Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.20.

Nuciferal (1).—Dried ether (50 ml) was placed in a 500-ml three-necked flask fitted with a magnetic stirrer, a dropping funnel and a thermometer. The air was swept out of the flask with dry nitrogen and a steady flow was maintained throughout the reaction. Finely cut lithium wire (2.78 g, 0.40 g-atom) was introduced and the stirred suspension was cooled to −10°. A solution of 30 g (0.21 mol) of methyl iodide in 150 ml of ether was added in the course of 1 hr at −20 to −10°. Stirring was continued for 1 hr at 0°. Diisopropylamine (20. g, 0.20 mol) (distilled over NaH) was added over a period of 20 min at −5° and stirring was continued until methane evolution had ceased (~20 min). Freshly distilled propylidene-*t*-butylamine[12] (26 g; 0.23 mol) was then added at −5° over a period of 20 min and stirring was continued for 20 min. Finally, a solution of 24.6 g (0.14 mol) of aldehyde **5** in 40 ml of ether was added at −70 to −75° over a period of 1 hr. The mixture was allowed to stand overnight at room temperature. It was then poured into an ice-cold solution of 50 g of oxalic acid in 500 ml of water and stirred vigorously for 30 min. The mixture was extracted with ether twice, and the combined extracts were subsequently washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4 and evaporated. Distillation of the residue afforded 25.3 g (83%) of racemic nuciferal (1), bp 105–115° (0.1 mm). This product contained ~10% aldehyde **5**. An analytical sample was obtained by redistillation through a Vigreux column, followed by chromatography on silicic acid using hexane + 3% AcOEt as eluent. Pure nuciferal had bp 94° (0.05 mm); uv (EtOH) 222 mμ (ε 19,000), 231 (18,900), 264 (940), 267 (800) and 273 (710); ir ($CHCl_3$) 2710, 1680, 1640 cm^{-1}; nmr (CCl_4) 1.23 (d, 3, J = 7 Hz), 1.60 (s, broad, 3), 2.29 (s, 3), 2.9–1.4 (m, 5), 6.33 (t, 1, J = 7 Hz), 7.04 (s, 4) an 9.27 ppm (s, 1).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.46; H, 9.43.

Registry No.—**1**, 18744-24-6; **2**, 18742-02-4; **4**, 18742-03-5; **5**, 4895-19-6.

Acknowledgment.—We are indebted to Firmenich et Cie., Geneva, for generous financial support.

(12) R. Tiollais, *Bull. Soc. Chim. Fr.*, **14**, 708 (1947).

Sodium–Liquid Ammonia Reduction of *anti*-1-Phenyl-1-chloro-2,3-*cis*-dimethylcyclopropane[1]

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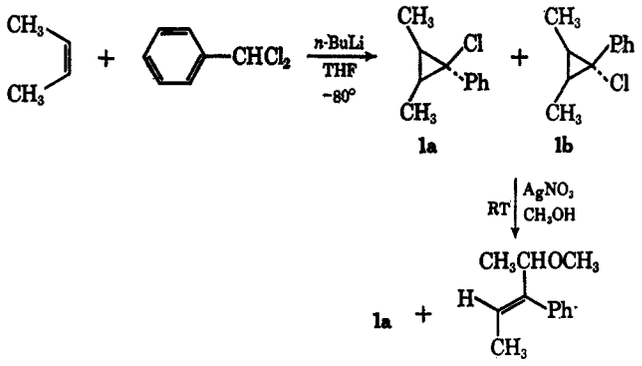
We would like to report the stereoselective reduction of *anti*-1-phenyl-1-chloro-2,3-*cis*-dimethylcyclopropane (**1a**) by sodium–liquid ammonia. A mixture of the two isomeric cyclopropanes **1a** and **1b** was obtained in a 50% yield from the reaction of *cis*-2-butene and benzal chloride with *n*-butyllithium (Scheme I). The two isomers could not be separated by gas chromatography; however, nmr showed **1a** and **1b** to be present in approximately a 3:1 ratio. The stereochemistry of the isomers has previously been assigned by Closs and coworkers on the basis of nmr considerations (isomer **1a** exhibits a multiplet at 1.2 ppm while **1b** has absorption

(1) Abstracted from the honors thesis of S. MacLean, Middlebury College, 1968.

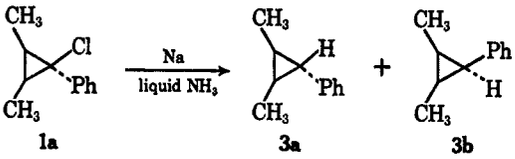
SCHEME I



at 0.8 ppm).[2] Treatment of the product mixture with methanolic silver nitrate (0.3 equiv) at room temperature afforded pure **1a** and the olefin **2a** which were readily separated by elution chromatography. The enhanced reactivity of **1b** under these conditions is in agreement with the rules governing electrocyclic transformations proposed by Woodward and Hoffmann[3] and lends credence to the stereochemical assignments made by Closs.

The structure of olefin **2a** was assigned on the basis of spectral data and a correct elemental analysis. The nmr of **2a** exhibits absorption at 1.07 (doublet, J = 6.5 cps, three protons), 1.58 (doublet, J = 7.0 cps, three protons), 3.28 (singlet, three protons), 3.79 (quartet, J = 6.5 cps, one proton), 5.69 (quartet, J = 7.0 cps, one proton), and 7.17 ppm (multiplet, five protons). The *cis* relationship of methyl and phenyl in **2a** is assumed from consideration of the two disrotatory modes of ring opening which are available to the cyclopropyl halide **1b**.[3]

Reduction of **1a** with sodium–liquid ammonia under paramagnetic conditions[4] afforded *anti*-1-phenyl-2,3-*cis*-dimethylcyclopropane (**3a**) in 63% yield (eq 1).[5]



(1)

The nmr spectrum of **3a** was in complete agreement with that reported by Closs. Gas chromatographic analysis of the product showed it to contain less than 1% isomer **3b**. Reduction of a 3:1 mixture of **1a** and **1b** afforded **3a** and **3b** in a 13:1 ratio. The reduction thus proceeds to give the thermodynamically more stable cyclopropane isomer as the predominent product.[5] It is difficult to reconcile our results with those of Hodgkins and coworkers,[6] who reported that a mixture of the epimeric 7-phenyl-7-chlorononcaranes underwent potassium–liquid ammonia reduction to afford *syn*-7-phenylnorcarane as the major product. Closs and Coyle[2] have questioned the assignments of the epimeric 7-phenylnorcaranes made by Hodgkins,

(2) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

(3) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

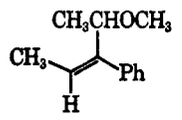
(4) (a) M. C. R. Symons, *Quart. Rev.* (London), **13**, 99 (1959); (b) C. A. Hutchison and R. A. Pastor, *J. Chem. Phys.*, **21**, 1959 (1953).

(5) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

(6) J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, *ibid.*, **86**, 4080 (1964).

et al., and reinvestigated their configurations. Their reassignments are consistent with our experimental results.

Interestingly, when **1a** was stirred with methanolic silver nitrate at reflux for 12 hr, a mixture of **2a** and what has tentatively been assigned structure **2b** was obtained in a 5:1 ratio.[7] This result would imply



2b

that ionization of **1a** is for the most part a nonconcerted process.

Experimental Section[8]

1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a + 1b).[9]—To a solution of 320 ml (3.76 mol) of *cis*-2-butene and 75.8 g (0.47 mol) of benzal chloride in 500 ml of tetrahydrofuran (THF) was added dropwise with stirring and under a nitrogen atmosphere 0.54 mol of *n*-butyllithium in hexane. The reaction mixture was kept at −80° while the addition took place and then stirred for 1 hr at this temperature. After warming to room temperature the THF was removed by vacuum distillation. Water and ether were added and the organic layer was separated. The aqueous layer was extracted with four 20-ml portions of ether. The ether extracts were combined with the organic layer, dried (magnesium sulfate), and concentrated. Fractional distillation afforded 42.3 g (50%) of **1a** and **1b**, bp 70–72° (1.25 mm) [lit.[2] bp 50–53° (0.3 mm)]. An nmr spectrum of the product exhibits multiplets at 0.8, 1.2, and 7.3 ppm. The relative intensities of high-field/low-field absorption was 8:5. The isomer ratio of **1a**:**1b**, determined by integrating the multiplets at 0.8 (**1a**) and 1.2 ppm (**1b**), was found to be 3:1. The infrared spectrum of the product was consistent with the desired structure. A vpc of the product on column a[8] at 150° gave one major peak which was collected. An nmr spectrum showed that **1a** and **1b** were present in the collected sample.

Sodium–Liquid Ammonia Reduction of *anti*-1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a).—A solution of 1.580 g (69 mg-atoms) sodium in 100 ml of liquid ammonia and 0.112 g (0.63 mmol) of **1a** were added dropwise and simultaneously to 250 ml of liquid ammonia. The reaction mixture was then stirred for 1 hr. Ammonium chloride was added until the solution became white, and the excess ammonia was evaporated. The reaction mixture was worked up in the usual manner. Analysis of the product mixture on column c[8] showed >99% **3a** and <1% **3b** to be present in a 63% yield.[10]

Sodium–Liquid Ammonia Reduction of 1a and 1b (3:1).—The reduction was carried out as described previously. Compounds **3a** and **3b** were obtained in a 60% yield (13:1 ratio).

Reaction of 1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a + 1b) with Silver Nitrate.—To a solution of 10 g (0.056 mol) of **1a** + **1b** in 20 ml of reagent grade methyl alcohol was added with stirring 3.2 g (19 mmol) of silver nitrate. The reaction mixture was stirred for 10 hr at room temperature. Water and ether were added and the organic layer was separated. The reaction mixture was worked up in the usual manner. Compound **1a** was separated from **2a** by column chromatography on silica gel and elution with ligroin. A 50% yield (5 g) of **1a** was obtained after distillation. *cis*-3-Phenyl-4-methoxy-2-pentene (**2a**) was eluted from the column with benzene. A mass spectrum of **2a** exhibits a molecular ion peak of *m/e* 176.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.76; H, 9.24.

An nmr spectrum of **1a** exhibits multiplets centered at 1.2 and 7.3 ppm. The infrared spectrum of **1a** differs from that of the mixture of **1a** and **1b** in that absorbance at 1179 and 939 cm^{-1} is absent. An ultraviolet spectrum of **1a** measured in hexane exhibits absorption maxima at 252 mμ (ε 1600) and 220 (7700).

Registry No.—Ammonia, 7664-41-7; **1a**, 13154-00-2; **2a**, 18744-16-6.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for support of this research, and to the University of Vermont for making its nmr facilities available to us.

(7) The structure of **2b** is assigned on the basis of a correct elemental analysis and nmr measurements made on the mixture, and a mass spectrum of pure **2b**.

(8) Infrared spectra (ir) were determined with a Perkin-Elmer Model 137 recording spectrophotometer. All spectra were measured in carbon tetrachloride unless otherwise stated. Ultraviolet spectra were determined on a Bausch and Lomb spectrophotometer, Model 505. The nmr spectra were determined at 60 Mc with a Varian Model A-60 spectrometer using tetramethylsilane (TMS) as the internal reference. Carbon-hydrogen analyses were carried out by C. F. Geiger, Ontario, Calif. Columns used for gas chromatography (vpc) were (a) 10% Carbowax 20M column, 6 ft × 0.25 in. glass tubing, (b) 10% Carbowax 20M column, 6 ft × 0.25 in. aluminum tubing, and (c) a 25% DC QF-1 column, 6 × 0.25 in. glass tubing. All yields were determined by gas chromatography.

(9) Prepared according to the procedure of D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4417 (1965).

(10) The retention times of both **3a** and **3b** were identical with those of authentic samples prepared by independent means.[5]

The Acid-Catalyzed Cyclization of 2-Substituted 3,3-Diphenylacrylophenones

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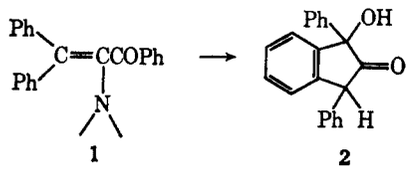
The cyclization of 2-substituted 3,3-diphenylacrylophenones to substituted 1,3-diphenylindenones, or their tautomers, under the influence of Brønsted acids, and some related cyclizations, were first described by Kohler and coworkers.[2,3] A previous publication from this laboratory[4] has described the cyclization of 2-amino-3,3-diphenylacrylophenones (**1**) to 1,3-diphenyl-1-hydroxyindan-2-one (**2**) with aqueous sulfuric acid. In this Note we present additional evidence for



1 **2**

the course of this reaction and correlate this and some similar cyclizations with a general reaction mechanism.

Barré and Kohler[2] obtained 2,3-dibromo-1,3-diphenylindene (**4**) by treating 2-bromo-3,3-diphenylacrylophenone (**3**) with hydrogen bromide in refluxing acetic acid, and also as a by-product of the bromination of 3,3-diphenylacrylophenone (**14**) in chloroform at room temperature. The major product of the latter reaction is 2-bromo-3,3-diphenylacrylophenone (**3**) which is formed exclusively when the reaction is done in refluxing chloroform. Kohler and Weiner[3] obtained 1-chloro-1,3-diphenylindan-2-one (**5**) by treating 3,3-

(1) To whom all inquires should be addressed.

(2) R. Barré and E. P. Kohler, *J. Amer. Chem. Soc.*, **50**, 2036 (1928).

(3) E. P. Kohler and N. Weiner, *ibid.*, **56**, 434 (1934).

(4) N. H. Cromwell and M. C. McMaster, *J. Org. Chem.*, **32**, 2145 (1967).