[Contribution from the Chemistry Department of the College of Arts and Sciences, University of Louisville]

REPLACEMENT REACTIONS OF α-BROMOETHYLBENZENESULFONYL CHLORIDE WITH ALKALI

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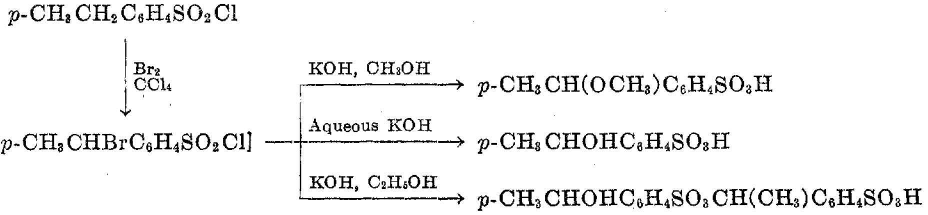
α-Haloethylbenzenesulfonic acid derivatives are of interest because they are readily available intermediates for the preparation of sulfostyrene derivatives. It has been suggested (1), in a reference not available until the research described herein was substantially complete, that α-chloroethylbenzenesulfonamide may be successfully dehydrohydrohalogenated to sulfonamidostyrene. We wish to record at this time our observations with this type of reaction using α-bromoethyl derivatives in which we have shown that replacement of the halogen to give α-hydroxy- and α-methoxy-ethyl compounds is favored over elimination.

p-Ethylbenzenesulfonyl chloride, prepared as previously described (2), was reacted with an equivalent amount of bromine in carbon tetrachloride. The bromination proceeded regularly when the reaction mixture was refluxed while exposed to light. Since extensive decomposition accompanied attempted distillation, the reaction product was used in the following reactions without further purification.

The products obtained on reaction of this brominated ethylbenzenesulfonyl chloride with alkali were replacement products of different types depending on the conditions used. With aqueous potassium hydroxide, the product was α-hydroxyethylbenzenesulfonic acid, isolated as its *p*-toluidine salt. Aqueous hydrolysis of α-bromoethylbenzene to α-hydroxyethylbenzene has been described previously (3). With potassium hydroxide in methanol, the product was α-methoxyethylbenzenesulfonic acid, also isolated as its *p*-toluidine salt. The formation of the methoxy instead of the hydroxy derivative on reaction of an α-bromoethylbenzene with methanolic potassium hydroxide has been previously observed (4). With potassium hydroxide in 95% ethanol, a toluidine salt was obtained whose neutral equivalent indicated that two molecules of the sulfonic acid had combined probably as a hydroxyethylbenzenesulfonate of the α-hydroxyethylbenzenesulfonic acid. Similar bimolecular products were obtained using the methyl ester in place of the sulfonyl chloride. These bimolecular reaction products could not be obtained reproducibly or analytically pure.



$$p\text{-}CH_3CH_2C_6H_4SO_2Cl \xrightarrow[CCl_4]{Br_2} [p\text{-}CH_3CHBrC_6H_4SO_2Cl]$$

$$[p\text{-}CH_3CHBrC_6H_4SO_2Cl] \xrightarrow{KOH,\ CH_3OH} p\text{-}CH_3CH(OCH_3)C_6H_4SO_3H$$

$$[p\text{-}CH_3CHBrC_6H_4SO_2Cl] \xrightarrow{\text{Aqueous KOH}} p\text{-}CH_3CHOHC_6H_4SO_3H$$

$$[p\text{-}CH_3CHBrC_6H_4SO_2Cl] \xrightarrow{KOH,\ C_2H_5OH} p\text{-}CH_3CHOHC_6H_4SO_3CH(CH_3)C_6H_4SO_3H$$

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[1] Taken from a thesis submitted by R. P. D. in partial fulfilment of the requirements for the M.S. degree.

In none of these reactions was there any evidence of formation of vinylbenzenesulfonic acid derivatives. Furthermore, attempts to dehydrohalogenate α-bromoethylbenzenesulfonyl chloride and methyl or butyl α-bromoethylbenzenesulfonate by vacuum distillation (pyrolysis) or with pyridine or quinoline gave only decomposition products. The esters were prepared by bromination of the previously described (2) esters and used without further purification.

During this study we have developed a procedure for isolating aryl sulfonic acid derivatives from salt mixtures. The procedure involves alkaline hydrolysis of the sulfonyl chlorides to the potassium sulfonates which are converted to and isolated as the water-insoluble *p*-toluidine salts. The *p*-toluidine salts, although recommended for characterization purposes (5), have apparently not previously been used in isolation of sulfonic acids (6). A study of the process using *p*-toluenesulfonyl chloride and *p*-ethylbenzenesulfonyl chloride has shown that the toluidine salt can be isolated in 73.7% of the theoretical amount.

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EXPERIMENTAL[2]

α-Bromoethylbenzenesulfonyl chloride. *p*-Ethylbenzenesulfonyl chloride (102 g., 0.499 mole) was dissolved in 400 ml. of carbon tetrachloride. To this solution was added 26.2 ml. (81.5 g., 0.51 mole) of bromine. The reaction mixture was warmed and illuminated with a 200 watt bulb. After the bromine had reacted, the mixture was filtered and the carbon tetrachloride was evaporated under a vacuum. Attempted distillation at reduced pressure led to extensive decomposition.

Attempts to characterize the α-bromoethylbenzenesulfonyl chloride by conversion to the amide with cold, concentrated ammonium hydroxide gave a product, m.p. 134°, recrystallized first from alcohol and then from toluene-petroleum ether, which did not analyze in agreement with the theoretical values.

α-Hydroxyethylbenzenesulfonic acid. To 27.5 g. of α-bromoethylbenzenesulfonyl chloride was added 19 g. of potassium hydroxide in 10% aq. solution. After two hours refluxing the solution, now homogeneous, was evaporated to dryness. To 5 g. of the total of 43.3 g. of residue in a few ml. of water was added 0.86 g. of *p*-toluidine in 0.66 ml. of conc'd hydrochloric acid. From this boiled and cooled solution 1.0 g. of the toluidine salt of α-hydroxyethylbenzenesulfonic acid, m.p. 185°, was obtained.

Anal. Calc'd for $C_{15}H_{19}NO_4S$: N, 4.53; S, 10.35; Neut. equiv., 309.

Found: N, 4.38; S, 10.62; Neut. equiv., 309.

α-Methoxyethylbenzenesulfonic acid p-toluidine salt. The crude α-bromoethylbenzenesulfonyl chloride obtained from 17 g. (0.083 mole) of *p*-ethylbenzenesulfonyl chloride and 4.7 ml. (14.7 g., 0.091 mole) of bromine was dissolved in 50 ml. of methanol and refluxed with a solution of 23 g. (0.42 mole) of potassium hydroxide in 50 ml. of methanol. The precipitated salts were collected and dried. Then 12.5 g. of this salt was dissolved in *ca.* 30 ml. of water and added to a solution of 10 g. of *p*-toluidine in 17 ml. of conc'd hydrochloric acid. The mixture was heated until all components were in solution, cooled, and filtered to collect the precipitated salt. After recrystallization from 25 ml. of water there was obtained 4.5 g. of the *p*-toluidine salt of α-methoxyethylbenzenesulfonic acid, m.p. 201–202°.

Anal. Calc'd for $C_{16}H_{21}NO_4S$: C, 59.5; H, 6.5; Neut. equiv., 323.

Found: C, 59.14; H, 6.46; Neut. equiv., 318.5 (322 after recrystallization from toluene).

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[2] Analyses by Micro Tech Laboratories, Skokie, Illinois.

Ethanolic potassium hydroxide hydrolysis. The toluidine salts obtained in several hydrolyses using 95% ethanolic potassium hydroxide following a procedure similar to that used in other hydrolyses, had neutral equivalents varying from 362 to 513. Other reagents and reactants have also given salts with neutral equivalents as high as 613. Most of these products have neutral equivalents in the range of 485–550.

Formation of toluidine salts of sulfonic acids. Following the procedure described for the α-bromoethylbenzenesulfonyl chloride, *p*-toluenesulfonyl chloride and *p*-ethylbenzenesulfonyl chloride were hydrolyzed and isolated as their toluidine salts. The *p*-toluenesulfonic acid was isolated in 73.7% (recrystallized) yield, m.p. 197°, Neut. equiv., 277 (5). The toluidine salt of *p*-ethylbenzenesulfonic acid, m.p. 190°, Neut. equiv., 292 (5) was similarly obtained from the sulfonyl chloride.

SUMMARY

α-Bromoethylbenzenesulfonyl chloride is converted by aqueous or alcoholic potassium hydroxide to α-hydroxyethyl, α-methoxyethyl, and perhaps sulfonate esters of α-hydroxyethylbenzene sulfonic acid. With these and other reagents there is no evidence that vinyl derivatives of benzenesulfonic acid can be obtained from α-bromoethyl compounds in this series. The sulfonic acids were isolated from salt mixtures as their *p*-toluidine salts by a procedure developed during this study.

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REFERENCES

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