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PROTOPHILIC DEUTEROEXCHANGE OF SOME ORGANOPHOSPHORUS (III) COMPOUNDS

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The electronic effects in organic compounds of trivalent phosphorus are as yet insufficiently elucidated, especially from a quantitative aspect. In particular, of considerable interest would be comparison of the electronic effects of substituents in compounds of phosphorus and nitrogen (see 1,2).

A valuable method for studying the electronic effects of substituents in organic compounds is determination of the hydrogen isotope exchange kinetics (3). The literature contains data on deuterium exchange in phosphonium salts (4,5), but as far as we know the isotopic method has here for the first time been employed to study the reactivity of organic compounds of trivalent phosphorus.

The rates of hydrogen exchange of the following substances with 0.8N t-C_4H_9OK solution in equal volumes of diglime ($CH_3OC_2H_4OC_2H_4OCH_3$) and deuterated t-butanol at 120° or with 0.03N potassium amide in liquid ammonia at 0 or 25° were measured: $C_6H_5P(CH_3)_2$ (b.p. 68-68.5° at 11 mm, n_D^{20}= 1.5650, d_4^{20}= 0.9670), $(C_6H_5)_2PCH_3$ (b.p. 146-147° at 7 mm, n_D^{20}= 1.6257, d_4^{20}= 1.0646),m-$CH_3C_6H_4P(C_6H_5)_2^{*}$ (m.p. 51-52°), p-CH_3 $C_6H_4P(C_6H_5)_2$ (m.p. 68-68.5°), $(C_6H_5)_3P$(m.p. 80-81°), m-$CH_3C_6H_4N(C_6H_5)_2$ (m.p. 69.5-70.5°), p-$CH_3C_6H_4N(C_6H_5)_2^{**}$ (m.p. 71-72°) $(C_6H_5)_3N$ (m.p.126.5-127°). It was found by test runs that the substances were stable under the experimental conditions. The results of the experiments are represented in Figs.1 and 2. n is the no of H atoms that underwent of change; t - time (hr).

Curve 2 of Fig.1 shows that in $C_6H_5P(CH_3)_2$ six hydrogen atoms undergo exchange much more rapidly than the others. This allows the rate constant of hydrogen exchange in the dimethylphosphino group with ND_3 + KND_2 (0.02N) to be calculated. The mean value is $k = 1.1x10^{-3}$ sec^{-1}at 0°. Exchange takes place twice as fast as in the CH_3 group (6) of toluene and 120 times as fast as in benzene (7) while it is about 10^4 times faster than in the dimethylamino group (8). Such a considerable difference is to be ascribed to stabilization of the dimethylphenylphosphine carbanion in the transition state of the exchange reaction with the base due to 2p, 3d conjugation.

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*Prepared from diphenylchlorophosphine and m-tolylmagnesium bromide.

Found: C 82.5, 82.7; H 6.1, 6.1; P 10.7, 10.9.

Calcd. for $C_{19}H_{17}P$: C 82.6, H 6.5, P 11.2.

** Prepared by arylation of p-toluidine with iodobenzene.

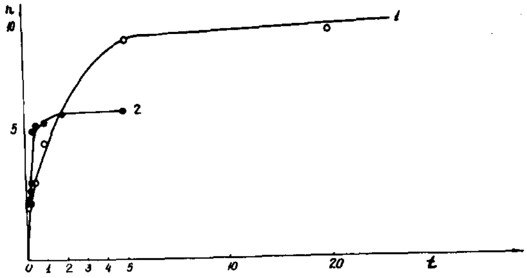

Fig.1

Deuterium exchange with 0.02N potassium amide solution in liquid ammonia, 0°.

1. $(C_6H_5)_2PCH_3$ 2. $C_6H_5P(CH_3)_2$.

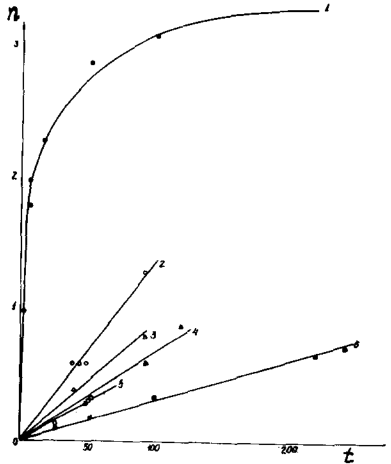

Fig.2

Deuterium exchange with 0.8N t-C_4H_9OK solution a mixture of equal volumes of butanol and diglime,120°.

1. p-$CH_3C_6H_4P(C_6H_5)_2$; 2. m-$CH_3C_6H_4P(C_6H_5)_2$;
3. m-$CH_3C_6H_4N(C_6H_5)_2$; 4. p-$CH_3C_6H_4N(C_6H_5)_2$;
5. $(C_6H_5)_3P$; 6. $(C_6H_5)_3N$.

It is well known (3) that deuteroexchange with base and metalation proceed by the ptorophilic hydrogen substitution mechanism. In fact, in accord with the deuterium exchange data, alkyllithiums selectively metalate dimethylphenylphosphine and methyldiphenylphosphine in the methyl group (9) in contrast to dimethylaniline and methyldiphenylamine (10) which are metalated in the ortho position of the aromatic ring.

Similar differences in the reactivity of compounds with elements of the second and third periods of the Mendeleev table due to the fact that only the latter possess vacant 3d levels can been observed in comparing, for instance, the rates of hydrogen exchange in the methoxy and methylthio groups, respectively, of anisole and thioanisole (11,12).

If the constant for the rate of hydrogen exchange in the CH_3 group of toluene with a solution of potassium amide in ammonia is taken equal to unity then the following order is obtained:

CH_3	OCH_3	SCH_3	$N(CH_3)_2$	$P(CH_3)_2$
1	0.003	10000	0.0001	2

Consequently the replacement of nitrogen by phosphorus will accelerate the exchange reaction by 10^4 fold, and the replacement of oxygen by sulfur will increase the rate by 10^7 times.

The measurements made on methyldiphenylphosphine (Fig.1, curve 1) do not allow the rate constant of hydrogen exchange in the PCH_3 group to be calculated because as it can be seen from the shape of the curve the rate of exchange of the most reactive aromatic and aliphatic CH bonds differ less than in the case of dimethylphenylphosphine.

Preliminary experiments on the exchange of triphenylphosphine and triphenylamine with ammonia reveal quite high values for the over-all rate of the reaction. Triphenylphosphine is somewhat more reactive, as is substantiated also by the results of measuring the deuteroexchange with t-butanol (Fig.2). For a degree of exchange $n < 1$, the mean numerical values for k_{120^o} are $2.7x10^{-7}$ and $1.6x10^{-7}$ sec^{-1} .

One may expect the effect of p,d conjugation to be manifested in the transition state on protonization of the hydrogen of the CH_3 group introduced into the para position of the triphenylphosphine molecule. This effect should be absent in protophilic deuteroexchange of the meta isomer of tolyldiphenylphosphine and in both isomers of tolyldiphenylamine.

The experimental results are in accord with the above said. In p-tolyldiphenylphosphine the three hydrogen atoms undergo exchange much faster than the rest (see Fig.2, curve 1). Thus, during the time required for the exchange of two hydrogen atoms in this compound hydrogen exchange begins only to be noticeable in m-tolyldiphenylphosphine and in p- and m- tolyldiphenylamine (see also (2)).

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