Tetrahedron Letters No.1, pp. 51-53, 1968. Pergamon Press Ltd. Printed in Great Britain.

# THE ALKYLATION OF PHOSPHORYL COMPOUNDS.

**L.V.Nesterov and R.I.Mutalapova.**

**The A.E.Arbuzov Institute of Organic**
**and Physical Chemistry, USSR Academy**
**of Sciences, Kazan, U.S.S.R.**

(Received in UK 27 September 1967)

**Quasi-phosphonium salts are supposedly formed as unstable intermediates when several alkylating agents (mostly alkyl halides) act on various ester phosphoryl compounds (I) or their sulfur (2) and nitrogen (3) analogues:**

$$R{-}O{-}\underset{|}{\overset{|}{P}}{=}Y + R'{-}X \longrightarrow R{-}O{-}\underset{|}{\overset{|\oplus}{P}}{-}Y{-}R' + \overset{\ominus}{X} \longrightarrow X{-}R + O{=}\underset{|}{\overset{|}{P}}{-}Y{-}R'$$

**( Y = >O, >S or >NR )**

**It is well known that alkyl halides act on tertiary phosphine sulfides (4) and substituted imides (5) to form rather stable quasi-phosphonium salts:**

$$R_3P{=}Y + R'{-}X \longrightarrow R_3\overset{\oplus}{P}{-}Y{-}R'\ \overset{\ominus}{X} \quad ( Y = {>}S \text{ or } {>}NR )$$

**A similar reaction is unlikely to take place when the interaction of tertiary phosphine oxides and alkyl halides occurs because of the reverse reaction described ten years ago (6):**

$$R_3\overset{\oplus}{P}{-}O{-}R'\ \overset{\ominus}{Hal} \longrightarrow R_3P{=}O + R'Hal$$

**One may yet expect the action of the stronger alkylating agents to give rise to stable quasi-phosphonium salts even while attacking the comparatively weak nucleophilic reagents such as phosphoryl compounds. The stable trialkyloxonium salts are the most appropriate reagents of this kind especially as they have anions of extremely low nucleophilicity which will not attack the newly formed quasi-phosphonium cations.**

And indeed, we have found the compounds $(C_2H_5)_n(C_2H_5O)_{3-n}P{=}O$ ( n = 0,I,2,3 ) to form stable quasi-phosphonium salts when treated with equivalent amounts of triethyloxonium fluoroborate. The reactions were carried out in the methylene chloride or ethylene chloride media, the solutions being refluxed for 2-3 hours:

$$(C_2H_5)_n(C_2H_5O)_{3-n}P{=}O + (C_2H_5)_3\overset{\oplus}{O}\,\overset{\ominus}{BF_4} \longrightarrow (C_2H_5)_n\overset{\oplus}{P}(OC_2H_5)_{4-n}\,\overset{\ominus}{BF_4} + (C_2H_5)_2O$$

The salts formed were precipitated by the addition of absolute ether and thoroughly washed with the same solvent.

The following salts $(C_2H_5)_n\overset{\oplus}{P}(OC_2H_5)_{4-n}\,\overset{\ominus}{BF_4}$ have been obtained (see Table I).

TABLE I.

| n | Yield % | M.p.(°C) | Formula | Analyses (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. | | | Found | | |
| | | | | C | H | P | C | H | P |
| 0* | 72.2 | -2I - -I8 | $C_8H_{20}BF_4O_4P$ | 32.24 | 6.77 | I0.39 | 32.90 | 6.95 | 9.I9 |
| I** | 40.4 | -I4 - -I0 | $C_8H_{20}BF_4O_3P$ | 34.07 | 7.I5 | I0.98 | 34.I2 | 7.00 | I0.65 |
| 2 | 83.0 | 3 - 5 | $C_8H_{20}BF_4O_2P$ | 36.II | 7.58 | II.64 | 36.39 | 7.58 | II.I0 |
| 3 | 84.6 | II8 - I20 | $C_8H_{20}BF_4OP$ | 38.43 | 8.06 | I2.39 | 38.84 | 8.04 | I2.03 |

* Unfortunately we did not succeed in purifying this substance to the desired degree perhaps owing to its relatively high instability and especially regarding air moisture.

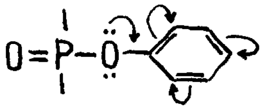
** Lit. (7) m.p. -I4 - -I0°.

The attempts to obtain stable quasi-phosphonium salts according to the following equation

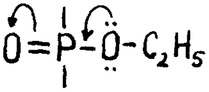
$$(C_6H_5)_n(C_6H_5O)_{3-n}P{=}O + (C_2H_5)_3\overset{\oplus}{O}\,\overset{\ominus}{BF_4} \longrightarrow$$
$$\longrightarrow (C_6H_5)_n(C_6H_5O)_{3-n}\overset{\oplus}{P}OC_2H_5\,\overset{\ominus}{BF_4} + (C_2H_5)_2O$$

proved successful only in case n = 3 ( triphenylethoxyphosphonium fluoroborate, m.p. I35-I37°. Anal. Calcd. for $C_{20}H_{20}BF_4OP$: C, 60.94; H, 5.II; P, 7.86. Found: C, 60.82; H, 5.26; P, 7.95. Yield 97% ). The reactions did not take place when n = 0, n = I or n = 2, with phosphoryl compounds being recovered in each case.

Our failure to alkylate the phenyl ester phosphoryl compounds can apparently be understood if the electron attraction from the ester oxygen to the phenyl group which prevents polarization of the phosphoryl group and reduces its nucleophilicity is admitted:



The electron displacement in the ethyl esters promotes the polarization of their phosphoryl groups and raises their nucleophilicities so that alkylation occurs:



$O=P-O-C_2H_5$

## References.

I. H.J.Harwood, D.W.Grisley Jr., J. Amer. Chem. Soc., 82, 423 (1960).

2. P.S.Pishchimuka, J. Russ. Phys.-Chem. Soc., 44, 1406 (1912).

3. V.A.Gilyarov, Khim. i Primenenie Fosfororgan. Soedinenii, Akad. Nauk S.S.S.R., Trudy I-oi Konferents., 1955, p.275 (Pub. 1957).

4. B.A.Hantzsch, H.Hibbert, Ber., 40, 1508 (1907).

5. H.Staudinger, E.Hauser, Helv. Chim. Acta, 4, 861 (1921).

6. A.I.Razumov, N.N.Bankovskaya, Doklady Akad. Nauk S.S.S.R., 116, 241 (1957).

7. K.Dimroth, A.Nurrenbach, Ber., 93, 1649 (1960).