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Alkylation of Triphenylsilyllithium with Trialkyl Phosphates

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High yields of methyl-, *n*-butyl- and isobutyltriphenylsilane were obtained from the equimolar reactions of triphenylsilyllithium with the respective trialkyl phosphates. The 3:1 reaction of triphenylsilyllithium with tri-*n*-butyl phosphate gave *n*-butyltriphenylsilane, hexaphenyldisilane, hexaphenyldisiloxane, 4-triphenylsilylbutanol and triphenylsilanol when forced conditions were employed. A possible mechanism for the formation of these products has been proposed.

In 1915 Michaelis and Wegner,[1] while attempting to prepare the phenyl ester of diphenylphosphinic acid *via* the reaction of phenyl dichlorophosphinate with phenylmagnesium bromide, obtained an unspecified yield of triphenylphosphine oxide. Not only were the chlorine atoms displaced by the Grignard reagent, but the phenoxide group as well. Similar displacements of —O—R groupings from triphenyl phosphite, triphenyl phosphate, and tri-*p*-cresyl phosphate by phenylmagnesium bromide have also been observed.[2]

The reaction, however, is not limited to aryl esters of this type, but appears to be quite general for compounds having either alkyl or aryl groups attached through oxygen to phosphorus. To illustrate, trialkyl phosphates,[3,4] trialkyl phosphites,[3-6] dialkyl phosphites,[4,7-11] alkyl,[12,13] and aryl[5] phosphonates and phosphorochloridates,[4,14,15] have all been found to undergo similar displacements when treated with organometallic compounds.

Triphenylsilyllithium, on the other hand, reacted with tri-*n*-butyl phosphate in tetrahydrofuran to give an 83.5% yield of *n*-butyltriphenylsilane, the alkylation product[16]:

$$(C_6H_5)_3SiLi + (n\text{-}C_4H_9O)_3PO \longrightarrow (C_6H_5)_3SiC_4H_9\text{-}n + (n\text{-}C_4H_9O)_2P(O)OLi$$

Alkylation reactions involving alkyl sulfates and sulfonates with Grignard reagents are well known[17]; however, this type of reaction has not been observed for alkyl esters of acids containing phosphorus as the central element, except for the reaction involving triphenylsilyllithium and tri-*n*-butyl phosphate.[16] This study describes further investigation of the scope and limitations of this alkylation reaction.

It was found that triphenylsilyllithium reacts smoothly and promptly with trimethyl, tri-*n*-butyl, and triisobutyl phosphate in a 1:1 mole ratio to give methyl-, *n*-butyl-, and isobutyltriphenylsilane in yields of 88, 97, and 87.8%, respectively. All three products were identified by mixed melting point determinations and infrared spectra.

As it was desirable to know whether all three alkyl groups of the ester could be utilized in this reaction, the reaction of triphenylsilyllithium with tri-*n*-butyl phosphate was repeated in a 3:1 mole ratio. The *n*-butyl ester was chosen for this purpose, because it gave the best yield of alkylation product of the three esters tested, although the yields in all three cases were satisfactory.

Forced conditions were required in order to consume all of the organosilyllithium reagent, but the yield of *n*-butyltriphenylsilane was found to be only 49.5%. In addition, hexaphenyldisilane (11.6%), hexaphenyldisiloxane (2.7%), 4-triphenylsilylbutanol (6.4%), and triphenylsilanol (5.9%) were isolated from the reaction mixture. A check-run gave *n*-butyltriphenylsilane (51.5%), hexaphenyldisilane (13.8%), 4-triphenylsilylbutanol (4.5%), and triphenylsilanol (9.05%).

As forced conditions (reflux and long reaction times) were required to obtain a negative Color Test I,[18] it is apparent that the removal of the second and third alkyl groups from the ester is much more difficult than is the removal of the first. This is probably due to repulsion by the nega-

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[1] A. Michaelis and F. Wegner, *Ber.*, **48**, 316 (1915).

[2] H. Gilman and C. C. Vernon, *J. Am. Chem. Soc.*, **48**, 1063 (1926).

[3] H. Gilman and J. Robinson, *Rec. trav. chim.*, **48**, 328 (1929).

[4] J. L. Willians, *Chem. & Ind.*, 235 (1957).

[5] P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952).

[6] M. H. Maguire and G. Shaw, *J. Chem. Soc.*, 2039 (1955).

[7] G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, **73**, 4101 (1951).

[8] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952); *J. Am. Chem. Soc*, **77**, 3411 (1955).

[9] R. C. Miller, J. S. Bradley, and L. A. Hamilton, *J. Am. Chem. Soc.*, **78**, 5299 (1956).

[10] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

[11] R. C. Miller, C. D. Miller, Wm. Rogers, Jr., and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).

[12] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).

[13] M. Janczewski, *Roczniki Chem.*, **33**, 185 (1959).

[14] A. Burger and N. D. Dawson, *J. Org. Chem.*, **16**, 1250 (1951).

[15] N. D. Dawson and A. Burger, *J. Org. Chem.*, **18**, 207 (1953).

[16] M. V. George, B. J. Gaj, and H. Gilman, *J. Org. Chem.*, **24**, 624 (1959).

[17] See, for example, M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, chapt. 21, Prentice-Hall, New York, 1954.

[18] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

tive charge on the ester after one alkyl group has been removed. In this connection, it has also been found that the second and third alkyl groups of phosphate esters are more difficult to hydrolyze.[19]

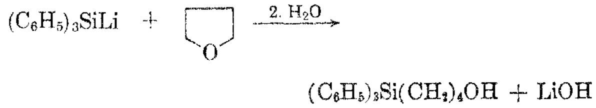
Secondly, it is apparent that all three alkyl groups of the ester are not functioning as alkylating agents, as *n*-butyltriphenylsilane was isolated in only 49.5 and 51.5% yields from these two reactions employing forced conditions. The isolation of hexaphenyldisilane also suggests that a different methanism is involved in the removal of the third alkyl group. The following reaction scheme is consistent with the observed results:

$$2(C_6H_5)_3SiLi + (n\text{-}C_4H_9O)_3PO \longrightarrow 2(C_6H_5)_3SiC_4H_9\text{-}n + \underset{\text{I}}{(LiO)_2P(O)(OC_4H_9\text{-}n)}$$

$$(C_6H_5)_3SiLi + \underset{\text{I}}{(LiO)_2P(O)(OC_4H_9\text{-}n)} \longrightarrow n\text{-}C_4H_9OLi + \underset{\text{II}}{(LiO)_2P(O)(Si(C_6H_5)_3)}$$

$$(C_6H_5)_3SiLi + \underset{\text{II}}{(LiO)_2P(O)(Si(C_6H_5)_3)} \longrightarrow (C_6H_5)_6Si_2 + \underset{\text{III}}{(LiO)_2P(O)Li}$$

$$\underset{\text{II}}{(LiO)_2P(O)(Si(C_6H_5)_3)} + 3H_2O \longrightarrow (C_6H_5)_3SiOH + (HO)_2P(O)H + 2LiOH$$



The first two alkyl groups of the ester react with triphenylsilyllithium to form I and *n*-butyltriphenylsilane. Although not indicated as such, this reaction probably occurs stepwise. Triphenylsilyllithium then reacts with I to give the silylphosphorus intermediate (II) by displacement of the *n*-butoxide group. Apparently after two of the alkyl groups have been removed from the ester, the steric hindrance around phosphorus is reduced sufficiently for the organolsilyllithium compound to attack the central phosphorus atom in the manner usually observed with compounds of this type.

Subsequent cleavage of the silylphosphorus intermediate (II) by triphenylsilyllithium leads to the formation of hexaphenyldisilane and lithium phosphite (III). Cleavages of this type have been used to explain the formation of hexaphenyldisilane from reactions of triphenylsilyllithium with halides of group V-B elements.[16] Similar reactions involving silicon-sulfur,[20] silicon-oxygen,[21] and silicon-mercury[22] bonds are also known.

As care was taken to exclude moisture from these reactions, the triphenylsilanol probably was formed *via* hydrolysis of the silylphosphorus compound (II). Compounds containing silicon-phosphorus bonds are known to undergo ready hydrolysis.[23] The hexaphenyldisiloxane isolated in the first reaction employing forced conditions was formed by dehydration of triphenylsilanol, and the 4-triphenylsilylbutanol, *via* cleavage of the solvent by triphenylsilyllithium.[24]

It would appear that steric requirements of the triphenylsilyl group are largely responsible for the occurrence of alkylation in these reactions. The large size of this anion prevents its attack on the ester at the central phosphorus atom. Apparently there is not too much difference, energywise, between these two possible reactions (alkylation *vs.* displacement), and the more favored displacement reaction gives way to the alkylation reaction when the organometallic compound is sufficiently hindered. An investigation to test this hindrance hypothesis employing Grignard reagents and organolithium compounds is presently being carried out. The results of this work will be reported later.

EXPERIMENTAL[25]

Reaction of triphenylsilyllithium with trimethyl phosphate (1:1). A solution of 0.04 mole of triphenylsilyllithium[26] in 75 ml. of tetrahydrofuran was added dropwise to a stirred solution of 5.6 g. (0.04 mole) of trimethyl phosphate in 50 ml. of the same solvent. Color Test I[18] was negative immediately after the addition was completed. Work-up by hydrolysis, addition of 100 ml. of diethyl ether, separation of the layers, extraction of the aqueous layer with diethyl ether, drying of the organic layer and removal of the solvents left an oil which was poured on a column of dry alumina.

Elution with 400 ml. of petroleum ether (b.p. 60–70°) gave 7.8 g. (71%) of methyltriphenylsilane, m.p. 63–65°, and an oil which contained triphenylsilane as the main constituent, as evidenced by strong absorption bands at 4.75 and 8.97 μ in its infrared spectrum, characteristic of the Si-H and sili-

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[19] G. M. Kosolapoff, *Organophosphorus Compounds*, chapt. 9, Wiley, New York, 1950.

[20] H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957); D. Wittenberg, T. C. Wu, and H. Gilman, *J. Org. Chem.*, **23**, 1898 (1958); D. Wittenberg, H. A. McNinch, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 5418 (1958).

[21] D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959); H. Gilman and T. C. Wu, *J. Org. Chem.*, **25**, 2251 (1960).

[22] M. V. George, G. D. Lichtenwalter, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 978 (1959).

[23] See, for example, G. Fritz, *Z. Naturforsch.*, **8b**, 776 (1953); G. Fritz, *Z. anorg. u. allgem. chem.*, **280**, 332 (1955); W. Keeber and H. W. Post, *J. Org. Chem.*, **21**, 507 (1956); G. Fritz and H. O. Berkénhoff, *Z. anorg. u. allgem. chem.*, **289**, 250 (1957); F. Fehér, G. Kuhlbörsch, A. Blüncke, H. Keller, and K. Lippert, *Chem. Ber.*, **90**, 134 (1957); G. W. Parshall and R. V. Lindsey, *J. Am. Chem. Soc.*, **81**, 6273 (1959).

[24] D. Wittenberg, D. Aoki, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 5933 (1958).

[25] Melting points are uncorrected. All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. The tetrahydrofuran was dried and purified by refluxing over sodium wire for at least 24 hr., followed by distillation into a refluxing suspension of lithium aluminum hydride under dry nitrogen. It was distilled immediately before use from this suspension.

[26] Prepared according to the procedure of H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

con-phenyl bond, respectively. Recrystallization of the solid from methanol raised the melting point to 65–66°. The product was identified by the method of mixed melting points and by a comparison of its infrared spectrum, as a carbon disulfide solution, with that of an authentic sample.

The reaction was repeated using the same quantities of triphenylsilyllithium and freshly distilled trimethyl phosphate. Hydrolysis and work-up as in the previous reaction gave 9.6 g. (88%) of methyltriphenylsilane, m.p. and mixed m.p. 67–68°, after crystallization from methanol.

Reaction of triphenylsilyllithium with tri-n-butyl phosphate (1:1). The addition of one-third of a solution of 0.04 mole of triphenylsilyllithium in 90 ml. tetrahydrofuran to a stirred solution of 3.99 g. (0.015 mole) of tri-*n*-butyl phosphate in 30 ml. of the same solvent gave a negative Color Test I and discharged the color of the silyllithium reagent. The addition of another 0.0133 mole of the organometallic compound resulted in a brown solution which gave a positive Color Test I even after stirring for 1 hr. An additional 6.65 g. (0.025 mole) of tri-*n*-butyl phosphate in 30 ml. of tetrahydrofuran was added and the remaining triphenylsilyllithium reagent then was added dropwise. Color Test I became negative and the mixture developed a pale pink coloration.

Hydrolysis with water, and the addition of 100 ml. of diethyl ether produced an emulsion which was cleared by the addition of a small amount of dilute hydrochloric acid. Work-up in the manner described for trimethyl phosphate gave 12.3 (97%) of *n*-butyltriphenylsilane, m.p. 85–87°, identified by mixed melting point and infrared spectra.

Reaction of triphenylsilyllithium with tri-n-butyl phosphate (3:1) *at reflux. Run 1.* A solution of 0.08 mole of triphenylsilyllithium in 160 ml. of tetrahydrofuran was added to a stirred solution of 7.1 g. (0.0267 mole) of freshly distilled tri-*n*-butyl phosphate in 50 ml. of the same solvent. The dark mixture was stirred for 2.5 hr. at room temperature (Color Test I positive), then at reflux for 18 hr. Hydrolysis, filtration, and washing of the insoluble material with water and diethyl ether left 2.2 g. of hexaphenyldisilane, m.p. and mixed m.p. 364–366°.

The filtrate, which had a strong phosphine-like odor, was acidified and the aqueous layer extracted with diethyl ether. Removal of the solvents from the dried organic phase left an oily solid which was washed with petroleum ether (b.p. 60–70°) and crystallized from benzene to give 0.1 g. of impure hexaphenyldisilane, identified by mixed melting point.

The petroleum ether extract was chromatographed on a column of alumina to give 12.5 g. (49.5%) of *n*-butyltriphenylsilane, 0.1 g. (2.7%) of hexaphenyldisiloxane (eluted with benzene), 0.1 g. of hexaphenyldisilane (total yield, 2.4 g., 11.6%), 1.7 g. (6.4%) of 4-triphenylsilylbutanol (eluted with ethyl acetate), and 1.3 g. (5.9%) of triphenylsilanol. All products were identified by mixed melting points.

Run 2. A solution of 0.06 mole of triphenylsilyllithium in 70 ml. of tetrahydrofuran was added to 5.3 g. (0.02 mole) of tri-*n*-butyl phosphate in a mixture of 40 ml. of tetrahydrofuran and 30 ml. of diethyl ether, and refluxed gently for 5 days with continuous stirring. At the end of this time, Color Test I was negative. Hydrolysis with 100 ml. of water and filtration gave 2.15 g. (13.8%) of hexaphenyldisilane, m.p. and mixed m.p. 363–365°. The filtrate had a strong phosphine-like odor.

Chromatographic separation of the organic layer gave 9.8 g. (51.5%) of *n*-butyltriphenylsilane, m.p. 86–88°. (mixed m.p.); 0.85 g. (4.5%) of 4-triphenylsilylbutanol, m.p. 107–109° (mixed m.p. and infrared spectra); and 1.5 g. (9.05%) of triphenylsilanol, m.p. 152–154° (mixed m.p.).

Reaction of triphenylsilyllithium with triisobutyl phosphate (1:1) *Run 1.* A mixture of 0.06 mole of triphenylsilyllithium and 16 g. (0.06 mole) of triisobutyl phosphate[27] in 170 ml. of tetrahydrofuran gave, after the initial heat of reaction had dissipated, a negative Color Test I. The pink solution was hydrolyzed with 50 ml. of half-saturated ammonium chloride, and 100 ml. of diethyl ether was added. Drying of the separated organic layer followed by removal of the solvents and boiling of the residue with 150 ml. of absolute ethanol gave upon filtration 0.3 g. (2%) of hexaphenyldisilane, m.p. 357–360° (mixed m.p.).

The ethanolic filtrate yielded upon concentration, two crops of isobutyltriphenylsilane (13.75 g., 72.3%), m.p. 75–76°. The product was identified by a mixed melting point with a sample prepared from the reaction of isobutyl chloride with triphenylsilyllithium,[28] and by infrared spectra.

Run 2. The previous reaction was repeated using 0.04 mole of each reactant in 110 ml. of tetrahydrofuran. Hydrolysis and removal of the solvents from the dried organic layer was accomplished as described in Run 1. The residue was purified by passing it through a column of alumina as a petroleum ether (b.p. 60–70°) solution. Removal of the solvent left 11.1 g. (87.8%) of isobutyltriphenylsilane, m.p. and mixed m.p. 74–76°. Elution with ethyl acetate gave, after crystallization from cyclohexane, 0.5 g. (4 5%) of triphenylsilanol, m.p. 151–153° (mixed m.p.).

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