

seem to interact strongly or to make coordinated complexes with sodium borohydride. Finally, in the presence of monosaccharides, sodium borohydride was found to be dissolved to some extent in THF in benzene and the reduction proceeded smoothly in either THF or benzene solution. In the absence of 1-6, sodium borohydride was only slightly soluble in THF (ca. 0.1 g/100 mL at 25 °C) and insoluble in benzene and hence the reaction was extremely sluggish in the former and did not take place in the latter solution.

Optically active additives, 1-6, are considered to be involved as chiral ligands or media in the present asymmetric reduction. These do not function as modified reagents but only enter into the reaction as intermediate complexes or solvates.

Experimental Section

Reagents. Ketones used here were purified by drying over CaH_2 and subsequent distillation in a nitrogen atmosphere. THF and benzene were heated under reflux over sodium wire and distilled over LiAlH_4 in a nitrogen atmosphere. Sodium borohydride was purified twice by recrystallization from 2,5,8-trioxanonane. The hydroxy-monosaccharide derivatives, 1,4:3,6-dianhydro-D-sorbitol (1),⁶ 1,4:3,6-dianhydro-D-mannitol (2),⁶ 1,2:5,6-di-*O*-isopropylidene-D-glucufuranose (3),³ 1,2:5,6-di-*O*-cyclohexylidene-D-glucufuranose (4),⁸ 2,3:4,5-di-*O*-isopropylidene- β -D-furctopyranose (5),⁹ and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (6),¹⁰ were prepared according to previous methods.

All the materials described were stored under a nitrogen atmosphere prior to use.

Instruments. Rotation were taken on a Zeiss Visual polarimeter with readings to $\pm 0.02^\circ$. Gas chromatographic determination was made on a Simazu GC-6A using a Silicone SE-30 prepared column.

Procedures. Under a nitrogen atmosphere, a benzene solution of the monosaccharide (30 mmol for 1 and 2 and 60 mmol for 3-6 in 50 mL of benzene) was added to sodium borohydride (30 mmol) in benzene. After stirring for 3 h at 25 °C, the ketone (30 mmol) was added and the mixture was stirred for 120 h. The mixture was hydrolyzed with 1 N hydrochloric acid. The ether extracts were washed (H_2O , three times), dried (NaSO_4), and concentrated (water aspirator) to give a colorless oil. The crude product was purified by distillation under reduced pressure. No monosaccharide was detected by TLC. Reaction procedure in THF solution was conducted in the same way. Reaction time in THF was 48 h.

References and Notes

- (1) (a) S. R. Landor and A. R. Tatchell, *J. Chem. Soc. C*, 2280 (1966); (b) S. R. Landor, B. J. Miller, and A. R. Tatchell, *ibid.*, 197 (1967); (c) O. Cervinka and O. Bělovský, *Collect. Czech. Chem. Commun.* **32**, 2897 (1967); (d) S. Yamaguchi and H. S. Mosher, *J. Org. Chem.*, **38**, 1870 (1973); (e) J. P. Vigneron and I. Jacquet, *Tetrahedron*, **32**, 939 (1976); (f) G. M. Giongo, F. DiGregorio, N. Palladino, and W. Marconi, *Tetrahedron Lett.*, 3195 (1973); (g) S. Yamaguchi, F. Yasuhara, and K. Koguto, *J. Org. Chem.*, **42**, 1578 (1977); (h) E. D. Lund and P. E. Shaw, *ibid.*, **42**, 2093 (1977); (i) T. Mukaiyama, M. Asami, J. Hanna, and S. Kobayashi, *Chem. Lett.*, 783 (1977).
- (2) D. Valentine, Jr., and J. W. Scott, *Synthesis*, 329 (1978).
- (3) (a) J. P. Massé and E. R. Parayre, *J. Chem. Soc., Chem. Commun.*, 438 (1976). They reported that optically active alcohol possessing the *R* configuration was produced in an enantiomeric excess of 39% in the reduction of acetophenone in the presence of *L*-*N*-methyl-*N*-dodecylphedrinium bromide. The latter experimental results reported^{3c} throw doubt on this high value by Massé et al. (b) J. Balcells, S. Colonna, and R. Fornasier, *Synthesis*, 266 (1976). (c) S. Colonna, R. Fornasier, and U. Pfeiffer, *J. Chem. Soc., Perkin Trans. 1*, 8 (1978); (d) S. Colonna and R. Fornasier, *J. Chem. Soc., Perkin Trans. 1*, 371 (1978).
- (4) T. Sugimoto, Y. Matsumura, S. Tanimoto, and M. Okano, Abstracts of the 6th Meeting for Organic Reaction Using Enzyme-Like Functional Compounds, March 1978, Tokyo, p 27.
- (5) O. Cervinka and A. Fabryová, *Tetrahedron Lett.*, 1179 (1967). It is however subsequently shown^{1a} that the reagent prepared by the reaction of equivalent amounts of LiAlH_4 with 3-*O*-benzyl-1,2-*O*,*O*-cyclohexylidene- α -D-glucufuranose reduced ketones with stereoselectivities as high as 38% in the case of propiophenone. Furthermore, addition of 1 equiv of ethanol to the LiAlH_4 -sugar complex results in the formation of the alkoxy complex. Subsequent reduction of ketones with this new reducing agent affords alcohol with 71% for acetophenone and 46% for propiophenone, respectively.^{1b}
- (6) R. Montgomery and L. F. Wiggins, *J. Chem. Soc.*, 390 (1946); 2204 (1948).
- (7) E. Fisher and C. Rund, *Ber.*, **49**, 88 (1916).
- (8) R. C. Hockett, R. E. Miller, and A. Scattergood, *J. Am. Chem. Soc.*, **71**, 3072 (1949).
- (9) R. F. Brady, Jr., *Carbohydr. Res.*, **15**, 35 (1970).
- (10) K. P. Link and H. M. Sell, *Biochem. Prep.*, **3**, 75 (1953).
- (11) U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, **23**, 1201 (1965).

- (12) P. A. Levene and L. Mikeska, *J. Biol. Chem.*, **70**, 355 (1926).
- (13) D. Nasipuri and G. Sarker, *J. Indian Chem. Soc.*, **44** (2), 165 (1967).
- (14) R. MacLeod, F. J. Welch, and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 876 (1960).
- (15) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).
- (16) S. R. Landor, B. J. Miller, and A. R. Tatchell, *J. Chem. Soc.*, 2282 (1966).

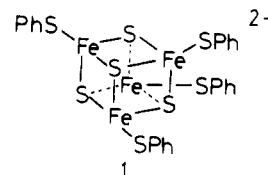
Bimolecular Reductions of Aromatic Ketones and Aldehydes with the *n*-Butyllithium- $\text{Fe}_4\text{S}_4(\text{SPh})_4$ System

Hiroo Inoue,* Michio Suzuki, and Norihiro Fujimoto

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

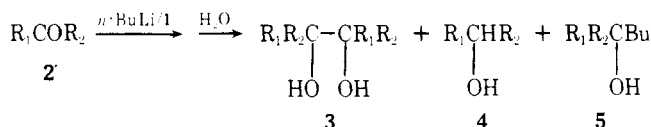
Received January 15, 1979

Although a tetrakis(mercapto- μ_3 -sulfido-iron) cluster¹ is attractive as a model for a biological reducing agent of the ferredoxin type,² detailed descriptions as to function of the cluster are lacking. Recent studies have disclosed that the cluster catalyzes the transfer of electrons from external reductants to a nitrogen complex of molybdenum.³ We have tried to utilize the cluster as an electron transfer carrier in a general organic redox reaction and found that $[\text{Fe}_4\text{S}_4(\text{SPh})_4](n\text{-Bu}_4\text{N})_2$ (1) mediates the transfer of electrons from



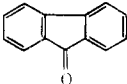
n-butyllithium to fluorenone.⁴ Herein, we wish to describe our findings that the *n*-butyllithium-1 system is effective as a reducing system for the bimolecular reductions of several aromatic ketones and aldehydes.

The *n*-butyllithium-1 system was prepared by treating the cluster 1 under argon with *n*-butyllithium in degassed hexane-diethyl ether at 0 °C for 30 min. The reactions of ketones and aldehydes with the *n*-butyllithium-1 system proceeded under mild conditions to give the corresponding pinacols 3, hydrols 4, and 1,2-addition products 5. In these reactions,



n-butyllithium was oxidized to octane, butane, and 1- and 2-butenes. The cluster 1 was regenerated in over 97% purity on addition of benzenethiol instead of water to the reaction mixtures after the reaction.⁵ In the iron ion-substrate molar ratio of 1:1, the yields of the products were dependent on the amount of *n*-butyllithium added. The optimum *n*-butyllithium-iron ion molar ratios to form predominantly pinacols are summarized in Table I. In the reduction of fluorenone having less negative reduction potential [$E_{1/2}$ (vs. SCE) = -1.29 and -1.95 V]⁶ than those of other ketones and aldehydes described in Table I, the formation of the fluorenone pinacol was observed in the *n*-butyllithium-iron ion molar ratio of 2:1 (entry 1). When the reduction of fluorenone was carried out in the molar ratio of 4:1, however, fluorenone was formed as a major product by a two-electron reduction.⁴ In the cases of benzophenone, acetophenone, and benzaldehyde which have the first reduction potentials near the second reduction potential of fluorenone,⁷ the *n*-butyllithium-iron ion molar ratio of

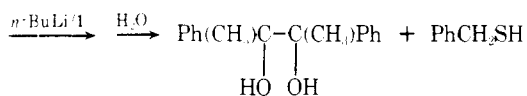
Table I. Reactions of Aromatic Ketones and Aldehydes with *n*-Butyllithium in the Presence of 1 or FeCl₃^a

entry	compd 2	iron complex	molar ratio <i>n</i> -BuLi/Fe ion	isolated yield, %			<i>dl</i> /meso ratio of 3	recovered 2, %
				3	4	5		
1		1 ^b	2:1	62	9	4		20
2		FeCl ₃ ^b	3:1	93	0	0		0
3	PhCOPh	1	2.7:1	57	12	6		22
4		1	3.6:1	44	27	12		17
5		FeCl ₃	2.7:1	0	24	0		75
6		FeCl ₃	3.6:1	3	55	6		25
7	PhCOCH ₃	1	4:1	57	3	12	2.2	10
8		1	5:1	34	6	38	2.3	3
9		FeCl ₃	3.5:1	43	30	0	2.8	12
10	PhCOCH ₂ CH ₃	1	3.7:1	57	6	16	1.9	5
11		FeCl ₃	3.7:1	25	44	0	2.4	9
12	PhCHO	1	3.7:1	58	0	29	1.6	0
13		1	3:1	44	0	47	1.5	0
14		FeCl ₃	3:1	65	10	0	1.9	0
15	<i>p</i> -ClC ₆ H ₄ CHO	1	3:1	52	7	35	1.2	0
16		FeCl ₃	3:1	68	24	0	1.7	0

^a Amounts of 2 used were 0.5–0.9 mmol. The molar ratio of Fe ion to 2 was 1. Solvent: ether (5 mL). ^b Reference 4.

3–4:1 was necessary to form their pinacols.⁸ The *dl*/meso ratios of pinacols were close to those in the electrolytic reductions in acidic media⁹ rather than nonaqueous aprotic media.¹⁰ In a control in which either the cluster 1 or *n*-butyllithium was omitted, pinacols were not produced in all cases.¹¹ In the case of *p*-chlorobenzaldehyde, the reductive cleavage of the carbon–chlorine bond did not occur at all (entry 15).

The reduction of 2-benzylthioacetophenone with the *n*-butyllithium–1 system (*n*-BuLi–iron ion–ketone 4:1:1) gave the acetophenone pinacol through the cleavage of the carbon–sulfur bond in 32% isolated yield with 46% recovery of the starting ketone.¹² Aliphatic ketones such as 2-undecanone and PhCOCH₂SCH₂Ph



cyclohexanone were not reduced to the corresponding pinacols under similar conditions, although minor quantities of hydrols were obtained. The increase of the *n*-butyllithium–iron ion molar ratio resulted in the formation of the 1,2-addition product.

The reducing ability of the *n*-butyllithium–1 system to form pinacols was compared with that of the *n*-butyllithium–FeCl₃ system. The best yields of pinacols in the reductions of ketones and aldehydes with the *n*-butyllithium–FeCl₃ system are shown in Table I. The pinacol–hydrol yield ratios are strongly dependent on the structure of the substrate. Particularly the remarkable difference in distribution of the yields is observed in the case of benzophenone (entries 3 and 6). Furthermore, hydrols rather than 1,2-addition products are produced predominantly in all cases using FeCl₃. These results reflect the important role of the iron ions constituting the cluster structure and indicate that the *n*-butyllithium–1 system acts effectively as a reducing system for the reductive dimerization of aromatic ketones and aldehydes.

Experimental Section

The carbonyl compounds are available commercially and were fully characterized prior to use. *n*-Butyllithium is the commercially available substance which is dissolved in hexane. The concentration of *n*-butyllithium, 1.26 M, was determined by Gilman's method using reaction with benzyl chloride.¹³ The cluster 1 was prepared according to Holm's method.¹ Anhydrous FeCl₃ was prepared by the sublimation of commercial FeCl₃ at 300 °C (1 mmHg) prior to use. UV spectra were obtained on a Hitachi EPS-3T spectrometer, IR spectra on a

Hitachi 215 grating infrared spectrometer as film and KBr pellets, and NMR spectra on a Hitachi R-24 A spectrometer in CDCl₃ with Me₄Si as an internal standard. All known products were isolated by column chromatography on silica gel and were confirmed by comparison of their IR and NMR spectra with authentic samples. Ether was refluxed over Na and distilled.

General Procedure for the Reactions of Ketones and Aldehydes with *n*-Butyllithium in the Presence of 1 or FeCl₃. The following is a typical experimental procedure. A 90-mL reaction tube, equipped with magnetic stirrer, was charged with 5 mL of ether and 1.22 mL (1.54 mmol) of a solution of *n*-butyllithium in hexane. After the air in the reaction tube was replaced by argon by a freezing method, the solution was cooled in a liquid nitrogen bath and 182 mg (0.143 mmol) of the cluster 1 was added to the frozen solution. The mixture was melted and stirred vigorously under argon at 0 °C for 30 min. The resulting black solution was again cooled in a liquid nitrogen bath. To the frozen solution was added 100.5 mg (0.552 mmol) of benzophenone. The reaction tube was degassed and sealed. The melted black solution was stirred vigorously at 10–20 °C for 20 h, during which time the black precipitate was formed. To the reaction mixture was added 20 mL of water with stirring. GC analysis of the ether layer done using a 1 m by 3 mm column packed with 10% SE-30 indicated the presence of octane in addition to 3, 4, and 5. The black precipitate was filtered under argon, washed with ether, and dried in vacuo; percent Fe was found to be 33.6. UV (DMF) showed a peak at 457 nm but the *E*(1%, 1 cm) value of the peak was reduced to about one-half its initial value. Adding 2 mL of benzenethiol instead of water to the mixture after the reaction, the precipitate showing properties (analysis, UV, and IR) consistent with those of the starting cluster 1 was obtained. The filtrate was partitioned in a 100-mL separatory funnel, the aqueous layer was then extracted with ether, and the combined ether layers were dried over Na₂SO₄. Filtration and removal of ether gave 126 mg of a white solid which was chromatographed on silica gel (10 g), eluting with carbon tetrachloride, giving first 24.9 mg of diphenyl disulfide then 22.4 mg (22%) of benzophenone. Further elution with benzene yielded 57.6 mg (57%) of benzopinacol, 8.4 mg (6%) of 1,1-diphenyl-1-pentanol, and 12.2 mg (12%) of benzhydrol. In a separate experiment, the gaseous materials were collected from the mixture after the reaction and analyzed to be a mixture of butane, 1-butene, and *cis*- and *trans*-2-butenes by GC analysis which was done using a 4 m by 3 mm column packed with DMS. The other control and comparison experiments outlined in the text were also carried out by the general procedure above. When product mixtures were obtained, these were often analyzed by NMR spectra. The amounts of the *dl* and meso isomers of 3 were determined by NMR spectroscopy.¹⁴

Registry No.—*dl*-3 (R₁ = Ph; R₂ = CH₃), 22985-90-6; *meso*-3 (R₁ = Ph; R₂ = CH₃), 4217-65-6; *dl*-3 (R₁ = Ph; R₂ = CH₂CH₃), 16020-87-4; *meso*-3 (R₁ = Ph; R₂ = CH₂CH₃), 16020-86-3; *dl*-3 (R₁ = Ph; R₂ = H), 655-48-1; *meso*-3 (R₁ = Ph; R₂ = H), 579-43-1; *dl*-3 (R₁ = *p*-ClC₆H₄; R₂ = H), 69483-09-6; *meso*-3 (R₁ = *p*-ClC₆H₄; R₂ = H), 37580-81-7.

References and Notes

- (1) B. A. Averill, T. Herskovitz, R. M. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).
- (2) D. O. Hall and M. C. W. Evans, *Nature* (London), **223**, 1342 (1969).
- (3) E. E. van Tamelen, J. A. Gladysz, and C. R. Brulet, *J. Am. Chem. Soc.*, **96**, 3020 (1974); G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *ibid.*, **97**, 7069 (1975).
- (4) H. Inoue, N. Fujimoto, and E. Imoto, *J. Chem. Soc., Chem. Commun.*, 412 (1977).
- (5) We assume that the product anions such as $R_1R_2C(O^-)C(O^-)R_1R_2$ complex the iron ions of the cluster after the reaction.
- (6) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).
- (7) The reduction potentials [$E_{1/2}$ (vs. SCE)] of benzophenone, acetophenone, and benzaldehyde in an aprotic medium are -1.83 and -2.09 V (CH_3CN), -1.87 and -2.32 V (DMF), and -1.93 and -2.51 V (DMF), respectively; T. J. Curphey, L. D. Trivedi, and T. Layloff, *J. Org. Chem.*, **39**, 3831 (1974); L. Meites, P. Zuman, W. J. Scott, B. H. Campbell, and A. M. Kardos, "Electrochemical Data", Part 1, A, 1974, pp 272 and 332.
- (8) The cathodic polarography of 1^{2-} [formally $2Fe(II) + 2Fe(III)$] in DMF reveals the $1^{2-} \rightarrow 1^{3-}$ and $1^{3-} \rightarrow 1^{4-}$ reduction processes with $E_{1/2} = -1.039$ and -1.748 V vs. SCE, respectively; B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 4159 (1974). From this fact, we assume that fluorenone would be reduced to its pinacol by the formally $3Fe(II) + Fe(III)$ cluster and other ketones and aldehydes by the formally $4Fe(II)$ cluster.
- (9) The *d/meso* ratios of pinacols were 0.93–1.41:1 for acetophenone, 1.40–1.42:1 for propiophenone, and 1.1:1 for benzaldehyde; J. H. Stocker, R. M. Jenevein, and D. H. Kern, *J. Org. Chem.*, **34**, 2810 (1969).
- (10) In the electroreduction of acetophenone in CH_3CN and DMF, the *d/meso* ratios were 7–9:1; J. H. Stocker and R. M. Jenevein, *Collect. Czech. Chem. Commun.*, **36**, 925 (1971).
- (11) J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973).
- (12) The reductive cleavage of the analogous C–S bond has been observed in the electrolytic reduction of 2-phenylthioacetophenone; C. P. Andrieux and J. M. Saveant, *Bull. Soc. Chim. Fr.*, 3281 (1972).
- (13) H. Gilman, F. K. Cantledge, and S. Y. Sim, *J. Organomet. Chem.*, **1**, 18 (1963).
- (14) J. H. Stocker, D. H. Kern, and R. M. Jenevein, *J. Org. Chem.*, **33**, 412 (1968); J. H. Stocker and R. M. Jenevein, *ibid.*, **33**, 2145 (1968).

Elimination Reactions. 3. Light-Assisted HCN Elimination from 2-[*p*-(*N,N*-Dimethylamino)phenyl]-2,3,3-tricyanopropionamide

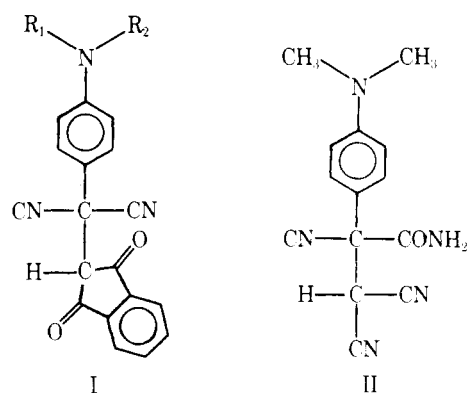
Patrick G. Farrell* and Fouad M. Fouad

Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6

Received November 22, 1977

The introduction of a new single bond between two carbon atoms via a photochemically induced elimination of a small, stable molecule (e.g., N_2 , CO_2 , SO_2 , and CO) is a well-known reaction.¹ There are also examples of both intra- and intermolecular photoinduced eliminations of hydrogen halides which lead to new single-bond formation,^{1,2} but relatively few reports of the analogous introduction of a double (or multiple) bond, although these include isolated examples of HCl , HBr , and HI photoeliminations.³ Similarly, a few examples of the photoinduced elimination of H_2O ,⁴ NH_3 ,⁵ and C_2H_4 ⁶ are known, together with a possible example of HCN photoelimination.⁷

In the course of some earlier work, we noted that some poly(cyano)ethanes eliminate HCN under photochemical conditions in addition to the expected base-catalyzed (thermal) HCN-elimination reaction.⁸ (Other workers have employed base-catalyzed HCN elimination from both cyclic and acyclic compounds to obtain the corresponding olefins.⁹) The C–CN bond is a fairly stable one under the usual photochemical conditions, except for that in compounds such as crystal violet or malachite green, leucocyanides, and there are few reports of its photochemical cleavage. Both homolytic and heterolytic cleavage of the C–CN bond is known for the leucocyanides, depending upon the nature of the solvent,¹⁰ while short-wavelength irradiation of nitriles usually leads to



homolytic bond cleavage (e.g., acetonitrile¹¹). A recent reference¹² to "an unusual photoelimination of HCN" from I to yield the corresponding olefin¹³ prompts us to report further on the similar HCN elimination from II. Unlike other poly(cyano)ethanes studied, II does not yield significant amounts of olefin under thermal, base-catalyzed reaction conditions, even after extended reaction times.

Experimental Section

Materials. Organic solvents were Fisher spectrograde, dried and redistilled twice before use. Doubly distilled water was deionized before use. 2-[4-(*N,N*-Dimethylamino)phenyl]-2,3,3-tricyanopropionamide (II) was prepared according to the literature procedure:⁸ decomposition above 190 °C; λ_{max} 262 nm (ϵ 18 000), λ_{sh} 295 nm (ϵ 7100) in methanol.

Method. Photolyses (3500 Å) were carried out in silica tubes in a Rayonet reactor, equipped with a merry-go-round unit. The temperature was maintained at 25 ± 1 °C. Five-milliliter portions of a 10^{-4} M solution of II in a given solvent were introduced into the silica tubes and each tube was flushed with oxygen-free nitrogen, saturated with the vapor of the solvent. The tubes were then closed, placed in the reactor, and irradiated. The reactions were analyzed spectroscopically by measuring the product development as a function of time (30-s or 1-min time intervals). Blank experiments confirmed that no reaction took place in the absence of irradiation, that reaction ceased on removal of the irradiation, and that 93–97% yields of product were obtained under the photochemical conditions employed. The intensity of the incident radiation was 6×10^{16} quanta/s, as determined by a potassium ferrioxalate actinometer.

In the presence of acid, solutions of the product are blue (λ_{max} 620 nm), whereas they are pink in methanol–water solutions (λ_{max} 426 nm). To confirm that rate determinations in the presence of acid were valid, runs in neutral media (90% MeOH–10% H_2O) were analyzed spectroscopically at both 620 and 426 nm (after addition of excess HCl). The data were identical within experimental error.

HCN elimination was followed to $65 \pm 5\%$ reaction in all cases and the data obtained were extrapolated to zero time. Good linear plots for first- or second-order kinetics were obtained with very little deviation over the range of reaction studied.

Results and Discussion

Values of first- or second-order rate coefficients for photoinduced HCN elimination from II in various media are shown in Table I. Reactions in pure alcohols exhibit first-order dependence on the substrate, whereas those in the presence of bases or of carbonyl compounds exhibit second-order substrate dependence. Although no thermal base-catalyzed elimination of HCN occurs in the time required for the photoinduced reaction to go to completion, examination of the data shows that the photochemical reaction rate in methanol is enhanced by the presence of bases. This presumably reflects the increased acidity of the excited species although the rate enhancement by aromatic bases is only slight, relative to that calculated from the data in Table I for an uncatalyzed second-order reaction in methanol. The reaction is not particularly sensitive to the strength of the base (as measured by their values of pK_b in water) however, as rates in the presence of either of the three weaker bases are effectively the same. Similar behavior is found in the presence of the stronger bases,