In addition to utility in ordinary desulfurizations, this method would serve uniquely in instances of carbonyl removal where the direct Wolff–Kishner procedure would be contraindicated, *e.g.*, with β-dicarbonyls or β-ketoesters (C–C cleavage),[5] some α,β-unsaturated carbonyls (C=C migration),[6] unstable α-substituted cycloalkanones (isomerized reduction products) and acyloins.[7]

Extension into the mechanism of this process and to other variously substituted sulfides including hemithioketals and sulfones is under investigation.

[5] H. Stetter and W. Dierichs, *Ber.*, **86**, 693 (1953), and earlier refs.

[6] R. Fischer, G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **34**, 1577 (1951), and earlier references.

[7] R. B. Turner, R. Anliker, R. Helbling, J. Meier and H. Heusser, *ibid.*, **38**, 411 (1955), and earlier references herein to related systems.

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RECEIVED SEPTEMBER 23, 1959

STEREOCHEMISTRY OF BASE-CATALYZED HYDROGEN-DEUTERIUM EXCHANGE REACTIONS

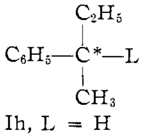
Sir:

In connection with our stereochemical studies of electrophilic substitution at saturated carbon,[1] we find that with hydrogen and deuterium as leaving groups, the reaction's course depends on solvent in a way similar to that when carbon is the leaving group.

TABLE I

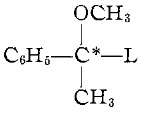
Run no.	Starting mat.[a] Compn.	Starting mat.[a] Concn., M	Solvent	Base Type	Base Concn., M	Temp., °C.	Time, hr.	% Exch.[b]	% Rac.[c]	Net steric course[d]
1	Ih	0.41	$(CH_3)_3COD$[e]	$(CH_3)_3COK$	0.41	218	75	37	4	89% Ret.[f]
2	Id[g]	.26	$(CH_3)_3COH$	$(CH_3)_3COK$	.26	225	69	73	9.5	87% Ret.
3	IIh	.11	$(CH_3)_3COD$[e]	$(CH_3)_3COK$	.33	220	26	51	9.5	80% Ret.[f]
4	IId[h]	.09	$(CH_3)_3COH$	$(CH_3)_3COK$	.55	220	10	13	1.8	88% Ret.
5	IId[h]	.19	$(CH_3)_2SO$[i]	$(CH_3)_3COK$	.26	85	14	31	31	Racem.

[a] Unless otherwise specified, starting material was optically pure. [b] Infrared analysis based on benzyl C–D band at 4.71 μ for Id and 4.725 μ for IId. [c] Optically pure starting materials had these observed rotations (l = 1 dm., neat): Ih, $\alpha^{25}\text{D}$ ±24.3°; Id (91% d), $\alpha^{26}\text{D}$ ±24.0°; IIh, $\alpha^{25}\text{D}$ ±120.0°; IId, $\alpha^{27}\text{D}$ ±120.0° (97% d). [d] Stereospecificity, calculated without correcting for racemization of product once formed, or for any isotope effects. [e] 97% deuterated (combustion and water analysis). [f] Not corrected for incompletely deuterated solvent. [g] Material 87% optically pure, and 81% deuterated. [h] Optically pure, 97% deuterated (combustion and water analysis). [i] Dimethyl sulfoxide containing *tert*-butyl alcohol at a concentration of 2 molar.



$C_6H_5-\overset{C_2H_5}{\underset{CH_3}{C^*}}-L$

Ih, L = H
Id, L = D

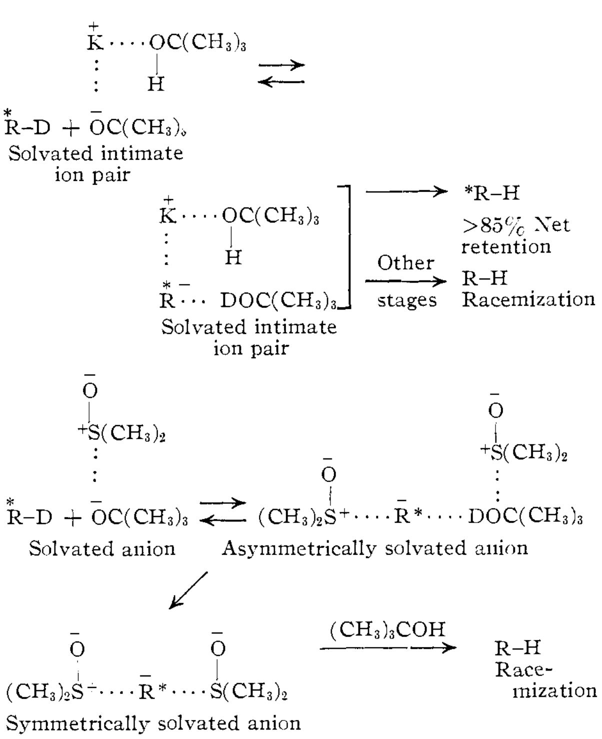


$C_6H_5-\overset{OCH_3}{\underset{CH_3}{C^*}}-L$

IIh, L = H
IId, L = D

The results indicate that hydrogen–deuterium exchange and the reverse reaction occur with high net retention in *tert*-butyl alcohol (runs 1–4), and with racemization in dimethyl sulfoxide (run 5). The values tabulated for the stereospecificity are minimal, since they are uncorrected for incompletely deuterated solvent (runs 1 and 3), or for racemization of product formed by stereospecific exchange reaction (runs 1–4).

Mechanistic schemes somewhat similar to those formulated for other leaving groups[1] would seem to apply.



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RECEIVED AUGUST 27, 1959

[1] (a) D. J. Cram, J. Allinger and A. Langemann, *Chem. and Ind.*, 919 (1955); (b) D. J. Cram, A. Langemann, J. Allinger, K. R. Kopecky, F. Hauck, W. Lwowski, W. D. Nielsen and C. A. Kingsbury, THIS JOURNAL, **81**, 5740 to 5790 (1959).

CYCLOPROPANES. VI. RETENTION OF OPTICAL ACTIVITY AND CONFIGURATION IN THE CYCLOPROPYL CARBANION[1]

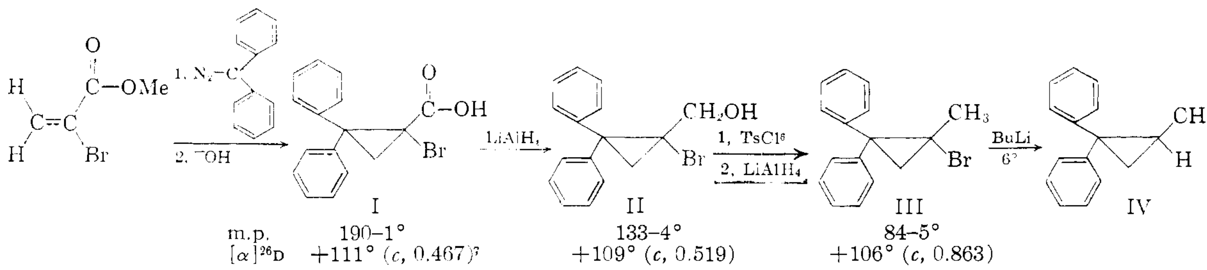
Sir:

We have shown previously that a cyclopropyl carbanion which is formed by the reaction of lithium diisopropylamide[2] or sodium methoxide[3] with 2,2-diphenylcyclopropyl cyanide is incapable of retaining its optical activity. It was recognized that the cyano grouping was playing a significant role in this racemization by participating in the delocalization of the negative charge. We wish to report some experiments which have a bearing on this question. Optically active 1-bromo-1-methyl-

[1] This work was supported by a grant from the National Science Foundation.

[2] H. M. Walborsky and F. M. Hornyak, THIS JOURNAL, **77**, 6126 (1955).

[3] H. M. Walborsky and F. M. Hornyak, *ibid.*, **78**, 872 (1956).



2,2-diphenylcyclopropane (III) prepared as described,[4,5] was chosen for study.

The bromide III (1.7 g., 0.0059 mole, $[\alpha]^{26}D$ + 106°) was dissolved in 50 ml. of 1:1 benzene–petroleum ether and cooled to 5°. A solution of 0.05 mole of butyllithium in 50 ml. of ether was added slowly (20 min.) so that the temperature did not rise above 6°. The solution was allowed to stir for an additional 15 min. at this temperature and then decomposed by the addition of methanol to yield pure 1-methyl-2,2-diphenylcyclopropane (IV) 0.342 g., 43%,[8] $[\alpha]^{26}D$ −78 ± 1° (C, 1.152, $CHCl_3$) whose infrared spectrum was identical in all respects with that of an authentic sample.[9,10]

The rotation of −78° corresponds to an optical purity of 80.5%[10] (80.5% (−)III, 19.5% (+)III), or to 60% retention and 40% racemization. The amount of retention of activity is indeed interesting in view of the observation that the acyclic 2-octyl carbanion retains only slight activity at a much lower (−70°) temperature.[11]

It has been shown that (−)-2,2-diphenylcyclopropanecarboxylic acid (V) was configurationally related to (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (VI)[12] and that the (−)-acid V was related to the (−) hydrocarbon IV.[10] By the use of Fredga's quasi-racemate technique[13] the (+) acid VI was shown to have the same configuration as the (+) acid I. It therefore follows that the conversion of III to IV proceeds with over-all retention of configuration.

As in the cases of the *trans*-butenyl anion (91% retention at −15°)[14] and the 2-octyl anion (20% retention at −70%) one also obtains retention of configuration in the cyclopropyl anion (60% at 6°).[15]

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(4) All substances described gave correct elemental analyses.

(5) The acid I (m.p. 184–5°) was resolved *via* its brucine salt.

(6) The tosylate derivative of II was not isolated.

(7) All rotations were taken in chloroform.

(8) Based on recovered III.

(9) H. M. Walborsky and F. J. Impastato, *Chemistry and Industry*, 1690 (1958).

(10) An optically pure sample of IV ($[\alpha]^{26}D$ − 127°) was prepared by the lithium aluminum hydride reduction of optically pure (−)-2,2-diphenylcyclopropanecarboxylic acid (V),[2] converting the resultant carbinol to the tosylate and then further reduction by lithium aluminum hydride.

(11) R. L. Letsinger, THIS JOURNAL, **72**, 4842 (1950).

(12) F. J. Impastato, L. Barash and H. M. Walborsky, *ibid.*, **81**, 1514 (1959). It should be noted that we have refrained from using absolute configuration notations since the assignment given[12] to the acids is in doubt. If one uses as a model the *transoid* configuration rather than the *cisoid* for the (−)-menthyl acrylate one would arrive at the opposite assignment. This problem is currently being investigated.

(13) A. Fredga, "The Svedberg Anniversary Volume," Almqvist and Wiksells Bocktryckeri A.B., Uppsala, 1945; for a recent application see K. Mislow and M. Heffler, THIS JOURNAL, **74**, 3668 (1952).

(14) A. S. Dreiding and E. E. Harris, *ibid.*, **73**, 4519 (1951); F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(15) That the carbanion is an intermediate in this reaction was demonstrated independently by treatment of (±)-III with butyllithium and pouring the reaction mixture on Dry Ice. The (±) acid VI isolated was identical in its infrared spectrum with that of an authentic sample.

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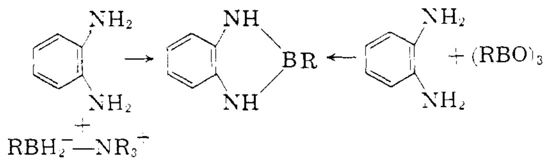
TRIALKYLAMINE ALKYLBORANES AND A NEW SYNTHESIS OF BORAZOLES

Sir:

Alkylboroxines are reduced readily with lithium aluminum hydride in the presence of trialkylamines and in diethyl ether at the reflux temperature. Such reductions are analogous to the previously reported reduction of triphenylboroxine[1] and consistently give 60–65% yields of the corresponding trialkylamine alkylborane.

$$(RBO)_3 + 3NR_3 \xrightarrow[Et_2O,\ 35^\circ]{LiAlH_4} 3RBH_2^-\!-\!NR_3^+$$

Trialkylamines such as trimethyl and triethylamine have been employed with such alkylboroxines as 1-propyl, 2-propyl, 1-butyl, 2-butyl, *i*-butyl, *t*-butyl, 1-pentyl, 1-hexyl, cyclohexyl and benzyl. The products were high boiling oils or low melting solids which could be purified easily by molecular distillation. Characterization was accomplished by C, H, B and N analyses as well as by direct conversion to the dihydrobenzoboradiazole which in every case was identical to that prepared from *o*-phenylenediamine and the corresponding alkyl boroxine.[2] Such interconversions illustrated the absence of alkyl group isomerization during reduction.



Treatment of trimethyl or triethylamine alkyl boranes with ammonia and a trace of ammonium chloride catalyst in diglyme solution at 100–150° results in the rapid evolution of hydrogen and nearly quantitative formation of the corresponding B,B,B-trialkylborazole. The borazoles were isolated by fractional distillation of the reaction mixtures at reduced pressures.

The borazoles were characterized by C, H, B and N analyses and by their characteristic infrared

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(1) M. F. Hawthorne, THIS JOURNAL, **80**, 4291 (1958).

(2) R. L. Letsinger and S. B. Hamilton, *ibid.*, **80**, 5411 (1958).