Table I. Reductive Silylation of Carbonyl Compounds by Trichlorosilane–Tri-*n*-propylamine

Run	Reactants (mole ratios) Carbonyl–$HSiCl_3$–$(n\text{-}C_3H_7)_3N$	Conditions	Products[a,c]
1	$(C_6H_5)_2CO$ (1:3:1)	Neat, 1 hr, 55–75°	$(C_6H_5)_2CHSiCl_3$ (95%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (99%)[b]
2	$p\text{-}ClC_6H_4COC_6H_5$ (1:3:1)	Neat, 1 hr, 52–77°	$p\text{-}ClC_6H_4CHSiCl_3C_6H_5$ (73%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (97%)[b]
3	$p\text{-}CH_3C_6H_4COC_6H_5$ (1:3:1.2)	CH_3CN (solvent), 24 hr, 60–67°	$p\text{-}CH_3C_6H_4CHSiCl_3C_6H_5$ (88%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (quantitative)[b]
4	C_6H_5CHO (1:3:1)	CH_3CN (solvent), 1 hr, 57–58°	$C_6H_5CH_2SiCl_3$ (5%)[c] $C_6H_5CHClSiCl_3$ (42%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (95%)[b]
5	$2,6\text{-}Cl_2C_6H_3CHO$ (1:3:1)	CH_3CN (solvent), 2 hr, 51–64°	$2,6\text{-}Cl_2C_6H_3CH_2SiCl_3$ (61%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (87%)[b]
6	C_6H_5COCl (1:1.25:1)	CH_3CN (solvent), 1 hr, 25°; 0.5 hr, 85°	$C_6H_5CHClSiCl_3$ (91%)[b,d] $(n\text{-}C_3H_7)_3N\cdot HCl$ (quantitative)[b,d]

[a] The distillation residues were resinous materials containing Si–O and Si–Cl linkages in accord with a structure like I. [b] Isolated yield. [c] Yield by glpc. [d] Yield based on $HSiCl_3$ and stoichiometry of eq 1. [e] Satisfactory elemental analyses and spectral data (nmr and ir) were obtained for all silicon compounds listed.

a polymeric structure similar to I[3]) whose ir spectrum was dominated by the Si–O absorption at 8.5–9.5 μ. Data for the transformation of a series of carbonyl compounds are summarized in Table I.

In contrast to the result described in entry 6 of Table I, benzoyl chloride, trichlorosilane, and tri-*n*-propylamine (mole ratio 1:3:1) combined in tetrahydrofuran (4 hr at −40 to +25°) produced, in addition to the amine hydrochloride (94%) and a small amount of α-chlorobenzyltrichlorosilane (II), a 59% yield of α-chlorobenzyltrichlorosilyloxydichlorosilane (III, $C_6H_5CHClSiCl_2OSiCl_3$): bp 110° (2 mm); nmr (CCl_4) δ 4.55 (s, 1), 7.35 (s, 5); ir band 9.0 μ. *Anal.* Calcd for $C_7H_6Si_2OCl_6$: C, 22.42; H, 1.61; Cl, 56.72; Si, 14.98. Found: C, 22.15; H, 1.74; Cl, 56.90; Si, 14.80. That III is a likely intermediate in the reductive silylation of benzoyl chloride was demonstrated by its rapid conversion to I and II on refluxing in acetonitrile in the presence of catalytic amounts of tri-*n*-propylamine.[4]

$$\text{III} \xrightarrow[\text{CH}_3\text{CN; 1 hr, 84°}]{\text{0.1 equiv of } (n\text{-}C_3H_7)_3N} \text{I} + \text{II (85\%)} \qquad (2)$$

If one assumes the general intermediacy of trichlorosilyloxy compounds similar to III in reductive silylations, the over-all reaction sequence may be represented by eq 3.

$$\begin{array}{l} \text{O} \qquad\qquad\qquad\qquad\qquad\quad \text{SiCl}_2\text{OSiCl}_3 \\ \quad\| \qquad\qquad\qquad\qquad\qquad\quad | \\ \text{R'CR''} + 2\text{HSiCl}_3 + \text{R}_3\text{N} \rightarrow \text{R'CHR''} + \text{R}_3\text{N}\cdot\text{HCl} \qquad (3) \\ \text{R'CHSiCl}_3\text{R''} + \text{I} \xleftarrow{\text{R}_3\text{N (catalyst)}} \end{array}$$

Based upon the reaction vigor, it appears that electron withdrawal from the carbonyl carbon facilitates the reductive silylation process. In substantiation of this premise, 2,4-dimethylbenzophenone was recovered virtually unchanged after refluxing for 4 hr with trichlorosilane and tri-*n*-propylamine.

Electronic and/or steric effects may be responsible for the rather anomalous behavior of benzaldehyde (entry 4 in Table I) compared to 2,6-dichlorobenzaldehyde (entry 5) and the other carbonyl compounds studied.

Acetophenone, cyclohexanone, and acetone each produced multicomponent mixtures when treated with the silane–amine combination, the last mentioned giving 2-trichlorosilyloxypropene[1] (IV) as the principal product

$$\begin{array}{l} \text{OSiCl}_3 \\ | \\ \text{CH}_2{=}\text{CCH}_3 \end{array}$$

IV

(45%). Whether other enolizable carbonyl compounds are unsuitable for reductive silylation is a point currently under investigation.

The general scope and mechanism of reductive silylations are under active investigation in our laboratory, since the reaction holds promise of becoming a powerful synthetic tool in both carbon and organosilicon chemistry.

Acknowledgment. The authors are grateful to the Purdue Research Foundation whose financial assistance made this work possible.

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(3) A similar (but phenyl-substituted) resinous substance was observed as the by-product in the high-temperature reduction of ketones by diphenylsilane. See H. Gilman and J. Diehl, *J. Org. Chem.*, **26**, 4817 (1961).

(4) This disproportionation can be regarded as a variant of that undergone by hexachlorodisiloxane, also with tertiary amine catalysis: G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, **82**, 5042 (1960).

Total Synthesis of *dl*-Cedrene and *dl*-Cedrol

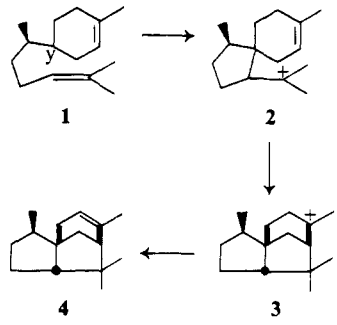
Sir:

Cation **1**, Y = +, as generated, for example, from the corresponding alcohol **1**, Y = OH, is potentially capable of cyclization *via* cations **2** and **3** to form cedrene (**4**)[1,2] in a

(1) Structure: (a) Pl. A. Plattner, A. Fürst, A. Eschenmoser, W. Keller, H. Kläui, St. Meyer, and M. Rosen, *Helv. Chim. Acta*, **36**, 1845 (1953); (b) G. Stork and R. Breslow, Jr., *J. Am. Chem. Soc.*, **75**, 3219 (1953).

(2) Absolute configuration: G. Büchi, R. E. Erickson, and N. Wakabayashi, *ibid.*, **83**, 927 (1961).

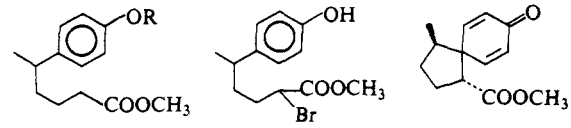
sequence which parallels the proposed biosynthesis.[3,4] The simplicity of this scheme as a synthetic pathway coupled with a moderate prospect for successful execution led to the development of the syntheses of cedrene which are reported here.[5,6]



1 2 4 3

A number of experiments on the acid-catalyzed cyclization of the alcohol **1**, Y = OH,[7,8] under varying conditions led to only trace amounts of material corresponding to cedrene by gas chromatographic analysis. Therefore, a study was made on the generation and behavior of the cation **2**.[9]

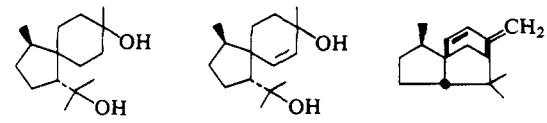
The spiro bicyclic skeleton corresponding to **2** was constructed starting with *p*-methoxyacetophenone *via* the methoxy ester **5**[8] which was obtained in 40% over-all yield by the sequence: (1) Reformatsky addition of methyl γ-bromocrotonate,[10] (2) dehydration to methyl 5-*p*-anisylhexa-2,4-dienoate,[8] mp 86–87°, using 0.2% toluenesulfonic acid in benzene at reflux for 2.5 hr, and (3) hydrogenation in methanol–ethyl acetate over 10% Pd–C catalyst. Treatment of **5** with 48% aqueous hydrobromic acid in acetic acid (1:1) at reflux for 5 hr, reesterification with methanolic hydrogen chloride, and reaction of the resulting phenolic ester with dihydropyran in methylene chloride containing a trace of toluenesulfonic acid gave the oily ester **6** in high yield. This ester was converted to the oily phenolic α-bromo ester **7** in 90% over-all yield by the sequence: (1) condensation with methyl oxalate using sodium hydride in dimethoxyethane to form the α-methoxallyl derivative, (2) bromination of the sodio derivative in methanol at 0° followed by deoxallylation *in situ* under the influence of sodium methoxide, and (3) removal of the tetrahydropyranyl group using a mixture of aqueous hydrochloric acid, ethylene glycol, and tetrahydrofuran. Treatment of the bromo phenol **7** with 1 equiv of potassium *t*-butoxide in *dry t*-butyl alcohol at 60° gave a mixture of *cis* and *trans* forms (ratio 53:47) of the diene **8**,[8,11] which upon exposure to methanolic sodium methoxide was converted largely to one (more stable) stereoisomer, considered to be the *trans* form **8**.[12] Catalytic hydrogenation of **8** using Pd–C catalyst in tetrahydrofuran afforded the saturated keto ester tetrahydro-**8** in good yield, a colorless liquid[8] showing nmr peaks (CCl_4 solution) due to $COOCH_3$ and $>CHCH_3$ at 3.64 (s) and 1.02 (d, J = 6.5 Hz), respectively. Treatment of tetrahydro-**8** with excess methyllithium gave the diol **9**. Exposure of **9** to anhydrous formic acid at room temperature produced a mixture of hydrocarbons from which pure *dl*-cedrene (**4**) (10–20%) was isolated by preparative glpc. The nmr, infrared, and mass spectra and glpc behavior on several different columns were identical for synthetic and natural samples.



5, R = CH_3
6, R = OTHP

7

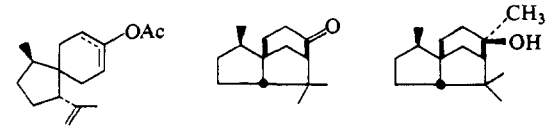
8



9 **10** **11**

An alternative synthesis of cedrene from the dienone **8** which proceeded more efficiently involved the conversion of **8** to a dihydro derivative by partial hydrogenation using 10% Pd–C catalyst in ethyl acetate (a much slower rate of reduction of **8** was noted after 1 equiv of gas was absorbed). The enone ester so formed gave the diol **10** after treatment with methyllithium. Exposure of the diol **10** to anhydrous formic acid gave a mixture of tricyclic formates which underwent thermolysis when passed as the vapor through a glass tube at 400° (0.2 mm) to form the diene **11**[8,13] in *ca.* 80% yield from **10**. Reduction of the diene **11** using excess lithium in ethylamine gave *dl*-cedrene,[8] spectroscopically and chromatographically identical with natural cedrene, as the only product.

Finally, exposure of the enol acetate **12**[14] to boron tri-



12 **13** **14**

(3) Biosynthesis: see W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev.* (London), **21**, 331 (1967).

(4) First synthesis: G. Stork and F. H. Clarke, Jr., *J. Am. Chem. Soc.*, **77**, 1072 (1955); **83**, 3114 (1961).

(5) The results herein described were presented previously in the Ernest Guenther (Fritzsche) Award Lecture at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., Abstract P-4, April 1, 1968.

(6) We recently learned (private communication, Dec 16, 1968) that Professor R. G. Lawton and T. G. Crandall have successfully completed a synthesis of *dl*-cedrene along similar lines.

(7) This alcohol was readily produced (as a mixture of diastereomers) by the reaction of 2-[6-methylhept-5-enyl]lithium with 4-methyl-3-cyclohexenone (for preparation of the latter see E. A. Braude, A. A. Weble, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958)). It is of interest that an isomer of **1**, Y = OH, has recently been found to occur naturally [see J. P. Minyard, A. C. Thompson, and P. A. Hedin, *J. Org. Chem.*, **33**, 909 (1968)].

(8) Elemental analysis or high-resolution mass, nuclear magnetic resonance (nmr), and infrared spectra were in accord with the assigned structure.

(9) A detailed report on the initial and ongoing investigations of the cyclization of **1** will be made at a later time.

(10) F. Bohlmann, *Ber.*, **90**, 1519 (1957).

(11) See R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **84**, 788 (1962), and previous papers cited therein.

(12) The stable isomer **8** and the less stable *cis* form show characteristically different nmr peaks; *e.g.*, those due to $COOCH_3$ occur at 3.45 ppm in **8** and 3.56 ppm in the *cis* form (in CCl_4 solution).

(13) This diene was identical (glpc, nmr, infrared, ultraviolet, and mass spectra) with an authentic sample[8] prepared from natural cedrene by monobromination (N-bromosuccinimide) and dehydrobromination (potassium *t*-butoxide in dry ether at 25°).

(14) This compound was prepared from the saturated keto ester tetrahydro-**8** by the sequence: (1) ketalization using ethylene glycol, (2) reaction with excess methyllithium, (3) deketalization, and (4) enol acetylation.

fluoride in methylene chloride at 0° led to efficient cyclization to tricyclic product. The ketone **13** so obtained was isolated in pure form[8] by preparative glpc and converted to *dl*-cedrol **14** by treatment with methyllithium.[4] Comparison of infrared and nmr spectra and glpc behavior of the synthetic product with natural cedrol confirmed the assigned structure **14**.[15]

(15) This work was supported by the National Science Foundation.

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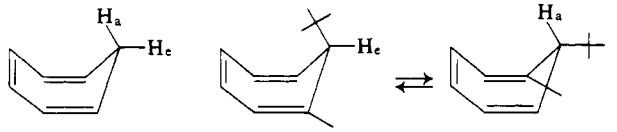
Hindered Ring Inversion of 1-Methyl-7-*t*-butylcycloheptatriene

Sir:

Nuclear magnetic resonance (nmr) spectroscopy has been especially fruitful in delineating not only the intimate structure of cycloheptatriene (**1**)[1,2] and its derivatives,[3-5] but also their energy barrier(s) and rates of interconversion. Whereas, from the studies of Anet[1] and Jensen,[2] extremely low temperatures (−170°) are necessary to slow



1 **2a** **2b**

the interconversion of **1**, we wish to report our studies of a simple derivative of **1** which, because of severe nonbonded interactions, undergoes *slow inversion at room temperature* and which shows further interesting spectral features.

Reaction of methyltropylium tetrafluoroborate with *t*-butyllithium[4b,6] gave as the minor product 1-methyl-7-*t*-butyl-1,3,5-cycloheptatriene (**2**).[7,8] The room temperature nmr spectrum[10] of this material exhibited (in addition to complex resonances for the olefinic protons) a broad absorption for the 7-*t*-butyl group centered at τ 9.17 and a singlet at τ 8.06 for the 1-methyl group of **2** (Figure 1A). When the temperature of the sample is progressively lowered, notable changes occur in the spectrum. More specifically, the *t*-butyl resonance sharpens and gives rise to two singlets of unequal intensity at τ 8.94 and 9.23 (ratio of the area of the low-field signal to that of the high-field signal 23:77), while the 1-methyl proton region under-

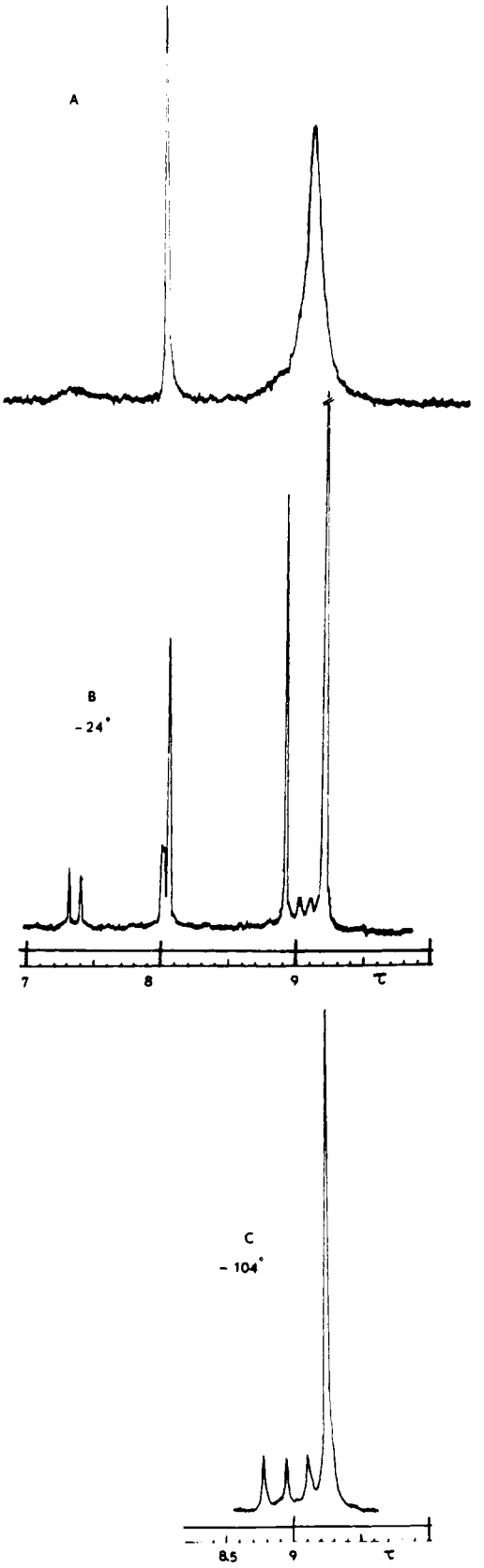


Figure 1. Partial 100-Mc spectra of **2** at different temperatures.

(1) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).
(2) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).
(3) K. Conrow, M. E. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).
(4) (a) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965); (b) H. Kessler and E. Muller, *Z. Naturforsch.*, **22b**, 283 (1967); (c) H. Gunther and H.H. Hinrichs, *Tetrahedron Letters*, 797 (1966); (d) K. W. Egger and W. R. Moser, *J. Phys. Chem.*, **71**, 3699 (1967); (e) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).
(5) H. Gunther, M. Gorlitz, and H. H. Hinrichs, *Tetrahedron*, **24**, 5565 (1968).
(6) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).
(7) A satisfactory analysis was obtained for this material.
(8) 1-Methyl-7-*t*-butyl-1,3,5-cycloheptatriene (**2**) was isolated from the reaction mixture by preparative gas chromatography on an 18% γ-methyl-γ-nitropimelonitrile column.[9] The experimental details and product distribution for this and other reactions of alkyltropylium ions with organolithium compounds will be reported in the full paper.
(9) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).
(10) Nmr spectra were measured on a Varian HA-100 spectrometer equipped with a variable-temperature probe. All spectra were obtained in carbon disulfide with chemical shifts reported as τ in parts per million relative to internal TMS.