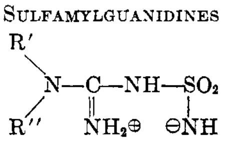
TABLE II

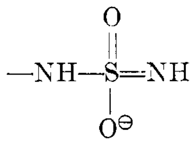
SULFAMYLGUANIDINES



I

R′	R″	M.p., °C	Yield, %	Recryst. solvent	Infrared μ	Calcd. C	N	N	Found C	H	N
(a) H	H	167–169	46	Ethanol	7.94,8.36,8.87	8.69	4.38	40.55	8.83	4.18	40.21
(b) CH_3	H	154–155	43	Ethanol	7.85,8.35,9.08	15.78	5.30	36.82	15.84	4.92	36.95
(c) $C_6H_5CH_2$	H	156.5–157.5	50	Acetone	7.95,8.56,8.90	42.09	5.30	24.54	42.19	5.18	24.72
(d) $CH_3(CH_2)_4$	H	83–84	16	Methylene chloride	8.04,8.55,9.01	34.60	7.74	26.90	34.64	7.89	27.22
(e) CH_3	CH_3	132–133.5	52	Ethanol–ether	7.88,8.60,8.95	21.68	6.06	33.71	21.62	5.98	34.10
IV [(Ie) HCl][a]		116–118	93	Ethanol–ether	7.38,8.46,none	17.78	5.47	27.64	17.90	5.12	27.85

[a] Prepared in water solution by addition of an equimolar amount of hydrochloric acid to (Ie) followed by evaporation to dryness under vacuum.

(b) Although the sulfamylguanidines exhibit the usual[6] strong sulfonamide S=O stretching absorptions in the infrared (approximately 7.8 and 8.6 μ), they in addition show a strong band near 9.0 μ (Table II) which may be due to the S—O⁻ stretching of the resonating anion:  $-NH-S(=O)(O^{\ominus})=NH$ in zwitterionic I. Spectra of authentic sodium salts of sulfamylamines exhibit this same strong peak near 9.0 μ while no absorption is seen near 9.0 μ in a hydrochloride salt of the sulfamylguanidine Ie (IV) (Table I).

Experimental[8]

A general method was employed in the preparation of all compounds of type I. This method is illustrated below for Ie.

N^1,N^1-Dimethyl-N^3-sulfamylguanidine (Ie).—Dimethylguanidine (free base) was prepared from 68 g. (0.50 mole) of the sulfate salt in 600 ml. of ethanol under a nitrogen atmosphere by treatment with 500 ml. of 1 *M* ethanolic sodium ethoxide, filtration of the precipitated sodium sulfate, and evaporation of the clear filtrate under vacuum. The residual cream colored solid was used immediately in the next step.

To a solution of 82 g. (0.50 mole) of N-sulfamylpiperidine[2] in in 100 ml. of dimethyl sulfoxide was slowly added a solution of the above free base in 150 ml. of dimethyl sulfoxide. Heating on the steam bath for 2 hr. followed by distillation of solvent under vacuum yielded a viscous orange oil. Trituration with ethanol readily yielded a pale yellow solid, 43.7 g. (52%), m.p. 126–129°. Recrystallization from ethanol–ether raised the m.p. to 132–133.5°.

Substitution of N-sulfamyldimethylamine for N-sulfamylpiperidine in the above reaction gave detectable evolution of a basic gas (dimethylamine) and 53% of identical product Ie, m.p. 131–132°, mixture m.p. 128–131°.

Table II summarizes pertinent physical data for compounds of type I.

Acknowledgment.—The author wishes to thank Mr. Nelson Treadway, Jr., for his technical assistance.

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(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 350.

(7) Kindly provided by Dr. J. M. McManus of these laboratories.

(8) Melting points were taken in open capillaries and are corrected. Infrared spectra were measured in potassium bromide pellets.

The Formation and Reactions of Some Phenylphosphonous Diamides and Diphenylphosphinous Amides

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Received August 14, 1962

The literature contains many references to the preparation of diphenylphosphinous amides,[1-3] but few references to phenylphosphonous diamides.[4]

In this investigation we prepared additional N-substituted phenylphosphonous diamides by the reaction of phenylphosphonous dichloride with *tert*-butylamine and 3-azabicyclo[3.2.2]nonane according to the general method of Michaelis.[5] These phenylphosphonous diamides behave as typical diphenylphosphinous amides. They add sulfur to give phenylphosphonothioic diamides, oxygen to produce phenylphosphonic diamides, and form adducts with some metal salts. They also form quaternary salts with aralkyl and alkyl halides in which the entering group is attached to phosphorus, not nitrogen.[4,5] P-Alkylation was also observed in our studies of the monoaminophosphonium halides.[6]

Finally, as a corollary to our previous studies of phosphorous–nitrogen compounds,[1,2] it was found that (3-azabicyclo[3.2.2]non-3-yl)diphenylphosphine reacts with methyl iodide to give (3-azabicyclo[3.2.2]non-3-yl) methyldiphenylphosphonium iodide and with carbon disulfide to give a crystalline adduct. On the basis of analogy with the work of Margulis and Templeton[7] the carbon disulfide adduct is tentatively assigned the following structure.

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(1) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

(2) N. L. Smith and H. H. Sisler, *ibid.*, **26**, 5145 (1961).

(3) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958.

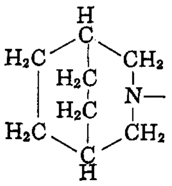
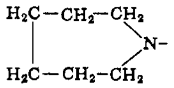
(4) A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).

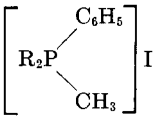
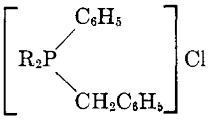
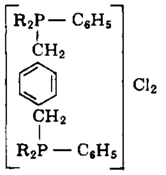
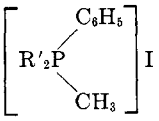
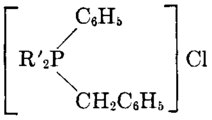
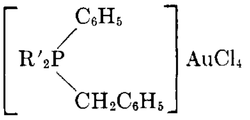
(5) A. Michaelis, *Chem. Ber.*, **31**, 1037 (1898).

(6) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 4733 (1961).

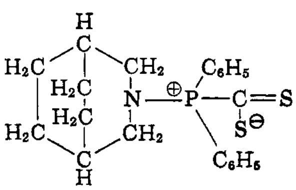
(7) T. N. Margulis and P. W. Templeton, *J. Am. Chem. Soc.*, **83**, 995 (1961).

TABLE I
PHENYLPHOSPHONOUS DIAMIDES AND THEIR DERIVATIVES

R = *tert*-C_4H_9NH— R' =  R'' = 

	Product	Formula	Yield, %	M.p., °C.	% C Calcd. Found	% H Calcd. Found	% N Calcd. Found	% P Calcd. Found	% X Calcd. Found
I	$R_2PC_6H_5$	$C_{14}H_{25}N_2P$	64	98–100/0.4 mm.[a]	66.63 66.36	9.99 9.75	11.10 11.26	12.28 12.22	
II	$R_2P(O)C_6H_5$[b]	$C_{14}H_{25}N_2OP$	71	188–189	62.66 62.83	9.39 9.39	10.44 10.32	11.55 11.80	
III	$R_2P(S)C_6H_5$[c]	$C_{14}H_{25}N_2PS$	39	108–109	59.12 58.91	8.86 9.90	9.85 9.90	10.89 10.83	11.28 (S) 11.37
IV		$C_{15}H_{28}IN_2P$	88	176–177	45.35 45.73	7.10 7.31			32.70 (I) 32.41
V		$C_{21}H_{32}ClN_2P$	69	232 dec.	66.56 66.43	8.51 8.30	7.39 7.29	8.18 8.08	9.36 (Cl) 9.38
VI		$C_{36}H_{58}Cl_2N_4P_2$	28	>335	63.61 63.48	8.60 8.35	8.24 8.35	9.11 9.12	10.43 (Cl) 10.41
VII	$R_2PC_6H_5 \cdot HgCl_2$	$C_{14}H_{25}Cl_2N_2PHg$	Quant.	198 dec.					13.54 (Cl) 13.15
VIII	$R'_2PC_6H_5$	$C_{22}H_{33}N_2P$	67	136–137	74.12 73.86	9.33 9.50	7.86 7.59	8.69 8.43	
IX	$R'_2P(O)C_6H_5$	$C_{22}H_{33}N_2OP$	97	160–161	70.94 70.99	8.93 8.92	7.52 7.36	8.32 8.20	
X	$R'_2P(S)C_6H_5$	$C_{22}H_{33}N_2PS$	Quant.	125–126			7.21 7.25	7.97 7.80	8.25 (S) 8.46
XI		$C_{23}H_{36}IN_2P$	43	236 dec.	55.43 55.66	7.26 7.03			25.43 (I) 25.51
XII		$C_{29}H_{40}ClN_2P$	44	273–274	72.10 72.35	8.35 8.18	5.80 6.02	6.41 6.32	7.34 (Cl) 7.55
XIII		$C_{29}H_{40}Cl_4N_2PAu$	88	166–167	44.28 44.18	5.12 5.10	3.56 3.59	3.94 4.03	18.03 (Cl) 18.03
XIV	$R''_2P(O)C_6H_5$[d]	$C_{18}H_{29}N_2OP$	19	188–190/0.25 mm.[a]	67.47 67.24	9.12 9.08	8.75 8.92		

[a] B.p. [b] See ref. 11. [c] Prepared by the reaction of *tert*-butylamine with phenylphosphonothioic dichloride. [d] Prepared by the reaction of hexahydro-1*H*-azepine with phenylphosphonic dichloride.



The analytical data, yields, and some physical properties for the various compounds synthesized in this investigation are compiled in Table I. Infrared absorption frequencies of the compounds listed are found in the ranges expected for P(O), P(S), P–N, P-phenyl, and phosphonium type structures.[1,6,8]

Experimental[9]

Materials.—Phenylphosphonic dichloride and phenylphosphonous dichloride were obtained from Victor Chemical Co.

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(8) Z. B. Papanastassiou and T. J. Bardos, *J. Med. Pharm. Chem.*, **5**, 1000 (1962).

(9) Analyses were performed by Gailbraith Microanalytical Laboratories, Knoxville, Tenn. The boiling and melting points are uncorrected.

Activated manganese dioxide was purchased from Beacon Chemicals Industries, Inc. The source of the amines were: *tert*-butylamine from Rohm and Haas, hexahydro-1*H*-azepine from E. I. DuPont de Nemours and Co., and 3-azabicyclo[3.2.2]nonane from Eastman Chemical Products, Inc. All compounds obtained from commercial sources were used as received.

Procedure for the Preparation of the Phenylphosphonous Diamides.[10]—The reaction of phenylphosphonous dichloride with *tert*-butylamine is described as an example of the preparation of the phenylphosphonous diamides.

A solution of 18.0 g. (0.1 mole) of phenylphosphonous dichloride in 75 ml. of benzene was added dropwise with stirring to a solution of 30.0 g. (0.4 mole) of *tert*-butylamine in 175 ml. of benzene. The temperature reached a maximum of 50° during the addition of the phenylphosphonous dichloride. At the completion of the addition, stirring at 50° was continued for 1.5 hr. The reaction mixture was filtered, and the amine hydrochloride precipitate was washed thoroughly with benzene and ethyl ether. The combined filtrate and washings were stripped of solvents by rotary evaporation at reduced pressure. The yellow, viscous residue was fractionated, b.p. 98–100°/0.4 mm., and the product weighed 14.9 g. (64% yield).

Procedure for the Oxidation of the Phenylphosphonous Diamides.—The phenylphosphonous diamides were converted to the corresponding phenylphosphonic diamides by reaction with activated manganese dioxide. The preparation of N,N'-di-*tert*-butyl-P-phenylphosphonic diamide (II) is described as an example of this method.

To a stirred solution of 5.0 g. (0.02 mole) of N,N'-di-*tert*-butyl-P-phenylphosphonous diamide (I) in 50 ml. of dry benzene was added 10.0 g. (0.12 mole) of activated manganese dioxide. The mixture was stirred at reflux for 2 hr., cooled, and filtered. The solids were washed with small portions of dry benzene. The solvent from the combined filtrate and washings was removed by rotary evaporation at reduced pressure, and the residue was air-dried. The product weighed 3.8 g. (93% yield). It crystallized from ethyl acetate as white needles, m.p. 188–189°.[11]

Procedure for the Formation of Phenylphosphonothioic Diamides by the Direct Addition of Sulfur to Phenylphosphonous Diamides.—A mixture of 1.2 g. (3.0 mmoles) of di(3-azabicyclo-[3.2.2]non-3-yl)phenylphosphine, 0.1 g. (3.0 mg.-atom) of sulfur and 50 ml. of dry benzene was stirred at reflux for 2 hr., filtered, and the solvent removed from the filtrate by rotary evaporation at reduced pressure. The product weighed 1.3 g. (quantitative yield), and crystallized from aqueous acetone in fine needles.

Procedure for the Quaternization of Phenylphosphonous Diamides.—A mixture of 2.5 g. (0.01 mole) of N,N'-di-*tert*-butyl-P-phenylphosphonous diamide, 1.4 g. (0.01 mole) of methyl iodide, and 50 ml. of benzene was stirred at 45–50° for 1 hr. The reaction product was filtered, and the solids washed thoroughly with ethyl ether, and air-dried. The white, crystalline product weighed 3.5 g. (88% yield) and melted at 168–170°. It crystallized from aqueous ethanol as white, glistening prisms, m.p. 176–177°.

Bis(*tert*-butylamino)benzylphenylphosphonium chloride (V), *p*-phenylenedimethylene)bis[bis-(*tert*-butylamino)phenylphosphonium chloride] (VI), bis(3-azabicyclo[3.2.2]non-3-yl)benzylphenylphosphonium chloride (XII), and bis(3-azabicyclo[3.2.2]-non-3-yl)methylphenylphosphonium iodide (XI) were prepared by the procedure described except that monochlorobenzene was used as solvent for the chloromethyl compounds.

Adduct of Carbon Disulfide and (3-Azabicyclo[3.2.2]non-3-yl)-diphenylphosphine.—A mixture of 3.1 g. (0.01 mole) of (3-azabicyclo[3.2.2]non-3-yl)diphenylphosphine,[1,2] 0.75 g. (0.01 mole) of carbon disulfide, and 35 ml. of dry benzene was stirred at 35–40° for 30 min. and then allowed to stand overnight at room temperature. The white powder which separated was filtered and washed with petroleum ether (39–50°). The product melted at 168–169°. The mother liquors yielded an additional crop, making a total of 3.1 g. (81% yield).

Its infrared spectrum in Nujol mull showed absorption bands (cm.$^{-1}$) at 695, 715, 746, 825, 945, 1010, 1120, 1260, 1345, 1440, 1460, and 2900.

Anal. Calcd. for $C_{21}H_{24}NPS_2$: C, 65.33; H, 6.29; N, 3.64; P, 8.06; S, 16.68. Found: C, 65.00; H, 6.52; N, 3.47; P, 8.35; S, 16.66.

Bis(hexahydro-1*H*-azepin-1-yl)phenylphosphine Oxide (XIV).—A solution of 19.5 g. (0.1 mole) of phenylphosphonic dichloride in 75 ml. of benzene was added with stirring to a solution of 40.0 g. (0.4 mole) of hexahydro-1*H*-azepine in 175 ml. of benzene. After the addition of phenylphosphonic dichloride, the reaction product was stirred at reflux for 1 hr. The product was filtered while hot, and the solids were washed thoroughly with boiling ethyl ether. The solvents were removed from the combined filtrates and washings at reduced pressure, and the residue fractionated, b.p. 188–190°/0.25 mm. The yellow oil weighed 6.0 g. (19% yield).

Bis(3-azabicyclo[3.2.2]non-3-yl)benzylphenylphosphonium Tetrachloroaurate (III) (XIII).—To a solution of 1.0 g. (2.0 mole) of $AuCl_3 \cdot HCl \cdot 4H_2O$ in 10 ml. of water was added with stirring a solution of 1.0 g. (2.0 mmoles) of bis(3-azabicyclo[3.2.2]non-3-yl) benzylphenylphosphonium chloride. A yellow precipitate formed immediately. The product was filtered and the solids washed with water. It crystallized from acetone in yellow granules, m.p. 166–167°, and weighed 1.4 g. (88% yield).

(3-Azabicyclo[3.2.2]non-3-yl)methyldiphenylphosphonium Chloride.—A mixture of 0.50 g. (1.6 mmoles) of 3-azabicyclo-[3.2.2]non-3-yl)diphenylphosphine, 0.25 g. (1.6 mmoles) of methyl iodide, and 25 ml. of dry benzene was stirred at reflux for 1 hr. The reaction product was cooled and filtered. The solids were washed thoroughly with ethyl ether and air-dried. It crystallized from benzene and ethyl ether as white granules, m.p. 206° dec. and weighed 0.4 g. (55% yield).

Anal. Calcd. for $C_{21}H_{27}INP$: C, 55.88; H, 6.03; N, 3.10; P, 6.86; I, 28.12. Found: C, 56.00; H, 6.03; N, 3.22; P, 6.67; I, 28.26.

Acknowledgment.—The author expresses his appreciation to Dr. Leonard T. Capell of the Chemical Abstracts Service for suggestions on nomenclature.

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[10] There is no spectral evidence that compound $(tert\text{-}C_4H_9NH)_2PC_6H_5$ exists in the tautomeric form $tert\text{-}C_4H_9N = \underset{H}{P}(C_6H_5)(tert\text{-}C_4H_9NH)$ since the PH (2440–2350 cm.$^{-1}$) and N = P (1300 cm.$^{-1}$) linkages are absent. The existence of a tautomeric form was suggested as a possibility by one of the referees.

[11] V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh. Chem.*, **91**, 836 (1960), reported the same melting point for the diamide prepared by the reaction of phenylphosphonic dichloride with *tert*-butylamine.

The Reaction of Phenyl Sulfoxide with Phenyllithium

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Received October 18, 1962

The reaction of sulfoxides with organomagnesium or organolithium compounds leads to various products depending on the nature of the sulfoxide, the organometallic compound, and the reaction conditions. Present evidence indicates sulfoxides containing the methylsulfinyl group react with organomagnesium halides to give sulfides derived from the parent sulfoxide[2,3]:

$$RMgX + CH_3SOR' \longrightarrow RCH_2SR'$$

Phenyl sulfoxide and arylmagnesium halides react to give diphenylaryl sulfonium salts[4] or phenyl sulfide[5] depending on the conditions. Some dialkyl sulfoxides have been reported to give the alkyl sulfide derived from the sulfoxide plus alcohols and olefins derived

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[1] National Science Foundation Fellow, Summer, 1962.

[2] H. Potter, Abstracts of Papers, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 3-0.

[3] R. Oda and K. Yamamoto, *J. Org. Chem.*, **26**, 4679 (1961).

[4] B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Am. Chem. Soc.*, **73**, 1965 (1951).

[5] H. Hepworth and H. W. Clapham, *J. Chem. Soc.*, 1188 (1921).