lization from ligroin the product melted at 91–92°. Mixed melting point with an authentic sample of α-benzyllactic acid (m.p. 98°) was depressed to 67–68°.

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Zinc Complex of Toluene-3,4-dithiol as a Reagent for Ketose Sugars

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Aliphatic and aromatic aldehydes and ketones react readily with 1,2-dimercapto compounds to form cyclic derivatives which are often intensely colored or easily oxidized to intensely colored compounds. Thus 1,2-dimercaptobenzene, I, condenses with benzaldehyde to give II which, in turn, is easily oxidized to salts of the cation III.[2] Similarly, 1,2-dimercaptoethane is a well recognized reagent for ketones.[3,4] In view of these facts it might be expected that the commercially available toluene-3,4-dithiol ("dithiol"), IV, would likewise afford a useful reagent for aldehydes and ketones.[5]

The poor keeping qualities of dithiol make it a difficult reagent to use. Recently, however, it has been found that its colorless zinc derivative, "zinc dithiol," V (or possibly VI), is surprisingly stable.[6] This is now available[1] as a very bulky pure white powder, the marked non-wettability of which appears to protect it from attack even on considerable exposure to acid vapors. It can generally be used in place of free dithiol and has application in the testing for trace quantities of numerous cations.[7]

It has been found that most common aldehydes do in fact react to give yellow colorations, or oily precipitates, when warmed with zinc dithiol in acid solution. Of immediate interest, however, is a reaction which occurs with sugars. When fructose or sorbose in dilute hydrochloric acid solution is heated to boiling with zinc dithiol a strong yellow color begins to develop within a few seconds and, after about 60 seconds, an oily yellow or orange precipitate separates. With sucrose a similar color develops, but much more slowly, doubtless owing to hydrolysis with formation of fructose. Among the sugars it appears that the reaction is given only by ketoses. In 4*N* hydrochloric acid none of the following available sugars or related compounds was found to give a reaction: arabinose, citric acid, galactose, glucose, inositol, lactose, mannitol, mannose, raffinose,[8] rhamnose, tartaric acid, xylose. Furfural gave a pale yellow color, much less intense than that given by the ketoses. In 2*N* acid the same distinction was observed, but the rate of development of color with fructose and sorbose was rather slow.

The reaction affords a quick and easy method by means of which ketoses may be immediately distinguished from aldoses. For example, fructose may be distinguished from glucose, or may be detected in the presence of the latter. The test is easily applied to qualitative work since neither the exact concentration of the acid nor the relative proportions of the reactants are critical. Since, under the conditions of the experiment, dithiol does not combine with such sugars as glucose, and since the excess of dithiol present may readily be titrated with mercuric chloride in presence of pyridine with a trace of a cobalt salt as indicator,[6] it appears that the reaction could be adapted to the quantitative estimation of ketoses.

This method was compared with others previously described for the detection of ketose sugars (8, 9). Although the anthrone reagent of Johanson is effective for developing chromatograms, and in spot test analysis, for qualitative identification in solution it was found to be inferior to dithiol. For example, addition of anthrone reagent to a dilute solution of fructose required three minutes for the color to develop, whereas less than 25 seconds was required for a strong yellow coloration employing the zinc complex of IV. The final color intensity and the sensitivity appeared to be of the same order of magnitude for both methods.

EXPERIMENTAL

General procedure for sugar analysis. To 0.25 ml. of dilute hydrochloric acid[10] was added 0.3–0.5 mg. (or more) of the sugar to be tested together with approximately the same amount of zinc dithiol. The mixture was heated to boiling, with shaking, and held at the boiling point for 30–60 sec. In presence of a ketose the liquid begins to become yellow within a few seconds, with deposition of a yellow or orange-yellow precipitate within 0.5–2.0 min., depending upon the concentration. With sucrose the color develops more slowly but is easily visible within 30–60 sec. The precipitate is readily visible when formed in a 0.2% fructose solution.

Comparison of anthrone with zinc dithiol in detection of fructose. Anthrone reagent was prepared by the method of Johanson.[9] Three min. was required for color to develop when fructose (1.0 mg.) was added to 0.25 ml. of reagent. Using zinc dithiol a strong yellow color developed within 25 sec. in presence of 0.5 mg. fructose. The final color intensities and sensitivities appeared to be comparable for both rea-

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(1) Reprints of this article, diacetyl-3,4-dithiol, dibenzoyl-3,4-dithiol, and the zinc complex of toluene-3,4-dithiol are available from Dr. Roy G. Neville, 783 Cereza Drive, Palo Alto, Calif.

(2) W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 534 (1927).

(3) H. Hauptmann, *J. Am. Chem. Soc.*, **69**, 562 (1947).

(4) L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(5) W. H. Mills and R. E. D. Clark, *J. Chem. Soc.*, 175 (1936).

(6) R. E. D. Clark, *Analyst*, **82**, 182 (1957).

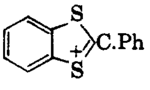
(7) R. E. D. Clark, *Analyst*, **61**, 242 (1936); **82**, 177, 760 (1957); **83**, 103, 396, 431 (1958).

(8) H. W. Rabin, *J. Am. Chem. Soc.*, **55**, 2603 (1933); **59**, 1402 (1937).

(9) R. Johanson, *Nature*, **172**, 956 (1953).

(10) One volume of concentrated hydrochloric acid diluted with 2 vol. of water.

gents. The solid sugar is required when using anthrone as this reagent must be employed in the presence of very little water. With zinc dithiol an aqueous solution of the sugar may be used.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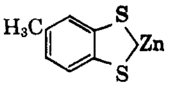
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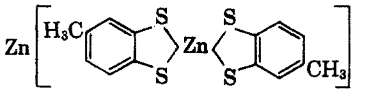
VI

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Synthesis of 4-Acetylphenylmethylsilanes Using 2-(4-Bromophenyl)-2-methyl-1,3-dioxolane

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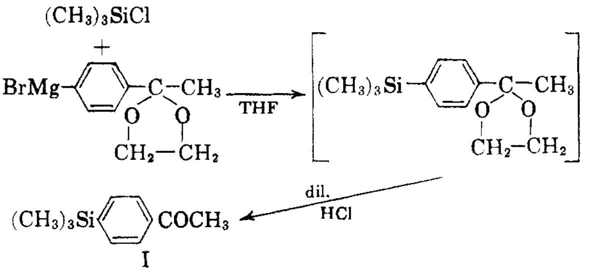
When acylation of trimethylphenylsilane is conducted under the usual Friedel-Crafts conditions the aryl-silicon bond is cleaved by the aluminum chloride used as catalyst.[2,3] This fact has limited the availability of 4-trimethylsilylacetophenone (I), and similar acetyl compounds of silicon.

Recently, Szmant and Skendrovich[4] obtained approximately 35% yields of I using a modification of the Friedel-Crafts reaction in which trimethylphenylsilane is treated with acetyl fluoride in chloroform saturated with boron trifluoride. Apart from the low yield, the method is disadvantageous in that acetyl fluoride boils at room temperature and requires special care in handling to achieve the maximum reaction.

Continuing our work on organosilanes,[5] in this paper we wish to report that yields of I approximating 80% may be obtained by avoiding a Friedel-Crafts reaction. The Grignard reaction of the ethylene ketal of 4-bromoacetophenone, *i.e.*, 2-(4-bromophenyl) - 2 - methyl - 1,3 - dioxolane, with trimethylchlorosilane produces I in excellent yield. In addition to the high over-all yield this method offers the advantage that the acetyl substituent is in a known position. The possibility of isomeric contaminants, as in the Friedel-Crafts procedure, is thereby eliminated. The reaction occurs smoothly in tetrahydrofuran, but attempts to form the Grignard reagent of the ketal in diethyl ether were unsuccessful.



The method has been extended to the preparation of the new compound di(4-acetylphenyl)dimethylsilane[6] in 50–60% yield. New derivatives of these compounds have also been prepared and are reported here.

EXPERIMENTAL

2-(4-Bromophenyl)-2-methyl-1,3-dioxolane (II). In a 3-l. flask, fitted with a Dean-Stark trap and reflux condenser, were placed 4-bromoacetophenone[7] (300 g., 1.5 moles), anhydrous ethylene glycol (93 g., 1.5 moles), 4-toluenesulfonic acid (1.2 g.), and anhydrous benzene (1500 ml.). The mixture was heated at brisk reflux until no more water distilled (20–25 hr.). Sodium acetate (1.2 g.) was added and the mixture stirred or shaken for 30 min., then filtered. The filtrate was washed thoroughly with water and dried over anhydrous sodium sulfate, and the benzene was distilled off at atmospheric pressure. The ketal was obtained as 300 g. (82%) of a colorless liquid, b.p. 175–180°/20–30 mm., which crystallized on standing in the receiver, m.p. 44–45°.[8] The infrared spectrum of the freshly prepared compound has a doublet at 1038 and 1078 cm.$^{-1}$ (C—O of a ketal) with no absorption in the carbonyl region.[9]

Anal. Calcd. for $C_{10}H_{11}BrO_2$: C, 49.34; H, 4.56; Br, 32.87. Found: C, 49.10; H, 4.51; Br, 32.90.

Hydrolysis of the ketal in the standard manner yielded 4-bromoacetophenone, m.p. 50°, which was characterized by its phenylhydrazone, m.p. 125°.[10]

4-Trimethylsilylacetophenone (I). Magnesium turnings (40 g., 1.65 g. atom), methyl iodide (5 ml.), and sodium-dried tetrahydrofuran (THF, 600 ml.), were placed in a 5-liter flask fitted with reflux condenser, motor-driven stirrer, thermometer, and dropping funnel. The mixture was heated at gentle reflux on the water bath and, after the methylmagnesium iodide had formed, a solution of the ketal (II) (334 g., 1.38 moles) dissolved in anhydrous THF (400 ml.) was run in, dropwise, during a period of about one hour. Gentle reflux was maintained for a further hour, then trimethylchlorosilane (150 g., 1.38 moles) was added with stirring to the solution cooled to 40°. After refluxing for an hour the mixture was allowed to cool overnight then 2 l. of water (containing 100 ml. of concentrated hydrochloric acid) was added to dissolve the crystalline magnesium salts. The lower aqueous layer was separated and the yellow oil was first washed several times with saturated calcium chloride

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[1] (1) For reprints: 783 Cereza Drive, Palo Alto, Calif.

[2] (2) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931).

[3] (3) The phenyl-silicon bond of trimethylphenylsilane is also cleaved by bromine. See R. A. Benkeser and A. Torkelson, *J. Am. Chem. Soc.*, **76**, 1252 (1954).

[4] (4) H. H. Szmant and S. Skendrovich, *J. Am. Chem. Soc.*, **76**, 2282 (1954).

[5] (5) R. G. Neville, *J. Org. Chem.*, **23**, 937 (1958).

[6] (6) Other acetylphenylsilanes are currently being synthesized in these laboratories.

[7] (7) R. Adams and C. R. Noller, *Org. Syntheses*, Coll. Vol. I, 2nd edition, 109 (1951).

[8] (8) All melting points are uncorrected.

[9] (9) H. O. House and J. W. Blaker, *J. Org. Chem.*, **23**, 335 (1958).

[10] (10) A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 743.