Reactions of Bistrichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric Acid with Certain Grignard Reagents[1]

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Bistrichlorophosphazosulfone and some new dialkylamides of trichlorophosphazosulfuric acid are obtained in nearly quantitative yields by the reaction of phosphorus(V) chloride with sulfamide and its N,N-disubstituted derivatives, respectively. These compounds undergo readily nucleophilic replacement of the chlorine atoms by phenyl and *p*-tolyl groups when treated with the corresponding Grignard reagents. However, such nucleophilic replacement is much less facile when the *m*-tolyl Grignard is used and non-existent with the *o*-tolyl compound, suggesting the importance of steric hindrance in such reactions. A prominent infrared absorption in the 1260–1300-cm.$^{-1}$ region appears to be characteristic of the entire $—SO_2N=P\langle$ grouping rather than of a pure P=N mode.

Certain of the striking analogies between the chemistry of sulfamide and that of urea have been emphasized in previous publications.[2] Another analogy is found in the synthesis of the corresponding phosphazo chlorides by reaction of these amides with phosphorus(V) chloride. When this reaction is carried out with sulfamide or its N,N-dialkyl derivatives, either in the presence or absence of an inert solvent, bistrichlorophosphazosulfone, $Cl_3P=NSO_2N=PCl_3$, or the N,N-dialkylamides of trichlorophosphazosulfuric acid, $R_2NSO_2N=PCl_3$, respectively, result in nearly quantitative yields.[3,4]

It has been of interest to extend these reactions to the synthesis of a variety of compounds of the second type [$R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$, C_4H_8O (from morpholine)]. Furthermore, since the nucleophilic replacement of chlorine atoms in compounds of both types has not been investigated extensively,[5,6] it has also been of interest to study this kind of reaction with various Grignard reagents. Both bistrichlorophosphazosulfone and the N,N-dialkylamides of trichlorophosphazosulfuric acid have been found to react readily at room temperature with either solutions of phenyl or *p*-tolyl (=Ar) magnesium bromide to give, in reasonable yields, the completely substituted products, as

$$Cl_3P=NSO_2N=PCl_3 + 6ArMgBr \longrightarrow Ar_3P=NSO_2N=PAr_3 + 6MgClBr$$

$$R_2NSO_2N=PCl_3 + 3ArMgBr \longrightarrow R_2NSO_2N=PAr_3 + 3MgClBr$$

The somewhat larger solubilities of the *p*-tolyl compounds result in their recovery in somewhat lower yields than are obtained with the corresponding phenyl derivatives.

When *m*-tolylmagnesium bromide is used, complete nucleophilic attack appears to be more difficult, and with *o*-tolylmagnesium bromide it is essentially non-existent. Even prolonged refluxing with excess Grignard reagent gives low yields with the *meta* compound and fails to produce any completely substituted derivative with the *ortho* compound. It is reasonable to conclude on this basis that steric hindrance plays an important role in determining the ease with which such reactions proceed.

However, the reduced solubility of adducts formed between intermediate substitution products and the magnesium halide may also be a determining factor. It is known, for example, that in the reaction of phosphorus(V) oxytrichloride with organo-magnesium compounds for the synthesis of phosphine oxides such adducts form and are converted to disubstituted phosphinic acid derivatives when branched-chain alkyl or aryl substituents are present.[7,8] Both the quantitative formation of such adducts with hindered aryl groups, as judged by the complete absence of residue upon evaporation of the initial solvent, and lack of reaction with any solvent except one that effects decomposition indicate the stability of these products. It is possible, therefore, that the formation of such a species may remove reactant before complete substitution can result.

Acidic hydrolysis may then lead to phosphinic acid derivatives—*e.g.*, $R_2NSO_2N=PAr_2OH$ or $R_2NSO_2NH—P(O)Ar_2$. Attempts to identify such compounds have given only negative results. Molecular weight determinations by the vapor-pressure procedure indicate the existence of phosphinic acid derivatives, but microanalytical results for carbon differ from the corresponding theoretical values by *ca.* 0.3%. However, that such species are present is suggested by the ready solubility of such compounds in aqueous sodium hydroxide and their ready reprecipitation upon addition of acid to pH 6. By contrast, the trisubstituted compounds

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[2] A. Vandi, T. Moeller, and L. F. Audrieth, *J. Org. Chem.*, **26**, 1136, 3478 (1961).

[3] A. V. Kirsanov, *Zh. Obshch. Khim.*, **22**, 1346 (1952).

[4] A. V. Kirsanov and Z. D. Nekrasova, *ibid.*, **27**, 1253 (1956).

[5] A. V. Kirsanov and L. L. Matveenko, *ibid.*, **28**, 1892 (1958).

[6] A. V. Kirsanov and Z. D. Nekrasova, *ibid.*, **27**, 3241 (1957).

[7] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **64**, 2982 (1942).

[8] K. A. Petrov, N. K. Bliznyuk, and V. P. Korotkova, *J. Gen. Chem. U.S.S.R.*, **30**, 2967 (1960). (English translation.)

TABLE I

PROPERTIES AND ANALYSES OF BISTRIARYLPHOSPHAZOSULFONES AND N,N-DIALKYLTRIARYLPHOSPHAZOSULFONES

Compound	Empirical formula	Yield, %	M.p.,[a] °C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Bistriphenylphosphazosulfone[b]	$C_{36}H_{30}N_2O_2P_2S$	46	245–246	70.12	70.16	4.90	4.98	4.54	4.70
N,N-Dimethyltriphenylphosphazosulfone[c]	$C_{20}H_{21}N_2O_2PS$	37	156–158	62.49	62.52	5.50	5.33	7.28	7.18
N,N-Diethyltriphenylphosphazosulfone[c]	$C_{22}H_{25}N_2O_2PS$	66	127	64.07	63.90	6.11	6.17	6.79	6.89
N,N-Di-*n*-propyltriphenylphosphazosulfone[c]	$C_{24}H_{29}N_2O_2PS$	50	178–179	65.44	65.49	6.63	6.48	6.36	6.58
N,N-Di-*n*-butyltriphenylphosphazosulfone[c]	$C_{26}H_{33}N_2O_2PS$	52	149	66.65	66.76	7.10	7.10	5.98	6.21
N-Morpholinetriphenylphosphazosulfone[c]	$C_{22}H_{23}N_2O_3PS$	47	181–182	61.96	61.72	5.43	5.39	6.57	6.39
Bistri-*p*-tolylphosphazosulfone[b]	$C_{42}H_{42}N_2O_2P_2S$	30	226	72.02	71.79	6.04	6.10	4.00	3.94
N,N-Dimethyltri-*p*-tolylphosphazosulfone[c]	$C_{23}H_{27}N_2O_2PS$	35	196	64.77	64.68	6.38	6.43	6.56	6.26
N,N-Diethyltri-*p*-tolylphosphazosulfone[c]	$C_{25}H_{31}N_2O_2PS$	40	160	66.06	66.14	6.87	6.97	6.16	6.38
N,N-Di-*n*-propyltri-*p*-tolylphosphazosulfone[c]	$C_{27}H_{35}N_2O_2PS$	35	175	67.19	66.99	7.31	7.30	5.80	5.93
N,N-Di-*n*-butyltri-*p*-tolylphosphazosulfone[c]	$C_{29}H_{39}N_2O_2PS$	48	155	68.21	68.34	7.70	7.59	5.48	5.55
N-Morpholinetri-*p*-tolylphosphazosulfone[c]	$C_{25}H_{29}N_2O_3PS$	43	129	64.09	64.36	6.24	6.26	5.98	5.91
N,N-Dimethyltri-*m*-tolylphosphazosulfone[c]	$C_{23}H_{27}N_2O_2PS$	22	159	64.77	64.91	6.38	6.45	6.56	6.31
N,N-Morpholinetri-*m*-tolylphosphazosulfone[c]	$C_{25}H_{29}N_2O_3PS$	24	124–125	64.09	64.06	6.24	6.28	5.98	6.10

[a] Uncorrected. [b] Type formula: $Ar_3P{=}NSO_2N{=}PAr_3$. [c] Type formula: $R_2NSO_2N{=}PAr_3$.

resist hydrolysis even when boiled with aqueous sodium hydroxide.

Compounds prepared, together with important data relating to their syntheses and properties, are summarized in Table I. All of the completely substituted products are white, crystalline, nonhygroscopic substances that are insoluble in water, *n*-heptane, petroleum ether, and diethyl ether; sparingly soluble in ethanol, benzene, and carbon tetrachloride; and soluble in acetone and chloroform.

The infrared spectra of compounds containing the $-\mathrm{N}{=}\mathrm{P}\!\begin{smallmatrix}/\\ -\\ \backslash\end{smallmatrix}$ group are of interest. Cyclic trimeric and tetrameric phosphonitrilic compounds show absorption at 1225 cm.$^{-1}$ and 1320 cm.$^{-1}$, respectively, which frequencies are believed to be P=N stretching frequencies.[9] Intense absorptions in the region 1350–1385 cm.$^{-1}$ in the spectra of a number of phosphoroimidates and phosphonimidates has been associated with the $-\mathrm{N}{=}\mathrm{P}\!\begin{smallmatrix}/\\ -\\ \backslash\end{smallmatrix}$ grouping.[10] On the other hand, absorption in the 1260–1290-cm.$^{-1}$ region for esters of alkyl sulfonimido-N'-phosphoric acid has also been associated with this grouping.[11] For comparison, infrared data for potassium bromide pellets of the compounds described herein are summarized in Table II. The strong absorptions in the 1125–1160-cm.$^{-1}$ region are characteristic of the symmetric S—O vibration.[2,12] The asymmetric vibration that usually occurs in the 1320–1340-cm.$^{-1}$ region has disappeared, however, and a new strong band at 1255–1300 cm.$^{-1}$ is always present. This is in good agreement with the observations of Goerdeler and Ullmann, but it seems more probable that these absorptions characterize the entire $-\mathrm{SO_2}-\mathrm{N}{=}\mathrm{P}\!\begin{smallmatrix}/\\ -\\ \backslash\end{smallmatrix}$ arrangement rather than the $-\mathrm{N}{=}\mathrm{P}\!\begin{smallmatrix}/\\ -\\ \backslash\end{smallmatrix}$ arrangement alone. This conclusion is supported by the fact that in most of the spectra reported herein the bands in this region are not well resolved but appear rather as shoulders, thus indicating the possibility of coupling between the —N=P vibration and the S—O asymmetric stretch shifted to a lower frequency by the substitution of more electropositive groups on the phosphorus atom.

Experimental

Bistrichlorophosphazosulfone and Dialkylamides of Trichlorophosphazosulfuric Acid.—The first of these compounds and the N,N-dimethyl and N,N-diethyl compounds of the second type were prepared as outlined by Kirsanov.[3,4] Previously undescribed compounds of the second type (N,N-di-*n*-propyl, N,N-di-*n*-butyl, and morpholino) were prepared by modifications of the Kirsanov procedure.

N,N-Di-*n*-propyltrichlorophosphazosulfone.—Thirty-four and two-tenths grams (0.189 mole) of N,N-di-*n*-propylsulfamide, 39.53 g. (0.189 mole) of phosphorus(V) chloride, and 100 ml. of carbon tetrachloride were placed in a 500-ml., round-bottomed flask equipped with a reflux condenser and a drying tube. The reaction takes place at room temperature with evolution of hydrogen chloride. Gentle heating on the steam bath was continued for 3 hr., after which time the evolution of gas ceased. The excess of carbon tetrachloride was removed *in vacuo* and the oily material which was left purified by distillation under reduced pressure. The pure compound is a slightly yellow oil, b.p. 113°/0.005 mm., $n^{25}\mathrm{D}$ 1.5010. Yield: 50.0 g. (83.5%).

Anal. Calcd. for $C_6H_{14}N_2O_2SPCl_3$: C, 22.83; H, 4.47; N, 8.87. Found: C, 22.99; H, 4.41; N, 8.97.

N,N-Di-*n*-butyl-trichlorophosphazosulfone.—Thirty grams (0.144 mole) of N,N-di-*n*-butylsulfamide, 30.0 g. (0.144 mole) of phosphorus(V) chloride, and 100 ml. of carbon tetrachloride were placed in a 500-ml., round-bottomed flask fitted with a reflux condenser and a drying tube. An exothermic reaction started at room temperature. Gentle refluxing on the steam bath was continued for 3 hr., after which time the reaction was completed. The excess of solvent was removed *in vacuo*, leaving a viscous, oily material. The pure compound obtained by vacuum distillation,

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(9) L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

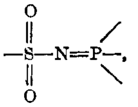
(10) M. I. Kabachnik, V. A. Gilyarov, and E. N. Tsvetkov, *Bull. Acad. Sci. U.S.S.R.*, 2036 (1959). (English translation.)

(11) J. Goerdeler and H. Ullmann, *Ber.*, **94**, 1067 (1961).

(12) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

TABLE II

INFRARED DATA FOR BISTRIARYLPHOSPHAZOSULFONES AND N,N-DIALKYLTRIARYLPHOSPHAZOSULFONES

Compound	Frequency S—O sym., cm.$^{-1}$	  cm.$^{-1}$
Bistriphenylphosphazosulfone	1125	1262
N,N-Dimethyltriphenylphosphazosulfone	1140	1300
N,N-Diethyltriphenylphosphazosulfone	1155	1290
N,N-Di-*n*-propyltriphenylphosphazosulfone	1140	1295
N,N-Di-*n*-butyltriphenylphosphazosulfone	1145	1295
N-Morpholinetriphenylphosphazosulfone	1150	1295
Bistri-*p*-tolylphosphazosulfone	1125	1255
N,N-Dimethyltri-*p*-tolylphosphazosulfone	1140	1300
N,N-Diethyltri-*p*-tolylphosphazosulfone	1140	1290
N,N-Di-*n*-propyltri-*p*-tolylphosphazosulfone	1140	1290
N,N-Di-*n*-butyltri-*p*-tolylphosphazosulfone	1140	1290
N-Morpholinetri-*p*-tolylphosphazosulfone	1140	1300
N,N-Dimethyltri-*m*-tolylphosphazosulfone	1140	1300
N-Morpholinetri-*m*-tolylphosphazosulfone	1140	1295

was a yellow oil, b.p. 140°/0.05 mm., n^{25}_{D} 1.4952. Yield 39.5 g. (80.0%).

Anal. Calcd. for $C_8H_{18}N_2O_2SPCl_3$; C, 27.96; H, 5.28; N, 8.15. Found: C, 27.75; H, 5.33; N, 8.31.

N-Morpholinetrichlorophosphazosulfone.—Eight and three-tenths grams (0.05 mole) of N-morpholinesulfamide, 10.41 g. (0.05 mole) of phosphorus(V) chloride, and 50 ml. of carbon tetrachloride were placed in a 240-ml., round-bottomed flask fitted with a reflux condenser and a drying tube. Gentle heating on the steam bath was continued for 5 hr., after which time the evolution of hydrogen chloride ceased and a clear solution was obtained. Upon cooling at 0°, a white precipitate was formed. It was filtered in a drybox, washed with cold carbon tetrachloride, and dried. The pure compound is a white, hygroscopic, crystalline material which melts at 94°. Yield: 14.0 g. (93.0%).

Anal. Calcd. for $C_4H_8N_2O_3SPCl_3$: C, 15.94; H, 2.67; N, 9.29. Found: C, 16.14; H, 2.76; N, 9.38.

Grignard Reagents.—These were prepared according to the classical method—*i.e.*, by dropping the appropriate aryl bromide into an ether suspension of clean, dry magnesium turnings with stirring. A small crystal of iodine and a short period of heating were initially required to shorten the induction period.

Bistriarylphosphazosulfones and N,N-Dialkyltriarylphosphazosulfones.—Inasmuch as the procedure followed in each condensation reaction was essentially the same, only typical syntheses are described in detail. In all cases, except with N,N-dimethyltrichlorophosphazosulfone and the morpholino derivative for which benzene was used as a solvent, the reactions were carried out in diethyl ether.

Bistriphenylphosphazosulfone.—Nine and sixteen-hundreths grams (0.025 mole) of bistrichlorophosphazosulfone in 50 ml. of anhydrous ether was slowly added at room temperature and over a period of 2 hr. to a well stirred ether solution of phenylmagnesium bromide (36.26 g., 0.2 mole). After the addition was completed, gentle refluxing was continued for an additional 6 hr. The excess of Grignard reagent was decomposed by pouring the reaction mixture into a flask containing 300 g. of crushed ice and 50 ml. of 12 *M* hydrochloric acid. The solid which separated was filtered, washed several times with water, and dried. The pure product could be obtained by extracting the crude material in a Soxhlet apparatus with ethanol and ultimately cooling the alcoholic solution.

N,N-Dimethyltriphenylphosphazosulfone.—Twelve and ninety-seven hundreths grams (0.05 mole) of N,N-dimethyltrichlorophosphazosulfone in 150 ml. of anhydrous benzene was slowly added, with stirring and at room temperature, to an ether solution of phenylmagnesium bromide (36.26 g., 0.2 mole), after which time the mixture was gently refluxed for an additional 6 hr. The cold mixture was then poured into a flask containing 300 g. of crushed ice and 50 ml. of 12 *M* hydrochloric acid. The solid which separated was extracted with benzene. The benzene layer was dried over calcium chloride and the excess of solvent removed *in vacuo*. The resulting colored residue was purified by several recrystallizations from ethanol.

N,N-Di-*n*-butyltri-*p*-tolylphosphazosulfone.—Eight and six-tenths grams (0.025 mole) of N,N-di-*n*-butyltrichlorophosphazosulfone in 50 ml. of ether was added in small portions at room temperature to a well stirred solution of *p*-tolylmagnesium bromide (19.52 g., 0.1 mole). After the addition of the chloride, the mixture was stirred and refluxed for 12 hr. The excess of Grignard reagent was decomposed by careful addition to the reaction mixture of 200 ml. of a saturated solution of ammonium chloride. The product was then extracted with benzene. After drying the benzene layer over calcium chloride, the excess of solvent was removed *in vacuo* and the residue purified by recrystallization from ethanol.

N,N-Dimethyltri-*m*-tolylphosphazosulfone.—Six and forty-eight hundredths grams (0.025 mole) of N,N-dimethyltrichlorophosphazosulfone in 100 ml. of anhydrous benzene was slowly added at room temperature to a well stirred ether solution of *m*-tolylmagnesium bromide (19.53 g., 0.1 mole). After the addition, stirring and refluxing were continued for an additional 24 hr., and the excess of Grignard reagent was decomposed by pouring the reaction mixture into a flask containing 200 g. of crushed ice and 50 ml. of 12 *M* hydrochloric acid. The solid which separated was extracted with benzene, and the crude product was obtained upon removal of the solvent under reduced pressure. Final purification was achieved by several recrystallizations from dilute ethanol.

Infrared Spectra.—These were measured with a Perkin-Elmer Model 21 instrument, using a sodium chloride prism.

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