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Nik. A. NESMEYANOV, S. T. ZHUZHLIKOVA, Corresponding Member of the Academy of Sciences of the USSR

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Abstract

Full Text

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Nik. A. NESMEYANOV, S. T. ZHUZHLIKOVA, Corresponding Member of the Academy of Sciences of the USSR
O. A. REUTOV

SULFONATION OF PHOSPHORUS YLIDES

SULFOBETAINES

The so-called Wittig reagents, or phosphorus ylides, are prone to electrophilic addition reactions. It is known that acids add to them with the formation of phosphonium salts. The first stage of the well-known Wittig reaction should likewise be regarded as electrophilic addition of aldehydes or ketones to ylides ([1]). Seyferth and Grim showed that triphenylphosphinemethylene adds compounds of trivalent boron ([2])

$$(C_6H_5)_3P = CH_2 + BX_3 \rightarrow (C_6H_5)_3\overset{\oplus}{P}CH_2\overset{\ominus}{B}X_3$$

and certain organometallic salts, for example: ([3])

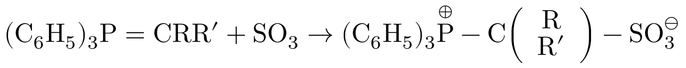
$$(C_6H_5)_3P = CH_2 + R_3SnCl \rightarrow [(C_6H_5)_3\overset{\oplus}{P} - CH_2 - SnR_3]\overset{\ominus}{Cl}.$$

Diphenylphosphine bromide adds similarly ([4]). It has also been shown that acid halides give phosphonium salts with ylides, which enter into a re-ylidation reaction with unreacted ylide ([5,6])

$$(C_6H_5)_3P = CHR + ClCOR' \rightarrow [(C_6H_5)_3P - CHR - COR']Cl,$$

$$(C_6H_5)_3PCHR{-}COR'Cl + (C_6H_5)_3P = CHR \rightarrow (C_6H_5)_3P = C(R)COR' + [(C_6H_5)_3\overset{\oplus}{P}CH_2R]\overset{\ominus}{Cl}.$$

Here we describe a new electrophilic addition reaction to phosphorus ylides, namely the reaction with sulfuric anhydride, which proceeds as follows:



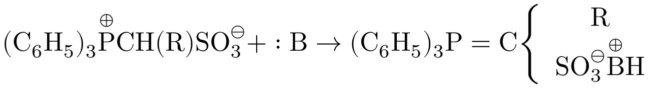
$$(C_6H_5)_3P = CRR' + SO_3 \rightarrow (C_6H_5)_3\overset{\oplus}{P} - C\left(\begin{matrix} R \\ R' \end{matrix}\right) - SO_3^{\ominus}$$

(I) (II)

a) $R = R' = C_6H_5$
b) $R = H,\ R' = COOCH_3$
c) $R = H,\ R' = COC_6H_5$
d) $R = H,\ R' = COCH_3$

This reaction proceeds with free sulfuric anhydride in dichloroethane or, better, with dioxane sulfotrioxide in the same solvent. Betaines of type II are thereby formed in yields of 40–95%; they are colorless crystalline substances, insoluble in water and in nonpolar organic solvents. Triphenylphosphine sulfotrioxide, obtained by us from triphenylphosphine in an analogous manner, possesses the same properties. It does not decompose on treatment with soda solution or on prolonged standing in air, and crystallizes from nitromethane.

Sulfobetaines containing a mobile hydrogen atom (II, $R = H$) readily eliminate a proton under the action of bases, being converted into salts of sulfonic acids that have the structure of Wittig reagents:



$$(C_6H_5)_3\overset{\oplus}{P}CH(R)SO_3^{\ominus} + :B \rightarrow (C_6H_5)_3P = C\left\{\begin{matrix} R \\ SO_3^{\ominus}\overset{\oplus}{B}H \end{matrix}\right.$$

These Wittig reagents are passivated by two electron-acceptor groups and therefore do not react with aldehydes.

Elimination of a proton from sulfobetaines of type II should occur more readily than from the corresponding phosphonium salts $[(C_6H_5)_3PCH_2R]X$ owing to the electron-acceptor action of the sulfo group. For this reason, in sulfonation one should expect "re-ylidation" between the betaine

and with the ylide that has not entered into the reaction, according to the following scheme

$$(C_6H_5)_3\overset{\oplus}{P}CH(R)SO_3{}^{\ominus} + (C_6H_5)_3P = CHR \rightarrow [(C_6H_5)_3P = C(R)SO_3{}^{\ominus}][(C_6H_5)_3\overset{\oplus}{P}CH_2R].$$

This, however, is not observed. For example, the yield of sulfobetaine in the sulfonation of acetylmethylene-triphenylphosphorane exceeds 90%. Evidently, the rate of reylidation is relatively low, and this reaction does not proceed to an appreciable extent during the sulfonation. Reylidation is effected to some extent by two-hour heating of equimolar amounts of acetylmethylene-triphenylphosphorane and the corresponding sulfobetaine in dichloroethane; in this case a complex salt is obtained in accordance with the scheme given. Carbomethoxymethylene-triphenylphosphorane behaves analogously.

Experimental Part

1) Sulfonation of diphenylmethylene-triphenylphosphorane (7). To a solution of freshly prepared diphenylmethylene-triphenylphosphorane (5.2 g, 0.012 mole), recrystallized from abs. benzene, in 25 ml of abs. dichloroethane, a solution of dioxanesulfur trioxide in dichloroethane (from 1.0 ml of dioxane and 0.93 g (0.012 mole) of sulfuric anhydride in 10 ml of dichloroethane) was added over 5 min in a stream of nitrogen, after which the mixture was left overnight. The solvent was then distilled off in vacuo to a small volume, and the residue was removed in a stream of warm air; the oil obtained was triturated in benzene and then in petroleum ether, giving 4.3 g of crystals Ia. After recrystallization from a tetrahydrofuran—methanol mixture, the yield of sulfobetaine was 2.55 g, 40% of theoretical, mp 195-198° (the substance begins to shrink at 187°); the sulfobetaine crystallizes with one molecule of methanol:

$$(C_6H_5)_3P^{\oplus}C(C_6H_5)_2SO_3^{\ominus} \cdot CH_3OH$$

Found %: C 71.07; 71.19; H 5.67; 5.49; P 5.33; 5.13; S 5.90; 5.80
$C_{32}H_{29}PSO_4$. Calculated %: C 71.04; H 5.40; P 5.73; S 5.92

2) Sulfonation of carbomethoxymethylene-triphenylphosphorane (8). 0.021 mole of this ylide was sulfonated analogously to the preceding experiment. The residue after removal of the solvent was triturated with water and washed with water and benzene; the product was reprecipitated with ether from nitromethane, giving $(C_6H_5)_3P^{\oplus}CH(COOCH_3)SO_3^{\ominus}$ (Ib), 66.6%. Mp 199-200° (with decomposition, from nitromethane-tetrahydrofuran).

Found %: C 60.71; 60.66; H 4.66; 4.61; P 7.70; 7.42; S 7.61; 7.85
$C_{21}H_{19}SO_5P$. Calculated %: C 60.92; H 4.62; P 7.49; S 7.74

1.0 g of the sulfobetaine obtained was dissolved in a minimum amount of 5% sodium hydroxide solution with gentle heating; the solution was filtered, and a saturated sodium chloride solution was added to the filtrate. Colorless needles precipitated: $(C_6H_5)_3P = C(COOCH_3)SO_3Na \cdot H_2O$, yield almost quantitative, mp 245-250° (from an acetone—methanol mixture).

Found %: C 56.04; 55.88; H 4.53; 4.52; P 6.36; 6.51
$C_{21}H_{20}O_6SPNa$. Calculated %: C 55.55; H 4.44; P 7.06

From the sodium salt a benzylthiuronium salt was obtained with mp 178°.

Found %: C 60.01; 60.20; H 4.97; 5.03; P 5.58; 5.63; S 11.28; 11.34
$C_{29}H_{28}S_2N_2O_5P$. Calculated %: C 60.05; H 4.84; P 5.35; S 11.31

3) Sulfonation of benzoylmethylene-triphenylphosphorane. The starting ylide was prepared by the action of liquid ammonia on triphenylphenacylphosphonium bromide, in 50% yield. We did not succeed, by the adopted procedure, in obtaining this ylide in satisfactory yield (by the action of sodium hydroxide solution on the phosphonium salt (9)). 6.0 g of benzoylmethylene-triphenylphosphorane was sulfonated similarly to the preceding ylides; the residue after removal of the solvent was triturated with water and washed on the filter with benzene; the yield of sulfobetaine II was 91% of theoretical, mp 234-

235°, after recrystallization from nitromethane, m.p. 227-228° (depressed)

$$(C_6H_5)_3P^{\oplus}CH(COC_6H_5)SO_3^{\ominus}$$

Found, %: C 67.54; 67.55; H 4.72; 4.78; P 6.89; 6.89; S 7.02; 6.93
$C_{26}H_{21}SO_4P$. Calculated, %: C 67.88; H 4.55; P 6.73; S 6.96

To 0.5 g of the product was added 10 ml of liquid ammonia; after an hour the ammonia was gradually removed, the residue was dissolved in water, and the solution was filtered. A solution of benzylthiuronium hydrochloride was added to the filtrate. The yield of the benzylthiuronium salt was 80%, m.p. 131-135° (shrinks at 120°).

Found, %: C 63.75; 63.88; H 5.09; 5.07; P 4.84; 4.92; S 10.35; 10.53;
N 4.73; 4.71
$C_{34}H_{31}PN_2S_2O_4$. Calculated, %: C 64.05; H 5.07; P 4.75; S 10.10;
N 4.44

4) **Sulfonation of acetylmethylene-triphenylphosphorane**[9]. 0.015 mole of this ylide was prosulfurated analogously to the preceding experiment. After evaporation of the solvent in a stream of hot air, the remaining crystals were washed with water and dried; yield of $(C_6H_5)_3P^{\oplus}—CH(COCH_3)SO_3^{\ominus} \cdot H_2O$ 5.7 g (92% of theory), after recrystallization from nitromethane (twice), m.p. 176-179° (crystallizes with one molecule of water).

Found, %: C 61.06; 61.18; H 5.27; 5.36; P 7.74; 7.67; S 7.57; 7.26
$C_{21}H_{21}PSO_5$. Calculated, %: C 60.62; H 5.09; P 7.45; S 7.68

When ammonia is passed into a solution of this sulfobetaine in chloroform, an ammonium salt is formed, readily soluble in water. The difficultly crystallizing benzylthiuronium salt melts at 158-160°.

5) **Sulfonation of triphenylphosphine.** The sulfonation was carried out in dichloroethane by analogy with the preceding experiments. The triphenylphosphine-sulfur trioxide obtained, almost insoluble in dichloroethane, was recrystallized twice from nitromethane; m.p. 181-182°, yield of purified product almost quantitative.

Found, %: C 63.27; 63.44; H 4.47; 4.52; P 8.72; 8.94
$C_{18}H_{15}PSO_3$. Calculated, %: C 63.18; H 4.39; P 9.06

6) **Reylidation between acetylmethylene-triphenylphosphorane and sulfobetaine II g.** A solution of 0.010 mole of acetylmethylene-triphenylphosphorane with m.p. 196-198° and 0.010 mole of betaine II

g in dichloroethane was heated for 2 hours; the solvent was removed in a stream of air, and the remaining viscous mass was extracted several times with warm water. The aqueous solution was divided into 2 parts; from one part, by addition of aqueous ammonia, acetylmethylenetriphenylphosphorane, insoluble in water, was precipitated, with melting point and mixed melting point with the starting substance 191–194°. From the other part of the aqueous solution the benzylthiuronium salt with m.p. 158–160° was precipitated. Thus, the presence in the aqueous solution of both the cation and the anion of the salt $[(C_6H_5)_3PCH_2COCH_3]^{\oplus}[(C_6H_5)_3P = C(COCH_3)SO_3{}^{\ominus}]$ was demonstrated. Yield about 10%.

Moscow State University
named after M. V. Lomonosov

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