# EQUILIBRIUM CH-ACIDITY OF ORGANOPHOSPHORUS COMPOUNDS

## COMMUNICATION 2. OXIDES OF SUBSTITUTED BENZYLPHOSPHINES AND SOME OF THEIR ANALOGS

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In [1] data were cited on the equilibrium CH-acidity (pK) of a number of phosphine oxides and phosphine sulfides of analogous structure, obtained by the method of transmetallation, using alkali-substituted aliphatic—aromatic indicators in diglyme (DG) and in DMSO.

In this work we measured pK of compounds with the general formula $\begin{matrix} X \\ \diagdown \\ \quad P(O)CH_2C_6H_4Z\text{-}p \\ \diagup \\ Y \end{matrix}$ to determine the influence of electronic effects of the substituents, as well as the polarity of the solvent, on the CH-acidity.

## DISCUSSION OF RESULTS

The compounds studied in this work are cited in Table 1. The synthesis of (I) and (V) was described earlier [1]. The oxide (II) was produced from diisopropylchlorophosphine and benzyl magnesium chloride, followed by oxidation of the intermediate diisopropylphosphine. The phosphine oxides (III) and (IV) were synthesized through the organomagnesium compounds of their chlorides of benzylphosphonic and phenylbenzylphosphinic acids. To obtain (VI) and (VII) we used the method of synthesis of nonsymmetrical phosphine oxides [3], based on alkylation of Mg salts of diarylphosphinous acids, formed under the action of aryl magnesium halides on diethyl phosphite.

The esters (VIII)-(XI) were produced according to the Michaelis—Becker reaction from salts of the corresponding acid esters of acids of trivalent phosphorus. Amides of benzylphosphonic acid (XII) and (XIII) were synthesized from the dichloride of the acid and secondary amines.

The condensation of diphenylphosphine with aldehydes in acid medium [15] led to the phosphine oxides (XIV) and (XV). Probably substituted hydroxybenzylphosphines are formed in these syntheses and undergo a pseudoallyl rearrangement [16]

$$(C_6H_5)_2PH \xrightarrow[HCl]{p\text{-}ZC_6H_4CHO} (C_6H_5)_2PCHC_6H_4Z\text{-}p \xrightarrow[HCl]{} (C_6H_5)_2P(O)CH_2C_6H_4Z\text{-}p$$

$$Z = CH_3,\ CH_3O$$

Diphenylphosphine was synthesized by the cleavage of ethyldiphenylphosphinite with sodium in liquid $NH_3$. The initial ethyldiphenylphosphinite was produced by the reaction of $PCl_3$ with benzene in the presence of $AlCl_3$, followed by alcoholysis of the reaction mixture in the presence of triethylamine [17].

The phosphine oxides (XVI) and (XVII) were produced by an Arbuzov rearrangement of ethyldiphenylphosphinite by substituted benzyl bromides. The nitration of diphenylbenzylphosphine oxide (V) led to the nitro derivative (XVIII), the structure of which as a p-isomer was assumed on the basis of analogy with the nitration of benzylphosphonic acid [18].

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TABLE 1. Derivatives of Benzylphosphinic Acid and Substituted Benzylphosphine Oxides

| Compound | Formula | Yield, % | Mp, °C | Bp, °C (p, mm Hg) | Literature reference |
|---|---|---|---|---|---|
| (I) | $(C_2H_5)_2P(O)CH_2C_6H_5$ | | 42—43 | 155—156 (2) | [1] |
| (II) | $(i\text{-}C_3H_7)_2P(O)CH_2C_6H_5$ | 50 | 47,5—48,5 (pet. ether) | 160—162 (2) | — |
| (III) | $(C_4H_9)_2P(O)CH_2C_6H_5$ | 46 | 68—69 (pet. ether) | 174—176 (3) | [2] |
| | | | | — | [3] |
| (IV) | $C_2H_5C_6H_5P(O)CH_2C_6H_5$ | 73 | 115—116,5 (benzene) | — | [4] |
| | | | | — | [5] |
| | | | | — | [6] |
| (V) | $(C_6H_5)_2P(O)CH_2C_6H_5$ | | 198—199 | — | [1] |
| (VI) | $(p\text{-}CH_3C_6H_4)_2P(O)CH_2C_6H_5$ [a] | 39 | 178—179 (heptane) | — | — |
| (VII) | $(m\text{-}CF_3C_6H_4)_2P(O)CH_2C_6H_5$ [b] | 53 | 142—143 (benzene-hexane) | — | — |
| (VIII) | $C_2H_5O(C_6H_5)P(O)CH_2C_6H_5$ | 50 | 63—63,5 (pet. ether) | 175—177 (2) | [7] |
| | | | | | [8] |
| (IX) | $(C_2H_5O)_2P(O)CH_2C_6H_5$ [c] | 76 | — | 135—136 (4) | [9] |
| (X) | $(C_4H_9O)_2P(O)CH_2C_6H_5$ [d] | 66 | — | 157—159 (2) | [10] |
| (XI) | $(i\text{-}C_5H_{11}O)_2P(O)CH_2C_6H_5$ [e] | 89 | — | 157—158 (2) | — |
| (XII) | $[(CH_3)_2N]_2P(O)CH_2C_6H_5$ | 81 | 82,5—83,5 (pet. ether) | 141—142 (2) | [11] |
| (XIII) | $[(C_2H_5)_2N]_2P(O)CH_2C_6H_5$ [f] | 40 | 52—53 (heptane) | 158—160 (2) | — |
| (XIV) | $p\text{-}CH_3OC_6H_4CH_2P(O)(C_6H_5)_2$ | 78 | 223—224 (alcohol) | — | [12] |
| (XV) | $p\text{-}CH_3C_6H_4CH_2P(O)(C_6H_5)_2$ | 64 | 198—199 (alcohol) | — | [13] |
| (XVI) | $p\text{-}C_2H_5COOC_6H_4CH_2P(O)(C_6H_5)_2$ [g] | 83 | 197—198 (alcohol) | — | — |
| (XVII) | $p\text{-}CNC_6H_4CH_2P(O)(C_6H_5)_2$ | 84 | 221—222 (ethyl acetate) | — | [14] |
| (XVIII) | $p\text{-}NO_2C_6H_4CH_2P(O)(C_6H_5)_2$ [h] | 84 | 206—208 (alcohol) | — | — |

[a] Found: C 78,6; H 6,8; P 9,7%. $C_{21}H_{21}OP$. Calculated: C 78,7; H 6,6; P 9,7%.

[b] Found: C 58,8; H 3,6; P 7,3%. $C_{21}H_{15}F_6OP$. Calculated: C 58,9; H 3,5; P 7,2%.

[c] $n_D^{20}$ 1,4968; $d_D^{20}$ 1,1116; *MR*, found: 60,11; calculated: 60,26.

[d] $n_D^{20}$ 1,4838; $d_D^{20}$ 1,0312; *MR*, found: 78,98; calculated: 78,74.

[e] $n_D^{20}$ 1,4790; $d_D^{20}$ 1,0032; *MR*, found: 88,22; calculated: 87,97.

[f] Found: C 64,0; H 9,8; P 10,8%. $C_{11}H_{27}N_2OP$. Calculated: C 63,9; H 9,6; P 11,0%.

[g] Found: C 72,8; H 5,9; P 8,7%. $C_{22}H_{21}O_3P$. Calculated: C 72,5; H 5,8; P 8,5%.

[h] Found: C 67,5; H 4,8; P 9,5%. $C_{19}H_{16}NO_3P$. Calculated: C 67,6; H 4,7; P 9,2%.

The values of pK of substituted benzylphosphine oxides and their analogs were measured by the method of transmetallation in DG (counter ion $Li^+$) and in DMSO (counter ion $Cs^+$) (Table 2). The selection of various counter ions in DG and DMSO was substantiated earlier [1]. Derivatives of diphenylbenzylphosphine oxide, substituted in the benzyl group, are poorly soluble in DG; therefore, their acidity was determined only in DMSO (Table 3). The acidity of the compounds studied in both solvents was determined relative to 9-phenylfluorene (18.5) [1].

In the case of a change in the polarity of the solvent (see Table 2), the acidity of compounds (I)-(XIII) is displaced relative to the scale of pK of aliphatic—aromatic CH-acids in DMSO, organophosphorus compounds are relatively weaker CH-acids than in DG. Thus, when DG is replaced by DMSO, the values of pK of the phosphine oxides (I)-(VII) and dialkylamides of benzylphosphonic acid (XII) and (XIII) increase by 4.7-5.6 units of pK, and of esters of benzylphosphonic and phenylbenzylphosphonic acids (VIII)-(XI) by 3.7-4.0 units of pK (see Table 2).

The observed changes in pK are evidently due to the ability of the phosphoryl group for coordination with the metal cation, the degree of which depends on the solvation and polar properties of the solvent [1]. The different values of pK for the oxide (V) with $Cs^+$ (27.9) and, found earlier [1], with $K^+$ (27.1), can evidently be explained by the ability of the phosphoryl group for coordination to a definite degree in the polar DMSO as well.

The relative acidity of the compounds studied is practically independent of the polarity of the medium, which is evidenced by the existence of a linear relationship between the values of pK in DG and DMSO, which phosphine oxides and amides of benzylphosphonic acid obey [Fig. 1, Eq. (1)]. The group of points corresponding to compounds with axial substituents at the phosphorus atom (VIII)-(XI) deviates from a linear dependence:

TABLE 2. Equilibrium CH-Acidity (pK) of the Compounds X, $YP(O)CH_2C_6H_5$ in Diglyme and Dimethyl Sulfoxide

| Compound | X | Y | DG | DMSO | ΔpK |
|---|---|---|---|---|---|
| (I) | $C_2H_5$ | $C_2H_5$ | 25,2* | 30,8* | 5,6 |
| (II) | $i$-$C_3H_7$ | $i$-$C_3H_7$ | 26,2 | 30,7 | 4,5 |
| (III) | $C_4H_9$ | $C_4H_9$ | 25,6 | 30,7 | 5,1 |
| (IV) | $C_2H_5$ | $C_6H_5$ | 24,0 | 29,3 | 5,3 |
| (V) | $C_6H_5$ | $C_6H_5$ | 23,1* | 27,9 | 4,8 |
| (VI) | $p$-$CH_3C_6H_4$ | $p$-$CH_3C_6H_4$ | 23,5 | 28,2 | 4,7 |
| (VII) | $m$-$CF_3C_6H_4$ | $m$-$CF_3C_6H_4$ | 20,7 | 25,5 | 4,8 |
| (VIII) | $C_6H_5$ | $C_2H_5O$ | 23,9 | 27,8 | 3,9 |
| (IX) | $C_2H_5O$ | $C_2H_5O$ | 23,9 | 27,9 | 5,0 |
| (X) | $C_4H_9O$ | $C_4H_9O$ | 24,1 | 28,0 | 3,9 |
| (XI) | $i$-$C_5H_{11}O$ | $i$-$C_5H_{11}O$ | 24,2 | 27,9 | 3,7 |
| (XII) | $(CH_3)_2N$ | $(CH_3)_2N$ | 25,1 | 30,0 | 4,9 |
| (XIII) | $(C_2H_5)_2N$ | $(C_2H_5)_2N$ | 25,7 | 30,9 | 5,2 |

*The values of pK were taken from [1].

$$pK_{DMSO} = 4.0 \pm 1.04\ pK_{DG} + 0.3;\ s_\rho = 0.06;\ r = 0.987 \quad (1)$$

The influence of substituents on the phosphorus atom on the CH-acidity can be estimated from the values of pK in DG, where the effects of the structure were more clearly manifested. In DMSO pK of (I)-(III), (XII), and (XIII) were practically the same, which may be associated with an approach to the limit of reliable measurements.

A comparison of the pK values of phosphine oxides in DG and DMSO with the constants $\sigma_p$ of the substituents at the phosphorus atom gave linear correlations, which have almost equal slopes and differ in the free factor by approximately five units of pK [Fig. 2, Eqs. (2) and (3)]

$$pK_{DG} = 20.4 - 2.20\ \Sigma\sigma^P \pm 0.1;\ s_\rho = 0.05;\ r = 0.993 \quad (2)$$

$$pK_{DMSO} = 25.3 - 2.22\ \Sigma\sigma^P \pm 0.4;\ s_\rho = 0.20;\ r = 0.982 \quad (3)$$

The points corresponding to substances with alkoxyl or amide substituents at the phosphorus atom deviate from the functions (2) and (3); moreover, the deviations have different signs for the ester and amide groups. The causes of the indicated deviations are not yet clear.

The introduction of substituents Z into the p-position of the benzyl group of diphenylbenzylphosphine oxide (see Table 3) greatly influences the CH-acidity. Thus, the $NO_2$ group increases the acidity by almost 10 orders of magnitude. The influence of substituents on the CH-acidity is well described by Eq. (4), in which the constants $\sigma^-$, considering the direct polar conjugation of the substituent with the reaction center, were used:

$$pK = 27.6 - 7.13\ \sigma^- \pm 0.5;\ s_\rho = 0.34;\ r = 0.996 \quad (4)$$

The Hammett $\sigma$-constants give a poorer correlation (r = 0.978, $s_\rho$ = 1.0).

## EXPERIMENTAL

All the operations were performed in an atmosphere of argon. The purity of the substances obtained was monitored by the method of gas—liquid chromatography under the conditions of [1]. The yields, constants, and analyses of the compounds obtained are cited in Table 1. The yields are given on the basis of the products obtained after the first recrystallization; the melting points of the latter and an analytical sample differ by 1-3°C.

TABLE 3. Equilibrium CH-Acidity (pK) of the Compounds p-$ZC_6H_4CH_2P(O)(C_6H_5)_2$ in Dimethyl Sulfoxide

| Compound | Z | pK | Compound | Z | pK |
|---|---|---|---|---|---|
| (XIV) | $CH_3O$ | 29,2 | (XVI) | $CO_2C_2H_5$ | 23,0 |
| (XV) | $CH_3$ | 28,6 | (XVII) | CN | 21,9 |
| (V) | H | 27,9 | (XVIII) | $NO_2$ | 18,2 |

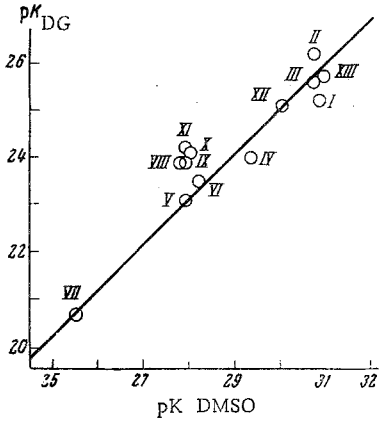


Fig. 1

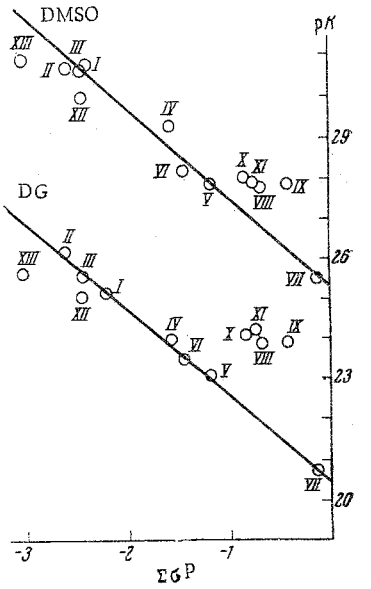


Fig. 2

Fig. 1. Relationship between pK of derivatives of benzylphosphonic acid and substituted benzylphosphine oxides in DG and DMSO. The numeration of the points corresponds to the compounds.

Fig. 2. Dependence of pK of derivatives of benzylphosphonic acid and substituted benzylphosphine oxides in DG and DMSO on the constants $\sigma_p$ of the substituents at the phosphorus atom. The numeration of the points corresponds to the compounds.

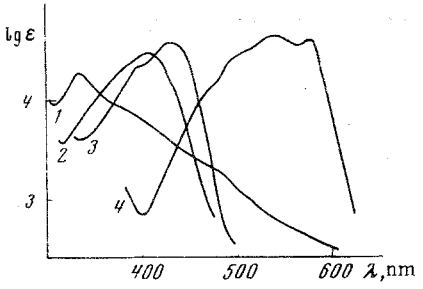


Fig. 3. UV spectra of phosphorus-containing carbanions in DMSO: 1) (V); 2) (XVII); 3) (XVI); 4) (XVIII).

Diisopropylbenzylphosphine Oxide (II). To a Grignard reagent (from 1.3 g Mg and 7.1 g $C_6H_5CH_2Cl$ in 50 ml abs. ether) we added with mixing 8.5 g diisopropylchlorophosphine [19] at 20°C. The mixture was treated with 40 ml of sat. $NH_4Cl$. The aqueous layer was extracted with benzene. The combined extract was dried with anhydrous $Na_2SO_4$ and evaporated under vacuum. To the residue we added 25 ml of acetone and then dropwise 5.1 g of 33% $H_2O_2$. The solution was mixed for 2 h, evaporated under vacuum, the residue dissolved in $CHCl_3$, washed with a solution of Mohr's salt, with water, and dried with anhydrous $Na_2SO_4$. The residue after evaporation of the solvent was redistilled under vacuum. We obtained 6.2 g of the oxide (II).

Dibutylbenzylphosphine Oxide (III). A Grignard reagent (from 2.7 g Mg and 15.7 g $CH_4H_9Br$ in 50 ml abs. THF) was added dropwise with mixing at the temperature −20 to −10°C to 10.7 g of the chloride of benzylphosphonic acid in 25 ml THF. The mixture was boiled for 1 h and treated with dilute (1:10) $H_2SO_4$. The aqueous layer was extracted with ether, and the combined extract evaporated under vacuum. The residue was boiled for 3 h with 10 ml of 20% aqueous-alcoholic KOH. The alcohol was evaporated under vacuum, the residue diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was redistilled. Yield 5.5 g (III).

Ethylphenylbenzylphosphine Oxide (IV). To 6.2 g $PCl_5$ in 70 ml abs. benzene, while boiling, we added 7.4 g phenylbenzylphosphinic acid in portions [20]. The mixture was boiled for 3 h and evaporated under vacuum. To a solution of the acid chloride obtained in 25 ml abs. THF with mixing, we added dropwise a Grignard reagent (0.9 g Mg and 4.2 g $C_2H_5Br$ in 35 ml abs. THF) at −20 to −10°C. Then the synthesis was conducted analogously to the production of (III). After recrystallization from benzene, we obtained 5.7 g (IV).

TABLE 4. Equilibrium Constants of Reactions of Transmetallation

| Compound | Diglyme | | | Dimethyl sulfoxide | | |
|---|---|---|---|---|---|---|
| | indicator* (pK) | K | n | indicator* (pK) | K | n |
| (I) | PF (23,7) | 0,045±0,005 | 2 | DHA (30,4) | 0,28±0,03 | 3 |
| (I) | TPP (25,9) | 3,3±0,6 | 3 | BDM (29,7) | 0,08±0,02 | 5 |
| (II) | TPP (25,9) | 0,45±0,1 | 3 | BDM (29,7) | 0,096±0,007 | 4 |
| (III) | TPP (25,9) | 1,4±0.14 | 3 | BDM (29,7) | 0,10±0,013 | 6 |
| (III) | PX (27,8) | 170±25 | 3 | | | |
| (IV) | PF (23,7) | 0,52±0,05 | 6 | PX (28,3) | 0,10±0,4 | 3 |
| (IV) | | | | BDM (29,7) | 2,2±0,3 | 3 |
| (V) | F (23,4) | 2,1±0,3 | 7 | PX (28,3) | 2,8±0,1 | 4 |
| (V) | PF (23,7) | 3,9±0,5 | 3 | | | |
| (VI) | F (23,4) | 0,79±0,09 | 5 | FK (28,3) | 1,4±0,2 | 6 |
| (VII) | BF (22,0) | 19,3±2,2 | 6 | TPP (26,2) | 4,6±0,6 | 6 |
| (VIII) | F (23,4) | 0,26±0,04 | 6 | PX (28,3) | 3,4±0,4 | 4 |
| (IX) | F (23,4) | 0,29±0,03 | 3 | PX (28,3) | 2,3±0,1 | 3 |
| (X) | F (23,4) | 0,17±0,04 | 5 | PX (28,3) | 1,8±0,1 | 3 |
| (XI) | F (23,4) | 0,15±0,01 | 6 | PX (28,3) | 2,7±0,2 | 3 |
| (XII) | PF (23,7) | 0,05±0,002 | 3 | PX (28,3) | 0,022±0,001 | 3 |
| (XII) | TPP (25,9) | 4,9±1,4 | 3 | BDM (29,7) | 0,41±0,03 | 3 |
| (XIII) | PX (27,8) | 108±15 | 3 | TPM (31,1) | 1,7±0,2 | 6 |
| (XIV) | | | | PX (28,3) | 0,14±0,01 | 4 |
| (XV) | | | | PX (28,3) | 0,50±0,1 | 5 |
| (XVI) | | | | F (22,9) | 0,86±0,05 | 5 |
| (XVII) | | | | BF (21,9) | 0,81±0,06 | 6 |
| (XVIII) | | | | PF (18,5) | 2,15±0,05 | 5 |

*PF) 9-isopropylfluorene; TPP) 1,1,3,3-tetraphenylpropene; PX) 9-phenylxanthene; F) fluorene; BF) 9-benzylfluorene; DHA 9,10-dihydroanthracene; BDM) p-biphenylyldiphenylmethane; TPM) triphenylmethane; PF) 9-phenylfluorene; n is the number of measurements.

Di-p-tolylbenzylphosphine Oxide (VI). To a Grignard reagent (from 2.4 g Mg and 17.1 g p-bromotoluene in 80 ml abs. ether) we added 4.6 g diethyl phosphite dropwise with mixing, maintaining weak boiling of the mixture, and after 30 min of boiling, 17.7 g $C_6H_5CH_2Cl$. The mixture was boiled for 4 h and treated with 80 ml of diluted (1:2) HCl. The aqueous layer was extracted with ether. The combined extract was washed with a saturated solution of soda, with water, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was recrystallized from heptane. Yield 12.2 g (VI).

Di(m-trifluoromethylphenyl)benzylphosphine Oxide (VII). The oxide (VII) was produced analogously to (VI) from m-bromobenzotrifluoride and diethyl phosphite.

Ethyl Ester of Phenylbenzylphosphinic Acid (VIII). To sodium ethylphenylphosphonite, produced by boiling (6 h) 16.3 g ethylphenylphosphonite with 2.2 g Na in 100 ml abs. THF, we added dropwise 12.2 g $C_6H_5CH_2Cl$. After 8 h of boiling, 50 ml of benzene and 40 ml of water were added to the mixture. The aqueous layer was extracted with benzene. The combined extract was washed with water, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was redistilled. Yield 12 g (VIII).

Ethyl Ester of Benzylphosphonic Acid (IX). To a solution of $C_2H_5ONa$ (from 3.7 g Na and 90 ml abs. alcohol) we added 22.3 g diethylphosphite, then dropwise with mixing 20.5 g $C_6H_5CH_2Cl$ and boiled for 6 h. Most of the alcohol was removed under vacuum. To the residue we added 100 ml of benzene and 70 ml of water. The aqueous layer was extracted with benzene. The combined extract was washed with water, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was distilled off. Yield 26.5 g (IX).

The dibutyl (X) and diisoamyl (XI) esters of benzylphosphonic acid were synthesized analogously.

Tetramethyldiamide of Benzylphosphonic Acid (XII). Gaseous dimethylamine was passed through a solution of 10 g of the chloride of benzylphosphonic acid in 130 ml abs. benzene at ≤45°C until the end of spontaneous heating of the mixture. The mixture was boiled for 1 h in a stream of dimethylamine and treated with water. The organic layer was evaporated under vacuum. The residue was boiled for 4 h with 35 ml of 20% aqueous alcoholic NaOH. The alcohol was evaporated under vacuum, the residue diluted with water and extracted with $CHCl_3$. The combined extract was dried with anhydrous $Na_2SO_4$ and evaporated under vacuum. The residue was redistilled. Yield 8.7 g (XII).

Tetraethyldiamide of Benzylphosphonic Acid (XIII). The amide (XIII) was synthesized analogously to (XII), the only difference being that the chloride of benzylphosphonic acid was added to diethylamine, dissolved in benzene, at 20-30°C.

Diphenyl-p-methoxybenzylphosphine Oxide (XIV). A mixture of 6.9 g diphenylphosphine, 5 g p-methoxybenzaldehyde, 50 ml AcOH, and 1 ml conc. HCl was boiled for 13 h. The residue was filtered off, washed with ether, and dissolved in a large quantity of $CHCl_3$. The solution was washed with 5% NaOH, with water, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was recrystallized from alcohol. Yield 8.9 g (XIV).

Diphenyl-p-methylbenzylphosphine Oxide (XV). The oxide (XV) was synthesized analogously to (XIV).

Diphenyl-p-carboethoxybenzylphosphine Oxide (XVI). To 8 g of the ethyl ester of $\alpha$-bromo-p-toluic acid we added dropwise at 20°C under a vacuum of 60 mm 7.7 g ethyldiphenylphosphinite [17]. The mixture was heated under vacuum for 4 h at 120°C. After recrystallization from alcohol we obtained 10.1 g (XVI).

Diphenyl-p-cyanobenzylphosphine oxide (XVII) was synthesized analogously (180°C, 3 h, vacuum ~60 mm).

Diphenyl-p-nitrobenzylphosphine Oxide (XVIII). To 80 ml of a mixture (1:1) of conc. $HNO_3$ and $H_2SO_4$ we added in portions over a period of 30 min at 0°C 5.7 g of diphenylbenzylphosphine oxide, mixed for 3 h at 20°C, and poured out into ice water with vigorous mixing. The precipitate was filtered off, washed several times with water, and dried. After recrystallization from alcohol we obtained 5.5 g (XVIII).

Diphenylphosphine. To a solution of 3.1 g Na in 250 ml abs. $NH_3$ we added 15.7 g ethyldiphenylphosphinite [17]. The mixture was mixed for 2 h. Ammonia was removed, 70 ml of benzene and 70 ml of dilute (1:1) HCl were added to the residue. The aqueous layer was extracted with benzene. The combined extract was washed with a saturated solution of $NaHCO_3$, dried with anhydrous $Na_2SO_4$, and evaporated under vacuum. The residue was redistilled. We obtained 10 g (76%) diphenylphosphine, bp 134-136°C (2 mm) [21].

Measurements of the equilibrium constants K (Table 4) of reactions of the investigated compounds with alkali substituted CH-indicators were conducted according to [1]. In a number of cases pK was determined by measurements with two indicators. The numeration of the compounds in Table 4 is given according to Table 1. The values of pK sought are equal to the difference of the values of pK for the indicators and log K, indicated in Table 4.

In DG the equilibrium for Li-substituted TPP and PX is reached within a long period of time (up to seven days), which hinders the reliable determination of K. Metallation of (VIII)-(XI) in both solvents, as well as that of (VI) in DMSO, is accompanied by a side process (possibly decomposition of the phosphorus-containing carbanions), leading to the formation of a loose deposit. However, the rate of this process is comparatively low and reproducible values of K can be obtained with successive displacements of the equilibrium of transmetallation in both directions. The error in the determination of pK does not exceed ±0.1 pK unit.

Solutions of the carbanions (I)-(XV) have a yellow-brown color, to which a broad absorption band (Fig. 3) with a maximum in the near UV region corresponds. The spectra of carbanions of this series differ negligibly in position of the maximum (by 10-15 nm). In DG the maximum of the band is somewhat shifted in the direction of shorter waves, but its exact position was determined in view of the strong general absorption in the UV region of the reaction mixture. The carbanions (XVI)-(XVIII) in DMSO have the characteristic absorption bands in the visible region (see Fig. 3, curves 2-4). The color of solutions of the carbanions (XVI) and (XVII) is yellow-green, that of (XVIII) purple. Values of $\lambda_{max}$, nm ($\varepsilon \cdot 10^{-3}$, liters/mole·cm): (XVI) 430 (40 ± 4), (XVII) 405 (30 ± 2), (XVIII) 535 (43 ± 4) and 570 (36 ± 3).

## CONCLUSIONS

1. The equilibrium CH-acidity (pK) of benzylphosphine oxides, as well as esters and tetraalkylamides of benzylphosphonic acid in diglyme (DG) and DMSO was determined by the method of transmetallation.

2. The acidity in DMSO is 4-6 units of pK lower than in DG, which can be explained by supplementary stabilization in DG of the carbanions of phosphine oxides and their analogs on account of coordination of the cation with the phosphoryl group.

3. A linear relationship is observed between the values of pK of phosphine oxides and amides of benzylphosphonic acid in DG and DMSO, which is not observed for compounds with alkoxyl groups at the phosphorus atom.

4. The linear correlations of the values of pK in the two solvents with the constants of substituents at the phosphorus atoms $\sigma_p$ of benzylphosphine oxides have close values of the slopes. Amides and esters of benzylphosphonic acid do not obey this dependence.

5. There is a linear relationship between the values of pK of derivatives of diphenylbenzylphosphine oxide with substituents in the paraposition of the benzyl group and the substituent constants $\sigma^-$.

## LITERATURE CITED


1. S. P. Mesyats, E. N. Tsvetkov, É. S. Petrov, M. I. Terekhova, A. I. Shatenshtein, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2489 (1974).
2. M. Sander, Chem. Ber., 93, 1220 (1960).
3. M. I. Kabachnik, T. A. Mastryukova, and A. É. Shipov, Zh. Obshch. Khimii, 35, 1574 (1965).
4. K. L. Marsi and L. D. Homer, J. Organ. Chem., 28, 2150 (1963).
5. A. K. Hoffman and A. L. Fesch, USA Patent No. 3032589, 1962; Chem. Abstrs., 57, P9882C (1962).
6. M. Höring, W. Lauter, L. Lichtenstaat, and W. Samuel, Liebigs Ann. Chem., 449, 213 (1926).
7. H. L. Henning, J. Prakt. Chem., 29, 93 (1965).
8. L. Horner, H. Hoffman, W. Klink, H. Ertel, and V. L. Toscano, Chem. Ber., 95, 581 (1962).
9. B. A. Arbuzov and N. P. Bogonostseva, in: Collection of Articles on General Chemistry [in Russian], Izd-vo AN SSSR, Vol. 2 (1953), pp. 1144.
10. N. I. Rizpolozhenskii, M. A. Zvereva, and A. V. Stepashkina, in: The Chemistry of Organic Compounds of Phosphorus [in Russian], Nauka, Leningrad (1967), p. 202.
11. H. Normant and G. F. Brault, Compt. Rend., 264C, 708 (1967).
12. R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem. Soc., C, 1547 (1967).
13. L. Horner, W. Klink, and H. Hoffman, Chem. Ber., 96, 3133 (1963).
14. R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem. Soc., C, 1700 (1968).
15. M. Epstein and S. A. Buckler, Tetrahedron, 18, 1231 (1962).
16. M. I. Kabachnik and E. N. Tsvetkov, Dokl. Akad. Nauk SSSR, 143, 592 (1962).
17. Kh. Nokhira, M. Taniguti, and K. Simamura, J. Synth. Org. Chem. Japan, 28, 969 (1970); RZhKhim, 6zh570 (1971).
18. G. M. Kosolapoff, J. Amer. Chem. Soc., 71, 1876 (1949); F. Kagan, R. D. Birkenmeyer, and B. E. Strube, J. Amer. Chem. Soc., 81, 3026 (1959).
19. W. Voskuil and J. F. Arens, Recueil. Trav. Chim., 302, 82 (1963).
20. F. F. Blicke and S. Raines, J. Organ. Chem., 29, 204 (1964).
21. W. Kuchen and H. Buchwald, Chem. Ber., 91, 2871 (1958).