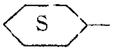
# NOTES

## Esters of 2-Furanacrylic Acid

By Paul D. Bartlett and Sidney D. Ross

In connection with the insect repellent program of the O.S.R.D., it became necessary to prepare a series of esters of 2-furanacrylic acid. Although esters of 2-furanacrylic acid are known, there is no satisfactory general preparative method available. Fischer esterification almost invariably gives low yields and impure products. The most commonly employed methods are the Claisen condensation of furfuraldehyde with the appropriate ester of acetic acid,[1] the alkylation of an alkali metal salt of 2-furanacrylic acid,[2] and treatment of 2-furanacrylyl chloride with an alcohol in benzene.[2] We have found that good yields of esters can be obtained from a variety of alcohols if 2-furanacrylyl chloride is treated with the alcohol in benzene in the presence of excess pyridine. Table I lists the esters prepared, their physical constants, the yields obtained, and the analyses. In cases where the ester is reported in the literature a reference is given.

Table I

| R | B. p. °C. | B. p. Mm. | M. p., °C. | $n_D$ | Yield, % | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3CH_2CH_2$—[2] | 91–94 | 3 | | 1.5392/24 | 86 | | | | |
| $CH_2{=}CHCH_2$—[3] | 131–133 | 16 | | 1.5573/25 | 100 | | | | |
| $CH_3OCH_2CH_2$— | 118–120 | 3 | 33–34 | | 97 | | | | |
| $(CH_3)_2CHCH_2$— | 94–95 | 2 | | 1.5277/24 | 75 | 68.03 | 7.27 | 68.16 | 7.47 |
| $CH_2{=}C(CH_3)CH_2$— | 93.5–94 | 3 | | 1.5500/25 | 90 | 68.73 | 6.30 | 68.12 | 6.43 |
| $CH_3CH_2OCH_2CH_2$— | 124–126 | 3 | | 1.5398/25 | 91 | 62.84 | 6.77 | 62.44 | 6.71 |
| $CH_3CH_2CH_2CH_2CH_2$—[2] | 116.5–118 | 2 | | 1.5289/24 | 88 | 69.22 | 7.75 | 68.67 | 7.93 |
| $(CH_3)_2CHCH_2CH_2$—[1] | 123–124 | 5 | | 1.5253/25 | 92 | | | | |
| $(CH_3CH_2)_2CHCH_2$— | 119–120 | 3 | | 1.5239/25 | 54 | 70.25 | 8.16 | 70.45 | 8.18 |
|  | 121–124 | 3 | 52–53 | | 80 | 70.90 | 7.33 | 71.55 | 7.58 |
| $C_6H_5CH_2$—[2] | 131–132 | 3 | 42–43 | | 86 | | | | |
| $C_6H_5CH_2CH_2$— | 155–156 | 3 | | 1.5872/25 | 72 | 74.36 | 5.82 | 74.01 | 6.03 |

### Experimental

2-Furanacrylic acid was prepared by the method of Dutt.[4] A more satisfactory procedure has since been reported by Rajagopalan and Raman.[5]

2-Furanacrylyl chloride was prepared by the method of Sasahi.[6] The product boils at 126° at 30 mm. Yields as high as 87% can be obtained by avoiding local superheating during the distillation.

The preparation of the esters can be illustrated by the procedure used to prepare the allyl ester. 2-Furanacrylyl chloride (403 g., 2.33 moles) was dissolved in 600 cc. of benzene in a three-necked flask, fitted with a mercury sealed stirrer, a condenser, and a dropping funnel. Pyridine (395 g., 5 moles) was added with stirring. Allyl alcohol (232 g., 4 moles) in 600 cc. of benzene was then added dropwise. After the addition the reaction mixture was heated for two hours on the steam-bath with stirring. The reaction mixture was cooled and poured into a large volume of water. The benzene layer was separated, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The benzene was removed *in vacuo* and the product was distilled. The yield was 415 g. (100%), b. p. 131–133 (16); $n^{25}_D$ 1.5573.

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(1) Posner, *J. prakt. Chem.*, **82**, 425 (1910), Schimmel and Co. Reports 225 (1929).

(2) Gilman and Wright, *Iowa State College J. Sci.*, **3**, 109 (1929).

(3) Bliche, *Ber.*, **47**, 1353 (1914).

(4) Dutt, *J. Indian Chem. Soc.*, **1**, 297 (1925).

(5) Rajagopalan and Raman, *Org. Syn.*, **25**, 51 (1945).

(6) Sasahi, *Biochem. Z.*, **25**, 272 (1910).

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## Urea Alkyl Sulfates

By C. L. Carter and P. A. Ongley

In an attempt to prepare alkyl isoureas by the alkylation of urea using the reaction products of alcohols and either sulfuryl chloride or chlorosulfonic acid, it was found that the main product of the reaction in either case was not alkyl isourea but urea alkyl sulfate, $[CO(NH)_2H]^+RSO_4^-$. As these salts apparently are not recorded in the literature, a number of them have been prepared and their properties studied.

### Experimental

The urea alkyl sulfates were prepared by adding dropwise to one mole of sulfuryl chloride in a beaker cooled with ice slightly more than two moles of the required alcohol. One mole of urea was then stirred in with continued

Table I

Urea Alkyl Sulfates

| Alkyl | Formula | Neutralization equivalent Calcd. | Found |
|---|---|---|---|
| Methyl | $C_2H_8O_5N_2S$ | 172 | 175 |
| Ethyl[a] | $C_3H_{10}O_5N_2S$ | 186 | 186 |
| *i*-Propyl | $C_4H_{12}O_5N_2S$ | 200 | 196 |
| *n*-Butyl | $C_5H_{14}O_5N_2S$ | 214 | 213 |
| *s*-Butyl | $C_5H_{14}O_5N_2S$ | 214 | 210 |

[a] This salt recrystallized gave a constant m. p. of 126°. It yielded a picrate m. p. 252–255° (with charring) and a nitrate m. p. 158°.