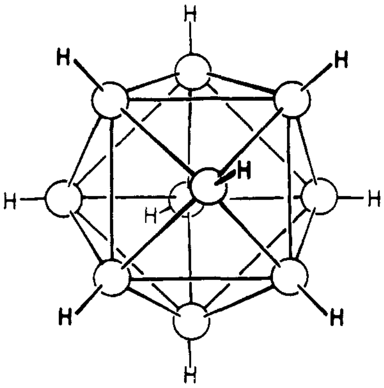

Fig. 1.—Proposed structure of the $B_{10}H_{10}^{-2}$ ion viewed approximately along the $\bar{8}$ axis.

The molecular structure (Fig. 1) has only two kinds of boron atoms in the ratio of 2 (apex) to 8 (approximately equatorial) in a polyhedron of symmetry D_{4d}. The valence orbitals of the apical boron atoms are slightly less symmetrical than those of the equatorial boron atoms, and hence the temperature-independent paramagnetism should be slightly greater for the apical boron atoms. This explanation, based upon a choice of origin at the boron nucleus, forms a more satisfactory basis for understanding B^{11} resonance shifts than that based strictly on formal charge and diamagnetism. Thus the n.m.r. results are well satisfied.

The valence orbitals can best be described by recognition of the two B_5H_5 groups, like those in B_5H_9 molecules, with almost equatorial boron atoms replacing bridge hydrogens. Of the twenty-one electron pairs, ten are used for BH single bonds, and three for each of the framework B_5 groups like those[3] in B_5H_9, and five for bonding among the sixteen remaining sp^3 orbitals of the eight almost equatorial B atoms. In D_{4d} these sixteen orbitals have the representation $A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2 + 2E_3$. Assuming all close interactions as the same, we find[3] A_1 at $H_0 + 2\beta$, E_3 at $H_0 + (2 + 2^{1/2})^{1/2}\beta$ and E_1 at $H_0 + 2^{1/2}\beta$ as strongly bonding orbitals to be occupied by these five electron pairs. The very weakly bonding E_2 at $H_0 + (2 - 2^{1/2})^{1/2}\beta$ and non-bonding B_1 and B_2, as well as all of the antibonding orbitals are unfilled. Thus MO theory in its simplest form leads to a closed shell electronic structure for $B_{10}H_{10}^{-2}$.

(3) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

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RECEIVED OCTOBER 3, 1959

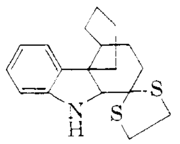
A NEW CHEMICAL DESULFURIZATION METHOD

Sir:

Hydrogenolytic desulfurization employing Raney nickel has proved to be a most useful tool in structural and small scale synthetic transformational work.[1] Other methods, catalytic and chemical, of reductive C–S cleavage have had limited utility.[2]

Hydrazine with or without alkali has been found to desulfurize cyclic or acylic dithioketals. Although the full scope and mechanism of this reaction has not as yet been established, preliminary results indicate satisfactory yields (60–95%), facility of manipulation, application to large or small scale, and freedom from the common disadvantages of the Raney nickel procedure. The substrate, 1 part by weight, in 8–20 parts by volume diethylenegycol or triethylene glycol, 3–5 parts by volume hydrazine hydrate, and 1.5–2.5 parts by weight potassium hydroxide is heated in a simple distillation apparatus. Provision may be made to collect the evolved gas over water, as the progress of reduction may be followed conveniently by this means. When the internal reaction temperature reaches the range 90–135°, depending on the nature of the substance being desulfurized, evolution of gas commences. Heating is continued at the same temperature or at gradually increasing temperatures so as to maintain a steady gas evolution and ultimately may be raised to the range 155–190° for a final completion. Times required varied from thirty minutes to three hours.

Although alkali was found not to be necessary in some cases, it lowered the effective temperature of reaction considerably. Thus, these dithioketals were desulfurized to the parent substances: 4-phenylcyclohexanone ethylenedithioketal, fluorenenone ethylenedithioketal, fluoreneone di-β-hydroxyethylthioketal, compounds I and II,[3] and *p*-menth-4-enone ethylenedithioketal, the 3-p-menthene being produced as the sole product as discerned by vapor phase chromatography.[4]



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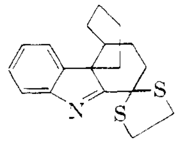

II

The gaseous by-products, collected over water, were shown to be combustible and to reduce permanganate. The sulfur was reduced completely to sulfide, no mercaptan being regenerated in the reaction. This fact plus the recognized stability of thioketals to alkali and the significantly lower reaction temperatures than those required in the Wolff–Kishner reduction vitiate an apparent relationship to the latter reaction.

(1) R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

(2) A. C. Cope and E. Farkas, *J. Org. Chem.*, **19**, 285 (1954); P. Charpentier, *Compt. rend.*, **225**, 306 (1947); H. Gilman and J. J. Dietrich, THIS JOURNAL, **80**, 381 (1958); E. Lieber and S. Somasekhara, *Chem. and Ind.*, 1367 (1958); Truce and Tate, abs. 132, Amer. Chem. Soc. Mtg., Sept. (1957) 43-P; R. Ireland, T. Wrigley and W. G. Young, THIS JOURNAL, **80**, 4604 (1958); M. S. de Winter, C. M. Siegmann and S. A. Szpilfogel, *Chem. and Ind.*, 905 (1959); F. W. Hoffmann, R. J. Ess, T. C. Simmons and R. S. Hanzel, THIS JOURNAL, **78**, 6414 (1956).

(3) The preparation of compounds I and II and the corresponding desulfurized bases will be described fully in a forthcoming publication under the authorship of V. Georgian, R. Harrisson and L. Skaletzky. Satisfactory elemental analyses were obtained for all new substances dealt with herein.

(4) This experiment was performed by Mr. James-Frederick Sauvage.

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.

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(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

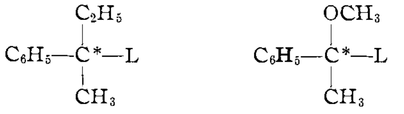
Sir:

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.



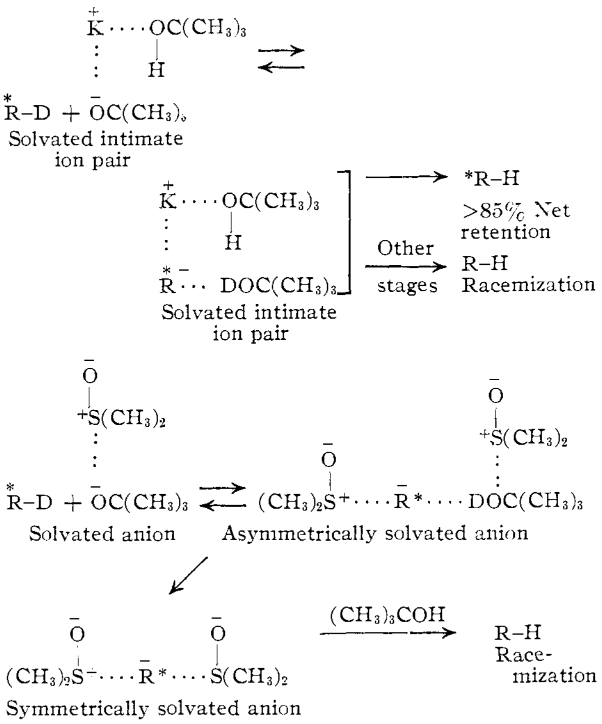
$C_6H_5-C^*(C_2H_5)(CH_3)-L$ $C_6H_5-C^*(OCH_3)(CH_3)-L$

Ih, L = H
Id, L = D

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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(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).

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RECEIVED AUGUST 27, 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-

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(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).