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).

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

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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

the ether solution for three or four hours with three successive portions of powdered calcium chloride. I only employed a quantity just sufficient to fix the alcohol which was mixed with ketene acetal. When being shaken in this way ketene acetal is held by the great surplus of solid calcium chloride, which is not the case when a concentrated aqueous solution of calcium chloride is used. The separation of alcohol is better performed in such a manner. The directions given by me should be changed as follows.

After drying with anhydrous sodium sulfate, the ethereal solution from the extraction of the "primary reaction product" triturated with water, is distilled through a fractionating column. The residue containing ether only in a little amount is shaken intermittently during six hours with four parts of saturated aqueous solution of calcium chloride. Then it is extracted with ether in a continuous extraction apparatus and the resulting solution is dried with anhydrous sodium sulfate. Observing the precautionary measures mentioned before, ether and finally ketene acetal are distilled; yield, 13 g. or 11.2% of the calculated amount based on 23 g. of sodium used.

The preparation of dimethyl ketene diethyl acetal from ethyl isobutyrate was not successful with sodium ethoxide. It was performed in another manner which will be described later.

TECHNISCHE HOCHSCHULE OF BERLIN
LABORATORY OF ORGANIC CHEMISTRY
BERLIN-LICHTERFELDE, GERMANY
HELMUTH SCHEIBLER

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KINETICS OF THE MERCURY SENSITIZED REACTION BETWEEN HYDROGEN AND OXYGEN

Sir:

Investigations of the mercury sensitized photo-reaction between hydrogen and oxygen have given rise to a large number of conflicting and unconnected data. These have been used to set up mutually conflicting theories of the mechanism of the reaction of hydrogen atoms with oxygen. It can, however, be demonstrated that almost all the known facts can be correlated and be completely in accord if we assume as the true mechanism:

$$\begin{array}{rcll}
Hg + h\nu & \longrightarrow & Hg' & I\ \mathrm{abs} \\
Hg' + H_2 & \longrightarrow & 2H + Hg & k_{H_2} \\
Hg' + O_2 & \longrightarrow & O_2' + Hg & k_{O_2} \\
H + O_2 & \longrightarrow & HO_2 & k_1 \\
HO_2 + H_2 & \longrightarrow & H_2O_2 + H & k_2 \\
HO_2 + HO_2 & \longrightarrow & H_2O_2 + O_2 & k_3
\end{array}$$

These give the kinetic expression

$$\frac{d\,[H_2O_2]}{dt} = \frac{k_2\,[H_2]}{\sqrt{k_3}}\sqrt{\frac{[H_2]\,k_{H_2}\,I\ \mathrm{abs}}{[H_2]\,k_{H_2} + [O_2]\,k_{O_2}}} + \frac{[H_2]\,kH_2\,I\ \mathrm{abs}}{[H_2]\,k_{H2} + [O_2]\,k_{O_2}}$$