TABLE II

MOLECULAR-ORBITAL DATA FOR STYRENE

Position	$A(-\beta)$	F	Position	$A(-\beta)$	F
β	1.704	0.821	m	2.546	0.395
α	2.424	.415	p	2.424	.415
o	2.370	.443			

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Metathetical Reactions of Silver Salts in Solution. III. The Synthesis of Nitrate Esters[1]

BY ARTHUR F. FERRIS, KATHARINE W. MCLEAN, IRMA G. MARKS AND WILLIAM D. EMMONS

RECEIVED APRIL 27, 1953

It has been found in this Laboratory that the use of silver nitrate in acetonitrile is a very convenient method for preparing laboratory quantities of extremely pure nitrate esters. The method has an additional advantage in that the reaction may be conveniently followed by periodic weighing of the silver halide precipitated.

The reaction of alkyl halides with silver nitrate under heterogeneous conditions has been used for many years as a preparative method for alkyl nitrates. Experiments wherein ethanol was used as a solvent for the reaction[2] have led largely to nitric acid and the mixed ethyl alkyl ether derived from the alkyl halide. The enormous solubility of silver nitrate in acetonitrile is well known,[3] and the use of silver nitrate in acetonitrile to prepare 2,4,6-trinitrobenzyl nitrate from the corresponding bromide has been described.[4] It would appear, however, that the virtues of silver nitrate in acetonitrile for synthesis of nitrates have not been generally recognized, since in even very recent work[5] nitrates have been prepared by the heterogeneous reaction.

Most primary and secondary alkyl iodides, many bromides and active chlorides react rapidly enough at room temperature or slightly above to be useful in preparative work. The following nitrates were prepared in the yields indicated: *n*-hexyl nitrate from *n*-hexyl bromide (77%) and from *n*-hexyl iodide (67%), *n*-octyl nitrate from *n*-octyl iodide (61%), benzyl nitrate from benzyl chloride (64%), methallyl nitrate from methallyl chloride (45%), 2-octyl nitrate from 2-octyl iodide (46%), 2-nitratoethanol from 2-bromoethanol (70%), nitratoacetonitrile from iodoacetonitrile (32%), ethyl lactate nitrate from ethyl α-bromopropionate (59%), and ethyl hydracrylate nitrate from ethyl β-bromopropionate (58%). These yields undoubtedly do not represent the optimum obtainable, since most of the experiments were carried out on a small scale with consequent large mechanical losses.

Experimental[6]

The procedures described herein for ethyl hydracrylate nitrate and methallyl nitrate are typical of those used for the preparation of the other esters. All boiling points are uncorrected.

Ethyl Hydracrylate Nitrate.—To a solution of 20.0 g. (0.118 mole) of silver nitrate in 100 ml. of dry, distilled acetonitrile was added a solution of 9.1 g. (0.05 mole) of ethyl β-bromopropionate in 25 ml. of acetonitrile. After three days at room temperature 9.0 g. (96%) of silver bromide was recovered by filtration. The filtrate was poured into a liter of ice-water, and the oil which separated extracted into two 50-ml. portions of methylene chloride. After drying, the solvent was removed by distillation at atmospheric pressure, and the residue was distilled at reduced pressure to yield 4.7 g. (58%) of ethyl hydracrylate nitrate, b.p. 60–64° (1.5 mm.), $n^{25}\text{D}$ 1.4258, d^{20}_4 1.262.

Anal. Calcd. for $C_5H_9O_5N$: C, 36.81; H, 5.56; N, 8.59. Found: C, 37.11; H, 5.72; N, 8.46.

Methallyl Nitrate.—To a solution of 18.7 g. (0.11 mole) of silver nitrate in 30 ml. of dry acetonitrile was added 9.1 g. (0.10 mole) of methallyl chloride. After five days at room temperature a total of 13.1 g. (92%) of silver chloride was collected on a filter. The filtrate was worked up as described above, and the residue was fractionated through a short packed column to give 5.3 g. (45%) of methallyl nitrate, b.p. 83–88° (215 mm.), $n^{25}\text{D}$ 1.4221, d^{20}_4 1.064.

Anal. Calcd. for $C_4H_7O_3N$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.51; H, 6.40; N, 12.19.

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] K. A. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904); J. W. Baker, *ibid.*, 987 (1934).

[3] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 68.

[4] L. F. Fieser and W. von E. Doering, THIS JOURNAL, **68**, 2252 (1946).

[5] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

[6] We are indebted to Mr. Al Kennedy and Miss Annie Smelley for analytical data.

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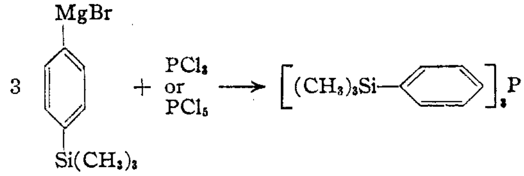
Silicon-containing Aromatic Phosphorus Derivatives

BY KURT C. FRISCH[1] AND HAROLD LYONS

RECEIVED APRIL 15, 1953

The purpose of this investigation was the preparation of aromatic silanes containing nuclear substituted phosphorus groups. The presence of phosphorus groups in aromatic silanes should impart certain physical properties useful in applications such as plasticizers, lubricants and oil additives. This paper deals with the preparation of some model compounds of this type.

p-Trimethylsilylphenylmagnesium bromide (I) was treated with phosphorus tri- and pentachloride, using equimolecular amounts of the reactants. In both cases, the main product consisted of tris-(*p*-trimethylsilylphenyl)-phosphine (II)



I II

In the reaction with phosphorus pentachloride, in addition to the above described crystalline phosphine (II), another liquid product was obtained which is presumably bis-(*p*-trimethylsilyl)-chlorophosphine (III).

Tris-(*p*-trimethylsilyl)-phosphine (II) is very resistant to oxidation. Refluxing the phosphine

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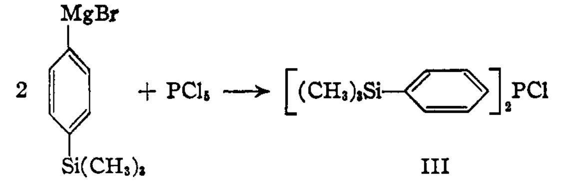
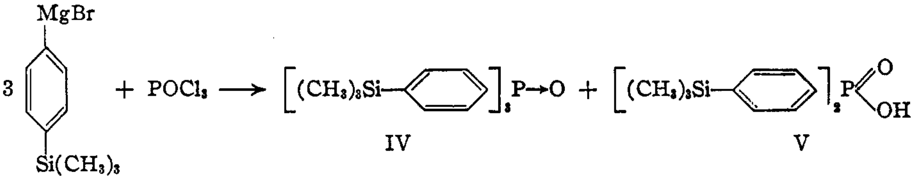
[1] E. F. Houghton & Co., Philadelphia, Penna.



(II) with potassium permanganate in aqueous and in pyridine solution did not result in the formation of the corresponding phosphine oxide. This result is not surprising in view of the well-known resistance of aromatic phosphines toward oxidation.



p-Trimethylsilylphenylmagnesium bromide (I) when treated with phosphorus oxychloride yields both the phosphine oxide (IV) as well as the diphosphonic acid (V). The procedure was essentially that of Kosolapoff.[2]

Experimental

***p*-Trimethylsilylphenylmagnesium bromide (I)** was prepared from 12.2 g. of magnesium turnings, 114.5 g. of *p*-bromophenyltrimethylsilane and 550 cc. of anhydrous ether. The reaction was initiated by means of a small amount of ethylmagnesium bromide.

Tris-(*p*-trimethylsilylphenyl)-phosphine (II). (A).—In a three-necked flask, equipped with stirrer, reflux condenser and dropping funnel, were placed 34.4 g. of phosphorus trichloride and 100 cc. of ether. Half of the above prepared Grignard solution was added gradually through a dropping funnel. Afterwards the mixture was refluxed for three hours. The inorganic precipitate was filtered off and washed with ether. The solvent was then removed from the filtrate. The weight of the residual material was 68.1 g. On standing in the refrigerator, crystals formed which were recrystallized from alcohol, yielding colorless needles, m.p. 95–96° (uncor.).

B.—Half of the above described Grignard solution was added slowly to a solution of 52.1 g. of phosphorus pentachloride in 100 cc. of ether. The product was worked up in the same way as described in A. The residual material weighed 63 g. It was vacuum distilled. Tris-(*p*-trimethylsilylphenyl)-phosphine (II) distilled at 112–117° at 31 mm. It was recrystallized from alcohol, yielding colorless needles, m.p. 95–96° (uncor.). A mixed melting point taken with the products obtained by procedures A and B showed no depression, establishing thereby the identity of the two materials. The yields of the pure product ranged from 35–45%.

Anal. Calcd. for $C_{27}H_{39}PSi_3$: Si, 17.6; P, 6.5. Found: Si, 17.2; P, 6.8.

In the above distillation, another fraction was isolated, distilling at 72° at 43 mm. as a colorless liquid.

Anal. Calcd. for $C_{18}H_{26}ClPSi_2$: Si, 15.4; P, 8.5. Found: Si, 13.1; P, 8.9.

While this compound evidently was not pure, it probably contained **bis-(*p*-trimethylsilylphenyl)-chlorophosphine** (III). The presence of chlorine was proven by means of a qualitative test.

Tris-(*p*-trimethylsilylphenyl)-phosphine Oxide (IV).—*p*-Trimethylsilylphenylmagnesium bromide, prepared from 57 g. of *p*-bromophenyltrimethylsilane, was added gradually to a solution of 38 g. of phosphorus oxychloride in 300 cc. of ether which was brought to reflux before the addition. The reaction mixture was then refluxed for 15 hours. After cooling, the yellow liquid was decanted from the residual solid. The solid was hydrolyzed in ice-water forming a white precipitate. The yellow liquid was concentrated on the steam-bath and formed a yellowish-white solid. Both the white precipitate and the residual solid obtained from the liquid portion of the reaction mixture were combined and washed first with dilute sodium hydroxide and then with water. The residual product was extracted with ether and the ether extract dried over anhydrous sodium sulfate. After removal of the ether, the remaining solid was recrystallized from alcohol, yielding a colorless, crystalline product, m.p. 259° (uncor.). The yield was 30%.

Anal. Calcd. for $C_{27}H_{39}OPSi_3$: Si, 17.0; P, 6.3. Found: Si, 17.4; P, 6.8.

Bis-(*p*-trimethylsilylphenyl)-phosphonic Acid (V).—The sodium hydroxide extract from the combined solid products of the reaction of *p*-trimethylsilylphenylmagnesium bromide and phosphorus oxychloride was acidified with dilute hydrochloric acid, resulting in a colorless, crystalline product, m.p. 213–214.5° (uncor.). The yield was 15%.

Anal. Calcd. for $C_{18}H_{27}O_2PSi_2$: Si, 15.5; P, 8.6. Found: Si, 16.5; P, 8.9.

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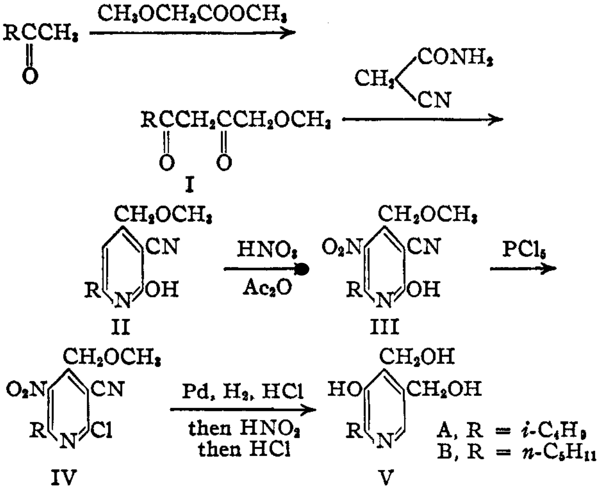
[2] G. M. Kosolapoff, THIS JOURNAL, 64, 2982 (1942).

Chemistry of Vitamin B_6. X. Some Homologs of the Vitamin B_6 Group

BY DOROTHEA HEYL, EILEEN LUZ, STANTON A. HARRIS AND KARL FOLKERS

RECEIVED APRIL 22, 1953

An ethyl homolog of pyridoxine, 2-ethyl-3-hydroxy-4,5-bis-(hydroxymethyl)-pyridine, was reported previously.[1] Two higher homologs have been prepared: the corresponding isobutyl and *n*-amyl derivatives. These compounds were synthesized in general by the sequence of reactions which was used for preparation of the ethyl homolog, the main difference being that several of the intermediates were not isolated. The compounds actually isolated are represented by the formulas I through V.



2-Ethyl-3-hydroxy-4,5-bis-(hydroxymethyl)-pyridine[1] was oxidized to 2-ethyl-3-hydroxy-4-formyl-5-hydroxymethylpyridine, which was isolated as the oxime VI. The latter was con-

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[1] S. A. Harris and A. N. Wilson, THIS JOURNAL, 63, 2526 (1941).