ether (b.p. 70°) solution. The effluent gave 6.2 g. of V, m.p. 115–119°, containing solvent of crystallization. Evacuation for 5 days gave 5.2 g. (99%) of V, a new compound, m.p. 119–120°. After recrystallization from ethanol the melting point remained at 119.0–119.5°. A second run gave the same results.

*Anal.* Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.72.

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## Reaction of Triphenylsilylpotassium with Formaldehyde

BY HENRY GILMAN AND T. C. WU

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It is generally known that an organometallic compound adds to the carbonyl group of an aldehyde or ketone to give the carbinol derivatives. Recently, however, it has been observed that when triphenylsilylpotassium is treated with benzophenone, followed by hydrolysis, the product obtained is a substituted alkoxysilane rather than the carbinol which one normally would expect.[1] In an extension of these studies to the addition reactions of triphenylsilylpotassium to a carbonyl group, we examined the reaction of triphenylsilylpotassium with formaldehyde. When a triphenylsilylpotassium suspension in ether was treated with formaldehyde for a period of one hour, a small amount of hydroxymethyltriphenylsilane was formed in addition to other products to be reported later.

$$(C_6H_5)_3SiK + C_6H_5COC_6H_5 \xrightarrow{(H_2O)} (C_6H_5)_3SiOCH(C_6H_5)_2$$

$$(C_6H_5)_3SiK + HCHO \xrightarrow{(H_2O)} (C_6H_5)_3SiCH_2OH$$

In this reaction triphenylsilylpotassium reacts with formaldehyde in the same way as does triphenylmethylsodium. In the latter case β,β,β-triphenylethanol is formed.[2]

### Experimental

A triphenylsilylpotassium suspension in ether was prepared by cleaving 0.01 mole of hexaphenyldisilane with sodium–potassium alloy, the excess of which was removed by the amalgamation procedure.[3] Formaldehyde gas, generated by heating paraformaldehyde,[4] was introduced over the surface of the stirred triphenylsilylpotassium suspension by a stream of dry nitrogen. It was observed that the brown color of the triphenylsilylpotassium suspension turned gray rapidly when the formaldehyde gas was introduced. After 1 hour the gray mixture gave a negative Color Test I.[5] The reaction mixture was allowed to stand overnight. Ethanol was added to the reaction product and the mixture was heated and filtered hot. On standing, 0.3 g. of paraformaldehyde separated. This apparently came from the recombination of the formaldehyde. The ethanol was distilled from the mother liquor, and a mixture of water and ether was added to extract the residue. From the ethereal solution there was obtained a gummy residue. Two recrystallizations from petroleum ether (b.p. 60–70°) yielded 0.7 g. (12%) of colorless crystals melting at 116–118° (uncor.). This compound has the characteristic absorption band of a hydroxyl group, but not that of an Si–O bond,[6] which would have been expected if addition had occurred in the manner of addition of triphenylsilylpotassium to benzophenone.[1]

*Anal.* Calcd. for $C_{19}H_{18}OSi$: C, 78.57; H, 6.24. Found: C, 78.67, 78.73; H, 6.31, 6.27.

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## On the Periodic Acid Oxidation of Diethanolamine

BY MANNING A. SMITH AND B. R. WILLEFORD, JR.

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It has been reported by Nicolet and Shinn[1] that diethanolamine is oxidized by periodic acid to yield four moles of formic acid. The product to be expected from this reaction is formaldehyde as indicated by the equation

$$HOCH_2CH_2NHCH_2CH_2OH + 2HIO_4 \longrightarrow 4H_2CO + 2HIO_3 + NH_3$$

This work has been repeated in connection with another study,[2] and the consumption of two moles of periodic acid per mole of diethanolamine has been confirmed. The presence of formaldehyde in the reaction mixture has been established by the precipitation of its dimedon derivative. The error in the identification of the reaction product mentioned above has been carried over in the review of periodic acid oxidations by Jackson.[3] Shupe[4] has reported that "tests have failed to confirm the literature statement that diethanolamine yields 4 mols of formic acid," but apparently did not identify the product. The abstract of this paper[5] contains conflicting statements concerning Shupe's work with diethanolamine, undoubtedly because of a typographical error. In view of this confusion in the literature, we feel that it is desirable to call attention to it here.

### Experimental

Ten ml. of 0.1078 *M* periodic acid solution was added to 48.4 mg. (0.461 mmole) of diethanolamine. The reaction mixture was heated on a steam-bath for 2.5 hours. After cooling, solid sodium bicarbonate (0.1–0.5 g.) was added followed by an excess of standard arsenite solution and 2 ml. of 20% potassium iodide. The solution was allowed to stand for 10 minutes, and the excess arsenite was then titrated with standard iodine solution. This is the standard procedure for the determination of periodic acid described by Jackson.[6] A consumption of 0.909 mmole of periodate by the diethanolamine was indicated. This gives a ratio of moles of periodate consumed per mole of diethanolamine of 0.909/0.461 or 1.98.

Another sample of diethanolamine (0.1059 g.) was treated with periodic acid according to the procedure of Reeves,[7] and the formaldehyde formed was precipitated as its dimedon derivative. The white crystalline solid had a melting point of 191°. The melting point showed no depression on mixing with an authentic sample. The yield was 0.9930 g. This corresponds to 84% of the theoretical amount.

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