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SYNTHESIS OF N-VINYL SULFONAMIDES

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During an investigation of acetylene chemistry, it was found that N-vinyl sulfonamides (I) could be prepared by direct vinylation of N-monoalkylated sulfonamides with acetylene. The vinylations were conveniently carried out in water using potassium hydroxide as catalyst at acetylene pressures of 7–16 atmospheres. In this way, four N-monoalkylated sulfonamides have been vinylated in yields of 45–85%. Vinylation of the N-monoarylated sulfonamide, *p*-toluenesulfonanilide, or the unsubstituted sulfonamides, *p*-toluenesulfonamide and butanesulfonamide was not effected with acetylene under these conditions.

$$RSO_2\overset{R'}{N}CH{=}CH_2$$

I

The characterization of these new vinyl monomers included elemental analyses, spectral analyses, and reduction in the case of one example to the N-ethyl derivative for comparison with a sample made by another method.

In a study of catalysts, it was found that powdered potassium hydroxide in anhydrous benzene was also satisfactory for promoting the vinylation whereas mercuric chloride and cuprous acetylide were ineffective.

N-Vinyl sulfonamides of the type I have been mentioned in the literature but apparently have not been described or characterized (1, 2). Other N-alkenyl sulfonamides, for example N-allyl-*p*-toluenesulfonamide, have been described (3).

EXPERIMENTAL

Materials. N-Methylbenzenesulfonamide was prepared by adding two equivalents of methylamine to a benzene solution of benzenesulfonyl chloride at 0°. The product distilling at 152–154°/1 mm. was collected, n_D^{25} 1.5441. *N-Methylcyclohexanesulfonamide* was similarly prepared, boiling point 131–132°/2 mm., m.p. 62°.

Anal. Calc'd for $C_7H_{15}NO_2S$: S, 18.05. Found: S, 17.95, 17.92.

p-Toluenesulfonanilide, m.p. 101–102°, was obtained from the Organic Chemicals Department of the du Pont Company. *N-Ethyltoluenesulfonamide* was an *ortho-para* mixture sold commercially as "Santicizer 8" and the fraction distilling at 152–157°/2 mm., n_D^{25} 1.5399, was used. *p-Toluenesulfonamide* was prepared from *p*-toluenesulfonyl chloride and ammonia and the product after recrystallization from 95% ethyl alcohol melted at 139–140°. *Butanesulfonamide* and the *N-methylbutanesulfonamide* were isomeric mixtures obtained from the Organic Chemicals Department of the du Pont Company. Commercial grade *acetylene* obtained from the Air Reduction Company was passed through a series of scrubbers containing, in order, Fieser's solution, calcium chloride, activated alumina, and sodium hydroxide pellets. The infrared spectra were determined on a Perkin-Elmer Model 21 double beam spectrometer.

Vinylation of N-methylbenzenesulfonamide. A mixture of 45 g. of N-methylbenzenesulfonamide, 200 ml. of distilled water, and 7 g. of potassium hydroxide was transferred to a 500-ml. stainless steel rocker bomb which previously had been flushed with nitrogen. The bomb was pressure-tested with nitrogen at 36 atm. pressure, then cooled in a "Dry Ice"/

methanol cooling bath and evacuated to about 10 mm. pressure. The equipment was installed behind a heavy barricade, and all operations with acetylene were controlled from the outside. With a bomb temperature slightly under 0°, acetylene at 8 atm. pressure was introduced and the reaction mixture was heated to 180°. When this temperature was reached, additional acetylene pressure was applied until the bomb gauge reached 13 atm. The pressure was maintained at 12–13 atm. by periodic repressuring with acetylene for 14.5 hours. The bomb was then cooled to room temperature, the pressure was released, and the contents were removed. The reaction mixture was shaken with 200-ml. of benzene, and the benzene layer was separated and washed twice with 5% aqueous caustic. The benzene layer then was dried over "Drierite" and distilled. After stripping off the benzene, the residual liquid was distilled and the fraction distilling at 120°/2 mm. weighed 38 g. (74% yield), n_D^{25} 1.5468.

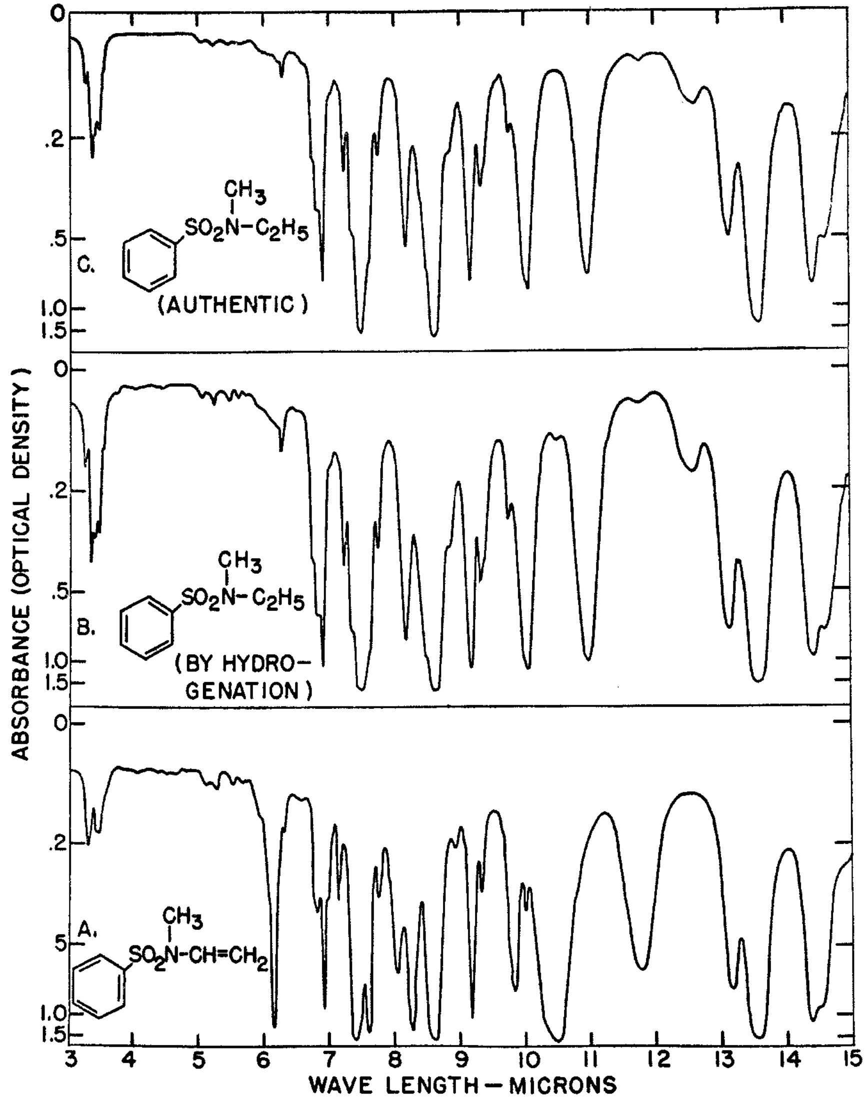

Fig. 1

Anal. Calc'd for $C_9H_{11}NO_2S$: C, 54.9; H, 5.6; N, 7.1; S, 16.2; H_2 No., 0.0102.
Found: C, 55.0; H, 5.7; N, 7.8; S, 16.4; H_2 No., 0.0106.

The infrared spectrum shows carbon:carbon unsaturation at 6.15 microns as well as sulfonamide (—$SO_2N<$) absorption at 7.4 and 8.6 microns (Figure 1).

Hydrogenation of N-vinyl-N-methylbenzenesulfonamide. Catalytic hydrogenation of a 20-g. sample of this vinyl compound with palladium-on-charcoal catalyst at room temperature in dioxane gave 10 g. of N-ethyl-N-methylbenzenesulfonamide, b.p. 120°/1.5 mm., n_D^{25} 1.5270. An "authentic" sample of N-ethyl-N-methylbenzenesulfonamide, made by reacting benzenesulfonyl chloride with N-ethyl-N-methylamine in aqueous sodium hydroxide, also distilled at 120°/1.5 mm., n_D^{25} 1.5272. As shown in Figure 1, the 6.15 micron band in the vinyl derivative indicative of the carbon:carbon double bond stretching disappeared in the reduced product. Likewise, the absorption in the 10.5 micron region present in the vinyl derivative and ascribed to the out-of-plane bending vibrations of ethylenic hydrogen also virtually disappeared in the reduced product. The spectra of the "hydrogenated" sulfonamide and the "authentic" control are virtually identical.

Vinylation of N-methylcyclohexanesulfonamide. A mixture of 45 g. of N-methylcyclohexanesulfonamide, 200 ml. of distilled water, and 7 g. of potassium hydroxide was treated with acetylene under a gauge pressure of 11–16 atm. during 16 hours at 180°. The reaction mixture was worked up as described previously and 35 g. of N-vinyl-N-methylcyclohexanesulfonamide distilling at 115–118°/3 mm., (62% yield), n_D^{25} 1.5022, was obtained.

Anal. Calc'd for $C_9H_{17}NO_2S$: C, 53.4; H, 8.4; N, 6.9.
Found: C, 53.8; H, 8.6; N, 6.9.

Vinylation of N-methylbutanesulfonamide. A mixture of 50 g. of N-methylbutanesulfonamide, 150 ml. of distilled water, and 5 g. of potassium hydroxide was treated with acetylene under a gauge pressure of 7–16 atm. during 16 hours at 180–184°. The oily layer was separated from the water layer and distilled. The fraction distilling at 93–120°/2 mm. weighed 35 g. Redistillation gave 19 g. of product distilling at 82–87°/1 mm. (45% yield), n_D^{25} 1.4702. There was recovered 14 g. of unreacted N-methylbutanesulfonamide, b.p. 120–123°/2 mm., n_D^{25} 1.4579.

Anal. Calc'd for $C_7H_{15}NO_2S$: S, 18.1. Found: S, 18.4.

Vinylation of N-ethyltoluenesulfonamide. A mixture of 100 g. of N-ethyltoluenesulfonamide, 4 g. of powdered potassium hydroxide, and 250 ml. of benzene was treated with acetylene under a gauge pressure of 13–17 atm. during 16 hours at 160°. The light tan reaction mixture was filtered, the filtrate was stripped of benzene, and from the residual liquid there was obtained 56 g. of product distilling at 125–139°/1.5 mm., n_D^{25} 1.5430 (50% yield). Most of this material distilled at 133–139°/1.5 mm., n_D^{25} 1.5426.

Anal. Calc'd for $C_{11}H_{15}NO_2S$: C, 58.8; H, 6.7; N, 6.2.
Found: C, 59.0; H, 6.8; N, 6.1.

SUMMARY

N-Vinyl-N-alkyl sulfonamides have been prepared by direct vinylation of the N-monoalkylated sulfonamides with acetylene in yields of 45–85%. The vinylations were carried out in water using potassium hydroxide as catalyst at acetylene pressures of 7–16 atmospheres.

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REFERENCES

(1) REPPE, KRZIKALLA, DORNHEIM, AND SAUERBIER, U. S. Patent No. 2,317,804 (April 27, 1943); REPPE, KRZIKALLA, AND DORNHEIM, German Patent No. 877,757 (May 26, 1953).
(2) DICKEY AND STANIN, U. S. Patent No. 2,475,424 (July 5, 1949).
(3) DIETRICH, U. S. Patent No. 2,236,168 (March 25, 1941).