mers of **2g** was individually converted to the corresponding isomer of **2c**,[17] neither of which was identical[18] with the compound obtained from the irradiation of **1c**[3] (see Figure 2).

It is clear that none of the reported photoproducts of **1a–c** has structure **2**. The dramatically different photochemical behavior of compounds **2d–g** is probably due to amide resonance precluding charge-transfer interaction between nitrogen and the carbonyl group in the excited state. This interaction is presumably responsible for the photochemistry of amino ketones.[4,18–20]

Photochemical 3-oxetanol formation[16,21,22] from α-alkoxy ketones serves as analogy to the α-amido ketone reaction, and many of the mechanistic details[22b] are probably the same. The products of the described α-tosyl amido ketone photochemistry are accounted for by either ring closure or type II cleavage (monitored by acetophenone formation); however, it is not at all clear at this time why ring formation is the highly preferred pathway.

Studies toward elucidating the scope and mechanism of this reaction are being continued.

[17] Acetaldehyde used for the reductive alkylation. Cis, mp 45–48°; trans, mp (HCl salt) 176–177°; free base a viscous oil.

[18] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969).

[19] (a) S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3741 (1967); (b) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); (c) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968).

[20] S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

[21] P. Yates and A. Szabo, *Tetrahedron Lett.*, 485 (1965).

[22] (a) N. J. Turro and F. D. Lewis, *ibid.*, 5845 (1968); (b) F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

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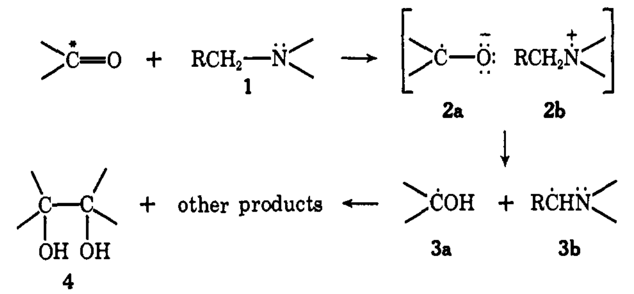
Asymmetric Induction of Photopinacolization in a Chiral Amino Ether[1]

Sir:

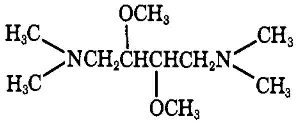
Attempts to isolate optically active products of ketone photoreduction by chiral hydrogen donors[2–5] have been unsuccessful. The excess donors (chiral secondary alcohols[2–4] and silanes[5]) were recovered without loss of activity; the products (pinacols, secondary carbinols, and their silyl ethers) showed no optical rotation. Furthermore, to the best of our knowledge there is only one case known in which asymmetry has been induced in a photochemical reaction using nonpolarized light.[6] We wish to report here a result pertinent to the mechanism of the photochemistry of carbonyl compounds, namely an example of asymmetric photoreduction in a chiral amine acting as a solvent *and* as hydrogen donor.

According to the work of Cohen[7] and others[8,9] the photoreaction of ketones in aliphatic amines takes the course outlined in Scheme I. Pinacols **4** could be formed either by dimerization of hydroxy radical **3a**[7] or by reaction of ion **2a** with itself,[9] with **3a**, or with a molecule of ketone. In any event, there is attachment of the reactive species to a nitrogen-containing molecule, **2a** being linked to **2b** ionically, **3a** forming hydrogen bonds with, *e.g.*, **1**. Therefore we thought that the conditions for preferential formation of one enantiomer of a *d,l* isomer **4** from an unsymmetrical ketone would be better with a chiral amine than with the hydrogen donors above.

Scheme I

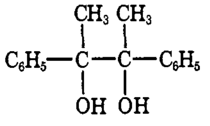


A solution of acetophenone in (+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane (DAB),[10] **5** (15.0 g in 130 ml), was irradiated under argon below 0° in a Pyrex immersion apparatus[11] until tlc (silica gel plates) analysis of samples showed the absence of ketone (*ca.* 14 hr); besides *d,l*- and *meso*-pinacol **6**, only nitrogen-containing products[7–9] ($R_f = 0$ in benzene–10% ethyl acetate) could be detected; the solution irradiated under these conditions remained colorless. Work-up in ether with careful removal of amines and other nitrogen compounds by successive extractions with hydrochloric acid led to the isolation of a crystalline product (8.9 g, 58% yield) which consisted of the *d,l* and meso diastereomeric pinacols **6** in the ratio of 0.85 (nmr assignment[8,12]). This mixture showed an optical rotation of $[\alpha]_D$ +1.05° (*c* 5, ethanol) which corresponds to a 6% optical yield of (*R*,*R*)-**6**.[13] The DAB recovered in 80% yield from the acidic aqueous solutions was of the same optical purity[10] as before use in the irradiation. The *d,l* form of **6** obviously crystallizes as a racemic compound



$(H_3C)_2NCH_2CH(OCH_3)CH(OCH_3)CH_2N(CH_3)_2$

5



$C_6H_5-C(CH_3)(OH)-C(CH_3)(OH)-C_6H_5$

6

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[1] We gratefully acknowledge generous support of this investigation by the Deutsche Forschungsgemeinschaft.

[2] C. Weizmann, E. Bergmann, and Y. Hirshberg, *J. Amer. Chem. Soc.*, **60**, 1530 (1938).

[3] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

[4] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

[5] A. Ritter and M. Lindemann, unpublished results; M. Lindemann, Dissertation, Universität Düsseldorf, Dec 1970.

[6] Hammond and Cole observed *asymmetric induction during energy transfer* using an optically active sensitizer for photoequilibration of the 1,2-diphenylcyclopropanes: G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, **87**, 3257 (1965).

[7] S. G. Cohen and R. J. Baumgarten, *ibid.*, **87**, 2996 (1965); S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967); S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); S. G. Cohen and B. Green, *ibid.*, **91**, 6824 (1969); S. G. Cohen and G. Parsons, *ibid.*, **92**, 7603 (1970).

[8] R. S. Davidson, *Chem. Commun.*, 575 (1966).

[9] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 1270 (1968).

[10] D. Seebach, H. Dörr, B. Bastani, and V. Ehrig, *Angew. Chem., Int. Ed. Engl.*, **8**, 982 (1969).

[11] Methanol of −30°, from a kryostat, was pumped through the cooling jacket of the immersion well; an external bath was kept between −30 and −20°. A 450-W Hanovia high-pressure mercury lamp was used.

[12] J. H. Stocker, *J. Amer. Chem. Soc.*, **88**, 2878 (1966), and footnote 5 therein.

[13] Assuming a value of 34.4° for optically pure product.[14]

[14] D. J. Cram and K. R. Kopecki, *J. Amer. Chem. Soc.*, **81**, 2748 (1959).

enabling us to extract the excess *d* enantiomer:[15] refluxing the photoproduct with pentane, decanting, and cooling the solution at 0° for 2 days gave a mixture of needlelike and rhombic crystals, the needles[14] showing a specific rotation of +31.4° (*c* 0.5, ether). To confirm that the enantiomeric crystals of **6** have a solubility different from that of the racemic compound, we prepared samples containing an excess of one enantiomer independently by chromatography of a *d,l*–meso mixture of **6** (from reduction of acetophenone with Al–Hg[16]) through cellulose-2.5-acetate.[17] With pentane we extracted an enriched enantiomer of high optical rotation from the optically active samples thus obtained, while extracts from the original inactive mixtures had zero rotations. To confirm that the induction had occurred during the step forming the central carbon–carbon bond of **6**, and not by asymmetric destruction after *d,l*-pinacol formation or by some resolution process, we subjected a solution of *d,l–meso*-**6** (ratio 1.8) in DAB after a storage period at room temperature of 16 hr and an irradiation period below 0° of 18 hr to exactly the work-up procedure described above. The pinacol recovered quantitatively was inactive and contained the *d,l* and meso diastereomers in an unaltered ratio.

Preliminary experiments indicate that photoreductions leading to secondary alcohols with asymmetric carbinol carbons can also be asymmetrically induced when carried out in the presence of **5**.

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(15) *Cf.* T. Leigh, *Chem. Ind.* (*London*), 1016 (1970).

(16) K. Sisido and H. Nozaki, *J. Amer. Chem. Soc.*, 70, 776 (1948).

(17) For this method see comments by A. Lüttringhaus and R. Cruse, translators, in E. L. Eliel, "Stereochemie der Kohlenstoffverbindungen," Verlag Chemie, Weinheim/Bergstr., Germany, 1966, p 73, footnote 38b. Meso, *l*, and *d* isomer-enriched fractions were eluted consecutively with benzene.

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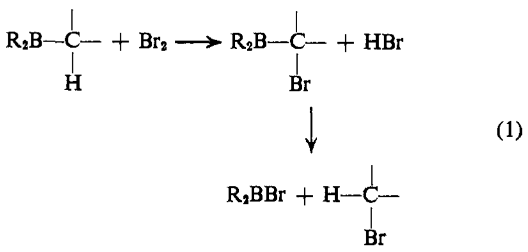
Rearrangement of α-Bromoethyldiethylborane Induced by Nucleophilic Reagents. An Unusually Facile Rearrangement Applicable to the Synthesis of Carbon Structures

Sir:

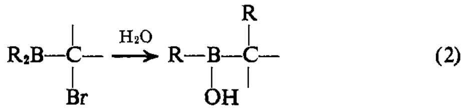
α-Bromoethyldiethylborane is readily synthesized by the photochemical reaction of triethylborane with bromine in the absence of water. It is quite stable in the absence of added nucleophiles, but is rapidly rearranged to derivatives of *sec*-butylethylborane by nucleophilic reagents, such as pyridine, water, methanol, acetonitrile, propylene oxide, and tetrahydrofuran. 2,6-Lutidine, 2,6-di-*tert*-butylpyridine, and diethyl ether are less effective than less-hindered nucleophiles, indicating that the rearrangement involves coordination of the nucleophile with the boron atom of the α-bromoorganoborane. This essentially quantitative formation of carbon–carbon bonds under such mild conditions has major implications for synthesis.

It was recently reported that the reaction of trialkylboranes with bromine in inert solvents, such as cyclohexane and methylene chloride, appears to involve a relatively rapid free-radical substitution in the α position to produce the α-bromoorganoborane and hydrogen bromide in the initial stage.[1,2] These then react to produce the alkyl bromide[1a] (eq 1). However,



$$R_2B{-}\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}{-} + Br_2 \longrightarrow R_2B{-}\overset{|}{\underset{\underset{\displaystyle Br}{|}}{C}}{-} + HBr \;\big\downarrow\; R_2BBr + H{-}\overset{|}{\underset{\underset{\displaystyle Br}{|}}{C}}{-} \qquad (1)$$

if water is present, the protonolysis is avoided and a facile rearrangement of an alkyl group from boron to carbon occurs[1b] (eq 2).



$$R_2B{-}\overset{|}{\underset{\underset{\displaystyle Br}{|}}{C}}{-} \xrightarrow{H_2O} R{-}\underset{\underset{\displaystyle OH}{|}}{B}{-}\overset{\overset{\displaystyle R}{|}}{\underset{|}{C}}{-} \qquad (2)$$

Previously, chloromethyldimethylborane was prepared and isolated.[3] The authors treated this derivative with water, but did not report any rearrangement of the kind postulated above. Matteson and Mah did report rearrangement of *B*-alkyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinates, but utilized sodium butoxide to achieve it.[4] Consequently, it appeared desirable to undertake to prepare and isolate[5] an α-bromotrialkylborane in order to confirm the fact that the postulated rearrangement can occur under the exceptionally mild conditions of the earlier bromination experiments.

It appeared possible that bromination of triethylborane in the absence of water, with rapid removal of the hydrogen bromide, prior to its reaction with the intermediate (eq 1), might provide the desired α-bromoorganoborane. Indeed, this proved to be practical, and the desired α-bromoethyldiethylborane could be isolated by distillation at low pressures.

A dry 200-ml flask, equipped with a septum inlet, magnetic stirrer with Teflon collar, reflux condenser connected to a water aspirator, and a dropping funnel was flushed with nitrogen. The flask was charged with 50 ml of dry *n*-pentane and 14.2 ml (100 mmol) of triethylborane.[6] Then 2.5 ml (50 mmol) of bromine in 10 ml of *n*-pentane was slowly added to the reaction mixture illuminated with a 150-W light bulb. A slow nitrogen stream and moderate suction with an aspirator were utilized to remove the hydrogen bromide as rapidly as possible. Distillation gave 6.2 g (35 mmol) of α-bromoethyldiethylborane (**1**), bp 57–58° (20 mm), a yield of 70% based on the bromine introduced (eq 3).

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(1) (a) C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970); (b) C. F. Lane and H. C. Brown, *ibid.*, **93**, 1025 (1971).

(2) J. Grotewold, E. A. Lissi, and J. C. Sianiano, *J. Organometal. Chem.*, **19**, 431 (1969).

(3) R. Schaeffer and L. J. Todd, *J. Amer. Chem. Soc.*, **87**, 488 (1965).

(4) D. S. Matteson and R. W. H. Mah, *ibid.*, **85**, 2509 (1963).

(5) α-Haloalkylboranes, $RCHXBH_2$, have been formed as intermediates in the hydroboration of certain vinyl chlorides. For example, hydroboration of 1-chloro-2-methylpropene yields α-chloroisobutylborane: H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968); D. J. Pasto, J. Hickman, and T.-C. Cheng, *ibid.*, **90**, 6259 (1968). See also D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966); D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 5608 (1967). However, we have been unable to find any report for the preparation and isolation of an α-haloorganoborane other than the chlorotrimethylborane of Schaeffer and Todd.[3]

(6) Excess triethylborane was used to minimize polybromination.