8,8-Dimethyl-7-(mercaptomethyl)-5-thia-1-azabicyclo-[4.3.0]-6-nonen-9-one (3d): 64% yield; mp 82–84 °C; IR 1680 cm^{-1}; ^1H NMR δ 1.24 (s, 6 H, 8-CH_3), 1.78 (t, J = 6.9 Hz, 1 H, D_2O exchangeable, SH), 2.1–2.2 (m, 2 H, 3-CH_2), 2.9–3.0 (m, 2 H, 4-CH_2), 3.34 (d, J = 6.9 Hz, 2 H, CH_2SH), and 3.5–3.6 (m, 2 H, 2-CH_2); ^{13}C NMR δ 18.3 (t, 7-CH_2SH), 22.8 (q, 8-Me), 24.0 (t, 3-C), 24.6 (t, 4-C), 39.4 (t, 2-C), 47.4 (s, 8-C), 118.6 (s, 7-C), 126.9 (s, 6-C), 181.8 (s, C=O). Anal. Calcd for $C_{10}H_{15}NOS_2$: C, 52.36; H, 6.59; N, 6.10. Found: C, 52.15; H, 6.53; N, 6.06.

2-(5',5'-Dimethyl-4'-oxo-3'-thiolanyl)-2-oxazine (2e): 77% yield; mp 77–79 °C; IR 1660 and 1685 cm^{-1}; ^1H NMR δ 1.04 (s, 3 H, 5'-Me), 1.29 (s, 3 H, 5'-Me), 1.8–1.9 (m, 2 H, 5-CH_2), 2.84 (dd, J = 10.8 and 6.6 Hz, 1 H, 1'-CH), 3.18 (dd, J = 11.7 and 6.6 Hz, 1 H, 2'-CH), 3.4–3.5 (m, 2 H, 6-CH_2), 3.55 (dd, J = 11.7 and 10.8 Hz, 2'-CH) and 4.1–4.2 (m, 2 H, 4-CH_2); ^{13}C NMR δ 19.6 (q, 5'-Me), 21.9 (t, 5-C), 24.4 (q, 5'-Me), 29.5 (t, 2'-C), 42.2 (t, 6-C), 51.4 (s, 5'-C), 53.8 (d, 1'-C), 65.0 (t, 4-C), 157.4 (s, C=N), and 211.7 (s, C=O). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.08; N, 6.56. Found: C, 56.25; H, 7.06; N, 6.55.

Registry No. **1a**, 141249-21-0; **1b**, 141249-22-1; **1c**, 125880-12-8; **1d**, 141249-23-2; **1e**, 141249-24-3; **2a**, 141249-25-4; **2b**, 141249-26-5; **2c**, 141249-27-6; **2e**, 141249-28-7; **3d**, 141249-29-8; 2,2-dimethylbutenoyl chloride, 57690-96-7; thiazolidine-2-thione, 96-53-7; oxazolidine-2-thione, 5840-81-3; pyrrolidine-2-thione, 2295-35-4; tetrahydro-1,3-thiazine-2-thione, 5554-48-3; tetrahydro-1,3-oxazine-2-thione, 17374-18-4.

Sulfonation of Aromatic Compounds in HSO_3F–SbF_5

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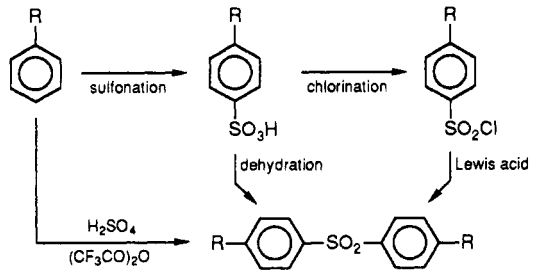
Sulfonyl compounds are useful raw materials for engineering plastics which are clear and thermostable. The synthesis of diaryl sulfones and disulfonyl compounds has been extensively studied and reviewed.[1,2] Generally, diaryl sulfones have been prepared from aromatic compounds by two- or three-step reactions via aryl sulfonic acids or sulfonyl chlorides.



The main synthetic methods for preparing diaryl sulfones have been Friedel–Crafts sulfonylations between arylsulfonyl halides and aromatic compounds in the presence of a suitable Lewis acid.[1] Other synthetic methods are the condensation of arylsulfonic acids with aromatic compounds using dehydration reagents[3] such as H_3PO_4 and P_2O_5. A one-pot synthesis of diaryl sulfones from aromatic compounds using H_2SO_4 and $(CF_3CO)_2O$ has been reported.[4]

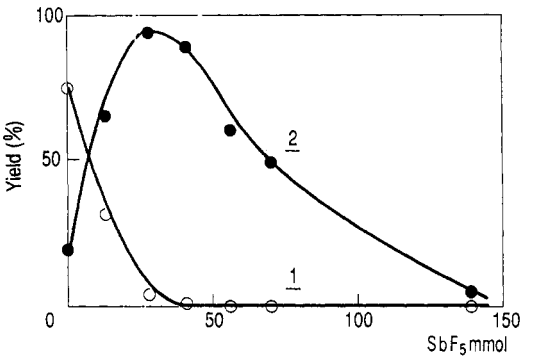
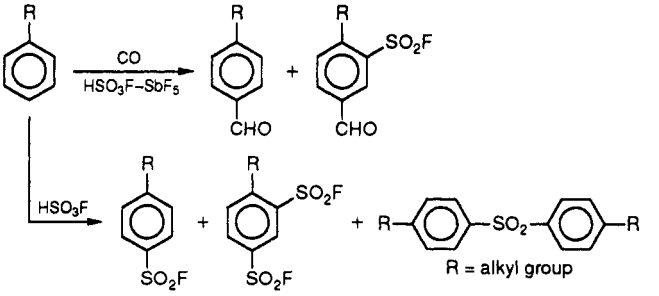


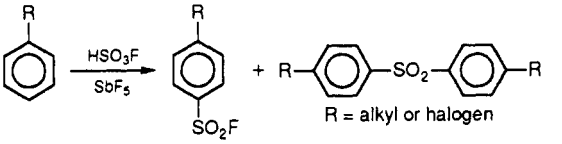
Figure 1. Influence of HSO_3F–SbF_5 Compositions. Sulfonation was carried out using 174 mmol of HSO_3F and 20 mmol of benzene at 50 °C for 1 h: (1) benzenesulfonyl fluoride; (2) diphenyl sulfone.

In our previous work on the formylation of alkylbenzenes with CO in HSO_3F–SbF_5, unexpected products, namely bis(alkylphenyl) sulfones and alkylbenzenedisulfonyl fluorides, were formed in a one-pot reaction as follows:[5]



Therefore, we focused on a convenient synthesis of diaryl sulfones and disulfonyl compounds in HSO_3F–SbF_5 and wish to report herein the results of these studies.

Aromatic compounds reacted with HSO_3F[6] in the presence of a suitable amount of SbF_5 to give arylsulfonyl fluorides and diaryl sulfones as the main products at 0–50 °C:



The results of application of this reaction to a variety of aromatic compounds are summarized in Table I. Diaryl sulfones were obtained in high yield from benzene, toluene, xylenes, 1,2,4-trimethylbenzene, and fluoro-, chloro-, and bromobenzene by a one-pot reaction when an excess amount of SbF_5 relative to the substrate was added to HSO_3F. The appropriate amount of SbF_5 depended on the reactivity of the aromatic compounds for the electrophilic substitution, and the required amount of SbF_5 decreased with increasing reactivity of the aromatic compounds. In the case of polyalkylbenzenes such as 1,3,5- and 1,2,3-trimethylbenzene and tetramethylbenzenes, attempts to obtain diaryl sulfones with good yield were unsuccessful, and arylsulfonyl fluorides were formed as the main products. Although the sulfonyl group was mainly

(1) Olah, G. A. *Friedel-Crafts and Related Reaction*; Wiley-Interscience: New York, 1964; Vol. III, p 1319.
(2) See ref 1, p 1355.
(3) (a) Graybill, B. M. *J. Org. Chem.* **1967**, *32*, 2931. (b) Sipe, H. J., Jr.; Clary, D. W.; White, S. B. *J. Chem. Soc., Chem. Commun.* **1984**, 283. (c) Ueda, M.; Uchiyama, K.; Kano, T. *J. Chem. Soc., Chem. Commun.* **1984**, 323. (d) Tedder, J. M. *Chem. Rev.* **1955**, *55*, 787. (e) Field, L. *J. Am. Chem. Soc.* **1952**, *74*, 394.
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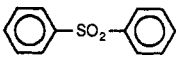
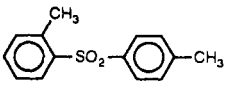
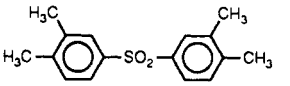
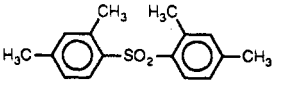
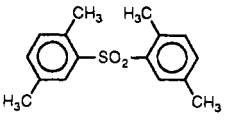
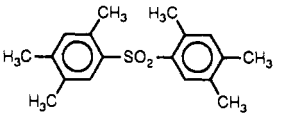
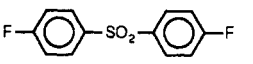
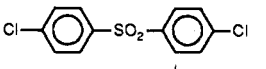
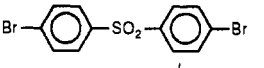
Table I. Synthesis of Diaryl Sulfones[a]

substrate	temp/°C	SbF_5/mmol	products, yield/%	
			sulfonyl fluoride	diaryl sulfone
benzene	50	27.6	4	 94
toluene	0	27.6	1 (100:0:0)[b]	 95 (30:58:4:5:3)[c]
o-xylene	0	27.6	3 (64:16:20)[d]	 92 (53:45:2)[e]
m-xylene	0	27.6	4 (87:13)[f]	 83 (75:25:0)[g]
p-xylene	25	27.6	2 (100:0)[h]	 83 (93:5:2)[i]
1,2,4-trimethylbenzene	0	20.7	20 (55:23:22)[j]	 71 (67:24:9)[k]
fluorobenzene	50	69.0	0	 83 (80:17:3)[l]
chlorobenzene	50	69.0	0	 94 (66:27:7)[l]
bromobenzene	50	69.0	3 (100:0)[m]	 63 (67:22:11)[l]

[a] Sulfonation was carried out using 174 mmol of HSO_3F and 20 mmol of aromatic compounds for 1 h. The structures of the main diaryl sulfone were depicted. [b] Isomer ratio of 4-toluenesulfonyl fluoride–3-toluenesulfonyl fluoride–2-toluenesulfonyl fluoride. [c] Isomer ratio of bis(4-methylphenyl) sulfone–2-methylphenyl 4′-methylphenyl sulfone–bis(2-methylphenyl) sulfone–3-methylphenyl 4′-methylphenyl sulfone–2-methylphenyl 3′-methylphenyl sulfone. [d] Isomer ratio of 3,4-dimethylbenzenesulfonyl fluoride–2,3-dimethylbenzenesulfonyl fluoride–2,4-dimethylbenzenesulfonyl fluoride. [e] Isomer ratio of bis(3,4-dimethylphenyl) sulfone–2,3-dimethylphenyl 3′,4′-dimethylphenyl sulfone–bis(2,3-dimethylphenyl) sulfone. [f] Isomer ratio of 2,4-dimethylbenzenesulfonyl fluoride–2,6-dimethylbenzenesulfonyl fluoride. [g] Isomer ratio of bis(2,4-dimethylphenyl) sulfone–2,4-dimethylphenyl 2′,6-dimethylphenyl sulfone–bis(2,6-dimethylphenyl) sulfone. [h] Isomer ratio of 2,5-dimethylbenzenesulfonyl fluoride–2,4–dimethylbenzenesulfonyl fluoride. [i] Isomer ratio of bis(2,5-dimethylphenyl) sulfone–2,4-dimethylphenyl 2′,5′-dimethylphenyl sulfone–bis(2,4-dimethylphenyl) sulfone. [j] Isomer ratio of 2,4,5-trimethylbenzenesulfonyl fluoride–2,3,6-trimethylbenzenesulfonyl fluoride–2,3,5-trimethylbenzenesulfonyl fluoride. [k] Isomer ratio of bis(2,4,5-trimethylphenyl) sulfone–2,3,6-trimethylphenyl 2′,4′,5′-trimethylphenyl sulfone–2,3,5-trimethylphenyl 2′,4′,5′-trimethylphenyl sulfone. [l] Isomer ratio of bis(4-halophenyl) sulfone–2-halophenyl 4′-halophenyl sulfone–bis(2-halophenyl)sulfone. [m] Isomer ratio of 4-bromobenzenesulfonyl fluoride–2-bromobenzenesulfonyl fluoride.

introduced to the para position of the substituent, the selectivity was not high. The 1,2-shift of the methyl group occurred in *o*- and *p*-xylene during sulfonation to give *m*-xylene derivatives. This behavior has also been observed in Friedel–Crafts alkylations, and the migration of the methyl group was interpreted to be caused by the formation of the arenium ion, σ-complex, in strong acid.[7]

Sulfonation of benzene was carried out in various compositions of HSO_3F–SbF_5. The results are shown in Figure 1. The yield of benzenesulfonyl fluoride decreased with increasing amounts of SbF_5. On the other hand, diphenyl sulfone was obtained in the highest yield when the molar ratio of SbF_5/benzene was 1:1.5. Diphenyl sulfone was also obtained in the absence of SbF_5, and this result showed that the reaction path to diphenyl sulfone was not only the Friedel–Crafts sulfonylation. Furthermore, the formation of benzenesulfonic acid was confirmed in the HSO_3F–SbF_3 system. Consequently, benzenesulfonyl fluoride and diphenyl sulfone are secondary products, and the initial product is benzenesulfonic acid, a similar situation to sulfonation using HSO_3Cl.[8] Therefore, the re-

(7) (a) Marvell, E. N.; Graybill, B. M. *J. Org. Chem.* **1965**, *30*, 4014. (b) Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 1103.

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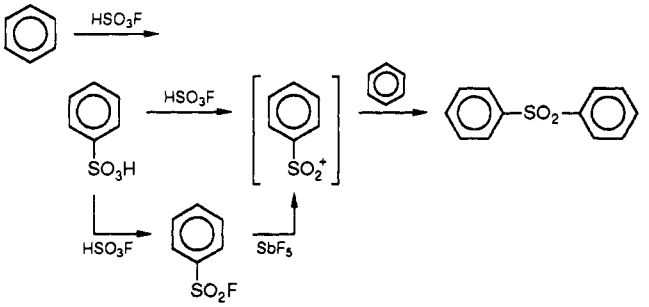
action path of diphenylsulfone can be represented as follows:



Furthermore, we found out that HSO_3F became an extremely strong sulfonation reagent by the addition of SbF_5 in disulfonyl compounds synthesis from arylsulfonyl fluorides and diaryl sulfones.[9]

In summary, the HSO_3F–SbF_5 system was useful for a one-pot synthesis of diaryl sulfones and disulfonation of aromatic compounds under mild conditions.

Experimental Section

All aromatic starting materials, HSO_3F (Moritakagaku), and SbF_5 (Aldrich) were of highest available purity and were used without further purification. A Yanagimoto G-3800 and G-6800 gas chromatography equipped with an on-line automatic integrator was used for GC analysis. A 25-m capillary column (OV-1701) and a 1.5-m packed column (FFAP) were used for isomer separation, whereas a 1.5-m packed column (OV-17) was utilized for yield determination. MS analysis (GC–MS) was performed on a Hitachi M-2000 fitted with a 50-m capillary column (OV-1701). ^{1}H-NMR spectra were recorded on a Hitachi R-24B, and ^{13}C-NMR spectra were recorded on a Nihondenshi FX-200. Infrared analysis was accomplished on a Nihonbunko IRA-1.

Sulfonation Procedures. The required amount of HSO_3F and SbF_5 were added into a 300-mL three-necked flask under temperature control, and then aromatic compounds were added with vigorous stirring into the mixture of HSO_3F and SbF_5. After the reaction was over, the reaction mixture was quenched in ice–water and extracted by benzene. Products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectroscopy and elemental analysis, and the yields of them were determined by GC using internal standards. Products isolation was carried out by vacuum distillation or recrystallization in acetone–*n*-hexane system.

Supplementary Material Available: Spectral data for diaryl sulfones and disulfonyl compounds and the results of disulfonyl compound synthesis experiments (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(9) Refer to supplementary material.

A Preparation of Unsymmetrical α-Diketones

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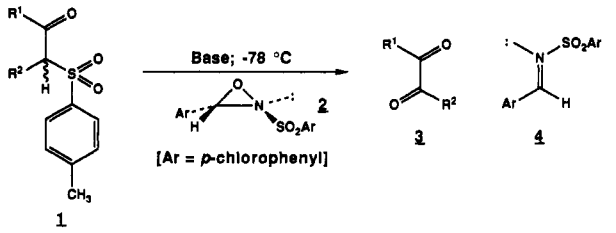
An efficient preparation of unsymmetrical α-diketones has long been of interest,[1] and several important methods have been developed.[2,3] We have sought to uncover a general and convergent strategy which would provide formation of the central carbon bond between two unsymmetrical carbonyl segments. Such a scheme would provide an efficient pathway for ongoing studies in the construction of highly oxygenated spiro ketal natural products.[4,5] In the course of our investigations, it became clear that the numerous routes for preparation of α-sulfonyl ketones, as well as the stable nature of these substances, would make them ideal starting materials. Furthermore, the direct oxidative desulfonation of alkyl, allylic, and benzylic sulfones was recently reported.[6] Herein, we wish to report a convenient procedure which allows conversion of readily available α-sulfonyl ketones **1** to the corresponding α-diketones **3** through a mild oxidative desulfonylation utilizing 2-[(*p*-chlorophenyl)sulfonyl]-3-(*p*-chlorophenyl)oxaziridine (**2**).



Pioneering efforts of Franklin Davis have documented the utility of *N*-sulfonyloxaziridines as a new family of oxidants.[7] These reagents have been used for epoxidations of alkenes,[8] heteroatom (S, Se, N) oxidations,[9] and the synthesis of alcohols and phenols from organometallic intermediates.[10] More recently this methodology has been developed as a practical route for the direct oxidation of ketone, ester, and amide enolates.[11] Furthermore, the

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