mass spectrographic analysis. The first crop of Ia was obtained by filtration at room temperature, the second after addition of an ether wash to the filtrate; total crude weight after being vacuum dried, 109.5 g., (84%). Vacuum sublimation at 300–330° and 1–5 mm. gave colorless needles in asbestoslike mats, m.p. 321–324°.

A similar reaction, in which tribromoborane was added through a pressure-equalized funnel to the stirred *o*-anisidine solution, gave an 84% yield of Ia after 5 hr. of reflux time. Methyl bromide (90%) appeared in the trap only after approximately half the theoretical amount of hydrogen bromide had been collected.

ii. **From *o*-Aminophenol.**—A 4-hr. reflux period was sufficient to convert the adduct of 71 g. (0.65 mole) of *o*-aminophenol and 80 g., (0.68 mole) of trichloroborane in 1 l. of chlorobenzene to 64 g. (84%) of product Ia. The initial adduct, formed immediately and exothermally, remained dissolved; hydrogen chloride evolution was accompanied by slow product precipitation all during reflux.

iii. **From *o*-Phenetidine.**—Under conditions described in i, 147 g. (1.07 moles) of *o*-phenetidine and 129 g. (1.10 moles) of trichloroborane gave 74 g. of mixed ethyl chloride and hydrogen chloride as volatile products and, as precipitate, 15.3 g. (12.5%) of product Ia. Evaporation of the filtrate at 2–10 mm. and 100° gave (after washing with ethyl ether and drying) 120.3 g. of granular white solid, m.p. 205–210°, that liberated hydrogen chloride upon exposure to air. This solid, held 1 hr. at 310° and 5 mm., lost approximately 15% of its weight in being converted to Ia.

A second run was made, using 66.6 g. (0.485 mole) of *o*-phenetidine and 58.7 g. (0.50 mole) of trichloroborane in 1 l. of refluxing benzene. Although after 8 hr. no more ethyl chloride was evolved, the cooled reaction mixture contained only small amounts of Ia. Vacuum evaporation of the filtrate left 65 g. of tan foam, softening without definite melting at 105°, containing 3.55% hydrolyzable chlorine, and having molecular weight (ebullioscopic benzene) of 1040. A macrocycle obtainable from VI (n = 6) of linear formula $C_{42}H_{33}B_7ClN_7O_7$ would have a calculated molecular weight of 959 and a chlorine content of 3.7%. A portion of the foam, when refluxed 24 hr. in chlorobenzene, was converted to Ia, with only a minor quantity of ethyl chloride evolution.

A mixture of 137.3 g. (1.00 mole) of *o*-phenetidine and 117.2 g. (1.00 mole) of trichloroborane in a liter of chlorobenzene was stirred overnight at room temperature, then treated with 120 g. (1.12 moles) of 2,6-lutidine. The mixture was stirred at 60°, then cooled and filtered to give, as a precipitate, a mixture of lutidine hydrochloride and Ia. A considerable yield of incompletely cyclized product remained in the filtrate.

The other products, Ib to If, were obtained by refluxing chlorobenzene suspensions of the corresponding trichloroborane–aniline adduct for 8–13 hr., then working up as previously described. Compound Ic was obtained in the stated yield only by holding the solvent insoluble product at 300–350° and 0.5–5 mm. until no more sublimation occurred (about 12 hr.). The gray-green insoluble polymer, obtained from 0.95 mole of trichloroborane and 0.425 mole of bi-*o*-anisidine, contained residual chlorine indicative of only 90% cyclization.

Reaction of Trichloroborane with 3-Methoxypropylamine or 2-Methoxyethylamine.—The reaction of 137 g. (1.14 moles) of trichloroborane with 101 g. (1.14 moles) of 3-methoxypropylamine in refluxing chlorobenzene gave methyl chloride and a hard, tacky solid insoluble in the reaction medium. No chlorobenzene soluble products were found in the solvent. No sublimate formed when the solid was heated to 259° at reduced pressure. Elementary analysis indicated a B–N–Cl ratio of 1.0:0.83:1.25. A broad absorption band at 3.7–4.2 μ indicated that the product contained amine hydrochloride. Similar results were obtained with 2-methoxyethylamine.

Acknowledgment.—We wish to acknowledge our indebtedness to Dr. Philip Brumfield and Mr. James Morrison for some of the laboratory work reported here.

Carbodiimides. III. Conversion of Isocyanates to Carbodiimides. Catalyst Studies

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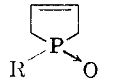
Oxides and sulfides from a number of organic compounds of Group V-B and Group VI-B elements are effective catalysts for converting organic isocyanates to carbodiimides.

Carbodiimides have been prepared from isocyanates in excellent yield under mild conditions by the catalytic action of the phosphine oxides I and II[1b]:

$$2RNCO \xrightarrow{\text{I or II}} RN{=}C{=}NR + CO_2$$



I. R = C_2H_5
II. R = C_6H_5

A mechanism study[2] indicated that the reaction proceeded through the formation of an intermediate phosphinimide III which formed carbodiimide by reaction with a second molecule of isocyanate. The initial step in the reaction is believed to be a nucleophilic attack of the oxygen atom of the polarized phosphorus–oxygen bond in the catalyst on the isocyanate carbonyl:

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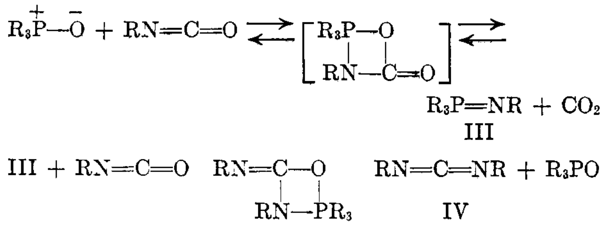
[1] (a) Present address: New Mexico State University, University Park, N. M. (b) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, in press.

[2] J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *J. Am. Chem. Soc.*, in press.



$$\overset{+}{R_3P}—\overset{-}{O} + RN=C=O \rightleftharpoons \left[\begin{matrix} R_3P—O \\ | \quad\ | \\ RN—C=O \end{matrix}\right] \rightleftharpoons \underset{\text{III}}{R_3P=NR} + CO_2$$

$$\text{III} + RN=C=O \quad \begin{matrix} RN=C—O \\ | \quad\ | \\ RN—PR_3 \end{matrix} \quad \underset{\text{IV}}{RN=C=NR} + R_3PO$$

According to this mechanism, the only requirement for catalytic activity is the polar coordinate bond between the phosphorus and oxygen atoms, so it would be predicted that other compounds with the same type of bonding should also exhibit catalytic activity. This type of bonding is found for the most part in certain compounds of Group V-B and Group VI-B elements.[3] Furthermore, catalytic activity, though modified by the influence of attached groups, should be found in all phosphorus derivatives having the appropriate bonding, regardless of the other groups attached to the phosphorus.

To test these predictions concerning the catalyst system, organic oxides of nitrogen, arsenic, antimony, and sulfur as well as other phosphine oxides and several other phosphorus derivatives of varying structures were tested as catalysts.

Experimental

Materials.—Hexamethylphosphoramide (Monsanto and Aldrich), bis(β-chloroethyl) vinylphosphonate (Monsanto and Eastman), dimethyl sulfoxide (Stepan), triphenyl phosphate (Eastman), and pyridine *N*-oxide (Reilly) were distilled before use. Triphenylphosphine oxide (Oldbury Electrochemical) was resublimed. Triethyl phosphate, bis(β-chloroethyl) β-chloroethylphosphonate, diphenyl sulfoxide, diphenyl sulfone, phenyl isocyanate, and phenyl isothiocyanate (Eastman) were used as received. 4-Nitropyridine *N*-oxide (Beacon) was used as received. Dilauryllaurylphosphonamide, triphenylphosphoramide and 2-octyl isocyanate were obtained from a laboratory supply. Diethyl phosphoramidate, triallyl phosphate, and ethylene phenylthiophosphonate were obtained from Shea Chemical.

Trimethylamine Oxide.—Trimethylamine oxide was prepared by the method of Hickinbottom.[4] The compound was dried by azeotropic distillation of water with benzene, heating at 105° and 200 mm. for several hours, sublimation at 180–200°/15 mm. and storage over phosphorus pentoxide in a vacuum desiccator for 2 weeks, m.p. 213–214° dec. (lit.[5] m.p. 208°). Elemental analysis indicated that even under these strenuous conditions not all of the water was removed.

Anal. Calcd. for C_3H_9NO: C, 47.9; H, 12.1; N, 18.6. Found: C, 47.7, 46.5; H, 12.1, 12.3, 11.9; N, 17.1, 17.6, 17.2. Calcd. for $C_3H_{11}NO_2$: C, 38.7; H, 11.9; N, 15.0.

Triethylphosphine Oxide.—Triethylphosphine was prepared by the method of Yoke.[6] The oxide was prepared by a modification of the procedure of Mann[7]:

Twenty milliliters of 15% hydrogen peroxide was added to a solution of triethylphosphine (10 g., 0.083 mole) in 100 ml. of dry acetone over a period of 0.5 hr. The solution was stirred and held below 15° during the addition. After an additional 0.5 hr. at room temperature, the acetone was removed by distillation and replaced by 100 ml. of benzene. Water was removed by azeotropic distillation and the residue was vacuum distilled to yield 6.2 g. (54%) of clear, slightly yellow product, b.p. 57–99°/25 mm.

Anal. Calcd. for $C_6H_{15}OP$: C, 53.7; H, 11.3; P, 23.0. Found: C, 51.2, 51.8, 52.2; H, 10.7, 10.6, 11.0; P, 22.5, 22.4.

Triphenylarsine Oxide.—Triphenylarsine oxide was prepared by method of Shriner[8] in 85% yield. After recrystallization from benzene, the compound melted at 200–201° (reported m.p. 189°).

Anal. Calcd. for $C_{18}H_{15}AsO$: C, 67.0; H,4.7; As, 23.3. Found: C, 66.8, 66.9; H, 4.5, 4.6; As, 22.3, 22.4.

Triphenylstibine Oxide.—Triphenylstibine oxide was prepared from triphenylstibine by the same general procedure as for the arsine derivative in 90% yield, m.p. 249–251° (lit.[9] m.p. 212°).

Anal. Calcd. for $C_{18}H_{15}SbO$: C, 58.3; H, 4.1; Sb, 32.7. Found: C, 58.4; H, 4.0; Sb, 32.8. The compound reported previously may have been the dihydroxide.

In an attempt to prepare the compound by the hydrolysis of triphenylstibine dichloride in ethanol,[10] a white solid was obtained, m.p. 226–229°, which did not give a correct analysis for either the oxide or the dihydroxide.

Anal. Calcd. for $C_{18}H_{17}SbO$: C, 55.8; H, 4.4; Sb, 31.4. Found: C, 57.1, 57.7; H, 5.4, 5.1; Sb, 26.4, 26.4. This analysis is in agreement with the formula $(C_6H_5)Sb(OC_2H_5)_2.H_2O$: Calcd. for $C_{22}H_{27}SbO_3$: C, 57.3; H, 5.4; Sb, 26.8.

Attempted Preparation of Triphenylbismuth Oxide.—Although triphenylbismuth dihydroxide was reported to be unstable,[11] an attempt was made to prepare it by the hydrogen peroxide oxidation of triphenylbismuth. In agreement with the earlier work, an exothermic reaction occurred and an infusible solid was obtained.

Tri(*m*-nitrophenyl)phosphine Oxide.—Tri(*m*-nitrophenyl)-phosphine oxide was prepared in 67% yield by the method of Michaelis,[12] m.p. 238–240° (lit.[13] m.p. 242°).

Anal. Calcd. for $C_{18}H_{12}N_3O_7P$: C, 51.9; H, 3.6; N, 10.1; P, 7.4. Found: C, 51.6; H, 2.7; N, 10.1; P, 6.7.

Tri(*m*-nitrophenyl)arsine Oxide.—Tri(*m*-nitrophenyl arsine oxide was prepared by the procedure of Michaelis[12] in 55% yield. Recrystallization from dimethylformamide gave feathery, yellow needles, m.p. 259–261° (lit.[14] m.p. 254°).

Anal. Calcd. for $C_{18}H_{12}N_3O_7As$: C, 47.3; H, 2.6; N, 9.2. Found: C, 47.2; H, 2.5; N, 9.6, 9.3.

1-Phenylarsolidine 1-Oxide.—The cyclic arsine was prepared according to a modification of the procedure of Gruttner[15]:

1-Phenylarsolidine.—A 1-l. four-necked flask was fitted with an air-driven stirrer, dropping funnel, nitrogen inlet, and condenser with a drying tube. Prepurified nitrogen was passed through the system during all operations. Magnesium (14.1 g., 0.58 g.-atom) was placed in the flask and covered with 200 ml. of anhydrous ether. A small portion of a solution of 1,4-dibromobutane (61.4 g., 0.19 mole in 300 ml. of ether) was added to the flask to start the reaction and then the remainder was added at a rate which maintained a rapid reflux. The reaction mixture was refluxed for 1.5 hr. after addition was completed. The Grignard solution was then transferred to a 500-ml. dropping

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[3] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, Vol. 1, p. 655; Vol. 2, p. 926.

[4] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans Green and Co., New York, N.Y., 1936, p. 277.

[5] J. Meisenheimer, *Ann.*, **397**, 273 (1913).

[6] J. T. Yoke, *Univ. Microfilms Pub.*, **12**, 671 (1954), (Michigan Univ.).

[7] F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948).

[8] R. L. Shriner and C. N. Wolf, *Org. Syn.*, **30**, 95 (1950).

[9] L. Kaufman, Ger. Patent 360,973; *Chem. Abstr.*, **18**, 841 (1924)

[10] G. Gruttner and M. Wiernik, *Ber.*, **48**, 1485 (1915).

[11] F. Challenger and V. Richards, *J. Chem. Soc.*, 405 (1934).

[12] A. Michaelis and A. Von Soden, *Ann.*, **229**, 324 (1885).

[13] L. Kaufman, *Ber.*, **41**, 2762 (1908).

[14] B. Philips, *ibid.*, **19**, 1031 (1886).

[15] G. Gruttner and E. Krause, *ibid.*, **49**, 1441 (1916).

funnel and attached to a 2-l. creased flask equipped with stirrer, nitrogen inlet, condenser and an additional 500-ml. addition funnel. In the latter funnel was placed a solution of phenylarsine dichloride[16] (50 g., 0.22 mole) in 500 ml. of ether. Ether (300 ml.) was added to the flask and then both solutions were added simultaneously at a rate sufficient to maintain a moderate reflux of ether (addition time 1$^1/_3$ hr.). The solution was stirred and allowed to reflux overnight. The flask was then cooled in ice water, and water (100 ml.) was added dropwise. The mixture was filtered (with some difficulty) to remove the precipitated oxides. The water layer was extracted with ether, the combined ether solutions were dried over sodium sulfate and the ether was removed by distillation. The residue was vacuum distilled through a 10 × $^1/_2$ " Vigreux column to yield a water-white liquid, b.p. 110–127°/10 mm., 8.2 g. (18%) and 16.9 g. polymeric residue (lit.[17] b.p. 125–128°/12–14 mm.).

Oxidation of 1-Phenylarsolidine.—The oxidation of the 1-phenylarsolidine by air was noted by Gruttner,[15] but the oxide was not characterized. The arsine was oxidized here essentially according to the procedure used for triethylphosphine oxide. A 125-ml. one-necked flask was equipped with magnetic stirrer, condenser, and thermometer extending into the flask through the condenser. To the flask was added 5.0 g. of the arsine dissolved in 10 ml. of acetone followed by 3.0 g. of 30% hydrogen peroxide. A vigorous reaction ensued with the temperature rising to 60°. The flask was cooled to room temperature in ice water, an additional 10 ml. of acetone was added, and the solution was stirred at room temperature for 1.5 hr. Acetone was removed under vacuum, 50 ml. of benzene was added and distilled under vacuum (water aspirator) to remove water. The white solid residue was sublimed at 200° and 1 mm. pressure overnight to give 5.2 g. (96%) of hygroscopic cream-colored solid.

Anal. Calcd. for $C_{10}H_{13}AsO$: C, 53.6; H, 5.8; As, 33.4. Found: C, 52.7, 52.5, 52.4; H, 5.7, 5.7, 5.6; As, 32.6, 32.5. Analysis indicates that the compound is the oxide possibly contaminated with the dihydroxide. Calcd. for dihydroxide: C, 49.6; H, 6.2; As, 30.9.

Procedure for Catalyst Testing.—The same procedure was used for all catalysts. A 250-ml. flask was equipped with a magnetic stirrer, condenser, and thermometer. When solid catalysts were used they were added to the reaction flask along with 25 ml. of dry benzene; traces of water were removed by azeotropic distillation. Phenyl isocyanate (50 ml., 0.45 mole) was then pipetted into the flask and the catalyst was added (from a weighed hypodermic syringe for liquids). The condenser outlet was connected to a gas bubbler containing saturated calcium hydroxide solutions to follow the evolution of carbon dioxide. The reaction mixture was then heated and stirred for the designated time. Unchanged phenyl isocyanate was removed at a low temperature under vacuum and the residue was distilled under vacuum through a 10 × $^1/_2$" Vigreux column. Diphenylcarbodiimide was identified by its infrared spectrum and elemental analysis. In general, the distillate contained small amounts of impurities, but no further attempt was made to fractionate the products.

In a comparative experiment in the absence of catalyst, no carbodiimide was obtained from phenyl isocyanate after 46.5 hr. of refluxing.[1b]

Reaction of 2-Octyl Isocyanate with Triphenylarsine Oxide.—The usual reaction procedure for catalyst testing was used. Triphenylarsine oxide (5.2 g., 0.016 mole) was dried by azeotropic distillation of water with 25 ml. of dry benzene. 2-Octyl isocyanate (0.14 mole) was added. Carbon dioxide evolution began immediately and continued slowly for 1 hr. The solution was heated slowly to 85°. At this point, carbon dioxide evolution was rapid. The reaction mixture was stirred at 85° for 4 hr. and then vacuum distilled. After removal of unchanged isocyanate, the product was obtained as a colorless oil, b.p. 107–109°/0.15–0.25 mm. The yield was 17 g. (79%).

Anal. Calcd. for $C_{17}H_{34}N_2$: C, 76.6; H, 12.8; N, 10.5. Found: C, 75.8; 75.9; H, 12.5, 12.6; N, 10.4, 10.5. An infrared spectrum confirmed the carbodiimide structure with contamination by a small amount of isocyanate.

Reaction of Phenyl Isothiocyanate with Triphenylarsine Oxide.—Triphenylarsine oxide (5.2 g., 0.016 mole) was dried as before. When phenyl isothiocyanate (56.2 g., 50 ml., 0.42 mole) was added, the temperature rose from 33° to 38° and a gas was evolved. The solution was stirred at room temperature until gas evolution ceased. The reaction mixture was then heated slowly to 110° and held at this temperature for 2 hr. Distillation of the reaction mixture gave 53.4 g. of recovered phenyl isothiocyanate, b.p. 96–26°/50–10 mm. and 1.7 g. of carbodiimide fraction, b.p. 96–142°/0.2 mm. The diphenylcarbodiimide was identified by its infrared spectrum which also indicated contamination with isothiocyanate.

Reaction of 1-Phenylarsolidine 1-Oxide with Phenyl Isocyanate.—The usual procedure for catalyst testing was used. A mixture of 54.1 g. (50 ml., 0.45 mole) of phenyl isocyanate and 0.41 g. (0.002 mole) of catalyst was heated at 99–108° for 1 hr. A white solid was formed and carbon dioxide was evolved. The reaction mixture was cooled, triturated with 100 ml. of petroleum ether (b.p. 30–60°) and filtered to obtain 28 g. of product, b.p. 160–200°. Recrystallization from ethanol–acetone raised the melting point to 294–296°.

Anal. Found: C, 75.2; H, 4.5; N, 13.4.

Results

The compounds were screened for catalytic activity by reaction with phenyl isocyanate to form diphenylcarbodiimide. Results are shown in Table I. The presence of traces of impurities, especially in the isocyanate, had a large effect on the yield and the data reported represent the best results obtained.

Table I

Group V-B and VI-B Oxides as Catalysts for Carbodiimide Formation[a]

Catalyst	Amount, moles	Temp.	Time, hr.	Yield, %
Triphenylphosphine oxide	0.004	115–120	2	5
	.004	160–162	3	27
	.004	160–162	8	56
Triphenylarsine oxide	.004	70–75	1	85
Triphenylstibine oxide	.004	115–120	2	41
Tri(*m*-nitrophenyl) phosphine oxide	.004	160–164	3	16
Tri(*m*-nitrophenyl) arsine oxide	.004	90	3	85
Triethylphosphine oxide	.006	122–125	3	64
Pyridine *N*-oxide	.027	110–123	1.5	33
Dimethyl sulfoxide	.006	162–164	2.5	13
Diphenyl sulfoxide	.004	145	7	0
Diphenyl sulfone	.004	145	5	0
Trimethylamine oxide	.004	111–126	1.5	0
1-Phenylarsolidine 1-oxide	.002	99–108	1	0
4-Nitropyridine *N*-oxide	.007	160	1.5	0

[a] Phenyl isocyanate (0.45 mole) used in each case.

In accord with the proposed mechanism, trimethylamine oxide showed no catalytic activity for carbodiimide formation but yielded instead phenyl isocyanate trimer. Triethylphosphine ox-

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[16] R. L. Barker, E. Booth, W. E. Jones, A. F. Mullidge, and A. N. Woodward, *J. Soc. Chem. Ind.*, **68**, 289 (1949).

[17] H. Landolt, *Ann.*, **89**, 301 (1854).

TABLE II

PHOSPHORUS COMPOUNDS AS CATALYSTS FOR CARBODIMIDE FORMATION[a]

Catalyst	Formula	Amount, moles	Temp.	Tine, hr.	Yield, %
Hexamethylphosphoramide	$[(CH_3)_2N]_3PO$	0.008	113–135	1.6	27
Dilauryllaurylphosphonamide	$C_{12}H_{25}P(O)(NHC_{12}H_{25})_2$	.0004	162–163	102	14.4
Triphenylphosphoramide	$(C_6H_5NH)_3PO$	.004	141–200	20	66.6
Diethyl phosphoramidate	$(C_2H_5O)_2P(O)NH_2$	.004	140–200	19	77.6
Triethyl phosphate	$(C_2H_5O)_3PO$	.004	150–175	3	32
Triallyl phosphate	$(CH_2{=}CHCH_2O)_3PO$	.004	142–164	3	4.8
Triphenyl phosphate	$(C_6H_5O)_3PO$	.04	160–190	21.5	62.8
Bis(β-chloroethyl) vinylphosphonate	$CH_2{=}CHP(O)(OCH_2CH_2Cl)_2$	.005	147–191	1	88
		.004	160–164	4	8
Bis(β-chloroethyl)β-chloroethylphosphonate	$ClCH_2CH_2P(O)(OCH_2CH_2Cl)_2$	.005	145–172	5	20
Ethylene phenylthiophosphonate	$(CH_2O)_2P(S)C_6H_5$	.004	162	16.5	20

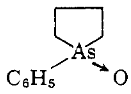
[a] Phenyl isocyanate (0.45 mole) used in each case.

ide and the triphenylphosphine, -arsine and -stibine oxides all catalyzed the formation of carbodiimide although elevated temperatures were required to obtain significant yields. In a test tube experiment, triethylarsine oxide gave an exothermic reaction with complete solidification of the reaction mixture to an unidentified white solid; this oxide was not studied further.

In the aromatic series, maximum catalytic activity was exhibited by triphenylarsine oxide. Introduction of nitro groups into the aromatic rings apparently had no effect on the activity of the aryl-phosphine or -arsine oxides.

Because of its high activity, triphenylarsine oxide was also tested with an aliphatic isocyanate and with phenyl isothiocyanate. With 2-octyl isocyanate, carbon dioxide was evolved slowly at room temperature and rapidly at 85°. After four hours at 85°, a 75% yield of essentially pure di-2-octylcarbodiimide was obtained. With phenyl isothiocyanate, gas was evolved at room temperature but after two hours at 110° only a 4% yield of a carbodiimide fraction was obtained.

In view of the much higher activity of triphenylarsine oxide compared to triphenylphosphine oxide, it was expected that the cyclic arsine oxide analog of Catalyst II, 1-phenylarsolidine 1-oxide V would exhibit more powerful catalytic activity than I or II.



The compound was readily prepared but difficult to dry completely. Quite surprisingly, no carbodiimide was obtained in the reaction with phenyl isocyanate. At elevated temperatures (100°), carbon dioxide was evolved at a moderate rate but in all trials an unidentified solid product was obtained.

A fair yield of diphenylcarbodiimide was obtained using pyridine *N*-oxide as catalyst. No catalytic activity was shown by 4-nitropyridine *N*-oxide.

In the sulfur series, diphenyl sulfoxide and diphenyl sulfone were inactive. Dimethyl sulfoxide gave a low yield of diphenylcarbodiimide as well as a large amount of unidentified white solid.

Attention was next directed to other phosphorus derivatives containing the coordinate bond to oxygen. Results are shown in Table II. Although catalytic activity was observed in each case, the catalysts were all considerably less active than the cyclic phosphine oxides and in most cases less active than triethylphosphine and triphenylphosphine oxides. Variations in yields were also observed with these catalysts and the results shown were again the best obtained. With the less active catalysts best yields were obtained by allowing the temperature to rise to the boiling point of the solution as carbodiimide was formed.

Discussion

The catalytic activity of the organic oxides of phosphorus, arsenic, and antimony and of the various phosphorus derivatives furnishes additional support for the proposed mechanism.[2] Although the required imides of triphenylarsine and triphenylstibine have not been reported, the unsubstituted imide of triphenylarsine is known,[18] and a stibine–methylene derivative has been reported.[19]

The maximum in catalytic activity observed with triphenylarsine oxide should result from a combination of factors. First, the highest nucleophilic activity would be expected from the compound having the greatest negative charge on oxygen. This variation in activity would be expected to parallel the dipole moments with the highest dipole moment being exhibited by the compound having the greatest contribution from the form $R_3\overset{+}{M}—\overset{-}{O}$.[20] By this reasoning, comparison of the dipole moments of triphenyl-arsine oxide (5.50 D.) and triphenylphosphine oxide (4.31 D.)[21] shows that the former should be more active, in agreement with present findings. No dipole moment for triphenyl-

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[18] R. Appel and D. Wagner, *Angew. Chem.*, **72**, 209 (1960).

[19] M. C. Henry and G. Wittig, *J. Am. Chem. Soc.*, **82**, 563 (1960).

[20] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell Univ. Press, Ithaca, N. Y., 1948, p. 74.

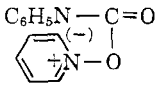
[21] K. A. Jensen, *Z. Anorg. Chem.*, **250**, 268 (1943).

stibine oxide could be found, although it should be close to that of the tri-(*p*-tolyl)stibine oxide (2.0 D.). The activity of triphenylarsine oxide in the conversion of 2-octyl isocyanate to carbodiimide as compared to the reduced activity of the cyclic phosphine oxides in this reaction may be due in part to this factor.

The second effect which should be of importance in the relative activity of the aryl derivatives is that of steric hindrance of the groups attached to the metalloid atom to the formation of the planar four-membered ring transition state proposed for the reaction.[2] On this basis, the compounds with the larger atoms should show higher activity. Kinetic studies are planned to sort out the determining factors.

From the standpoint of the mechanism, the order of catalytic activity of the various phosphorus derivatives tested should vary in the order: phosphine oxide > phosphinate > phosphonate > phosphate, this being the order of nucleophilicity (and polarity) of the phosphoryl groups in question.[22] The reactivities of the compounds tested are in qualitative agreement with this order, phosphine oxides being most active and phosphates least active. Further work is in progress to set up a quantitative order of reactivity.

According to the proposed mechanism, neither trimethylamine oxide nor pyridine *N*-oxide should be a catalyst for the reaction since formation of the transition state would require pentacovalent nitrogen. Since isocyanate will go to carbodiimide under certain conditions without catalyst,[1] there may be a bimolecular process possible involving two molecules of isocyanate in the product-forming step. It may be that the catalytic effect of pyridine *N*-oxide comes from the simple polarization of the —N=C=O by dipole–dipole interaction, or *via* an intermediate such as



which reacts as such with another molecule of isocyanate with simultaneous elimination of carbon dioxide and regeneration of catalyst.

The behavior of triethylarsine oxide and the cyclic arsine oxide III was also surprising. Their behavior may be a result of the strongly basic character of the aliphatic arsine oxides. The relative base strengths as shown by formation of the dihydroxides of some of the aliphatic derivatives of interest, are shown in Table III.[23] The "normal" behavior of triethylphosphine oxide would be expected since it has little tendency to form the dihydroxide.

TABLE III

RELATIVE BASE STRENGTHS

$$R_3AO + H_2O \longrightarrow R_3A\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$$

Compound	Log p*K* Association[a]
Me_3PO	0
Et_3PO	0
Me_2SO	0
Et_2SO	0
Et_3AsO	3.71
Me_3AsO	3.75
Me_3NO	4.65
Et_3NO	5.13
Me_3SbO	5.36

[a] Compounds with high pK_a form stable hydroxides.

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[22] H. J. Harwood and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **82**, 423 (1960).

[23] (a) P. Nylen, *Z. Anorg. Allgem. Chem.*, **246**, 227 (1941); *Chem. Abstr.*, **36**, 1295 (1942). (b) P. Nylen, *Tids. Kjemi Bergvesen*, **18**, 48 (1938); *Chem. Abstr.*, **32**, 8888 (1938).