Triisobutylantimony Diacetate.—The diacetate was prepared from the oxide by reaction with acetic acid in refluxing benzene using a Dean and Stark trap. It was obtained in 54% yield as a colorless oil with b.p. 144–147° (3.3 mm.).

Anal. Calcd. for $C_{16}H_{33}O_4Sb$: C, 46.6; H, 8.0; Sb, 29.8. Found: C, 45.6; H, 8.0; Sb, 30.7.

Tri-*n*-butylantimony Diethoxide.—The diethoxide was prepared from the oxide and excess ethanol in refluxing benzene using a Dean and Stark trap. It was obtained in 44% yield as a colorless oil with b.p. 104–109° (0.10 mm.).

Anal. Calcd. for $C_{16}H_{37}O_2Sb$: C, 50.3; H, 9.7; Sb, 3.17. Found: C, 50.0; H, 9.1; Sb, 30.4.

Procedures for the Trimerization of Isocyanates.—Trimerization of reactive liquid isocyanates could be induced by adding the required amount of catalyst to the isocyanate in a stoppered, dry flask and allowing it to stand at room temperature with occasional swirling until complete solidification was noted. Obtained in this way, using 2 mole % of tri-*n*-butylantimony oxide, were the following isocyanurates: phenyl, 94%, m.p. 281° (lit.[1] m.p. 280°); *m*-chlorophenyl, 100%, m.p. 221° (lit.[1] m.p. 218°); toluene diisocyanate, ~70%, m.p. >300°; hexamethylene diisocyanate, ~60%, m.p. >300°.

Less reactive isocyanates required heating at 80°. Trimers obtained in this manner were: *o*-methoxyphenyl, 1 hr., 95% (lit.[1] m.p. 95°); *p*-tolyl, 6 hr., 22%, m.p. 268° (lit.[1] m.p. 264°).

Trimers obtained at room temperature in heptane or DMSO over a period of 24 hr. were: *m*-chlorophenyl, 97%; phenyl, 96%; *m*-nitrophenyl, 71%, m.p. 245° dec.; toluene diisocyanate, 100%, m.p. >300°; hexamethylene diisocyanate (5 mole % oxide used), 100%, m.p. >300°; the latter two were run in DMSO.

Reaction of Tri-*n*-butylantimony Oxide and Phenyl Isocyanate.—When 7.14 g. of phenyl isocyanate (0.06 mole) was added to 15.4 g. of tri-*n*-butylantimony oxide (0.05 mole) in a drybox, an exothermic reaction was noted. After 4 days at room temperature, the reaction mixture was triturated with heptane to yield some triphenyl isocyanurate (m.p. 278–281°); the heptane-soluble fraction, upon distillation of solvent, yielded 17.1 g. of a nondistillable oil ($n^{24}D$ 1.5275) whose elemental analysis indicated it to be a stoichiometric complex of tri-*n*-butylantimony oxide and phenyl isocyanate.

Anal. Calcd. for $C_{19}H_{27}NO_2Sb$: N, 3.3. Found: N, 3.4.

The structure of this complex was confirmed by infrared analysis which indicated the absence of NH absorption, unreacted isocyanate ($\gamma_{C=O}$ 2240 cm.$^{-1}$), or triphenyl isocyanurate ($\gamma_{C=O}$, 1705 cm.$^{-1}$); a strong carbonyl absorption at 1725 cm.$^{-1}$ was noted. Attempts to prepare this complex by heating triphenyl isocyanurate and the oxide were unsuccessful. The complex was an active trimerizing agent.

Synthesis of Isocyanatoorganosulfonyl Isocyanates and Organodisulfonyl Isocyanates[1]

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Phosgenation of *p*-aminobenzenesulfonamide (VII) in an inert medium at 150° gave *p*-isocyanatobenzenesulfonyl isocyanate (III), while at 90° the product was *p*-isocyanatobenzenesulfonamide (IX). Several derivatives of III were prepared illustrating the difference in the reactivity of the sulfonyl and phenyl isocyanate groups contained in this molecule. Organodisulfonyl isocyanates IV–VI were prepared by the direct phosgenation of organodisulfonamides.

(1) This paper was presented at the Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov. 1963.

A few aliphatic and aromatic monosulfonyl isocyanates are described in the literature. These materials were prepared either by the reaction of sulfonyl chlorides with silver cyanate,[2] by the reaction of sulfonic anhydrides with silver cyanate,[3] or by the direct phosgenation of monosulfonamides.[4] By the silver cyanate methods, the yields were generally low (5 to 38%); phosgenation gave yields of about 80%.

$$\left.\begin{array}{l} CH_3SO_2Cl + AgCNO \\ (CH_3SO_2)_2O + AgCNO \end{array}\right\} \longrightarrow CH_3SO_2NCO$$

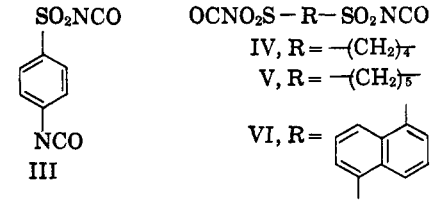
$$C_6H_5SO_2NH_2 + COCl_2 \longrightarrow C_6H_5SO_2NCO$$

Sulfonyl diisocyanates I and II, respectively, were prepared by the reactions of chlorosulfonyl isocyanate with silver cyanate,[5] and potassium cyanate with sulfur trioxide.[6]

$$CNCl + SO_3 \longrightarrow ClSO_2NCO \xrightarrow{AgCNO} OCNSO_2NCO \quad (I)$$

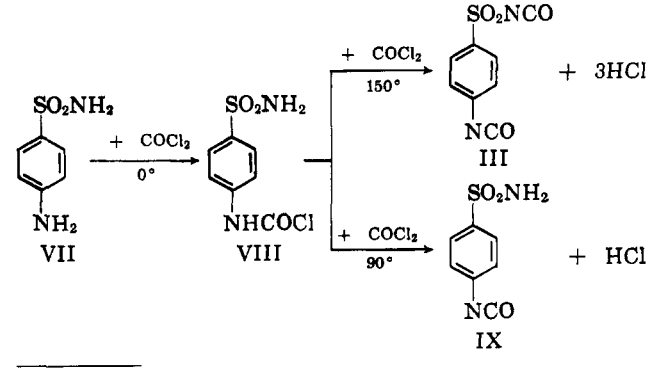
$$4SO_3 + 2KCNO \longrightarrow K_2S_2O_7 + S_2O_5(NCO)_2 \quad (II)$$

p-Isocyanatobenzenesulfonyl isocyanate (III) and the organodisulfonyl isocyanates IV–VI, representing new classes of diisocyanates, have now been prepared by the direct phosgenation of *p*-aminobenzenesulfonamide (VII) and organodisulfonamides, respectively.



Synthesis and Derivatives of *p*-Isocyanatobenzenesulfonyl Isocyanate (III).—Two-stage phosgenation of VII in nitrobenzene solvent afforded III in 87% yield. This new diisocyanate is nonlachrymatory at room temperature, is obtainable in a high degree of purity by a simple distillation, and is extremely reactive with active hydrogen-containing materials, *i.e.*, water, alcohols, etc.

The conversion of VII to III involves: (1) addition of a slurry of VII in nitrobenzene to a solution of phosgene in nitrobenzene at 0° to form presumably a mixture of *p*-aminobenzenesulfonamide hydrochloride and



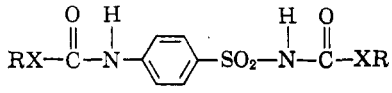
(2) O. C. Billeter, *Ber.*, **38**, 2013 (1905).
(3) L. Field, *J. Am. Chem. Soc.*, **74**, 394 (1952).
(4) H. Krzekalla (to Badische Anilin- and Soda-Fabrik Aktiengesellschaft), U. S. Patent 2,666,787 (1950).
(5) R. Appel and H. Gerber, *Ber.*, **91**, 1200 (1958).
(6) R. Appel and H. Gerber, *Angew. Chem.*, **70**, 271 (1958).

p-(chloroformamido)benzenesulfonamide (VIII); (2) elevating the temperature of the reaction mixture to 150° and maintaining this temperature while passing phosgene through the reaction mixture for 3 hr.; (3) removal of the solvent by flash distillation; and (4) distillation of the product under reduced pressure.

Low-temperature (90°) phosgenation of the reaction product of VII and phosgene in the cold (0°) gave IX in 71% yield.

III was allowed to react with amines and alcohols to give the derivatives shown in Table I.

TABLE I

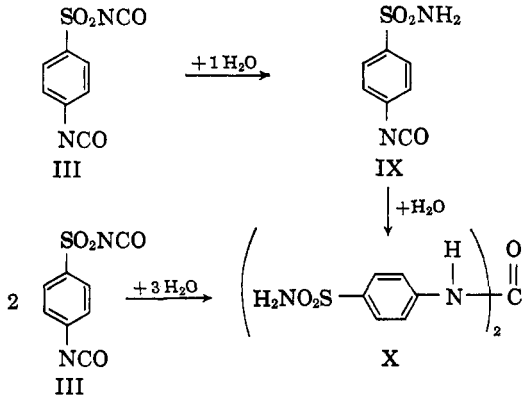


X	R	M.p., °C.[a]	Yield, %
>NH	CH_2=$CHCH_2$–	203–204	60
>NH	C_4H_9–	192–193.5	85
–O–	CH_3–	203–205	38
–O–	CH_2=$CHCH_2$–	158–159	96

[a] Temperatures are uncorrected.

Sulfonyl isocyanates have been reported to be much more reactive with common protic reagents than are aryl and alkyl isocyanates. This difference is shown by the products obtained from the reaction of water with III, which contains both the aryl and sulfonyl isocyanate group.

The reaction of equimoles of III and water gave a white, crystalline solid which was identical with IX. Further reaction of IX with water gave 4,4′-ureylenebis(benzenesulfonamide) (X), identical with the compound prepared by the reaction of 2 moles of III with 3 moles of water.



Synthesis of Organodisulfonyl Isocyanates.—Organodisulfonyl isocyanates were prepared by the direct phosgenation of organodisulfonamides. IV and V were prepared in 57 and 62% yields, respectively, by the phosgenation of the corresponding disulfonamides in nitrobenzene at 170–180°. At temperatures less than 150°, no appreciable reaction was noted after several hours of phosgenating.

To prepare VI it was necessary to utilize a temperature of 250° and a chlorinated phenyl ether (Arochlor 1260) as solvent for the phosgenation. This was presumably due to the insolubility of the aromatic disulfonamide at the lower temperatures. VI was precipitated from the solvent in 54% yield and subsequently refined by sublimation.

Experimental[7]

***p*-Isocyanatobenzenesulfonyl Isocyanate (III).**—A slurry of 172 g. (1.0 mole) of *p*-aminobenzenesulfonamide in 1000 g. of nitrobenzene was added to a solution of 396 g. (4.0 moles) of phosgene in 548 g. of nitrobenzene while the kettle temperature was maintained at −10 to 0°. The temperature of the resulting mixture was raised to 157° and the mixture was sparged with phosgene for 3 hr. The resulting clear solution was treated with phosgene for an additional 2 hr., and subsequently with nitrogen to remove phosgene and by-product hydrogen chloride. The solvent was removed by flash distillation and the product was distilled to give 194 g. (86.7%) of III with a boiling point of 108–109° (0.15 mm.), and a freezing point of 42.5°. The product had infrared absorption at 4.45 (NCO), 6.25 and 6.55 (phenyl C=C), 7.40 and 8.60 (SO_2), and 11.95 μ (*para* disubstitution).

Anal. Calcd. for $C_8H_4N_2O_4S$: C, 42.80; H, 1.78; N, 12.48; S, 14.30. Found: C, 42.62; H, 1.96; N, 12.25; S, 14.25.

***p*-Isocyanatobenzenesulfonamide (IX).**—The same general procedure was used as described for the preparation of III, except the temperature was maintained at 90°. III (172 g., 1.0 mole) in nitrobenzene treated with liquid phosgene at 0° and then with gaseous phosgene at 90° for 4 hr. was purged free of phosgene with nitrogen, cooled, and filtered. The solid product was washed with ethyl ether and dried to yield 141 g. (71.2%) of IX, which on recrystallization from toluene had m.p. 156–157°. The product had infrared absorption at 2.99 (NH_2), 4.45 (NCO), and 7.50 and 8.70 μ (SO_2).

Anal. Calcd. for $C_7H_6N_2O_3S$: C, 42.4; H, 3.03; N, 14.13. Found: C, 42.22; H, 3.30; N, 14.19.

IX in methyl isobutyl ketone reacted with aniline to give the anilide, m.p. 229–230°. Infrared maxima at 5.95 (substituted urea C=O), 7.6 and 8.7 (SO_2), and 13.35 and 14.4 μ (monosubstituted aromatic) are consistent with the proposed structure.

Anal. Calcd. for $C_{13}H_{13}N_3O_3S$: N, 14.43. Found: N, 14.41.

***p*-Isocyanatobenzenesulfonamide (IX) by Reaction of Equimoles of III and Water.**—Water (1.8 g., 0.1 mole) was added to 22.4 g. (0.1 mole) of III dissolved in 250 ml. of benzene. The reaction temperature rose from 28 to 38° during the addition. When the reaction had subsided, the mixture was filtered to yield 15 g. (75.8%) of IX, which on recrystallization from toluene had m.p. 155–157°.

Anal. Calcd. for $C_7H_6N_2O_3S$: C, 42.4; H, 3.03; N, 14.13. Found: C, 42.3; H, 3.42; N, 13.98.

A mixture melting point of this material with that prepared by phosgenation was 156–157°.

4,4′-Ureylenebis(benzenesulfonamide) (X) by Reaction of III with an Excess of Water.—To an agitated solution of 22.4 g. (0.1 mole) of III in 100 ml. of acetone there was added 9.0 g. (0.5 mole) of water in 25 ml. of acetone. Stirring was continued for 30 min. at ambient temperature, after which the temperature was elevated to reflux (55°) and maintained for 2 hr. Cooling and filtration afforded X (10.0 g., 28% of theory) which on recrystallization from water had m.p. 285–286°. Infrared absorption at 3.02 and 3.1 (NH, NH_2), 5.91 (substituted urea C=O), and 7.55 and 8.7 μ (SO_2) are consistent with the proposed structure.

Anal. Calcd. for $C_{13}H_{14}N_4O_5S_2$: C, 42.15; H, 3.81; N, 15.13. Found: C, 42.26; H, 3.97; N, 15.21.

4,4′-Ureylenebis(benzenesulfonamide) (X) Prepared from IX and an Excess of Water.—IX (1.98 g., 0.01 mole) prepared by the reaction of III with equimoles of water, was stirred for 4 hr. with an excess of water in acetone. Subsequent filtration and drying under reduced pressure afforded X (1.4 g., 82% of theory) which on recrystallization had m.m.p. 284–286° with X, prepared from III and an excess of water.

N-(Methoxycarbonyl)-4-methoxyformamidobenzenesulfonamide.—To a solution of 8.25 g. (0.04 mole) of III in 80 ml. of dry acetone was added slowly 5.9 g. (0.18 mole) of methanol in 20 ml. of dry acetone. The mixture was allowed to stir at ambient temperature for 30 min. after the addition, the temperature was elevated to 40°, and heating was continued for 2 hr. Subsequent filtration and recrystallization from water gave the product (4.1 g., 38% of theory), m.p. 203–205°. Infrared absorption at 2.95 (NH), 3.3 (aromatic CH), 3.35 (CH_3), 5.78 (carbamate C=O), 6.47 (carbamate NH), 6.65 (aromatic C=C), 7.37 and 8.55 (SO_2), and 8.1 μ (carbamate C—O) are consistent with the structure.

(7) All temperatures are uncorrected.

Anal. Calcd. for $C_{10}H_{12}N_2O_6S$: C, 41.7; H, 4.17; N, 9.73. Found: C, 41.99; H, 4.22; N, 9.48.

N-(Allylcarbamoyl)-4-allylureylenebenzenesulfonamide.—In a manner similar to that employed in the synthesis of the allyl alcohol derivative, 97 g. (1.7 moles) of allylamine in benzene was treated with 168 g. (0.75 mole) of III in benzene. The product obtained in 60% yield was recrystallized from ethanol, m.p. 203–204°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4S$: C, 49.75; H, 5.36; N, 16.56. Found: C, 49.79; H, 5.67; N, 16.15.

N-(*n*-Butylcarbamoyl)-4-(*n*-butylureylene)benzenesulfonamide.—In a manner similar to that employed in the synthesis of the allyl alcohol derivative, 73.1 g. (1.0 mole) of *n*-butylamine in benzene was treated with 101 g. (0.45 mole) of III. The product, obtained in 85% yield, melted at 192–193.5°.

Anal. Calcd. for $C_{16}H_{26}N_4O_4S$: C, 51.90; H, 7.70; N, 15.10. Found: C, 52.0; H, 7.50; N, 14.80.

1,4-Butanedisulfonyl Isocyanate (IV).—Phosgene was sparged through a nitrobenzene (279 g.) solution of 31 g. (0.15 mole) of 1,4-butanedisulfonamide at a rate of 1.0 mole/hr. for 2 hr. at 100°, and then for 5 hr. at 160°. The resulting solution was sparged with nitrogen for 1 hr., filtered, and the nitrobenzene was removed under reduced pressure. The residual liquid solidified on cooling. The solid was washed with anhydrous ether and dried. The product (22.5 g., 57%) was isolated with a melting point of 60–63° and infrared maxima at 4.45 (NCO) and 7.5 and 8.60 μ (SO_2).

Anal. Calcd. for $C_6H_8N_2O_6S_2$: C, 26.9; H, 2.99; N, 10.45. Found: C, 26.66; H, 3.86; N, 10.78.

1,5-Pentanedisulfonyl Isocyanate (V).—The same general procedure was used as described for the synthesis of IV. Phosgene was sparged through a 10% nitrobenzene solution of 1,5-pentanedisulfonamide (23 g., 0.1 mole) for 5 hr. at 165°. The crude product (17 g.) was isolated in 60.2% yield which was subsequently flash distilled at 200° (0.1 mm.). Infrared absorption has the expected maxima at 4.45 (NCO) and 7.4 and 8.6 μ (SO_2).

Anal. Calcd. for $C_7H_{10}N_2O_6S_2$: C, 29.8; H, 3.55. Found: C, 29.45; H, 3.90.

1,5-Naphthalenedisulfonyl Isocyanate (VI).—A slurry of 143 g. (0.5 mole) of 1,5-naphthalenedisulfonamide in 2000 g. of Arochlor 1260 (chlorinated phenyl ether) was maintained at 250° as gaseous phosgene was added at a rate of 1.0 mole/hr. for 10 hr. The resulting solution was sparged with nitrogen for 1 hr. and then filtered. Anhydrous ether (500 ml.) was added to the filtrate and 91 g. (54%) of product was isolated which melted at 185–190°. The analytical sample was purified by sublimation at 240–260° and 0.1 mm.

Anal. Calcd. for $C_{12}H_6N_2O_6S_2$: C, 42.79; H, 1.77; N, 8.31; S, 18.36. Found: C, 42.84; H, 1.96; N, 7.92; S, 18.56.

Syntheses and Reactions of Some Hindered Organophosphorus Compounds[1]

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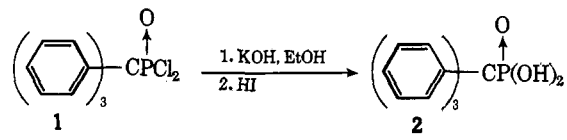
Received July 8, 1964

There has been little discussion in the literature of the effect of steric hindrance on the reactions of organophosphorus compounds. Triphenylmethylphosphonyl dichloride (1) can be hydrolyzed to the corresponding phosphonic acid 2 only with difficulty.[3-6] This is probably due to the steric shielding of the phosphorus atom by the three phenyl groups. Application of the synthetic procedure by which phenylphosphorus dichloride was obtained from benzene[7] (namely by the use of phosphorus trichloride and aluminum chloride with the aromatic hydrocarbon) to mesitylene, durene, and pentamethylbenzene primarily produced the corresponding diarylphosphinic chlorides.[8] Hydrolysis of these hindered phosphinic chlorides resulted in the formation of some surprisingly stable secondary diarylphosphine oxides which could not be oxidized to phosphinic acids by the normal procedure using alkaline hydrogen peroxide.[8] Resistance to oxidation by alkaline ferricyanide seemed to increase with increasing methyl substitution on the ring. These observed phenomena would appear to be due largely to steric effects.



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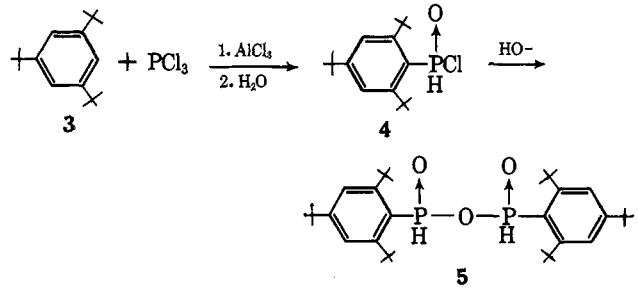
Resistance to both hydrolysis and oxidation by organophosphorus chlorides which possess a substantial amount of steric hindrance, as illustrated by the examples mentioned above, has been found to an even greater extent in a more radically hindered organophosphorus chloride, namely 2,4,6-tri-*t*-butylphenylphosphinic chloride (**4**). This compound was readily synthesized in a 71% yield by treating 1,3,5-tri-*t*-butylbenzene[9] (**3**) with phosphorus trichloride and anhydrous aluminum chloride followed by hydrolysis.



3 4 5

The attempts to oxidize 2,4,6-tri-*t*-butylphenylphosphinic chloride with alkaline hydrogen peroxide or chlorine were not successful as shown by complete recovery of unchanged starting material. A substitution product, 2,4,6-tri-*t*-butylphenylphosphinic anhydride (**5**), was obtained in a small yield (15%) from the attempted oxidation of compound **4** with alkaline potassium ferricyanide.

Use of potassium permanganate in refluxing alkaline solution as an oxidizing agent for compound **4** strikingly illustrated the difficulty of oxidizing the phosphorus–hydrogen bond in this compound. It did oxidize one of the *t*-butyl groups to a carboxylic acid and hydrolyze the phosphorus chloride, thereby producing 2,6-di-*t*-butyl-4-carboxylphenylphosphinic acid (**6**) in a very small yield (7%); but the phosphorus–hydrogen bond in this product remained intact. It was shown to be a dibasic acid by the two breaks in its titration curve. The infrared spectrum of **6**, when run

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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