

# Selective Reductions. XI. The Reaction of Sodium Borohydride with Alkyl Halides under Solvolytic Conditions. Borohydride as a Convenient Trap for Carbonium Ions<sup>1,2</sup>

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**Abstract:** In nonionizing solvents, secondary and tertiary alkyl halides react with sodium borohydride only slowly, in many cases yielding the olefin, rather than the desired saturated hydrocarbon. However, the addition of water to produce typical solvolysis conditions brings about a rapid reaction, providing the corresponding hydrocarbon in good yield, along with the concomitant formation of the alcohol and the olefin as the usual solvolytic products. Evidence is presented which indicates that the mechanism of the reduction involves the trapping of the intermediate carbonium ions formed in the solvolysis. Consequently, the reaction should be useful, both synthetically, to convert reactive alkyl halides and their derivatives to the corresponding hydrocarbons, and mechanistically, to trap carbonium ions in investigations of their nature. A number of synthetic applications is described.

The reduction of alkyl halides and related derivatives by complex metal hydrides has been the subject of several investigations.<sup>5,6</sup> Because of the lower reactivity of sodium borohydride, most of the work reported has utilized lithium aluminum hydride in the usual ethereal solvents.<sup>7</sup>

The reduction of primary and secondary alkyl derivatives by lithium aluminum hydride in ether is believed to involve a typical S<sub>N</sub>2 mechanism. The reaction follows second-order kinetics<sup>8</sup> and proceeds with inversion of configuration at the reaction center,<sup>9,10</sup> and the rate decreases from primary to secondary to tertiary.<sup>5</sup> However, lithium aluminum hydride is of little utility for the reduction of tertiary and of some secondary derivatives which can undergo ready elimination. In such cases the product is predominantly olefin, with only low yields of the desired hydrocarbon.<sup>5</sup>

It is generally recognized that S<sub>N</sub>2 displacements proceed slowly and with difficulty with tertiary and many secondary derivatives. Such compounds, however, exhibit an enhanced reactivity in reactions of the S<sub>N</sub>1 type. Accordingly, it appeared desirable to explore the possibility of utilizing this characteristic to achieve a simple reduction of such derivatives by carrying the reaction out under conditions where the compound is readily converted into carbonium ions. Lithium

aluminum hydride is not stable in the usual solvolytic media. However, sodium borohydride is quite stable in water and many mixed aqueous systems suitable for the solvolytic generation of carbonium ions. Accordingly, we undertook a study of the reaction of sodium borohydride with reactive secondary and tertiary halides under solvolytic conditions.

## Results

After some experimentation, 80% (by volume) aqueous diglyme was selected for detailed study of the reaction characteristics. This solvent could be made 1.80 *M* in sodium borohydride and 0.25 *M* in the organic derivative without loss of homogeneity. Any higher concentration of one of the reactants was not possible, however, without a decrease in the concentration of the other. As the reaction proceeds, there is formed sodium halide and boric acid. Consequently, a small lower phase separates toward the end of the reaction. However, this did not appear to cause any difficulty. Benzhydrol chloride was selected as a convenient derivative for some of the exploratory studies.

**Rate Studies.** Under anhydrous conditions the rate of reaction of sodium borohydride with benzhydrol chloride was quite slow. Thus only 6% of diphenylmethane was produced in 4 hr at 45° in a solution in diglyme which was 1.80 *M* in sodium borohydride and 0.25 *M* in benzhydrol chloride. The pseudo-first-order constant for this reaction was calculated to be  $3.5 \times 10^{-6} \text{ sec}^{-1}$ .

On the other hand, in the 80% aqueous diglyme solvent, the reaction proceeded some 60 times faster. The first-order rate constant for the reaction was  $2.1 \times 10^{-4} \text{ sec}^{-1}$ . There was formed 72–75% of diphenylmethane, with benzhydrol being the remaining product. In the same solvent, with sodium borohydride absent, the benzhydrol chloride underwent solvolysis with a first-order rate constant of  $1.34 \times 10^{-4} \text{ sec}^{-1}$ . The product consisted entirely of benzhydrol.

The results are therefore consistent with the proposal that there is a rate-determining ionization of the benzhydrol chloride to form the benzhydrol cation. This reacts with water in the absence of sodium borohydride

(1) This paper is based on a thesis submitted by Harold M. Bell in partial fulfillment of the requirements of the degree of Doctor of Philosophy, Purdue University.

(2) Reported in part as a preliminary communication: H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

(3) National Defense Education Act, College Science Teaching Fellow, 1960–1963.

(4) Ethyl Corporation Fellow, 1963–1964.

(5) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p 889.

(6) H. C. Brown and P. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

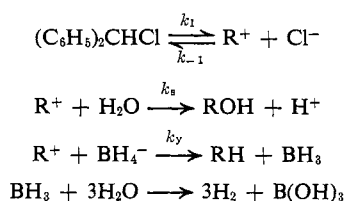
(7) The generalization that sodium borohydride possesses low reactivity in its reaction with alkyl halides may be misleading. Although the reaction with benzhydrol chloride is sluggish, as reported in this paper, the corresponding reaction with methyl chloride is rapid and quantitative.<sup>6</sup> We are undertaking a systematic study of the reaction of sodium borohydride with alkyl halides under typical S<sub>N</sub>2 conditions to parallel the present study of the reaction under S<sub>N</sub>1 conditions.

(8) D. J. Malter, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **78**, 1311 (1956).

(9) E. L. Eliel, *ibid.*, **71**, 3970 (1949).

(10) G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957).

to yield benzhydrol exclusively. In the presence of sodium borohydride, a large fraction of the carbonium ions are diverted to react preferentially with the borohydride ion to yield diphenylmethane.



It should be noted that the first-order rate constant in the presence of the sodium borohydride is approximately 50% greater than the value observed in absence of the sodium borohydride. However, this is a reaction which is quite sensitive to salt effects and the increase is in the direction predicted for the presence of the borohydride.

**Effect of Borohydride Concentration.** A series of solvolyses of benzhydryl chloride was carried out under the usual conditions, but with variable concentrations of sodium borohydride in order to ascertain the influence of the borohydride concentration on the yield. The results are summarized in Table I.

**Table I.** Effect of Borohydride Concentration on the Yield of Diphenylmethane<sup>a</sup>

| Boro-<br>hydride,<br>M | — Diphenylmethane, % —<br>Obsd | Calcd <sup>b</sup> |
|------------------------|--------------------------------|--------------------|
| 0.2                    | 15                             | 20                 |
| 0.50                   | 27                             | 33                 |
| 1.00                   | 50                             | (50)               |
| 1.4                    | 59                             | 58                 |
| 1.8                    | 73                             | 65                 |

<sup>a</sup> Benzhydryl chloride, 0.25 M, in 80% aqueous diglyme at 45°.

<sup>b</sup> The calculated values are based on the experimental value obtained with 1.0 M borohydride, utilizing the equation,  $[\text{ROH}]/[\text{RH}] = k_s/k_y[\text{BH}_4^-]$ . For 1.0 M borohydride,  $k_s/k_y = 1.0$ . The calculated values are obtained by applying this constant to the other concentrations of borohydride.

During the reaction some hydrolysis of the sodium borohydride occurs, brought about by the acid produced in the solvolysis. At the higher concentrations of borohydride, this loss is insignificant. However, at the lower borohydride concentrations, the actual borohydride concentration present in the reaction mixture may be appreciably lower than the amount introduced into the solution. This factor may be responsible for the fact that at the lower concentrations the yield of diphenylmethane is somewhat lower than the calculated values.

**Effect of Solvent Composition.** In order to examine the effect of the water content of the solvent medium on the yield, the reactions of sodium borohydride with benzhydryl chloride and *t*-cumyl chloride<sup>11</sup> were studied in a series of solvents ranging from 65 to 88% aqueous diglyme. The results are summarized in Table II.

Greater variation in the solvent composition could not be examined because of the homogeneity limits with high water concentrations and the slowness of the reaction with low.

(11) For convenience, this common name will be utilized for 2-chloro-2-phenylpropane.

**Table II.** Effect of Aqueous Content of the Solvent on Yield of Solvolytic Reduction Product<sup>a</sup>

| Diglyme,<br>vol % | Diphenyl-<br>methane,<br>% | Cumene,<br>% |
|-------------------|----------------------------|--------------|
| 65                | 75                         | 58           |
| 72                | 77                         | 61           |
| 80                | 73                         | 60           |
| 88                | 77                         | 59           |

<sup>a</sup> Benzhydryl and *t*-cumyl chlorides with 1.8 M sodium borohydride at 45°. The halides were 0.25 M in 80 and 88 vol % diglyme, and 0.125 M in the more aqueous solvents (to maintain homogeneity).

The insensitivity of the yield to the water concentration is convenient for the practical applications of the reaction but is unexpected from simple mechanistic considerations. However, in the case of *t*-cumyl chloride a complete examination of all the products (Table IV) reveals an increase in the yield of alcohol with increasing aqueous content of the solvent, with a compensating decrease in olefin formation.

**Effect of Leaving Group.** Under the standard conditions (0.25 M RX, 1.8 M sodium borohydride, 80% aqueous diglyme, 45°) benzhydryl bromide gives an 87% yield of diphenylmethane, significantly better than the 73% yield realized with the chloride.

Furthermore, in 65% aqueous diglyme,  $\alpha$ -phenylethyl bromide, 0.125 M, produced ethylbenzene in an 80% yield, as compared to only 39% from the chloride. Again, this is not consistent with a mechanism involving fully dissociated carbonium ions.

**Effect of Structure.** A number of representative derivatives were subjected to the reaction in order to explore the effect of structure on the applicability of the reaction. The results are summarized in Table III. (Results previously mentioned are included for convenience.)

**Table III.** Reaction of Representative Alkyl Halides with Sodium Borohydride under Solvolytic Conditions<sup>a</sup>

| Compound                                | — Reaction product, % —         |                                  |
|---|---------------------------------|----------------------------------|
|   | 80%<br>diglyme,<br>0.25<br>M RX | 65%<br>diglyme,<br>0.125<br>M RX |
| Benzhydryl chloride                     | 73                              | 75                               |
| Benzhydryl bromide                      | 87                              |                                  |
| <i>p</i> -Chlorobenzhydryl<br>chloride  | 62                              |                                  |
| <i>p</i> -Methoxybenzhydryl<br>chloride | 97                              |                                  |
| Triphenylmethyl chloride                | 97                              |                                  |
| Diphenylmethylcarbonyl<br>chloride      | 52                              |                                  |
| <i>t</i> -Cumyl chloride                | 60                              | 58                               |
| $\alpha$ -Phenylethyl chloride          |                                 | 39                               |
| $\alpha$ -Phenylethyl bromide           |                                 | 80                               |
| Cinnamyl chloride                       | 93                              |                                  |
| 1-Phenylallyl chloride                  | 86                              |                                  |

<sup>a</sup> Sodium borohydride, 1.8 M, 45°.

In many cases it was established that the side products were alcohol and olefin (where elimination is possible). Complete product analysis by gas chromatography was made where it was practical. In some cases the low volatility of the alcohols made such an analysis impractical. The results are summarized in Table IV.

**Table IV.** Products of Solvolysis in Aqueous Diglyme Containing Sodium Borohydride<sup>a</sup>

| Compound                        | Concn, <i>M</i> | Di-glyme, % | —Product, %—<br>Redn Olefin Alcohol |
|---------------------------------|-----------------|-------------|-------------------------------------|
| Diphenylmethylcarbinyl chloride | 0.25            | 80          | 52 38 <i>b</i>                      |
| <i>t</i> -Cumyl chloride        | 0.25            | 88          | 59 21 14                            |
|                                 | 0.25            | 80          | 60 13 22                            |
|                                 | 0.125           | 72          | 61 11 26                            |
|                                 | 0.125           | 65          | 58 8 34                             |
| $\alpha$ -Phenylethyl chloride  | 0.125           | 65          | 39 7 56                             |
| $\alpha$ -Phenylethyl bromide   | 0.125           | 65          | 80 1 14                             |
| Cinnamyl chloride               | 0.25            | 80          | 93 <sup>c</sup> 2                   |
| 1-Phenylallyl chloride          | 0.25            | 80          | 86 <sup>d</sup> 12                  |

<sup>a</sup> Sodium borohydride, 1.8 *M*, 45°. <sup>b</sup> Not analyzed. <sup>c</sup> Propenylbenzene, 89%; allylbenzene, 4%. <sup>d</sup> Propenylbenzene, 71%; allylbenzene, 15%.

**Synthetic Applications.** The above experiments were carried out utilizing concentrations which permitted maintenance of homogeneous conditions for the greater portion of the reaction. However, this is not a significant factor in reactions carried out primarily for synthetic purposes. Here it is far more important to achieve a satisfactory yield with minimum dilution of the reaction products by solvent. Consequently, we explored several possible solvents. Sodium hydroxide, 1.0 *M*, was utilized to avoid hydrolysis of the sodium borohydride.

The results are summarized in Table V. On the basis of these results we elected to use 65% aqueous diglyme for the preparative reductions.

**Table V.** Effect of Solvent on Yield in the Reduction of *t*-Cumyl Chloride by Sodium Borohydride under Preparative Conditions<sup>a</sup>

| Solvent                  | Cumene, % | $\alpha$ -Methylstyrene, % | <i>t</i> -Cumyl alcohol, % |
|--------------------------|-----------|----------------------------|----------------------------|
| 50% diglyme <sup>b</sup> | 59        | 8                          | 22                         |
| 65% diglyme <sup>b</sup> | 66        | 11                         | 16                         |
| 80% diglyme <sup>b</sup> | 64        | 19                         | 7                          |
| 80% ethanol              | 47        | 5                          | 8 <sup>c</sup>             |
| Water                    | 37        | 7                          | 57                         |

<sup>a</sup> *t*-Cumyl chloride, 0.5 *M*; sodium borohydride, 2.0 *M*; sodium hydroxide, 1.0 *M*; 45°. <sup>b</sup> Small losses of products, approximately 10%, occurred during the isolation procedure. <sup>c</sup> No analysis was made for *t*-cumyl ethyl ether.

Further tests showed that the effect of temperature is small, with 50° being slightly more satisfactory than 25 or 75°. As was to be expected, the borohydride concentration was the most important factor controlling the yield of reduction product. A concentration of 4.0 *M* was considered to be a practical upper limit and this was therefore adopted.

These considerations led to the adoption of the final preferred procedure. A solution was prepared of 65% aqueous diglyme at 50°, containing 4.0 *M* sodium borohydride and 1.0 *M* sodium hydroxide. An amount of alkyl chloride or tosylate to make the gross composition 0.5 *M* (had the solution remained homogeneous) was then added and the reaction mixture was stirred vigorously for several hours (or until tests show the absence of the reactant). Pentane was then added, followed by sodium hydroxide pellets to remove the

water, yielding an upper diglyme-pentane phase containing the organic components. The diglyme-pentane phase was then examined gas chromatographically. The results are summarized in Table VI.

**Table VI.** Reduction of Selected Organic Derivatives with Sodium Borohydride under Solvolytic Conditions<sup>a</sup>

| Compound <sup>b</sup>                        | — Reaction products, % —<br>Redn Olefin Alcohol |
|--|---|
| <i>t</i> -Cumyl chloride                     | 81 8 6  |
| $\alpha$ -Phenylethyl chloride               | 75 2 21   |
| Benzhydryl chloride                          | 99 <i>c</i>                                     |
| Diphenylmethylcarbinyl chloride <sup>d</sup> | 66 32 <i>c</i>                                  |
| Triphenylmethyl chloride                     | 96  |
| <i>t</i> -Amyl chloride                      | 40 35 <sup>e</sup> 25                           |
| 1-Chloro-1-methylcyclopentane                | 40 46 12  |
| Cyclooctyl tosylate                          | 40 49 11  |

<sup>a</sup> Diglyme, 65%; sodium borohydride, 4.0 *M*; sodium hydroxide 1.0 *M*. <sup>b</sup> 0.5 *M*. <sup>c</sup> Not analyzed for. <sup>d</sup> 15°. <sup>e</sup> 9% 2-methyl-1-butene and 26% 2-methyl-2-butene.

## Discussion

It is apparent from the experimental results that this reaction should be quite useful for the conversion of reactive alkyl halides and related derivatives into the corresponding hydrocarbons. In cases where the system produces a relatively stable carbonium ion which cannot undergo elimination, the yields are very high. Thus benzhydryl chloride was converted into diphenylmethane in a yield of 99%, and triphenylmethyl chloride was converted into triphenylmethane in a yield of 96%.

In cases where elimination can occur, or the carbonium ion is less stable, the yields decrease. However, the yields of 66 to 81% realized for diphenylmethylcarbinyl chloride,  $\alpha$ -phenylethyl chloride, and *t*-cumyl chloride must still be considered satisfactory. In the case of *t*-amyl chloride, 1-chloro-1-methylcyclopentane, and cyclooctyl tosylate, the elimination reaction becomes of major importance and the yield decreases to 40%. However, even here the simplicity of the reaction would suggest that it may well be useful for such reductions in spite of the lower yields.

This study was initiated on the assumption that sodium borohydride would serve as an efficient trap for carbonium ions and that such a trap would be useful for mechanistic as well as synthetic applications. Indeed, several such applications of the reaction have already been reported.<sup>12,13</sup> It is pertinent to inquire whether the data are consistent with a trapping of the carbonium ion produced in the solvolysis by the borohydride.

It was pointed out that the reaction of sodium borohydride with benzhydryl chloride in anhydrous diglyme is very slow. The reaction rate is enhanced by a factor of 60 through the use of 80% aqueous diglyme instead of the anhydrous solvent. Typical S<sub>N</sub>2 reactions of this type are generally hindered, rather than facilitated, by an increase in the aqueous content of the solvent.<sup>14</sup>

(12) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); **86**, 5006 (1964); H. M. Bell and H. C. Brown, *ibid.*, **86**, 5008 (1964).

(13) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

Supporting the conclusion that we are dealing with a rate-determining ionization of the benzhydryl chloride, followed by a fast reaction of the ion with borohydride or solvent, is the near identity in the rate constants for the reaction in the presence ( $2.1 \times 10^{-4} \text{ sec}^{-1}$ ) and absence of sodium borohydride ( $1.34 \times 10^{-4} \text{ sec}^{-1}$ ). A unimolecular ionization reaction should be subject to a positive salt effect. The increase in rate observed in the presence of the 1.80 M sodium borohydride is in the direction expected for such a salt effect. Winstein and his co-workers recently reported kinetic data for the solvolysis of *anti*-7-dehydronorbornyl chloride in 65% aqueous diglyme, both in the presence and absence of borohydride. In this case also a near identity of the reaction rates was observed.<sup>13,15</sup>

The effects of varying the borohydride concentration likewise supports the proposed carbonium ion mechanism (Table I). Reasonable agreement was realized for the yield of diphenylmethane estimated on the basis of a competition of the carbonium ion for water and borohydride.

On the other hand, it is puzzling that an increase in the aqueous content of the solvent (over the narrow range enforced by the need to maintain homogeneity) failed to produce an increase in the yield of benzhydrol with a corresponding decrease in the yield of diphenylmethane (Table II). It is also unexpected in terms of the formation of simple dissociated carbonium ions that the bromides examined gave higher yields of the hydrocarbons than the corresponding chlorides (Table III).

Both apparent anomalies could be explained if the mechanism were elaborated to include the reaction of borohydride with ion pairs.<sup>16</sup> In this event, the reaction course would not be independent of the leaving group. Moreover, the carbonium ion could then react preferentially with water clustered about the anion, rather than with water in the bulk.

The data clearly establish that both the rate and the yield of reduction product are related to the stability of the carbonium ion produced by the system. For example, triphenylmethyl chloride reacts exceedingly rapidly, forming triphenylmethane in high yield, whereas  $\alpha$ -phenylethyl chloride reacts relatively slowly and produces ethylbenzene in a much lower yield. Similarly, the *p*-chloro substituent in *p*-chlorobenzhydryl chloride should be expected to destabilize the carbonium ion slightly. A decrease in the yield of hydrocarbon is observed (from 73% for benzhydryl chloride to 62%). On the other hand, the *p*-methoxybenzhydryl chloride gives a yield of 97%. Apparently the more stable the carbonium ion the more selective it is in choosing between borohydride and water in its reaction.

The experiments with cinnamyl and 1-phenylallyl chlorides were originally carried out in part with the hope of trapping and identifying the carbonium ions involved. However, it soon became apparent that the

reaction in this system has complications which will require a detailed kinetic study for its full understanding. For example, the reaction of borohydride with cinnamyl chloride may have a large  $\text{S}_{\text{N}}2$  component. In ordinary solvolysis, much more attack at the secondary position occurs than the 3–4% observed in the present reaction.<sup>17</sup> Also 1-phenylallyl chloride rearranges to cinnamyl chloride at a rate faster than its rate of solvolysis.<sup>18</sup>

In conclusion, the reaction clearly possesses promise as a rapid, convenient synthetic procedure for reducing reactive tertiary and secondary halides and related derivatives to the corresponding hydrocarbons. Perhaps even more important, the reaction promises to serve as a convenient trap of carbonium ions to give relatively stable products, easily isolated and identified.

## Experimental Section

**Materials.** All of the materials were either commercial products or were synthesized by standard procedures. Liquid products were distilled and fractions of constant refractive index were combined for use. Solid products were recrystallized to constant melting point. In all cases the physical constants agreed satisfactorily with the constants available in the literature. The thesis<sup>1</sup> should be consulted for details.

**Procedure.** Water and diglyme were mixed (by volume) to give the solvent of the desired aqueous composition. Sodium borohydride was then dissolved, together with sodium hydroxide if the reaction mixture was to contain that component. The entire mixture was contained in a flask equipped with a reflux condenser and magnetic stirrer. (Hydrogen is evolved in considerable quantities from reaction mixtures not containing sodium hydroxide. In such cases, where loss of volatile components might occur, a small vapor trap was attached to the condenser.) The alkyl halide was added dropwise for rapidly reacting components, or rapidly for the usual case of slow reacting components. For reactions carried out under homogeneous conditions, the time allowed for complete reaction was set equal to the time for complete solvolysis in the same aqueous solvent in the absence of borohydride (measured titrimetrically in a parallel experiment). For nonhomogeneous reduction, the reaction was allowed to proceed for approximately twice this time.

At the end of the reaction, pentane was added, followed by sodium hydroxide pellets to give a dense lower phase of aqueous caustic and a dry upper phase of diglyme–pentane which could be analyzed directly by gas chromatography.

Alternatively, the reaction mixture could be diluted with water and the reaction products extracted with pentane. (Diglyme is soluble preferentially in the aqueous phase.) Two specific experiments are described in detail to illustrate the alternative procedures.

**Reduction of Benzhydryl Chloride (Homogeneous).** In a stirred, 100-ml flask, maintained at 45°, was placed 3.4 g (90 mmoles) of sodium borohydride and 50 ml of 80% aqueous diglyme, followed by 2.53 g (12.5 mmoles) of benzhydryl chloride. The reaction mixture was stirred magnetically for 4 hr. It was cooled to 25° and 20 ml of pentane was added, followed by pellets of solid sodium hydroxide. Analysis of the upper layer indicated 72% diphenylmethane.

**Reduction of *t*-Cumyl Chloride (Heterogeneous).** In a stirred, 200-ml flask, maintained at 50°, was placed 15.1 g (0.4 mole) of sodium borohydride, 4.0 g (0.1 mole) of sodium hydroxide, 65 ml of diglyme, and 35 ml of water, followed by 7.74 g (50 mmoles) of *t*-cumyl chloride. The reaction mixture was stirred for 1 hr. Then 20 ml of water was added, the upper layer was separated, and the lower layer was extracted four times with 15-ml portions of petroleum ether, bp 35–37°. The combined extracts were washed with water, dried, and analyzed by gas chromatography. The analysis indicated 81% cumene, 8%  $\alpha$ -methylstyrene, and 7% phenyldimethylcarbinol.

**Analysis.** All products were analyzed by gas chromatography, except those whose low volatility made the procedure inconvenient. In all cases, authentic samples, prepared by an independent method, were utilized for comparison. In addition to the gas chromatography

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 347–350.

(15) In cases where the reaction is utilized for synthetic purposes, it is unimportant whether the product is formed *via* the trapping of carbonium ions or *via* a bimolecular displacement reaction. However, in cases where the reaction is used primarily for mechanistic purposes to trap a carbonium ion, it is desirable that the investigator establish the essential absence of a significant bimolecular displacement reaction by the usual kinetic techniques.

(16) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3348 (1961).

(17) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(18) G. Valkanas and E. S. Waight, *J. Chem. Soc.*, 2720 (1959).

graphic analysis, a small amount of the reaction product was isolated by this technique for confirmatory identification by refractive index and infrared spectrum.

The yields were measured by comparing the peak area of the reaction product with the peak area of a standard solution of the same material. Thus all yields reported are actual, rather than normalized values. There were two exceptions to this procedure. Triphenylmethane was isolated and weighed to establish the yield, and the products from *t*-amyl chloride, because of their high volatility, were analyzed utilizing an internal standard.

Checks of the analytical procedure, utilizing synthetic mixtures, indicated that the actual compositions could be reproduced with an uncertainty of  $\pm 2\%$  for each component. Since the values are as likely to be high or low, it is not surprising that in some cases the actual yields total slightly more than 100%.

**Rate Measurements.** The rate of solvolysis of benzhydryl chloride in the presence of borohydride was measured by following the rate of formation of diphenylmethane, determined by gas chromatographic examination of aliquots. The rate in the absence of borohydride was measured by the usual titrimetric technique.

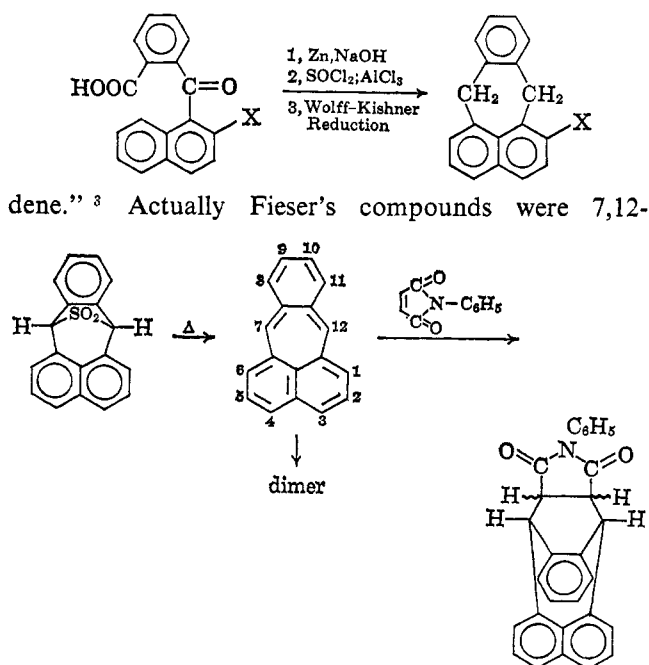
## 7,12-Dihydropleiadenes. I. Free-Energy Barriers to Conformational Inversion<sup>1</sup>

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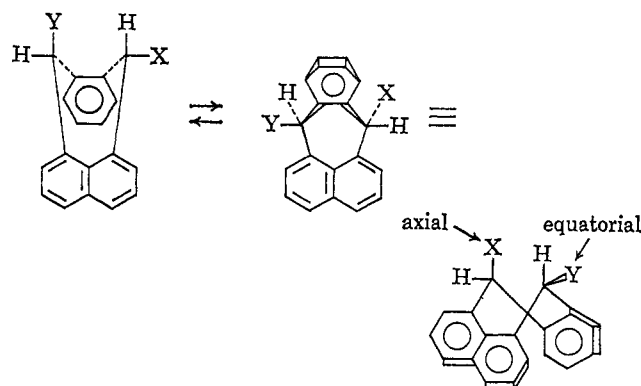
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received October 25, 1965

**Abstract:** A variety of 7,12-dihydropleiadenes has been prepared by multistep syntheses from 1,8-naphthalic anhydride and aryl Grignard reagents. These nonplanar molecules, whose seven-membered rings are "boat shaped," undergo conformational inversion at rates too fast to permit isolation of enantiomeric or diastereomeric atropisomers. From variable temperature nmr measurements, free energies of interconversion of 13.2–15.6 kcal/mole were calculated for the ring "flip" of several dihydropleiadenes. The transition state for the inversion is deduced to be planar.

Some time ago, Fieser and co-workers prepared a variety of polycyclic cyclohepta[*d,e*]naphthalenes from the condensation of phthalic anhydride and 2-substituted naphthalenes.<sup>3</sup> Reduction of the keto acids, followed by intramolecular acylation and further reduction of the resultant ketones, gave polynuclear products containing a central cycloheptane ring, whose parent structure was given the trivial name "pleia-



dihydro analogs of the fully conjugated system that resisted synthesis until Cava and Schlessinger's successful generation and "trapping" experiments (above).<sup>4</sup> The parent pleiadene molecule proved to be a highly reactive "o-xylylene," which dimerizes or polymerizes unless trapped by dienophiles. Unlike planar pleiadenes, 7,12-dihydropleiadenes (hereafter abbreviated DHP) are stable molecules which exist in folded conformations with geometry not unlike the more common 9,10-dihydroanthracenes.<sup>5</sup>



Several consequences of conformational interconversion in dihydropleiadenes can be distinguished. In the first case ( $X = Y$ ), a degenerate process occurs in which the conformer flips into *itself* (cf. compounds I, IV, VII, VIII, and IX in Tables I and II). A second group of compounds, exemplified by 8-methyl-7,12-

(1) Partially reported in preliminary form: P. T. Lansbury and J. F. Bieron, *J. Am. Chem. Soc.*, **86**, 2524 (1964).

(2) (a) Alfred P. Sloan Foundation Fellow, 1963–1967; (b) National Science Foundation Predoctoral Fellow, 1962–1964.

(3) L. F. Fieser and M. A. Fieser, *J. Am. Chem. Soc.*, **55**, 3010, 4963 (1933).

(4) M. P. Cava and R. H. Schlessinger, *ibid.*, **85**, 835 (1963); *Tetrahedron*, **21**, 3073 (1965).

(5) A. H. Beckett and B. A. Mulley, *Chem. Ind. (London)*, 146 (1955).