compared to the major isomer. This is consistent with other findings on sterically compressed systems.[18] Examination of models of these substances indicates that the minor should suffer severe nonbonded interactions between the methyl groups, leading to the observed shift trend.

We had hoped to resolve the question of the favored migratory mode for **12** and **13** by acid-catalyzed rearrangement, but the cis material is inert to *p*-TsOH/benzene/reflux, and the trans merely epimerizes to the cis.

(17) Comparison spectra were graciously supplied by Professor Zalkow. Though the melting point reported here is the same as that for the natural product, this must be purely coincidental as ours is obviously produced in racemic form.

(18) J. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 116.

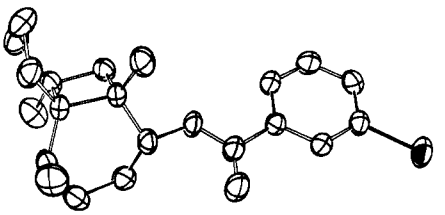
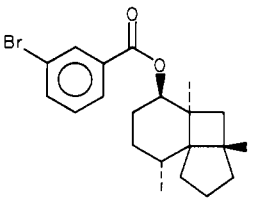


Figure 1. Perspective view of the molecular structure of **14**.

We also attempted to correlate the ^{13}C NMR spectrum of **6** with **12** and **13** but were unsuccessful. We obtained the multiplicities of all of the carbons in **6**, but a full assignment was not possible. Additionally, the complex nature of the coupled spectra of **12** and **13** as epimeric mixtures made interpretation impossible.

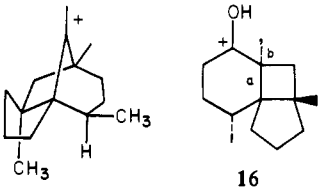
Finally, in a two-step sequence (1, LAH/THF; 2, *m*-BrC_6H_4COBr, pyridine), derivative **14** was prepared and submitted for single-crystal X-ray analysis. The structure as shown in Figure 1 possesses the cis-fused bicyclo [4.2.0] ring system.



14

Discussion

The synthetic approach described here has shown that intramolecular [2 + 2] photocycloaddition followed by molecular rearrangement is a viable, efficient means for constructing complex polycyclic systems. The solvolytic behavior of the synthetic intermediates proved interesting. For example, **6** displays a 5:1 preference for fused mode migration. Furthermore, **10** is rearranged exclusively to isocomene. No products derived from the bicyclo [3.2.1] cation **15**, obtained by bridged mode migration,



15 **16**

are observed. We must point out though that our first synthesis shows that cation **15** is converted to isocomene, so the fact that we obtain only isocomene from **10** is not necessarily a reflection of the partition between the fused and bridged pathways. It is interesting that migration through **15** provides a product in which the original angular methyl group remains at the angle, while fused migration places this methyl at the vinyl position.

We originally[1] considered that fused-mode migration could be explained by the formation of a trans-fused bicyclo [4.2.0] ring system. The unambiguous structural proof of **14** shows this to be incorrect. Furthermore, as mentioned above, no distinction between fused- and bridged-mode migration may be made on the basis of the rearrangement of **10**. However, we have considered two explanations for the favored fused migration of **6**. Both are kinetically based, but our results do support the contention that the rearrangement is irreversible.

The first relies on an extrapolation of the bond angles in **14** to the hypothetical cation **16**, in which bond a has better orbital overlap (by ca. 23°) with the adjacent p orbital. The hazards in the extrapolation from **14** to **16** and in the prediction of a favored transition state from a ground-state conformation must be acknowledged, however. The second possible explanation is that product development control in the first step of the ketone rearrangement favors the tricyclo [6.3.0.$0^{1,5}$] system, which then undergoes a second bond migration to yield **7**. While force field

calculations[19] indicate the two unsubstituted tricycloundecanes to be of roughly comparable stability, the trimethyltricyclo-[5.3.1.$0^{1,5}$]undecane would seem to suffer more torsional strain. The greater stability of the [6.3.0.$0^{1,5}$] ring system as compared to the [5.3.1.$0^{1,5}$] ring system is also suggested by the exclusive formation of isocomene from **15**. If the isocomyl cation were not appreciably more stable than all other cations on the energy surface, it seems unlikely that the formation of a cyclopentene instead of a methylenecyclopentane would possess enough driving force to exclude all other products.

Summary

The total synthesis of isocomene as described herein was achieved in seven steps and 34% overall yield. The value of the synthetic approach lies not only in this work but in its potential application to other natural products of our interest. Cyclobutyl carbinyl cation rearrangements would seem to hold great promise in total synthesis.

Experimental Section

All melting points were taken on a Buchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrometer. Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer. The solvent was $CDCl_3$ with internal Me_4Si. ^{13}C NMR spectra were recorded at 25.144 MHz on a Nicolet Technology Corporation TT-23 spectrometer. Chemical shift values are given in ppm relative to solvent ($CDCl_3$, 77.0 ppm). Gas chromatography (VPC) was performed on a Varian A90-P3 instrument with helium as carrier gas. The column was $^1/_4$ in. × 10 ft, packed with 8% SE-30/Chromosorb G, operated at 180 °C. Thin-layer chromatography was performed on Analtech glass plates coated with silica gel (GF, 250 μm). Column chromatography was performed by using Baker 60–200 mesh silica gel. Preparative high-pressure LC was performed on a Waters Prep LC/System 500 using PrepPak columns. THF was distilled from sodium/benzophenone immediately prior to use. Mass spectra were obtained with Atlas MS-12 and Consolidated 12-110B mass spectrometers. Elemental analyses were performed by the microanalytical laboratory operated by the College of Chemistry, University of California, Berkeley, Calif. UV spectra were obtained on a Cary Model 118 recording spectrophotometer.

4-Methyl-4-penten-1-ol. A 1-L 4-neck round-bottom flask equipped with a glass filter was fitted with a mechanical stirrer, reflux condenser, and serum stoppers. Magnesium (28 g, 1.15 mol) was placed in the flask and covered with 50 mL of THF. In a syringe on a syringe pump was placed 2-methyl-3-chloropropene (50 mL, 0.51 mol), and a few drops were added to the flask. After initiation was complete, the reaction was diluted with 500 mL of THF and the remainder of the halide added over ca. 4 h. After addition was complete, the Grignard solution was filtered into a 1-L 3-neck round-bottom flask containing a stir bar. Titration showed this solution to be ca. 0.65 M in Grignard. The solution was cooled to −70 °C, and ethylene oxide (16 mL, 0.32 mol) was added from a chilled (0 °C) graduated cylinder in one portion. After a short induction period, the temperature rose to 20 °C. The reaction mixture was then refluxed for 30 min, cooled, and quenched into ice. Concentrated HCl (25 mL, 0.32 mol) was added, and the layers were separated. The aqueous phase was extracted with Et_2O (2 × 500 mL) and the combined organic phases were washed with $NaHCO_3$ and NaCl. The solution was dried ($MgSO_4$), and the solvents were removed in vacuo. Fractional distillation (10 cm Vigreux, 25 torr) gave two fractions, bp 64–77 °C and 77–79 °C. VPC analysis (90 °C) showed both to be >95% pure. The combined weight was 29.92 g (93%).

2,4-Dimethyl-1-ethoxy-1-cyclohexen-3-one. In a 300-mL 3-neck round-bottom flask, LDA was prepared in 60 mL of THF from diisopropylamine (17.2 mL, 124 mmol) and *n*-BuLi (82 mL of a 1.50 M hexane solution). After the mixture was cooled to −70 °C, 2-methyl-1-ethoxy-1-cyclohexen-3-one (16.92 g, 109.9 mmol) was added by syringe in 30 mL of THF, washing the container with an additional 10 mL of THF. After the solution was stirred for 1 h at −70 °C, MeI (7.70 mL, 124 mmol) was added neat and the cooling bath removed. After being stirred overnight, the solution was diluted with H_2O and the layers were separated. The aqueous phase was extracted with Et_2O (2 × 100 mL), and the combined organic phases were washed with 100 mL portions of the following solutions: 5% HCl, $Na_2S_2O_3$, and NaCl. Drying ($MgSO_4$), filtration, and removal of solvents in vacuo gave the crude product which was Kugelrohr distilled (160 °C (0.6 torr)) to give 16.74 g (91%) of a white solid. Recrystallization of a small sample from hexane gave material with mp 48 °C. IR: 1640, 1620, 1450, 1380, 1360, 1290, 1260, 1240, 1190, 1140, 1120, 1075, 1040, 1030, 1000, 950, 920, 895, 865, 740 cm^{-1}. ^1H NMR: δ 1.10 (3 H, d, J = 7 Hz), 1.30 (3 H, t, J = 7 Hz), 1.60 (3 H, br s), 4.00 (2 H, q, J = 7 Hz). Anal. ($C_{10}H_{16}O_2$): C, H.

2,6-Dimethyl-1-(4-methyl-4-pentenyl)-1-cyclohexen-3-one (5). In a 100-mL oven-dried flask fitted with reflux condenser and stir bar was placed 3.63 g of Mg (149 mmol). This was covered with 5 mL of THF, and a few drops of 1-bromo-4-methyl-4-pentene were added. Initiation proceeded easily, and the reaction was diluted with 40 mL of THF. The remainder of the halide (12.50 g, 76.7 mmol) was added by syringe pump over 1 h. The flask containing the halide was rinsed with an additional 5 mL of THF. The solution was heated at reflux for 10 min and then cooled. Titration showed this solution to be 1.28 M in Grignard.

In a 100-mL round-bottom flask fitted with a reflux condenser was placed 2,4-dimethyl-1-ethoxy-1-cyclohexen-3-one (8.24 g, 49.0 mmol) which was dissolved in 20 mL of THF. The Grignard solution from above (55 mL, 70.4 mmol) was added by syringe and the solution refluxed for 20 min. After being cooled, the reaction mixture was poured into 30 g of ice and 40 mL of 10% HCl and stirred at room temperature for 2 h. The solution was saturated with NaCl, and the layers were separated. The aqueous phase was extracted with Et_2O (2 × 100 mL), and the combined organic layers were washed with H_2O, $NaHCO_3$, and NaCl. Drying, filtering, and removal of solvents in vacuo gave the crude product. This was purified by washing it through a 60-g plug of silica gel by using 10% ether/hexane (R_f = 0.21), monitoring the eluant by UV (wt 9.12 g, 90%). Further purification could be performed by preparative high-pressure LC or Kugelrohr distillation (150 °C (0.4 torr)). VPC analysis indicated the presence of a single compound (retention time = 7 min). IR: 1660, 1620, 1450, 1420, 1380, 1350, 1190, 1080, 880 cm^{-1}. ^1H NMR: δ 1.17 (3 H, d, J = 7 Hz), 1.73 (6 H, br s), 1.9–2.5 (11 H, m), 4.66 (2 H, br s). UV (hexane): 240 nm (log ε = 4.14); 324 nm (log ε = 1.52). Preparative VPC gave the analytical sample. Anal. ($C_{14}H_{22}O$): C, H.

2α,6α,8β-Trimethyltricyclo[6.3.0.$0^{1,6}$]undecan-5-one (6). Nitrogen was bubbled through a solution of **5** (6.18 g, 30 mmol) in 3 L of high-pressure LC grade hexane in a 3-L round-bottom flask for 30 min. This was sealed and placed in a Rayonet reactor fitted with 350-nm lamps and irradiated for 24 h. The solvent was removed in vacuo and the residue purified by preparative high-pressure LC (10% ether/hexane). The material obtained (4.72 g) consisted of pure **6** by VPC (retention time = 5.6 min). This could be further purified by Kugelrohr distillation (130 °C (0.4 torr)) to give a waxy solid, mp 63–68 °C, with >95% recovery of material. On a smaller scale (3 mmol), the yield was 77% and the product purified by column chromatography with the same solvent (R_f = 0.39). IR: 1705, 1460, 1450, 1440, 1380, 1320, 1275, 1180, 1080, 1060, 1040, 1020, 1000, 940 cm^{-1}. ^1H NMR: δ 0.83 (3 H, d, J = 7 Hz), 1.00 (3 H, s), 1.10 (3 H, s), 1.33 (1 H, d, J = 12 Hz), 2.30 (1 H, d, J = 12 Hz). ^{13}C NMR: δ 18.1 (q), 19.4 (q), 22.2 (q), 24.8 (t), 26.7 (t), 28.9 (t), 33.3 (d), 36.7 (t), 39.6 (t), 41.0 (t), 44.5 (s), 46.4 (s), 56.5 (s), 217.7 (s). UV (hexane): 283 nm (log ε = 1.50), tail to 340 nm. Anal. ($C_{14}H_{22}O$): C, H.

Cargill Reaction of 6. Cycloadduct **6** (1.116 g, 5.42 mmol) was dissolved in benzene (65 mL) and *p*-toluenesulfonic acid (1.08 g) was added. This was heated at reflux for 2 h, cooled, and poured into water. Separation, extraction of the aqueous phase with ether, washing the combined organic layers with NaOH, H_2O, $NaHCO_3$, and NaCl, and drying gave a solution which was filtered and evaporated. Preparative high-pressure LC (10% ether/hexane) or, on a smaller scale, column chromatography easily separated these two products.

5β,7α,10α-Trimethyltricyclo[5.3.1.$0^{1,5}$]undecan-11-one (7) was obtained in 75% yield (839 mg). R_f = 0.68. IR (film): 1740, 1450, 1380, 1320, 1300, 1270, 1260, 1190, 1140, 1015, 985, 920, 800 cm^{-1}. ^1H NMR: δ 0.80 (3 H, d, J = 7 Hz), 1.00 (3 H, s), 1.13 (3 H, s). Preparative VPC (Ret. time = 5.2 min) gave the analytical sample. Anal. ($C_{14}H_{22}O$): C, H.

5β,8α,11α-Trimethyltricyclo[6.3.0.$0^{1,5}$]undecan-7-one (8) was obtained in 15% yield (167 mg). R_f = 0.38. Retention time = 6 min. Mp 149 °C. IR: 1730, 1460, 1380, 1260, 1120, 1040, 1020, 910, 800, 740 cm^{-1}. ^1H NMR: δ 0.97 (3 H, d, J = 7 Hz), 1.10 (3 H, s), 1.12 (3 H, s), 2.28 (2 H, AB, J = 17 Hz). High-resolution mass spectrum calcd for $C_{14}H_{22}O$, 206.1670. Found: 206.1667.

(±)-Isocomene (1). In a 50-mL round-bottom flask were placed 20 mL of THF and 6 mL (7.8 mmol) of a 1.30 M solution of MeLi in ether. Next, **7** (0.779 g, 3.78 mmol) was added neat, rinsing the container with THF (2 × 1 mL). The solution was heated at reflux for 3 h, cooled, and poured into 40 mL of brine. The solution was acidified with 10 mL of 10% HCl, and the layers were separated. The aqueous phase was extracted with Et_2O (30 mL), and the combined organic phases were washed with H_2O, $NaHCO_3$, and NaCl. The solution was dried ($MgSO_4$) and filtered, and the solvents were removed in vacuo to give 0.854 g (100%) of a mixture of tertiary alcohols, as evidenced by a

(19) E. Osawa et al., *J. Am. Chem. Soc.*, **99**, 5361 (1977).

complex methyl region in the ^1H NMR spectrum. IR: 3400, 2950, 1460, 1380, 1260, 1180, 1140, 1080, 1050, 960, 920, 900, 800, 760 cm^{-1}. This was not further characterized and was used without purification.

The crude tertiary alcohols were dissolved in 30 mL of 95% HCO_2H and stirred at room temperature. After 15 min, a white solid precipitated. After 2 h, this was filtered to give pure isocomene (400 mg, 50%) with mp 57–59 °C. The mother liquors were evaporated to a small volume and taken up in Et_2O. The organic phase was washed with $NaHCO_3$ and NaCl and dried ($MgSO_4$). Filtration and removal of solvents in vacuo gave an oil (141 mg) which solidified. Both materials showed a single peak on VPC (retention time = 3.6 min). TLC (hexane) showed a single spot (R_f = 0.74). IR (CCl_4, 10%): 3020, 2950, 2870, 1670, 1455, 1375, 1330, 1190, 1005, 845 cm^{-1}. ^1H NMR: δ 0.83 (3 H, d, J = 7 Hz), 1.03 (6 H, s), 1.56 (3 H, br s), 4.83 (1 H, br s). ^{13}C NMR: δ 12.9, 17.3, 23.2, 23.8, 24.1, 32.1, 33.6, 37.4, 40.0, 42.7, 56.7, 60.0, 64.0, 132.8, 142.9. Purification by preparative VPC gave a transparent solid, mp 60–62 °C. Anal. ($C_{15}H_{24}$): C, H.

5β,7α,10α-Trimethyl-11-hydroxytricyclo[5.3.1.0^{1,5}]undecane. Lithium aluminum hydride (27 mg) was dissolved in THF (1 mL), and **7** (11.3 mg, 55 μmol) was added in 0.5 mL of THF, washing the flask with two additional 0.5-mL portions of THF. After being stirred at room temperature for 2 h, the reaction was quenched by the addition of 27 μL of H_2O, 27 μL of 15% NaOH, and 81 μL of H_2O. Drying ($MgSO_4$) and removal of solvents in vacuo gave 5.7 mg (50%) of alcohol. This showed a complex methyl region and two singlets in ^1H NMR: major δ 3.53; minor δ 3.73. IR (film): 3500, 2920, 1460, 1375, 1360, 1260, 1160, 1060 cm^{-1}. High-resolution mass spectrum calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1819.

5β,8α,11α-Trimethyl-7-hydroxytricyclo[6.3.0.0^{1,5}]undecane. Lithium aluminum hydride (31 mg) was dissolved in 1 mL of Et_2O, and **8** (11 mg, 53 μmol) was added in 0.5 mL of Et_2O, washing the flask with two additional portions of Et_2O. After being stirred at room temperature for 1 h, the reaction was quenched by the addition of 31 μL of H_2O, 31 μL of 15% NaOH, and 93 μL of H_2O, dried, and filtered, and the solvents were removed in vacuo to give 8 mg (73%) of alcohol. This showed a very complex ^1H NMR spectrum. IR (film): 3350, 1460, 1375, 1260, 1120, 1040, 800 cm^{-1}. High-resolution mass spectrum calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1820.

2α,6α,8β-Trimethyl-5-methylenetricyclo[6.3.0.0^{1,6}]undecane (10). In a 50-mL round-bottom flask was placed a stir bar and NaH (750 mg of a 50% suspension, 15.6 mmol). This was washed with petroleum ether (2 × 5 mL), and 15 mL of Me_2SO was added. After being heated at 60 °C for 1 h, the solution was cooled and triphenylmethylphosphonium bromide (5.50 g, 15.4 mmol) was added. After the mixture was stirred 10 min, **6** (1.593 g, 7.73 mmol) was added, and the solution was heated at 70 °C for 72 h. The reaction mixture was cooled and poured into a mixture of H_2O and petroleum ether. The layers were separated, and the organic phase was washed repeatedly with H_2O. Washing with $NaHCO_3$, 1% HCl, and NaCl followed by drying ($MgSO_4$), filtering, and removal of solvents in vacuo gave the crude product. This was placed on a 30-g silica gel column which was eluted with hexane. The eluant was monitored by TLC (R_f = 0.74). This gave 1.214 g (77%) of **10** as a water white liquid which showed a single peak on VPC (retention time = 3.8 min). IR (film): 1640, 1450, 1370, 1255, 1240, 880 cm^{-1}. ^1H NMR: δ 0.70 (3 H, d, J = 7 Hz), 1.00 (3 H, s), 1.03 (3 H, s), 4.77 (2 H, br s). High-resolution mass spectrum calcd for $C_{15}H_{24}$: 204.1878. Found: 204.1880. Preparative VPC gave the analytical sample. Anal. ($C_{15}H_{24}$): C, H.

Conversion of 10 to Isocomene. In a 50-mL round-bottom flask were placed **10** (1.52 g, 7.45 mmol), 25 mL of benzene, and *p*-toluenesulfonic acid (0.42 g, 2.20 mmol). The solution was heated at reflux for 1 h, cooled, and poured into water. The layers were separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with $NaHCO_3$ and NaCl, dried ($MgSO_4$), and filtered. Removal of the solvents in vacuo gave 1.488 g (98%) of isocomene.

4-Methyl-1-ethoxy-1-cyclohexen-3-one. In a 200-mL 3-neck round-bottom flask was prepared LDA (from 12.2 mL of diisopropylamine (87.2 mmol) and 58 mL of a 1.50 M solution of *n*-BuLi in hexane (87 mmol)) in 60 mL of THF. After the solution was cooled below −70 °C, 3-ethoxycyclohexenone (10.64 g, 76.0 mmol) was added in 15 mL of THF. After the mixture was stirred for 1 h at −70 °C, MeI (5.4 mL, 87 mmol) was added and the solution was warmed to room temperature and stirred overnight. The reaction mixture was diluted with H_2O, and the layers were separated. Extraction of the aqueous phase (2 × 100 mL of Et_2O), washing (5% HCl, $Na_2S_2O_3$, H_2O, and NaCl), drying, filtering, and evaporation gave the crude product. This was Kugelrohr distilled (140 °C (0.5 torr)) to give 10.0 g (86%) of material which solidified when being cooled in a refrigerator but was liquid at room temperature. IR (film): 2950, 1660, 1610, 1455, 1380, 1360, 1235, 1190, 1015, 1040, 900, 815 cm^{-1}. ^1H NMR: δ 1.10 (3 H, d, J = 7 Hz), 1.30 (3 H, t, J = 7 Hz), 3.83 (2 H, q, J = 7 Hz), 5.23 (1 H, br s). Anal. ($C_9H_{14}O_2$): C, H.

6-Methyl-1-(4-methyl-4-pentenyl)cyclohexen-3-one (11). Following the same procedure used for **5** on a 10-mmol scale, there was obtained an 85% distilled (Kugelrohr, 120 °C (0.3 torr)) yield. VPC analysis indicated >90% a single compound with a retention time of 8 min. IR (film): 3070, 2950, 1670, 1620, 1450, 1255, 1200, 890 cm^{-1}. ^1H NMR: δ 1.12 (3 H, d, J = 7 Hz), 1.70 (3 H, br s), 4.67 (2 H, br s), 5.80 (1 H, br s). UV (hexane): 228 nm (log ϵ = 4.14), 339 nm (log ϵ = 1.43). Preparative VPC gave the analytical sample. Anal. ($C_{13}H_{20}O$): C, H.

Cycloaddition of 11. In 300 mL of hexane was placed **11** (570 mg, 3.0 mmol), and the solution was purged with N_2 for 30 min. The container was sealed and placed in a Rayonet reactor, irradiating at 350 nm for 2 h. The solvent was removed in vacuo and the residue purified by preparative high-pressure LC (25% ether/hexane) to give fraction 1 (R_f = 0.20, cis product, 188 mg, 33%) and fraction 2 (R_f = 0.19, trans product, 364 mg, 64%). Cis cycloadducts (3:1 mixture): (major) ^1H NMR δ 0.87 (3 H, d, J = 6 Hz), 1.06 (3 H, s); ^{13}C NMR δ 17.0, 22.7, 23.0, 29.4, 31.1, 32.3, 33.1, 37.3, 41.9, 45.7; (minor) ^1H NMR δ 1.06 (3 H, d, J = 7 Hz), 1.26 (3 H, s); ^{13}C NMR δ 15.7, 23.0, 24.4, 30.0, 34.3, 36.4, 40.3, 40.5, 43.1, 46.2; IR (film): 1700, 1450, 1380, 1315, 1220 cm^{-1}. VPC analysis showed a single peak, retention time = 6 min; preparative VPC gave the analytical sample; Anal. ($C_{12}H_{20}O$) for C, H. Trans cycloadducts (3:1 mixture): the mixture of epimers in this material was not readily evident in its NMR spectrum, but followed from its conversion to the cis (vide infra); IR (film): 1715, 1450, 1380, 1170, 915, 730 cm^{-1}; ^1H NMR: δ 0.77 (d, J = 7 Hz), 1.27 (2d's, 1s), 3.35 (m); resonances for the minor isomer in ^{13}C NMR are shown in parentheses; ^{13}C NMR: δ 15.6, (18.5), 21.5, 23.9, (26.3), (29.4), 30.6, (34.9), 35.2, 37.3, 37.9, 38.4, 38.8, (39.8), 42.5; VPC analysis showed two peaks, the first corresponding to cis adduct, apparently due to partial thermal equilibration, and the second with retention time = 7 min; preparative VPC gave the analytical sample; Anal. ($C_{13}H_{20}O$) for C, H.

Equilibration of 12. Submission of fraction 2 to the photochemical reaction conditions and workup provided a quantitative recovery of unchanged trans cycloadduct. This was dissolved in 5 mL of MeOH, and a few K_2CO_3 crystals were added. The solution was heated at reflux for 2 h, cooled, and poured into water. Ether extraction, drying, filtering, and evaporation gave in 74% recovery a 3:1 mixture of cis cycloadducts in which the major component corresponded to the minor obtained in the cycloaddition.

2α,6α,8β-Trimethyl-5-hydroxytricyclo[6.3.0.0^{1,6}]undecane. Lithium aluminum hydride (80 mg, 2.10 mmol) was dissolved in 10 mL of THF and cooled to 0 °C. Cycloadduct **6** (691 mg, 3.35 mmol) was added slowly in 2 mL of THF and stirred at 0 °C for 2 h. TLC analysis showed the reaction was complete, so it was quenched by the addition of 80 μL of H_2O, 80 μL of 15% NaOH, and 240 μL of H_2O and dried ($MgSO_4$). The solvents were evaporated to give a residue which was chromatographed on a 25-g silica gel column using 10% ether/hexane. IR (film): 3400, 1460, 1440, 1375, 1065, 1010, 900 cm^{-1}. 5β-Alcohol: 346 mg (50%), R_f = 0.18. ^1H NMR: δ 0.77 (3 H, d, J = 7 Hz), 1.00 (3 H, s), 1.17 (3 H, s), 3.50 (1 H, t, J = 6 Hz). Anal. ($C_{14}H_{24}O$): C, H. 5α-Alcohol: 262 mg (38%), R_f = 0.07. ^1H NMR: δ 0.66 (3 H, d, J = 7 Hz), 0.87 (3 H, s), 1.13 (3 H, s), 4.00 (1 H, m). Anal. ($C_{14}H_{24}O$): C, H.

2α,6α,8β-Trimethyl-5β-(3′-bromobenzoyloxy)tricyclo[6.3.0.0^{1,6}]undecane (14). The 5β-alcohol from above (190 mg, 0.91 mmol) was dissolved in pyridine (5 mL), and to this was added *m*-bromobenzoyl bromide (0.55 g, 2.08 mmol). After the mixture was stirred overnight, TLC analysis indicated a single UV-active component with R_f = 0.52 (10% ether/hexane). The reaction mixture was poured into H_2O and Et_2O, the layers were separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with H_2O, 2 × 10% HCl, H_2O, $CuSO_4$, $NaHCO_3$, and NaCl. Drying ($MgSO_4$), filtering, and evaporation gave a residue which was chromatographed on a 20-g column of silica gel to give 324 mg (91%) of **14**. Dissolution of this in boiling hexane followed by slow crystallization gave prisms, mp 91 °C. IR: 1720, 1670, 1420, 1280, 1260, 1200, 995, 750 cm^{-1}. ^1H NMR: δ 0.83 (3 H, d, J = 7 Hz), 1.07 (3 H, s), 1.17 (3 H, s), 5.03 (1 H, t, J = 5 Hz), 7.23 (1 H, t, J = 7.8 Hz), 7.60 (1 H, dt, J = 7.8, 1.2 Hz), 7.93 (1 H, dt, J = 7.8, 1.2 Hz), 8.10 (1 H, t, J = 1.2 Hz). Anal. ($C_{21}H_{27}O_2Br$): C, H, Br.

X-Ray Crystal Structure of 14. Large, tabular crystals were obtained as described above. Several fragments of one crystal were mounted on glass fibers in air by using Eastman 910 cement. Preliminary precession photographs indicated triclinic Laue symmetry and yielded rough cell dimensions. A crystal fragment ~0.29 × 0.32 × 0.35 mm in the shape of a rough parallelepiped with rounded edges was then mounted on a Nonius CAD-4 four-circle, κ-geometry diffractometer automated by a PDP 8/e minicomputer and Nonius software. The crystal was accurately centered in the beam and a preliminary orientation matrix determined

Table I. Crystal and Data Collection Parameters

(A) Crystal Parameters at 25 °C[a,b]	
$a = 7.9388$ (14) Å	$M_r = 391.37$ amu
$b = 11.0544$ (15) Å	$d_{calcd} = 1.394$ g cm^{-3}
$c = 11.6775$ (19) Å	$\mu_{calcd} = 21.90$ cm^{-1}
$\alpha = 66.094$ (14)°	space group $P\bar{1}$ (C_i^1, No. 2)
$\beta = 84.768$ (14)°	$Z = 2$
$\gamma = 86.500$ (13)°	dimens: 0.32 × 0.35 × 0.29 mm
$V = 932.6$ Å^3	

(B) Data Measurement

diffractometer: Nonius CAD-4
radiatn: Mo Kα ($\bar{\lambda} = 0.710\ 73$ Å)
monochromator: highly oriented graphite ($2\theta_m = 12.2°$); perpendicular mode, assumed 50% perfect
reflctns measd: $h,\pm k,\pm l$
2θ range: $3° \rightarrow 46°$
scan type: θ(crystal)–2θ(counter)
scan speed: variable, min, 0.694°/min; max, 5.0°/min (θ)
scan width: $\Delta\theta = 0.65 + 0.347 \tan\theta°$, centered on θ(Mo $K\alpha_1$)
bkgd: θ(crystal)–2θ(counter) counted over a range $0.25(\Delta\theta)$ beyond each end of the scan
std reflctns: ($3\bar{6}5$), (162), ($4\bar{1}4$); measured after every 2 h of X-ray exposure time. Over the period of data collection they dropped monotonically an average of 2% in intensity.
orientatn: checked after every 250 measurements. Orientation was redetermined if any of the three orientation check reflections was offset from its predicted position by more than 0.10. Reorientation was performed once during data collection.
vert aperture: 3.0 mm; aperture-crystal distance = 173 mm
horiz aperture: $(2.0 + 1.0 \tan\theta)$ mm
reflctns collected: 2579 excluding std
unique reflctns used [$F^2 > 3\sigma(F^2)$]: 2139

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ components of 24 reflections with 2θ between 22 and 30°. [b] In this table, the esds are given in parentheses right-justified to the least significant digits given.

by searching reciprocal space in the region near $2\theta = 10°$ and indexing the reflections found. Inspection of the Niggli values for the primitive cell confirmed the choice of the triclinic Laue group. Accurate cell dimensions and orientation matrix were then determined by centering 12 pairs of Friedel-related reflections, all with 2θ between 22 and 30°. Table I gives the derived crystal parameters and details of the data collection procedure.

Structure Solution and Refinement. The 2579 unique data were reduced to squared structure factor amplitudes and their esds by correction for Lorentz and polarization effects (including monochromator) scan time and background by using the equations $F_o^2 = (\omega/Lp)(C - 2B)$ and $\sigma_o(F^2) = (\omega/Lp)(C + 4B)^{1/2}$, where C and B are the observed total counts in the scan and background reflections, ω is the scan speed in θ (deg/min), and $1/Lp = (\sin 2\theta)(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m - \sin^2 2\theta)$ is the correction for Lorentz and polarization effects at 2θ for the reflection and a monochromator, assumed 50% perfect, set at $2\theta_m$. Inspection of the standard reflections showed a linear drop in intensity of ~2% of the original intensities over the data collection period. All reflections were corrected for decay.

Observation of the intensities of several reflections near $\chi = 90°$ at 10° increments of rotation around the diffraction vector showed deviations of only ±3.66% maximum. Absorption was not corrected for, due to the low magnitude of the effect and the difficulty of properly defining the crystal shape.

The location of the bromine atom was easily determined from a three-dimensional Patterson map. A difference Fourier phased by the refined bromine revealed the positions of all other nonhydrogen atoms. After three cycles of full-matrix least squares with isotropic and three cycles with anisotropic thermal parameters for all atoms, the residuals were $R = 5.80\%$, $wR = 9.45\%$, and "goodness-of-fit" = 5.38 for 2139 reflections with $F_o^2 > 3\sigma(F^2)$. The residuals are defined by the equations $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variable parameters. A difference Fourier map clearly showed the positions of all 27 hydrogen atoms. These were included in the final cycles of least-squares refinement with their isotropic thermal parameters fixed at reasonable values. The final refinement of 298 parameters against 2139 reflections with $F^2 > 3\sigma(F^2)$ converged to final residuals of $R = 2.88\%$, $wR = 3.78\%$, and GOF = 2.20. The final difference Fourier was essentially flat with no significant peaks. Analysis of the residuals with respect to $(\sin\theta)/\lambda$, $|F_o|$, and index values and parities showed no abnormal features.

Throughout the structural analysis the analytical scattering factor tables for the neutral atoms were used.[20a] The structure factors of the nonhydrogen atoms were corrected for the real and imaginary components of anomalous dispersion for molybdenum radiation.[20b] The quantity minimized by least squares was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o)$ and where $\sigma(F_o) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}/2F_o$. The "$p$ factor", introduced to lower the weights of very strong reflections, which are subject to systematic errors, was set to 0.025 throughout the refinement.

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Supplementary Material Available: Tables of positional and thermal parameters (Tables II and III), tables of bond lengths and bond angles (Tables IV and V), and a table of selected torsional angles (Table VI) (6 pages). Ordering information is given on any current masthead page.

(20) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England, 1974: (a) Vol. IV, pp 99–101; (b) Vol. IV, pp 149–150.