out as described above. Tap water was circulated through an ice bath and then through the condenser during the decomposition to prevent the distillation of the solvent.

Analysis of Gaseous Decomposition Products.—After completion of a decomposition run, the gaseous product was collected in a trap at −70° and subsequently transferred to a second vacuum line in series with a gas sample valve and a gas chromatograph. Analysis of the decomposition product was made on a 20 ft. × 0.25 in. column with 20% didecyl phthalate substrate on Chromasorb-P treated with hexamethyldisilazine. Peaks were identified by comparison of retention times with standards supplied by The Matheson Company. Quantitative analysis of the decomposition products was made by measuring the area under each peak, with appropriate thermal conductivity corrections. A synthetic mixture containing known partial pressures of the isomeric butenes was prepared and used to calibrate the detector. The temperature and the flow rate were 41° and 4.7 cc./min. The retention times of 1-butene, *cis*-2-butene, and *trans*-2-butene are 3.9, 5.7, and 5.1 min., respectively, under these conditions, which provided base-line separation. The percentages of products listed in Table I are within ±1% of all runs analyzed.

Infrared spectra from 2–16 μ of the decomposition products and a synthetic mixture prepared from the pure olefins in the appropriate amounts were essentially the same. The spectra were taken on a Perkin-Elmer 237 infrared spectrophotometer in a 10-cm. path-length cell.

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Trimerization of Isocyanates by Trialkylantimony and -arsenic Oxides

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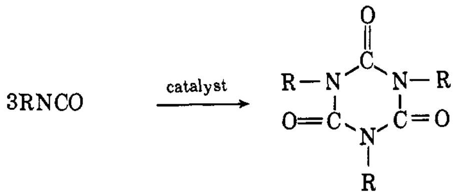
While investigating the properties of the group Va organometallics, it was noted that tri-*n*-butylantimony and triisobutylarsenic oxides, among others, were highly efficient catalysts for the trimerization of isocyanates to trialkyl and triaryl isocyanurates. With 2 mole % of either oxide, for example, *m*-chlorophenyl and phenyl isocyanates could be trimerized in bulk in 94–100% yields at room temperature over periods of time ranging from 15 min. to 1 hr.[1]



Trimers of the less reactive *o*-methoxyphenyl and ethyl isocyanates were obtained in 95 and 77% yields, respectively, by heating at 80° in the presence of tri-*n*-butylantimony oxide. The products obtained from both toluene and hexamethylene diisocyanates at room temperature were infusible, cross-linked resins with varying amounts of unreacted isocyanate. With dimethyl sulfoxide as a solvent, no unreacted isocyanate was noted in the latter. Trimers of *m*-nitrophenyl, *m*-chlorophenyl, and phenyl isocyanates were obtained in 71, 97, and 96% yields, respectively, at room temperature in heptane or benzene.

A variety of group Va oxides and esters were evaluated as trimerizing agents (Table I). Along with the oxides, tri-*n*-butylantimony diethoxide (expt. 1) and triisobutylantimony diacetate (expt. 2) were also found to be effective trimerizing agents. Noteworthy is the ability of triphenylarsenic oxide to trimerize methyl isocyanate and to catalyze both trimer (~30%) and carbodiimide formation with *m*-chlorophenyl isocyanate (expt. 3). This oxide had previously been reported to catalyze carbodiimide formation with phenyl and *sec*-octyl isocyanates.[2] The more basic trialkylantimony and -arsenic oxides, as well as isocyanates more susceptible toward nucleophilic attack, appear to enhance trimer formation.

TABLE I

ACTIVITY OF TRIMERIZING AGENTS

Expt. no.	Catalyst[a]	Results
1	$(n\text{-Bu})_3Sb(OEt)_2$	Phenyl and *m*-chlorophenyl isocyanates trim. in 1 hr. at 28°
2	$(i\text{-Bu})_3Sb(OAc)_2$	*m*-Chlorophenyl isocyanate trim. in 4 days at 28°
3	$(Ph)_3AsO$	Methyl isocyanate trim. in 15 min. at 28°; *m*-chlorophenyl isocyanate yielded trimer (~30%) and carbodiimide (~70%)
4–5	$(n\text{-Bu})_3Sb$, $(n\text{-Bu})_3SbCl_2$	No trim. of *m*-chlorophenyl isocyanate noted in 10 days at 28°

[a] 2 mole %.

Addition of a slight excess of phenyl isocyanate to tri-*n*-butylantimony oxide under anhydrous conditions yielded some triphenyl isocyanurate along with a nondistillable oil believed to be a stoichiometric complex of the oxide and isocyanate. This suggests that an "isocyanate–oxide" complex originally formed in the trimerization reacts with excess isocyanate to generate the trimer.

Experimental

Materials.—Isocyanates were purchased from either Eastman Chemical Co. or Matheson Coleman and Bell and were used as received. Hexamethylene diisocyanate was obtained from Ott Chemical Co. and was used as received. Triphenylarsenic oxide (Eastman) was recrystallized from heptane (m.p. 195–196°). Tri-*n*-butyl- and triisobutylantimony, as well as triisobutylarsenic, were prepared in this laboratory by a previously described procedure.[3] Their dichlorides were also prepared by a previously described procedure.[4]

Tri-*n*-butylantimony Oxide.—Tri-*n*-butylantimony oxide was prepared in 92% yield by the method of Dyke and Jones.[4]

Triisobutylarsenic Oxide.—This oxide was obtained in 94% yield by the caustic hydrolysis of triisobutylarsenic dichloride. After recrystallization from heptane, the product was obtained as white crystals with m.p. 158–160°.

Anal. Calcd. for $C_{12}H_{27}AsO$: C, 54.8; H, 10.6; As, 28.5. Found: C, 54.4; H, 10.0; As, 27.7.

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[1] By contrast, triphenyl isocyanurate is conventionally prepared by heating phenyl isocyanate for 25 hr. at 125° in the presence of ethanol and N-methylmorpholine: see I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

[2] J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

[3] W. Stamm and A. Breindel, *Angew. Chem.*, **76**, 99 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 66 (1964).

[4] W. J. C. Dyke and W. J. Jones, *J. Chem. Soc.* (London), 1921 (1930).

Triiosobutylantimony 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.

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%.

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

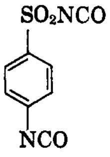
$$C_6H_5SO_2NH_2 + COCl_2 \longrightarrow C_6H_5SO_2NCO$$

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]

$$CNCl + SO_3 \longrightarrow ClSO_2NCO \xrightarrow{AgCNO} \underset{\text{I}}{OCNSO_2NCO}$$

$$4SO_3 + 2KCNO \longrightarrow K_2S_2O_7 + \underset{\text{II}}{S_2O_5(NCO)_2}$$

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.

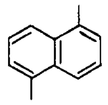

III

$$OCNO_2S-R-SO_2NCO$$

IV, R = $-(CH_2)_4-$

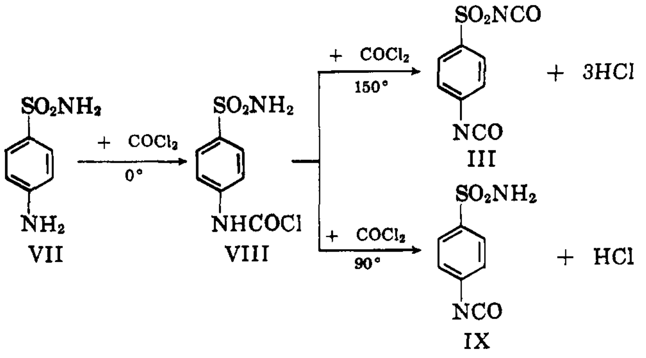
V, R = $-(CH_2)_5-$

VI, R =



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



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

[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).