3-Alkoxy-2-oxanorcaranes. Synthesis of Labile Cyclopropanes from Labile Olefins Using an Improved Lithium–Ammonia Reduction Procedure on the Dichlorocarbene Adducts[1]

Angelina J. Duggan[2] and Stan S. Hall*

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, New Jersey 07102

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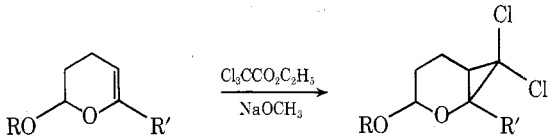
The most serious limitation of the Simmons–Smith cyclopropane synthesis procedure is that labile olefins, which can be polymerized by the strong Lewis acid zinc iodide, sometimes give poor yields.[3] Consequently, it was not too surprising for us to find *no* cyclopropane adducts when the extremely sensitive 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a–d**)[4] were subjected to these conditions. Evidently the major problem with attempts to convert **1a–d** to the corresponding 3-alkoxy-2-oxanorcaranes (**3a–d**) is that both the starting olefins **1a–d** and the cyclopropane products **3a–d** are very acid sensitive. This obstacle was circumvented by first adding dichlorocarbene, generated from ethyl trichloroacetate with sodium methoxide,[5] to the olefins **1a–d**, and then reducing the adducts **2a–d** using an improved metal–ammonia procedure.

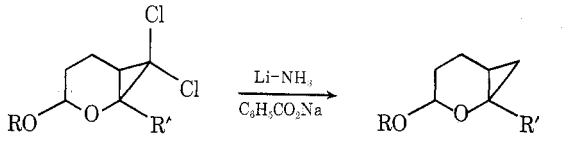
Trans–cis mixtures of 3-alkoxy-2-oxa-7,7-dichlorononorcarane (**2a,b**) and 3-alkoxy-1-methyl-2-oxa-7,7-dichlorononorcarane (**2c,d**) were prepared by the addition of dichlorocarbene to 2-alkoxy-3,4-dihydro-2*H*-pyran (**1a,b**) and 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyran (**1c,d**), respectively.[1] Subsequent reduction of the adducts **2a–d** in lithium–



1a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = CH_3; R′ = CH_3
d, R = C_2H_5; R′ = CH_3

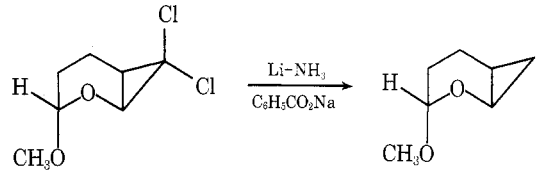
trans- and *cis*-**2a–d**

ammonia, followed by a sodium benzoate quench,[6] gave reasonable isolated yields (62–78%, distilled) of the corresponding trans–cis mixtures of 3-alkoxy-2-oxanorcaranes (**3a,b**) and 3-alkoxy-1-methyl-2-oxanorcaranes (**3c,d**).[7]



trans- and *cis*-**2a–d** *trans-* and *cis*-**3a–d**

The trans to cis ratios did not change during the reduction of the dichlorocarbene adducts **2a–d**; and when a pure isomer, obtained by careful column chromatography, was reduced the configuration was retained. For example, *trans*-3-methoxy-2-oxa-7,7-dichlorononorcarane (*trans*-**2a**) yielded *trans*-3-methoxy-2-oxanorcarane (*trans*-**3a**), exclusively.



trans-**2a** *trans*-**3a**

Quenching the lithium–ammonia reduction step with sodium benzoate[6] is essential. When protonic quenches, such as ammonium chloride or alcohol, were used additional products were detected (GLC) and the isolated yields were substantially lower. In addition, the result obtained with the sodium benzoate quench indicates that the reduction of 1,1-dichlorocyclopropane to cyclopropane is complete in lithium–ammonia and does not require an added proton source.

Experimental Section[8]

The 3-alkoxy-2-oxa-7,7-dichlorononorcaranes (**2a,b**) and 3-alkoxy-1-methyl-2-oxa-7,7-dichlorononorcaranes (**2c,d**) were prepared by a method previously described.[1] All reactions were performed in dry glassware under a static prepurified nitrogen atmosphere which was connected by a T tube to the assembly and to a soda lime drying trap. Anhydrous ammonia was distilled, through a KOH column, directly into the reaction vessel and anhydrous ethyl ether was used directly from freshly opened containers. The lithium wire (0.125 in., 0.01% Na, Ventron Corp.) was wiped free of oil, rinsed in petroleum ether, and cut into small pieces (0.5 cm) just prior to use. Gas chromatography (GLC) was performed on a Hewlett-Packard Model 7610A high-efficiency chromatograph (flame detector) using a 4 ft × 6 mm (all glass) 5% Carbowax 20M on 60–80 Chromosorb W column. Distillations were accomplished with a short-path distillation apparatus at atmospheric pressure. All boiling points are uncorrected.

***trans*-3-Methoxy-2-oxanorcarane (*trans*-3a).** A solution of 4.13 g (21 mmol) of *trans*-3-methoxy-2-oxa-7,7-dichlorononorcarane (*trans*-**2a**) in 25 ml of Et_2O was added dropwise (ca. 5 min) to a stirred solution of 882 mg (126 mg-atoms) of lithium in 25 ml of Et_2O and 125 ml of ammonia. After 30 min the dark-blue color of the solution was discharged by the cautious addition of ca. 4 g of sodium benzoate (ca. 5 min). Pentane (50 ml) was added and the ammonia was allowed to evaporate. The residue was partitioned between pentane and water; then the organic phase was separated, washed with 5% $NaHCO_3$, and dried ($MgSO_4$). Analysis (GLC) indicated one product (*trans*-**3a**), which after distillation yielded 1.80 g (70%) of a colorless oil: bp 125–130° (760 mm); ir (film) 3080, 3010, 2940, 2835, 1455, 1440, 1370, 1210, 1150, 1100, 1045, 940, 900, 810, 720 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.32 (1 H, t, J = 3 Hz, equatorial anomeric proton), 3.31 (3 H, s), 3.27–3.08 (1 H, m), 2.28–1.88 (1 H, m), 1.68–1.35 (3 H, m), 1.11–0.76 (1 H, m), 0.66–0.22 (2 H, m); mass spectrum *m/e* (rel intensity) 100 (8), 97 (15), 72 (10), 71 (10), 68 (14), 67 (14), 59 (16), 58 (100), 45 (12), 43 (10), 41 (34), 39 (13).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.59; H, 9.42.

***trans*- and *cis*-3-Ethoxy-2-oxanorcarane (*trans*- and *cis*-3b).** Treatment of 4.36 g (20.6 mmol) of a 78:22 mixture of *trans*- and *cis*-3-ethoxy-2-oxa-7,7-dichlorononorcarane (*trans*- and *cis*-**2b**) as described above for *trans*-**2a** afforded a 78:22 mixture (analyzed by GLC) of *trans*- and *cis*-**3b** which distilled together, yielding 2.16 g (74%) of a colorless oil: bp 130–135° (760 mm); ir (film) 3080, 3010, 2940, 1440, 1370, 1210, 1150, 1105, 1050, 960, 910, 815, 720 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.44 (0.78 H, t, J = 3 Hz, equatorial anomeric proton), 4.32 (0.22 H, d of d, J = 2.5 and 7.5 Hz, axial anomeric proton), two overlapping quartets centered at 3.73 (1 H, d of q, J = 7 and 10 Hz), and two overlapping quartets centered at 3.39 (1 H, d of q, J = 7 and 10 Hz) superimposed on 3.28–

3.06 (1 H, m), 2.39–1.75 (1 H, m), 1.67–1.34 (3 H, m), two overlapping triplets centered at 1.19 (2.34 H, t, J = 7 Hz) and 1.13 (0.66 H, t, J = 7 Hz), 1.06–0.72 (1 H, m), 0.66–0.21 (2 H, m); mass spectrum m/e (rel intensity) 114 (6), 97 (19), 86 (14), 79 (6), 73 (12), 72 (100), 68 (15), 67 (17), 57 (14), 44 (59), 43 (51), 41 (41).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.66; H, 9.90.

***trans*- and *cis*-3-Methoxy-1-methyl-2-oxanorcarane (*trans*- and *cis*-3c).** Treatment of 5.05 g (24 mmol) of a 80:20 mixture of *trans*- and *cis*-3-methoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*trans*- and *cis*-**2c**) as described above for *trans*-**2a**, except that 945 mg (135 mg-atoms) of lithium was used, afforded a 80:20 mixture (analyzed by GLC) of *trans*- and *cis*-**3c** which distilled together, yielding 2.10 g (62%) of a colorless oil: bp 145–155° (760 mm); ir (film) 3080, 3010, 2960, 2880, 2840, 1450, 1365, 1240, 1210, 1120, 1100, 1040, 1010, 970, 920, 900, 880, 855 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.31 (0.8 H, t, J = 3 Hz, equatorial anomeric proton), which overlaps slightly with 4.23 (0.2 H, d of d, J = 2.5 and 7 Hz, axial anomeric proton), 3.31 (2.4 H, s), 3.28 (0.6 H, s), 2.25–1.76 (1 H, m), 1.75–1.32 (3 H, m), 1.29 (3 H, s), 1.00–0.52 (1 H, m), 0.51–0.25 (2 H, m); mass spectrum m/e (rel intensity) 142 (M^+, 0.7), 114 (8), 112 (5), 111 (12), 72 (20), 71 (18), 67 (14), 58 (100), 55 (8), 45 (15), 43 (55), 41 (24).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.31; H, 9.87.

***trans*- and *cis*-3-Ethoxy-1-methyl-2-oxanorcarane (*trans*- and *cis*-3d).** Treatment of 3.32 g (14.8 mmol) of a 95:5 mixture of *trans*- and *cis*-3-ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*trans*- and *cis*-**2d**) as described above for *trans*-**2a**, except that 640 mg (91 mg-atoms) of lithium was used, afforded a 95:5 mixture (analyzed by GLC) of *trans*- and *cis*-**3d** which distilled together, yielding 1.80 g (78%) of a colorless oil: bp 170–175° (760 mm); ir (film) 3080, 3010, 2970, 2880, 1460, 1380, 1250, 1120, 1105, 1055, 1030, 965, 930, 890, 860, 840 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.45 (ca. 0.95 H, t, J = 3 Hz, equatorial anomeric proton), slightly detectable apparent quartet at ca. 4.34 (ca. 0.05 H, axial anomeric proton), two overlapping quartets centered at 3.78 (1 H, d of q, J = 7 and 10 Hz), two overlapping quartets centered at 3.38 (1 H, d of q, J = 7 and 10 Hz), 2.33–1.76 (1 H, m), 1.70–1.35 (3 H, m), 1.30 (3 H, s), 1.19 (ca. 2.85 H, t, J = 7 Hz) superimposed on 1.15 (ca. 0.15 H, t, J = 7 Hz), 1.03–0.60 (1 H, m), 0.54–0.27 (2 H, m); mass spectrum m/e (rel intensity) 156 (M^+, 2), 141 (1), 128 (25), 112 (17), 111 (28), 99 (8), 95 (8), 93 (15), 86 (39), 72 (100), 67 (24), 57 (23), 55 (25), 44 (46), 43 (79), 41 (24), 39 (14).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 68.90; H, 10.29.

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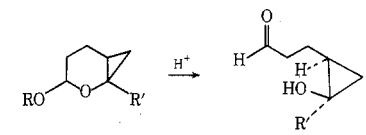
Registry No.—*trans*-**2a**, 30823-17-7; *trans*-**2b**, 30823-19-9; *cis*-**2b**, 30823-18-8; *trans*-**2c**, 55123-04-1; *cis*-**2c**, 55089-06-0; *trans*-**2d**, 55123-05-2; *cis*-**2d**, 55089-07-1; *trans*-**3a**, 55298-07-2; *trans*-**3b**, 55298-08-3; *cis*-**3b**, 55332-71-3; *trans*-**3c**, 55255-15-7; *cis*-**3c**, 55298-09-4; *trans*-**3d**, 55255-16-8; *cis*-**3d**, 55298-10-7; lithium, 7439-93-2.

References and Notes

(1) Part IV in a series "The Chemistry of 2-Alkoxy-3,4-dihydro-2*H*-pyrans". Part III: A. J. Duggan and S. S. Hall, *J. Org. Chem.*, in this issue.
(2) Taken in part from the Ph.D. Thesis of A.J.D. which was submitted to the Graduate Faculty, Rutgers University, Oct 1974.
(3) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); (b) *ibid.*, **81**, 4256 (1959); (c) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
(4) (a) R. I. Longley, Jr., and W. S. Emerson, *Org. Synth.*, **34**, 71 (1954); (b) *J. Am. Chem. Soc.*, **72**, 3079 (1950).
(5) (a) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959); (b) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960); (c) W. E. Parham, E. E. Schweizer, and S. A. Mierzwa, Jr., *Org. Synth.*, **41**, 76 (1961).
(6) The potential advantages of using sodium benzoate as a quenching agent for metal–ammonia reductions was first suggested by (a) M. Smith in R. L. Augustine, Ed., "Reduction", Marcel Dekker, New York, N.Y., 1968, p 105; and successfully applied in (b) S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); (c) S. S. Hall, *J. Org. Chem.*, **38**, 1738 (1973).
(7) Hydrolysis of these compounds, using the method described in ref 4a, would yield the corresponding cyclopropanol. The overall sequence, then, should provide a selective procedure to synthesize these unique structures.



(8) The ir spectra were determined with a Beckman Model IR-10 infrared recording spectrophotometer. The NMR spectra were determined at 100 MHz with Varian Associates Model XL-100 and Model HA-100 NMR spectrometers. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B mass spectrometer.

An Improved Synthesis of Dicyclohexylidene Diperoxide

John R. Sanderson,* Andrew G. Zeiler, and Randall J. Wilterdink

Story Chemical Corporation, Muskegon, Michigan 49445

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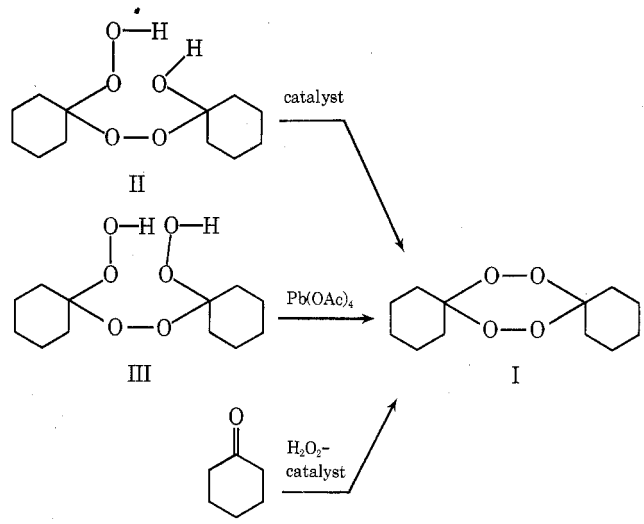
Dicyclohexylidene diperoxide (I) has been prepared by the "dehydration" of 1-hydroxy-1′-hydroperoxydicyclohexyl peroxide (II)[1,2] and by reaction of 1,1′-dihydroperoxydicyclohexyl peroxide (III) with lead tetraacetate.[3–5] Dicyclohexylidene diperoxide (I) has also been prepared "directly" from cyclohexanone and hydrogen peroxide[6] (Scheme I).

Scheme I



The disadvantages of preparing diperoxides such as I from the "open" peroxides such as II and III follow. For optimum results, the intermediate open peroxides should be purified by recrystallization before use. In general, "open" peroxides are more hazardous to work with owing to the shock sensitivity of these materials. The yields of the diperoxides prepared using this procedure are generally low.[1–5]

The former procedures for the direct conversion of cyclohexanone to the diperoxide also give low yields. Furthermore, the procedures often give mixtures of I, the triperoxide (IV), and "open" peroxides such as II and III that can be difficult to purify.[6]