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A NOVEL P^{III} - P^{V} REARRANGEMENT OF N-ALKYLAMIDO PHOSPHORAMIDITES

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Aromatic isocyanates react with N-aryl phosphoramidites to give amidino phosphonates (e.g. I) in highly exothermic reactions (1)

$$(EtO)_2P\text{—}NHPh + PhNCO \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}\text{—}\overset{NPh}{\overset{\|}{C}}\text{—}NHPh$$

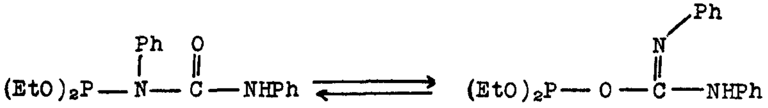
I

However the reaction at lower temperatures gives an oil (II), with a ^{31}P n.m.r. peak at -137 p.p.m. and a carbonyl peak in the i.r. spectrum at 1675 cm^{-1}. On heating this oil to 100° for one hour, I was formed in ca. 90% yield as shown by the ^{31}P n.m.r. absorption at -3 p.p.m. This re-arrangement appears to be general for derivatives of aromatic isocyanates, but the yield of product depends on the solvent, the substituent in the aromatic nucleus and the temperature. Usually small yields of dialkyl phosphonate (^{31}P n.m.r. absorption at -21 and +8 p.p.m.) and a product so far unidentified with ^{31}P n.m.r. absorption at +2 p.p.m. are formed.

We have followed the rearrangement kinetically by mixing equivalent proportions of the phosphoramidite and appropriate isocyanate in a bath cooled in ice, and allowing the reaction to proceed to give the P^{III} insertion product, II. When the peak in the i.r. spectrum corresponding to isocyanate had disappeared, a toluene solution of known concentration was held at 60° in a thermostat. The rate of rearrangement was followed by the decrease in the intensity of the amide C═O band at 1670 - 1680 cm^{-1}.

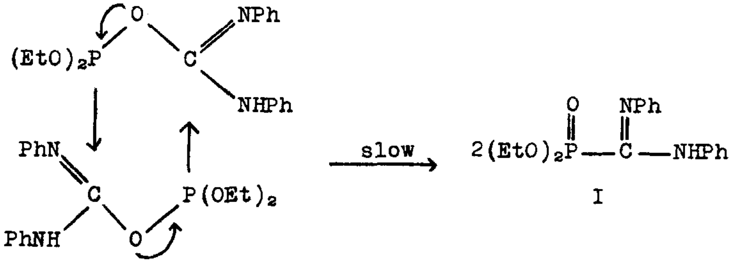
The reaction appeared to be second order (Table) although at low concentrations a first order component was detected, i.e.

$$\text{Rate} = k_1[II] + k_2[II]^2$$



$$(EtO)_2P-\overset{Ph}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-NHPh \rightleftharpoons (EtO)_2P-O-\overset{\overset{\diagup Ph}{N}}{\overset{\|}{C}}-NHPh$$

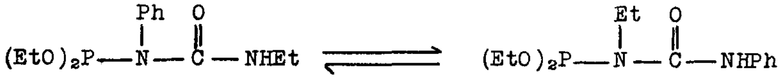
II



I

The overall rate of such a reaction, the second stage of which is a type of Arbusov reaction, would increase with the substitution of electron attracting substituents in the aromatic group, as observed.

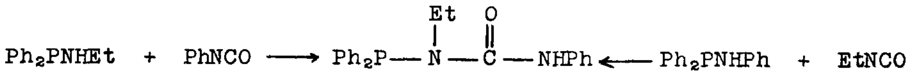
Moreover a rearrangement of the kind proposed in the first stage of this reaction scheme may explain the formation (1) of mixtures of isomers in the reaction of N-alkylphosphoramidites with aromatic isocyanates, e.g.



$$(EtO)_2P-\overset{Ph}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-NHEt \rightleftharpoons (EtO)_2P-\overset{Et}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-NHPh$$

III IV

recognised by the ^{31}P n.m.r. absorption at -134.7 p.p.m. (III) and -140.3 p.p.m. (IV). A similar process could also explain the formation (1) of a common product from the reaction of an N-alkyl phosphinous amide with phenyl isocyanate and N-phenyl phosphinous amide with alkyl isocyanate, e.g.



$$Ph_2PNHEt + PhNCO \longrightarrow Ph_2P-\overset{Et}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-NHPh \longleftarrow Ph_2PNHPh + EtNCO$$

1. R. F. Hudson and R. J. G. Searle, J.Chem.Soc.B., 1349, 1968.
2. R. F. Hudson, R. J. G. Searle and F. Devitt, J.Chem.Soc.B., 789, 1966.

TABLE

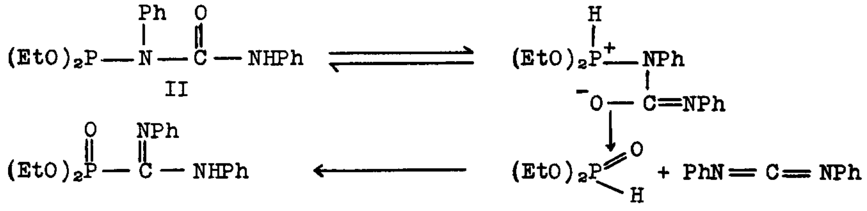
Rate constants for the rearrangement of several phosphite ureas at 60° in toluene.

Compound	Conc. (M)	$10^5 k_2$ (ℓ.mole^{-1}sec^{-1})
$(EtO)_2PN(Ph)CONHPh$*	0.12	8.3
"	0.12	8.0
"	0.08	9.3
"	0.0624	8.7
"	0.0624	9.0
"	0.0324	9.7
"	0.04	9.6
$(EtO)_2PN(C_6H_4-NO_2-p)CONHPh$	0.12	55.0
$(EtO)_2PN(C_6H_4-OMe-p)CONHPh$	0.12	0.9

*$k_1 = 1.05 \times 10^{-6} sec^{-1}$

The rate order for the substituted compounds is $pNO_2 > H > pMeO$, the values in the Table giving an approximate value of the Hammett ρ parameter of + 1.1.

By analogy with the reaction of phosphoramidites with aldehydes and ketones (2), a mechanism of the Staudinger-Wittig type is possible,



However, we find that diethylphosphonate and aromatic carbodiimides do not react under the conditions of the re-arrangement.

Moreover the second order rate law supports a bimolecular mechanism, which may be of the following type.