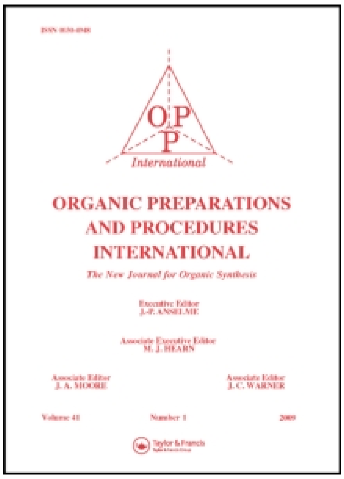

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SULFONIC-CARBOXYLIC ANHYDRIDES

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SULFONIC-CARBOXYLIC ANHYDRIDES

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Mixed sulfonic-carboxylic anhydrides have previously been shown to be excellent acylating agents.[2] In this paper the preparation of several new anhydrides is reported.

$$ArSO_3^- Ag^+ + Ar'COCl \longrightarrow \underset{I}{ArSO_2\text{-}O\text{-}COAr'} + AgCl$$

a) $Ar = Ar' = p\text{-}CH_3C_6H_4$

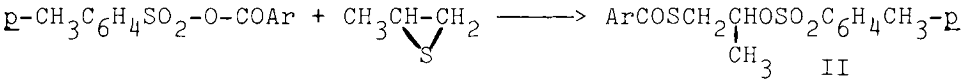
b) $Ar = p\text{-}CH_3C_6H_4$, $Ar' = p\text{-}ClC_6H_4$

c) $Ar = Ar' = p\text{-}ClC_6H_4$

As anticipated, each was found to be an active acylating agent. Aniline and phenol, for example, reacted with Ia to give p-methylbenzanilide and phenyl p-toluate in 95% and 81% yields respectively. In addition, aromatic substitution occurred with anisole in the presence of triethylamine affording 4-methyl-4'-methoxybenzophenone in 62% yield.

$$Ia + C_6H_5OCH_3 \longrightarrow p\text{-}CH_3OC_6H_4COC_6H_4CH_3\text{-}p$$

With propylene sulfide, several thioethyl p-toluenesulfonates(II) were obtained in moderate yield.



II

The benzoylation of ℓ-menthol in dioxane was followed polarimetrically and second order rate constants of 6.11 and 2.44 x 10^{-4} l/m min. at 29.90° and 21.40° respectively were calculated. From this, $E_a = 19.2$ Kcal. and $S^{\ddagger} = -20.2$ eu.

Experimental[3]

p-Toluyl p-Toluenesulfonate (Ia). To a solution of 27.9 g (0.1 mole) of silver p-toluenesulforate in 200 ml of acetonitrile there was added dropwise and with stirring 15.1 g (0.1 mole) of p-toluyl chloride in 50 ml of acetonitrile. Stirring at room temperature was continued for 3 hr. after which time the solvent was removed under vacuum. The residual solid was extracted several times with ether. Cooling the ether extracts below 0° afforded 11.6 g (40%) of Ia, m.p. 80-82°. Some softening before melting was observed for this and the other anhydrides. Infrared absorption was exhibited at 1780 cm^{-1}.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86; S, 11.05. Found: C, 62.27; H, 5.01; S, 10.91.

p-Chlorobenzoyl p-Toluenesulfonate (Ib). This compound was prepared as described above. From 27.9 g (0.1 mole) of silver p-toluenesulfonate and 17.5 g (0.1 mole) of p-chlorobenzoyl chloride, there was obtained 13.5 g (43%) of Ib, m.p. 111-113°.

Anal. Calcd. for $C_{14}H_{11}ClO_4S$: C, 54.10; H, 3.57; Cl, 11.41; S, 10.32. Found: C, 53.82; H, 3.83; Cl, 11.70; S, 10.22.

p-Chlorobenzoyl p-Chlorobenzenesulfonate (Ic). This compound was prepared as described above except that benzene was used instead of ether for the extraction of the anhydride. From 26.8 g (0.1 mole) of silver p-chlorobenzenesulfonate and 17.1 g (0.1 mole) of p-chlorobenzoyl chloride, there was obtained 12.7 g (38%) of Ic, m.p. 135-137°.

Anal. Calcd. for $C_{13}H_8Cl_2O_4S$: C, 47.14; H, 2.43; Cl, 21.41; S, 9.68. Found: C, 46.95; H, 2.63; Cl, 21.20; S, 9.69.

Reaction of Ia with Anisole. To 10.0 g (0.034 mole) of Ia and 3.5 g (0.034 mole) of triethylamine in 100 ml of ether, there was added 3.7 g (0.034 mole) of anisole. After a reflux period of 12 hr. the solution was extracted first with dilute hydrochloric acid and then with a saturated solution of sodium carbonate. Evaporation of the ether afforded a brown solid which was recrystallized from ethanol-water to give 4.8 g (62%) of 4-methyl-4'-methoxybenzophenone, m.p.

93-94° (lit.[4] m.p. 92°). The infrared spectrum exhibited a strong band at 1675 cm^{-1}.

Reaction of Ia with Aniline. To 6.25 g (0.022 mole) of Ia in 150 ml of ether there was added 4.1 g (0.044 mole) of aniline. Precipitation occurred immediately. The ether was evaporated to dryness and the residual solid treated with a saturated solution of sodium carbonate. The water insoluble material was recrystallized from ethanol-water, affording 4.3 g (95%) of p-methylbenzanilide, m.p. 143-144° (lit.[5] m.p. 144-145°). The infrared spectrum was identical to that of an authentic sample.

Reaction of Ia with Phenol. To 5.0 g (0.017 mole) of Ia in 100 ml of ether there was added 1.6 g (0.017 mole) of phenol. The solution was stirred overnight and then extracted with a saturated solution of sodium carbonate. After evaporation of the ether, the residual solid was recrystallized from ethanol-water, affording 2.7 g (81%) of phenyl p-toluate, m.p. 73-74° (lit.[6] m.p. 75-76°). The infrared spectrum was identical to that of an authentic sample.

1-Methyl-2-Benzoylthioethyl p-Toluenesulfonate. Benzoyl chloride (14.1 g; 0.1 mole) was added dropwise to silver p- toluenesulfonate (27.9 g; 0.1 mole) in 200 ml of acetonitrile. Silver chloride precipitated but was not removed. After 0.5 hr., propylene sulfide (11.1 g; 0.19 mole) was added to the mixture while the temperature was maintained between 20-30°. After a reflux period of 1 hr. the solvent was removed and the residual solid extracted with benzene. The benzene solution was washed with a saturated solution of sodium carbonate and then evaporated to dryness. The residual solid was recrystallized from hexane, affording 7.9 g (22%) of 1-methyl-2-benzoylthioethyl p-toluenesulfonate, m.p. 90.5-92°. Infrared absorption was exhibited at 1665, 1185, and 1020 cm^{-1}. The H^1 nmr spectrum showed a multiplet for the aromatic protons (τ 2.0-2.8), a multiplet for the methine proton (τ 5.2), a multiplet for the methylene protons (τ 6.75), a singlet for the methyl group attached to the aromatic ring (τ 7.7), and a doublet for the remaining methyl group (τ 8.5). The integrated intensities were in accord with the proposed structure.

Anal. Calcd. for $C_{17}H_{18}O_4S_2$: C, 58.26; H, 5.18; S, 18.30. Found: C, 58.11; H, 5.21; S, 18.39.

1-Methyl-2-p-Nitrobenzoylthioethyl p-Toluenesulfonate. Propylene sulfide (1.6 g; 0.021 mole) was slowly added to p-nitrobenzoyl p-toluenesulfonate[2] (5.7 g; 0.017 mole) in 100 ml of acetonitrile. After a reflux period of 2 hr. the solvent was removed and the residual solid recrystallized from methanol, affording 2.8 g (42%) of 1-methyl-2-nitrobenzoylthioethyl p-toluenesulfonate, m.p. 130-131°. Infrared absorption was exhibited at 1665, 1540, and 1350 cm^{-1}.

Anal. Calcd. for $C_{17}H_{17}NO_6S_2$: C, 51.63; H, 4.33; S, 16.21. Found: C, 51.21; H, 4.16; S, 16.23.

1-Methyl-2-Acetylthioethyl p-Toluenesulfonate. Acetyl chloride (9.8 g; 0.12 mole) was added to silver p-toluenesulfonate (27.9 g; 0.1 mole) in 150 ml of acetonitrile. Silver chloride precipitated but was not removed. After stirring the mixture for 15 min., propylene sulfide (8.1 g; 0.11 mole) was added dropwise while the temperature was maintained between 20-30°. After an additional 0.5 hr., the mixture was filtered and the solvent evaporated, affording a red oil which crystallized after washing with sodium carbonate solution. The solid was extracted with boiling hexane which on cooling afforded 5.78 g (20%) of 1-methyl-2-acetylthioethyl p-toluenesulfonate, m.p. 58-59°. Infrared absorption was exhibited at 1690, 1185, and 1025 cm^{-1}.

Anal. Calcd. for $C_{12}H_{16}O_4S_2$: C, 50.31; H, 5.55; S, 22.24. Found: C, 49.94; H, 5.59; S, 22.23.

Kinetic Results.[7] The reaction of benzoyl p-toluenesulfonate[2] and ℓ-menthol, $[\alpha]_D^{21.4}$ -49.4 (methanol), was followed by observing the change in optical rotation attending the disappearance of ℓ-menthol and the appearance of ℓ-menthyl benzoate. Rotations were measured on a Rudolph Photoelectric Polarimeter, model 200S-340-8026. The concentration of alcohol and ester were determined by reference to a previously prepared plot of optical rotation versus composition of various mixtures of ℓ-menthol and ℓ-menthyl benzoate. At the completion of each run, the solvent, dioxane, was removed in vacuo and the residual material dissolved in ethanol. Cooling of the ethanol afforded ℓ-menthyl benzoate, m.p. 54-55°, $[\alpha]_D^{21.4}$ -86.6 (chloroform).

Table I

Variation in Optical Rotation During the Reaction of ℓ-Menthol and Benzoyl p-Toluenesulfonate in Dioxane[a,b]

Run	[-α] (deg.)	Time (min.)	ℓ-Menthol M	Anhydride M	k x 10^4 1/m min.
1.	12.66	316	0.3575	0.3575	6.11
	15.84	1125	0.3030	0.3030	6.19
	16.29	1279	0.2949	0.2949	6.15
	16.58	1380	0.2899	0.2899	6.13
	17.20	1624	0.2792	0.2792	6.02
2.	13.50	1240	0.6940	0.3059	2.50
	13.70	1374	0.6835	0.2990	2.50
	13.96	1558	0.6751	0.2906	2.48
	15.83	2905	0.6121	0.2276	2.64
	18.85	7032	0.5092	0.1247	2.64

a. The initial concentrations were: Run 1: ℓ-menthol 0.3840 M; anhydride 0.3840 M; Run 2: ℓ-menthol 0.7680 M; anhydride 0.3835 M.

b. Data obtained at a wavelength of 589 mμ: Run 1 temp. 29.90°, pathlength 4 decimeters; Run 2 temp. 21.40°, pathlength 2 decimeters.

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7. Interestingly benzoyl chloride did not react with ℓ-menthol under conditions similar to those used here. This indicates that these anhydrides are more reactive than benzoyl chloride.

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