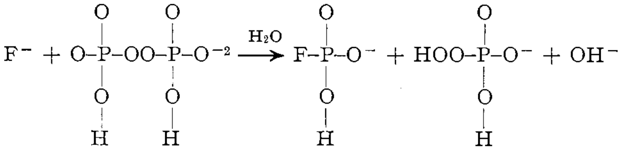
second reaction, not involving hydrolysis, is introduced by the presence of fluoride ion. In view of this, together with the observation that the pH of the reaction solutions containing fluoride ion increased from 4.6 to 4.9 over the course of about 40% reaction, it is felt that the observed acceleration is due to the reaction



$$F^- + O\text{–}\overset{O}{\underset{OH}{P}}\text{–}OO\text{–}\overset{O}{\underset{OH}{P}}\text{–}O^{-2} \xrightarrow{H_2O} F\text{–}\overset{O}{\underset{OH}{P}}\text{–}O^- + HOO\text{–}\overset{O}{\underset{OH}{P}}\text{–}O^- + OH^-$$

for which we have some evidence.[29]

Table V lists values of rate constants for a number of acid-catalyzed hydrolyses of substituted phosphates carried out under similar reaction conditions. It is particularly noteworthy that the rate obtained in this research, with RO = HOO, is three to four orders of magnitude larger than that for any of the other substituents. Thus the perhydroxyl ion is an excellent leaving anion, being better than the less basic phenolate ion; this observation deserves particular comment.

TABLE V

RATE CONSTANTS FOR THE ACID-CATALYZED HYDROLYSES OF PHOSPHATES OF THE TYPE $ROPO_3H_2$[a]

RO[b]	Rate constant	Ref.
OH	$0.55 \times 10^{-6}\ M^{-1}$ sec.$^{-1}$	25
OCH_3	$1 \times 10^{-6}\ M^{-1}$ sec.$^{-1}$ [c]	24a
OC_6H_5	$<4 \times 10^{-6}\ M^{-1}$ sec.$^{-1}$	26
OOH	1900×10^{-6} sec.$^{-1}$ [d]	This work

[a] At 100° in aqueous solution. [b] Leaving anion is RO^-. [c] For P–O bond fission. [d] At 1.0 M $HClO_4$; estimated using $k_1 = 7.83 \times 10^{-5}$ sec.$^{-1}$ at 61° and $E_a = 20.2$ kcal. mole^{-1}.

It is well established that the anions of monosubstituted peroxides are remarkably reactive nucleophiles,[27] and the available data suggest that this is a transition-state effect rather than abnormal binding strength in the product. This being the case, it is a consequence of the law of microscopic reversibility that peroxy anions should be good leaving groups in displacement reactions. This is exactly what is observed, for both H_3PO_5 and $H_4P_2O_8$ hydrolyze rapidly in comparison with other substituted phosphates. It seems reasonable to conclude that the "alpha effect"[27] will also be observed with leaving groups in nucleophilic displacements.

All of the data obtained here (rates, acid dependence, activation parameters, fluoride ion catalysis, etc.) can be readily explained by a mechanism involving attack of water as a nucleophile on the phosphorus atom in the peroxyphosphates.

Acknowledgments.—We wish to thank Drs. Robert L. Kay and K. M. Ibne-Rasa for helpful suggestions, the U. S. Atomic Energy Commission Contract AT-(30-1)-1983 for continued support, and the Eastman Kodak Co. for a fellowship.

[29] The actual presence of the monofluorophosphate ion in such experiments has been shown by Miss Reet Paju and Mr. Bruce Fitch of this laboratory. Identification was made by preferential precipitation and identification of the silver salt Ag_2FPO_3 and by n.m.r. spectra of the solutions after reaction was complete.

CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
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Linear Deammonation Products of Sulfamide and Their Derivatives[1]

BY PIERO NANNELLI, AMEDEO FAILLI, AND THERALD MOELLER[2]

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Although both imidodisulfuric diamide (imidodisulfamide) and diimidotrisulfuric diamide are cleaved by phosphorus(V) chloride, the analogous 3-methylimidodisulfuric diamide and 3,5-dimethyldiimidotrisulfuric diamide react smoothly with this reagent to yield the highly reactive and synthetically useful bis(trichlorophosphazo) derivatives. The chlorine atoms in these compounds are readily replaced by phenyl and phenoxy groups *via* nucleophilic substitution, with the formation of more hydrolytically stable products. An analysis of the infrared spectra of a number of these derivatives has permitted assignments of observed frequencies to the significant structural units. Data on other physical properties are given also.

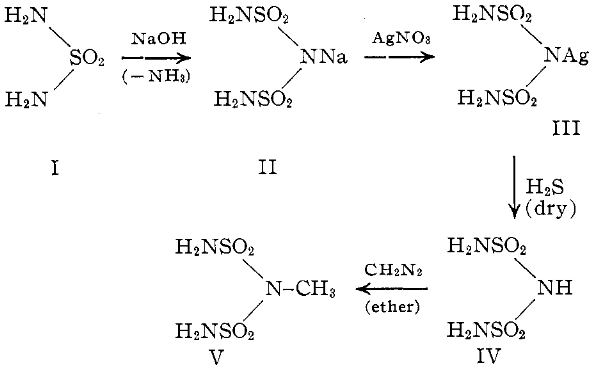
The synthesis of phosphazo chlorides by the reaction of sulfamide or its N,N-dialkyl derivatives with phosphorus(V) chloride was first reported by Kirsanov.[3,4] This type of reaction and the properties of its products have been investigated more recently and in considerable detail by Moeller and Vandi.[5] It has been of interest to extend the latter study to the synthesis of phosphazochlorides from the linear imidopolysulfamides that form as deammonation condensation products of sulfamide and to an evaluation of the physical and chemical characteristics of these compounds.

Although the $-NH_2$ groups of both imidodisulfuric diamide (IV) and diimidotrisulfuric diamide (VII) undergo the Kirsanov reaction with phosphorus(V) chloride, reaction of the NH groups results in cleavage of the sulfur–nitrogen bonds. This difficulty is obvi-

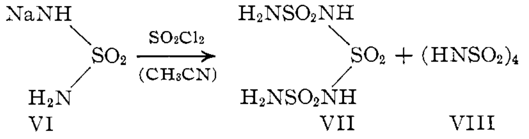
[1] Presented to the Inorganic Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1964.
[2] To whom correspondence should be directed.
[3] A. V. Kirsanov, *Zh. Obshch. Khim.*, **22**, 1346 (1952).
[4] A. V. Kirsanov and Z. D. Nekrasova, *ibid.*, **27**, 1253 (1957).
[5] T. Moeller and A. Vandi, *J. Org. Chem.*, **27**, 3511 (1962).

ated by prior selective methylation of the strongly acidic imido groups with ethereal diazomethane.

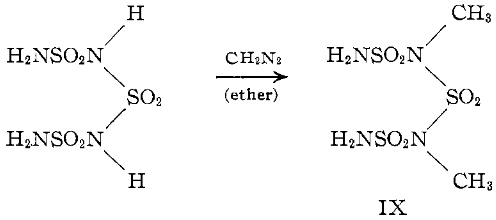
A further difficulty lies in the unavailability and relative instability of the linear imidopolysulfamides. The sequence of reactions leading to 3-methylimidodisulfuric diamide (V) is as follows[6–8]



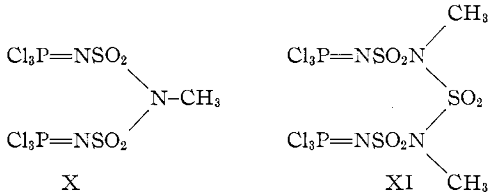
The resulting compound, a white crystalline substance that dissolves readily in water, acetone, or ethyl acetate, gives, when freshly prepared, neutral aqueous solutions that hydrolyze rapidly even at room temperature. A comparable procedure[9] works well for the synthesis of the disilver salt of diimidotrisulfuric diamide, but this compound is not converted to the parent diimidotrisulfuric diamide by dry hydrogen sulfide. It has been shown, however, that that compound can be obtained in an impure state by the reaction scheme[10]



The desired substance (VII) is the principal product at low reaction temperatures. The limited solubility of tetrasulfimide (VIII) in diethyl ether, as compared with that of compound VII, permits ready separation of the two, but the strongly hygroscopic natures of both substances make complete purification difficult. The crude diimidotrisulfuric diamide so obtained is readily converted to the desired 3,5-dimethyldiimido compound (IX) as in 81–86% yield. Compound IX is a white, nonhygroscopic, crystalline solid that is readily soluble in acetone, methanol, dioxane, or tetrahydrofuran; moderately soluble in ethanol or water; and only slightly soluble in diethyl ether. Freshly prepared aqueous solutions are neutral, by contrast with those of compound VII, which are strongly acidic. It is of interest that compounds of the same composition but slightly different melting point (134–135° *vs.* 137.5–138°) were obtained by recrystallization of the dimethyl derivative from benzene–acetonitrile (or ethyl acetate) and acetonitrile (Table I).



The corresponding trichlorophosphazo derivatives (X, XI) are obtained in excellent yields by reaction of phosphorus(V) chloride with compounds V and IX in refluxing carbon tetrachloride under completely anhydrous conditions,[5] followed by cooling to 5°. The products, after recrystallization from carbon tetrachloride, are colorless, crystalline solids that are soluble in benzene and less soluble in carbon tetrachloride. Like bis(trichlorophosphazo)sulfone,[5] they undergo ready hydrolysis, but at observably slower rates.



Compounds X and XI are susceptible to nucleophilic displacement of chlorine atoms, as are bis(trichlorophosphazo)sulfone and the N,N-dialkylamides of trichlorophosphazosulfuric acid.[5,11] Thus, the bis(triphenyl) and bis(triphenoxy) derivatives are readily obtained by reaction with phenylmagnesium bromide and sodium phenoxide, respectively. The resulting colorless products are soluble in chloroform and readily crystallizable from ethanol.

Certain of the properties of the compounds described are given in Table I.

Infrared Spectra

The spectra (NaCl region, KBr pellets) of compounds V, IX, XII, XIII, and XIV are given in Figure 1. Certain aspects of these spectra, together with appropriate comparisons with spectra of related compounds, follow.

3-Methylimidodisulfuric Diamide (V) and 3,5-Dimethyldiimidotrisulfuric Diamide (IX).—Assignment of the two strong bands at 3390 and 3290 cm.$^{-1}$ to the NH stretch in the sulfonamide group is in accord with a similar assignment of the 3280 cm.$^{-1}$ band appearing in the solid-state spectra of substituted sulfamides of the types $R_2NSO_2NH_2$ and R_2NSO_2NHR.[12] Furthermore, two bands in the 3340–3365 and 3265–3285 cm.$^{-1}$ regions in the solid-state spectra of unsubstituted sulfonamides have been similarly attributed to the NH group.[13]

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[6] A. V. Kirsnov and Yu. M. Zolotov, *Zh. Obshch. Khim.*, **20**, 1637, 1650 (1950).

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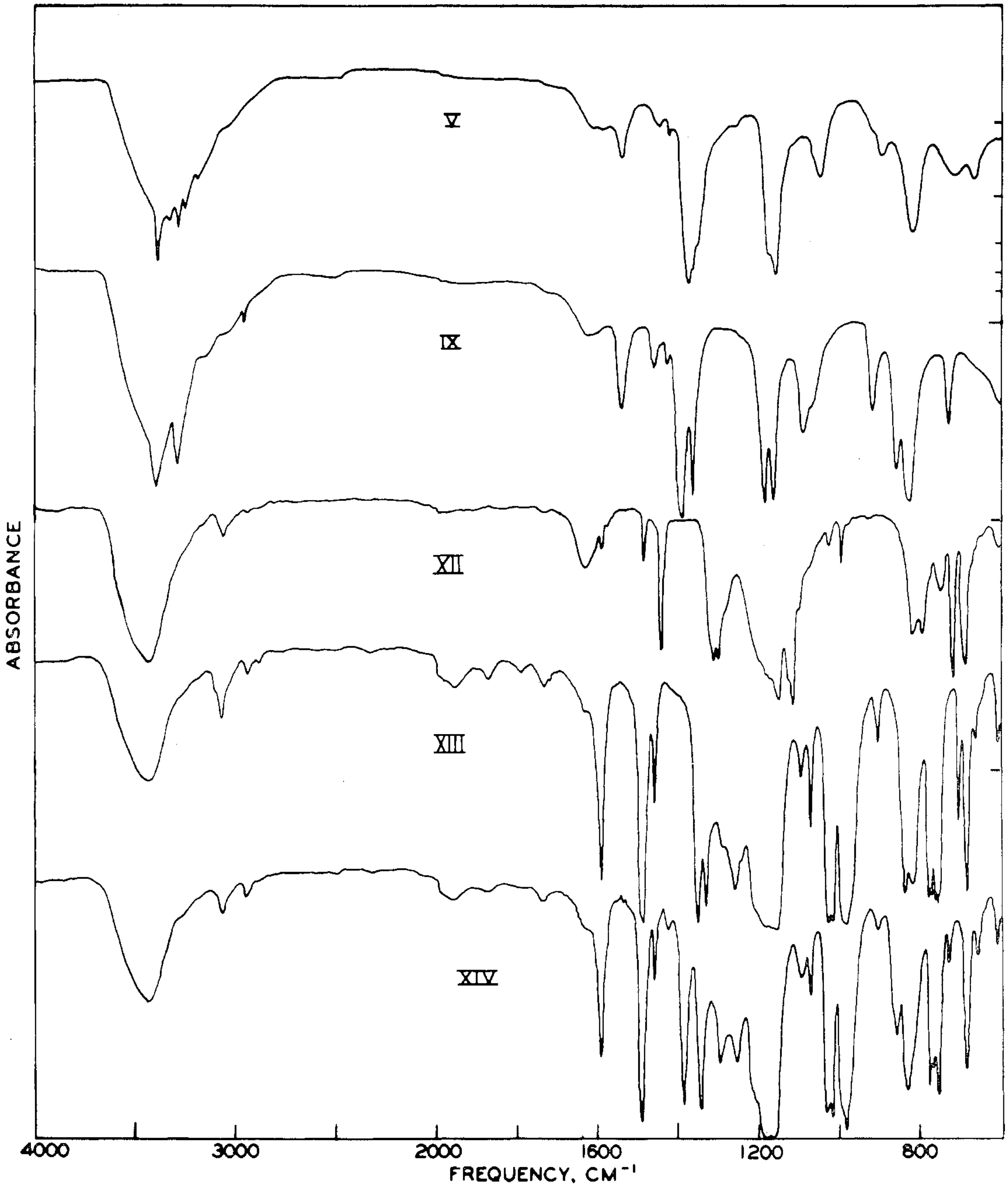

Figure 1.—Infrared spectra: V, $(H_2NSO_2)_2NCH_3$; IX, $[H_2NSO_2N(CH_3)]_2SO_2$; XII, $[(C_6H_5)_3P{=}NSO_2]_2NCH_3$; XIII, $[(C_6H_5O)_3P{=}NSO_2]_2NCH_3$; XIV, $[(C_6H_5O)_3P{=}NSO_2N(CH_3)]_2SO_2$.

Prominent in the spectrum of compound V are two intense absorptions in the 1410–1320 cm.$^{-1}$ (maximum at 1380 cm.$^{-1}$) and the 1210–1130 cm.$^{-1}$ (maximum at 1160 cm.$^{-1}$) regions. The same bands also appear in the spectrum of compound IX, but are each resolved into two closely separated peaks of nearly equal intensity (maxima at 1395, 1365 cm.$^{-1}$ and 1185, 1165 cm.$^{-1}$, respectively). These absorptions are of particular interest since they occur in spectral regions where the asymmetric and symmetric SO_2 stretching frequencies should appear. Thus, these modes are represented, respectively, by the 1350 and 1160 cm.$^{-1}$ bands for the N,N-disubstituted sulfonamides,[13,14] by the 1350–1320 and 1145–1140 cm.$^{-1}$ regions for the N-substituted sulfamides,[12] and by the 1317 and 1170 cm.$^{-1}$ bands for N-methyltoluene-*p*-sulfonamide.[15] Absorption in the 1350–1300 cm.$^{-1}$ region is also characteristic of sulfones,[16] and strong bands in the 1160–1125 cm.$^{-1}$ region, as shown by many compounds containing the SO_2 group, are assigned to a symmetric SO_2 mode.[17]

A third strong band between 1100 and 1070 cm.$^{-1}$, and usually near 1090 cm.$^{-1}$, observed for many sulfonamides was originally tentatively identified as an S–N stretching frequency.[13] More recently, the band found at 1092 cm.$^{-1}$ in the spectrum of N-methyltoluene-*p*-sulfonamide has been associated with the group of

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[14] R. Adams and J. J. Tjepkema, *J. Am. Chem. Soc.*, **70**, 4204 (1948).

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TABLE I

PROPERTIES OF IMIDOSULFAMIDES

Compound	Yield, %	M.p.,[a] °C.	Mol. wt.[c,d]	Analysis,[d] % C	H	N	Cl
3-Methylimidodisulfuric diamide $(H_2NSO_2)_2NCH_3$ (V)	58	114–115	189	6.34	3.72	22.21	
				6.91	3.85	21.91	
3,5-Dimethyldiimidotrisulfuric diamide $[H_2NSO_2N(CH_3)]_2SO_2$ (IX)	81–86[b]		282	8.51	3.57	19.85	
		134–135	280, 257, 256	8.72	3.63	20.10	
		137.5–138		8.67	3.64	20.06	
				8.77	3.67	19.84	
Bis(trichlorophosphazo)-3-methylimidodisulfone $(Cl_3P{=}NSO_2)_2NCH_3$ (X)	70	103–104	460	2.61	0.66	9.14	46.26
			446	2.75	0.67	9.09	46.56
Bis(trichlorophosphazo)-3,5-dimethyldiimidotrisulfone $[Cl_3P{=}NSO_2N(CH_3)]_2SO_2$ (XI)	54–58[b]	118	553 dec.	4.34	1.09	10.13	38.47
				4.72	1.44	9.84	38.69
Bis(triphenylphosphazo)-3-methylimidodisulfone $[(C_6H_5)_3P{=}NSO_2]_2NCH_3$ (XII)	21	228–229	710	62.61	4.68	5.92	
				62.37	4.61	5.72	
Bis(triphenoxyphosphazo)-3-methylimidodisulfone $[(C_6H_5O)_3P{=}NSO_2]_2NCH_3$ (XIII)	32.3	91–92	806	55.15	4.12	5.21	
				55.11	4.25	5.28	
Bis(triphenoxyphosphazo)-3,5-dimethyldiimidotrisulfone $[(C_6H_5O)_3P{=}NSO_2N(CH_3)]_2SO_2$ (XIV)	80[b]	90	899	50.77	4.04	6.23	
			860	50.79	4.08	6.22	

[a] In sealed capillary; uncorrected. [b] For crude product. [c] By vapor pressure lowering in acetone (IX), benzene (X, XIV). [d] First line for each substance calculated; others found.

SO_2 variations.[18] In the light of observed alterations between the C–O and S–O stretching frequencies, it has been suggested[15] that the S–N stretching frequency should appear at lower wave numbers than the C–N frequency. Thus, in agreement with the assumed position of the C–N band for the simple amines,[19] the 1062 cm.$^{-1}$ band for N-methyltoluene-*p*-sulfonamide is associated with the C–N group,[15] and the 904, 918, and 909 cm.$^{-1}$ bands for sulfonamides and the 839 cm.$^{-1}$ band for N-methyltoluene-*p*-sulfonamide with the S–N group.[15] Some support is given by the S–N lines found at 900–800 cm.$^{-1}$ in the Raman spectra of sulfonamides.[20]

On this basis, the absorptions in the regions (cm.$^{-1}$) 1080–1030 (maximum, 1050), 900, and 870–790 (maximum, 820) for compound V can be assigned, respectively, to the C–N, S–N of the $-SO_2-NH_2$ group, and SO_2-N-R stretching modes. The bands for compound IX at (cm.$^{-1}$) 1120–1045 (maximum, 1090; shoulder, 1070), 920, and 830 are similarly assigned.

Bis(triphenyl) and Bis(triphenoxy) Derivatives of Compounds X and XI.—These compounds contain the $\geqslant P{=}N{-}SO_2-$ group. The $\geqslant P{=}N-$ stretching frequency for the trimeric and tetrameric phosphonitrilic chlorides lies at 1125 and 1320 cm.$^{-1}$, respectively.[21] However, for phosphonimidates and phosphorimidates, it is reported to lie in the 1385–1325 cm.$^{-1}$ region,[22] and the strong absorption noted in the 1375–1325 cm.$^{-1}$ region for monomeric and dimeric trichlorophosphazoaryls and phenyldichlorophosphazoaryls has been associated with the $\geqslant P{=}N-$ group.[23] Furthermore, an analysis of the spectra of compounds of the type $RSO_2N{=}P(OR)_3$ led to an assignment of strong absorption in the 1290–1260 cm.$^{-1}$ region to the $\geqslant P{=}N-$ group.[24] Similarly, the strong absorption in the region 1300–1255 cm.$^{-1}$ for compounds of the types $(Ar_3P{=}N)_2SO_2$ and $RR'NSO_2N{=}PAr_3$ has been ascribed to this grouping.[5]

The spectrum of compound XII has a strong absorption at 1445 cm.$^{-1}$ (related to the phenyl groups), a broad absorption in the region 1250–1090 cm.$^{-1}$ (maxima, 1150 and 1120 cm.$^{-1}$) (associated with the symmetric SO_2 stretch), and an absorption in the region 1350–1270 cm.$^{-1}$ (maxima, 1315 and 1305 cm.$^{-1}$) (associated with the asymmetric SO_2 and $\geqslant P{=}N-$ stretches). The spectrum of compound XIII is better resolved, with absorptions at 1590 and 1490 cm.$^{-1}$ (phenyl group), 1350–1330 cm.$^{-1}$ (asymmetric SO_2 stretch), 1260 cm.$^{-1}$ ($\geqslant P{=}N-$ stretch), and 1230–1140 cm.$^{-1}$ (P–O–C and SO_2 stretches). The band at 1030–1015- cm.$^{-1}$ also reflects the P–O–C stretch.[19]

The spectrum of compound XIV shows comparable absorptions for the phenyl group at 1580 and 1480

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(18) S. Detoni and D. Hadži, *Spectrochim. Acta*, **11**, 601 (1957).

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1960, pp. 295, 315.

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(23) I. N. Zhmurova, A. A. Kisilenko, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **32**, 2580 (1962); *Russ. J. Gen. Chem.*, **32**, 2544 (1962).

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

cm.$^{-1}$ and for the SO_2 group (asymmetric) at 1345 cm.$^{-1}$. In the 1310–1240 cm.$^{-1}$ region, two separated peaks of nearly equal intensity at 1295 and 1255 cm.$^{-1}$ are characteristic of the solid but only one (1290 cm.$^{-1}$) of a solution in benzene. The broad absorption at 1230–1140 cm.$^{-1}$ probably reflects the P–O–C and SO_2 (symmetric) groups and that at 1040–1010 cm.$^{-1}$ the P–O–C group.

Experimental

Materials.—Thiophene-free benzene was dried over sodium wire. Commercial acetonitrile was distilled six times from phosphorus(V) oxide and once from fused potassium carbonate. Commercial sulfamide was recrystallized twice from absolute ethanol. Absolute ethanol, absolute diethyl ether, and cylinder (dry) hydrogen sulfide were used directly. Ethereal solutions of diazomethane were prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide,[25] dried for 3 hr. over potassium hydroxide pellets, and standardized.

Infrared Spectra.—All infrared spectra were obtained with a Model 21 Perkin-Elmer double-beam instrument with sodium chloride optics, using the potassium bromide pellet technique.

Silver Salt of Imidodisulfuric Diamide (III).—This compound was obtained as the crystalline 2-hydrate by a modification of previously reported procedures[6,7] and dehydrated *in vacuo;* yield 86%.

Anal. Calcd. for $AgH_4N_3O_4S_2$: Ag, 38.24. Found: Ag, 38.20.

Imidodisulfuric Diamide (IV).—An anhydrous methanolic suspension of compound III was treated with hydrogen sulfide as previously described,[7] and the desired substance was precipitated from an acetone solution of the reaction product with benzene.[26] Melting point, after purification; 167–169°; yield 42.5%.

Anal. Calcd. for $H_5N_3O_4S_2$: H, 2.87; N, 23.99. Found: H, 2.98; N, 23.93.

3-Methylimidodisulfuric Diamide (V).—This compound was prepared essentially as previously described[8]; yield 58%.

Bis(trichlorophosphazo)-3-methylimidodisulfone (X).—To a 200-ml. flask, equipped with a reflux condenser bearing a calcium chloride drying tube, 5.67 g. (0.03 mole) of compound V, 13.53 g. (0.065 mole) of phosphorus(V) chloride, and 90 ml. of carbon tetrachloride were added. The reaction mixture was refluxed at *ca.* 80° for 24 hr., by the end of which period evolution of hydrogen chloride had ceased. The product was crystallized by storing the resulting solution in a refrigerator. It was recrystallized by dissolving in 80 ml. of hot carbon tetrachloride and cooling to 5°; yield 9.7 g. (70%).

Bis(triphenylphosphazo)-3-methylimidodisulfone (XII).—To an ethereal solution of phenylmagnesium bromide, prepared from 2.43 g. (0.1 g.-atom) of magnesium turnings and 15.70 g. (0.1 mole) of bromobenzene, was added, with magnetic stirring, 4.59 g. (0.01 mole) of compound X dissolved in 150 ml. of dry benzene. The system was refluxed for 4 hr. The Grignard reagent was then destroyed with ice and hydrochloric acid, and the benzene–ether solution was dried with calcium chloride and evaporated. The resulting yellow oil solidified after standing under ethanol. Recrystallization from ethanol gave a pure product; yield 1.5 g. (21%).

Bis(triphenoxyphosphazo)-3-methylimidodisulfone (XIII).—Twenty grams (0.212 mole) of dry phenol dissolved in 150 ml. of dry benzene was treated with 4 g. (0.174 g.-atom) of sodium. This mixture was refluxed overnight. The resulting suspension of sodium phenoxide was then added, with vigorous stirring, to a solution of 2.295 g. (0.005 mole) of compound X in 100 ml. of benzene. After being refluxed for 3 hr., the mixture was shaken repeatedly with water until the water extract was neutral. After being dried over potassium carbonate, the benzene solution was evaporated *in vacuo*. The oily residue was dissolved in 70 ml. of dry ethanol and the product crystallized by cooling to −5°. Recrystallization from ethanol gave a yield of 1.3 g. (32.3%).

Impure Diimidotrisulfuric Diamide (VII).—This compound was prepared from the dry sodium salt of sulfamide[27] as described by Meuwsen and Papenfuss.[10] The impure product melted at 159–161°; yield 64.5%. The dipotassium salt, obtained by reaction with potassium hydroxide and precipitation with ethanol, was analyzed.

Anal. Calcd. for $K_2H_4N_4S_3O_6$: K, 23.7; N, 16.9. Found: K, 23.3; N, 17.04.

3,5-Dimethyldiimidotrisulfuric Diamide (IX).—To a 1-l., three-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a calcium chloride tube, were added 5 g. (0.0197 mole) of dry, pulverized compound VII and 400 ml. of dry ether. The flask was cooled to 0°, and an ethereal solution containing 0.039 mole of diazomethane was added dropwise with stirring. A slight excess of diazomethane was then added (yellow color persisting for 15–20 sec.). The colorless solution was stirred for 10–15 min., then filtered, and the solvent was removed *in vacuo* with water-bath heating to a residual volume of 70 ml. Then 200 ml. of dry benzene was added slowly with vigorous shaking. The solution was allowed to stand for 3 hr. to crystallize. Evaporation of the mother liquor to *ca.* 100 ml. yielded a second crop of crystals. The product was washed with dry benzene and dried *in vacuo;* yield 4.5–4.8 g. (81–86%).

Bis(trichlorophosphazo)-3,5-dimethyldiimidotrisulfone (XI).—This compound was prepared in the same manner as compound X, using 2.82 g. (0.01 mole) of dry, pulverized compound IX; yield 3–3.2 g. (54–58%).

Bis(triphenoxyphosphazo)-3,5-dimethyldiimidotrisulfone (XIV).—This compound was prepared in the same manner as compound XIII, using 2.76 g. (0.005 mole) of compound XI; yield (crude) 3.6 g. (80%).

Acknowledgment.—The generous support provided by the Army Research Office (Durham) under Contract DA-31-124-ARO(D)-35 is gratefully acknowledged.

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