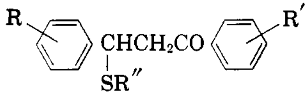
TABLE I

BASIC KETOSULFIDES



R	R′	R″	M.p., °C.	Yield, %	Formula	Nitrogen Calc'd	Nitrogen Found
H	H	$(C_2H_5)_2NCH_2CH_2$	113–115	92	$C_{21}H_{28}ClNOS^a$	3.71	3.67
H	H	$(C_2H_5)_2NCH_2CH_2CH_2$	112–113	—	$C_{23}H_{32}INOS^b$	2.82	2.90
p-$(CH_3)_2N$	*p*-CH_3O	$(C_2H_5)_2NCH_2CH_2$	145–146	88	$C_{24}H_{35}ClN_2O_2S^a$	6.22	6.28
p-$(CH_3)_2N$	*p*-Cl	$(C_2H_5)_2NCH_2CH_2$	142–143	71	$C_{23}H_{32}Cl_2N_2OS^a$	6.16	6.14
p-$(CH_3)_2N$	*p*-CH_3CONH	$(C_2H_5)_2NCH_2CH_2$	153–154	87	$C_{25}H_{36}ClN_3O_2S^a$	8.80	8.75
o-Cl	*p*-CH_3CONH	*p*-C_7H_7	148–149	85	$C_{24}H_{22}ClNO_2S$	3.32	3.57
p-CH_3O	*p*-CH_3CONH	*p*-C_7H_7	130–131	91	$C_{25}H_{25}NO_3S$	3.34	3.35

[a] Purified as the hydrochloride. [b] Methiodide.

cone,[3d] and 4-dimethylamino-4′-chlorochalcone[3e] have been reported.

The ketosulfides. The compounds listed in Table I were prepared by the following general procedure. Molar equivalents of the mercaptan and chalcone were refluxed for some hours (8–30) in absolute ethanol. The solution was concentrated, and the crystalline mass was filtered and washed with ethyl acetate. The basic ketosulfides could be recrystallized from ethanol, but the excess solvent had to be removed immediately upon isolating the product. If not, the crystals acquired a dark brown color on exposure to the air. Washing with ethyl acetate or petroleum ether gave a pure product.

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β-Ethylacrylamide

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The preparation and dehydration of β-ethylacrylamide to β-ethylacrylonitrile has been reported recently.[1] This potentially useful synthesis, however, falls short in one important respect, namely—low yields of β-ethylacrylamide. The need for relatively large quantities of β-ethylacrylonitrile as an intermediate in certain synthetic studies led us to reëxamine the condensation of malonmonoamide with propionaldehyde.

It is well known that the Knoevenagel reaction is reversible and, at the elevated temperatures often used, the water formed in the reaction can effect hydrolysis of the condensation product. Moreover, a not uncommon competing reaction is the removal of the reacting aldehyde through self-condensation (aldol).[2] Since the low boiling point of propionaldehyde precluded using continuous distillation as a means of water removal, it was thought that the gross reaction equilibrium might be favorably displaced by employing a larger proportion of propionaldehyde (which incidentally is more accessible than the other reactant, malonmonoamide). The use of an excess of aldehyde should also compensate for aldol losses.

It has been found that the yield of β-ethylacrylamide can be increased nearly four-fold by condensing malonmonoamide with 2 moles of propionaldehyde instead of with 0.5 mole as heretofore reported.

EXPERIMENTAL

To a mixture of 103 g. (1 mole) of malonmonoamide,[3] 100 ml. of dry pyridine, 2 ml. of piperidine, and 0.5 ml. of glacial acetic acid was added 116 g. (2 moles) of freshly distilled propionaldehyde and the system was heated under reflux (oil-bath at 80–82°) for 24 hours. As much pyridine as possible was distilled off (water pump) at 80°, and the cooled residue was triturated with alcohol-free ether and collected by filtration. After a second ether treatment, and air-drying, there remained 47.1 g. of practically colorless crystals, m.p. 150° (softening at 145°). Recrystallization from acetone afforded 42 g. (in two crops) of colorless plates, m.p. 151.5–153°. This represents a yield of 42.5% of *pure* material (based on malonmonoamide) as compared with 11.5% reported earlier.[1] A sample, sublimed at 120–130°/0.5 mm., melted at 152.5–154° (uncorr.), (lit.,[1,4] 148°, 152°).

Anal. Calc'd for C_5H_9NO: C, 60.6; H, 9.15. Found: C, 60.8; H, 9.14.

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[4] J. Seib, *Ber.*, **60**, 1390 (1927).