intermediate radical **2** (eq 3) which then rearranges with opening of the epoxide ring to **3** (eq 4). The alkoxy radical **3** reacts with the trialkylborane (eq 5) to form a borinate **4**, displacing an alkyl radical[1b,6] which continues the chain. Hydrolysis of the intermediate borinate produces the 4-alkyl-2-buten-1-ol **5** (eq 6).

$$R_3B + O_2 \longrightarrow R\cdot + R_2BO_2 \quad (2)$$

$$R\cdot + CH_2{=}CHCH{-}CH_2 \longrightarrow \underset{\textbf{2}}{RCH_2\dot{C}HCH{-}CH_2} \quad (3)$$

$$\textbf{2} \longrightarrow \underset{\textbf{3}}{RCH_2CH{=}CHCH_2O\cdot} \quad (4)$$

$$\textbf{3} + R_3B \longrightarrow \underset{\textbf{4}}{RCH_2CH{=}CHCH_2OBR_2} + R\cdot \quad (5)$$

$$\textbf{4} + H_2O \longrightarrow \underset{\textbf{5}}{RCH_2CH{=}CHCH_2OH} + R_2BOH \quad (6)$$

Thus, this new reaction appears to be one of wide generality and provides a convenient, one-step four-carbon-atom homologation, leading to a variety of 4-alkyl-2-buten-1-ols. Both primary and secondary trialkylboranes react satisfactorily. Although the yields realized with secondary trialkylboranes are somewhat lower, they can be improved by the use of diethyl ether as the solvent (Table I), in spite of the competitive reaction with the solvent (**5**, R = 1-ethoxyethyl), analogous to that observed in THF.

The following procedure is representative. A 25-ml flask equipped with a side-arm inlet containing a rubber septum was fitted with a condenser and magnetic stirring bar and flushed with nitrogen. To the flask was added 5 ml of benzene, followed by 0.71 ml (5 mmol) of triethylborane, and finally 1.2 ml (15 mmol) of 1,3-butadiene monoxide (Aldrich). The mixture was vigorously stirred at 25° as air was passed into the flask at the rate of 1 ml/min through a syringe needle placed through the rubber septum to a point just above the reaction mixture. Samples were removed periodically and analyzed by glpc on a Dow 710 column. Analysis after 1.5 hr indicated that all of the borane had reacted. At this point 1.6 ml of 3 *N* sodium hydroxide was added followed by the gradual addition of 1.6 ml of 30% hydrogen peroxide. The mixture was stirred for an additional hour at room temperature. Potassium carbonate was added until the aqueous layer was saturated. Analysis of the organic layer by glpc indicated that 3.75 mmol (75%) of 2-hexen-1-ol had formed. Distillation of the organic layer from a reaction conducted on a 25-mmol scale yielded 1.7 g (68%) of 2-hexen-1-ol, bp 69–72° (20 mm); $n^{20}D$ 1.4363.

In our earlier reports[1,2] of the synthetic potential of organoboranes *via* free-radical processes, the substrates employed all contained an "activated" double bond in that it was conjugated with a carbonyl function and produced an intermediate radical which was resonance stabilized (eq 7). Even though the reaction with 1,3-butadiene monoxide requires that the alkyl radical add to a relatively "unactivated" double bond that does not produce a resonance-stabilized intermediate, its addition is quite facile and produces good yields of 4-alkyl-2-buten-1-ols. This suggests that compounds containing double bonds that are not in direct conjugation with a carbonyl function, such as dehydronorcamphor, are possible substrates for this reaction.[7]

$$R\cdot + CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}R' \longrightarrow RCH_2\dot{C}H{-}\overset{\overset{O}{\|}}{C}R' \longleftrightarrow RCH_2CH{=}\overset{\overset{O\cdot}{|}}{C}R' \quad (7)$$

Our observations with the oxygen-induced addition of organoboranes to acetylacetylene[2b] suggests that trialkylboranes may also react with 3,4-epoxy-1-butynes to yield allenic alcohols. This reaction is currently under investigation.

(7) Experiments with dehydronorcamphor and other homoconjugated compounds are currently in progress.

(8) National Institutes of Health Postdoctorate Fellow at Purdue University, 1969–1971.

(9) Postdoctorate research associate on a research grant (DA 31-124 ARO(D) 453) supported by the U. S. Army Research Office (Durham).

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Photolysis of α-*N*-Alkylamidoacetophenones, a Direct Route to 3-Azetidinols[1]

Sir:

To our knowledge there are only three synthetic routes to 3 functionally substituted azetidines,[2] all of which have inherent limitations. Our attempts to repeat a reported fourth rather general procedure, involving the photolysis of α-*N*,*N*-dialkylamino ketones (eq 1, **a**–**c**),[3] were unsuccessful. In the photolysis of **1c** for example, a 95% yield of acetophenone (*i.e.*, Norrish type II cleavage) was obtained and glc analysis of the distilled basic fraction revealed a minimum of seven components. The ability of α-phenacylamines to undergo virtually exclusive type II photoelimination,[4] albeit with low quantum efficiency,[5] renders our results unexceptional.

We now wish to report that the photolysis of α-*N*-alkylamidoacetophenones (**1d**–**g**), especially when Z = tosyl, results in very high yields (74 to >95%) of the corresponding N-substituted 3-azetidinols (**2d**–**g**),[6] which can readily be converted into the corresponding amines **2a**–**c**. Furthermore, the azetidines **2a**–**c** prepared in this manner have physical properties fully consistent with their assigned structures, but very different from

(1) E. H. Gold, Abstracts, 2nd Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct 1970, p 53.

(2) (a) V. R. Gaertner, *J. Org. Chem.*, **32**, 2972 (1967); V. R. Gaertner, *Tetrahedron Lett.*, 4691 (1966); (b) B. J. Gaj and D. R. Moore, *ibid.*, 2155 (1967); (c) J. L. Kurz, B. K. Gillard, D. A. Robertson, and A. G. Hortmann, *J. Amer. Chem. Soc.*, **92**, 5008 (1970).

(3) (a) R. A. Clasen, Ph.D. Thesis, Kansas State University, Manhattan, Kan., 1966; (b) R. A. Clasen and S. Searles, Jr., *Chem. Commun.*, 289 (1966).

(4) A. Padwa, W. A. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

(5) P. Wagner, personal communication on type II photoelimination of **1a**.

(6) The only analogous reaction that we are aware of involves the photocyclization of 2-oxoamides to 3-hydroxy-β-lactams (B. Akermark and N-G. Johansson, *Tetrahedron Lett.*, 371 (1969)).

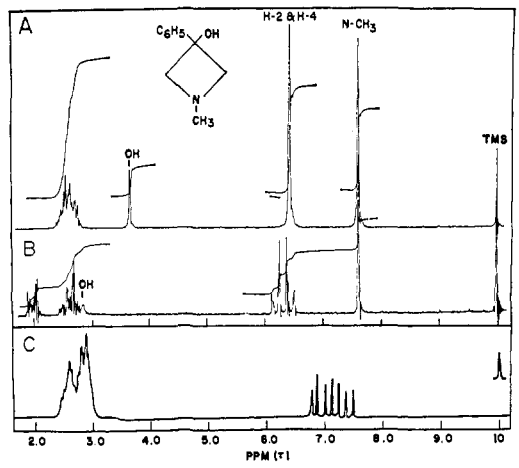
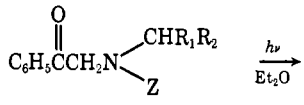


Figure 1. Nmr spectra (60 MHz, with TMS as internal standard): trace A ($CDCl_3$) and trace B (pyridine-d_5) of **2a** prepared in this work; trace C (neat) of the photolysis product of **1a** obtained by Clasen and Searles.[3a]

the physical properties reported for the photoproducts obtained by Clasen and Searles.[3]



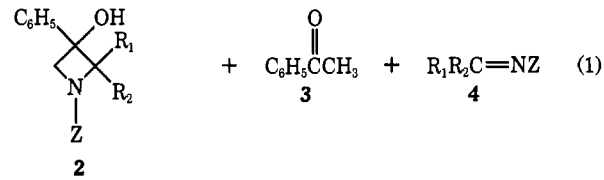
1

1 and 2

$R_1 = R_2 = H$

$R_1 = R_2 = CH_3$

$R_1 = H; R_2 = CH_3$



2 **3** **4** (1)

Z =		
CHR_1R_2	$C_6H_5C{=}O$	Ts
a	**d**	**e**
b		**f**
c		**g**

Photolysis[7] of **1d**[8] affords, in addition to acetophenone,[9] a 50–55% yield of **2d**, mp 101.5–103.5°.[10] The structure of **2d** follows from its hydrolysis to the known 3-phenyl-3-azetidinol (**5**),[11] which can be benzoylated to afford the photoproduct. In contrast to **1d**, photolysis of the *N*-tosyl analog **1e** yields only **2e** (>95%, mp 142.5–143°), and no detectable acetophenone. The structure of azetidinol **2e** is established by obtaining it from the tosylation of **5**, and by the fact that **2e** can be reductively cleaved back to **5** after suitably protecting the hydroxyl group (*i.e.*, $-CH_2OCH_3$). Reductive alkylation of **5** with formaldehyde gives a quantitative yield of solid **2a** (mp 54–56°, bp 85–86° (0.05 mm)) reported by Clasen and Searles[3] to be a liquid (bp 56–57° (0.05 mm)). As can be seen from Figure 1, the nmr spectra[12] of **2a** are fully consistent with our assigned structure and quite different from the spectra recorded[3a] for the photoproduct of **1a**.[13] For example, in our nmr spectrum of **2a** in $CDCl_3$, the ring protons coincidentally appear as a singlet at τ 6.45, but show the expected AA'-BB' pattern at τ 6.18 and 6.45 in pyridine-d_5.

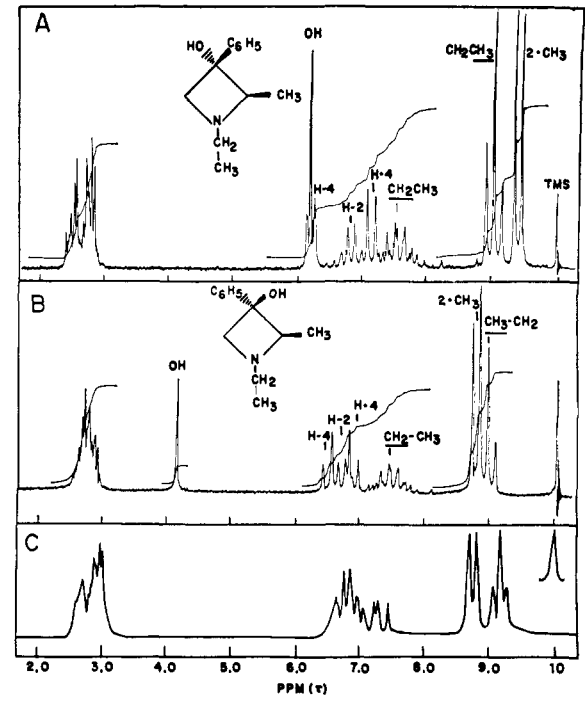


Figure 2. Nmr spectra (60 MHz, TMS as internal standard): traces A and B (CCl_4), respectively, of *trans*-**2c** and *cis*-**2c** prepared in this work; trace C (CCl_4) of the photolysis product of **1c** obtained by Clasen and Searles.[3a]

Similarly, **2f** [(74%, mp 118–118.5°) and acetophenone (18%)] are obtained upon photolysis of **1f**, and can be converted to azetidinol **2b**.[14] Once again, the ir and nmr spectra[13] of **2b** are totally in accord with the structural assignment but are very different from the recorded spectra[3a] of the photoproduct of **1b**. Thus, for example, the ring CH_3 groups cis (τ 8.68, s) and trans (τ 9.30, s) to OH, the nonequivalent isopropyl CH_3 groups (τ 9.07, d, J = 6.0 Hz and 9.10, d, J = 6.0 Hz), and the AB pattern (τ 6.36 and 6.84, J = 7.5 Hz) of the two ring protons are clearly seen in our nmr spectrum of **2b**.

Finally, irradiation of **1g** results in the formation of the cis and trans isomers[15] of **2g** (78%, ratio 53:47) and acetophenone (19%). As before, each of the two iso-

(7) Photolyses were carried out internally through Pyrex in *ca.* 0.03 *M* ethereal solutions, employing a 450-W Hanovia medium-pressure mercury lamp. Chemical yields were obtained by chromatographic separation (column chromatography and preparative tlc for solids and quantitative glc for acetophenone).

(8) D. G. Ott, F. N. Hayes, and V. N. Kerr, *J. Amer. Chem. Soc.*, 78, 1941 (1956).

(9) A *ca.* 15–20% yield of an as yet unidentified isomeric amido ketone, mp 119–120°, was also obtained.

(10) Satisfactory elemental analyses and mass spectra (observable molecular ions) were obtained for all compounds reported. Melting points are corrected.

(11) E. Testa and L. Fontanella, *Justus Liebigs Ann. Chem.*, 671, 106 (1964).

(12) Because **2a** is a solid, its nmr spectrum could not be recorded neat for comparative purposes.

(13) Ir and nmr spectral comparisons made under identical conditions with those reported in ref 3a.

(14) Free base obtained as a viscous oil from analytically pure hydrochloride, mp 209–210°.

(15) Cis: CH_3 cis to OH, mp 161.5–163°. Trans: CH_3 trans to OH, mp 142–142.5°. Configurational assignments follow from nmr ($CDCl_3$) chemical shifts of the CH_3 signals (doublets, J = 6.5 Hz);[16] cis τ 8.61, trans τ 9.15. The isomers are readily separated by fractional crystallization from ethanol.

(16) R. B. La Count and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965).

mers of **2g** was individually converted to the corresponding isomer of **2c**,[17] neither of which was identical[13] 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]

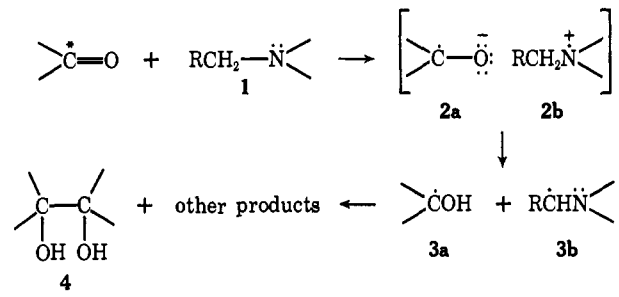
Sir:

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.

(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).

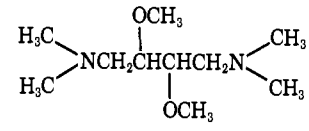
According to the work of Cohen[7] and others[8,9] the photoreaction of ketones in aliphatic amines takes the course outlined in Scheme I. Pinacols **4** could be

Scheme I

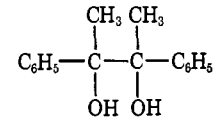


formed either by dimerization of hydroxy radical **3a**[7] or by reaction of ion **2a** with itself,[9] with **3a**, or with a molecule of ketone. In any event, there is attachment of the reactive species to a nitrogen-containing molecule, **2a** being linked to **2b** ionically, **3a** forming hydrogen 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.

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)



5



6

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

(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).