

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. X. Rates of Reaction of Bis-3-methyl-2-butylborane with Representative Cycloalkenes and Isomeric *cis-trans* AlkenesBY HERBERT C. BROWN AND A. W. MOERIKOFER^{1,2}

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The reaction of bis-3-methyl-2-butylborane (dimer) with cyclopentene in tetrahydrofuran solution is second order, first order in cyclopentene and first order in dimeric bis-3-methyl-2-butylborane (disiamylborane). The rate constant for cyclopentene, $k_2 = 14.0 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹, decreases by a factor of 100-fold for cyclohexene, $k_2 = 0.134 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹, but rises sharply again for cycloheptene, $k_2 = 72 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹. *cis*-2-Butene, with $k_2 = 23 \times 10^{-4}$, reacts at a rate slightly faster than cyclopentene, whereas the rate for *trans*-2-butene, with $k_2 = 3.8 \times 10^{-4}$, is slower by a factor of 6. As the alkyl groups on the double bond, RCH=CHR', are varied from methyl (2-butene) to ethyl (2-pentene, 3-hexene), to isopropyl (4-methyl-2-pentene, 2,5-dimethyl-3-hexene), and finally to *t*-butyl (4,4-dimethyl-2-pentene), the rates of reaction with disiamylborane invariably decrease with the increasing steric requirements of the alkyl substituents. However, in each case, the *cis* isomer reacts at a considerably greater rate than the corresponding *trans* structure. Consequently, the reaction of aliphatic olefins with disiamylborane should be generally applicable to the selective removal of the *cis* isomer from the *trans*, as well as to differentiate between isomeric structures. The higher reactivities of the *cis* isomers over the *trans*, as well as that of cyclopentene and cycloheptene over cyclohexene, are attributed to the strained condition of the double bonds in the more reactive olefins.

In earlier studies attempts were made to follow the rates of reaction of diborane with representative olefins. However, the reaction proved to be too fast to measure in the ether solvents utilized for the hydroboration reaction.³

In the course of exploring the selective hydroboration of olefins, it was observed that bis-3-methyl-2-butylborane (disiamylborane) possesses very useful characteristics as a hydroborating agent. Thus it reacts with terminal olefins to give (after oxidation) the primary alcohol in very high purity. In the case of 1,2-dialkylethylenes, RCH=CHR', the boron atom preferentially combines with the less hindered carbon atom of the double-bond. Moreover, disiamylborane proved to be highly selective between olefins of different structures, permitting the quantitative separation of 1-hexene from 2-hexene, and of cyclopentene from cyclohexene. Even more remarkable, it permitted the removal of *cis*-2-pentene from *trans*-2-pentene.^{4,5}

These characteristics suggested the desirability of a more quantitative study of the influence of olefin structure upon its rate of reaction with disiamylborane. Ideally, such a comparison of reactivity should be based on the rate constants for the reactions of the reagent with the different olefins. Accordingly, we undertook a detailed study of the kinetics of the reaction, utilizing cyclopentene as a representative olefin. Although the experimental difficulties were great, the kinetics proved to be relatively simple. Consequently, we extended this procedure to cyclohexene and cycloheptene, in order to establish the influence of ring-size on olefin reactivity, and then examined a number of isomeric *cis-trans* alkenes, in order to establish the magnitude and generality of the

marked difference in reactivity observed previously for *cis*- and *trans*-2-pentene and 2-hexene.

Results

Kinetics of the Reaction of Disiamylborane with Cyclopentene.—Disiamylborane is a white solid, highly susceptible to oxidation by air and to hydrolysis by moisture.⁵ Because of these difficult characteristics, it appeared impractical to undertake the isolation of the analytically pure product for preparation of standard solutions to be utilized in the rate studies. Instead, standard solutions of 2-methyl-2-butene and of diborane, both in tetrahydrofuran, were prepared, and the reagent synthesized *in situ* by mixing two moles of the olefin per mole of borane. The mixture was permitted to stand for 6–9 hours at 0° to complete the synthesis of the reagent.

In this procedure it was necessary to operate with the rigorous exclusion of air and moisture, as well as to mix the two reagents in precisely the stoichiometric amounts. A slight deficiency of the olefin (or a slight excess of diborane) results in the presence of monosiamylborane, a much more reactive intermediate. Alternatively, a small excess of 2-methyl-2-butene introduces complications since it reacts with disiamylborane at a rate competitive with that of several of the olefins of interest in this study.

The reaction was initiated by adding standard solutions of cyclopentene and methylcyclohexane (internal standard) in tetrahydrofuran to the solution of disiamylborane. Aliquots, removed and quenched with 1-decene then were analyzed for the cyclopentene/methylcyclohexane ratio by vapor phase chromatography.

Diborane, which exists in the dimeric state in many ether solvents, dissociates to form the monomeric borane C₄H₉O:BH₃ in tetrahydrofuran.⁶ In order to proceed with the interpretation of the rate data, it was necessary to know the molecular state of disiamylborane in tetra-

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(2) Post-doctorate research assistant, 1960–1961, on a Research Award (585-C) provided by the Petroleum Research Fund of the American Chemical Society.

(3) Unpublished studies with Dr. Laura Case.

(4) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).

(5) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

(6) J. R. Elliott, W. L. Roth, G. F. Roedel and E. M. Boldebeck, *J. Am. Chem. Soc.*, **74**, 5211 (1952); B. Rice, J. A. Livasy and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955).

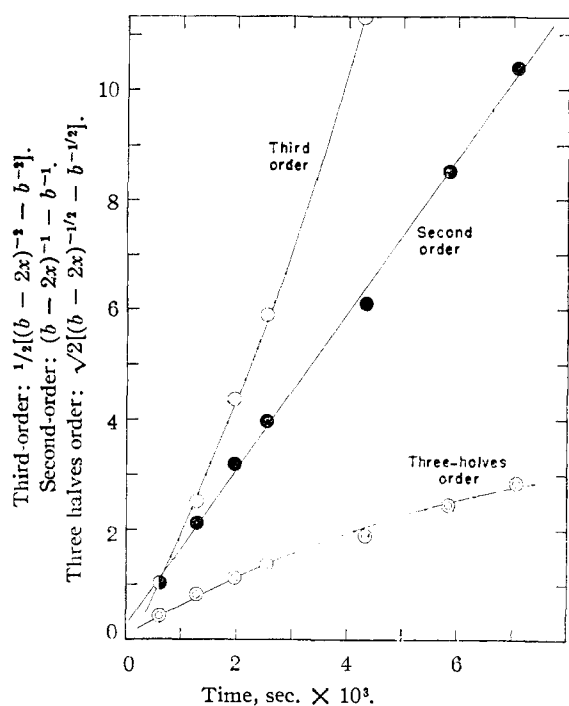
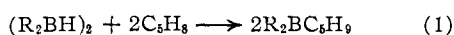


Fig. 1.—Three-halves, second and third-order plots of the reaction of dimeric disiamylborane (0.020 *M*) with cyclopentene (0.400 *M*) in tetrahydrofuran at 0°. Third-order ordinate values are one-third of their true value.

hydrofuran. Molecular weight determinations by vapor pressure lowering and infrared examination of the solutions revealed that disiamylborane is almost completely dimeric in this solvent, with only minor amounts of monomer possibly present.⁷ Consequently, in this study the concentrations of the disiamylborane will be expressed as the dimer.⁸

Data for a typical rate study are summarized in Table I.

The stoichiometry of the reaction requires two moles of cyclopentene per mole of disiamylborane dimer (1).



If this equation represents the reaction mechanism, the reaction should exhibit third order kinetics, first order in the dimer and second order in cyclopentene (2).

$$dx/dt = k_3[(R_2BH)_2][C_5H_8]^2 \quad (2)$$

Integrated, this becomes expression 3.

$$k_3t = \frac{1}{2} \left[\frac{1}{(b-2x)^2} - \frac{1}{b^2} \right] \quad (3)$$

However, a plot of the data utilizing this relationship exhibits a definite curvature (Fig. 1).

(7) A detailed study of the mono- and dialkylboranes containing bulky substituents has been completed by G. Klender and A. W. Moerikofer and will be reported shortly.

(8) Strictly speaking, we should term the reagent, "tetrasiamyldiborane," instead of "disiamylborane." However, it is common practice to refer to a number of species, such as trimethylaluminum and gallium trichloride, by their monomeric names, even though these substances normally exist in the dimeric state. In working with these alkylboranes, we have found it very convenient to refer to them as borane derivatives, except in cases where the structure of the diborane skeleton becomes important in dealing with the experimental observations.

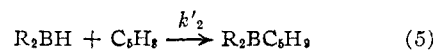
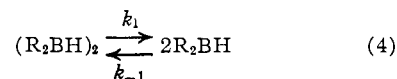
TABLE I

RATE DATA FOR THE REACTION OF DISIAMYLBORANE (DIMER) WITH CYCLOPENTENE IN TETRAHYDROFURAN AT 0°

| Time, sec. | Cyclopentene, <i>M</i> | (Disiamylborane) ₂ , <i>M</i> | Rate constants ^a <i>k</i> ₃ , 10 ⁻⁴ l. mole ⁻¹ sec. ⁻¹ |
|------------|------------------------|--|---|
| 0 | 4.00 | 2.00 | .. |
| 610 | 2.84 | 1.42 | 16.7 |
| 1270 | 2.16 | 1.08 | 16.7 |
| 1950 | 1.76 | 0.88 | 16.4 |
| 2530 | 1.55 | .78 | 15.6 |
| 4320 | 1.16 | .58 | 14.2 |
| 5820 | 0.91 | .46 | 14.6 |
| 7080 | .78 | .39 | 14.7 |
| 8760 | .61 | .31 | 16.0 |

^a Calculated from the equation, $k_3t = \left(\frac{1}{b-2x} - \frac{1}{b} \right)$, where *b* is the initial concentration of cyclopentene and *b* - 2*x* is the concentration at time *t*.

The observation that disiamylborane exists as a dimer in tetrahydrofuran solution does not exclude the possibility that the reaction of this reagent with olefins proceeds through the formation of a small equilibrium concentration of monomer (4), followed by a rate-determining reaction of the monomer with the olefin (5).



Such a mechanism would require three-halves-order kinetics (6).

$$\frac{dx}{dt} = \left(\frac{k_1}{k_{-1}} \right)^{1/2} k'_2 [(R_2BH)_2]^{1/2} [C_5H_8] \quad (6)$$

Integrated for the case where the initial concentration of disiamylborane (dimer) is one-half the concentration of cyclopentene, this becomes expression 7

$$k_3t = \sqrt{2} \left[\frac{1}{(b-2x)^{1/2}} - \frac{1}{b^{1/2}} \right] \quad (7)$$

However, the three-halves plot in Fig. 1 likewise exhibits a marked curvature. Consequently, the reaction of cyclopentene with disiamylborane (dimer) does not proceed through an equilibrium concentration of the monomeric disiamylborane.

Treatment of the data as a simple second-order reaction, first order in disiamylborane dimer and first order in cyclopentene (8,9), yields a good fit (Fig. 1).

$$dx/dt = k_2[(R_2BH)_2][C_5H_8] \quad (8)$$

$$k_2t = \frac{1}{b-2x} - \frac{1}{b} \quad (9)$$

This unexpected result was confirmed by running additional kinetic determinations at other concentrations. In each case the second-order plot yielded a straight line, whereas the three-halves and third-order treatments exhibited major deviations. Moreover, good agreement was realized between the second-order constants determined from the graphical analysis of the data for each kinetic run (Table II).

Finally, this conclusion that the reaction conforms to second-order kinetics was checked by

TABLE II
RATE CONSTANTS FOR THE REACTION OF DISIAMYLBORANE
(DIMER) WITH CYCLOPENTENE IN TETRAHYDROFURAN AT 0°

| Initial concentrations, M | Rate constant, ^a k_2 (10^{-4} l. mole ⁻¹ sec. ⁻¹) | Time, (sec. $\times 10^3$) to complete fraction of reaction |
|-----------------------------|---|--|
| Cyclo- pentene | (Disiamyl- borane) ₂ | 0.50 0.75 |
| 0.400 | 0.200 | 14.2 1.54 5.4 |
| .200 | .200 | 14.6 1.18 2.9 |
| .200 | .100 | 13.2 3.50 11.9 |

^a From graphical treatment of data.

calculating the times for 50% and 75% completion (Table II) and substituting the values into expression⁹ 10

$$n = 1 + \frac{\log(T_1/T_2)}{\log(a_2/a_1)} \quad (10)$$

where T_1 and T_2 are the respective half-lives or three-quarter lives at initial concentrations a_1 and a_2 . In this way, the value of n was calculated to be 2.18 and 2.14, confirming the conclusion that the reaction follows second-order kinetics.

Effects of Ring Size.—The reaction of cyclohexene with disiamylborane proved to be very slow, much slower than the corresponding reaction with cyclopentene. Accordingly, in order to complete the reaction in a reasonable time, the initial concentrations were increased to 0.4 M for disiamylborane (dimer) and 0.8 M for cyclohexene.

Here also, the rate data follow second-order kinetics (Fig. 2) and yield a rate constant of $k_2 = 0.131 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹ less than 1/100 the rate constant for cyclopentene.

The next larger ring, cycloheptene, exhibited a much greater reactivity, even greater than that of cyclopentene itself. Because of the high reactivity, it was possible to obtain only a few experimental points. However, these correspond to a second-order plot (Fig. 2) and yield the rate constant, $k_2 = 72 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹.

Reaction with *cis-trans* Isomeric Alkenes.—The reaction of *cis*-2-butene with disiamylborane is 50% faster than that of cyclopentene, with a rate constant of 23×10^{-4} l. mole⁻¹ sec.⁻¹. On the other hand, *trans*-2-butene exhibits a much slower reaction, with $k_2 = 3.9 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹. In both cases the kinetic data fit the second-order treatment satisfactorily, easily within the precision of the experimental data (Fig. 3).

In order to explore the influence of the steric requirements of the alkyl substituents, as well as the generality of this enhanced reactivity of the *cis* isomer, the study was extended to a large number of isomeric *cis*- and *trans*-alkenes (rate constant $\times 10^4$ in parentheses): *cis*-2-butene (23), *trans*- (3.9); *cis*-2-pentene (21), *trans*- (3.0); *cis*-4-methyl-2-pentene (4.8), *trans*- (1.2); *cis*-4,4-dimethyl-2-pentene (0.78), *trans*- (0.10); *cis*-3-hexene (21), *trans*- (2.2); *cis*-2,5-dimethyl-3-hexene (1.1), *trans*- (0.42).

The rates decrease with increasing steric requirements of the alkyl substituents, with the *trans* isomer invariably reacting at a lower rate than the *cis* derivative.

(9) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 14.

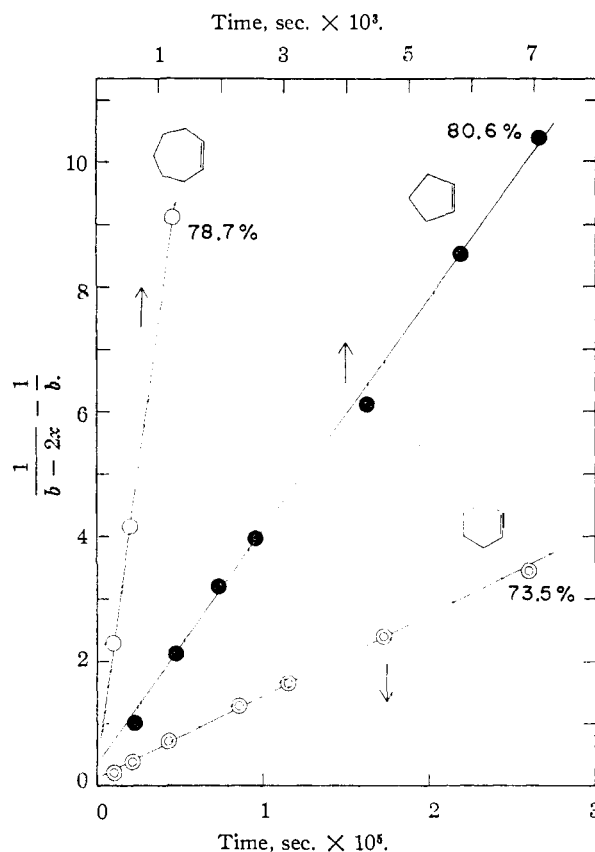
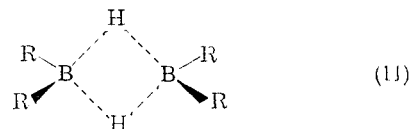


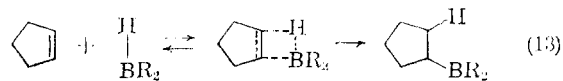
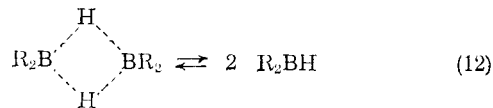
Fig. 2.—Second-order plots for the reaction of dimeric disiamylborane with cyclopentene, cyclohexene and cycloheptene.

Discussion

Disiamylborane exists in tetrahydrofuran solution as the dimer. The structure is presumably related to tetramethyldiborane with a double hydrogen bridge¹⁰ (11).



The simplest possible mechanism for the reaction of this molecule with olefins would appear to involve a dissociation into a small equilibrium concentration of monomer (12), followed by a *cis* addition¹¹ of the R_2BH monomer to the double bond (13).



(10) K. Hedberg, M. E. Jones and V. Schomaker, Second International Congress of Crystallography, Stockholm, 1951, as reported in "Tables of Interatomic Distances and Configuration in Molecules and Ions," L. E. Sutton, Editor, The Chemical Society, London, 1958, p. M177.

(11) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

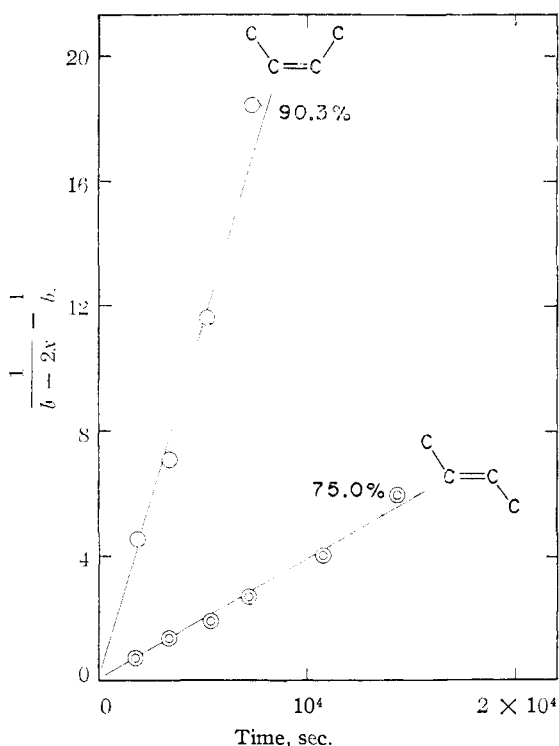
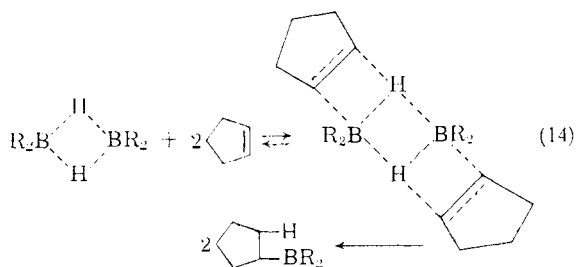


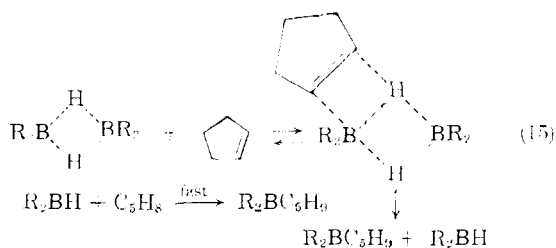
Fig. 3.—Second-order plots for the reaction of dimeric disiamylborane with *cis*- and *trans*-2-butene.

However, this mechanism requires three-halves-order kinetics (6). The failure to observe such kinetics appears to rule out a preliminary dissociation of the tetrasiamyldiborane molecule as an essential initial stage in the reaction of the reagent with the olefin.

The alternative mechanism in which the dimeric molecule reacts simultaneously with two cyclopentene molecules (14) requires third-order kinetics.



The second-order kinetics appear to require a reaction of the dimer with one cyclopentene molecule, presumably resulting in the formation of the product and one molecule of monomer. The latter presumably reacts with a second molecule of olefin in a rapid second step (15).



The present study was carried out in tetrahydrofuran, and no attempt was made to vary the solvent. However, it is probable that tetrahydrofuran plays an important role in this reaction by coordinating with the disiamylborane monomer, the "leaving group" in this particular reaction.

The reaction of diborane with olefins in the gas phase and in hydrocarbon media is very slow. Small quantities of various ethers greatly accelerate the reaction.³ It may be that this powerful catalytic effect of ethers is likewise due to their ability to coordinate with the borane leaving group in the initial alkylation stage.

Diborane exists in the monomeric stage in tetrahydrofuran solution.⁶ Under these circumstances there should be no "leaving group" and the details of the hydroboration stage should differ significantly from those cases where the reaction involves the dimer.

With the kinetic order established, it is possible to determine rate constants for the reaction of disiamylborane with various olefins and to compare quantitatively the effect of structure upon the reactivity of various olefins. The rate constants established in the present study are summarized in Table III.

TABLE III

RATE CONSTANTS FOR THE REACTION OF DISIAMYLBORANE WITH OLEFINS IN TETRAHYDROFURAN SOLUTION AT 0°

| Olefin ^a | Rate constant $k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹ | $\frac{k_{cis}}{k_{trans}}$ |
|---|--|-----------------------------|
| Cyclopentene | 14 | |
| Cyclohexene | 0.13 | |
| Cycloheptene | 72 | |
| <i>cis</i> -2-Butene | 23 | |
| <i>trans</i> -2-Butene | 3.9 | 6.0 |
| <i>cis</i> -2-Pentene | 21 | |
| <i>trans</i> -2-Pentene | 3.0 | 7.0 |
| <i>cis</i> -4-Methyl-2-pentene ^b | 4.8 | |
| <i>trans</i> -4-Methyl-2-pentene | 1.2 | 4.0 |
| <i>cis</i> -4,4-Dimethyl-2-pentene | 0.78 | |
| <i>trans</i> -4,4-Dimethyl-2-pentene | 0.10 | 7.8 |
| <i>cis</i> -3-Hexene | 21 | |
| <i>trans</i> -3-Hexene | 2.2 | 9.5 |
| <i>cis</i> -2,5-Dimethyl-3-hexene | 1.1 | |
| <i>trans</i> -2,5-Dimethyl-3-hexene | 0.42 | 2.5 |

^a Olefin purities approximately 99%. ^b Olefin purity approximately 95%.

The order of reactivity, cyclopentene > cyclohexene < cycloheptene, was observed previously for the related reaction involving the addition of diethylaluminum hydride to the cyclic olefins.¹² At 78° the observed half-lives of these reactions in minutes are: cyclopentene, 200; cyclohexene, 1880; cycloheptene, 110. The addition of diethylaluminum hydride to the cycloalkenes proceeds at a much slower rate than the addition of disiamylborane and the variation of reactivity with ring size is less (Table III).

This change in reactivity of the cyclic olefins with ring size appears to be general for reactions involving a simple *cis* addition to the double bond. Thus in the reaction at 78° with hexachlorocyclopentane-

(12) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 99 (1954). These authors determined the half-lives for all of the cyclic olefins from cyclobutene through cycloundecene.

diene, the following half-lives (in minutes) were observed¹³: cyclopentene, 80; cyclohexene, 1760; cycloheptene, 61.

The decrease of 100-fold observed in the reaction of disiamylborane with cyclopentene and cyclohexene might at first sight be attributed to the increased steric requirements of the relatively non-planar cyclohexene as compared with the more planar cyclopentene system. However, the marked increase observed with cycloheptene argues against this factor as being the dominant one in these large variations in reactivity with ring size.¹⁴

It is well recognized that the cyclopentane and cycloheptane ring systems are strongly strained compared to cyclohexane itself.¹⁵ Calculations based on the heats of hydrogenation of the corresponding cycloalkenes¹⁶ show that both cyclopentene and cycloheptene are strained as compared to cyclohexene. Consequently, it appears that the increased reactivities of the five- and seven-membered ring olefins as compared to cyclohexene must be the result of the greater strain to which the double bonds are subjected in the cyclopentene and cycloheptene molecules.¹⁷ This conclusion is supported by the observation that *trans*-cyclononene and *trans*-cyclododecene are far more reactive than the corresponding *cis* isomers toward diethylaluminum hydride.¹⁷

For the above interpretations to be acceptable, the transition state must be very close to the olefin-disiamylborane structure. Cyclopentane and cycloheptane are considerably less stable thermodynamically than cyclohexane. If the transition states resembled products closely, the markedly lower stability of cyclopentyl- and cycloheptyldisiamylborane would have been expected to favor the reaction of the reagent with cyclohexene, leading to the more stable derivative, cyclohexyldisiamylborane.

The difference in the reactivities of *cis*- and *trans*-2-butene is likewise interpretable in terms of the greater strain present in the *cis*-olefin.¹⁸

The phenomenon appears to be general for open-chain *cis-trans* olefins (Table III).

The reaction also appears to be sensitive to the steric requirements of the olefin. As one of the methyl groups in *cis*-2-butene is varied from methyl to ethyl to isopropyl to *t*-butyl, the rate of reaction decreases, slowly at first but more rapidly with the more bulky substituents ($k_2 \times 10^4$ l. mole⁻¹ sec.⁻¹): Me, 23; Et, 21; *i*-Pr, 4.8; *t*-Bu, 0.78. A similar effect is observed in the *trans* derivative: Me, 3.9; Et, 3.0; *i*-Pr, 1.2; *t*-Bu, 0.10. Simultaneous variation in the structure of both alkyl groups produces

similar effects: *cis*-Me₂, 23; *cis*-Et₂, 21; *cis*-*i*-Pr₂, 1.1; *trans*-Me₂, 3.9; *trans*-Et₂, 2.2; *trans*-*i*-Pr₂, 0.42.

Disiamylborane is a reagent of large steric requirements.^{4,5} This marked decrease in rate observed in both the *cis* and *trans* derivatives with an increase in the bulk of the alkyl substituents is attributed to the conflicting steric requirements of the two reactants in the transition state.

Consequently, it appears that both the strains to which the double bonds are subjected in the olefin and the steric requirements of the olefin represent important factors in controlling the rate of reaction of disiamylborane with double bonds.

The difference in reactivity previously noted for *cis*- and *trans*-2-pentene was utilized to achieve the removal of the *cis* isomer from the *trans*.⁵ The present results reveal that the phenomenon is quite general and should prove generally useful to remove the more reactive *cis*-olefin from the *trans* isomer in aliphatic derivatives.

However, in the medium ring olefins, the available evidence indicates that it is the more strained *trans* isomers which possess the greater reactivities toward hydridic reagents.¹⁷ In these derivatives disiamylborane would be expected to remove the *trans* isomer selectively. Consequently, disiamylborane should be generally applicable to remove the more strained olefin from an isomeric pair—the *cis*-olefin in acyclic systems or the *trans*-olefin in alicyclic (medium ring) systems.

Experimental Part

Materials.—Diglyme, tetrahydrofuran and boron trifluoride etherate were purified as previously described.⁵ Sodium borohydride from Metal Hydrides, Inc., (~98%) was utilized without purification.

Cyclopentene, cyclohexene, 2-methyl-2-butene, cyclohexane and methylocyclohexane were Phillips Petroleum Co. products, certified to be at least 99% pure, and were utilized after distillation over sodium. Cycloheptene, from Columbia Organic Chemical Co., was distilled over sodium in a Podbielniak Heli-grid column under nitrogen: b.p. 113.2° at 747 mm., n_D^{20} 1.4588 (lit.¹⁹ b.p. 114.4 at 760 mm., n_D^{20} 1.4580).

The *cis*- and *trans*-2-butene were pure grade products from Phillips Petroleum Co. and were used after drying over calcium hydride. *trans*-4-Methyl-2-pentene was Phillips research grade, whereas *cis*-4-methyl-2-pentene was the technical grade, approximately 95%. These olefins were dried over calcium hydride.

All other olefins were products of certified purity from American Petroleum Institute Project No. 45 at Ohio State University and were utilized directly from sealed ampoules without drying or other treatment.

Diborane was generated by treating a solution of sodium borohydride in diglyme with boron trifluoride etherate and the gas passed through a wash bottle containing a small quantity of sodium borohydride in diglyme (to remove traces of boron trifluoride) into dry tetrahydrofuran maintained at 0°. Standard solutions in the range 2.0 to 2.4 *M* were prepared and stored at 0° in the cold room. No measurable changes in titer were noted in periods of 30 to 60 days under these conditions.

Standard solutions of 2-methyl-2-butene (6.0 *M*) in tetrahydrofuran were prepared and stored at 0°.

Kinetic Procedure.—All standard solutions were prepared and stored at 0° to minimize volumetric errors and loss of volatile components. All equipment and apparatus were dried vigorously and transfers were made with hypodermic syringes in order to minimize exposure to contaminants. The syringes were lubricated with halocarbon oil and maintained at 0° before use. In order to minimize the loss of active hydride in the syringe, a small amount of diborane

(13) K. Ziegler and H. Froitzheim-Kühlhorn, *Ann.*, **589**, 157 (1954).

(14) Ziegler and his co-workers (ref. 12, 13) observed that the rate increased moderately from cycloheptene to cyclooctene, but then decreased with cyclononene and cyclododecene. In the latter cases, steric effects arising from the puckering of the ring systems might play a role in the decreased reactivities.

(15) W. G. Dauben and K. S. Pitzer, "Conformational Analysis," Chapter 1 in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(16) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).

(17) K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn and J. Schneider, *Ann.*, **589**, 126 (1954).

(18) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 867 (1935).

(19) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1059 (1939).

solution was used to rinse the syringe, removing traces of residual moisture, before the syringe was utilized to transfer the standard diborane solution.

The disiamylborane reagent was prepared as follows. To the carefully dried 200-ml. reaction flask, flushed with nitrogen and fitted with a side-arm containing a rubber serum cap, was added 20 ml. of the standard tetrahydrofuran solution, 6.0 *M* in 2-methyl-2-butene (120 mmoles). The flask was cooled to -20° to compensate for the heat of reaction and 24.25 ml. of the diborane solution in tetrahydrofuran (2.47 *M*, 60 mmoles) was added slowly. The reaction was permitted to proceed over 6 to 9 hours in order to attain 98-99% reaction of the 2-methyl-2-butene, maintaining a slight excess static nitrogen pressure.

To the reagent was added 85.5 ml. of tetrahydrofuran (0°) and the entire mixture was cooled to -2° . A standard solution of cyclopentene, 3.0 *M*, and methylcyclohexane, 1.5 *M*, in tetrahydrofuran was prepared and maintained at 0° . The reaction was initiated by injecting over 30 seconds 20 ml. of this solution, containing 4.08 g. (60 mmoles) of cyclopentene and 2.94 g. (30 mmoles) of methylcyclohexane. The heat of mixing brought the temperature of the reaction mixture, 150 ml. of a homogeneous solution, to 0° , where it was maintained during the reaction.

To follow the course of the reaction, aliquots of 0.50 ml. were withdrawn with a syringe (precooled to 0°) and in-

jected into rubber-capped vials, which contained 0.10 ml. of 1-decene to react with residual disiamylborane and quench the reaction. The vials were maintained at -78° until the reaction mixtures were analyzed.

The samples, 1-3 μ l., for the v.p.c. analysis were removed with a Hamilton syringe, precooled to -78° and injected into the Perkin-Elmer 154C fractometer containing a 1-m. adiponitrile column maintained at $40-50^{\circ}$. The injection block was maintained at a low temperature, $50-70^{\circ}$, to avoid pyrolysis of the injected mixture. Symmetrical peaks were obtained and the areas determined by graphical integration.

Data for a typical kinetic study are presented in Table I. Other kinetic data are shown graphically in Figs. 2 and 3.

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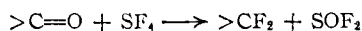
Chemistry of Sulfur Tetrafluoride.¹ VI. Fluorination of Thiocarbonyl Compounds

BY R. J. HARDER AND W. C. SMITH

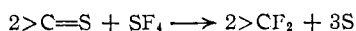
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The reactions of several thiocarbonyl compounds with SF_4 have been investigated. Fluorine atoms are introduced with ease at specific sites in the molecule by replacement of sulfur, with complete utilization of the fluorine in SF_4 .

An earlier paper² in this series described the use of sulfur tetrafluoride (SF_4) as a highly selective agent for the replacement of oxygen by fluorine in organic compounds. Thus, SF_4 converts a carbonyl group to a difluoromethylene group, thionyl fluoride being formed as a by-product.



We have found that the thiocarbonyl group is fluorinated by SF_4 in a similar manner. This reaction differs from that of SF_4 with carbonyl compounds, however, in that a formal oxidation-reduction of the sulfur atoms in the thiocarbonyl compound and SF_4 occurs, resulting in the formation of free sulfur and the complete utilization of the fluorine atoms in SF_4 .



The course of reaction, therefore, parallels that of SF_4 with inorganic sulfides, which are converted to the corresponding fluorides and sulfur.³

Ethylene trithiocarbonate reacts smoothly with SF_4 at 110° in the absence of catalyst to give 2,2-difluoro-1,3-dithiolane (I) in 82% yield, by-product sulfur being obtained in 90% of the theoretical amount. Dithiolane I is readily hydrolyzed

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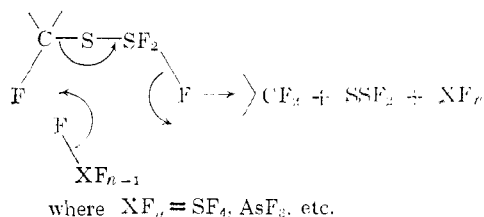
(2) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(3) A. L. Oppgaard, W. C. Smith, E. L. Muettterties and V. A. Engelhardt, *ibid.*, **82**, 3835 (1960).

to ethylene dithiocarbonate, demonstrating that no rearrangement of the ring system occurred during fluorination.

Fluorination of thiuram sulfides (II) with SF_4 also proceeds with ease, affording a novel series of compounds, the dialkyltrifluoromethylamines (III). Typical of this transformation is the reaction of SF_4 with bis-(pentamethylene)-thiuram disulfide (IIc) at 100° , providing a 70% yield of 1-trifluoromethylpiperidine (IIIc). It is interesting to note that both the thione and sulfidic sulfur atoms of the thiuram compound and the sulfur atom of SF_4 appear as free sulfur among the products.

A mechanism can be written for the initial stages of the SF_4 -thiocarbonyl reaction which parallels that proposed for the SF_4 -carbonyl reaction.² However, if the analogy between these two reactions were carried to completion, the result would be the elimination of a fragment SSF_2 .



A fluoride of sulfur, S_2F_2 , is known, but the structure has not been determined. It has been found in this Laboratory that S_2F_2 disproportionates moderately fast at room temperature to give SF_4 and