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			

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES
UNIVERSITY COLLEGE
LONDON, W.C.1, ENGLAND

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.

---

[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.

ROHM AND HAAS COMPANY
JOSIAH GORGAS LABORATORY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

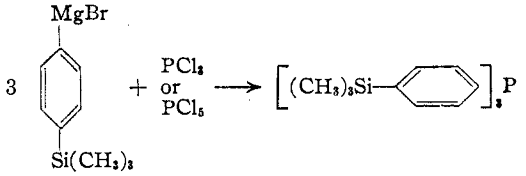
Silicon-containing Aromatic Phosphorus Derivatives

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

---

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