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Optical Purity and Optical Rotatory Power of Dehydronorcamphor[1a]

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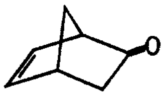
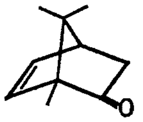
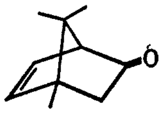
The optical properties of dehydronorcamphor have been reinvestigated. The previously reported absolute rotation and ORD amplitude of the n → π* transition have been confirmed by an independent determination of the optical purity by nmr spectroscopy. The circular dichroism has been found to match closely the corresponding values reported for the n → π* transition of dehydrocamphor and dehydroepicamphor.

Bicyclo[2.2.1]hept-5-en-2-one (dehydronorcamphor, **1**) a simple archetype of the dissymmetric β,γ-unsaturated carbonyl chromophore, figures as a key compound in studies of the relationship between optical rotatory power and chemical structure, both from the theoretical[2] and the experimental[3-6] points of view.

It is therefore of interest to note that while (+)-**1** and dehydrocamphor [(−)-**2**] are reported to have similar molecular amplitudes for the Cotton effect of their lowest lying n → π* transition (*a* +780 ± 40[4] and *ca.* −840,[7] respectively), corresponding to similar extinction coefficients [ε 277 (λ_{max} 307.5 mμ) and 308 (λ_{max} 304 mμ) for **1**[2a] and **2**[6]], the corresponding molecular ellipticites are reported to differ significantly ($[\theta]_{max}$ +3.18 × 10^4 and −5.89 × 10^4 for **1**[5] and **2**,[6] respectively). This result is contrary to expectations since, even taking into account that the values cited for **1** and **2** refer to different solvents (hydrocarbon and ethanol, respectively), **1** and **2** do have similar chromophoric geometries and the rotational strengths should clearly manifest parallel behavior in ORD and CD.[2] In terms of the semiquantitative expression relating molecular amplitude and circular dichroism of ketones,[8] $[\theta]_{max}$ values of +6.4 and −6.9 × 10^4 might have been predicted from the *a* values of **1** and **2**, respectively, or, conversely, *a* values of +390 and −720 might have been predicted from the reported $[\theta]_{max}$ values of **1** and **2**, respectively. Whereas calculated and reported values for *a* and $[\theta]_{max}$ of **2** are in reasonable agreement, the corresponding values for **1** are grossly mismatched.


(+)-1


(−)-2


(+)-3

Similar considerations were advanced by Bays, Cookson, and MacKenzie who pointed out that, given the similarity in the extinction coefficients of the lowest n → π* transition of **1**, **2**, and dehydroepicamphor (**3**) [ε 325 (λ_{max} 310 mμ)], and given the roughly linear relationship of extinction coefficients (log ε) to optical rotatory power (log *a* or log Δε) of ketones,[9] the $\Delta\epsilon_{max}$ values in the CD curves of **1**–**3** would be expected to be closely similar. In fact, reported values for $\Delta\epsilon_{max}$ in hydrocarbon solvents are +9.6, −18.5, and +19.9 for **1**,[5] **2**,[6] and **3**,[6] respectively, once again identifying **1** as the source of the discrepancy. However, because of the close agreement in $\Delta\epsilon_{max}$ values of **2** and **3**, it is the reported circular dichroism of **1** to which the finger of suspicion points, the more so since the $\Delta\epsilon_{max}$ value of **1** calculated[6,8] from the published[4] ORD amplitude is +19.4.

To resolve this discrepancy, we have reinvestigated the ORD and CD of **1**.

Compound **1** was prepared as previously described, *i.e.*, by asymmetric hydroboration of norbornadiene to *exo*-dehydronorborneol (**4**), followed by oxidation to **1**. Use of (−)-α-pinene in the asymmetric hydroboration gave the enantiomer (*i.e.*, (−)-**1**) of the previously studied[4,5] sample.

Since the asymmetric hydroboration furnishes optically impure material, it is crucial to obtain an accurate measure of the optical purity of **1** for purposes of comparison with **2** and **3**, which are obtained from natural sources and are presumed to be optically pure. The optical purity of **1** had previously been estimated[4] by relating **4** and the derived (+)-**1** to *exo*-norborneol, whose optical purity had been established by the isotope dilution method.[10] To be doubly sure, the optical purity of **1** was established in the present work by an entirely independent method, *i.e.*, by nuclear magnetic resonance spectroscopy.[11]

Reaction of racemic dehydronorborneol (*exo*/*endo* ratio 87:13) with an equimolar amount of racemic O-methylmandelyl chloride gave a mixture of esters whose nmr spectrum at 60 MHz in benzene solution showed

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[1] (a) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67; (b) National Aeronautics and Space Administration Fellow, 1965–1968.

[2] (a) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962); (b) R. E. Ballard, S. F. Mason, and G. W. Vane, *Trans. Faraday Soc.*, **59**, 775 (1963); (c) A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolymers, Symp.*, **1**, 75 (1964); (d) A. Moscowitz, *Proc. Roy. Soc.*, **A297**, 16, 40 (1967); (e) E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

[3] (a) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962); (b) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, pp 235–236; (c) R. C. Cookson, *Proc. Roy. Soc.*, **A297**, 27 (1967); (d) G. Snatzke, *ibid.*, 43 (1967).

[4] K. Mislow and J. G. Berger, *J. Amer. Chem. Soc.*, **84**, 1956 (1962).

[5] E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *ibid.*, **84**, 2823, 5003 (1962).

[6] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., Sect. B*, 215 (1967).

[7] P. J. Mälkönen and R. Frostell, *Suomen Kemistilehti, Sect. B*, **40**, 84 (1967).

[8] Reference 3b, p 19, gives $a = 0.0122[\theta]_{max}$; $a = 40.28\,(\Delta\epsilon_{max})$.

[9] S. F. Mason, *J. Chem. Soc.*, 3285 (1962); S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

[10] J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **81**, 4088 (1959).

[11] (a) M. Raban and K. Mislow, "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 216 ff; (b) M. Raban and K. Mislow, *Tetrahedron Lett.*, 3961 (1966); J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.*, **33**, 1142 (1968), and references cited therein.

the following relevant features: the diastereotopic methoxymethine protons (CH_3OCH) of the diastereomers derived from **4** were not perceptibly anisochronous; the signals of the methoxy protons (CH_3O) of the diastereomers derived from either **4** or *endo*-dehydronorborneol (**5**) were separated by *ca.* 1 Hz; the signals of the methoxymethine protons of the diastereomers derived from **5** were separated by *ca.* 2 Hz. The chemical shift nonequivalence of the diastereotopic methoxymethine protons derived from **5** could therefore be used as the basis for estimating the optical purity by nmr. Reaction of racemic **5** with an excess of optically pure O-methylmandelyl chloride gave a 1:1 mixture of diastereomers, as judged by integration of the methoxymethine proton resonances at 100 MHz.

Sodium borohydride reduction of (−)-**1**, $[\alpha]^{23}_{\mathrm{D}}$ −525° (isooctane), gave a mixture of diastereomeric dehydronorborneols, (−)-**5** and (−)-**4**, in a ratio of 91:9. Reaction of this mixture with optically pure (*R*)-O-methylmandelyl chloride gave a mixture of diastereomeric esters. The ratio of esters derived from (−)-**5** was 2.65:1.00 as judged by integration and area measurement of the appropriate methoxymethine proton resonances at 100 MHz.[12] This corresponds to an optical purity of 45.2% in the precursor alcohol (−)-**5**. The starting ketone was therefore also 45.2% optically pure, and the absolute rotation of (−)-**1**, *i.e.*, the rotation of the pure enantiomer, is calculated to be $[\alpha]_{\mathrm{D}}$ −1160° (isooctane). This value is in satisfactory agreement with the value of $[\alpha]_{\mathrm{D}}$ +1140° (isooctane) which may be calculated from the previously reported[4] rotation ($[\alpha]_{\mathrm{D}}$ +548° (isooctane)) and optical purity (48.0%). To our knowledge, this is the first example in which the absolute rotation of a compound has been independently established by isotope dilution and nmr spectroscopy.

It may be noted in this connection that the elegant approach developed by Pirkle,[13] in which the chemical shift nonequivalence of corresponding nmr signals in diastereomerically solvated enantiomers (*i.e.*, enantiomers dissolved in a chiral medium) affords a measure of optical purity which is absolute in the sense that no reference to a standard of optical purity is required, is inconvenient to apply in the present instance where the substances whose optical purities are to be determined (*i.e.*, **1**, **4** or **5**) show complex spin–spin coupling.

The ORD of (−)-**1** in isooctane was found to be substantially the same in shape and amplitude as the one previously reported[4] for the enantiomer. The molecular amplitude, corrected to optical purity, was a −840 ± 20 for the transition centered near 308 mμ, in satisfactory agreement with the previous determination,[4] a +780 ± 40, and identical with the value found[7] for **2** in ethanol. However, the CD intensity of (−)-**1** in isooctane differed substantially in magnitude from that previously reported[5] for the enantiomer. The molecular ellipticity of (−)-**1**, corrected to optical purity, was found to be $[\theta]_{\max}$ -6.80×10^4 for the transition centered at 308 mμ, in excellent agreement with the value of $[\theta]_{\max}$ -6.9×10^4 calculated[8] from the measured amplitude of the ORD curve, but in poor agreement with the earlier measurement[5] on (+)-**1**, $[\theta]_{\max}$ $+3.18 \times 10^4$. It must be concluded that the latter value is in error, as had been surmised.[6]

Cookson, *et al.*,[3c,6] have suggested that in β,γ-unsaturated ketones such as **1–3**, the rotational strengths of the $n \rightarrow \pi^*$ and short-wavelength ("charge-transfer") transitions should be nearly equal in magnitude and opposite in sign; indeed, the CD curves of **2** and **3** do change sign at shorter wavelengths.[6] However, in the case of (−)-**1** we have been able to record the complete CD curve in isooctane corresponding to the transition near 212 mμ, and have observed a negative Cotton effect with $[\theta]_{\max}$ -2.5×10^4 at 215 mμ.[14] Consequently, the Cotton effects associated with the long-wavelength and short-wavelength transitions of **1** are of the *same* sign, in contrast to the behavior observed[6] for the closely analogous β,γ-unsaturated ketones **2** and **3**.

Experimental Section[15]

(−)-**Dehydronorcamphor** (1) was prepared in the manner previously described,[4] using (−)-α-pinene ($[\alpha]^{23}_{\mathrm{D}}$ −39.4° (neat)) for the preparation of (+)-*sym*-tetraisopinocampheyldiborane. Crude 1 was purified by preparative glpc (a 20 ft × $^3/_8$ in. 30% Carbowax 20M on 45–60 mesh Chromosorb W column at 190–200°, helium flow rate 200 cc/min). Under these conditions 1 had a retention time of 12–13 min. The material collected was further purified by distillation (Kugelrohr, 40–60° at 2 mm) to give a colorless liquid which solidified easily on cooling, n^{25}_{D} 1.4840 (lit. n^{25}_{D} 1.4857[16] and n^{25}_{D} 1.4839[17] for racemic 1, and n^{25}_{D} 1.4834[4] for optically active 1), $[\alpha]^{23}_{\mathrm{D}}$ −525° (c 0.169, isooctane). The material was homogeneous by glpc analysis both on a 2-ft 10% Carbowax 20M on 60–80 mesh Chromosorb W column at 130° (helium flow rate 30 cc/min, retention time 4.9 min), and on a 6-ft 10% Carbowax 4000 on 60–80 mesh Chromosorb W column at 150° (helium flow rate 30 cc/min, retention time 9.6 min). The infrared spectrum was indistinguishable from that of the enantiomer.[4] The ultraviolet spectrum in isooctane solution exhibited the following features: $\lambda_{\max}$ mμ (ϵ) 320 (176), 307.5 (267), 297 (232), 287.5 (156.5), 212 (2550), 204 (2400) [lit.[2a] 319.5 (177), 307.5 (277), 296.5 (242), 287.5 (162); lit.[17] 320, 308 (266), 297; lit.[18] *ca.* 210 mμ]; ORD in isooctane (c 0.0752 g/100 ml at $\lambda > 230$ mμ, c 0.00752 at $\lambda < 230$ mμ, corrected to optical purity), $[\phi]_{321}$ −48,900°, $[\phi]_{316}$ −20,300°, $[\phi]_{309.5}$ −29,000°, $[\phi]_{306}$ 0°, $[\phi]_{300}$ +9560°, $[\phi]_{298}$ +8520°, $[\phi]_{289}$ +30,300°, $[\phi]_{287.5}$ +30,000°, $[\phi]_{280}$ +34, 960°, $[\phi]_{275}$ +33,600°, $[\phi]_{228}$ +6740°, $[\phi]_{203}$ +90,000° (lit.[4] corrected to optical purity, $[\phi]_{322}$ +46,350°, $[\phi]_{316}$ +26,500°, $[\phi]_{311}$ +30,800°, $[\phi]_{305}$ −4430°, $[\phi]_{303}$ −3670°, $[\phi]_{292}$ −24,300°, $[\phi]_{289}$ −24,300°, $[\phi]_{281}$ −31,300°, $[\phi]_{270}$ −25,000°); CD in isooctane, corrected to optical purity (c 0.094 g/100 ml at $\lambda > 230$ mμ, c 0.0094 at $\lambda < 230$ mμ), $\lambda_{\max}$, mμ ($[\theta]$), 340 (0), 318 (−47,300), 306.5 (−68,000), 296 (−55,300), 286 (−34,600), 215 (−25,000), 205 (0), $[\theta] > 0$ below 205 mμ.

Racemic dehydronorcamphor (1) was prepared from racemic dehydronorborneol (Aldrich *exo–endo* mixture) in the same manner as the optically active material.

Racemic *endo*-dehydronorborneol (5) was prepared by sodium

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[12] The methoxymethine proton resonance of the O-methylmandelates of **4** appears as a signal which is well separated from the signals of the esters derived from **5**.

[13] W. H. Pirkle, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); T. G. Burlingame and W. H. Pirkle, *ibid.*, 4294 (1966); W. H. Pirkle and T. G. Burlingame, *Tetrahedron Lett.*, 4039 (1967); W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **89**, 5485 (1967).

[14] In the previous CD measurement[5] carried out on (+)-**1**, the beginnings of a positive Cotton effect at shorter wavelengths could be discerned, but the maximum could not be reached.

[15] Elemental analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Nmr spectra were measured on a Varian A-60A or Varian HA-100 spectrometer in *ca.* 10% benzene solution. Chemical shifts in the 60-MHz spectra are reported in hertz upfield from internal benzene, and those in the 100-MHz spectra are reported in parts per million downfield from internal tetramethylsilane. We thank the National Science Foundation for providing the funds for the purchase of the Varian HA-100 spectrometer. ORD measurements were taken on a Cary 60 spectropolarimeter and CD measurements were taken on a Cary 6001 CD accessory.

[16] N. J. Toivonen and J. Kaila, *Suomen Kemistilehti, Sect. B*, **28**, 91 (1955).

[17] P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, **78**, 2473 (1956).

[18] C. A. Grob and A. Gagneux, unpublished work, cited by H. Labhart, and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

borohydride reduction of racemic 1.[19a] Sodium borohydride (0.91 g, 24 mmol) was stirred in isopropyl alcohol (5 ml) at 0°. Racemic 1 (2.0 g, 18.5 mmol) in isopropyl alcohol (5 ml) was added over a period of 10 min, and the mixture was stirred overnight at room temperature. Water and saturated ammonium chloride were added to decompose excess borohydride. The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to give an oily residue whose infrared spectrum indicated the absence of a carbonyl band. The residue was purified by Kugelrohr distillation to give 0.42 g (21%) of a white solid, mp 104.5–113° (lit.[19b] mp 109.4–110.8°), which had an infrared spectrum in satisfactory agreement with the reported[19b] spectrum of 5.

(−)-*endo*-**Dehydronorborneol** (5) was prepared from (−)-1 in a manner analogous to that described above for the racemic compound. The product was purified by distillation (Kugelrohr, 30–50° at 0.005 mm) to give 0.36 g (39%) of a white solid: mp 105–111°; $[\alpha]^{23}\mathrm{D}$ −73.4° (*c* 2.62, chloroform). Analysis by glpc on a 2-ft 10% Carbowax 20 M on 60–80 mesh Chromosorb W column at 131° (helium flow 30 cc/min) indicated an *endo/exo* ratio of 91:9; retention time of the *endo* and *exo* isomers were 5.2 and 6.5 min, respectively.

Anal. Calcd for $C_7H_{10}O$: C, 76.31; H, 9.16. Found: C, 75.98; H, 9.05.

Racemic dehydronorborneol was prepared as previously described.[20] The product was a white solid, mp 60–84° (lit.[20] mp 92–93° for racemic *exo*-dehydronorborneol), which was shown to have an *exo/endo* ratio of 87:13 by glpc analysis, as for 5, above.

Dehydronorbornyl O-Methylmandelate.—Racemic O-methylmandelyl chloride, prepared[11b] from O-methylmandelic acid (1.09 mmol) was stirred magnetically in benzene solution. Pyridine (0.98 g, 12.4 mmol) was added and a precipitate formed. Racemic dehydronorborneol (*exo/endo* ratio 87:13, 0.12 g, 1.09 mmol) in benzene solution was added, and the mixture was stirred at room temperature for 45 min. The work-up was carried out as described for the O-methylmandelamides.[11b] Since impurities were indicated in the nmr spectrum of the crude ester, the product was chromatographed on florisil and eluted with 75:25 v/v benzene–hexane followed by benzene, and 90:10 v/v benzene–ether. The 60-MHz nmr spectrum of the chromatographed material featured a single methoxymethine proton signal at 149 Hz and a single methoxy proton signal at 238 Hz for the mixture of diastereomers from 4. An analytical sample was collected by glpc (2-ft 10% Carbowax 20M at 210°, helium flow 60 cc/min, retention time 8.2 min).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.05; H, 6.81.

endo-**Dehydronorbornyl O-Methylmandelate.**—Optically pure O-methylmandelyl chloride, prepared[11b] from (−)-(*R*)-O-methylmandelic acid (1 mmol), was treated with pyridine (0.24 g, 3 mmol) and racemic 5 (0.0539 g, 0.49 mmol) as above, for 13 hr at room temperature. The crude ester mixture was chromatographed on florisil, as above. The 60-MHz nmr spectrum of the chromatographed material featured the following signals. The methoxymethine protons in the mixture of diastereomers derived from the *exo* contaminant appeared as a singlet at 149 Hz, and the corresponding protons in the diastereomers derived from 5 appeared at 152.5 and 154.5 Hz. The methoxy protons appeared at 238 (shoulder) and 239 Hz. Electronic integration of the methoxymethine resonances for the diastereomers from 5 in the 100-MHz spectrum indicated a ratio of 1:1. An analytical sample was obtained by distillation (Kugelrohr, 110–115° at 0.02 mm).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.30; H, 7.16.

Determination of the Optical Purity of (−)-*endo*-**Dehydronorborneol** (5).—Optically pure O-methylmandelyl chloride, prepared[11b] from (−)-O-methylmandelic acid (1.61 mmol), was treated with pyridine (0.40 g, 5.1 mmol) and (−)-5 (0.0805 g, 0.71 mmol), $[\alpha]^{23}\mathrm{D}$ −73.4° (*c* 2.62, chloroform), as above, for 13 hr at room temperature. The sample used for the nmr measurement was collected by chromatography as described above for racemic dehydronorbornyl O-methylmandelate. The 100-MHz spectrum of the mixture of diastereomers featured the following signals. The methoxymethine protons in the mixture of diastereomers derived from 4 appeared as a singlet at δ 4.63, and the corresponding protons in the diastereomers derived from 5 appeared at 4.59 and 4.55, with that at 4.59 being the more intense. The methoxy protons appeared at δ 3.19 and 3.17. Electronic integration and peak area measurements of expanded scale spectra of the resonances at δ 4.59 and 4.55 indicated that the ratio of diastereomers in the O-methylmandelate derived from (−)-5, and hence the ratio of enantiomers in (−)-5 was 2.65:1.00.

Registry No.—(−)-1, 16620-79-4; (−)-*endo*-5, 16620-80-7; dehydronorbornyl O-methylmandelate, 16620-82-9; *endo*-dehydronorbornyl O-methylmandelate, 16620-81-8.

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[19] (a) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966); (b) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[20] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

Multinuclear Ferrocenes. V. Allylic Oxidation of 1-Ferrocenylcyclopentene[1]

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Allylic oxidations of 1-ferrocenylcyclopentene (3) by selenium dioxide, chromium trioxide, mercuric acetate, and lead tetraacetate have been studied with the view toward development of a suitable entry into the syntheses of new multinuclear ferrocenes. All oxidations were attended by fairly high degrees of decomposition, and products were obtained in low yields. In all cases oxidation was shown to take place exclusively α to the side of the double bond bearing the ferrocenyl group. Thus, **2-ferrocenyl-2-cyclopenten-1-one** (5), **2-ferrocenyl-3-acetoxy-1-cyclopentene** (7), and **2-ferrocenyl-3-ethoxy-1-cyclopentene** (8) were the oxidation products. While the unsaturated ketone (5) underwent unexpected conjugate hydride addition with sodium borohydride to give the saturated alcohol, **2-ferrocenyl-1-cyclopentanol** (9); the unsaturated alcohol, **2-ferrocenyl-2-cyclopenten-1-ol** (6), obtained from hydrolysis of 7, was not reduced upon similar treatment with sodium borohydride.

Whereas general methods of synthesis of systems consisting of directly bonded ferrocene nuclei have not been developed to any significant extent, two basic approaches have been used. One, which involves coupling of substituted ferrocenes, has been shown[2] to proceed without rearrangement to substituted biferrocenyls. This approach, however, is attended with serious difficulties at the present time since good general methods of synthesis of a useful range of coupling components is still undeveloped, particularly for appropriately constituted bi- and terferrocenyls.

The second approach lies in the construction of ferrocenylcyclopentadienes, which may then be complexed or "sandwiched" around iron to give the corresponding multinuclear ferrocene systems. The syn-

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[1] Previous paper in this series: S. I. Goldberg, W. D. Loeble, and T. T. Tidwell, *J. Org. Chem.*, **32**, 4070 (1967).

[2] S. I. Goldberg and R. L. Matteson, *ibid.*, **29**, 323 (1964).