pure to be used without purification; mp 83–84 °C (recrystallized from Skellysolve B). Anal. Calcd for $C_{17}H_{17}NO_4S$: c, 61.63; H, 5.17; N, 4.23; S, 9,66. Found: C, 61.80; H, 5.29; N, 4.17; S, 9.56.

Registry No. 1 (R = H), 2382-96-9; 1 (R = 3,4,5-trimethoxybenzyl, 86971-23-5; 1 (R = benzyl), 86971-24-6; 1 (R = *sec*-heptyl), 86971-25-7; 1 (R = *n*-heptyl), 86971-26-8; 1 (R = cyclohexyl), 86971-27-9; 1 (R = 3-picolyl), 86971-28-0; 2 (R = benzyl), 538-74-9; 2 (R = 2-benzothiazolylmethyl), 86971-29-1; 2 (R = *n*-heptyl), 629-65-2; 2 (R = *sec*-heptyl), 45162-42-3; 2 (R = 2-picolyl), 5832-32-6; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = *n*-heptyl), 86971-30-4; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = *sec*-heptyl), 86971-31-5; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = benzyl), 86971-32-6; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = *n*-butyl), 86971-33-7; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = allyl), 86971-34-8; 4 (R = 3,4,5-trimethoxybenzyl; R = ethyl), 86971-35-9; 4 (R = 3,4,5-trimethoxybenzyl; $R^1 = (CH_2)_5CO_2H$), 86971-36-0; 4 (R = 3,4,5-trimethoxybenzyl; R^1 = H), 80192-89-8; 4 (R = benzyl; R^1 = *n*-butyl), 5184-47-4; 4 (R = benzyl; $R^1 = CH(CH_3)CH{=}CH_2$), 75238-62-9; 4 (R = benzyl; $R^1 = CH_2CH{=}CHCH_3$), 31409-96-8; 4 (R = *n*-heptyl; R^1 = benzyl), 58587-21-6; 4 (R = *n*-heptyl; R^1 = *sec*-heptyl), 86971-37-1; 4 (R = 3-picolyl; $R^1 = (CH_2)_5CO_2CH_3$), 86971-38-2; 4 (R = 3-picolyl; R^1 = 2-picolyl), 86971-39-3; 4 (R = cyclohexyl; R^1 = benzyl), 19843-98-2; benzyl chloride, 100-44-7; 2-(chloromethyl)benzothiazole, 37859-43-1; *n*-heptyl bromide, 629-04-9; *sec*-heptyl bromide, 1974-04-5; 2-picolyl chloride hydrochloride, 6959-47-3; 3,4,5-trimethoxybenzyl bromide, 21852-50-6; cyclohexyl bromide, 108-85-0; 3-picolyl chloride hydrochloride, 6959-48-4; *n*-butyl chloride, 109-69-3; allyl chloride, 107-05-1; ethyl bromide, 74-96-4; methyl 6-bromohexanoate, 14273-90-6; 3-chloro-1-butene, 563-52-0.

1,3,4-Dioxazol-2-ones: A Potentially Hazardous Class of Compounds†

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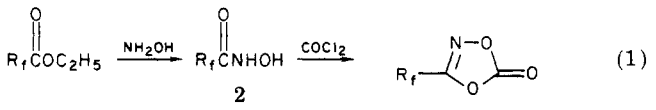
Trifluoromethyl isocyanate and other perfluoroaliphatic isocyanates are usually prepared by the classical Curtius rearrangement.[1] However, the acyl azide precursors are capriciously explosive, and more than one investigator has been injured while trying to prepare trifluoromethyl isocyanate by this method.

In a search to find a safer method of generating perfluoroaliphatic isocyanates, we examined several other precursors that could be used in place of acyl azides. One class of compounds investigated was the cyclic carbonates of perfluoroaliphatic hydroxamic acids (5-(perfluoroalkyl)-1,3,4-dioxazol-2-ones, 1).[2] We found that these compounds are indeed efficient intermediates to isocyanates, but they are surprisingly similar to acyl azides in that they are also dangerously explosive.

The cyclic carbonates (1) were prepared in high yield by the reaction of phosgene with perfluoroaliphatic hydroxamic acids in diglyme solvent (eq 1). No base was

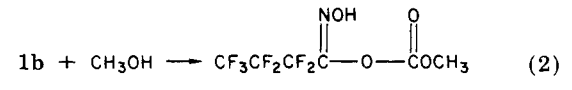


(1)

1a, $R_f = CF_3$
b, $R_f = CF_2CF_2CF_3$
c, $R_f = (CF_2)_6CF_3$

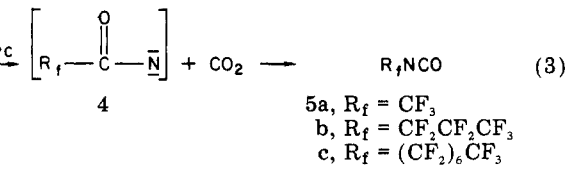
needed to remove the hydrogen chloride. In fact, if a base was added to the reaction mixture, cyclic carbonates were not obtained, probably because of their extreme reactivity toward nucleophiles.

1,3,4-Dioxazol-2-ones can be regarded as mixed anhydrides of carbonic acid and hydroxamic acids, and so it is not surprising that they react vigorously with water, alcohols, and amines. With methanol, 5-(heptafluoropropyl)-1,3,4-dioxazol-2-one (**1b**) gives the adduct ester **3** (eq 2).



(2)

Pyrolysis of the cyclic carbonates **1** at 275 °C and atmospheric pressure (eq 3) results in expulsion of carbon



(3)

5a, $R_f = CF_3$
b, $R_f = CF_2CF_2CF_3$
c, $R_f = (CF_2)_6CF_3$

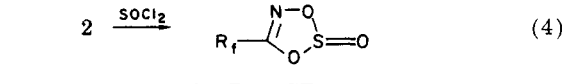
dioxide, and the resulting acylnitrenes (**4**) rearrange to give a nearly quantitative yield of perfluoroalkyl isocyanates. Trifluoromethyl, heptafluoropropyl, and perfluoroheptyl isocyanates (**5a–c**) were prepared by this method. Pyrolysis at lower tempertures gave incomplete conversions.

Our first attempts to prepare **5a** by the pyrolysis of **1a** were highly successful, but a later attempt resulted in a forceful explosion when the remaining (ca. 20 g) unpyrolyzed **1a** contained in a glass dropping funnel (25 °C) detonated. Subsequently, we found that an electrically heated wire will cause an unconfined sample of **1a** to detonate. A sample of **1a** contained in a sealed stainless steel tube also detonated when heated rapidly to 220 °C, but it was not sensitive to mechanical shock.

1,3,4-Dioxazol-2-ones that contain larger perfluoroalkyl substituents apparently are safer to handle. A hot wire failed to initiate a propagating decomposition (detonation) of **1b**. Nonetheless, **1b** cannot be considered safe, for in a subsequent preparation, it detonated while being distilled at atmospheric pressure.

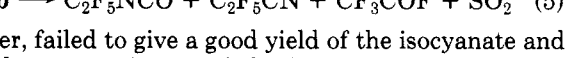
Our conclusions are that cyclic carbonates of hydroxamic acids (1,3,4-dioxazol-2-ones) can be pyrolyzed under certain conditions to give high yields of isocyanates, but the process is hazardous and offers no advantage over the pyrolysis of acyl azides.

In related work, several cyclic sulfites **6** were prepared by the reaction of perfluoroaliphatic hydroxamic acids with thionyl chloride (eq 4). Pyrolysis of sulfite **6b** (eq 5),



(4)

6a, $R_f = CF_3$
b, $R_f = C_2F_5$
c, $R_f = CF_2CF_2CF_3$



(5)

however, failed to give a good yield of the isocyanate and instead gave a mixture of the isocyanate, pentafluoropropionitrile, and trifluoroacetyl fluoride.

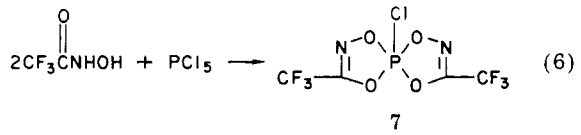
A bicyclic phosphorane (**7**) was also prepared from trifluoroacetohydroxamic acid and phosphorous penta-

† Contribution No. 3237.

(1) Barr, D. A.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 3428. Sprenger, G. H.; Wright, K. J.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 2890.
(2) Eibler, E.; Sauer, J. *Tetrahedron Lett.* **1974**, 2565. These authors report low yields of arylisocyanates by the pyrolysis of 5-aryl-1,3,4-dioxazol-2-ones in dimethyl sulfoxide.

0022-3263/83/1948-3845$01.50/0

chloride (eq 6), but pyrolysis of this compound also failed to give satisfactory yields of the isocyanate.



$$2CF_3CNHOH + PCl_5 \longrightarrow \mathbf{7} \quad (6)$$

Experimental Section

Warning: Fluoroalkyl dioxazolones prepared in this study are prone to explosive decomposition and should be handled with extreme caution. Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz with $CFCl_3$ as an internal standard. Downfield shifts are reported as positive values.

5-(Trifluoromethyl)-1,3,4-dioxazol-2-one (1a). Phosgene (160 mL, measured at −78 °C, 2.3 mol) was slowly distilled into a solution of 198.7 g (1.54 mol) of trifluoroacetohydroxamic acid in 500 mL of diglyme contained in a 1-L flask equipped with a dry ice cooled condenser. The temperature of the reaction mixture was slowly increased from 25 to 60 °C, and the rate of addition of phosgene was adjusted so that this temperature could be maintained. After the addition, heating was continued until no more HCl was evolved (about 4 h). The volatile portion of the reaction mixture was distilled out under reduced pressure into a cold trap, and the distillate was redistilled in a spinning-band still to give 192.25 g (86;) of **1a**: bp 65–66 °C; ^{19}F NMR ($CDCl_3$) δ −69.3 (s); mass spectrum, mol wt calcd 155, Found m/e 155; IR (liquid) 1887 (C=O), 1640 cm^{-1} (C=N). Anal. Calcd for $C_3F_3NO_3$: C, 23.24, F, 36.76; N, 9.04; Found: C, 23.35; F, 36.80; N, 9.16. **Warning**: This compound will detonate if heated rapidly (10 °C/min) to 227 °C or if contacted with a hot nichrome wire.

5-(Heptafluoropropyl)-1,3,4-dioxazol-2-one (1b). Phosgene (63 mL measured at −78 °C, ca. 0.9 mol) was slowly distilled into a stirred solution of 103.2 g (0.45 mol) of heptafluorobutyrohydroxamic acid in 300 mL of tetraglyme heated to 65–70 °C in a 1-L flask fitted with a dry ice condenser. Heating was continued until no further evolution of HCl was observed. The volatile portion of the reaction mixture was distilled into a cold trap under reduced pressure, and the distillate was redistilled to give 70.68 g (62%) of **2a** as a colorless liquid: bp 101.4–102.8 °C; ^{19}F NMR (CCl_3F) δ −81.0 (t, J = 9 Hz, 3 F), −118.2 (q, J = 9 Hz, 2 F), −127.0 (s, 2 F). Anal. Calcd for $C_5F_7NO_3$: C, 23.55; F, 52.14, N, 5.49. Found: C, 23.56; F, 52.43; N, 5.18.

5-(Perfluoroheptyl)-1,3,4-dioxazol-2-one (1c). Phosgene (13.8 mL, measured at −78 °C, 0.2 mol) was distilled into a stirred solution of 42.9 g (0.1 mol) of perfluorooctanohydroxamic acid in 300 mL of glyme at 25–60 °C. The reaction mixture was heated at reflux for 1.5 h and then distilled to give 29.6 g (65%) of **1c** as a colorless liquid: bp 65 °C (7 mm); IR (liquid) 1895 (C=O), 1630 cm^{-1} (C=N). Anal. Calcd for $C_9F_{15}NO_3$: C, 23.75; F, 62.62; N, 3.08. Found: C, 24.02; F, 62.37; N, 3.00.

Heptafluoropropyl Isocyanate (5b). A 14.36-g (56.3 mmol) sample of **1b** was added over a period of 15 min to a 100-mL flask packed with stainless steel sponge (flash arrestor) and connected to a horizontal $^1/_2$ in. × 16 in. stainless steel tube heated to 285–312 °C. During the addition, the tube and flask were evacuated to 30 mm, and the pyrolysate that passed through the tube was condensed in successive traps cooled with dry ice–acetone and liquid nitrogen. The flask containing the stainless steel sponge was heated periodically to ensure complete volatilization of the dioxazolone. The liquid nitrogen cooled trap contained solid carbon dioxide. The dry ice cooled trap contained a liquid, which was distilled to give 12.45 g (93%) of **5b** as a colorless liquid: bp 25.5–26.0 °C; ^{19}F NMR ($CClF_3$) δ −128.45 (s, 2 F), −81.36 (m, 5 F).

Perfluoroheptyl isocyanate (5c) was prepared by a pyrolysis of **1c** and was obtained as a colorless liquid: bp 121–122 °C; IR (liquid) 2280 cm^{-1}; ^{19}F NMR ($CDCl_3$) δ −80.0 (t, J = 11 Hz, 2 F), −81.6 (t, J = 10 Hz, 3 F), −122.0 (m, 4 F), −122.9 (m, 2 F), −123.7 (m, 2 F), −126.5 (m, 2 F). Anal. Calcd for $C_8F_{15}NO$: C, 23.38; F, 69.33; N, 3.41. Found: C, 23.57; F, 69.01; N, 3.50.

Trifluoromethyl Isocyanate (5a). Dioxazole **1a** was pyrolyzed to **5a** by passing it through an unpacked platinum tube or a stainless steel tube ($^1/_2$ in. × 12 in.) inclined at an angle of 40° and heated to about 400 °C. The pyrolysate was condensed in a cold trap (−78 °C) and then distilled from trap to trap to give trifluoromethyl isocyanate as a colorless liquid: bp 35.5 °C; ^{19}F NMR (CCl_3F) δ −46.6 (br s).

Warning: This pyrolysis should not be repeated under these conditions. In one of these pyrolyses, the remaining dioxazolone (in the dropping funnel) detonated when the addition was about half completed. The reason for the detonation is not known.

5-(Trifluoromethyl)-1,3,2,4-dioxathiazole 2-Oxide (6a). Thionyl chloride (18 g, 0.15 mol) was added dropwise to 19.0 g (0.147 mol) of trifluoroacetohydroxamic acid, and the reaction mixture was heated until evolution of HCl ceased. Distillation gave 14.32 g of **6a** as a colorless liquid: bp 76–77 °C; IR (liquid) 6.10 μm; ^{19}F NMR (CCl_3F) δ −66.4 (s). Anal. Calcd for $C_2F_3NO_3S$: C, 13.72; F, 32.55; N, 8.00; S, 18.31. Found: C, 13.84; F, 33.05; N, 7.71; S, 17.90.

5-(Pentafluoroethyl)-1,3,2,4-dioxathiazole 2-Oxide (6b). Thionyl chloride (23.8 g (0.2 mol) was added dropwise to a 35.8-g (0.2 mol) sample of pentafluoropropionohydroxamic acid. The reaction mixture was warmed gently to reflux, and the liquid reaction product was distilled to give 23.0 g (51%) of **6b** as a colorless liquid: bp 90–91 °C; IR (liquid) 1634 cm^{-1}; ^{19}F NMR (CCl_3F) δ 83.8 (q, J = 2 Hz, 3 F), −120.1 (t, J = 2 Hz, 2 F). Anal. Calcd for $C_3F_5NO_3S$: C, 16.01; F, 42.20; N, 6.22. Found: C, 16.24; F, 42.13, N, 6.28. A sample of dioxadiazole oxide hydrolyzed rapidly back to the hydroxamic acid when a few drops of water were added to a sample.

Pyrolysis of 6b. A 10-g (0.044 mol) sample of **6b** was added dropwise through a $^1/_2$-in. platinum tube inclined at an angle of 30° and heated to 400 °C over a length of 12 in. at a rate of 1 drop/s. The exhaust gases were condensed in a trap cooled by dry ice to give 6.5 mL of liquid. Analysis by ^{19}F NMR, IR, and GC indicated that three fluorine-containing products were formed: pentafluoropropionitrile (45% yield), pentafluoroethyl isocyanate (21% yield), and trifluoroacetyl fluoride (19% yield).

5-(Heptafluoropropyl)-1,3,2,4-dioxathiazole 2-Oxide (6c). Thionyl chloride (30 g, 0.25 mol) was added dropwise to 57.3 g (0.25 mol) of heptafluorobutyrohydroxamic acid, and the reaction mixture was warmed to 50 °C. An additional 15 g (0.125 mol) of thionyl chloride was added. When the evolution of HCl ceased, the reaction mixture was distilled to give 40.26 g (59%) of **6c** as a colorless liquid: bp 109–110 °C; n^{25}_D 1.3330; IR (liquid) 1620 cm^{-1}; ^{19}F NMR (CCl_3F) δ −80.9 (t, J = 9 Hz, 3 F), −114.1 (m, 2 F), −126.6 (m, 2 F). Anal. Calcd for $C_4F_7NO_3S$: C, 17.46; F, 48.34; N, 5.09; S, 11.66. Found: C, 17.25; F, 48.02; N, 4.92; S, 11.30.

5-Chloro-3,8-bis(trifluoromethyl)-1,4,6,9-tetraoxa-2,7-diaza-5-phosphaspiro[4.4]nona-2,7-diene (7). A mixture of 40.0 g (0.31 mol) of trifluoroacetohydroxamic acid and 40.0 g (0.19 mol) of phosphorous pentachloride was heated in a simple still until the contents liquified and then distilled. Redistillation through a spinning-band still gave 26.85 g (50%) of **7** as a colorless liquid (bp 143 °C) that solidified on cooling: mp 27 °C; ^{19}F NMR (CCl_3F) δ −71.6 (d, J = 2.4 Hz); IR (liquid) 1634 cm^{-1} (C=N). Anal. Calcd for $C_4ClF_6N_2O_4P$: C, 14.99; F, 35.57; N, 8.74; P, 9.67. Found: C, 14.76; F, 35.01; N, 8.75; P, 9.68.

Perfluorooctanohydroxamic acid was prepared by adding 200 g (0.45 mol) of ethyl perfluorooctanote dropwise to a solution of hydroxylamine in methanol [prepared by dissolving 24.45 g (0.45 mol) of sodium methoxide and then 31.45 g (0.45 mol) of hydroxylamine hydrochloride in 300 mL of methanol and then filtering off the precipitated sodium chloride]. The resulting solution was stirred overnight and then evaporated to dryness to give 168.28 g (87% yield) of the hydroxamic acid as a colorless solid. A sample was recrystallized from acetonitrile: mp 115–116 °C; IR (KBr) 1690 cm^{-1} (C=O); ^{19}F NMR (CD_3CN) δ −81.2 (m, 3 F), −119.1 (m, 2 F), −122.2 (m, 8 F), −126.3 (m, 2 F). Anal. Cald for $C_8H_2F_{15}NO_2$: C, 22.39; H, 0.47. Found: C, 22.61; H, 0.63.

Heptafluorobutyrohydroxamic acid was prepared in a similar manner from ethyl heptafluorobutyrate and hydroxylamine. Recrystallization from benzene gave colorless crystals: mp 89–92 °C; IR (KBr) 1686 cm^{-1}; ^{19}F NMR (Me_2SO-d_6) δ −80.4 (q, 3 F), −119.8 (t, 2 F), −126.8 (s, 2 F). Anal. Calcd for $C_4H_2F_7NO_2$: C, 20.97; H, 0.88; F, 58.06; N, 6.12. Found: C, 21.09; H, 0.68; F, 57.84; N, 5.97.

Pentafluoropropionohydroxamic acid was prepared in a similar manner from ethyl pentafluoropropionate and hydrox-

ylamine. Recrystallization from benzene gave colorless crystals: mp 65–69 °C; IR (KBr) 1692 cm^{-1}; ^{19}F NMR (ether) δ −83.9 (q, 3 F), −124.0 (t, 2 F). Anal. Calcd for $C_3H_2F_5NO_2$: C, 20.12; H, 1.13; F, 53.05; N, 7.82. Found: C, 19.91; H, 1.11; F, 52.87; N, 7.71.

Trifluoroacetohydroxamic acid[3] was prepared in a similar manner from ethyl trifluoroacetate and hydroxylamine. Recrystallization from methylene chloride gave colorless plates: mp 49–51 °C; ^{19}F NMR (ether) δ −75.2 (s). Anal. Calcd for $C_2H_2F_3NO_2$: C, 18.61; H, 1.56; F, 44.14; N, 10.86; Found: C, 19.13; H, 1.62; F, 43.51; N, 10.58.

Methoxycarbonyl 2,2,3,3,4,4,4-Heptafluoro-*N*-hydroxybutanimidate (3). Methanol (18 mL, 0.43 mol) was added dropwise to 54.5 g (0.21 mol) of **1b** cooled in a water bath to keep the temperature below 40 °C. The reaction mixture was evaporated to dryness under reduced pressure, and the resulting solid was collected on a filter and washed with hexane to give 51.13 g (85%) of **3** as colorless crystals: mp 42–43 °C; ^{19}F NMR ($CDCl_3$) δ −82.2 (t, J = 9 Hz, 3 F), −121.4 (m, 2 F), −127.5 (m, 2 F); ^1H NMR ($CDCl_3$) δ 3.96 (s, 3 H), 9.8 (NOH). Anal. Calcd for $C_6H_4F_7NO_4$: C, 25.10; H, 1.40; F, 46.33; N, 4.88; Found: C, 25.24; H, 1.48; F, 46.46; N, 4.98.

Registry No. **1a**, 87050-94-0; **1b**, 87050-95-1; **1c**, 87050-97-3; **2** (R_f = CF_3), 1514-45-0; **2** (R_f = $CF_3(CF_2)_2$), 87050-96-2; **2** (R_f = $CF_3(CF_2)_6$), 15435-88-8; **2** (R_f = CF_3CF_2), 87051-00-1; **3**, 87051-03-4; **5a**, 460-49-1; **5b**, 424-62-4; **5c**, 335-91-1; **6a**, 87050-98-4; **6b**, 87050-99-5; **6c**, 87051-01-2; **7**, 87051-02-3; $COCl_2$, 75-44-5; $SOCl_2$, 7719-09-7; CF_3CF_2CN, 422-04-8; CF_3CF_2NCO, 356-74-1; CF_3COCl, 354-34-7; PCl_5, 10026-13-8; $CF_3(CF_2)_6CO_2Et$, 3108-24-5; $CF_3(CF_2)_2CO_2Et$, 356-27-4; $CF_3CF_2CO_2Et$, 426-65-3; CF_3CO_2Et, 383-63-1.

(3) Knunyants, I. L.; Sokol'skii, G. A. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 602.

Photochemistry of Benzyl Sulfite

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Received March 8, 1983

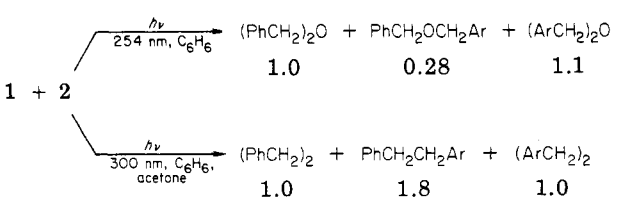
Photoextrusion reactions have been the subject of considerable recent attention. In addition to posing interesting mechanistic questions, photoextrusions are occasionally of preparative value.[1] A functional group that offers the potential for such reactions is the sulfite ester (e.g., benzyl sulfite (**1**)). Examination of the photochemical literature

$$PhCH_2OS(O)OCH_2Ph$$
1

reveals little information regarding sulfite photochemistry. Kobayashi et al. suggested that the photochemical fragmentation of *n*-butyl sulfite occurred via homolysis of the S–O bond.[2] A low-temperature ESR study of several acylic sulfites including **1** reported by Gilbert et al. appears to confirm this suggestion.[3] The photochemistry of cyclic sulfite esters of some 1,2-diols has also been examined, and pathways involving photoextrusion of both SO_2 and SO_3 have been observed.[4,5] To date, however, no systematic study of the products and mechanism of the photolysis of benzyl sulfite has been reported. We describe here the results of such a study.

(1) For a recent review of photoextrusion reactions, see: Givens, R. S. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 227 ff.
(2) Kobayashi, M.; Minato, H.; Miyaji, Y.; Yoshioka, T.; Tanaka, K.; Honda, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2817.
(3) Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *J. Chem. Res., Synop.* **1977**, 173.
(4) Griffin, G. W.; Manmade, A. *J. Org. Chem.* **1972**, *37*, 2589.
(5) Olsen, R. J.; Butler, F. M. *J. Chem. Res., Synop.* **1982**, 175.

Scheme I



Ar = 3-methylphenyl

Results and Discussion

The UV spectrum of **1** is nearly identical with that of benzyl alcohol, indicating that the benzyl groups are acting as the chromophore. In contrast, aliphatic sulfites are essentially transparent in the near UV[6] region.

The photochemistry of **1** was examined in a variety of aprotic solvents (acetonitrile, benzene, cyclohexane, dioxane, and ethyl acetate). Both direct irradiations (0.095 M, 254 nm) and acetone–sensitized irradiations (0.095 M, 4.5 M acetone, 300 nm) were performed. Results were similar in all solvents, and the outcome in benzene is reported in Table I.

Direct irradiation resulted in the efficient decomposition of **1**; the quantum yield for the disappearance of **1** in cyclohexane was found to be 0.39 ± 0.04 by using potassium ferrioxalate actinometry. Photolysis produced benzyl alcohol, benzyl ether, and the rearrangement product, benzyl phenylmethanesulfonate along with trace amounts of bibenzyl, toluene, and benzaldehyde. Isolation of the rearranged product indicates that at least part of the photochemistry proceeds via C–O bond cleavage and was unexpected on the basis of Kobayashi's work with benzyl *p*-toluenesulfinate.[2] When the reaction was sensitized with acetone, the yield of sulfonate decreased, only a trace of benzyl ether was produced, and bibenzyl emerged as a major product. Of the photoproducts that were observed, only the rearranged product was photolabile, some photodecomposition being observed after prolonged irradiation (>80% conversion of **1**).

A point of interest bearing on the mechanism of the reaction is the magnitude of the solvent-cage effects in the recombination reactions that produce the benzyl ether and bibenzyl. For examination of this, equimolar mixtures of benzyl sulfite and 3-methylbenzyl sulfite (**2**) were irradiated under conditions identical with those above. The benzyl ethers in the direct irradiation and bibenzyls in the sensitized irradiation were separated from the other products by columm chromatography, and the product ratios were determined by NMR spectroscopy. The results are shown in Scheme I. The formation of only a minor amount of unsymmetrical ether in the direct irradiation indicates a large cage effect (ca. 85%) in the ether-forming reaction. The nearly statistical distribution of bibenzyls obtained in the sensitized reaction is consistent with recombination after escape from the solvent cage and argues against the extrusion of SO_3.

A final point that must be considered is the high yield of benzyl alcohol obtained under both direct and sensitized irradiation conditions. A similar results was reported by Kobayashi in the direct irradiation of *n*-butyl sulfite.[2] A possible route to benzyl alcohol involves cleavage of the S–O bond followed by extrusion of SO. Hydrogen abstraction by the resulting benzyloxy radicals could produce benzyl alcohol. Precedent for a sulfinyl photoextrusion

(6) "Atlas of Spectral Data and Physical Constants for Organic Compounds", 2nd Ed.; Grasselli, J. G., Ritchey, W. M., Eds.; CRC Press, Cleveland, **1975**; Vol. IV, p 575.

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