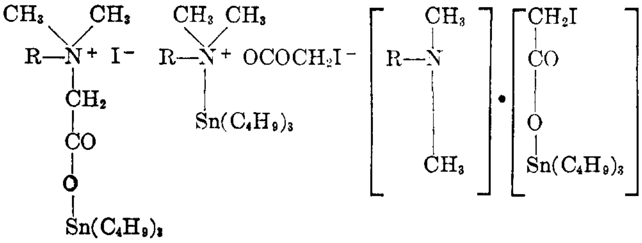

A B C

R = mercurated base

Fig. 1.—Possible structural formulas.

rated aqueous I or IV but II precipitated mercuric sulfide, instantly, and III on standing 12 to 24 hr.

Trimethyltin iodoacetate reacted with both dimethylamino groups of mercuribisdimethylaniline. The other tin halo esters combined with only one. Several attempts to add a second tri-*n*-butyl- or propyltin halo ester or methyl iodide failed.

The compounds prepared are believed to be the iodide of the quaternary ammonium base (Fig. 1A). Figure 1B represents a substituted acetate of the quaternary ammonium base. Figure 1C represents the addition of the tri-*n*-butyltin iodoacetate as a double salt of a tertiary base as suggested by Kraus and Greer[12] for the addition of trimethyltin salts to bases such as pyridine or aniline. The latter two compounds should be obtainable with esters or salts other than the bromoacetic or iodoacetic ester. However, when the chloroacetate, acetate, or iodide reacted at 100° with mercuribis-4-dimethylaniline, the only identifiable compounds obtained were the starting materials. Feigl's test[13] for iodide was positive. It is recognized that no rigorous proof of the proposed structure of I and analogous products has been possible; however, it does seem that the fact that several similar pairs of compounds do react to yield products with compositions which indicate that corresponding types of reactions must have occurred in the several instances gives substantial justification to the proposed structure.

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[12] C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, **45**, 3708 (1923).

[13] F. Feigl, "Spot Tests, Inorganic Applications," Elsevier Publishing Company, Amsterdam, 1954, p. 248.

Temperature Dependence of Stereochemistry of Complex Metal Hydride Reductions

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Although appreciable attention recently has been focused on the effect of solvent and reagent composition on the stereochemistry of reduction by complex metal hydrides,[1] little data appear in the literature on temperature effects on stereochemistry when other variables are held constant. Vail and Wheeler[2] have recently observed minor changes in the relative amounts of 3α- and 3β-cholestanols when reductions of 3-cholestanone were performed with various reducing agents and solvents at several temperatures. The general trend was toward increasing amounts of axial alcohol at higher temperature.[2] We wish to report results on the temperature dependence of product stereochemistry, utilizing conformationally pure ketones, in which case increased temperature may result in either an increase or decrease in the relative amount of axial alcohol, although both cases actually involve greater proportions of the major product at low temperature (an enthalpy effect).

The table shows some typical results of reduction of 3,3,5-trimethylcyclohexanone (I) (a hindered ketone) and 4-*t*-butylcyclohexanone (II) (an unhindered ketone) by excess lithium aluminum hydride and sodium borohydride ($>$one mole of reducing agent/mole of ketone) in various solvents, each combination of reagent and solvent being studied at several temperatures. The molar ratios of the complex metal hydride to the ketone were not kept constant, but it is felt that this has no effect on the stereochemistry since Haubenstock and Eliel[1] have shown that the stereochemistry of reductions of 3,3,5-trimethylcyclohexanone with lithium aluminum hydride in either diethyl ether or tetrahydrofuran is independent of the proportion of reactants and order of addition. Entries 5a–d likewise show that this also applies in pyridine. Eliel and Haubenstock have also shown that the relative proportion of ketone and reducing agent does not affect the stereochemical result in the reductions with sodium borohydride. It can be seen that I gives substantially greater amounts of axial alcohol (the major product) at lower temperatures, whereas there is a slight decrease in per cent axial (the minor product) when reduction of II is performed at lower temperatures, as was observed with 3-cholestanone.[2] These data are rationalizable according to the earlier views of Dauben, Fonken, and Noyce[3] on "steric approach control" and "product development control" and by assuming that the transition state for reduction of unhindered ketones (*e.g.*, II) does *not* resemble reactants but is well along the reaction coordinate toward product,[4] thus leading mainly to equatorial alcohol. This latter view is supported by several recent studies of borohydride reduction of unhindered ketones where linear-free energy relationships are obeyed[5,6] with highly positive ρ values being observed (+2.6 for *p*-substituted acetophenones[5] and +2.65 for 2- and 3-substituted fluorenones[6]). Hindered ketones, on the other hand, reach the transition state earlier ("steric approach control"), thus leading to a predominance of *exo*-attack.

The present work provides further examples of the effect of temperature and solvent on the stereochemistry of reduction of cyclic ketones. A practical aspect of the data is the indication that greatest stereoselectivity in the reduction of hindered ketones to axial alcohols can be achieved in good solvating media[1] at low temperature.

Experimental

In all the complex metal hydride reductions the ketone (approximately 7 mmoles) was dissolved in 25 ml. of the indicated solvent (Table I), protected from the atmosphere, and cooled in a bath to the desired temperature. A molar excess of the complex metal hydride was then added in powdered form to the system and stirred for 15–30 min. with a magnetic stirrer, except for the sodium borohydride reductions in isopropyl alcohol which were stirred approximately 48 hr.

All reductions run at 0° or higher were essentially complete in the reduction period (less than 1% unchanged ketone),

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[1] H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

[2] O. R. Vail and D. M. S. Wheeler, *J. Org. Chem.*, **27**, 3803 (1962).

[3] W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

[4] M. G. Coombe and H. B. Henbest, *Tetrahedron Letters*, 404 (1961).

[5] H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962).

[6] G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962).

TABLE I

COMPLEX METAL HYDRIDE REDUCTIONS OF 3,3,5 TRIMETHYLCYCLOHEXANONE (I) AND 4-*t*-BUTYLCYCLOHEXANONE (II)

Entry	Reagent	Solvent	Temp., °C.	Molar ratio, metal hydride to ketone I	% Axial alcohol from I (normalized)	% Unreduced ketone I	Molar ratio, metal hydride to ketone II	% Axial alcohol from II (normalized)	% Unreduced ketone II
1[a]	$LiAlH_4$	Et_2O	30	1.1[a]	55[a]	2.6[a]	1.2	8	<1
2	$LiAlH_4$	Et_2O	0	1.3	58	<1	1.2	7.5	<1
3	$LiAlH_4$	Et_2O	−40	1.1	61.5	<1	1.0	5	2.6
4	$LiAlH_4$[b]	C_5H_5N	27	1.0	71	<1	1.1	11.5	<1
5a	$LiAlH_4$	C_5H_5N	0	1.05	75	<1	1.7	10.5	<1
b	$LiAlH_4$	C_5H_5N	0	0.77	74	1.3	. . .	. . .	. . .
c	$LiAlH_4$	C_5H_5N	0	0.50	76	0.8	. . .	. . .	. . .
d	$LiAlH_4$	C_5H_5N	0	0.30	76	41.3	. . .	. . .	. . .
6	$LiAlH_4$	C_5H_5N	−40	1.05	83	<1	1.1	8.5	30
7	$LiAlH_4$	THF	65	0.38[a]	74[a]	7[a]	. . .	. . .	. . .
8	$LiAlH_4$	THF	27	1.2	76.5	<1	1.2	8	<1
9	$LiAlH_4$	THF	0	1.3	82	<1	2.0	7.5	<1
10	$LiAlH_4$	THF	−40	1.1	87.5	<1	2.0	4.0	<1
11	$NaBH_4$	CH_3OH	27	1.2	80.5	<1	1.2	20	<1
12	$NaBH_4$	CH_3OH	0	1.3	86	<1	2.0	16.5	<1
13	$NaBH_4$[c]	CH_3OH	−40	1.2	98	<1	1.3	12.0	2
14	$NaBH_4$[d]	CH_3OH	−70	1.2	98	27.4	. . .	. . .	. . .
15	$NaBH_4$	*i*-C_3H_7OH	27	1.4	57.5	<1	1.4	12.5	<1
16	$NaBH_4$	*i*-C_3H_7OH	0	1.4	62.0	<1	1.5	13.0	<1

[a] Results taken from ref. 1. [b] There is no opportunity for lithium tetrakis(N-dihydropyridyl)aluminate to play a significant role in these reductions since it is slowly formed under these conditions and reduces dialkyl ketones only with great difficulty (P.T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, **83**, 3537; **84**, 1756 (1962)). The present reductions were accomplished within a few minutes by addition of lithium aluminum hydride to pyridine solutions of I and II. [c] Although $NaBH(OCH_3)_3$ may be involved at 0° and 27°, there was very little hydrogen evolution at −40° and none at −70°, so one may consider solvated sodium borohydride to be the major reducing species. [d] Since large amounts of ketone remain unchanged under these conditions it is conceivable that some reduction might occur during work-up. This possibility was shown to be extremely remote since a semiquantitative kinetic run at −75°, using the usual work-up for each aliquot taken, showed that good second-order kinetics were obeyed ($k_2 = 6.7 \times 10^{-4}$ l./mole-sec.) when the data were treated by the method of Brown, *et al.*, *Tetrahedron*, **1**, 214 (1957).

whereas several of the reductions at −40° did not proceed to completion in the allotted time. When the reducing agent was lithium aluminum hydride, the excess hydride was neutralized with methanol at the temperature at which the reduction was run before continuing with the work-up. The reaction mixtures were then poured into a mixture of ice, water, and ether and acidified with dilute hydrochloric acid. The crude product was taken up in ether, washed with sodium bicarbonate solution, saturated salt solution, and dried over anhydrous sodium sulfate. The ether solution was concentrated and the mixtures of *cis*- and *trans*-3,3,5-trimethylcyclohexanols and *cis*- and *trans*-4-*t*-butylcyclohexanols were analyzed by gas–liquid partition chromatography using an F & M Model 300 programmed temperature–gas chromatograph. Peak areas were calculated from the product of the peak height and half-height width.

Synthetic mixtures of the pure *cis*- and *trans*-3,3,5-trimethylcyclohexanols, as well as mixtures of the alcohols and I were prepared and analyzed by gas chromatography. Since experimental and calculated results agreed within ±1%, no correction factors were used. The separation was carried out on a 5-ft. column freshly prepared using 20% by weight of the benzene extract from commercial "Tide" detergent on Chromosorb P. Helium flow rate was approximately 120 ml. per min. and the temperature was programmed from 90° at a rate of 4.6° per minute. The ketone had a retention time of 7.67 min., the *trans* alcohol 10 min., and the *cis* alcohol 12.67 min.

Synthetic mixtures of pure *cis*- and *trans*-4-*t*-butylcyclohexanols were prepared and analyzed by gas chromatography in the same manner. The experimental results agreed with the calculated results within 1% in the absence of 4-*t*-butylcyclohexanone up to 20% of the ketone present in the mixture and within 2–3% up to 40% of the ketone in the mixture, the ketone partially masking the *cis* alcohol when it is present in large amounts. The separation was carried out on the same 5-ft. "Tide" column using a flow rate of approximately 200 ml. per min. The temperature was programmed from 90° at 4.6° per min. The retention time of the ketone was 13.5 min., that of the *cis* alcohol 14.67 min., and that of the *trans* alcohol 16.67 min.

The crude product mixtures from the hydride reductions were analyzed in the previous manner. The only peaks observed were those corresponding to the ether solvent, which immediately flashed off, the two alcohols and, in some cases where the reduction was incomplete, the ketones. In the table the yields of axial alcohols are normalized to 100%.

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The Preparation of Certain Cyclopolymethylenecyclosiloxanes

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The hydrolysis of organosilicon dihalides generally results in the formation of a mixture of cyclic and linear organopolysiloxanes with the latter predominating. A survey reveals that usually the hydrolysis involves the use of dialkyl, diaryl, or alkyl–aryl substituted dichlorosilanes. Siloxane polymers resulting from the hydrolysis of 1,1-dichloro-1-silacyclobutane and 1,1-dichloro-1-silacyclopentane have been described by Hersch.[1] This paper records the preparation and characterization of four crystalline polymers of the type $[(CH_2)_xSiO]_y$ where x is 4 or 5 and y is 3 or 4.

(1) J. M. Hersch, U. S. Patent 2,464,231 (1949).