TABLE I

Hindered ketone	Grignard reagent	Product	Melting point, °C.	Yield, %	Analyses, % Calcd. C	H	Found C	H
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–CN[a]	t-C_4H_9MgCl	p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$C(CH_3)_3$	115.5–116.8	45	85.65	9.95	85.60	9.88
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–CN	C_6H_5–CH_2MgCl	p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$CH_2C_6H_5$	119.5–120.5	35	87.39	8.60	87.15	8.54
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$OCH_3$	t-C_4H_9MgCl	p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$C(CH_3)_3$[b]	114.5–115.5	54				
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$OCH_3$	C_6H_5–CH_2MgCl	p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$CH_2C_6H_5$[b]	118–120	9				
p-Dur$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$OCH_3$	t-C_4H_9MgCl	p-Dur$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$C(CH_3)_3$[b]	125.5–126.5	78				
p-Mes$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$OCH_3$	t-C_4H_9MgCl	p-Mes$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$C(CH_3)_3$[c]		88	85.67	8.63	85.40	8.68
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$\text{O}\overset{\text{O}}{\text{C}}CH_3$	t-C_4H_9MgCl	p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$C(CH_3)_3$[b]	115.5–116.8	56				
p-Tip$\overset{\text{O}}{\text{C}}$–$C_6H_4$–$\text{O}\overset{\text{O}}{\text{C}}CH_3$	C_6H_5–CH_2MgCl	No displacement prod.						

[a] Tip = 2,4,6-triisopropylphenyl radical; Dur = 2,3,5,6-tetramethylphenyl radical; Mes = 2,4,6-trimethylphenyl radical. [b] A mixed melting point with an authentic sample showed no depression. [c] B.p. 143–150° (0.25 mm.); $n^{20}D$ 1.5638. The infrared spectrum of this material was identical with that of an authentic sample obtained by treating mesitylene with p-t-butylbenzoyl chloride. A trinitro derivative made by adding the ketone, dissolved in petroleum ether, to fuming nitric acid at 0° melted at 200–201.5° dec. *Anal.* Calcd. for $C_{20}H_{21}N_3O_7$: C, 57.83; H, 5.10; N, 10.12. Found: C, 57.86; H, 5.30; N, 10.13.

to each mole of ketone to be employed, was filtered through a glass wool plug into refluxing ether. Then the p-substituted hindered diaryl ketone, dissolved in benzene, was added during 5 to 10 minutes. The mixture generally developed a dark red-brown color, which gradually faded to a light tan in 30 minutes to 5 hours, indicating the reaction had gone to completion. Decomposition was accomplished by pouring the reaction mixtures into iced dilute hydrochloric acid. After the organic layer had been dried, the solvent was removed by evaporation. The resulting light yellow viscous oils could be induced to crystallize from methanol, and the products were then recrystallized from ethanol. The results are shown in Table I.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Friedel–Crafts Alkylation of Aromatic Compounds with Vinyl Sulfones[1]

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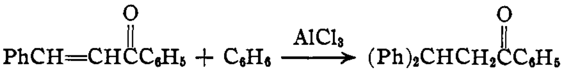
RECEIVED JULY 6, 1953

Methyl ω-styryl sulfone in the presence of 97% sulfuric acid alkylates benzene and toluene to give β,β-diphenylethyl methyl sulfone and β-phenyl-β,p-tolylethyl methyl sulfone, respectively. Under the same conditions ω-styryl p-tolyl sulfone alkylates toluene to give β-phenyl-β,p-tolylethyl p-tolyl sulfone. Methyl vinyl sulfone does not alkylate toluene, benzene, m-xylene or mesitylene under the conditions studied.

Vinyl ketones have been used to alkylate aromatic compounds under Friedel–Crafts conditions.[2] However, similar reactions with vinyl sulfones



$$\text{PhCH}{=}\text{CH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCl}_3} (\text{Ph})_2\text{CHCH}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\text{C}_6\text{H}_5$$

do not appear to have been reported previously. During a study of the conversion of ω-styrenesulfonyl chloride (I) to α,β-unsaturated sulfones, equations 1 and 2

$$C_6H_5CH{=}CHSO_2Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH{=}CHSO_2C_6H_5 \quad (1)$$

$$C_6H_5CH{=}CHSO_2Cl + C_7H_8 \xrightarrow{AlCl_3} C_6H_5CH{=}CHSO_2C_6H_4CH_3\text{-}p \quad (2)$$

the formation of β-phenyl-β,p-tolylethyl p-tolyl sulfone (III) was observed in the aluminum chloride-catalyzed reaction of the sulfonyl chloride I with toluene at reflux temperature. The structure of product III was established by the following independent synthesis.

$$p\text{-}CH_3C_6H_4(C_6H_5)C{=}CH_2 + p\text{-}C_7H_7SH \xrightarrow{(C_6H_5CO)_2O_2} p\text{-}CH_3C_6H_4(C_6H_5)CHCH_2SC_7H_7\text{-}p \xrightarrow{H_2O_2} \underset{\text{III}}{p\text{-}CH_3C_6H_4(C_6H_5)CHCH_2SO_2C_7H_7\text{-}p}$$

Product III may have been formed by the condensation of toluene with the sulfone II which is prepared in good yield when I is treated with toluene at room temperature.[3] This hypothesis is supported by the observation that when II[4] is treated with toluene in the presence of 97% sulfuric acid, III is obtained in good yield.

The aluminum chloride-catalyzed condensation of methyl ω-styryl sulfone, prepared from sodium ω-styrenesulfinate, with toluene at room temperature for 59 hours or with benzene at reflux tempera-

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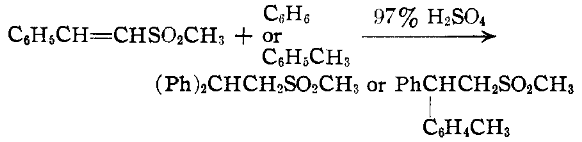
[1] Taken from Mr. Simms's and Mr. Hill's M.S. Theses.

[2] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 236–237.

[3] The reaction of ω-styrenesulfonyl chloride with toluene to give the *trans*-sulfone also was reported recently by A. P. Terent'ev, R. A. Gracheva and Z. F. Shcherbatova, *Doklady Akad. Nauk S.S.S.R.*, **84**, 975 (1952); *C. A.*, **47**, 3262 (1953).

[4] E. P. Kohler and H. A. Potter, THIS JOURNAL, **57**, 1316 (1935).

ture was attempted; but most of the starting sulfone (60–73%) was recovered. However, using 97% sulfuric acid as the alkylation catalyst, condensation products of methyl ω-styryl sulfone with benzene and toluene were obtained in good yield. When too short a reaction time was used, mixtures of saturated and unsaturated sulfones were obtained, in which case the unsaturated sulfone could be destroyed by oxidizing the mixture with an acetone solution of potassium permanganate.



$$C_6H_5CH{=}CHSO_2CH_3 + \begin{matrix}C_6H_6\\ \text{or}\\ C_6H_5CH_3\end{matrix} \xrightarrow{97\%\ H_2SO_4}$$

$$(Ph)_2CHCH_2SO_2CH_3 \text{ or } \underset{\displaystyle C_6H_4CH_3}{\underset{|}{PhCH}}CH_2SO_2CH_3$$

The orientation of the tolyl group was assigned by analogy with III.

Several unsuccessful attempts were made to establish the structure of the product assumed to be β,β-diphenylethyl methyl sulfone. α,α-Diphenyl-β-methylsulfonylethanol[5] could not be reduced with phosphorus and iodine. The corresponding vinyl sulfone, methyl β,β-diphenylvinyl sulfone, could not be reduced catalytically or with zinc and acetic acid. 1,1-Diphenyl-2-chloroethane[6] was treated with sodium methyl mercaptide followed by oxidation. No sulfone was obtained and it appears that dehydrohalogenation instead of sulfide formation took place. In an attempt to establish the structure of the toluene alkylation product, presumably β-phenyl-β,*p*-tolylethyl methyl sulfone, methyl mercaptan was treated with 1-phenyl-1-*p*-tolylethylene in the presence of benzoyl peroxide. Subsequent oxidation of the reaction product with hydrogen peroxide in acetic acid failed to produce the sulfone.

The condensation of methyl vinyl sulfone with a series of aromatic compounds in the presence of aluminum chloride did not proceed as expected. The only products isolated were small quantities of dark colored oil or tar. Since aluminum chloride was not effective as a catalyst, boron trifluoride-etherate was used as a catalyst in the reaction of mesitylene and *m*-xylene with methyl vinyl sulfone. These reactions also resulted in only small quantities of non-crystallizable oils, which were probably polymers of methyl vinyl sulfone. Nor was methyl β-phenylethyl sulfone isolated when a mixture of benzene and methyl vinyl sulfone was treated with 97% sulfuric acid.

Experimental

Friedel–Crafts Reactions with ω-Styrenesulfonyl Chloride.—Anhydrous aluminum chloride (16 g., 0.12 mole) was added in small portions to a solution of 20.3 g. (0.1 mole) of ω-styrenesulfonyl chloride[7] in 100 ml. of benzene. The reaction mixture was heated on a steam-bath until the evolution of hydrogen chloride had ceased. Hydrolysis with a mixture of ice and hydrochloric acid was followed by separation of the benzene layer and extraction of the water layer with ether. The organic extracts were combined and the solvent was evaporated. The product, phenyl ω-styryl sulfone, after decolorization with charcoal and recrystallization from methanol, weighed 13.3 g. (54.5%) and had m.p. 73.5–74.5°. It decolorized an acetone solution of permanganate.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95. Found: C, 68.64, 68.73; H, 4.71, 4.89.

Anhydrous aluminum chloride (15.0 g., 0.11 mole) was added to a solution of 20.3 g. (0.1 mole) of ω-styrenesulfonyl chloride in 100 ml. of toluene cooled in an ice-bath. The reaction mixture was allowed to warm to room temperature, and after the evolution of hydrogen chloride had subsided it was heated on a steam-bath for one half hour. The product, ω-styryl *p*-tolyl sulfone (II), isolated as described above for the phenyl analog, weighed 10.9 g. (42%) and had m.p. 121–122°, reported[4] m.p. 121°. It did not depress the m.p. of an authentic sample.[8]

Anhydrous aluminum chloride (36 g., 0.27 mole) was added to a solution of 45.7 g. (0.23 mole) of ω-styrenesulfonyl chloride in 100 ml. of toluene at reflux temperature. After the evolution of hydrogen chloride had ceased, the product, isolated as described for the preceding experiment, weighed 10.1 g. (12.5%) and had m.p. 128.5–129.5°; m.p. 130–130.5°, after recrystallization from petroleum ether (b.p. 90–100°).

Anal. Calcd. for $C_{22}H_{22}O_2S$: C, 75.39; H, 6.33. Found: C, 75.86, 75.54; H, 6.17, 6.29.

An authentic sample of β-phenyl-β,*p*-tolylethyl *p*-tolyl sulfone (III) was prepared by adding 12.4 g. (0.1 mole) of *p*-thiocresol to 19.4 g. (0.1 mole) of 1-phenyl-1,*p*-tolylethylene in the presence of a few crystals of benzoyl peroxide. After 24 hours of standing at room temperature, the resulting product was dissolved in glacial acetic acid and an excess of 30% hydrogen peroxide was added dropwise to the resulting hot solution. The reaction mixture was poured onto ice and filtered. Recrystallization of the residue from methanol gave 22 g. (62.9%) of sulfone with m.p. 131–133°; mixed m.p. with the aforementioned Friedel–Crafts product, 131–132°.

Methyl ω-Styryl Sulfone, its Preparation and Alkylation Reactions.—ω-Styrenesulfonyl chloride (88 g., 0.43 mole) was added to a stirred mixture of 88 g. (1.34 moles) of zinc dust in 1.5 l. of 95% ethanol. The mixture was stirred for 2 hours and allowed to stand overnight. The solution was heated to boiling and the zinc chloride and excess zinc were filtered off. The precipitate was washed with boiling 50% ethanol until this residue was no longer inflammable. This washing removed most of the zinc sulfinate and required 2.5 to 3 l. of alcohol. The combined filtrate was evaporated to 2 l. Sodium carbonate (104 g., 1 mole) was added to form sodium ω-styrenesulfinate, and the precipitate of zinc carbonate was filtered off. The solution was evaporated to 1 l., methyl iodide (0.6 mole) was added, and the mixture was heated at reflux for 2 hours and allowed to stand overnight. The solution was evaporated to 500 ml. and a crop of crystals weighing 31 g. was collected. This material (m.p. 70–75°) decolorized a solution of potassium permanganate in acetone and a solution of bromine in carbon tetrachloride. It was recrystallized from a mixture of methanol and water to give 28.0 g. (32% yield) of methyl ω-styryl sulfone, m.p. 78–79°.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.34; H, 5.49. Found: C, 59.39; H, 5.57.

Methyl ω-styryl sulfone (5 g., 0.025 mole) was added to a stirred mixture of 97% sulfuric acid (10 g., 0.1 mole) in 100 ml. of benzene cooled in an ice-bath. The mixture was dark brown in color, and most of the sulfone appeared to be dissolved in the sulfuric acid layer. Stirring was continued for 2 hours at ice-bath temperature and then for 4 hours at room temperature. The reaction mixture was poured into ice-water and the aromatic layer was separated. The water layer was washed with 200 ml. of ether and the combined solvents were evaporated to dryness under an air jet. A solid residue (5.5 g.) was obtained which gave 5.46 g. (76% yield) of white crystals (m.p. 104–105°) after recrystallization from methanol and water.

Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.23; H, 6.15. Found: C, 68.96; H, 6.31.

The above procedure was repeated except that toluene was substituted for benzene and the reaction time at room temperature was extended to 9 hours. The semi-solid product was dissolved in 100 ml. of absolute methanol, decolorized with charcoal, and crystallized in three fractions: (1) 0.92 g., m.p. 77–83°; (2) 0.96 g., m.p. 92–93°; (3) 1,60 g., m.p. 83–86°. Fractions 1 and 3 evidently contained some

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(5) Furnished by K. R. Buser, this Laboratory.

(6) E. Hepp, *Ber.*, **7**, 1409 (1874).

(7) F. G. Bordwell, *et al.*, THIS JOURNAL, **68**, 139 (1946).

(8) Furnished by Prof. H. A. Potter, Alma College, Alma, Michigan.

of the unreacted methyl ω-styryl sulfone; they were combined and dissolved in acetone, and potassium permanganate was added until a purple color persisted. The manganese dioxide was filtered off and the acetone was evaporated. Water was added and the saturated sulfone was extracted with 200 ml. of ether. Evaporation of the ether left a residue, which was recrystallized from methanol and water to give 1.8 g. of methyl β-phenyl-β,*p*-tolylethyl sulfone; m.p. 92–93°, total yield 2.76 g. (37% of theory).

Anal. Calcd. for $C_{16}H_{18}O_2S$: C, 69.82; H, 6.57. Found: C, 69.85; H, 6.75.

Alkylation of Toluene with *p*-Tolyl ω-Styryl Sulfone.—This compound[4] (II) (10 g., 0.039 mole) was added to a stirred mixture of toluene (100 ml.) and 97% sulfuric acid (20 g.) cooled in an ice-bath. The mixture was stirred at ice-bath temperature for 1 hour and then at room temperature for 6 hours. The reaction mixture was poured into ice-water and the aromatic layer was separated. The water layer was extracted with 200 ml. of ether and the combined aromatic layer and ether extract was evaporated to dryness under an air jet. The solid obtained was dissolved in absolute methanol and crystallized in three fractions: (1) 4.3 g., m.p. 130–132°; (2) 1.5 g., m.p. 124–127°; (3) 3.8 g., m.p. 106–111°. A mixture of 0.09 g. of fraction (1) and 0.08 g. of the known sample[3] (m.p. 131–132.5°) had mp. 130.5–132.5°.

Alkylations with Methyl Vinyl Sulfone.—The quantities of reactants used were: 0.1 mole of methyl vinyl sulfone,[9] 0.22 mole of aluminum chloride, and a large excess of the aromatic compound. In all cases a solution of the sulfone in the aromatic compound or in nitrobenzene was added to a stirred mixture of the catalyst and the aromatic compound, in some cases using nitrobenzene as the solvent. The first reactions were run at about 30° for 2 hours generally following the procedure given in ref. (2). In three cases some dry hydrogen chloride was added to the reaction mixtures containing aluminum chloride as a catalyst. When no condensation was obtained the temperature of the subsequent reactions was raised to 90°. The only result of this increase in temperature was an increase in the amount of tar-like product formed. In each case the reaction mixture was decomposed by pouring it into an ice-water–hydrochloric acid mixture. The organic layer was then separated, washed with water and steam distilled. The product, if any, should have remained in the pot residue since the sulfone produced by the condensation would be water insoluble and not appreciably steam distillable.

Methyl vinyl sulfone (10.6 g., 0.1 mole), was added to a stirred mixture of benzene (150 ml.) and sulfuric acid (97%, 20 g.) cooled to ice-bath temperature. This mixture was stirred 2 hours at ice-bath temperature, 3 hours at room temperature and 1 hour at 60°. The reaction mixture was hydrolyzed by pouring it into ice-water. The organic layer was separated and evaporated down to a small quantity of oil, which could not be crystallized. The water layer was extracted with two 100-ml. portions of ether and the ether was evaporated; however, no appreciable amount of residue remained.

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[9] G. D. Buckley, *et al.*, *J. Chem. Soc.*, 1514 (1947).

NOTES

The Adsorption of Cupric and Mercuric Ions by a Weak-base Anion Exchange Resin

By John Andelin and Norman Davidson

Received April 25, 1953

Weak-base anion-exchange resins in their "basic" form take up an anion X^- by virtue of the reaction $RNH_2 + H^+ + X^- \rightarrow RNH_3^+ + X^-$, that is, by addition of a proton to the unshared pair of the nitrogen atom. It is reasonable to expect that other cations which form ammine complexes will be adsorbed by the resin. Sussman has briefly reported on the adsorption of cupric ions by an anion-exchange resin.[1] The results of a fragmentary study of the adsorption of Cu^{++} and Hg^{++} ions by the weak-base resin, Amberlite IR-4B, are reported here.

Experimental

A sample of the resin hydrochloride was treated with excess sodium hydroxide, washed with water until on standing for 24 hours the *p*H remained 7–8, and stored over saturated sodium sulfate (vapor pressure 22.3 mm. at 25°, 95% relative humidity).

Cupric solutions were prepared from C.P. copper nitrate and were analyzed iodometrically, using the directions of Swift.[2a] Using 25-ml. portions of solutions at a *p*H of 3–5, Cu^{++} concentrations as low as 2×10^{-4} *M* could be determined to 1% provided the solutions were deoxygenated by bubbling CO_2 gas through them. Mercuric solutions, prepared from mercuric nitrate, were analyzed by thiocyanate titration.[2b] Hydrogen ion in the Hg^{++} solutions was determined by titration with NaOH to a brom thymol blue end-point, in the presence of 0.3 *M* KI to complex the Hg^{++}. The first color change of the indicator gives the end-point, but it subsequently fades.

The adsorption experiments were done at an ionic strength of *ca.* 0.10 volume molar maintained with sodium nitrate. Weighed samples of resin were equilibrated with measured volumes of an aqueous phase in a glass-stoppered erlenmeyer flask by constant end-over-end rotation of the flask. The amount of copper or mercury adsorbed or eluted was computed from the change in concentration of the aqueous phase, and the known initial amount of metal in the resin, or, when necessary, by elution of the copper from the resin with acid. Concentrations of adsorbed constituents in the resin are reported in units of weight molality, *m*, *i.e.*, moles per kilogram of the free base form of the resin. Solution concentrations are reported in units of volume molarity, *M*. Titration curves of the resin, at the ionic strength used in our experiments, are shown in Fig. 1.

Results and Discussion

In order to do experiments at a *p*H at which there was no question about possible precipitation of basic copper compounds, it was necessary to use a resin which was at least 2 *m* in acid. Figure 2 displays the results of a series of experiments on the adsorption and elution of Cu^{++} by the resin. After 5 or 6 days exposure to the aqueous Cu^{++} solution (curves A and B), the rate of adsorption of Cu^{++} fell to a low value. The resin, which was normally amber colored, became blue-green upon adsorbing Cu^{++} and almost black when more

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[1] F. C. Nachod (editor), "Ion Exchange," Academic Press, Inc., New York, N. Y., 1949, p. 244.

[2] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., N. Y., 1950, (a) p. 210, (b), p. 101.