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PROTOPHILIC DEUTEROEXCHANGE OF CERTAIN TERTIARY ARYLPHOSPHINES AND THEIR OXIDES

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Abstract—In order to study the electron effects of phosphorus-containing substituents, the rate constants of protophilic isotope exchange at *ortho, meta* and *para* positions for deuterated triphenylphosphine, triphenylamine, triphenylphospine oxide and at *meta* and *para* positions for dimethylphenyl-phosphine have been determined. In addition, the rate constants have been determined for protophilic isotope exchange in deuteromethyl groups of diphenyl-*m*- and *p*-tolyphosphines, their oxides and methyldiphenylphosphine. Based on the data obtained, the electronoacceptor effect of trivalent phosphorus is similar to that of pentavalent phosphorus and qualtatively different from the effects of trivalent nitrogen. This may possibly account for the p_π–d_π-conjugation and complete absence or negligible contribution of p–π-conjugation.

INTRODUCTION

THE influence of the trivalent P atom on the distribution of electron density over the benzene ring was studied [1–8] by its effect on the properties of functional groups at the corresponding positions of the benzene ring. The only example of direct substitution orientated by trivalent phosphorus known at present is the metalation of triphenylphosphine[9] which however has not been studied quantitatively.

To understand the nature of the electron effects of phosphorus containing substituents,[10] the isotope hydrogen exchange kinetics in aromatic amines and phosphines have been studied as models of the substitution reaction.[11] The results show that there is a pronounced difference in the electron effect of phosphorus and nitrogen. The direct hydrogen–deuterium isotope exchange experiments do not reveal all the details of this process whereas the reverse reaction kinetics-dedeuteration of aromatic phosphines and amines containing deuterium at certain positions in the ring or side chain, reveals them easily.

In this paper we report the rate of dedeuteration in the presence of a base for triphenylamine, dimethylphosphine, triphenylphosphine and its oxide, all containing deuterium at definite positions of the benzene ring. Evidence has been obtained for the influence of tri- and pentavalent phosphorus on the rate of deuterium exchange in Me groups, bonded to phosphorous directly or via the benzene ring.

Synthesis

The preparation of deuterated triphenylphosphines is discussed in the Experimental:

$$(C_6H_5)_2PR \xleftarrow{(C_6H_5)_2PCl} RMgX \xrightarrow{PCl_3} R_3P$$

$$R = O\text{-}DC_6H_4,\ m\text{-}DC_6H_4,\ p\text{-}DC_6H_4$$

In the preparation of benzene deuterohalides, mixtures with deuterobenzene and the starting benzene dihalide were always obtained as proved by GLC. After separation in 30–50% yield, the isotopic purity of the compounds obtained exceeded 90%. Their individuality was confirmed by GLC which indicated no more than 1% impurity (ether, dideuterobenzene) in the compounds. The constants and the yields of the compounds obtained are tabulated (Table 1).

TABLE 1. DEUTERATED ARYLHALIDES

Compound	n_D^{20}		d_4^{20}		B.p. °C	Yield %
	X = D	X = H	X = D	X = H		
p-XC_6H_4Br	1·5586	1·5600[12]	1·4974	1·4939[12]	154	31
m-XC_6H_4Cl	1·5235	1·5248[12]	1·1146	1·1074[12]	132	56
o-XC_6H_4Cl	1·5246	1·5248[12]	1·1186	1·1074[12]	132	42
m-$CX_3C_6H_4Br$	1·5495	1·5538[13]	1·4226	1·4092[13]	183	73
p-$CX_3C_6H_4Br$[a]	—	—	—	—	183	65

[a] M.p. is 27–28°; According to Ref. 14; m.p. of p-bromotoluene is 28°.

TABLE 2. DEUTERATED TRIARYLPHOSPHINES RPR'_2

R	p-C_6H_4D	m-DC_6H_4	o-DC_6H_4	p-DC_6H_4	m-DC_6H_4	o-DC_6H_4	p-$CD_3C_6H_4$	m-$CD_3C_6H_4$
R'	C_6H_5	C_6H_5	C_6H_5	p-DC_6H_4	m-DC_6H_4	o-DC_6H_4	C_6H_5	C_6H_5
M.p. °C	82–83[a]	82–83[a]	82–83[a]	82–83[a]	82–83[a]	82–83[a]	67–68[b]	51–52[c]
Yield, %	68	74	67	60	59	71	74	65

[a] M.p. of tripehnylphosphine[15] is 80°.

[b] M.p. of diphenyl-p-tolylphopsphine[16] is 68°.

[c] M.p. of diphenyl-m-tolylphosphine[10] is 51–52°.

The m.ps and yields of deuterated triarylphosphines are listed in Table 2; their isotopic purity was also higher than 90%.

The corresponding phosphine oxides are given in Table 3.

TABLE 3. DEUTERATED TRIARYLPHOSPHINE OXIDES

R	M.p., °C	Yield, %
p-DC_6H_4[a]	157–158	76
m-DC_6H_4[a]	157–158	65
o-DC_6H_4[a]	157–158	80
p-$CD_3C_6H_4$[b]	134·5–135	76
m-$CD_3C_6H_4$[c]	126–127	88

[a] M.p. of triphenylphosphine[17] is 156°.

[b] M.p. of diphenyl-p-tolylphosphine[18] is 129–130°.

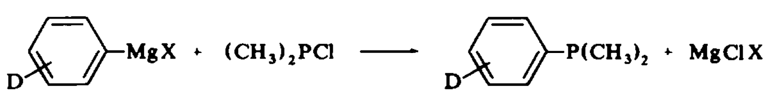
[c] M.p. of diphenyl-m-tolylphosphine[18] is 123–124°.

Similarly, the dimethylphenylphosphines prepared with deuterium at *meta* or *para* positions are given in Table 4.

TABLE 4. DEUTERATED DIMETHYLARYLPHOSPHINES OF $XC_6H_4P(CH_3)_2$ TYPE

Compound	n_D^{20}		d_4^{20}		B.p., °C/mm	Yield, %
	X = D	X = H	X = D	X = H		
p-$XC_6H_4P(CH_3)_2$[a]	1·5627	1·5650[10]	0·9757	0·9670[11]	65–66/8	69
m-$XC_6H_4P(CH_3)_2$[a]	1·5631	1·5650[10]	0·9809	0·9670[11]	64–65/8	60

[a] B.p. of dimethylphenylphosphine[10] is 68–68·5° at 11 mm.

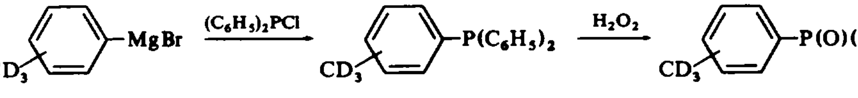


Dimethylchlorophosphine was obtained by reduction of dimethylchlorothiophosphinate with triphenylphosphine.

$$(CH_3)_2P(S)Cl + (C_6H_5)_3P \longrightarrow (CH_3)_2PCl + (C_6H_5)_3PS$$

α,α,α-Trideuterobromotoluenes necessary for the synthesis of diphenyltolylphosphines were prepared according to the Schlosser's method[19] with a modification of the isotope exchange conditions: the phosphonium salts obtained from triphenylphosphine and *m*- and *p*-bromobenzyl bromides were treated in the presence of deuterated sodium alkali using a mixture of deuterated water and tetrahydrofuran instead of deuterated water only. This reduced the requirements for water considerably (8 times). According to the GLC data, the compounds obtained were single substances (98–99%); the isotopic purity exceeded 90%. The PMR spectra of the deuterotoluenes show no reasonances of Me protons.

The deuterated diphenyltolylphosphines (Table 2) obtained were converted into the corresponding oxides given in Table 3.



Methyldiphenylphosphines containing deuterium in the Me group were synthesized by the reaction of diphenylchlorophosphine with deuterated methylmagnesium iodide.

$$CD_3MgI + ClP(C_6H_5)_2 \longrightarrow CD_3P(C_6H_5)_2 + Mg\ ICl$$

Tri-(*p*-deuterophenyl)amine was obtained from tri-(*p*-bromophenyl)-amine butyllithium and deuterated water[20] using ether which gives better results than the hexane.[20]

Tri-(*o*,*o*′,*p*-trideuterophenyl)amine was obtained by deuteration of triphenylamine.[21] Tri-(*m*,*m*′-dideuterophenyl)amine was prepared by the twofold action of anhydrous trifluoroacetic acid on tri-(pentadeuterophenyl)amine synthesized from triphenylamine. The evidence for no exchange at the *meta* positions even with stronger acid (with liquid deuterium bromide) has been reported.[22]

The deuterium position in the compounds was confirmed by IR spectra.* The position in the spectra for the bands of out-of-plane C—H deformations[23] depend on the type of substitution used to identify the structure. The corresponding bands together with their assignments for isomeric deuterated halobenzenes, triphenylphosphines and triphenylamine are tabulated (Table 5). Each isomer was characterized by an intense band not present in the spectra of other isomers. These band positions are known to be little dependent on the type of substituent in the aromatic ring. The data also provide evidence for the isomeric purity of the compounds obtained.

TABLE 5. THE FREQUENCIES OF INFRARED SPECTRA IN THE RANGE OF CH OUT-OF-PLANE DEFORMATION OF DEUTERATED BENZENE HALIDES, TRIPHENYLPHOSPHINES AND TRIPHENYLAMINE

Compound	Adjacent 4H-atoms	Adjacent 3H-atoms	Adjacent 2H-atoms	Adjacent 1H-atom
o-DC_6H_4Cl	772 (very strong)[a]	—	—	—
m-DC_6H_4Cl	—	800 (very strong)	—	902 (medium)
p-DC_6H_4Br	—	—	850 (very strong)	—
(*o*-$DC_6H_4)_3P$	780 (very strong)	—	—	—
(*m*-$DC_6H_4)_3P$	—	810 (very strong)[b]	—	913 (medium)
(*p*-$DC_6H_4)_3P$	—	—	856 (very strong)	—
(*p*-$DC_6H_4)_3N$	—	—	850 (very strong)	—
m-$DC_6H_4P(CH_3)_2$	—	808 (strong)[c]	—	900 (very strong)[d]
p-$DC_6H_4P(CH_3)_2$	—	—	850 (very strong)	903 (very strong)[d]

[a] There are very weak bands in the range of 850–860 cm^{-1} typical for *para*-isomer. A similar (855 cm^{-1}) fairly intensive band is observed also in triphenylphosphine but vanishes in tri-(*o*-deuterophenyl) phosphine.

[b] There is a weak band 855 cm^{-1} in the spectrum which may be interpreted in terms of admixture of *para*-isomer. This band is also, however, observed in triphenylphosphine. In *m*-deuterochlorobenzene this absorption peak is not present.

[c] The band 808 cm^{-1} has two satellites 850 cm^{-1} and 868 cm^{-1} of average intensity which may be assigned to the *para*-isomer. A similar doublet of lower intensity is present in undeuterated dimethylphenylphosphine.

[d] Very strong bands at about 900 cm^{-1} are observed in both dimethylphenylphosphine and dimethyl-*p*-deuterophenylphosphine.

The structures of *p*-deuterobromobenzene, α,α,α-tri-deutero-*p*-bromotoluene and tri-(*p*-deuterophenyl)amine were confirmed by PMR spectra† which are symmetrical quadruplets and correspond to the AB type. Such spectra are typical for particular *para* disubstituted benzene.[24] The spectra of *ortho* and *meta* deuterochlorobenzenes appear as complicated multiplets different from each other.

The PMR spectra of deuterotriphenylphosphine solutions in THF (0·36 m) are doublets ($\delta = 7{\cdot}15$ ppm, $J = 3{\cdot}5$ c/s ($\pm 0{\cdot}2$)) and do not differ from those of triphenylphosphine under similar conditions. The relative intensity of doublet resonances depends on the concentration used. Shaw *et al.*[25] suggest that all of the triphenylphosphine protons are approximately magnetically equivalent and show the same chemical shift while the splitting of the signal is caused by the spin–spin interaction of protons with phosphorus. Although this interpretation is in agreement with our

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* The authors express their appreciation to E. I. Matrosov and B. C. Chikildin for IR spectral determinations.

† The PMR spectra were determined by I. D. Rubin for which the authors wish to thank him.

data on spectra of deuterated derivatives (otherwise the spectra of different isomers would not be identical), we do not agree with the explanation of magnetic equivalence of protons. The donor mesomeric effect postulated[25] for the Ph_2P-group would obviously encourage the inequivalence of protons produced by the negative effect is more likely to account for the equivalence. This effect was experimentally found to occur for the Ph_2P-group.[1-8]

RESULTS

Table 6 gives the average values of the dedeuteriation rate constants at *ortho*, *meta* and *para* positions of isomers of deuterotriphenylphosphine, deuterotriphenylamine and dimethyldeuterophenylphosphine with liquid ammonia, potassium amide (0·02N) or sodium amide (the saturated solution) at 25°.

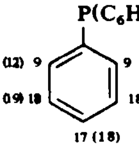
TABLE 6. THE AVERAGE VALUES OF THE RATE CONSTANTS OF DEDEUTERATION IN AROMATIC RING

Deudeuterated compound	Solvent, catalyst	Temp	k sec^{-1} for various position in ring[a]		
			ortho-	*meta-*	*para*
Triphenylphosphine	NH_3, KNH_2	25°	$5{\cdot}2(\pm0{\cdot}2).10^{-4}$	$10{\cdot}4(\pm0{\cdot}8).10^{-4}$	$9{\cdot}8(\pm0{\cdot}7).10^{-4}$
Triphenylphosphine	NH_3, $NaNH_2$	25°	$1{\cdot}2(\pm0{\cdot}15).10^{-4}$	$1{\cdot}9(\pm0{\cdot}1).10^{-4}$	$1{\cdot}8(\pm0{\cdot}1).10^{-4}$
Triphenylamine	NH_3, KNH_2	25°	$1{\cdot}7(\pm0{\cdot}1).10^{-3}$[b]	$5{\cdot}2(\pm0{\cdot}7).10^{-4}$	$2{\cdot}4(\pm0{\cdot}2).10^{-4}$
Triphenylamine	NH_3, $NaNH_2$	25°	—	$9{\cdot}2(\pm0{\cdot}1).10^{-5}$	$4{\cdot}2(\pm0{\cdot}4).10^{-5}$
Dimethylphenylphosphine	NH_3, KNH_2	25°	—	$1{\cdot}3(\pm0{\cdot}2).10^{-4}$	$1{\cdot}3(\pm0{\cdot}2).10^{-4}$
Triphenylphospine oxide	$t\text{-}C_4H_9OH$—diglime(50vol%) $t\text{-}C_4H_9OK$ (0·8N)	120°	$6{\cdot}6(\pm0{\cdot}6).10^{-6}$	$1{\cdot}2(\pm0{\cdot}2).10^{-6}$	$0{\cdot}8(\pm0{\cdot}1).10^{-6}$

[a] For the calculation of f-values the exchange rate constant of deuterobenzene with liquid ammonia and KNH_2 (0·02 N). ($k_{25} = 5{\cdot}7(\pm0{\cdot}7).10^{-5}$ sec^{-1}) and in the saturated solution $NaNH_2$ ($k_{25} = 1{\cdot}0 (\pm0{\cdot}1).10^{-5}$ sec^{-1}) at 25°.

[b] Is calculated using the experimentally determined total exchange rate of $(o,o',p\text{-}D_3C_6H_2)_3N$ and the value $k_{para} = 2{\cdot}4.10^{-4}$ sec^{-1}.

The values of deuteroexchange partial rate factors (f) are indicated below with the values obtained with sodium amide in brackets. The data for dimethylaniline have been reported.[26]



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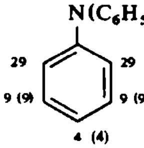

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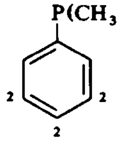
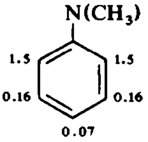


III



IV

A comparison of formula I and II as well as III* and IV shows that f_{meta} and f_{para} are practically equal when there is a hydrogen exchange in the phenyl rings of aryl-

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* The data on dimethylphenylphophine (III) are to be considered as preliminary since the structure of the compound containing deuterium at *meta*-position was not positively identified.

phosphines in contrast to the corresponding amines where $f_{meta} > f_{para}$. The higher exchange rate of *meta* and *para* atoms for organophosphorus compounds indicates the more powerful electronacceptor properties of phosphorus as compared with nitrogen. This may be accounted for by the p_π–d_π-conjugation since nitrogene electronegativity is higher than that of phosphorus. The equal exchange rates at *meta* and *para* positions of phosphines (I and III) apparently are due to this conjugation compensating the inductive effect extinction at *para* position and of the full absence or negligibility of p-π-conjugation as in phosphorus distinct from nitrogen.

Unfortunately, we have not determined the value of f_{ortho} for III. In triphenylphosphine (I) unlike triphenylamine (II) $f_{ortho} < f_{meta}$. This may be due to the steric hindrance of *ortho* positions in phosphines which is stronger than in amines (the valent angles at heteroatoms in triphenylphosphine[27] and triphenylamine[28] are 102–103° and 116° respectively). Conversion of trivalent into pentavalent phosphorus in the triphenyl derivative is accompanied by an increase in the C—P—C angle from 102–103° to approximately a tetrahedral one and is followed by a marked acceleration of the deuterium exchange at the *ortho* position compared with the *meta* and *para* positions. This may be related to the reduced steric hindrance of the *ortho* position. The growth of substituent inductive effect is of course of great importance.

Since the hydrogen exchange in triphenylphosphine oxide in liquid ammonia is very fast with sodium amide as catalyst the measurements of dedeuteriation kinetics were performed in a mixture of equal volumes of t-butyl alcohol and diglime (or diethylene glycol) with t-BuOK (0·8N) at 120° (Table 6). The electronoacceptor properties of the Ph_2P-group are more distinct than in triphenylphosphine on confrontation of exchange rates in Me groups bonded to one of the phenyl rings of triphenylphosphine at *meta* or *para* position. We measured the dedeuteriation kinetics of the corresponding diphenyltolylphosphines with deuterium in Me group in a mixture t-butyl alcohol-diglime with BuOK (120°). The exchange in the *para* Me group was found to be approximately 25 times faster than the *meta* Me group (Table 7). This indicates p_π–d_π-conjugation in the transition state of exchange in

TABLE 7. THE AVERAGE VALUES OF DEDEUTERIATION RATE CONSTANTS IN METHYL GROUPS OF DIPHENYLTOLYLPHOSPHINES, OF THEIR OXIDES AND METHYLDIPHENYLPHOSPHINE

The compound	Solvent catalyst	Temp	sec^{-1} for various positions in ring	
			meta	*para*
$(C_6H_5)_2PC_6H_4CD_3$	$t\text{-}C_4H_9OH$— diglime (50 vol.%), $t\text{-}C_4H_9OK$	120°	1·1 (±0·1) . 10^{-6}	2·6 (±0·4) . 10^{-5}
$(C_6H_5)_2P(O)C_6H_4CD_3$	$t\text{-}C_4H_9OH$— diglime (50 vol.%), $t\text{-}C_4H_9OK$	120°	4·5 (±0·1) . 10^{-5}	1·1 . 10^{-2}[a]
$(C_6H_5)_2PCD_3$	NH_3, KNH_2	−20°	2·1 (±0·1) . 10^{-3}	
$C_6H_5CD_3$	NH_3, KNH_2	−20°	7·9 (±0·3) . 10^{-5}	

[a] The approximate rate constant is calculated using the value of apparent activation energy of reaction (~20 kcal/mole), determined from the exchange rate constants at 25, 50 and 75°: 2·7 (±0·1) . 10^{-6}; 3·4 (±0·6) . 10^{-5}; 3·6 . 10^{-4} sec^{-1}.

diphenyl-*p*-tolyplphosphine which apparently possesses the carbanion structure. The d-orbital conjugation effects are more powerful here than in triphenylphosphine.

This is probably caused by the difference in structure of carbanion centres arising during exchange of Ph and Me groups and in their interaction with substituents in phenyl rings. The carbanion centre appearing during exchange of the Me group is capable of direct polar conjugation with the substituent in the benzene ring (in this case with trivalent P atoms possessing the vacant d-orbitals) which reduces the transition state energy. When hydrogen exchange at the *para*-position of ring takes place, the carbanion centre arising in the transition state apparently does not come into direct conjugation with the substituent since the electrons of the breaking C—H bond are located in the benzene ring plane. In this case the substituent conjugation with the benzene exerts indirect influence on the carbanion centre through the change in π-electron density at the *para* C atom.

The deuterium exchange in the Me group of diphenyl-*p*-tolylphosphine oxide is so fast that we could not measure its rate at 120° (in the mixture with t-butyl alcohol-diglime). The rate constant was estimated on the basis of the approximately determined value of apparent activation energy of the reaction ($\sim$20 kcal/mole). The deuterium exchange rate in the Me group of diphenyl-*m*-tolylphosphine oxide is approximately 200 times slower than that in the *para*-isomer (Table 7).

Consequently, the electron influence of trivalent phosphorus in the Ph_2P-group is quantitatively but not qualitatively different from that of pentavalent P in the $Ph_2P(O)$-group. Trivalent phosphorus and nitrogen are essentially different in this respect.

Trivalent phosphorus exerts a strong influence on the hydrogen exchange rate in Me groups directly bonded to phosphorus. It has been shown earlier[11] that the exchange in Me groups of dimethylphenylphosphine is twice as fast as that in toluene Me groups and 10^4 times as fast as that in Me groups of dimethylaniline. This reaction illustrates the difference between the electron influence of nitrogen and phosphorus.

We have also studied the exchange in the deuteromethyl group of methyldiphenylphosphine with liquid ammonia in the presence of potassium amide ($-20°$). The reaction rate is approximately 25 times faster than in the Me group of toluene (Table 7). Consequently, substitution of Me group by a Ph group in dimethylphenylphosphine is accompanied by a 12-fold increase in the deuterium exchange rate in the Me group bonded to phosphorus (a similar substitution of Me group for Ph in dimethylaniline accelerates the exchange reaction twice only). The increased effect of a Ph group bonded to phosphorus may account for its participation in the carbanion negative charge delocalization which arises in the transition state. This means that one can suppose a through charge delocalization over the P atom. The possibility of such a delocalization in cyclic phosphonitrile chlorides was theoretically investigated by Craig and Mitchell.[29] This type delocalization of a negative charge through the N atom is evidently impossible since it would increase the number of electrons in the nitrogen valent shell above eight.* The increase in deuterium exchange

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* The successive substitution of methyls for phenyls in tetramethylphosphonium iodide is known to increase the hydrogen exchange rate in methyl groups by nearly 20 times per each substitution.[30] The additivity in the changes of constants suggests an idea of dominant contribution of inductive effect. It is, however, by no means to be considered as evidence for no delocalization.

rate in the Me group of methyldiphenylamine compared with dimethylaniline seems to be due to the inductive effect of the Ph group.

In conclusion, the deuteroexchange kinetics of several aromatic phosphines and their oxides show that the electron effect of trivalent and pentavalent phosphorus are similar and differ qualitatively from the effects of trivalent nitrogen. Several of the phenomena may be interpreted in terms of conjugation using the vacant d-orbitals of the P atom. No evidence for p–π conjugation was observed for trivalent phosphorus compounds. The present data are in agreement with ionization constants of phosphorus substituted benzoic acids.[1–3]

EXPERIMENTAL

The purity of deuterated halobenzenes and bromotoluenes was tested using the chromatographed "Tsvet-1", with silicone oil PM S-4 as carrier.

The PMR spectra were measured using a NMR high resolution spectrometer Hitachi H-60, and IR spectra using a spectrometer UR-10. All the procedures were carried out under N_2.

Deuterated Triarylphosphines

Tri-(o-deuterophenyl) phosphine. To a soln of Grignard's reagent obtained from 14·2 g *o*-deuterchlorobenzene and 3,2 g Mg in 75 ml THF, a soln of 5·5 g PCl_3 in 25 ml THF was added drop-wise at −50° to −40°. In 40 min (−40°) the mixture was heated to the room temp and treated with NH_4Cl aq. The aqueous layer was extracted with benzene. The extract was dried over Na_2SO_4, the solvent was removed under reduced press and the reisude distilled. The tri-(*o*-deuterphenyl) phosphine was crystallized from alcohol.

Tri(-*m*-deuterophenyl) phosphine and tri-(*p*-deuterophenyl) phosphine were synthesized similarly.

Diphenyl-*o*-deuterophenylphosphine, diphenyl-*m*-deuterophenylphosphine, diphenyl-*p*-deuterophenylphosphine, diphenyl-α,α,α-trideutero-*p*-tolylphosphine, diphenyl-α,α,α-trideutero-*m*-tolylphosphine were obtained similarly, using diphenylchlorophosphine instead of PCl_3. All compounds were crystallized from alcohol.

Dimethyldeuterophenylphosphines

Dimethyl-p-deuterophenylphosphine. To a stirred Grignard's soln obtained from Mg (1·55 g) and *p*-deuterobromobenzene (9·2 g) in 60 ml ether, a soln of dimethylchlorophosphine (4·7 g) in 20 ml ether was added dropwise at −60° to −50°. In 1 hr (−40°) the reaction was raised to the room temp and the mixture treated with sat. NH_4Cl aq and extracted with benzene. The extract was dried over Na_2SO_4 and evaporated under reduced press. Dimethyl-*p*-deuterophenylphosphine was isolated by distillation.

Dimethyl-*m*-deuterophenylphosphine was synthesized in a similar manner.

Deuterated arylphosphine oxides

Diphenyl-m-tolylphosphine oxide. 2 ml 30%-H_2O_2 was added dropwise to a soln of diphenyl-*m*-tolylphosphine (3·0 g) in 25 ml acetone. The mixture was refluxed for 1 hr, the solvent was distilled off under reduced press and the residue dissolved in benzene. The solution was washed with water, with an acidified solution of Mohr's salt with water again and dried over Na_2SO_4. The solvent was distilled off under reduced press. Diphenyl-*m*-tolyphosphine oxide was isolated by crystallization from a mixture benzene–hexane to give 80% yield, the m.p. was 126–127°. (Found: C, 78·0; 78·1; H, 5·8; 5·8; P, 10·7; 10·6. Calc. for: C, 78·1; H, 5·9; P, 10·6%).

Oxides of diphenyl-*p*-deuterophenylphosphine, diphenyl-*m*-deuterophenylphosphine, diphenyl-*o*-deuterophenylphosphine, diphenyl-α,α,α-trideutero-*p*-tolylphosphine, diphenyl-α,α,α-tri-deutero-*m*-tolylphosphine were synthesized similarly. All compounds were crystallized from benzene–hexane mixtures.

The measurements of deuteroexchange kinetics

To avoid systematical errors, we used various products of the same compound containing deuterium at certain positions in one or three benzene rings and solutions of the catalyst were prepared independently in the corresponding solvents. There were from 200 to 800 moles of ammonia or from 60 to 80 moles of t-butyl alcohol per 1 mole of substance. To check the concentration of each potassium amide solution in liquid ammonia, we measured the deuterium exchange rate in the Me group of toluene at 0°. The following average values of the rate constants were obtained: $k \,.\, 10^{-4}$: 5·6, 5·2, 5·0.

For the calculation of the rate constant for the exchange reaction of deuterobenzene with liquid ammonia was determined in the presence of potassium amide (0·02 N): $5{\cdot}7\,(\pm 0{\cdot}7)\,.\,10^{-5}\ \text{sec}^{-1}$. In the experiments using a saturated soln of sodium amide the average value of the rate constant at 25° was obtained: $1{\cdot}0\,(\pm 0{\cdot}1)\,.\,10^{-5}\ \text{sec}^{-1}$.

The solns of triphenylphosphine in liquid ammonia in the presence of potassium or sodium amide were of orange-red in colour, the solns of triphenylamine were yellow in the presence of potassium amide and light yellow in the presence of sodium amide, those of dimethylphenylphosphine were light orange. The solns of all studied samples in mixture of t-butyl alcohol with diglime were colourless.

All compounds were insoluble in water. In order to stop the reaction and to isolate the compound the solns were poured into water. Liquid compounds came to the surface and were separated by pipette and distilled under reduced press over calcium hydride. The solids precipitated were filtered off, washed on the filter and dried under reduced press. In a few cases the compounds were extracted from aqueous soln by ether; the extract was washed, dried over $CaCl_2$ chloride, then the ether was distilled off and the residue was dried under reduced press. The constants of all compounds remained the same before and after experiments.

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