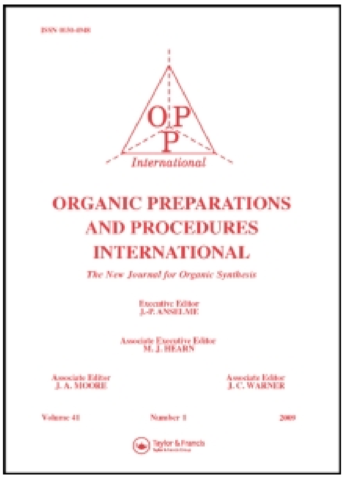

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

ACRYLYLOXYMETHYL METHYL SULFIDES

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To cite this Article Harville, R. L. and Reed Jr., Samuel F.(1969) 'ACRYLYLOXYMETHYL METHYL SULFIDES', Organic Preparations and Procedures International, 1: 4, 239 — 241
To link to this Article: DOI: 10.1080/00304946909458390
URL: http://dx.doi.org/10.1080/00304946909458390

ORGANIC PREPARATIONS AND PROCEDURES 1(4), 239-241 (1969)

ACRYLYLOXYMETHYL METHYL SULFIDES[1]

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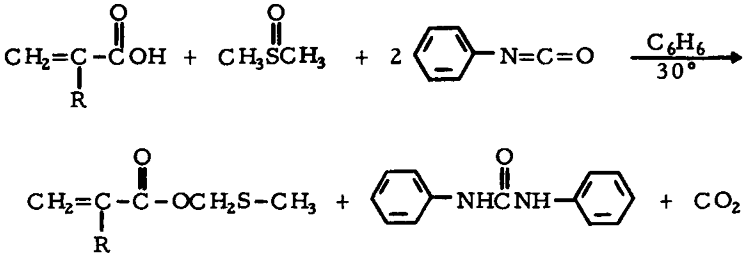

R = H, CH_3

It has been reported by Sorenson[2] that the reaction of benzoic acid with dimethyl sulfoxide in the presence of phenyl isocyanate gave benzoyloxymethyl methyl sulfide and diphenylurea. Both acrylic and methacrylic acids reacted readily with the DMSO-phenyl isocyanate mixture in dry inert solvents (benzene or diethyl ether) with the liberation of carbon dioxide. The reaction temperature was maintained below 30° to prevent the polymerization of products which were isolated by distillation at reduced pressure in the presence of a polymerization inhibitor such as diphenylpicrylhydrazyl.

Acrylyloxymethyl methyl sulfide was extremely sensitive to polymerization and was never obtained in yields greater than 40%. In contrast, methacrylyloxymethyl methyl sulfide was less susceptible to thermal polymerization and was isolated in yields of 60-70%. Distillation of the products[3] was always carried out at temperatures below 50° to insure minimum polymerization. Characterization data consisted of infrared and H^1 n.m.r. spectra and elemental analysis.

Experimental

Methacrylyloxymethyl Methyl Sulfide. - To a 300 ml three-necked flask fitted with mechanical stirrer, thermometer, reflux condenser connected to a gas bubbler, and dropping funnel was introduced 150 ml of dry benzene, 17.2 g (0.2 mole) methacrylic acid, and 15.6 g (0.2 mole) dimethyl sulfoxide. To this mixture was added with stirring 47.2 g (0.4 mole) of phenyl isocyanate over a period of 1 hour. The reaction started immediately as indicated by a rise in temperature and the evolution of CO_2. The flask was cooled so as to maintain the temperature below 30°C. Carbon dioxide was still being liberated after 6 hours and the reaction was continued for a total of 24 hours, during which time diphenylurea precipitated from the mixture. The solid urea was collected by filtration, washed with benzene, and air dried. A total of 40.36 g (96%), m.p., 236-237°C, was obtained.

The benzene solution was washed with saturated sodium bicarbonate solution, with water, and dried over anhydrous magnesium sulfate. After evaporation of the benzene, the liquid residue was distilled under reduced pressure in the presence of a trace of diphenylpicrylhydrazyl as inhibitor to yield 19.44 g (66%) of methacrylyloxymethyl methyl sulfide, b.p., 42° (0.8 mm), η_D^{20} 1.4770. The H^1 n.m.r. spectrum displayed absorption centered at τ 8.08 (m, CH_3-), 7.79 (s, CH_3-S-), 4.85 (s, $-CH_2-S-$) and 3.96 and 4.44 (m, $CH_2=$). Peak area ratios were 3:3:2:2.

Calc'd. for $C_6H_{10}O_2S$: %C, 49.31; %H, 6.85; %S, 21.92.
Found: %C, 49.19; %H, 6.73; %S, 21.98.

Acrylyloxymethyl Methyl Sulfide. - Under similar conditions, a mixture of 150 ml benzene, 14.4 g (0.2 mole) acrylic acid, and 15.6 g (0.2 mole) dimethyl sulfoxide, when treated with 47.6 g (0.4 mole) phenyl isocyanate, gave a 90% yield of diphenylurea and 9.35 g (35%) of acrylyloxymethyl methyl sulfide, b.p., 48° (1 mm), η_D^{20} 1.4744. A considerable portion of this material polymerized during distillation lowering the yield. The H^1 n.m.r. spectrum displayed absorptions centered at τ 7.78 (m, CH_3-S-), 4.93 (s, -CH_2S-), and 3.86 and 4.18 (m, CH_2=CH-). Peak area ratios were 3:2:3.

Calc'd. for $C_5H_8O_2S$: %C, 45.45; %H, 6.06; %S, 24.23.
Found: %C, 45.61; %H, 6.21; %S, 24.11.

References

1. This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama, under Contract DAAH01-67-C-0632.
2. W. R. Sorenson, J. Org. Chem., 24, 968 (1959).
3. Products should be stored at temperatures below 0° to prevent polymerization.

(Received April 22, 1969)