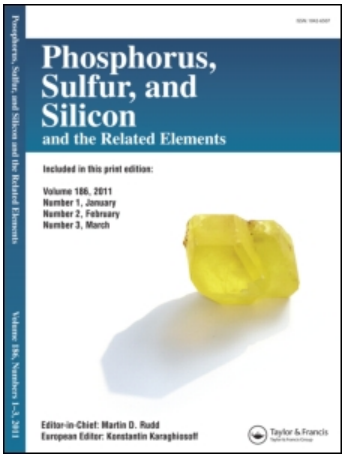

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THE SYNTHESIS, SOLVOLYSIS AND REARRANGEMENT OF BENZYL TRIFLUOROMETHANESULFINATES

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THE SYNTHESIS, SOLVOLYSIS AND REARRANGEMENT OF BENZYL TRIFLUOROMETHANESULFINATES

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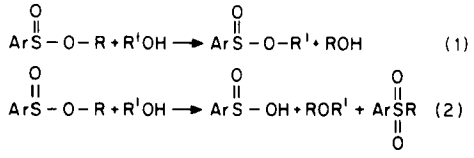
The synthesis and reactivity of benzyl trifluoromethanesulfinates have been investigated. These esters are easily and almost quantitatively obtained by selective oxidation of the corresponding sulfenates. A study of their behavior has revealed some unique features. In sharp contrast to benzyl arenesulfinates, which undergo ethanolysis with complete sulfur–oxygen bond fission, the corresponding trifluoromethanesulfinates undergo ethanolysis with exclusive carbon-oxygen bond fission, and with a rate enhancement by a factor of 6 powers of ten. The unusual high reactivity of these esters, comparable to that of the corresponding tosylates, is discussed. A kinetic study of the solvent and substituent effects on the rate of solvolysis has been performed. Also in contrast with benzyl arenesulfinates, these esters undergo facile rearrangement to sulfone on heating in polar nonhydroxylic solvents such as acetonitrile, in high yields. The mechanisms of solvolysis and rearrangement are discussed.

Key words: Benzyl trifluoromethanesulfinates; highly reactive sulfinates; synthesis; solvolysis; rearrangement; solvent and substituent effects.

INTRODUCTION

The synthesis and reactivity of esters of arenesulfinic acids[1] have received considerable attention in the past. The rearrangement and solvolysis of such esters have been of particular mechanistic interest, and the former subject has been recently reviewed.[2] The solvolysis of arenesulfinates can involve either sulfur–oxygen or carbon–oxygen bond fission. An unequivocal indication for S—O bond cleavage in the alcoholysis of sulfinate esters is the production of the parent alcohol and a new sulfinate ester, the latter corresponding to the alcohol used as solvent (Equation 1). On the other hand, if C—O bond fission occurred under the same conditions the product would be sulfinic acid, ether and/or sulfone (Equation 2). For example, Kenyon and coworkers[3] have found that ethyl



(1)

(2)

p-toluenesulfinate yields only *d*-2-octyl *p*-toluenesulfinate when heated with *d*-2-octanol and that on refluxing a solution of (−)-α-phenylethyl *dl*-*p*-toluenesulfinate in ethanol with added potassium acetate or carbonate, α-phenylethanol of retained configuration is formed. These results are clear evidence for S—O bond fission. More recently, Herbrandson and Cusano[4] have

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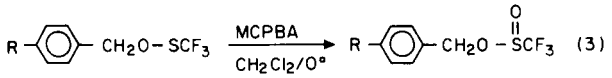
also observed S—O bond fission in the ethoxide-ion catalyzed ethanolysis of epimeric (−)-menthyl *p*-iodobenzenesulfinates. Bunton and Hendy[5] determined the position of bond fission in the hydrolyses of methyl and benzhydryl *p*-toluenesulfinates in aqueous dioxan by the use of H_2O^{18} enriched solvent. The base-catalyzed reaction of both esters, as well as the acid-catalyzed hydrolysis of the first ester, have thus been shown to involve S—O bond fission. In a subsequent and elegant study, using optically active methyl *p*-toluenesulfinate containing ^{14}C in the methoxy group, Mikolajczyk and coworkers[5b] obtained convincing kinetic evidence for complete inversion of configuration at sulfinyl sulfur in acid-catalyzed transesterification of sulfinates. The same type of cleavage has also been reported by Darwish and Noreyko[6] for the solvolysis of various *p*-methoxyneophyl arenesulfinates in aqueous and absolute ethanol in the presence of such bases as ethoxide ion, potassium acetate and 2,6-lutidine. On the other hand, exclusive carbon-oxygen bond fission by an ionization mechanism has been reported for the solvolysis of esters likely to develop stable carbonium ions such as *t*-butyl, *α*-phenylethyl, benzhydryl[7] and *p*-methoxybenzyl (*p*-anisyl)[8] arenesulfinates under conditions appropriate for the competing rearrangement to sulfone.

In recent years, considerable attention has been focused on the high reactivity of trifluoromethanesulfonates (triflates) in various substitution reactions. It is well known[9] that under solvolytic conditions these esters are more reactive than the corresponding tosylates or halides by a factor of 10^5–10^7. The triflate anion has therefore been considered as the most effective leaving group.[10] In accord with this observation, alkyl triflates have been reported as the most powerful alkylating agents of their type,[11] while vinyl triflates have been of immense value in the generation and study of the unstable vinylic cations[12] as well as in the generation of vinylidene carbenes.[13]

In view of the significant role played by triflates in mechanistic studies, and as a consequence of our interest in the chemistry of sulfinates in general[1a,2,14] and trihalomethanesulfinates in particular,[15] we have undertaken an investigation on the syntheses and reactivity of trifluoromethanesulfinates (triflinates).[16] A detailed report of our results is presented below.

RESULTS AND DISCUSSION

Although the preparation of several simple alkyl triflinates had been previously described in the literature[17] it involved the use of the unstable gas CF_3SOF, which is not easily accessible. Fortunately, we have found that these esters can also be prepared by the method used for the preparation of the corresponding chloro analogues.[15] We have thus synthesized benzyl, *p*-chloro, and *p*-methylbenzyl triflinates by a very convenient method, oxidation of the appropriate sulfenate ester[18] with *m*-chloroperbenzoic acid in methylene chloride at 0°C (Equation 3).



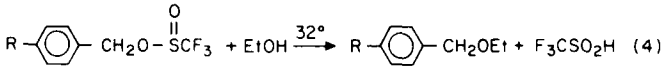
(3)

R = H, Me, Cl

All the esters prepared were obtained in almost quantitative yield. It is interesting to note that further oxidation of the sulfinate to the sulfonate does not take place even in the presence of an excess of oxidizing agent at room temperature. This contrasts with the observation that arenesulfinates are easily oxidized to sulfonates at 0°, a reaction used for the preparation of highly active arenesulfonates,[19] as well as with reports that benzyl trifluoro[20] and trichloromethyl[21] sulfides can be oxidized to the corresponding sulfones. It is also of interest that the *p*-methoxybenzyl (*p*-anisyl) triflinate could not be obtained by this method. Rearrangement to the corresponding sulfone took place under the normal reaction conditions. These observations are analogous to those reported for the trichloromethanesulfinates.[15]

Following our initial report,[16] Hendrickson and Skipper[22] reported a general procedure for the preparation of triflinates involving *in situ* generation of trifluoromethanesulfinyl chloride (CF_3SOCl) by reaction of potassium triflinate (CF_3SO_2K) with mesitylenesulfonyl chloride, followed by addition of the alcohol in acetonitrile at 0° in the presence of pyridine. Although this procedure also affords triflinate esters in good to excellent yields, it is much more expensive and also requires the preparation of the hygroscopic potassium triflinate by elimination of $CFSO_2^-$ from N-phenacylphenyltriflamide. On the other hand, our procedure uses cheap and readily available materials. The required sulfenate esters[18] are prepared by treatment of the alcohol with commercially available or readily accessible[23] CF_3SCl.

In order to test the reactivity of triflinates, we have first investigated their behaviour under solvolytic conditions. We have found that all benzyl triflinates prepared undergo facile ethanolysis with exclusive C—O bond fission as evidenced by formation of the corresponding ethyl ether and sulfinic acid (Equation 4).



(4)

In sharp contrast with these results, benzyl 2,6-dimethylbenzenesulfinate has been reported[14a] to undergo ethanolysis by complete S—O bond cleavage and at a much slower rate even at 90° ($k = 2 \times 10^{-7}\ sec^{-1}$). A comparison between the rate of this ester with that of the corresponding triflinate (see Table I), taking into account the difference in bond cleavage and temperature, indicates that the reactivity of the triflinate is higher by some 6 powers of ten. This factor is similar to that found for the triflate/tosylate ratio.[9] Furthermore, the reactivity of benzyl triflinates, somewhat surpassed by the analogous trichloromethanesulfinates is of the same order of magnitude as that of the corresponding tosylates,[24] as can be seen from the data shown in Table I.

The unusual high reactivity of the triflinates may be attributed to the high acid strength of CF_3SO_2H ($pKa = -0.6$)[25] compared to $ArSO_2H$ ($pKa = 2.76$),[1e] and the consequent high leaving group ability of the triflinate anion. On the other hand, the lack of rearrangement to sulfone during solvolysis, as normally observed with arenesulfinates, may reflect the reduced nucleophilicity of the sulfur atom in this case. The same explanation may also be advanced for the lack of triflinate to triflate oxidation.

TABLE I

Rate constants for the solvolysis of benzyl trifluoromethanesulfinates[a]

Trifluoromethane sulfinate	Solvent	[Ester]	[2,6-Lutidine]	$k \times 10^5$ m, sec^{-1}
Benzyl	EtOH	0.0101	0.0400	1.04 ± 0.03
	MeOH	0.0100	0.0400	3.21 ± 0.05
	80%EtOH—H_2O	0.0100	0.0400	4.31 ± 0.06
p-Chlorobenzyl	EtOH	0.0100	0.0400	0.92 ± 0.01
	MeOH	0.0103	0.0409	1.84 ± 0.02
	80%EtOH—H_2O	0.0100	0.0400	2.67 ± 0.02
p-Methylbenzyl	EtOH	0.0198	0.0400	6.90 ± 0.17
		0.0191	0.0751	6.56 ± 0.13
	MeOH	0.0200	0.0800	23.71 ± 0.90
	80%EtOH—H_2O	0.0197	0.0800	88.19 ± 2.96
Benzyl Tosylate[b]	EtOH	0.0200		5.33 ± 0.25
	MeOH	0.1200		16.70 ± 0.40
	80%EtOH	0.0500		32.40 ± 3.00

[a] Measured titrimetrically.
[b] At 25°. Data taken from Reference 24.

Further evidence for the mechanism of solvolysis was obtained from a kinetic study of the reaction. A summary of first-order rate constants for the solvolysis of benzyl triflinates in various solvents is presented in Table I. In order to analyze the kinetic results with respect to the substituent and solvent effects, we have examined the Hammett and Winstein correlations. The rates of solvolysis in methanol and 80% ethanol–water correlate quite well with σ. Although the size of $\rho = -2.69$ for the first solvent is smaller than usually observed with ionizing systems, it compares favourably with the value recorded for the solvolysis of other benzylic systems, such as chlorides and sulfonates.[26] On the other hand, the size of $\rho = -3.76$, obtained for 80% ethanol is suggestive of an ionization mechanism.

Good linear correlations were found when $\log k$ for solvolysis of *p*-chloro- and *p*-methylbenzyl triflinates, using the solvents mentioned in the Table at 32°, were plotted against $\log k$ for ionization of *p*-methoxyneophyl tosylate[27] in the same solvents at 25°. The slope (*a* value) of the straight line of 0.52 for the *p*-chlorobenzyl esters indicates a relatively low sensitivity to variation in solvent ionizing power. It is therefore suggested that this ester, as well as the unsubstituted one react by both S_N1 and S_N2 mechanisms. On the other hand, a slope of 1.2 was obtained for the *p*-methylbenzyl triflinate (Figure 1), similar to the values reported for other ionizing systems.[14a,c,15,28] Consequently it is suggested that in this case, capable of developing a more stable carbenium ion, complete ionization takes place.

Inspection of the data shown in Table II indicates a close resemblance between the reactivity of the trifluoro- and trichloromethanesulfinates. Although it has been stated[29] that trifluoroacetic acid is a stronger acid than trichloroacetic acid, the given pKa values, 0.3 and 0.08 respectively[29] point to the reverse. However, other available data[25,30] show that CF_3CO_2H is indeed several times stronger than CCl_3CO_2H, while the substituent constants of CF_3 and CCl_3 and their acid

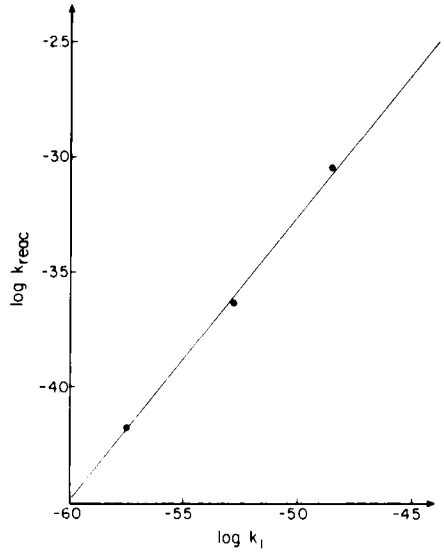


FIGURE 1 Plot of log k for solvolysis of p-methylbenzyl triflinate at 32° vs. log k for ionization of p-methoxyneophyl p-toluenesulfonate at 25° ($a = 1.22 \pm 0.00$, correlation coefficient = 0.999).

strengthening effects are almost identical. Assuming that this relation applies also for trihalomethanesulfinic acids, the observed resemblance between triflinates and trichlinates seems reasonable. In view of these findings one would predict that the practically unknown trichloromethanesulfonates may serve as good substitutes for the triflates. On the other hand, as judged by the results of a comparison between trifluoro- and trichloromethanesulfenates,[18] this prediction may not be exactly correct.

The evidence presented above with regard to an ionization mechanism for the solvolysis of benzyl triflinates is also supported by the results obtained from the study of their rearrangement to the corresponding sulfones. Rearrangements of sulfinates to sulfones have been studied extensively in the past.[2] With the exception of allylic and propargylic arenesulfinates which rearrange to sulfones

TABLE II

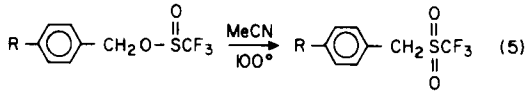
Rate constants for the solvolysis of benzyl trihalomethanesulfinates at 32°

		$10^5 k$, sec^{-1}		
Benzyl Ester	Solvent	p-Cl	p-H	p-Me
Triflinate	EtOH	0.92	1.04	6.56
	MeOH	1.84	3.21	23.71
	80%EtOH	2.67	4.31	88.19
Trichlinate[a]	EtOH	1.27	3.05	12.53
	MeOH	—	7.14	42.50
	80%EtOH	—	9.25	121.30

[a] Trichloromethanesulfinate. Data taken from Reference 15.

via a concerted [2, 3]-sigmatropic shift mechanism,[14b,e,f] the rearrangement of practically all other sulfinates proceeds by an ionic mechanism, as first suggested by Kenyon and coworkers.[31] More recently, however, the mechanistically detailed studies by Darwish and coworkers[7] have shown that the main route to sulfone-formation in the rearrangement of *t*-butyl, benzhydryl, α-phenylethyl and trityl arenesulfinates under various conditions is ion pair recombination and not recombination of free ions.

Previously, it has been reported[32] that no rearrangement of benzyl *p*-toluenesulfinate to benzyl *p*-tolyl sulfone takes place on heating the ester in a mixture of acetic and hydrochloric acids or in a homogeneous state. Similarly, on heating a solution of benzyl benzenesulfinate in formamide (dielectric constant 109) during 70 hr on a steam bath, the ester rearranged to benzyl phenyl sulfone in low yield.[14a] In contrast, we have found that benzyl triflinate rearranged to benzyl trifluoromethyl sulfone on heating in acetonitrile at 100° in the presence of 2,6-lutidine ($t_{\frac{1}{2}} \sim$ 3.5 hr). The *p*-chloro- and *p*-methylbenzyltriflinates also rearrange to the corresponding sulfones (Equation 5). The rearrangement to sulfone which clearly involves C—O bond cleavage is further evidence for the unusual reactivity of the triflinates and the high stability of the triflinate anion. The rearrangement of the *p*-anisyl ester at 0° in methylene chloride may be indicative of an ionization mechanism for the reaction.



(5)

The results described above are supported by the independent observations made by Hendrickson and Skipper[22] on the rearrangement of a number of primary triflinates to the corresponding triflones. For example, heptyl triflinate rearranged to the corresponding sulfone on heating at 145° in HMPA for 4 hr in 87% yield. This is in sharp contrast to the lack of reactivity of simple primary arenesulfinates. The triflones are of special interest for the synthetic chemist in the variety of ways they facilitate carbon–carbon bond construction, a subject extensively investigated and reviewed by Hendrickson.[33]

EXPERIMENTAL

Melting points and boiling points are uncorrected. Melting points were taken on a Thomas Hoover melting point apparatus. Infrared spectra were recorded on Perkin Elmer Grating Infrared Spectrometer Model 457. NMR spectra were recorded on Varian HA 100 NMR Spectrometer, and mass spectra on Perkin Elmer Hitachi RMU6 Mass Spectrometer.

Solvents and Reagents. Ethanol was dried by treatment with magnesium ethoxide, as described by Fieser.[34a] Methanol was dried by a similar method.[34b] X% ethanol–water means a solution prepared by mixing X volumes of ethanol with (100 – X) volumes of distilled water at 25°C. The same pipette was used for measuring all volumes. Acetonitrile was purified by the method described by Smith *et al.*[27] Eastman grade 2,6-lutidine was purified by refluxing with, and distillation from, barium oxide (bp 140–142°).

Preparation of Triflinates. p-Chlorobenzyl trifluoromethanesulfinate. To a solution of 2.00 g (0.008 mole) of *p*-chlorobenzyl trifluoromethanesulfenate[16a] in 10 ml of dry methylene chloride, cooled in an ice-water bath, was gradually added a solution of 2.20 g (0.01 mole) of Fluka grade 80%

MCPBA in 15 ml of methylene chloride during 5 min, with magnetic stirring. A few minutes later a white precipitate of *m*-chlorobenzoic acid appeared. Stirring of the reaction mixture at 0°C was continued for another two hours, followed by removal of the cooling bath, addition of 60 ml of ether and sequential washings with two portion of 15 ml of 5% KI solution, two portions of 10 ml of saturated $Na_2S_2O_3$ solution and 5 portions of 15 ml water. After drying ($MgSO_4$) and evaporation of the solvents at the water aspirator, 2.0 g (94% yield) of the expected ester was obtained as a clear and colorless liquid: ^{1}H NMR ($CDCl_3$) δ 7.39 (m, 5H); 5.15 (dd, J_{AB} = 12 Hz, $\Delta\nu$ = 32 Hz, 2H). The AB quartet at δ 5.15 ppm is due to the magnetic nonequivalence of the benzylic methylene protons which in turn is caused by the proximal asymmetric sulfur atom. This NMR absorption is quite general for sulfinate esters[35] and is very useful for their identification; IR (neat) 1195, 1130, 930 and 895 cm^{-1}; MS, m/e (%) 258 (M^+, 0.1), 189 (M—CF_3, 2), 125 (Cl—C_6H_4—CH_2, 100), 69 (CF_3, 13.5), 51 (CF_2H, 17.5), 50 (CF_2, 15).

Benzyl trifluoromethanesulfinate. To a solution of 1.50 g (0.007 mole) of benzyl trifluoromethanesulfenate[16a] in 10 ml of dry methylene chloride cooled at 0°, was added with magnetic stirring a solution of 2.0 g (0.009 mole) of 80% MCPBA in 10 ml of dry CH_2Cl_2. After further stirring for 1.5 hr at 0° and 0.5 hr at room temperature the product was isolated as described for the preparation of the *p*-chlorobenzyl analogue. The product was obtained as a clear and colorless liquid (1.45 g, 90% yield): ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 5H), 5.20 (dd, J_{AB} = 12 Hz, $\Delta\nu$ = 30 Hz, 2H); IR (neat) 1180, 1140, 950 and 920 cm^{-1}; MS *m/e* (%) 224 (M^+, 0.3), 205 (M—F, 0.8), 155 (M—CF_3, 10), 91 ($C_6H_5CH_2$, 100), 77 (C_6H_5, 90), 69 (CF_3, 50), 51 (CF_2H, 75), 50 (CF_2, 30).

p-Methylbenzyl trifluoromethanesulfinate was prepared by oxidation of the corresponding sulfenate ester,[16a] as described for the preparation of the *p*-chloro analogue, and was obtained as a clear and colourless liquid (yield 92%): ^{1}H NMR ($CDCl_3$) δ (7.20 (s, 4H), 5.17 (dd, J_{AB} = 12 Hz, $\Delta\nu$ = 30 Hz, 2H), 2.31 (s, 3H); IR (neat) 1200, 1130, 915 and 875 cm^{-1}; MS *m/e* (%) 238 (M^+, 1.8), 169 (M—CF_3, 0.4), 105 ($CH_3C_6H_4CH_2$, 100), 69 (CF_3, 7.5), 51 (CF_2H, 5.6), 50 (CF_2, 2.8).

Solvolysis of Triflinates. Ethanolysis of benzyl trifluoromethanesulfinate. The following is a typical procedure for the solvolysis of all benzyl sulfinates investigated. A 0.4480 g quantity (0.0020 mole) of benzyl triflinate and 0.8600 g (0.0080 mole) of 2,6-lutidine were dissolved in 50 ml of anhydrous ethanol. The solution was kept in a constant temperature oil bath at 32° for 10 days. After addition of 100 ml of distilled pentane and washing with 5 portions of 50 ml of 1% HCl, 3 portions of 50 ml of 5% $NaHCO_3$ and 5 times with 50 ml of water, the pentane solution was dried over anhydrous $MgSO_4$, and the solvent carefully evaporated at reduced pressure (>100 mm Hg) to a constant weight of the residue (0.260 g, 0.00193 mole, 96.3% yield). The product was identified as benzyl ethyl ether by ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 5H), 4.49 (s, 2H), 3.52 (q, J = 7 Hz, 2H), 1.24 (t, J = 6 Hz, 3H).

Kinetic Measurements. Solutions of the appropriate ester (~0.02 M) in the appropriate solvent, in the presence of 2,6-lutidine (~0.08 M) acting as a buffer, were prepared in a 50 ml volumetric flask and immersed in a 32° constant temperature bath. At different time intervals, 5 ml aliquots of the solution were removed by means of a pipette, diluted with 5 ml of distilled and boiled water, and titrated with a 0.0127 N solution of sodium methoxide in ethanol at 0°, using phenolphthalein as indicator. The rate constants were calculated from the first order kinetic expression $k = (2.303/t)\log(T_{(\infty)} - T_0/T_{(\infty)} - T_t)$. Errors were calculated by means of the least square method. All calculations and plots were obtained by means of an IBM 360/50 computer, using the APL language.

Rearrangement of Triflinates to Triflones. Solutions of 0.250 g of each of the three triflinates and 0.100 g of 2,6-lutidine in 10 ml of dry acetonitrile were heated in sealed tubes for 24 hr at 100°. After cooling to room temperature, 50 ml of ether were added to each solution, followed by washing with 1% HCl, 5% $NaHCO_3$ and water. After drying over anhydrous $MgSO_4$ and evaporation of the solvent, the sulfones were crystallized from the dark solid residues using pentane, and identified by IR and NMR as shown below. The data of *p*-anisyl triflinate, obtained by spontaneous rearrangement of the corresponding ester are also presented.

Benzyl trifluoromethyl sulfone. M.p. 101–2° (lit[33] = 103°); IR ($CHCl_3$) 1120, 1200, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 5H), 4.43 (s, 2H).

p-Chlorobenzyl trifluoromethyl sulfone M.p. 95–6°; IR ($CHCl_3$) 1120, 1200, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38 (s, 4H), 4, 43 (s, 2H).

p-Methylbenzyl trifluoromethyl sulfone. M.p. 92–3°; IR ($CHCl_3$) 1120, 1220, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.21 (s, 4H), 4.40 (s, 2H), 2.34 (s, 3H).

p-Methoxybenzyl trifluoromethyl sulfone. M.p. 100–1°; IR ($CHCl_3$) 1120, 1210, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (d, $J = 9$ Hz, 2H), 7.24 (d, $J = 9$ Hz, 2H); 4.44 (s, 2H), 3.77 (s, 3H).

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