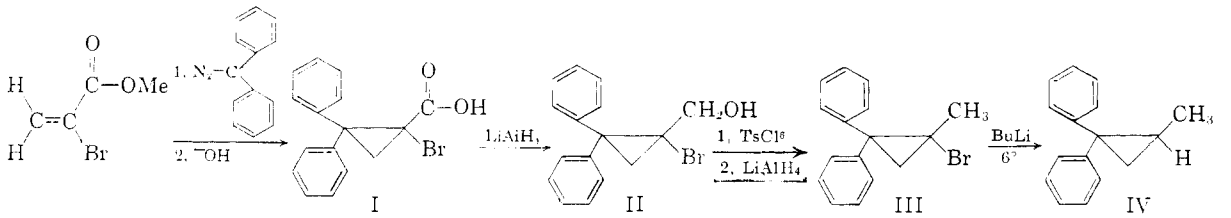


2,2-diphenylcyclopropane (III) prepared as described,[4,5] was chosen for study.

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]

(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 Boktryckeri 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.

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

H. M. WALBORSKY
F. J. IMPASTATO

RECEIVED AUGUST 19, 1959

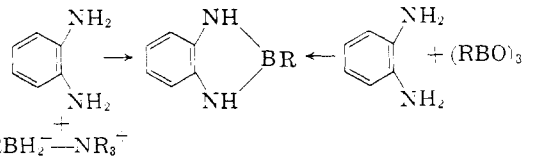
TRIALKYLAMINE ALKYLBORANES AND A NEW SYNTHESIS OF BORAZOLES

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.

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

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

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

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

TABLE I

INTERCONVERSION REACTIONS

Alkyl group	Derivative	Yield, %	M.p. (b.p.), °C.	Analyses Calcd. C	H	B	N	Found C	H	B	N
1-Propyl	Trimethylamine Borane	65		62.64	15.77	9.41	12.18	62.45	15.60	9.50	12.06
	Dihydrobenzoboradiazole	95	102–103								
	Borazole	88	108 (9 mm)	52.28	11.70	15.70	20.32	52.05	11.51	15.74	20.25
2-Propyl	Trimethylamine Borane	65		62.64	15.77	9.41	12.18	62.54	15.79	9.39	12.23
	Dihydrobenzoboradiazole	91	124–126								
	Borazole	79	(70/0.5)	52.28	11.70	15.70	20.32	51.95	11.62	15.60	20.51
1-Butyl	Trimethylamine Borane	64		65.14	15.62	8.38	10.86	64.88	15.38	8.23	10.83
	Dihydrobenzoboradiazole	85	66–67								
	Borazole	91	(110/0.6)	57.92	12.16	13.04	16.88	57.97	12.00	12.94	16.68
2-Butyl	Trimethylamine Borane	66		65.14	15.62	8.38	10.86	65.02	15.29	8.41	10.80
	Dihydrobenzoboradiazole	92	61–62								
	Borazole	85	(94/0.7)	57.92	12.16	13.04	16.88	57.90	11.91	12.90	16.72

spectra. The above table gives data concerning the transformations of four representative alkylboroxines.

$$RBH_2^- - NH_3^+ \xrightarrow[NH_4Cl]{NH_3} [RBH_2^- - NH_3^+] \longrightarrow 2H_2 + 1/3\ (^-RB{\equiv}NH)_3^+$$

The scope of these reactions are under investigation and will be reported later in greater detail.

ROHM AND HAAS COMPANY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA M. FREDERICK HAWTHORNE

RECEIVED SEPTEMBER 9, 1959

A TPN+ SPECIFIC GLYCEROL DEHYDROGENASE FROM LIVER*

Sir:

The DPN+ specific glycerol dehydrogenases of rat and swine liver have been described.[1] I wish to report here the occurrence of a TPN+ specific glycerol dehydrogenase which was found during the process of chromatography of the supernatant fraction of a rat liver sucrose (0.25 *M*) homogenate. This enzyme may be of general interest since it was found to oxidize tris-(hydroxymethyl)-aminomethane and other similar compounds used as biochemical buffers. A volume of 20 ml. of supernatant, containing about 200 mg. protein, which had been dialyzed against 5 m*M* tris phosphate, *p*H 8.0, was applied to a 1.1 × 30 cm. column of DEAE-cellulose,[2,3] and initially eluted with about 150 ml. of the same buffer to removed loosely bound proteins. The two glycerol dehydrogenases emerged as separate peaks of activity as shown in Fig. 1. The total activity of the TPN+ was about one-eighth that of the DPN+ enzyme. The purification of the enzyme during the chromatography was 40–50 fold.

The enzyme may be classed as a D-glyceraldehyde hydrogenase: the equilibrium of the reaction lies far toward the direction of glyceraldehyde reduction[1]; dihydroxyacetone was found to give less than one-fifth the activity obtained with DL-glyceraldeyde; and D-glyceraldeyde was found to be more active than the DL-form.

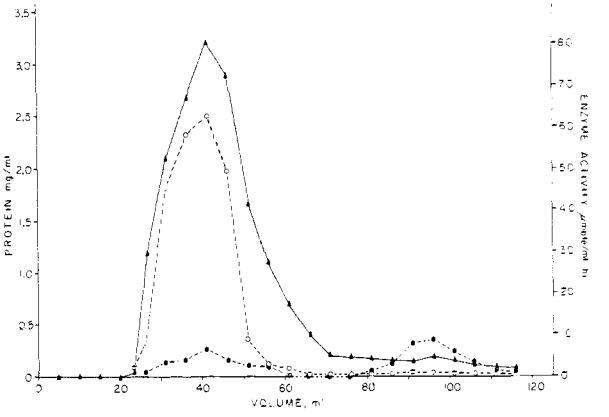


Fig. 1.—Separation of DPN+ and TPN+ D-glyceraldehyde hydrogenases on DEAE-cellulose. The reaction mixture contained 20 μmole of DL-glyceraldehyde, 4 μmole of triethanolamine *p*H 7.0, and 0.02 μmole DPNH or TPNH in a volume of 200 microliters. Incubation was 30 min. at 38°. Triangles represent protein (Lowry); open circles, enzyme activity with DPNH; closed circles, with TPNH.

The optimum *p*H for glyceraldehyde reduction was less than 7.0 with 0.1 *M* DL-glyceraldehyde, 0.02 *M* triethanolamine buffer, and 10^{-4} *M* TPNH. When the reaction was run in the opposite direction, at 0.1 *M* substrate concentration and at the optimum *p*H of 9.5 in triethanolamine buffer, glycerol was oxidized, but 2-amino-2-methyl-1, 3-propanediol (AMP_2) was oxidized at about twice the rate. Tris-(hydroxymethyl)-aminomethane and 2-amino-2-methyl-1-propanol (AMP_1) were oxidized at about two-thirds the rate of glycerol, and ethanol was not oxidized at a measurable rate. The K_m's at 38° for glycerol and AMP_2 were 0.63 *M* and 0.13 *M*, respectively. The K_m for TPN+ in the presence of 0.5 *M* AMP_2 was 1.7×10^{-4} *M*. The K_m for D-glyceraldehyde was 6.2×10^{-4} *M*. The enzyme was 95% inhibited by 10^{-5} *M* *p*-mercuribenzoate.

* These abbreviations are used: TPN+ and TPNH, oxidized and reduced forms of triphosphopyridine nucleotide, respectively; DPN oxidized diphosphopyridine nucleotide; DEAE-cellulose, diethylaminoethyl-cellulose.

This work was supported by grant C-4110 from the National Cancer Institute of the National Institutes of Health, United States Public Health Service.

(1) H. P. Wolf and F. Leuthardt, *Helv. Chim. Acta*, **36**, 1463 (1953).
(2) E. A. Peterson and H. A. Sober, THIS JOURNAL, **78** 751 (1956).
(3) H. A. Sober, F. J. Cutter, M. M. Wycoff and E. A. Peterson, *ibid.*, **78**, 756 (1956).