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THERMAL REACTIONS OF SOME PHOSPHORIMIDATES

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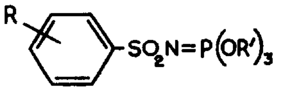
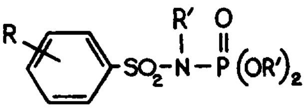
Arylsulphonylphosphorimidates have been prepared by the addition of trivalent phosphorus compounds to sulphonylazides(1), by the addition of trialkyl phosphites to the nitrene generated from chloramine - T(2), and by the reaction of phosphorus pentachloride and an alcohol with sulphonamides(3). These products have been assigned the general structure (I).



(I)



(II)

In the course of our work on compounds of potential insecticidal interest we have prepared several variously substituted compounds of type (I) by the addition of trialkyl phosphites to the corresponding sulphonylazide. The phosphorimidate structures (I) for the undistilled reaction products were confirmed by n.m.r. spectroscopy.

However, distillation of the phosphorimidate (I, R= 4-CH_3, R' = C_2H_5) caused striking changes in its infra-red spectrum, although the distillate possessed other physical characteristics (boiling point, refractive index) identical with those previously assigned to it.(2,3) Examination of the distillate by n.m.r. spectroscopy showed it to consist of a mixture of (I, R= 4-CH_3, R' = C_2H_5 ; 15%) and the rearranged phosphoramidate (II, R = 4-CH_3, R' = C_2H_5 ; 85%), the spectrum of which contained *inter alia* a double quartet centred at 6.5τ not present in the undistilled material and attributed to the methylene protons of the N-ethyl residue. This ratio was not altered on further distillation. p-Toluenesulphonethylamide was identified after alkaline hydrolysis of the distillate.

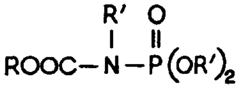
Distillation of the phosphoramidate (II, R = 4-CH_3, R' = C_2H_5), prepared from diethylphosphochloridate and the sodium salt of p-toluenesulphonethylamide, gave a similar mixture of compounds of structure (I and II), confirming a thermal interconversion (I $\rightleftharpoons$ II).

Brief heating at 200° caused a similar rearrangement of other variously ring-substituted phosphorimidates denoted by changes in their infra-red spectra, in particular the appearance of intense bands at ca. 910, 1270 (P=O) and 1300 $cm.^{-1}$

In contrast to the sulphonylphosphorimidates, another series of phosphorimidates (III, R=R' = alkyl) prepared analogously by the addition of trialkyl phosphites to azidoformic esters, gave on heating to 200° alkylisocyanate and trialkyl phosphate.

$$ROOC{-}N{=}P(OR')_3$$

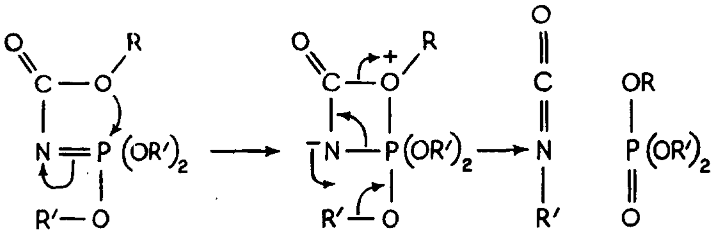
(III)



$$ROOC{-}\overset{R'}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{P}}(OR')_2$$

(IV)

By thermal decomposition of the mixed ester (III, R=C_2H_5,R' = CH_3) only methylisocyanate was detected, and it seemed to us a priori that the formation of isocyanate probably proceeded via the carbamate (IV) formed in an analogous manner to the sulphonylphosphoramidates (II). The thermal decomposition of phosphorylated carbamate anions giving isocyanates has been previously reported.(4) However, the carbamic esters (IV)(5) were found to be stable under the conditions used for the thermal decomposition of (III) for which the annexed mechanism is therefore proposed.



(III)

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REFERENCES

1. J. Goerdler and H. Ullmann, Chem.Ber., 94, 1067 (1961)

2. J.I.G. Cadogan and H.N. Moulden, J.Chem.Soc., 3079 (1961)

3. A.V. Kirsanov and V.I. Shevchenko, J.Gen.Chem. U.S.S.R., 24, 483, 1980 (1954)

4. W.S. Wadsworth and W.D. Emmons, J.Org.Chem., 29, 2816 (1964)

5. B.A. Arbuzov, P.I. Alimov and M.A. Zvereva, Izvest.Akad. Nauk. S.S.S.R., 1042 (1954) ; Chem.Abs., 50, 215 (1956)