On cooling, needle crystals separated which, after recrystallization from alcohol, gave 0.5 g. of light cream-colored needles which melted at 223°. The analytical data were satisfactory for the monofurfuryl ether of the diol.

*Anal.* Subs., 0.1886: $CO_2$, 0.5763; $H_2O$, 0.0928. Calcd. for $C_{31}H_{24}O_3$: C, 83.8; H, 5.41. Found: C, 83.4; H, 5.47.

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## Note on the Preparation of Trialkyl Phosphates and their Use as Alkylating Agents

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Alkyl halides, sulfates, sulfites and sulfonates appear to be the best general alkylating agents known but because none of these classes of compounds is entirely satisfactory, it was considered desirable to investigate the use of other esters for this purpose. Preliminary experiments indicated that the alkyl borates, carbonates, nitrites and phosphites would be of no value, but the trialkyl phosphates showed some promise and were further investigated.

None of the various methods for preparing alkyl phosphates reported in the literature[1] proved as convenient as the reaction of phosphorus oxychloride with the alcohol in the presence of pyridine. This method is an adaptation of that used by Milobendski and Sachnovski[2] for the preparation of alkyl phosphites, in which benzene has been used as a solvent instead of ether and in which the pyridine hydrochloride is removed by adding water and removing the water layer instead of filtering off the solid pyridine hydrochloride.

In order to compare the various esters as alkylating agents a standard procedure was developed using one equivalent of alkylating agent per mole of phenol. This method was not devised for producing the maximum yiel

TABLE I

YIELDS OF PHOSPHATES AND PHENOL ETHERS

| Ester | Phosphates | | Phenol Ethers | |
|---|---|---|---|---|
| | % Yield | B. p., °C. | % Yield | B. p., °C. |
| Ethyl sulfate | . . | . . . . . . . . . . . . . . . . | 73.0 | 168–170 |
| Ethyl phosphate | 51.7 | 104–107 (16 mm.) | 21.6 | 167–170 |
| *n*-Propyl phosphate | 63.5 | 128–134 (15 mm.) | Not run | |
| *n*-Butyl phosphate | 74.0 | 160–162 (15 mm.) | 39.0 | 204–211 |
| *Sec.*-butyl phosphate | 44.0 | 119–129 (8–12 mm.) | 18.7 | 188–198 |
| *n*-Amyl phosphate | 63.7 | 158–163 (6 mm.) | 15.0 | 125–128 (25 mm.) |

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[1] (a) Evans, Davis and Jones, *J. Chem. Soc.*, 1310 (1930); (b) Bannister, U. S. Patent 1,799,349 (1931); (c) Johnson, British Patent 330,228 (1930).

[2] Milobendski and Sachnovski, *Chemik Polski*, **15**, 34 (1917), [*Chem. Abs.*, **13**, 2865 (1919)].

of ether but for ease of controlling conditions so that the results would be comparable. This accounts for the fact that the yield of phenetole using ethyl sulfate is not as high as that reported by Cade.[3] The yields of phosphates and phenol ethers are given in Table I.

It should be noted that while the yields of phenol ethers from phosphates are low compared with that from the sulfate, they are based on the amount of alkyl radical available. Many of the higher yields from other esters reported in the literature are based on the substance being alkylated, using a large excess of alkylating agent.

[3] Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

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# COMMUNICATIONS TO THE EDITOR

## PREPARATION OF KETENE DIETHYL ACETAL

*Sir:*

According to the communication of Snell and McElvain [THIS JOURNAL, **55**, 416 (1933)] these authors were unable to duplicate the preparation of ketene diethyl acetal described by me [Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 28 (1927)]. This preparation, however, has often been accomplished in my laboratory by several young chemists. The above failure may have been due to two causes. (1) The residue obtained from sodium ethoxide and ethyl acetate after removal of the volatile substances, containing the so-called "primary reaction product of the acetoacetic ester synthesis," may have lost alcohol during the treatment and been transformed into the sodium derivative of acetoacetic ester which, treated with water, of course did not give ketene acetal [Scheibler and Marhenkel, *Ann.*, **458**, 6, 18 (1927)].

The evaporation of ether and the excess ester must be performed quickly at low temperature under diminished pressure. It is not surprising that Snell and McElvain, who dried the residue in a vacuum desiccator over sulfuric acid until it attained a constant weight, only obtained sodioacetoacetic ester. The weight of the dry residue obtained by them from 23 g. of sodium was only 90–100 g. instead of 125 g. A small amount of ethyl acetate may remain in the residue and be quickly saponified when it is treated with water, in contrast with ketene acetal, which does not undergo any decomposition in aqueous alkaline solution.

(2) The authors may have used too much calcium chloride in shaking