

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**, 1377 (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

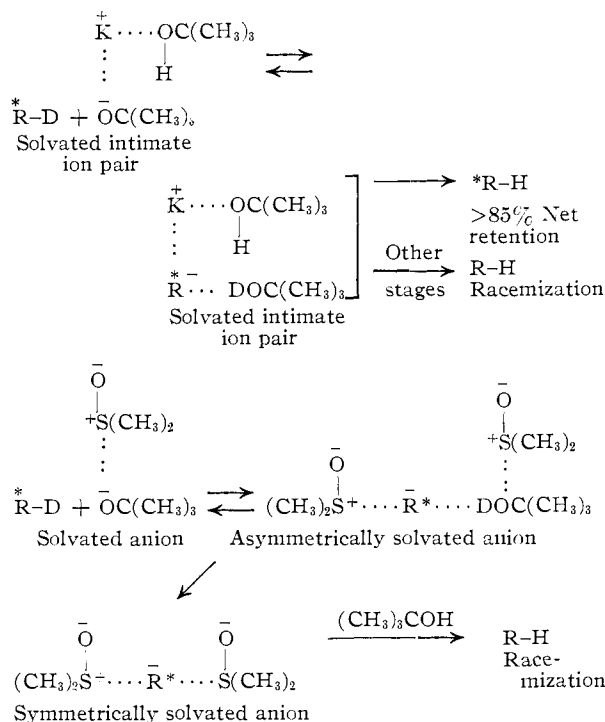
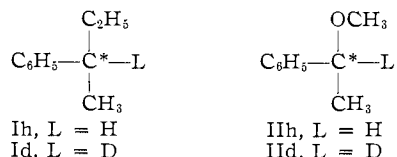


TABLE I

Run no.	Starting mat. a Concn., M	Solvent	Type	Base		Temp., °C.	Time, hr.	% Exch. b	% Rac. c	Net steric course d
				Concn., M						
1	Ih	0.41 (CH ₃) ₃ COD ^e	(CH ₃) ₃ COK	0.41		218	75	37	4	89% Ret. f
2	Id ^g	.26 (CH ₃) ₃ COH	(CH ₃) ₃ COK	.26		225	69	73	9.5	87% Ret.
3	Ih	.11 (CH ₃) ₃ COD ^e	(CH ₃) ₃ COK	.33		220	26	51	9.5	80% Ret. f
4	IIId ^h	.09 (CH ₃) ₃ COH	(CH ₃) ₃ COK	.55		220	10	13	1.8	88% Ret.
5	IIId ^h	.19 (CH ₃) ₂ SO ⁱ	(CH ₃) ₃ COK	.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 IIId. ^c Optically pure starting materials had these observed rotations (*l* = 1 dm., neat): Ih, α^{25D} \pm 24.3°; Id (91% d), α^{25D} \pm 24.0°; Ih, α^{25D} \pm 120.0°; IIId, α^{27D} \pm 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.

groups, the reaction's course depends on solvent in a way similar to that when carbon is the leaving group.



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 groups¹ would seem to apply.

(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 CARBANION¹

Sir:

We have shown previously that a cyclopropyl carbanion which is formed by the reaction of lithium diisopropylamide² or sodium methoxide³ 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).