

decomposed on distillation at reduced pressure. The p-nitrosulfones derived from these esters were crystalline and analyzed correctly, showing that the sulfide ester had been obtained.

Two methods were tried in an attempt to prepare pure β -alkylmercaptoethyl p-aminobenzoates. Reduction of the impure p-nitrosulfides was unsuccessful. Chemical reduction with tin or iron in hydrochloric acid led to complexes which were intractable. Low-pressure catalytic reduction using palladium chloride on charcoal resulted in hydrogenolysis of the sulfide linkage, so that ethyl p-aminobenzoate and the alkylmercaptan were obtained. The mercaptans were not isolated, but were evident by their odor and by strong nitroprusside tests. Coupling potassium alkylmercaptides with β -chloroethyl p-aminobenzoate in alcohol solution produced crude oils or low-melting solids which were extremely unstable, and only amorphous products which contained less than the calculated amount of sulfur were obtained.

Treatment of these impure p-aminosulfides with alkyl halides formed crude salts which were also unstable and were not further investigated. It would be of interest to determine whether the sulfide or the amine group coupled preferentially in this reaction.

Experimental

β -Ethylsulfonylethyl p-Nitrobenzoate:

A solution of 40.6 g. (0.38 mole) of β -ethylmercaptoethanol, prepared by the method of Fromm and Jorg (5), and an equimolar amount of p-nitrobenzoyl chloride (75 g.) in ether was shaken, and 35 g. of pyridine was added dropwise. The pyridine hydrochloride which precipitated was removed by filtration, and the ether removed under reduced pressure. The resulting yellow, viscous oil weighed 83 g., equivalent to 85% yield of pure product. A solution of 15 g. (0.06 mole) of the crude p-nitrosulfide was dissolved in 100 ml. of glacial acetic acid, and 40 ml. of 30% hydrogen peroxide added. After standing for 48 hours at room temperature, the solution was diluted with cold water, and the crystals which separated were filtered and dried. After recrystallization from ethanol, 16.6 g. (98%) of glistening white plates which melted at 110-111° were obtained.

Anal: Calcd. for $C_{11}H_{13}O_6NS$; %S, 11.17. Found, %S, 11.33

β -Ethylsulfonylethyl p-Aminobenzoate:

A 10 g. sample (0.035 mole) of β -ethylsulfonylethyl p-nitrobenzoate was dissolved in 150 ml. of ethanol and 0.2 g. of Adams platinum oxide catalyst (6) added to the solution in a pressure bottle. The bottle was placed in a low-pressure hydrogenation apparatus and shaken until a pressure drop of 9 lbs. of hydrogen had occurred. The catalyst was removed by filtration, and the ethanol solution distilled. The amine was obtained by dilution with water, and recrystallized from ethanol-water mixture. It was obtained as white crystals, soluble in acid and melting at 115-116°.

Anal: Calcd. for $C_{11}H_{15}O_4NS$; %S, 12.45. Found; %S, 12.69.

β -n-Butyl sulfonylethyl p-Nitrobenzoate:

Since the reaction of ethylene oxide and butyl mercaptan gave greatly reduced yields of β -n-butylmercaptoethanol, crude β -n-butylmercaptoethyl p-nitrobenzoate was prepared in a different way. A solution of potassium butylmercaptide was prepared by dissolving 4 g. (0.044 mole) of butylmercaptan in 20 ml. of ethanol containing 2.5 g. (0.044 mole) of potassium hydroxide. To this was added a solution of 10 g. (0.044 mole) of β -chloroethyl p-nitrobenzoate (7) in 30 ml. of ethanol. After standing at room temperature for 24 hours, the solution was diluted with water and extracted with ether. After drying, the ether was removed and 8.4 g. (67%) of a yellow oil was obtained. This crude sulfide was oxidized in theoretical yield to the sulfone, which was obtained in white plates, melting at 63-64°.

Anal: Calcd. for $C_{12}H_{17}O_6NS$; %S, 10.16. Found; %S, 9.90.

β -n-Butylsulfonylethyl p-Aminobenzoate:

Catalytic reduction of the purified β -n-butylsulfonylethyl p-nitrobenzoate proceeded smoothly and quantitatively, yielding β -n-butylsulfonylethyl p-aminobenzoate in white crystals which melted at 93-93.5° after purification.

Anal: Calcd. for $C_{13}H_{19}O_4NS$; %S, 11.23. Found; %S, 11.61.

Summary

The p-nitro- and p-aminobenzoates of β -ethylsulfonylethanol and β -n-butylsulfonylethanol have been prepared and characterized. These esters are apparently devoid of local anesthetic action.

Efforts to obtain the corresponding esters of β -ethylmercaptoethanol and β -n-butylmercaptoethanol were not successful.

References

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