+7.1°) gives ≡Si*Cl ([α]D +14.1), which furnished ≡Si*H ([α]D −6.4°). For the new system in which R = ethyl, ≡Si*H ([α]D +0.76°) gives ≡Si*Cl ([α]D +2.0°) which upon reduction gives ≡Si*H ([α]D −0.75°). The parallel behavior of the four systems in these cycles leaves little doubt that for the new systems, as for the original system, chlorination proceeds *via* retention and reduction by inversion of configuration.[8]

For the chlorosilanes having R = neopentyl or ethyl, coupling with α-naphthyllithium in ether gave back the α-NpPhMeSi*R derivatives which were enantiomers of the starting compounds. Since a high degree of conservation of optical activity obtains for these four-reaction sequences, it follows that the reactions involved are highly stereospecific.

$$\alpha\text{-NpPhMeSi*R} \xrightarrow[\text{inversion}]{Br_2} \text{PhMeRSi*Br} \xrightarrow[\text{inversion}]{LiAlH_4} \text{PhMeRSi*H}$$

I

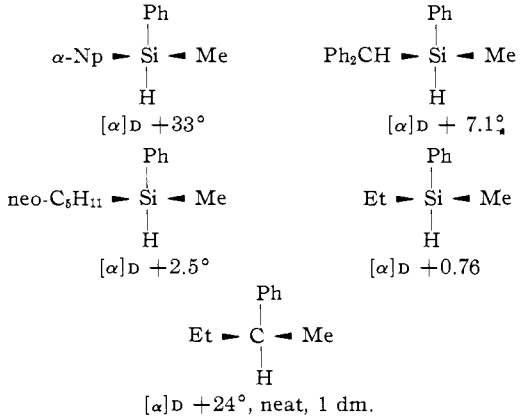
$$\xrightarrow[\text{retention}]{Cl_2} \text{PhMeRSi*Cl} \xrightarrow[\text{inversion}]{\alpha\text{-NpLi}} \alpha\text{-NpPhMeSi*R}$$

II

For R = neopentyl, I had [α]D +23.2° whereas II had [α]D −18.6°. For R = ethyl, I had [α]D −4.16° whereas II had [α]D +3.36°. For R = benzhydryl, probably due to the presence of active hydrogen in this group, the cycle was less stereospecific; I had [α]D +15.5° whereas II had [α]D −7.1°. The designated assignments of stereochemistry to each of the four reactions are in accord with previous stereochemical studies on the α-naphthylphenylmethylsilyl system,[1,2,5] and are also in accord with an assigned course of inversion of configuration for the cleavage of α-NpPhMeSi*$C_6H_4$-*p*-($OCH_3$) with bromine[6] to give α-NpPhMeSi*Br.

The above Walden cycles, previous determination of the stereochemistry of reactions of α-NpPhMeSi*– compounds, and the recent rigorous determination of the absolute configuration of (−)-α-NpPhMeSi*H by the X-ray method,[9] lead to assignment of absolute configuration for compounds containing four organosilicon systems. This is done below for the dextrorotatory ≡Si*H compounds.

The absolute configuration of the carbon analog[10] of phenylethylmethylsilane is included for comparison.




It is noteworthy that the above first comparison of analogous compounds containing asymmetric silicon and asymmetric carbon indicates the same sign of [α]D for the same configuration, and much smaller optical rotation for the silicon compound. In the phenylethylmethyl systems, methyl and ethyl must have nearly the same polarizability, and the lower rotation of the silicon analog may reflect, at least in part, lower selectivity in conformation distribution due to the larger size of Si.

All three α-NpPhMeSi*R compounds (rotations given above for I) were prepared by treatment of (−)-α-NpPhMeSi*Cl with RLi in ether. Syntheses of ≡Si*R, R = benzhydryl[3] or ethyl,[4] have been reported using this procedure. Cleavage of the α-naphthyl group was performed in benzene with equimolar bromine (*ca.* 2 *M* bromine) for 20 minutes at room temperature for R = neopentyl or ethyl and in carbon tetrachloride for 1 hr. for R = benzhydryl. Without isolation, the optically active bromosilanes were reduced to ≡Si*H and the latter purified by fractional distillation in all cases, and also by subsequent recrystallization for the benzhydryl compound. All three silanes were dextrorotatory (rotations given above); two were liquids and the benzhydryl compound had m.p. 55–56°. Chlorination in carbon tetrachloride gave a dextrorotatory ≡Si*-Cl compound (rotations given above) in all three cases; again, only the benzhydryl compound was crystalline and had m.p. 66–68°. Coupling of the dextrorotatory chlorides with α-naphthyllithium gave optically active α-NpPhMeSi*R compounds (rotations given above for II) which were purified by fractional distillation. Infrared spectra and analyses for the new compounds were all in accord with the assigned structures. Further work on the new optically active systems is in progress.

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(8) The new systems differ from the original system in that ≡Si*H and ≡Si*Cl having the same sign of [α]D have the same configuration in the new systems. This is also true of the original systems for rotations measured below 340 mμ. Discussion of these aspects is deferred to a later paper.

(9) T. Oshida, R. Pepinsky, and Y. Okaya, Abstracts, International Union of Crystallography Congress, Rome, Italy, September, 1963. These results are in accord with a less rigorous determination utilizing Cram's rule of asymmetric induction and some reasonable assumptions: A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(10) D. J. Cram and J. Allinger, *ibid.*, **76**, 4518 (1954).

## On the Stereochemistry of Homoenolization

*Sir:*

Recent work demonstrated that hydrogens beta to a carbonyl can be abstracted by alkali to produce homoenolate ions.[1] We have now studied the stereochemistry of the reverse process, the protonation of homoenolic species, and have found a high degree of stereospecificity whose mechanistic course depends on the medium. The results shed light on the stereochemistry of homoenolization and provide examples of electrophilic substitutions that proceed by inversion of configuration.

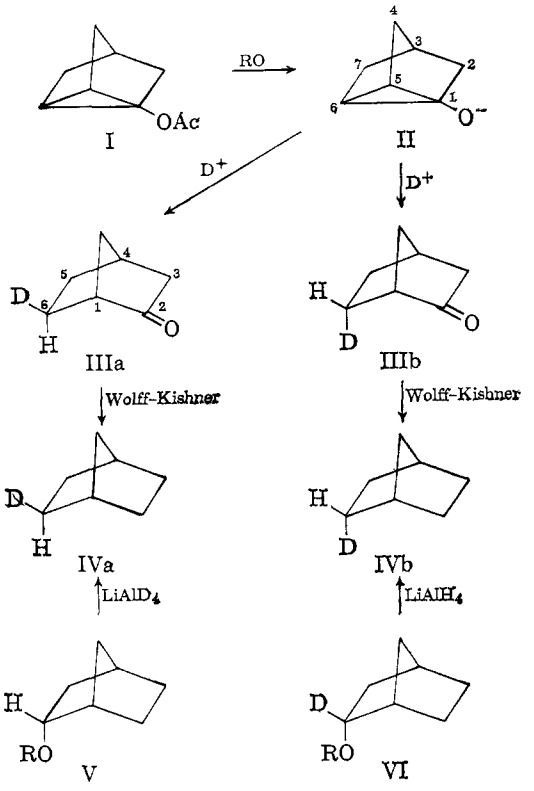
On mild treatment with alkalies, 1-acetoxynortricyclene[2] (I) yielded ion II, which collapsed to norbornan-2-one by protonation at either of the equivalent homoenolic carbons C-5 or C-6. In deuterated medium this homoketonization produced 6-deuterionorbornan-2-one with an *exo* deuterium (IIIa) or with an *endo* deuterium (IIIb) according to whether cleavage occurred with inversion or retention of configuration, respectively.[3] The 6-deuterionorbornan-2-one was converted to 2-deuterionorbornane (IV) by Wolff–Kishner reduction,[4] and the *exo*/*endo* ratio of deuterium in the hydrocarbon was determined by infrared spectroscopic comparison with authentic *exo*-2*d*-norbornane (IVa) and *endo*-2*d*-norbornane (IVb), which were separately synthesized as follows.

(1) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962).

(2) Prepared as reported by H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); *J. Am. Chem. Soc.*, **82**, 6362 (1960).

(3) Any deuterium subsequently incorporated at the enolizable position (C-3) in norbornan-2-one was removed after every run by repetitive treatment with potassium hydroxide in methanol–water.

(4) Deuterium analyses showed that no deuterium was lost during the Wolff–Kishner reduction.




a, R = H
b, R = *p*-$BrC_6H_4SO_2$

The *p*-bromobenzenesulfonate ester[5] (Vb) of *endo*-2-norborneol (Va)[6] was reduced with lithium aluminum deuteride in diethyl ether and gave *exo*-2*d*-norbornane (IVa), $\nu(CS_2)$ 781 and 858 cm.$^{-1}$, 98% monodeuterated by mass spectral analysis, and 0.95 atom excess of deuterium by combustion analysis. In the n.m.r. spectrum the intensity ratio of the bridgehead protons (centered at 2.22 p.p.m.) to the remaining protons (centered near 1.40 and 1.21 p.p.m.) was 1/4.4 (theoretical ratio 1/4.5).[7] The *exo* stereochemistry in IVa follows from the inversion of configuration expected for this type of reduction[8] and was independently confirmed by comparison with *exo*-2*d*-norbornane prepared by hydroboration of norbornene.[9] Reduction of norbornan-2-one with lithium aluminum deuteride gave the deuterioalcohol (VIa). Conversion to the corresponding *p*-bromobenzenesulfonate (VIb) followed by reduction with lithium aluminum hydride gave *endo*-2*d* norbornane, $\nu(CS_2)$ 790 and 840 cm.$^{-1}$, 99% monodeuterated (mass spectrum), and 0.98 atom excess of deuterium (combustion analysis). The n.m.r. intensity ratio of bridgehead protons to remaining protons was 1/4.5 (theory 1/4.5).[10]

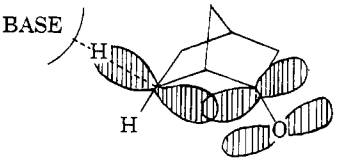
Table I summarizes the stereochemical results of homoketonization at room temperature. Under alkaline conditions (runs 1–4) the protonation occurred with high stereospecificity (>94.5%) and with inversion of configuration. Interestingly, these carbanion protonations are among the first cases of electrophilic substitutions where virtually complete inversion of configuration has been demonstrated.[11–13] In acid medium (run 5) the electrophilic cleavage went with >90% retention of configuration. In run 6 the 1-acetoxynortricyclene was first converted to 1-hydroxynortricyclene with lithium aluminum hydride. Without purification the isolated hydroxy compound was allowed to homoketonize in acid medium, and retention of configuration (>90%) was again observed.[14]

TABLE I

| Medium | Deuterium[a] configuration |
|---|---|
| 1. *t*-BuOK in *t*-BuOD | >94.5% *exo* |
| 2. KOMe in MeOD | >94.5% *exo* |
| 3. KOMe in MeOD/dimethyl sulfoxide (1/1)[b] | >94.5% *exo* |
| 4 $(CH_3)_4\overset{+}{N}\bar{O}D$ in *t*-BuOD | >94.5% *exo* |
| 5. $D_2SO_4$ in DOAc/$D_2O$ (1.2/1) | >90% *endo* |
| 6. $D_2SO_4$ in DOAc/$D_2O$ (1.7/1)[c] | >90% *endo* |

[a] The percentages are minimum values and represent the reliability limits of our infrared method. [b] In mixed solvents the ratios refer to weights. [c] In this run the substrate was 1-hydroxynortricyclene.

To the extent that these homoketonizations are the microscopic reverse of homoenolizations in the bicyclo[2.2.1]heptane system we conclude that the preferred transition state in the alkaline medium involves an *exo* hydrogen. Consequently, any direct orbital overlap with the carbonyl group would have to take place from the backside of the *exo* C–H bond. In contrast, homoenolization in the acid medium would involve preferential abstraction of the *endo* hydrogen. These findings may be relevant to other phenomena involving homoconjugative or *trans*-spatial orbital interactions (*e.g.*, 1,3-eliminations, fragmentation reactions, n.m.r. couplings,[15] etc.) and we are using the epimeric deuterium compounds to study some of these.




**Acknowledgment.**—We gratefully acknowledge support of this work by the Petroleum Research Fund, administered by the American Chemical Society, and by the Alfred P. Sloan Foundation.

(5) S. Winstein and D. Trifan, *Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

(6) K. Alder, H. Wirtz, and H. Koppelberg, *Ann.*, **601**, 138 (1956); S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).

(7) In deuteriochloroform at 60 Mc./sec. Chemical shifts are in p.p.m. downfield from internal tetramethylsilane.

(8) E. L. Eliel, *J. Am. Chem. Soc.*, **71**, 3970 (1949).

(9) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961). We are grateful to Professor Brown for sending us an infrared spectrum of their *exo*-2*d*-norbornane to confirm its identity with ours.

(10) The n.m.r. intensities rule out an alternative pathway for deuterium entry that involves preliminary ionization of the *endo*-brosylate to give a nonclassical norbornyl carbonium ion, which is then attacked by the reducing agent stereospecifically from the *exo* side. This pathway would not alter the stereochemistry of V → IVa; but in the case of VI → IVb a 1:1 mixture of IVb and 1*d*-norbornane would result (neglecting isotope effects). As a further check on this latter possibility we prepared 1*d*-norbornane by reduction of 1-chloronorbornane with sodium in methanol-*d*. Infrared and n.m.r. comparisons showed that if our *endo*-2*d*-isomer (IVb) contained any of the 1*d*-isomer, the amount would have to be less than about 10%.

(11) See D. S. Matteson and J. O. Waldbillig, *J. Am. Chem. Soc.*, **85**, 1019 (1963), for an interesting example of preferred inversion in a mercuride–boronation reaction.

(12) In their extensive studies of carbanion protonations, Cram and coworkers found examples of complete retention of configuration, of complete racemization, and of 60% net inversion of configuration. For similar alkaline media there are striking differences in stereochemical behavior between their open-chain systems and our cyclic ones [D. J. Cram, *et al.*, *ibid.*, **81**, 5740, 5774 (1959); **85**, 1108 (1963)].

(13) C. H. DePuy and F. W. Breitbeil [*ibid.*, **85**, 2176 (1963)] found that treatment of *cis*-1-methyl-2-phenylcyclopropanol in dioxan–$D_2O$ with NaOD in the one case and with DCl in the other gave optically active 4-phenyl-2-butanone with opposite signs of rotation. Their experiments did not reveal the degree of stereospecificity of each cleavage or permit them to make an unequivocal stereochemical assignment to each pathway.

(14) Although 1-hydroxynortricyclene is a special type of cyclopropane system, the stereochemical behavior in acidic medium might be more general for cyclopropane rings, and this point is being investigated.

(15) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

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