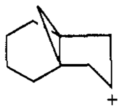
2, presumably as a result of acid catalysis by the 2,6-lutidine tosylate. The primary products of the solvolysis of **2** appear to be **5** and **6**, since the amounts of **7** and **8** increase as the solvolysis proceeds.

The data presented support the contention that **1** and **2** solvolyze to give two completely different ions. It appears that **1** gives products based on the migration of $C_6$ to the incipient cationic center to give **9**, while **2** is converted into products resulting from the migration of $C_8$ to the site of developing charge to yield **10**. Since there is no crossover of products, these rearrangements must be extremely stereospecific. The degree of stereospecificity is presumably controlled by the stability of the developing cation. Migration of $C_6$ in the solvolysis of **1** should lead to **9**, which is stereochemically well arranged for stabilization by the neighboring cyclopropyl ring as shown in **11**. Only products with the stereochemistry required by the intermediacy of **11** were found in the solvolysis of **1**. Migration of $C_6$ in the solvolysis of **2** would produce **12**, which is not well situated for stabilization by the neighboring cyclopropyl group.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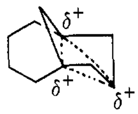

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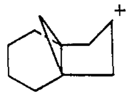
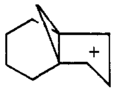


12

In the solvolysis of **2**, migration of $C_8$ should give the cyclopropylcarbinyl cation **10**. Support of this contention was provided by the solvolysis of each of the epimeric *p*-nitrobenzoates **13**, which gave a mixture of the same products as were obtained from **2**.[15] The derivation of **5**, **6**, and **7** from **10** is readily rationalized. Only the details of the conversion of **2**, **5**, **6**, and **7** into **8** remain to be elucidated.[16] Migration of $C_8$ in the solvolysis of **1** would produce **14**, which would be expected to have a destabilizing interaction of the hydrogens at $C_8$ and $C_{10}$ of **14**.



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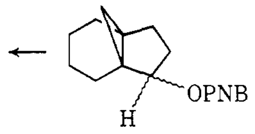

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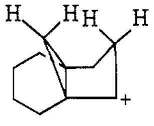

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In summary, this study demonstrated that the ring expansion from a cyclobutylcarbinyl to a cyclopentyl type cation can be an extremely selective process. In compounds such as **1** and **2**, where the cyclobutane moiety is part of a more highly strained ring system, interactions with the rest of the molecule can lead to products with unusual carbon skeletons due to the overall relief of ring strain.

**Acknowledgment.** We are indebted to the National Science Foundation for a grant in support of this investigation.

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[15] P. G. Gassman and E. A. Armour, unpublished work. The details of the solvolysis of **13** will be presented elsewhere.

[16] We are continuing to investigate this aspect of the problem.

[17] The Ohio State University Dissertation Fellow, 1972–1973.

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## Tetrabutylammonium Cyanoborohydride. A New, Exceptionally Selective Reducing Reagent

*Sir:*

The ever-present requirement for accomplishing reductions of specific functional groups with a minimum of damage to other sensitive portions of molecules has stimulated considerable interest in reagents capable of such selective conversions.[1] One successful approach to this problem has involved the modification of borohydride anion by the replacement of a hydrogen with a cyanide substituent. This strongly electron-withdrawing group increases the Lewis acidity of the corresponding cyanoborane and thus the cyanoborohydride anion is more reluctant to deliver a hydride. The result is a toned down reducing capability (and an increased stability) which allows more discriminate selection among functional groups.[2–5]

This communication reports the unique ability in this regard of tetrabutylammonium cyanoborohydride (TBAC), a new, versatile reducing agent.[6,7] In hexamethylphosphoramide (HMPA) solvent at 25°, TBAC is an exceptionally mild reagent which reduces only primary iodides and, to a lesser extent, bromides to the corresponding hydrocarbons. Figure 1 illustrates the rate plots for primary halides and tosylate. Thus, 1-iododecane afforded an 81% yield of decane in 21 hr with no olefin or other side products detected while the corresponding bromo, chloro, and tosyl derivatives suffered less nucleophilic attack (Figure 1). In addition, other normally sensitive groups including aldehydes, ketones, esters, amido, cyano, and aromatic nitro were practically inert to the reaction conditions.[8]

Remarkably, the addition of acid to the medium drastically alters the reducing ability of the reagent and permits the selective reduction of aldehydes to be performed facilely in the presence of most other functional groups including ketones. In Figure 2 are plotted the results from competitive reduction experiments of nonaldehyde and 2-undecanone using excess TBAC and varying acid concentration. As seen, increasing the

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[1] For a stimulating and educational review of selective reductions see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters 12 and 13.

[2] Recent applications of selective reductions with sodium cyanoborohydride include the reductive amination of aldehydes and ketones,[3] the selective reduction of alkyl halides and tosylates,[4] and the selective conversion of carbonyl tosylhydrazones to hydrocarbons.[5]

[3] R. F. Borch, M. Bernstein, and H. Durst, *J. Amer. Chem. Soc.*, **93**, 2897 (1971); R. F. Borch and A. Hassid, *J. Org. Chem.*, **37**, 1673 (1972); M. Boutigue and R. Jacquesy, *Bull. Soc. Chim. Fr.*, 750 (1973); A. Harmon and C. Hutchinson, *Tetrahedron Lett.*, 1293 (1973).

[4] R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *Chem. Commun.*, 1097 (1971).

[5] R. O. Hutchins, C. A. Milewski, and B. E. Maryanoff, *J. Amer. Chem. Soc.*, **93**, 1793 (1971); **95**, 3662 (1973); B. Ganem, *Tetrahedron Lett.*, 4105 (1971).

[6] The reagent was prepared in a similar manner as described for the corresponding borohydride.[7] Thus, 0.1 mol of $Bu_4NHSO_4$ suspended in 50 ml of water was treated with 35 ml of 5 *N* NaOH, and a solution of 0.11 mol of $NaBH_3CN$ in 40 ml of water was added at room temperature. After 15 min, the mixture was extracted three times with $CH_2Cl_2$ which was dried ($K_2CO_3$), decolorized with carbon, and concentrated at reduced pressure to afford white crystalline product (78%) which was recrystallized from ethyl acetate. The material (mp 144–145°) gave a satisfactory elemental analysis for $C_{17}H_{39}N_2B$.

[7] A. Brandstrom, U. Junggren, and B. Lamm, *Tetrahedron Lett.*, 3173 (1972).

[8] For instance, nonaldehyde gave 3% reduction in 59 hr while 2-undecanone was 5% reduced in 72 hr. Heptanenitrile, ethyl decanoate, dodecamide, and 4-nitrobiphenyl were virtually unaffected in 72 hr under the conditions described in Figure 1. Sodium cyanoborohydride in HMPA offers similar discrimination between alkyl iodides and other functional groups; see ref 4.

**Table I.** Reduction with Tetrabutylammonium Cyanoborohydride in Hexamethylphosphoramide[a] at 25°

| Compound | Acid concn, *N* | Time, hr | Product | % yield[b] |
|---|---|---|---|---|
| Nonaldehyde | 0.12 | 1.0 | Nonanol | 84 |
|  | 0.15 | 1.0 |  | 92 |
| 9-Anthraldehyde | 0.15 | 0.5 | 9-Anthrylmethanol | 95[c] |
| 4-Cyanobenzaldehyde | 0.15 | 0.5 | 4-Cyanobenzyl alcohol | 43[d] |
| 2-Undecanone | 1.5 | 0.5 | 2-Undecanol | 84 |
| Cholestan-3-one | 1.5 | 0.5 | 3-Cholestanol | 94[e] |
| 4-Acetylbiphenyl | 1.5 | 0.67 | 4-(α-Hydroxyethyl)-biphenyl | 86 |
| 4-*tert*-Butylcyclohexanone | 1.5 | 0.5 | 4-*tert*-Butylcyclohexanol | 88[f] |

[a] Solutions were 0.2 *M* in the compound and 0.8 *M* in TBAC. [b] Isolated yields, purified by recrystallization or distillation unless noted otherwise. [c] Yield of unpurified material; recrystallization led to partial air oxidation. [d] Water solubility resulted in substantial loss of product. [e] Composed of 79% β- and 15.5% α-isomers. [f] 15% cis, 73% trans isomers.

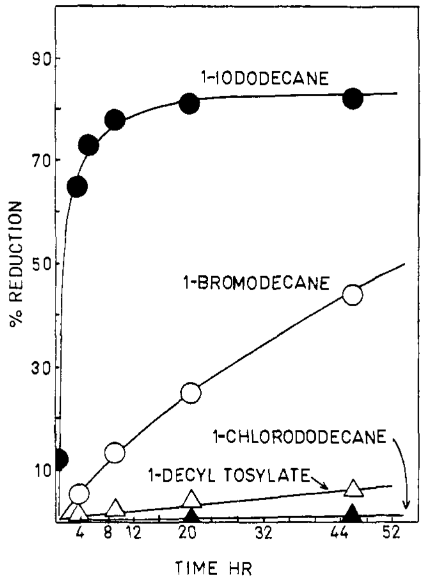

Figure 1. Reduction of primary halides and tosylate with TBAC in HMPA at 25°. All solutions were 0.2 *M* in the compound and 0.8 *M* in TBAC. The per cent reductions were determined by glpc using internal standards.

acidity rapidly accelerated the reduction rate of nonaldehyde such that in 0.1 or 0.12 *N* acid, nearly complete reduction occurred in 15 min while *the ketone was essentially untouched* (*ca.* 3% reduction).[9,10] Also worthy of note, the relatively slow reduction rate of primary iodides (an $S_N2$ process) was not concomitantly increased with increasing acid strength and in 15 min iododecane suffered only *ca.* 12% reduction in 1.5 *N* acid (at twice the relative TBAC concentration, Figure 1). Thus the reductive priority was almost completely reversed under acidic conditions allowing aldehydes to be selectively reduced even in the presence of normally labile iodides and ketones. As the concentration of acid was further increased, the rate of ketone reduction also increased until, in 1.5 *N* acid, complete reduction was observed in 15 min. Even under these conditions other functional groups including cyano, ester, amido, and nitro were not affected.

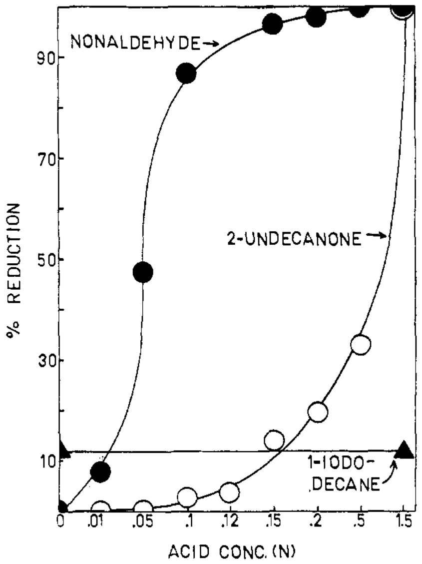

Figure 2. Competitive reduction of nonaldehyde and 2-undecanone and reduction of 1-iododecane with TBAC in HMPA at 25°. The reaction time in each case was 15 min. Competitive experiments were conducted with solutions 0.2 *M* in both carbonyl compounds and 0.8 *M* in TBAC. The reduction of 1-iododecane was conducted with solutions 0.2 *M* in iododecane and 0.8 *M* in TBAC. The per cent reductions were monitored by glpc analysis using internal standards.

Table I presents the results for a variety of reductions of aldehydes and ketones. As a representative example, the reduction of 4-acetylbiphenyl is described. A solution of 3 mmol of 4-acetylbiphenyl and 12 mmol of TBAC in 15 ml of HMPA containing 22.5 equiv of sulfuric acid was stirred at 25° for 40 min, then diluted with 20 ml of water and stirred for 30 min. The mixture was extracted four times with ether which was dried and concentrated to obtain a quantitative yield of essentially pure 4-(α-hydroxyethyl)biphenyl. Re-

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(9) The reduction rate of carbonyls by cyanoborohydride is greatly increased by protonation.[3] The marked difference in aldehyde and ketone reduction rates in the highly basic solvent HMPA[10] possibly results from a more discriminate deliverance of hydrogen ion to the less hindered aldehyde oxygen from the relatively hindered protonated HMPA phosphoryl oxygen. Other solvents including methanol and benzene did not provide substantial selectivity. For example, using conditions described in ref 3 with TBAC (methanol, pH ~4, 25°), complete disappearance of nonaldehyde and 85% reduction of 2-undecanone was obtained in 15 min. In this case, a small amount (*ca.* 10–15%) of nonaldehyde dimethyl acetal was observed in addition to the alcohol. Furthermore, sodium cyanoborohydride in HMPA was less effective for the selective reduction of aldehydes over ketones. For instance, $NaBH_3CN$ in 0.12 *N* acidic HMPA gave 78% reduction of nonaldehyde and 10% reduction of 2-undecanone in 15 min at 25°; in 1 hr the per cent reductions were 83 and 17% for the aldehyde and ketone, respectively. In addition, the faster rate of halide reductions by $NaBH_3CN$ (*i.e.*, ~51% reduction of iododecane in 1.0 hr at 25°, ref 4) decreases greatly the selectivity possible in the presence of these functional groups.

(10) H. Normant, *Angew. Chem., Int. Ed. Engl.*, 6, 1046 (1967).

crystallization from cyclohexane gave white needles (86%), mp 95–96° (lit.[11] 97°).

In conclusion, the mild conditions, high yields, convenience, and absence of side products coupled with the superior and controllable selectivity recommend the reagent for synthetic applications which would not tolerate harsher reagents. Particularly attractive possibilities include the removal of iodo groups in the presence of carbonyls or the reduction of aldehydes selectively in the presence of ketones or halides.

(11) W. Huber, M. Renoll, A. Rossow, and D. Mowry, *J. Amer. Chem. Soc.*, **68**, 1109 (1946).

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## Molecular Beam Chemistry. Persistent Collision Complex in Reaction of Oxygen Atoms with Bromine Molecules

*Sir:*

Crossed-beam experiments have demonstrated that many reactions proceed *via* formation and decomposition of a "sticky" collision complex which persists for many vibrational periods and at least a few rotational periods, or typically $\gtrsim 5 \times 10^{-12}$ sec. Among the well-studied examples are reactions involving alkali halide salts,[1–3] reactions of halogen atoms with olefins,[4,5] and several ion–molecule reactions.[6,7] For each of these systems the intermediate complex could be reasonably postulated to be a stable molecular species which correlates with the ground-state reactants and products. This communication reports a study of the reaction

$$O(^3P) + Br_2(^1\Sigma_g^+) \longrightarrow BrO(^2\Pi) + Br(^2P)$$

It is found to go *via* a persistent collision complex with large reaction yield and no activation energy, but the known, stable $Br_2O$ molecule does not correlate with the reactants.

Figure 1 shows the experimental results. The primary data comprise velocity distributions of BrO at seven scattering angles, obtained with an apparatus employing mass spectrometric detection and time-of-flight analysis.[8] The O beam comes from a rf discharge source; the $Br_2$ beam comes from a supersonic nozzle. The product velocity analysis makes possible a quantitative kinematic transformation of the laboratory data to determine the scattering distribution in the "center-of-mass" (CM) coordinate system.[8] This system pertains to an observer riding with the centroid of the three atoms and thus displays the relative motion of the reaction products.

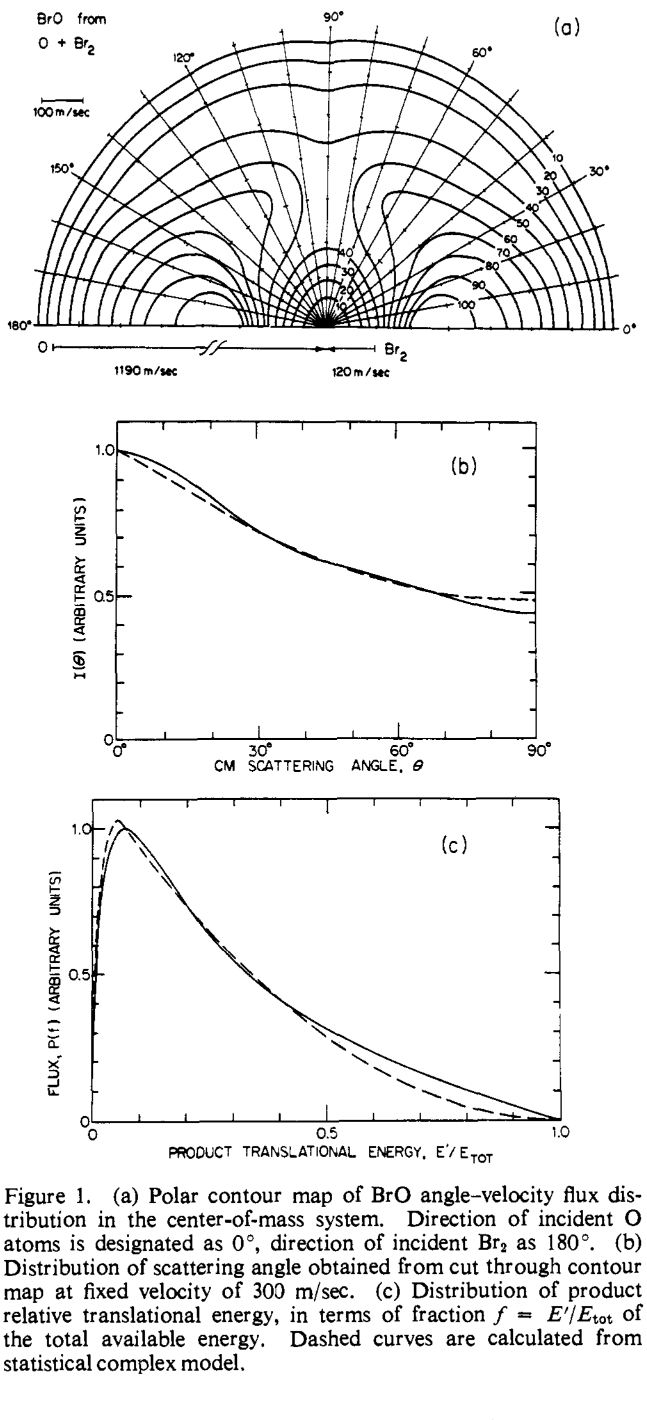

Figure 1. (a) Polar contour map of BrO angle–velocity flux distribution in the center-of-mass system. Direction of incident O atoms is designated as 0°, direction of incident $Br_2$ as 180°. (b) Distribution of scattering angle obtained from cut through contour map at fixed velocity of 300 m/sec. (c) Distribution of product relative translational energy, in terms of fraction $f = E'/E_{tot}$ of the total available energy. Dashed curves are calculated from statistical complex model.

In Figure 1, the CM distributions exemplify the properties expected for a persistent complex more accurately than any previously studied reaction. These properties include: forward–backward symmetry with respect to the initial relative velocity vector, velocity spectrum independent of scattering angle, and characteristic shapes of the angular distribution, $I(\theta)$, and relative translational energy distribution, $P(f)$. For comparison, Figure 1 includes curves calculated from a simple statistical model[1,9] akin to the RRKM theory of unimolecular decay.[10] According to the model, $I(\theta)$

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(1) W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss Faraday Soc.*, **44**, 108 (1967); *J. Chem. Phys.*, **56**, 3581 (1972).

(2) G. H. Kwei, A. B. Lees, and J. A. Silver, *J. Chem. Phys.*, **55**, 456 (1971); **58**, 1710 (1973).

(3) S. J. Riley and D. R. Herschbach, *J. Chem. Phys.*, **58**, 27 (1973).

(4) J. M. Parson and Y. T. Lee, *J. Chem. Phys.*, **56**, 4658 (1972); J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *ibid.*, in press.

(5) J. T. Cheung, J. D. McDonald, and D. R. Herschbach, *J. Amer. Chem. Soc.*, to be submitted for publication.

(6) M. H. Chiang, E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, *J. Phys. Chem.*, **75**, 1426 (1971).

(7) A. Lee, R. L. LeRoy, Z. Herman, R. Wolfgang, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 569 (1972).

(8) J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.*, **56**, 769 (1972).

(9) S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 564 (1972).

(10) O. K. Rice, "Statistical Mechanics, Thermodynamics, and Kinetics," W. A. Freeman, San Francisco, Calif., 1967, pp 495–573; R. A. Marcus, *J. Chem. Phys.*, **43**, 2658 (1965).