# PREPARATION OF PHLOROGLUCINOL TRIMETHYL ETHER*

By J. W. CLARK-LEWIS†

Preparation of alkyl ethers from phloroglucinol and alkyl halides or sulphates is complicated by formation of *C*-alkyl derivatives due to keto-enol tautomerism of the phenol. However, a further consequence of this tautomerism is that dialkyl ethers can be obtained from phloroglucinol and alcohols under conditions resembling Fischer-Speier esterification of acids. The dimethyl ether, prepared in this way by Weidel and Pollak (1900) and by Pratt and Robinson (1924), can then be methylated without difficulty to phloroglucinol trimethyl ether (Freudenberg 1920); Touchstone, Ashmore, and Huffman (1956) recently described various other trialkyl ethers obtained from phloroglucinol by this two-stage method. Bredereck, Hennig, and Rau (1953) have reported the first satisfactory preparation of phloroglucinol trimethyl ether (93 per cent.) directly from phloroglucinol, with inhibition of *C*-alkylation by maintaining pH 8–9 throughout the methylation by gradually adding aqueous sodium hydroxide. An experimentally simpler and more convenient alternative is the methylation of anhydrous phloroglucinol by the standard anhydrous acetone–potassium carbonate technique as described below.

*Experimental*

Anhydrous potassium carbonate (130 g; 4 equiv) was added to a solution of anhydrous phloroglucinol (30 g) in dried ($K_2CO_3$) acetone (300 c.c.), and the mechanically stirred suspension was warmed almost to the reflux temperature before adding four quantities ($3 \times 22 \cdot 5$ and $1 \times 10$ c.c.) of freshly washed and dried ($MgSO_4$) dimethyl sulphate (total 77·5 c.c.; 3·5 equiv) at intervals of 15 min. Heating was discontinued after 3 hr (total), and the suspension was stirred for a further 1 hr after the addition of water (300 c.c.) and aqueous ammonia (*d* 0·88; 25 c.c.); water was then added to dissolve salts and the solution was extracted with ether. The ether extract was washed once with dilute hydrochloric acid, three times with aqueous sodium hydroxide, and finally with water before evaporation of the solvent. The residue was distilled at the water-pump and the pale yellow distillate solidified (34·1 g, 85%), m.p. 45–48·5 °C; recrystallization from methanol (30 c.c.) at 0 °C gave phloroglucinol trimethyl ether in colourless prisms (24·8 g, 62%), m.p. 52–53 °C (Found: C, 64·1; H, 7·1; OMe, 55·1%. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·2; OMe, 55·4%), and a further quantity (2·2 g, total 27 g, 67·5%) was obtained from the mother liquors. In a similar experiment the anhydrous acetone solution of methylated product was filtered from inorganic salts, and the filtrate was concentrated by evaporation before being shaken with dilute aqueous sodium hydroxide and ammonia solution until the product (34 g, 85%) solidified (m.p. 42–46 °C); recrystallization from methanol (charcoal) gave colourless prisms of phloroglucinol trimethyl ether, m.p. 52–53 °C.

* Manuscript received May 22, 1957.

† Department of Organic Chemistry, University of Adelaide.

*References*

BREDERECK, H., HENNIG, I., and RAU, W. (1953).—*Chem. Ber.* **86**: 1085.
FREUDENBERG, K. (1920).—*Ber. dtsch. chem. Ges.* **53**: 1425.
PRATT, D. D., and ROBINSON, R. (1924).—*J. Chem. Soc.* **125**: 193.
TOUCHSTONE, J. C., ASHMORE, J., and HUFFMAN, M. N. (1956).—*J. Amer. Chem. Soc.* **78**: 5643.
WEIDEL, H., and POLLAK, J. (1900).—*Mh. Chem.* **21**: 22.