as 5. 2-Ethoxy-3-indolone (1) was not thermally reactive with less polar olefins such as styrene even at higher temperatures.

## Experimental Section

The nmr spectra were obtained using Varian A-60A and HA100 spectrometers, and ir spectra were recorded with a Perkin-Elmer 337 spectrophotometer. Elemental analysis was performed by Atlantic Microlabs, Atlanta, Georgia.

**2-Ethoxy-3-indolone (1).** 2-Ethoxy-3-indolone was prepared by the reaction of ethyl iodide with the silver salt of isatin. Silver nitrate (200 g, 1.18 mol) was dissolved in 500 ml of water and added with stirring to 128 g (1.2 mol) of sodium carbonate dissolved in 500 ml of water. The yellow precipitate was collected by suction filtration, washed with water, and dried at 140° in the dark until the weight was constant. Isatin (160 g, 1.09 mol), the dry silver carbonate (156 g, 1.13 equiv of silver), 2 g of silver nitrate and 3 l. of ethanol were placed in a 5-l. three-neck flask equipped with a mechanical stirrer and condenser and refluxed for 14 days. The silver salt of isatin was then removed by vacuum filtration and washed several times with ethanol. The salt was dried at ambient temperature under vacuum to a constant weight of 214 g. Evaporation of the ethanol washes gave 89 g (0.6 mol) of recovered isatin.

The dried silver salt (125 g) and 2 l. of chloroform were placed in a 5 l. three-neck flask equipped as above and brought to reflux for 1 hr. The mixture was cooled and 79 g (0.5 mol) of ethyl iodide was added. The reaction was stirred for 10 days at ambient temperature, the precipitate was removed by vacuum filtration through Celite, and the red chloroform filtrate was evaporated to give 29.5 g of crude 2-ethoxy-3-indolone. The precipitate collected on Celite was dried as before and allowed to react with an additional 48 g (0.3 mol) of ethyl iodide under the same conditions as described above. Work-up gave an additional 29 g of crude product. The crude material was sublimed four times at 50° (0.01 mm) to yield 32 g (38% based on isatin consumed), mp 61–62° (lit.[7] 52°). The purified 2-ethoxy-3-indolone gave the following spectral absorptions: nmr ($CDCl_3$) $\delta$ 1.49 (t, $J$ = 7 Hz, 3 H), 4.53 (q, $J$ = 7 Hz, 2 H), 7.01–7.42 ppm (m, 4 H); ir ($CHCl_3$) 1750 and 1600 $cm^{-1}$.

**Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2) in an Nmr Tube.** 1,1-Dimethoxyethene (40 mg, 0.45 mmol) and 0.5 ml of deuteriochloroform were placed in an nmr tube and the 100-MHz spectrum was recorded, $\delta$ 3.06 (s, 2 H) and 3.59 ppm (s, 6 H). Then 60 mg (0.34 mmol) of 2-ethoxy-3-indolone was added to the above solution. Three minutes after the addition, the spectrum was taken and consisted simply of the sum of the spectra of 1,1-dimethoxyethene and 2-ethoxy-3-indolone. After 10 min at 40° shoulders appeared on the low-field side of each of the peaks of the methylene quartet of 2-ethoxy-3-indolone. After 30 min at 40° each peak of the methylene quartet appeared as distinct doublets, a shoulder appeared to the high-field side of the methoxy peak at 3.59 ppm, a new singlet appeared at 3.42 ppm, and an AB pattern appeared at 2.78 and 3.29 ppm ($J$ = 12 Hz). After 2 hr in the probe of the spectrometer, these new peaks, along with the methyl triplet and aromatic proton absorptions, were the only significant peaks in the spectrum, discounting the residual 1,1-dimethoxyethene absorptions.

**Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2) Observed in an Ir Cell.** 2-Ethoxy-3-indolone (120 mg, 0.68 mmol), 1,1-dimethoxyethene (60 mg, 0.68 mmol), and 0.51 ml of chloroform were placed in an nmr tube and the thermal cycloaddition was followed by nmr until the reaction reached 90% completion as judged by observation of the change in the methylene quartet pattern of the spectrum at $\delta$ 4.53 ppm. An aliquot was then withdrawn from the nmr tube and diluted to a suitable concentration with chloroform. The ir spectrum contained a small absorbance at 1650 $cm^{-1}$ ($A$ = 0.1) due to residual 1,1-dimethoxyethene in addition to the carbonyl absorbance at 1750 $cm^{-1}$ ($A$ = 0.15) and the carbon–nitrogen double bond stretching band at 1600 $cm^{-1}$ ($A$ = 0.80) from residual 2-ethoxy-3-indolone and the cycloadduct (3). Thus, the ratio of the absorbances in the reaction mixture (C=O:C=N) was 0.19, whereas the ratio of absorbances (C=O:C=N) was 0.45 for pure 2-ethoxy-3-indolone in chloroform solution.

**Thermal Reaction of 2-Ethoxy-3-indolone (1) with 1,1-Dimethoxyethene (2).** A 100-ml three-neck flask equipped with a magnetic stirrer, condenser, and nitrogen inlet was charged with 0.50 g (2.9 mmol) of 2-ethoxy-3-indolone, 0.40 g (4.5 mmol) of 1,1-dimethoxyethene, and 50 ml of chloroform. The flask was heated at 40° for 12 hr and an additional 0.40 g of 1,1-dimethoxyethene was added. After the solution was heated for an additional 12 hr, it was transferred to a separatory funnel, 50 ml of water was added, and the mixture was shaken vigorously. The organic layer was separated and dried with magnesium sulfate, and the chloroform was removed by rotary evaporation. The residue solidified and was sublimed at 110° (0.01 mm). The sublimate was then recrystallized twice from ether–petroleum ether (bp 30–40°) to give 0.28 g of white crystals (40%), mp 108–110°. The product was identified as methyl 3-(2-ethoxy-3-hydroxyindoleninyl)acetate (4) from the following spectral absorptions: nmr ($CDCl_3$) $\delta$ 1.40 (t, $J$ = 7 Hz, 3 H), 2.83 (s, 2 H), 3.71 (s, 3 H), 4.42 (q, $J$ = 7 Hz, 2 H), 4.55 (broad, 1 H), and 7.25 ppm (m, 4 H); ir ($CHCl_3$) 3480, 1720, 1625, and 1590 $cm^{-1}$; mass spectrum (70 eV) $m/e$ 249 (41), 220 (4.9), 219 (15), 190 (6), 188 (6), 176 (21), 162 (10), 161 (14), 148 (21), 146 (base), 134 (6), 119 (8), 90 (23); (12 eV) $m/e$ 250 (18), 249 (base).

*Anal.* Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.06; N, 5.62. Found: C, 62.62; H, 6.11; N, 5.51.

**Acknowledgment.** The authors wish to thank the National Institutes of Health (GM-18349) and The American Cancer Society for generous support of this work.

**Registry No.**—1, 53153-60-9; 2, 922-69-0; 3, 53153-61-0; 4, 53153-62-1; ethyl iodide, 75-03-6; isatin silver salt, 5711-07-9.

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# Bis Homologation of a Naphthalene to a Dihydroheptalene *via* Carbenoid Addition[1a]

J. D. White*

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331*

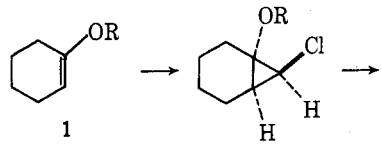
L. G. Wade, Jr.[1b]

*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*

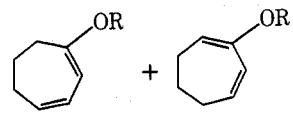
*Received July 15, 1974*

The homologation of a bicyclo[4.4.0]decane, with simultaneous enlargement of both rings to a bicyclo[5.5.0]dodecane, was first demonstrated by Anderson and Barlow[2] and subsequently was exploited by Dauben and Bertelli in their elegant synthesis of heptalene.[3] In a search for alternate approaches to heptalene derivatives, we have found that this double-ring expansion can be accomplished conveniently by a bis addition of dibromocarbene to a tetrahydronaphthalene.

Parham, *et al.*, have shown that ring enlargement of a 1-alkoxycyclohexene (1) to alkoxycycloheptadienes **3a** and **3b** occurs when the derived *endo*-chlorocyclopropane **2** is heated in the presence of pyridine.[4] The rigid requirement for the endo halide in this reaction implies firm control of the electrocyclic opening (disrotatory) of the cyclopropyl cation by orbital symmetry constraints.[5] Application of this

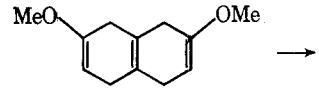


1 2

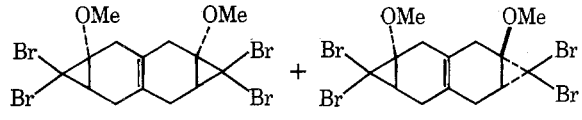


3a 3b

approach to 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene (4), prepared by Birch reduction of 2,7-dimethoxynaphthalene,[6] required selective addition of dibromocarbene to the two enol ether functions of 4, and this was achieved by the use of 2.2 equiv of bromoform in the presence of potassium *tert*-butoxide, which led to a mixture of syn (5) and anti (6) adducts in *ca.* 80% yield.[7] Mono- and tris(dibromocarbene) adducts were produced in only very minor amounts in this reaction, as determined by mass spectrometry and ascertained by thin-layer chromatography, but these were not separated.

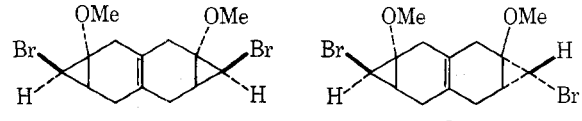


4



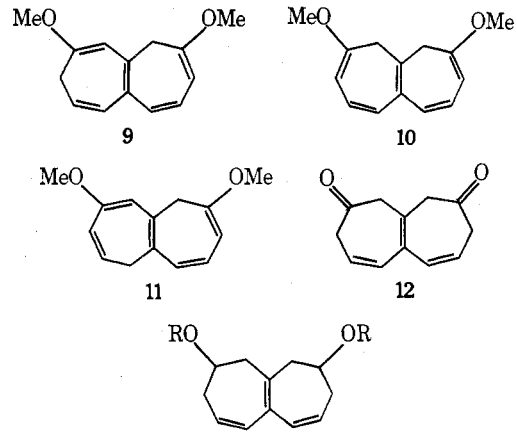
5 6

Stereoselective, reductive removal of the two exo halogens in 5 and 6 parallels similar results in related systems[4,8] and in the present case was most easily accomplished (on a 1-mmol scale) by electrolysis at a stirred mercury cathode in LiCl–DMF.[9] For larger scale reductions, transmetalation of 5 and 6 with 2 equiv of butyllithium at −78°, followed by methanolysis, proved to be the method of choice.[10] In both cases, virtually the sole products were the endo,syn,endo and endo,anti,endo dibromides (7 and 8, respectively), separable by thin-layer chromatography and characterized in each case by a coupling constant of 9 Hz between cis hydrogens on the cyclopropane rings.[11]



7 8

Upon heating at 100° in pyridine for 1 hr, the mixture of 7 and 8 was smoothly transformed to dihydroheptalene 9, isolated in pure form after column chromatography. In contrast, treatment of 7 and 8 with silver salts under a variety of conditions led to a large number of decomposition products.[12] Support for structure 9 comes from the uv spectrum, which reveals an extended chromophore (342 nm), and from the nmr spectrum, which shows nonequivalent methoxyl protons and six olefinic hydrogens. From the nmr data, the symmetrical dihydroheptalene 10 (but not 11) is eliminated. Gentle hydrolysis of 9 with aqueous oxalic acid gave the crystalline diketone 12, shown by ir (1710 $cm^{-1}$) to possess nonconjugated carbonyl groups. Although 12 is evidently the thermodynamically stable isomer, since no rearrangement to an $\alpha,\beta$-unsaturated ketone could be induced under acidic conditions,[13] the mild hydrolysis of 9 probably does not provoke a shift of non-enol double bonds.



9 10 11 12



13, R = H
14, R = $COCH_3$

The approach described here provides a potential route to various substituted heptalenes which is under investigation. In an attempt to bring our scheme into convergence with Dauben and Bertelli's synthesis of the parent heptalene,[3] 12 was reduced with sodium borohydride to diol 13 which was converted to diacetate 14. However, neither dehydration of 13 nor pyrolysis of the surprisingly stable 14 produced useful quantities of dihydroheptalene.

## Experimental Section

Mass spectra were determined on an AEI MS-9 double-focusing spectrometer, using a standard ionizing potential of 70 eV. All compounds subjected to mass spectrometric molecular weight determination were of high purity, as determined by nmr analysis and by homogeneity in thin-layer chromatography where applicable. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates T-60 or HA-100 spectrometer, in either the frequency sweep or Fourier transform mode. Absorptions are reported relative to an internal tetramethylsilane standard (0.00 ppm). Infrared spectra were obtained on a Perkin-Elmer Model 137, 237, or 457 spectrophotometer, and ultraviolet spectra were determined on a Cary Model 14 spectrometer. Elemental analysis was performed by Dr. Susan Rottschaefer, Department of Chemistry, University of Oregon. Melting points were determined on a Kofler hot-stage microscope, and all melting points and other temperatures are reported in degrees Celsius (uncorrected).

**2,7-Dimethoxy-1,4,5,8-tetrahydronaphthalene (4).** To a solution of 15 g (0.077 mol) of 2,7-dimethoxynaphthalene (mp 137–138°) in 400 ml of anhydrous *tert*-butyl alcohol, 400 ml of anhydrous THF, and 1 l. of liquid ammonia was added lithium wire (22 g, 3.1 mg-atoms) in small amounts over a 40-min period. The dark blue solution was stirred for 8 hr, after which the reaction was quenched with 400 ml of methanol. One liter of water was added, and the aqueous layer was extracted three times with methylene chloride. The combined methylene chloride washings were washed twice with water and once with saturated NaCl solution. Evaporation of solvent followed by crystallization of the residue from methanol at −40° gave 12.9 g (0.066 mol, 87%) of 4, mp 61–62° (lit.[6] mp 69–69.5°): ir (KBr) 1012, 1152, 1221, 1373, 1458, 1680, 1725 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 2.58 (8 H, s), 3.52 (6 H, s), 4.60 (2 H, s).

*Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.26; H, 8.35.

**1,5-Dimethoxy-6,6,12,12-tetrabromotetracyclo[9.1.0$^{3,9}$.0$^{5,7}$]-dodec-3(9)-ene (5 and 6).** A solution of 0.38 g (1.9 mmol) of 4 and 0.77 g (8.0 mmol) of potassium *tert*-butoxide in 16 ml of benzene and 10 ml of *tert*-butyl alcohol was cooled to 0°, and a solution of 0.7 ml (2.0 g, 8.0 mmol) of bromoform in 6 ml of benzene was added with stirring over a 0.5-hr period. The solution was then stirred for 1 additional hr at 0°. Approximately 20 ml of water and 20 ml of diethyl ether were added, and the layers were separated. The aqueous layer was extracted several times with ether, and the ether layers were combined, washed with water, dried over $MgSO_4$, and evaporated to yield 0.95 g of the crude tetrabromide. A rapid column chromatography (activity II alumina, eluted with methy-

lene chloride) afforded 0.8 g (1.5 mmol) of 5 and 6 as a clear, light yellow oil. Precipitation from chloroform–hexane gave 0.6 g (1.1 mmol, 58%) of 5 and 6 as an amorphous yellow solid: ir (film) 570, 663, 754, 863, 980, 1030, 1115, 1157, 1207, 1220, 1258, 1383, 1428, 1608, 1677, 1692, 1710, 2830, 2885, 2935, 2995 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 1.7–2.8 (10 H, m), 3.50 (6 H, s); mass spectrum *m/e* 536 (parent, pentuplet of spacing 2 mass units).

**1,5-Dimethoxy-6,12-dibromotetracyclo[9.1.0$^{3,9}$,0$^{5,7}$]dodec-3(9)-ene (7 and 8). A. Electrochemical Reduction.** A three-compartment electrolysis cell was constructed from a vigorously stirred mercury pool cathode, a platinum gauze anode, a catholyte consisting of 30 ml of 1.0 *N* LiCl in 96% DMF–4% water, and anolyte consisting of 4 ml of 1.0 *N* LiCl in 86% DMF–4% water–10% hydrazine, and a Ag–AgCl standard reference electrode. The cathode and anode chambers were separated by a fine-porosity fritted disk, and the standard electrode was isolated by a cracked-glass tube filled with the catholyte solution. All solutions were deoxygenated using argon, and argon was bubbled through the cell continuously during the electrolysis. The cell was positioned in an ice bath and operated for 15 min at a cathode potential of −2.00 V with respect to the reference electrode. A solution of 265 mg (0.5 mmol) of 5 and 6 in 4 ml of DMF was then added, and electrolysis was allowed to proceed (*ca.* 0.75 hr) until the cell current approached the previously determined background current of *ca.* 10 mA. The catholyte was poured into a mixture of 100 ml each of water and pentane, and the pentane layer was washed with water and evaporated to give 190 mg (0.5 mol, 100%) of 7 and 8.

**B. *Via* Halogen–Metal Exchange.** A solution of 265 mg (0.5 mmol) of tetrabromides 5 and 6 in 2 ml of THF was cooled to −80° and treated with 0.7 ml (1.1 mmol) of *n*-butyllithium (Foote, 1.6 *N*). The mixture was stirred at −80° for 15 min and then quenched by the addition of 0.5 ml of methanol. Approximately 10 ml each of ether and water were added, and the ether layer was washed, dried over $MgSO_4$, and evaporated to yield crude dibromide. Preparative-layer chromatography (silica gel, eluted with $CHCl_3$) yielded 160 mg (0.42 mmol, 85%) of 7 and 8: ir ($CDCl_3$) 605, 870, 1032, 1044, 1147, 1197, 1230, 1326, 1357, 1397, 1430, 1720, 2833, 2905, 2950, 3005, 3050, 3070 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 1.60 (2, H, d, $J$ = 9 Hz), 1.65 (2 H, d, $J$ = 9 Hz), 1.92 (2 H, s), 2.44 (6 H, broad s), 3.42 (6 H, s); mass spectrum *m/e* 377 (parent, triplet of spacing 2 mass units). This material was identical in all respects with the two dibromides prepared by method A above.

**2,9-Dimethoxy-1,8-dihyroheptalene (9).** A solution of 2.62 g (6.93 mmol) of 7 and 8 in 50 ml of anhydrous pyridine was stirred for 1 hr at 100°. The mixture was evaporated *in vacuo*, and the residue was taken up into ether, washed with 1 *N* $CuSO_4$ solution, dried over $MgSO_4$, and evaporated to yield 0.9 g of crude pyrolysate. Column chromatography (silica gel, eluted with $CHCl_3$) gave 0.53 g (2.46 mmol, 28%) of pure 9: ir 1020, 1170, 1204, 1225, 1268, 1423, 1544, 1620, 2840, 2963, 3010 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 2.50 (2 H, d, $J$ = 7 Hz), 2.67 (2 H, s), 3.55 (3 H, s), 3.71 (3 H, s), 5.1–6.5 (6 H, m); uv (EtOH) $\lambda_{max}$ 342 nm ($\epsilon$ 6000); mass spectrum *m/e* 216.114 (parent, calcd for $C_{14}H_{16}O_2$ 216.115).

**Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-dione (12).** A solution of 100 mg of 9 in 3 ml of acetone, 0.6 ml of water, and 0.3 ml of concentrated hydrochloric acid was stirred for 25 min at room temperature. The reaction mixture was poured into saturated $NaHCO_3$ solution, which was extracted three times with ether. The ether layers were combined, washed with water, dried over $MgSO_4$, and evaporated to yield 86 mg (0.46 mmol, 100%) of nearly pure 12. Recrystallization from EtOH–water gave 81 mg (0.43 mmol, 93%) of 12, mp 107–109°: ir 790, 972, 1143, 1188, 1240, 1405, 1574, 1707, 2920, 3015, 3400 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 3.06 (4 H, d, $J$ = 6 Hz), 3.26 (4 H, s), 5.89 (2 H, d of t, $J$ = 5.5, 6 Hz), 6.33 (2 H, d, $J$ = 11 Hz); uv (EtOH) showed end absorption only; mass spectrum *m/e* 188.085 (parent, calcd for $C_{12}H_{12}O_2$ 188.084).

*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.21; H, 6.37.

**Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-diol (13).** A solution of 130 mg (0.69 mmol) of 12 and 50 mg (1.3 mmol) of sodium borohydride in 10 ml of anhydrous EtOH was stirred for 1 hr at 0°. The reaction mixture was poured into water and extracted three times with ether. The combined ether layers were washed with water, dried over $MgSO_4$, and evaporated to yield 125 mg of crude diol. Preparative-layer chromatography gave 110 mg (0.58 mmol, 84%) of pure 13: ir ($CDCl_3$) 910, 1018, 1082, 1262, 1444, 2910, 2950, 3005, 3440, 3608 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 2.01 (2 H, broad s), 2.2–2.5 (2 H, m), 2.51 (4 H, d, $J$ = 6 Hz), 4.39 (2 H, quintet, $J$ = 6 Hz), 5.89 (4 H, s); mass spectrum *m/e* 192.118 (parent, calcd for $C_{12}H_{16}O_2$ 192.115).

**Bicyclo[5.5.0]dodeca-1,9,11-triene-4,7-diacetate (14).** A solution of 20 mg (0.104 mmol) of 13, 75 mg of acetic anhydride, and 135 mg of 4-(*N*,*N*-dimethylamino)pyridine in 2 ml of $CH_2Cl_2$ was stirred for 15 min at room temperature. The reaction mixture was cooled to 0°, 0.5 ml of methanol was added, and all volatiles were evaporated. The residue was taken up into ether, which was washed with 2 *N* HCl and then with saturated $NaHCO_3$ solution. The ethereal solution was dried over $MgSO_4$ and evaporated to give 27 mg (0.98 mmol, 94%) of pure 14: ir ($CHCl_3$) 1022, 1100, 1260, 1378, 1443, 1734, 2962 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 2.04 (6 H, s), 2.1–2.4 (4 H, m), 2.49 (4 H, d, $J$ = 6 Hz), 5.28 (2 H, m), 5.89 (4 H, d, $J$ = 2 Hz); mass spectrum *m/e* 276 (parent), 216 (loss of HOAc), 156 (base peak, loss of 2 HOAc).

**Acknowledgment.** We are grateful to Professor David Dolphin for assistance with electrochemical aspects of this work and to Professor Weston Borden for helpful discussions.

**Registry No.**—4, 1614-82-0; 5, 53165-97-2; 6, 53187-74-9; 7, 53165-98-3; 8, 53187-75-0; 9, 53165-99-4; 12, 53166-00-0; 13, 53166-01-1; 14, 53166-02-2; 2,7-dimethoxynaphthalene, 3469-26-9.

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# A New Fragmentation Reaction and Its Application to the Synthesis of (±)-Grandisol

Robert L. Cargill* and Ben W. Wright

*Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208*

*Received July 1, 1974*

Grandisol (1), a component of the pheromone released by the male boll weevil, *Anthonomus grandis* Boehman,[1] has been synthesized by a variety of routes.[2] We report here a convenient synthesis of racemic 1 that involves a novel fragmentation of an ozonide.

Condensation of 3 with benzaldehyde, furfural, or acetone provided an alkylidine derivative 4. Reaction of 4 with methyllithium yielded the corresponding tertiary alcohol 5. Ozonolysis of 5 at −70° in methylene chloride followed by decomposition of the presumed ozonide 6 in aqueous sodium bicarbonate gave keto acid 2 in an overall yield of 40–50% from 3. Conversion of 2 into 1 has been reported.[2]

Although all three alkylidine derivatives 5a–c gave 2 in acceptable yields, 5c is the preferred intermediate. Ozonol-