

of Colter and McKelvey.<sup>7</sup> The method assumes that the E1 product proportions are the same in both the presence and absence of strong base. Two or three base concentrations in the range 0.26–1.2 M were used in deriving each figure. The greatest contribution of the E1 reaction to the total elimination product was 21–22% at the lowest base concentrations. Sample data used in calculating the corrections are given in Table VI.

**Control Experiments.** The absence of a significant E1 component in the reactions of most of the tosylates was shown by runs at two or more base concentrations in the range 0.2–1.2 M. Only 2-

methyl-3-pentyl and 3-methyl-2-butyl tosylates (see above) showed a regular trend that exceeded experimental error. Synthetic mixtures of the olefins were neither fractionated nor isomerized on exposure to reaction conditions more stringent than those employed on the tosylates, followed by work-up using the procedure described above (conditions: 0.4–0.6 M *t*-butoxide in *t*-butyl alcohol at 80° for 20 hr on the pentenes, and 110° for 76 hr on the methylpentenes). While longer reaction times in the E1 reactions sometimes led to decreases in overall yields, olefin proportions were independent of reaction time.

## Mechanism and Kinetics of Radiolytically Initiated Cyclohexyl Radical Addition to *cis*- and *trans*-1,2-Dichloroethylene and of the Subsequent Chlorine Atom Elimination Reaction

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*Contribution from the Soreq Nuclear Research Centre, Yavne, Israel.*

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**Abstract:** The kinetics of  $\gamma$ -radiation induced formation of *cis*- and *trans*-1-cyclohexyl-2-chloroethylene by a free-radical chain mechanism in binary solutions of *cis*- and *trans*-1,2-dichloroethylene in cyclohexane was studied at 150°. The condensation reaction between the solvent and the two solutes resulted in the formation of equal ratios of *cis*- and *trans*- $c\text{-C}_6\text{H}_{11}\text{CH}=\text{CClH}$ . The condensation reaction was found to proceed *via* addition of cyclohexyl radicals to the olefins followed by subsequent elimination of a chlorine atom from the intermediate radical. The rate constants for the addition of cyclohexyl radicals to *cis*- and *trans*-1,2-dichloroethylene are estimated at  $3.1 \pm 0.4 \times 10^4$  and  $9.7 \pm 0.7 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively. The rate constants of the chlorine elimination reaction are estimated at  $8.6 \pm 2.6 \times 10^8$  and  $1.12 \pm 0.37 \times 10^4 \text{ sec}^{-1}$  for the radicals obtained from solutions of *cis* and *trans* isomers, respectively. The possible mechanisms of the addition and elimination reactions are discussed.

The free-radical interaction of olefins and saturated compounds has been the subject of numerous investigations. The interaction of geometrical isomeric olefins with saturated compounds is of particular interest since the steric structure of the products resulting from both isomers may possibly yield valuable information on the mechanism of such reactions.

In recently published work<sup>1</sup> we reported the occurrence of  $\gamma$ -radiation induced free-radical chain condensation reactions of alkanes (RH) with tetrachloroethylene and trichloroethylene.  $\gamma$  irradiation was found to offer some significant advantages in the kinetic study of such reactions. The condensation reactions were found to proceed *via* addition of R radicals to the chloroolefins followed by subsequent elimination of a chlorine atom. We thought it worthwhile to extend this study to solutions of *cis*- and *trans*-1,2-dichloroethylene in alkanes, expecting that in addition to the determination of rate constants for the addition and elimination steps the comparison of the reactivities of the two isomers and their product distributions might yield additional information on the mechanism of such reactions. Cyclohexane was chosen as the alkane solvent since it forms predominantly cyclohexyl radicals upon radiolysis, thus eliminating complications arising from the possibility of different alkyl radicals attaching themselves to the olefins.

(1) (a) A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **91**, 4626 (1969); (b) *ibid.*, **91**, 4631 (1969).

### Experimental Section

**Materials.** *cis*- and *trans*-1,2-dichloroethylene (Fluka purum) were purified by distillation. Phillips Research Grade cyclohexane, stated purity 99.99%, was used as received after it was found that treatment with sulfuric acid<sup>2a</sup> did not affect the yield of products, within the experimental error.

**Procedure.** The sample preparation and irradiation techniques were similar to those used by us previously.<sup>2</sup> The irradiations were carried out in Pyrex ampoules containing 2-ml solutions. The total volume of the ampoules was less than 3 ml. The irradiations were carried out at a dose rate of  $2.02 \times 10^{17} \text{ eV ml}^{-1} \text{ min}^{-1}$ . The total dose administered to the *cis*- and *trans*-dichloroethylene solutions was  $1.26 \times 10^{18}$  and  $6.28 \times 10^{17} \text{ eV ml}^{-1}$ , respectively. The liquid products were determined by gas chromatography (F & M Model 810). The cyclohexylchloroethylenes were analyzed with a 12-ft 20% Ucon on Diatoport column at 150°. The same column at 50° was used for the determination of *cis*- $\text{C}_2\text{Cl}_2\text{H}_2$ . *trans*- $\text{C}_2\text{Cl}_2\text{H}_2$  was analyzed with a 16-ft 20% silicon oil DC 200 on Diatoport column at 50°.  $c\text{-C}_6\text{H}_{11}\text{CHCClH}$  was identified by mass spectrometric analysis and combustion analysis.

*Anal.* Calcd for  $\text{C}_8\text{H}_{13}\text{Cl}$ : C, 66.4; Cl, 24.5; H, 9.1. Found: C, 66.2; Cl, 24.8; H, 8.9.

Nmr and ir techniques were used to differentiate between the *cis* and *trans* isomers of  $c\text{-C}_6\text{H}_{11}\text{CHCClH}$ . HCl was determined coulometrically.<sup>2b</sup>

### Results and Discussion

The main products of the radiolysis of solutions of *cis*- and *trans*-1,2-dichloroethylene are HCl and *cis*- and *trans*-1-cyclohexyl-2-chloroethylene. The yields

(2) (a) L. A. Rajbenbach and U. Kaldor, *J. Chem. Phys.*, **47**, 242 (1967); (b) A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **90**, 4105 (1968).

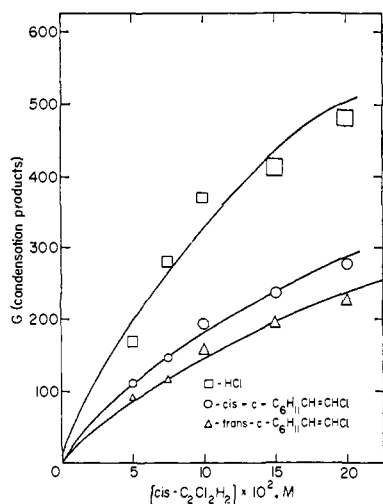
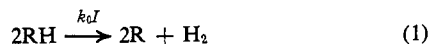


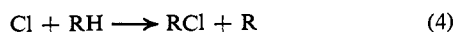
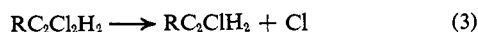
Figure 1. Yield of condensation reaction products vs. concentration of *cis*-1,2-dichloroethylene.

of these products, expressed in terms of  $G$  values (molecules per 100 eV energy absorbed), are shown in Figures 1 and 2 as a function of solute concentration. From these data it can be seen that in both solutions the yield of HCl is equal, within the experimental uncertainty, to the sum of the yields of *cis*- and *trans*-1-cyclohexyl-2-chloroethylene along the whole range of solute concentrations. The disappearance of the solute was checked against the yield of condensation products in 0.1  $M$  solutions. In the case of the *cis*-1,2-dichloroethylene, at a total dose of  $2.51 \times 10^{18}$  eV  $\text{ml}^{-1}$ ,  $G(-\text{C}_2\text{Cl}_2\text{H}_2)$  was found to be  $\sim 340$ , while the corresponding  $G$  value for the formation of *cis*- and *trans*- $c\text{-C}_6\text{H}_{11}\text{-C}_2\text{Cl}_2\text{H}_2$  was 310. In the case of *trans*- $\text{C}_2\text{Cl}_2\text{H}_2$  the corresponding values, determined at  $1.25 \times 10^{18}$  eV  $\text{ml}^{-1}$  total dose, were  $G(-\text{C}_2\text{Cl}_2\text{H}_2) = 585$  and  $G(c\text{-C}_6\text{H}_{11}\text{-C}_2\text{Cl}_2\text{H}_2) = 610$ . Given the uncertainty in the determination of  $G(-\text{solute})$  values, these results can be considered as proving that the solutes are removed from the system predominantly by a reaction sequence leading to the formation of  $c\text{-C}_6\text{H}_{11}\text{CHClH}$  accompanied by HCl.

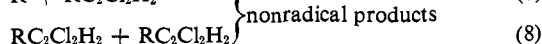
**Reaction Scheme.** The experimental results are discussed in terms analogous to that set up for the case of trichloroethylene solutions.<sup>1b</sup> The radiation intensity is represented by I and the cyclohexane by RH.



chain propagation



chain termination



The initiation step (reaction 1) represents the radiolytic process in a somewhat oversimplified way. However it can be reasonably assumed that cyclohexyl radicals are the only "long-lived" species which will enter into chemical reaction with the solute leading to a

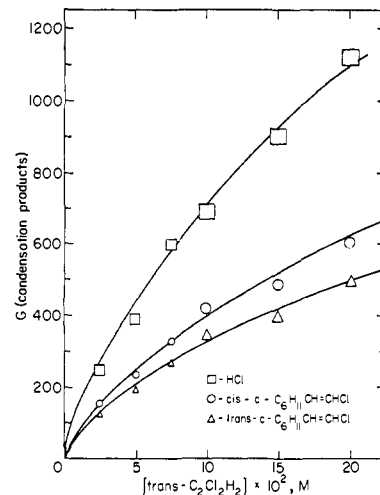
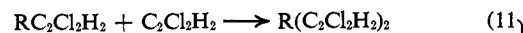
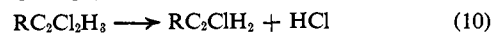


Figure 2. Yield of condensation reaction products vs. concentration of *trans*-1,2-dichloroethylene.

chain reaction. A more detailed description of the primary processes occurring in the radiolysis of solutions of chloroethylenes in alkanes has been presented elsewhere.<sup>3</sup>

Additional reactions which should be considered in the system studied are



Reactions 9 and 10 could constitute an alternative propagation sequence. However the thermodynamics of step 10 are considered to be highly unfavorable at 150°. We have some evidence<sup>4</sup> for the occurrence of reactions 9 and 11 in radiolysis at room temperature. The fact that we were unable to detect cyclohexyl-dichloroethane among the radiolysis products at 150°, and the finding that  $G(-\text{C}_2\text{Cl}_2\text{H}_2) \approx G(c\text{-C}_6\text{H}_{11}\text{-C}_2\text{Cl}_2\text{H}_2)$  indicates that under our experimental conditions reactions 9 and 11 do not occur to a significant extent.

Another possible complicating reaction is



Reaction 12 does not seem to be very plausible because of the large excess of  $c\text{-C}_6\text{H}_{12}$  over  $\text{C}_2\text{Cl}_2\text{H}_2$  and the fact that liquid-phase chlorination studies<sup>5</sup> have shown  $k_4$  to be approximately three to four times larger than  $k_{12}$ . In addition, reversal of step 12 would be expected to lead to geometrical isomerization of the starting olefin. No such isomerization of the recovered olefins could be detected, further supporting the contention that chlorine atoms react exclusively by reaction 4.

**Kinetics of Cyclohexylchloroethylene Formation. Determination of  $k_2$  and  $k_3$  Values.** Under the conditions of long kinetic chains it can be shown<sup>1b</sup> that the yield of the condensation products should be related to the solute concentration by the expression

$$1/G(\text{RC}_2\text{ClH}_2) = \left[ \frac{2\alpha(k_5 + k_6)}{G(R_0)} \right]^{1/2} (1/k_3 + 1/k_2[\text{C}_2\text{Cl}_2\text{H}_2]_{\text{av}}) \quad (I)$$

(3) A. Horowitz and L. A. Rajbenbach, *J. Chem. Phys.*, **48**, 4278 (1968).

(4) A. Horowitz and L. A. Rajbenbach, unpublished results.

(5) M. L. Poutsma and R. L. Hinman, *J. Amer. Chem. Soc.*, **86**, 3807 (1964).

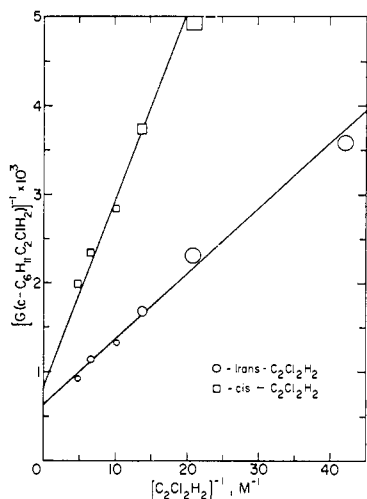


Figure 3. The reciprocal of  $G(c\text{-}C_6H_{11}C_2ClH_2)$  as a function of the reciprocal of the  $C_2Cl_2H_2$  concentration.

where  $[C_2Cl_2H_2]_{av}$  represents the average concentration of the solute during the reaction. To find  $[C_2Cl_2H_2]_{av}$  it is assumed that the final concentration of the solute is given by the difference between its initial concentration and the yield of the condensation products, *i.e.*, by assuming  $G(-C_2Cl_2H_2) = G(c\text{-}C_6H_{11}C_2ClH_2)$ .  $G(R_0)$  denotes the radiolytic yield of cyclohexyl radicals in pure solvent. The proportionality constant  $\alpha = 10D/N$ , where  $D$  represents the rate of energy absorption in  $eV\ ml^{-1}\ sec^{-1}$  and  $N$  is the Avogadro number, converts the  $G$  values into the rate of formation in units of  $M^{-1}\ sec^{-1}$ .

Inherent in expression I is the assumption that, as in the case of  $C_2Cl_4$  solutions in alkanes,<sup>1a</sup> the yield of radiolytically generated cyclohexyl radicals is unaffected by the presence of the solute in the concentration range used and equals that in pure irradiated solvent. The fact that expression I is obeyed (Figure 3) tends to support the assumption that no significant changes in the total radical yield occur in the solute concentration range used.

From the ratios of intercept to slope we obtain  $k_2/k_3$  ratios. The values of  $k_2$  and  $k_3$  can be estimated by taking  $2(k_5 + k_6) = 4.1 \times 10^9\ M^{-1}\ sec^{-1}$  (ref 6) and  $G(R_0) = 5$  (ref 7), under the assumption that the radiolytic yield of cyclohexyl radicals at  $150^\circ$  is not significantly different from that observed at room temperature. The  $k_2$  and  $k_3$  values obtained are shown in Table I.

**Mechanism of the Addition (Step 2) and Elimination (Step 3) Reactions.** The higher reactivity of the *trans* isomer of  $C_2Cl_2H_2$  toward cyclohexyl radical addition (see Table I) conforms to the general trend of the higher radical affinity of *trans* olefins as reported by Mayo<sup>8</sup> and Szwarc.<sup>9</sup> However, such a comparison is somewhat

(6) M. C. Sauer, Jr., and M. Mani, *J. Phys. Chem.*, **72**, 3856 (1968). These authors give the value  $2 \times 10^9\ M^{-1}\ sec^{-1}$  for the rate constant of cyclohexyl-cyclohexyl radical interaction, and an activation energy of 1.4 kcal/mole for hexyl-hexyl radical interaction in liquid *n*-hexane. Assuming equal activation energy for hexyl-hexyl and cyclohexyl-cyclohexyl radical interaction, we arrive at  $2(k_5 + k_6) = 4.1 \times 10^9\ M^{-1}\ sec^{-1}$  at  $150^\circ$ .

(7) R. A. Holroyd and G. W. Klein, *J. Amer. Chem. Soc.*, **87**, 4983 (1965). These authors have established the following  $G$  values for the parent-minus-hydrogen radicals in *n*-pentane, *n*-hexane, and cyclopentane: 5.4, 5.6, and 4.6, respectively.

(8) F. M. Lewis and F. R. Mayo, *ibid.*, **70**, 1533 (1948).

(9) R. A. Bader, R. P. Buckley, F. Leavit, and M. Szwarc, *ibid.*, **79**, 5621 (1957).

Table I. Rate Constants for the Addition of Cyclohexyl Radicals to *cis*- and *trans*-1,2-Dichloroethylene ( $k_2$ ), and for the Chlorine Atom Elimination from the 1,2-Dichloro, Cyclohexylethyl Radical ( $k_3$ )

| Solute                             | $k_2 \times 10^{-4}$ ,<br>$M^{-1}\ sec^{-1}$ | $k_3 \times 10^{-3}$ ,<br>$sec^{-1}$ | $G(cis\text{-}c\text{-}C_6H_{11}\text{-}CHCClH)/G(trans\text{-}c\text{-}C_6H_{11}\text{-}CHCClH)$ |
|------------------------------------|--|--------------------------------------|---|
| <i>cis</i> -1,2-Dichloroethylene   | $3.4 \pm 0.4$                                | $8.6 \pm 2.6$                        | $1.23 \pm 0.04$   |
| <i>trans</i> -1,2-Dichloroethylene | $9.7 \pm 0.7$                                | $11.2 \pm 3.7$                       | $1.22 \pm 0.03$   |

misleading since in the case of 1,2-dichloroethylene, rather exceptionally, the *trans* isomer represents the thermodynamically less stable form,<sup>10</sup> and could therefore be expected *a priori* to be more reactive. (The higher stability of the *cis* form of  $C_2Cl_2H_2$  results most probably from a more pronounced double-bond character of the C-Cl bond in this isomer.<sup>11</sup>) Both Mayo<sup>8</sup> and Szwarc<sup>9</sup> have suggested that the lower reactivity—despite their lesser stability—of the *cis* isomers studied by them is due to the greater steric interference of the substituents in the transition state of the addition reaction. The resulting lack of planarity in the activated complex, with its adverse effect on resonance stabilization, more than offsets the higher energy content of the *cis* olefins, leading to their lower reactivity as compared with the *trans* isomer. Szwarc has interpreted the lack of correspondence between, on the one hand, the heats of formation of the *cis* and *trans* isomers, and on the other, the difference in activation energy for the addition of methyl radical to the isomers, as an indication of the existence of two different transition states for the addition of the radicals in the two cases. This hypothesis was not verified by Szwarc for the case of 1,2- $C_2Cl_2H_2$  since he observed some side reactions, quite probably chlorine atom elimination from the  $CH_3\text{-}CHClCHCl$  radical (analogous to reaction 3 in our scheme) which interfered with the determination of the activation energies involved. In the addition of alkyl radicals to dichloroethylene, steric interference with resonance in the activated complex is not plausible, and thus, provided that the addition to both isomers proceeds *via* the same transition state, the less-stable energy-rich *trans*- $C_2Cl_2H_2$  could be expected to be the more reactive isomer of the pair.

It should be noted that under the assumption of the same transition state and equal preexponential factors for the addition of cyclohexyl radicals to both isomers of  $C_2Cl_2H_2$ , the difference in activation energies would equal the difference in the heats of formation of the isomers, namely 450 cal/mole.<sup>10</sup> Thus one would expect a reactivity ratio *trans/cis*  $\approx 1.8$ . The ratio obtained by us is  $\approx 3$ .

Turning to the elimination reaction, step 3, we observe that although the yield of the condensation products is smaller in the case of the *cis* isomer, the ratio  $G(cis\text{-}c\text{-}C_6H_{11}C_2ClH_2)/G(trans\text{-}c\text{-}C_6H_{11}C_2ClH_2)$  is the same for both isomers. Moreover, the values of the rate constants  $k_3$  for chlorine atom elimination from the  $c\text{-}C_6H_{11}CClHCClH$  radical can be considered equal in the two isomers, within experimental error. This

(10) K. S. Pitzer and J. Hollenberg, *ibid.*, **76**, 1493 (1954).

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 289.

means that at some stage, prior to the chlorine atom elimination reaction, the original stereochemical structure is lost. This might happen at the stage of the activated complex if the addition proceeds *via* the same transition state in both isomers, or it might be caused by a free rotation around the C-C axis of the original olefinic carbon atoms in the  $c\text{-C}_6\text{H}_{11}\text{C}_2\text{Cl}_2\text{H}_2$

radical if there is a different transition state in the two cases.

Another question which arises is whether the chlorine atom splitting reaction leading to the formation of the *cis* and *trans* forms of  $c\text{-C}_6\text{H}_{11}\text{CHCClH}$  proceeds *via* a single or two distinct transition states. This question cannot be answered on the basis of our results.

## Selective Reductions. XV. Reaction of Diborane in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

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Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. Received September 10, 1969

**Abstract:** The rates and stoichiometry of the reaction of diborane in tetrahydrofuran solution with selected organic compounds containing representative functional groups were examined under standardized conditions in order to compare its reducing characteristics with those of other selective reducing agents similarly examined and to establish the scope of its applicability as a selective reducing agent. The rate of evolution of hydrogen from active hydrogen compounds varied considerably with the nature of the functional group and the structure of the hydrocarbon moiety. Most aldehydes and ketones are reduced rapidly to the alcohol stage. However, the reduction of benzophenone is considerably slower. Norcamphor is reduced with much higher stereospecificity than is realized with the usual complex hydrides, yielding 2% *exo*-, 98% *endo*-norbornanol. *p*-Benzoquinone is reduced to hydroquinone at a moderate rate, whereas the reaction with anthraquinone is quite sluggish. Carboxylic acids are rapidly reduced, whereas the corresponding acid chlorides react much slower. Aliphatic acid esters are reduced at a moderate rate, whereas the reactions of aromatic esters are much slower. The reactions of diborane with epoxides are relatively slow and complex, yielding only 48% of butyl alcohols from the simplest epoxide examined, 1,2-butylene oxide, and none of the anticipated simple alcohols from 1-methyl-1,2-cyclohexene oxide. Tertiary amides and nitriles are reduced readily to the corresponding amines, whereas the reduction of primary amides is much slower. Azobenzene undergoes reduction to aniline, whereas 1-nitropropane, nitrobenzene, and azoxybenzene are stable to the reagent under the standard conditions. Cyclohexanone oxime, phenyl isocyanate, and pyridine *N*-oxide react with diborane at moderate rates, whereas pyridine forms an addition compound but fails to indicate further reaction. Finally dimethyl sulfoxide is reduced at a moderate rate to dimethyl sulfide. However, the other sulfur derivatives examined, disulfide, sulfide, and tosylate, are inert to the reagent under the standard conditions.

Diborane has proved to be a most versatile reagent for the hydroboration of olefins, dienes, and acetylenes,<sup>2</sup> making organoboranes readily available for synthetic purposes.<sup>3</sup> Previous explorations have also revealed that diborane is a powerful hydrogenating agent for functional groups.<sup>4</sup>

In these preliminary exploratory studies<sup>4</sup> we noted many unusual reducing characteristics of diborane, quite different from those we have observed for aluminum hydride,<sup>5</sup> lithium aluminum hydride,<sup>6</sup> and its

alkoxy derivatives.<sup>7,8</sup> In particular, it appeared that diborane, as a Lewis acid, functions as an "acidic" reducing agent,<sup>4b</sup> in marked contrast to the behavior of sodium borohydride or the alkoxy aluminohydrides<sup>7,8</sup> which function as "basic" reducing agents.

For example, acyl halides are rapidly reduced by all of the aluminum hydrides<sup>6-8</sup> as well as by sodium borohydride. However, reduction of acyl halides by diborane is remarkably slow.<sup>4a</sup> On the other hand, carboxylic acids are rapidly reduced by diborane,<sup>4b,c</sup> with the rate comparable to that exhibited by the exceedingly powerful reducing agent, lithium aluminum hydride. This reactivity toward the mild reagent, diborane, is in marked contrast to the behavior of the other mild reagents, lithium tri-*t*-butoxyaluminumhydride and sodium borohydride, neither of which reduce carboxylic acids under the usual mild standard conditions (THF, 0°).

(1) (a) Postdoctorate research associate, 1962-1964, on research grants supported by the Atomic Energy Commission, AT(11-1)-70, and the National Institute of Health, GM 10937; (b) graduate research assistant, 1963-1967, and postdoctorate research associate, 1967-1969, on Research Grants DA-31-124, ARO(D)-117, and -453 supported by the U. S. Army Research Office (Durham).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) (a) H. C. Brown, *Accad. Naz. Lincei*, 73 (1968); (b) H. C. Brown, *Accounts Chem. Res.*, 2, 65 (1969).

(4) (a) H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, 61, 673 (1939); (b) H. C. Brown and B. C. Subba Rao, *ibid.*, 82, 681 (1960); (c) H. C. Brown and W. Korytnyk, *ibid.*, 82, 3866 (1960).

(5) H. C. Brown and N. M. Yoon, *ibid.*, 88, 1464 (1966).

(6) H. C. Brown, P. M. Weissman, and N. M. Yoon, *ibid.*, 88, 1458 (1966).

(7) H. C. Brown and P. M. Weissman, *ibid.*, 87, 5614 (1965).

(8) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, 1, 430 (1963).