Anal. Calcd. for $C_{16}H_{24}O_6NP$: C, 53.69; H, 6.75; P, 8.67. Found: C, 53.47; H, 7.06; P, 8.68.

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Organic Phosphorus Compounds. VII.[1] The Preparation of Methylphosphonic Chlorofluoride

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For a study of preparative methods for isopropyl methylphosphonofluoridate, Sarin, a sample of the previously unknown methylphosphonic chlorofluoride, $CH_3P(O)ClF$ (I), was required. Although the complete replacement of chlorine by fluorine in methylphosphonic dichloride (II) by means of anhydrous hydrogen fluoride proceeds readily with the formation of methylphosphonic difluoride (III),[3] all attempts to replace only one of the chlorine atoms in II by fluorine under a variety of conditions were unsuccessful. The resulting reaction product yielded in all cases by distillation only II and III in varying ratios depending on the molar ratio of II to hydrogen fluoride employed. The desired I was obtained, however, from methylphosphonofluoridic acid, $CH_3P(O)(F)OH$ (IV), which gave the desired I by treatment with thionyl chloride.

While the hydrolysis of Sarin and of its chlorine analog, $CH_3P(O)(Cl)OCH(CH_3)_2$, proceeds with the formation of isopropyl methylphosphonate, $CH_3P(O)(OH)OCH(CH_2)_3$, IV was obtained readily by the thermal decomposition of Sarin at its boiling point by elimination of propene. Treatment of IV with refluxing thionyl chloride and subsequent fractionation of the reaction mixture yielded I as a relatively stable compound boiling at 126.0–126.5° under atmospheric pressure.

One of the fluorine atoms of III can be estimated as fluoride ion by the method of Sass *et al.*[4] while the P-to-F bond of I is stable under the conditions of this method. It is thus possible to determine III in the presence of I. The presence of small amounts of fluorine which can be detected as fluoride ion, even in carefully fractionated I, indicates that under the conditions of the distillation disproportionation of the I occurs to a small extent. A fractionated sample of I containing 0.83% fluoride ion, corresponding to 4.37% III, was found to undergo a slow disproportionation reaction at 60° with a further increase of 6.74% in the III content during a period of seventy hours.

EXPERIMENTAL

Thermal decomposition of isopropyl methylphosphonofluoridate. Isopropyl methylphosphonofluoridate[5] (46.7 g., 0.33 mole) in a 100-cc. round bottom flask, equipped with a reflux condenser and an attached Dry Ice–acetone trap, was immersed in an oil bath at 160–165°. After an induction period of about 30 min., the decomposition of I began with the evolution of a gas. During the decomposition the pot temperature dropped to 141° and remained steady until the gas evolution ceased after a total heating period of 50 min. The condensate in the attached cold trap consisted of 14.1 g. propene (14.03 g. corresponds to a quantitative yield) which was identified by its conversion to 1,2-dibromopropane, b.p. 139–140°; lit.,[6] b.p. 140.7–140.8°/740 mm. Hg.

After the removal of a small forerun at 30–33°/5 mm., distillation of the viscous oily pot residue (31.0 g.) of crude IV under reduced pressure gave the bulk of the methylphosphonofluoridic acid IV as a colorless oily liquid, b.p. 69–72°/2 mm.

Anal. Calcd. for CH_4PFO_2: P, 31,61; total F, 19.38. Found: P, 31.46; total F, 20.28.

A small amount of solid distillation residue was recrystallized from a 1:5 mixture of absolute ethanol and acetone to yield methylphosphonic acid, m. 105°; lit.[7], m.p. 105°.

Preparation of methylphosphonic chlorofluoride (I). Crude, undistilled IV (438.5 g.) from the thermal decomposition of Sarin was mixed in a 2-l. round bottom flask with 500 g. thionyl chloride, and the mixture refluxed for 6 hr. until the pot temperature rose to 80°. An additional 50 g. of thionyl chloride was then added, and the mixture heated for another 3 hr. during which the pot temperature finally reached 127°. Distillation of the crude reaction mixture through a 15-cm. column packed with glass helices at 68 mm. pressure yielded 389 g. of crude chlorofluoride I boiling at 52–67°. The product was redistilled through a 30-cm. helix-packed column to give 240 g. of a constant boiling fraction at 41°/30 mm. containing 1.77% of ionic fluorine. On the basis of the fluoride ion analysis, the chlorofluoride contained 9.3% of methylphosphonic difluoride.

The distilled I (230 g.) was solidified by cooling with a Dry Ice–acetone bath and then slowly thawed. The portion which was liquid at −23° was filtered from the crystal sludge, and the part of the filter residue melting at −23 to −19° separated by filtration. The residue melting above −19° was discarded. Estimation of fluoride ion in the fraction melting at −23 to −19° showed a content of 1.56% fluoride ion. Since further fractional crystallization did not lower the difluoride content markedly, 190 g. of recrystallized product was redistilled through a 30-cm. helix-packed column to yield 127 g. of distillate, b.p. 34–35°/14 mm. The fluoride ion content of 0.5% in this batch of I corresponded to 2.7% methylphosphonic difluoride.

A sample of I prepared as described above, but purified only by repeated distillation under reduced pressure was analyzed.

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(2) To whom inquiries about this note should be addressed.

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TABLE I

DISPROPORTIONATION OF METHYLPHOSPHONIC CHLOROFLUORIDE AT 60°

Time in hr.	Fluoride Ion, %	Difluoride, %
0	0.83	4.37
3.25	1.63	8.58
20.25	1.78	9.37
48.5	1.87	9.84
70	2.11	11.11

Anal. Calcd. for CH_3PClFO: Cl, 30.44; total F, 16.31; fluoride ion, 0. Found: Cl, 30.45; total F, 16.47; fluoride ion, 0.87.

Yields of 72–82% of crude distilled I, b.p. 120–144°, based on Sarin as the starting material, were obtained consistently in a large number of runs. The boiling point of the purified compound is 126.0–126.5° at atmospheric pressure.

Determination of disproportionation of I at 60°. Samples of approximately 0.40 g. of I having a fluoride ion content of 0.83% were sealed in bulbs, weighed, and kept in a thermostat at 60 ± 0.5° for various periods of time. The samples, removed from the thermostat, were cooled in ice water and immediately titrated for fluoride ion. The results are listed in Table I.

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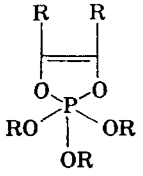
Communications TO THE EDITOR

A New Carbon-Carbon Condensation Reaction Induced by Phosphite Esters. Formation of a 2:1 Adduct in the Reduction of Acenaphthenequinone with Trimethyl Phosphite[1]

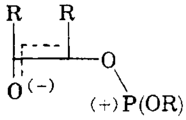
Sir:

We have described[2] crystalline *1:1 adducts* derived from the reaction of tertiary phosphite esters with 9,10 phenanthrenequinone and with α-diketones such as benzil. We favor a cyclic unsaturated oxyphosphorane structure I for these adducts, as they are remarkably soluble in alkanes and/or benzene, show no carbonyl or enolate bands in the infrared when pure, and give strong positive shifts in the phosphorus-NMR spectra relative to phosphoric acid implying considerable phosphorus shielding. An equilibrium with the open dipolar form II under certain conditions is, however, conceivable.

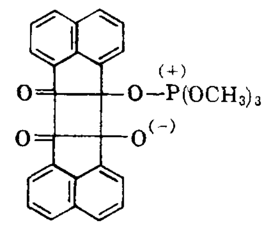
We should like to report now the formation of a crystalline 2:1 adduct (III) from acenaphthenequinone (IV) and trimethyl phosphite (V). The adduct (*Anal.* Calcd. for $C_{27}H_{21}O_7P$: C, 66.5; H, 4.3; P, 6.4. Found: C, 66.6; H, 4.4; P, 6.1.) was prepared as described below. It is unstable in moist air but can be handled in dry nitrogen, is practically insoluble in cold hexane, ether and benzene and has a single sharp band at 5.78 μ and a very strong set of bands in the 9.00–9.50 μ region characteristic of P—O—C vibrations. The spectra were determined in a methylene chloride solution which decomposed slowly. The 2:1 adduct could have structure III or the corresponding cyclic saturated oxyphosphorane.



I

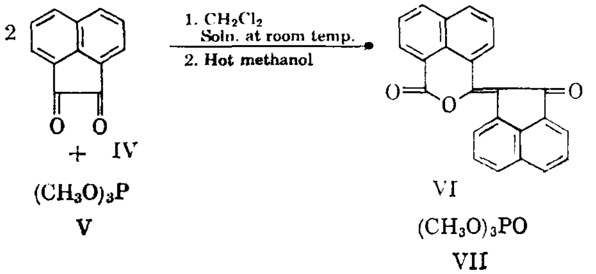


II



III

When the 2:1 adduct (III) was warmed with methanol, a clean molecular rearrangement took place. The products were trimethyl phosphate (VII) and the enol lactone VI. The over-all transformation is then



The following is a typical procedure: A mixture of acenaphthenequinone (18.2 g.; 0.1 mole), trimethyl phosphite (7 ml; *ca.* 0.05 mole), and methylene chloride (250 ml.) was stirred at 25°, under

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