To facilitate identification, the product was hydrogenated in methanol solvent over Raney nickel. Approximately one third of the mixture was lost by accidental spillage. After the methanol was removed, there was no intermediate fraction to the 1-octanol fraction (ruling out a possibility for 2-ethyloctanol which would have formed by the initial 1,2-addition of dimethoxy-2-butene to methoxybutadiene). There was 25 g. of 1-octanol which distilled at 87.5–89° (10 mm.); n^{20}D 1.4308; α-naphthylurethane, m.p. 64–65°.[13,14] After the octanol was removed, there was a trace of a mid-fraction followed by 10 g. of the previously identified 5-methoxy-1-octanol; b.p. 103–106° (10 mm.); n^{20}D 1.4380.

Anal. Calcd. for $C_9H_{20}O_2$: Equiv. wt. 160.2. Found: Equiv. wt. 159.8 (phthalation).

Reaction of 1,1-dimethoxy-2-butene and 1-methoxy-1,3-butadiene. To 10 ml. of diethyl ether and 0.24 ml. of concd. sulfuric acid there was added, with stirring and cooling (at 40°), a mixture of 348 g. (3 moles) of 1,1-dimethoxy-2-butene and 84 g. (1 mole) of 1-methoxy-1,3-butadiene over a period of 6 min. After an additional 4 min., the acid was neutralized with sodium hydroxide and the mixture distilled to recover 112 g. (56%) of 1,1,5-trimethoxy-2,6-octadiene which distilled at 72–83° (1–1.5 mm.). The infrared spectrum of this material was identical to that recorded for the 1,1,5-trimethoxy-2,6-octadiene isolated from the reaction of methanol and 1-methoxy-1,3-butadiene.

SOUTH CHARLESTON, W. VA.

(13) Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953, lists for 1-octanol; b.p. 90.2° (11.8 mm.) $n^{20.5}$D 1.43035.

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, 1956, p. 281, lists for 1-octanol α-naphthylurethane, m.p. 66°.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Phosphine as a Reducing Agent

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Phosphine readily reduces aromatic nitro and sulfonyl chloride groups in basic media. The reduction of the nitro compounds has been carried out under a standard set of conditions and the corresponding azoxy derivatives obtained in 80–95% yields. The products produced from sulfonyl chlorides vary markedly with the conditions employed. These products include mercaptans, disulfides and trithiophosphate esters. Some related reactions of secondary phosphines and arylsulfonyl chlorides are also reported.

One of the significant chemical properties of phosphine is the ease with which it reacts with inorganic oxidizing agents such as halogens, metal ions and oxygen.[1,2] However, little attention has been given to the reduction of organic compounds by phosphine. The only directly relevant literature which has been found describes the reduction by phosphine of *N*-chloro-*p*-toluenesulfonamide to *p*-toluenesulfonamide,[3] and α-naphthol to naphthalene.[4] In addition, Weyl has speculated that nascent phosphine is the active reducing agent in the conversion of nitrobenzene to aniline by red phosphorus and water.[5]

In considering areas in organic chemistry where phosphine might act as a reducing agent, our attention was drawn to oxygenated functionalities of nitrogen and sulfur by certain reports of the reducing action of other trivalent phosphorus species.[6] Exploratory experiments showed that under proper conditions some functional groups of this type were indeed reduced readily. This paper describes our findings in reducing aromatic nitro compounds and arylsulfonyl chlorides with phosphine, and some related reactions of secondary phosphines.

RESULTS AND DISCUSSION

Reduction of aromatic nitro compounds. Phosphine and nitrobenzene did not react at room temperature in a neutral solution or in solutions containing small amounts of ferric or cupric ions. However, in the presence of potassium hydroxide a reaction occurred readily and azoxybenzene was formed in high yield. Examination of other nitro compounds showed that the reaction was general; good yields of azoxy compounds were obtained in all cases. Further reduction products were not detected. The results are presented in Table I.

The general method of carrying out this reaction consisted of passing phosphine into a nearly saturated solution of the nitro compound in aqueous ethanol containing four molar equivalents of potassium hydroxide. The azoxy derivatives usually

(1) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., New York, 1928, Vol. VIII, p. 810.

(2) N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford University Press, London, 1950, p. 729.

(3) J. R. Bendall, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 157 (1942).

(4) H. Wichelhaus, *Ber.*, **38**, 1725 (1905).

(5) T. Weyl, *Ber.*, **39**, 4340 (1906); **40**, 970, 3608 (1907).

(6) A. H. Kohlase, *J. Am. Chem. Soc.*, **54**, 2441 (1932). W. H. Hunter and B. E. Sorenson, *J. Am. Chem. Soc.*, **54**, 3368 (1932). E. E. Gilbert and C. J. McGough, U.S. Patent **2,690,450** (1954). F. W. Hoffmann, T. R. Moore, and B. Kagan, *J. Am. Chem. Soc.*, **78**, 6413 (1956). A. C. Poshkus and J. E. Herweh, *J. Am. Chem. Soc.*, **79**, 4245 (1957). F. Ramirez and A. Aguiar, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958, p. 42. N. E. Howard, Jr., and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959).

TABLE I

$$2\ RNO_2 \xrightarrow{PH_3} RN(O)=NR$$

R	% Yield, RN(O)=NR	Melting Point, Found	Melting Point, Reported[a]
C_6H_5	96	35–36	36[b]
o-$CH_3C_6H_4$	80	57–58	59[c]
m-$CH_3C_6H_4$	85	35–36	38–39[c]
p-$CH_3C_6H_4$	85	67–68	70[c]
m-ClC_6H_4	79	98–99	96[c]
p-ClC_6H_4	88	153–154	157[d]

[a] The identity of each azoxy compounds was further confirmed by either mixture melting point or microanalysis. [b] H. E. Bigelow and A. Palmer, *Org. Syntheses*, **11**, 16 (1931). [c] L. Zechmeister and P. Rom, *Ann.*, **468**, 117 (1929). [d] J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 2929 (1928).

TABLE II

EFFECT OF VARYING THE AMOUNT OF ALKALI ON THE YIELD OF AZOXY PRODUCT

R	Mole Ratio KOH/RNO_2	% Yield, RN(O)=NR
o-$CH_3C_6H_4$	4	80
o-$CH_3C_6H_4$	2	39
p-ClC_6H_4	4	88
p-ClC_6H_4	2	89
p-ClC_6H_4	1	76

precipitated during the course of the reaction. Large amounts of alkali were not essential in all cases as indicated in Table II.

The fate of the phosphine was investigated in the case of the reduction of nitrobenzene. After acidification, the products were found to be hypophosphorous acid (82%) and phosphorous acid (18%) by iodimetric titrations. No phosphoric acid was formed. An independent total phosphorus determination gave results in excellent agreement with these findings. However, the amount of these phosphorus acids produced during the reaction with nitrobenzene was 20% greater than that required by the following stoichiometry:

$$4\ RNO_2 + 3\ PH_3 \longrightarrow 2\ RN(O)=NR + 3\ H_3PO_2$$

$$2\ RNO_2 + PH_3 \longrightarrow RN(O)=NR + H_3PO_3$$

The most obvious explanation for this is that some phosphorus intermediate is oxidized independently by the alkali. Although it was found that phosphine was not attacked by alkali under the reduction conditions in the absence of nitrobenzene, a reaction of this type has been reported with sodium hypophosphite under more vigorous conditions.[7]

$$NaH_2PO_2 + NaOH \longrightarrow Na_2HPO_3 + H_2$$

This type of oxidation should occur more readily with the probable intermediate phosphine oxide,[8] H_3PO, and thus account for the excess phosphine consumed in our experiment.

Some reactions were attempted with nitrobenzene in an autoclave at higher temperatures under neutral conditions. No reaction occurred upon heating a mixture of phosphine, water, and nitrobenzene at 100° for 27 hr. This experiment duplicated the conditions described by Weyl in which nitrobenzene was reduced to aniline,[5] except that the equivalent amount of phosphine was substituted for red phosphorus. Thus, the claim that phosphine is the actual reducing agent seems to be incorrect. In an experiment conducted at 250° the pressure in the autoclave rose and the gas present after reaction was nearly pure hydrogen. It is known that phosphine will reduce water at this temperature to give hydrogen and phosphoric acid.[9] Extensive decomposition of the organic material had occurred and no products could be isolated.

Reduction of aromatic sulfonyl chlorides by phosphine. As in the case of nitrobenzene, no reaction of p-toluenesulfonyl chloride was observed in the absence of a base. In a hydrocarbon solvent containing a molar equivalent of pyridine a slow reaction did occur. Much faster reactions were observed when pyridine was used as solvent and all subsequent experiments were carried out in this medium.

The products produced by the reduction of sulfonyl chlorides with phosphine varied with the conditions employed. A moderate temperature and addition of phosphine in several portions (method A) gave mainly the corresponding disulfides. When an initial excess of phosphine was added in a pressure reactor (method B), vigorously exothermic reactions took place preceded by induction periods characteristic and reproducible for each sulfonyl chloride. Fair yields of the corresponding thiophenols were obtained from these reactions. A third, intermediate set of conditions (method C) consisted of adding a substantial amount of the required phosphine initially to the pressure reactor with the balance added in two or three portions. Surprisingly, these conditions resulted in the formation of triaryl trithiophosphates in addition to thiophenols. In no case was a product detected which would correspond to the phosphorus analog of a sulfonamide, RSO_2PH_2. The facile oxidation-reduction reactions reported here suggest that it

(7) V. B. Blaser and K. H. Worms, *Z. Anorg. u. allgem. Chem.*, **300**, 229 (1959).

(8) E. Wiberg and G. Müller-Schiedmayer, *Z. Anorg. u. allgem. Chem.*, **308**, 352 (1961).

(9) I. N. Bushmakin and A. V. Frost, *Zhur. Priklad. Khim.*, **6**, (4), 607 (1933).

TABLE III

Reduction of Arylsulfonyl Chlorides by Phosphine

RSO_2Cl, R =	Products	% Yield	Method
C_6H_5	$(C_6H_5S—)_2$	40	A
	C_6H_5SH	13	
p-$CH_3C_6H_4$	$(p$-$CH_3C_6H_4S—)_2$	37	A
C_6H_5	C_6H_5SH	16	C
	$(C_6H_5S)_3PO$	26	
p-$CH_3C_6H_4$	p-$CH_3C_6H_4SH$	40	C
	$(p$-$CH_3C_6H_4S)_3PO$	9	
C_6H_5	C_6H_5SH	68	B
p-$CH_3C_6H_4$	p-$CH_3C_6H_4SH$	56	B
p-BrC_6H_4	p-BrC_6H_4SH	60	B
p-$NO_2C_6H_4$	p-$NO_2C_6H_4SH$	48	B
	$(p$-$NO_2C_6H_4S—)_2$	15	

will be difficult if not impossible to prepare a substance of this type. A summary of the results obtained in these reactions is given in Table III.

The oxidation products of phosphine were investigated in the reaction with benzenesulfonyl chloride (Method B). These consisted of hypophosphorous acid (11%) orthophosphorous acid (47%), and phosphoric acid (42%).

Reduction of aromatic sulfonyl chlorides by secondary phosphines. The reactions of two secondary phosphines with arylsulfonyl chlorides were investigated and proved to be similar to those observed with phosphine itself. Again, no reaction took place readily in the absence of a base, and the products obtained were dependent on reaction conditions. *S*-Arylphosphinothioates, $(CNCH_2CH_2)_2P(O)SR$, were formed with bis(2-cyanoethyl)-phosphine under suitable conditions but this type of product was not detected with di-*n*-butylphosphine. The results of these experiments are recorded in Table IV.

TABLE IV

Reactions of Secondary Phosphines with Arylsulfonyl Chlorides

R_2PH, R =	RSO_2Cl, R =	Products	% Yield
n-C_4H_9[a]	p-$CH_3C_6H_4$	p-$CH_3C_6H_4SH$	35
		$(n$-$C_4H_9)_2P(O)OH$	43
n-C_4H_9[b]	p-$CH_3C_6H_4$	$(p$-$CH_3C_6H_4S—)_2$	42
		p-$CH_3C_6H_4SH$	10
		$(n$-$C_4H_9)_2P(O)OH$	57
$CNCH_2CH_2$[a]	p-$CH_3C_6H_4$	$(p$-$CH_3C_6H_4S—)_2$	92
$CNCH_2CH_2$[b]	p-$CH_3C_6H_4$	$(CNCH_2CH_2)_2P(O)$-$SC_6H_4CH_3$—p	36
$CNCH_2CH_2$[b]	C_6H_5	$(CNCH_2CH_2)_2P(O)$-SC_6H_5	31

[a] Pyridine used as solvent. [b] Dioxane used as solvent with a molar equivalent of pyridine.

EXPERIMENTAL[10]

General method for the reduction of nitro compounds with phosphine. The apparatus consisted of a 3-necked Morton flask fitted with a gas inlet tube, a sealed stirrer, a thermometer, and a gas outlet connected to a water trap. The flask was charged with the appropriate solution and the system purged thoroughly with prepurified nitrogen. The phosphine was then passed in from a cylinder[11] through the gas inlet which was immersed below the level of the liquid. The solution was stirred and the phosphine stream was adjusted so that little escaped through the water trap. A moderate (10–20°) rise in temperature was noted and the solution became progressively darker. When the reaction was completed (1.5–3 hr.) the system was again purged with nitrogen and the mixture worked up. Details are presented below for the reduction of nitrobenzene. In the other cases indicated in Table I the work up procedure consisted of filtering the solid products from the mixture, washing with aqueous ethanol, and drying.

Reduction of nitrobenzene. A solution of 36.9 g. (0.3 mole) of nitrobenzene, 60 g. (1.5 moles) of sodium hydroxide, and 450 ml. of 85% aqueous ethanol was prepared and treated as described above for 3 hr. The resulting solution was evaporated and the residue taken up in water and ether. The layers were separated and the ether was dried with sodium sulfate and evaporated to give 28.5 g. (96%) of azoxybenzene, m.p. 35–36°.

The aqueous layer was diluted to 500 ml. and aliquots were analyzed for hypophosphorous and orthophosphorous acids by the method of Jones and Swift.[13] The absence of phosphoric acid was established using molybdate reagent.

Anal. Found: H_3PO_2, 0.203, 0.203 mole. H_3PO_3, 0.0437, 0.0440 mole. Total P found from these results: 15.3 mg./ml. Total P found by oxidation followed by precipitation with molybdate reagent: 15.23, 15.16 mg./ml.

High pressure experiments with nitrobenzene. Into a stainless steel autoclave was placed 25.0 g. (0.20 mole) of nitrobenzene, 100 ml. of water, and 29 g. (0.85 mole) of phosphine. The autoclave was heated to 100° and rocked for 27 hr. No significant pressure drop was observed. Examination of the resulting organic material indicated that it was unchanged nitrobenzene.

In a higher temperature experiment, a mixture of 25 g. (0.20 mole) of nitrobenzene, 100 ml. of water, and 14 g. (0.41 mole) of phosphine was placed in the autoclave and heated to 250° for 6 hr. The pressure at 0° was 250 p.s.i. and 1 hr. later at 250° was 1,000 p.s.i. At the end of six hours the pressure reached 2800 p.s.i. at 250°. A gas sample was examined by mass spectrographic analysis, which indicated that its composition was 99.8 mole % hydrogen and 0.2 mole % phosphine. The condensed phases consisted of a dark aqueous layer and an intractable black tar.

General procedure for reaction of phosphine with arylsulfonyl chlorides. These reactions were carried out using a standard Parr pressure reaction apparatus. A solution of the sulfonyl chloride in anhydrous pyridine was placed in the bottle which was attached to the phosphine reservoir of the Parr apparatus. After several preliminary evacuations and nitrogen purges, the flow of phosphine from the reservoir into the Parr bottle was controlled as desired. In removing the bottle from the apparatus, the evacuation and nitrogen purges were repeated.

Reduction of p-toluenesulfonyl chloride. Method A. A solution of 38.1 g. (0.2 mole) of *p*-toluenesulfonyl chloride in 70 ml. of pyridine was treated with 0.01 mole portions of phosphine every 30 min. until no more was taken up (4.5 hr.). The temperature was kept between 15–20°. The mixture was cooled to 0° and filtered to remove pyridine hydrochloride and the filtrate evaporated at reduced pressure. The residue was extracted with ether and the ether soluble solid was recrystallized from ethanol to give 9.0 g. of di-*p*-tolyl

(10) Melting points are uncorrected. Microanalyses were carried out under the supervision of Dr. J. Kuck.

(11) A phosphine generator[12] would probably do as well.

(12) W. A. Reeves, F. F. Flynn, and J. D. Guthrie, *J. Am. Chem. Soc.*, **77**, 3923 (1955).

(13) R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953)

TABLE V

REDUCTION OF ARYLSULFONYL CHLORIDES BY METHOD B

RSO_2Cl, R =	Grams	Moles	Pyridine, Ml.	Charge of Phosphine, Moles	Induction, Period, Min.	Temp.	Products	M.P.	Wt., G.
p-$CH_3C_6H_4$	30.0	0.16	200	0.13	11	23–106	p-$CH_3C_6H_4SH$	40–43	10.8
p-BrC_6H_4	35.0	0.14	225	0.13	3.5	23–105	p-BrC_6H_4SH	73–74	15.4
p-$NO_2C_6H_4$	30.0	0.13	195	0.12	1.5	23–130	$(p\text{-}NO_2C_6H_4S—)_2$	176–179	3.0
							p-$NO_2C_6H_4SH$	74–76	10.0
C_6H_5	35.2	0.20	240	0.15	13	23–145	C_6H_5SH	165–170[a]	15.0

[a] Boiling point.

disulfide, m.p. 46–47°, undepressed upon admixture with an authentic sample.

Reduction of benzenesulfonyl chloride. Method A. A solution of 35.2 g. (0.2 mole) of benzenesulfonyl chloride in 125 ml. of pyridine was treated with phosphine as described above. After evaporating the pyridine, the residual liquid was acidified with concentrated hydrochloric acid and extracted with ether. The ether solution was evaporated and the residue distilled to give thiophenol, 2.0 g., b.p. 26–27°/2.5 mm. and diphenyl disulfide, 6.0 g., b.p. 147°/2.0 mm., m.p. 59–61°. These materials were identified by infrared spectroscopy using authentic standards.

Reduction of p-toluenesulfonyl chloride. Method C. To a solution of 38.1 g. (0.2 mole) of p-toluenesulfonyl chloride in 130 ml. of pyridine was added 0.03 mole of phosphine. Additional phosphine was added at intervals so as to maintain a temperature of about 80°. The reaction was completed in 45 min. The mixture was filtered and the filtrate evaporated under reduced pressure. The residue was extracted with ether and the ether soluble material recrystallized from isopropyl alcohol to give 3.0 g. of *S,S,S*-tri-p-tolyl trithiophosphate, m.p. 138–140°. Identification was accomplished using an authentic specimen prepared by a standard procedure,[14] m.p. 138–140°.

Anal. Calcd. for $C_{21}H_{21}OPS_3$: C, 60.54; H, 5.08; P, 7.43. Found: C, 60.39; H, 5.13; P, 7.32.

The ether insoluble material was made alkaline, dried *in vacuo*, and acidified with aqueous hydrochloric acid. The resulting solution was extracted with ether and the ether soluble material recrystallized from water-methanol to give 10.0 g. of p-thiocresol, m.p. 42–43°. A mixed melting point showed no depression.

Reduction of benzenesulfonyl chloride. Method C. A solution of 35.2 g. (0.2 mole) of benzenesulfonyl chloride in 250 ml. of pyridine was treated with phosphine as described above. Obtained was 3.6 g. of thiophenol, b.p. 70°/25 mm. and 6.5 g. of *S,S,S*-triphenyl trithiophosphate, m.p. 114–115°, after recrystallization from cyclohexane. The identity of the latter was established by comparison with a sample prepared by the method of Michaelis and Linke.[14]

Reduction of arylsulfonyl chlorides. Method B. In this method of reduction an excess of phosphine was added in one portion to the solution of sulfonyl chloride in pyridine. After an "induction period" during which a temperature rise of only 5–20° was noted, the temperature rose suddenly by 60–100° in the course of 1 min. or less. The reaction was complete a few minutes later. The solution was filtered and aqueous sodium hydroxide added to the filtrate. The pyridine and water were then evaporated and the residue washed with ether and acidified with hydrochloric acid. The resulting mixture was extracted with ether and, after evaporating the solvent, the residue was recrystallized or distilled. Details are presented in Table V for the individual cases. In the case of benzenesulfonyl chloride reduction, the aqueous acid layer was analyzed for hyphosphorous and orthophosphorous acids and separately for phosphoric acid.

Anal. Found: H_3PO_2, 0.0127 mole; H_3PO_3, 0.0535 mole; H_3PO_4, 0.0477 mole.

Reaction of p-toluenesulfonyl chloride with di-n-butylphosphine. (a) Into a 3-necked flask fitted with an addition funnel, thermometer, condenser, and sealed stirrer was placed 14.1 g. (0.1 mole) of p-toluenesulfonyl chloride dissolved in 25 ml. of anhydrous pyridine. The apparatus was swept with nitrogen and 21.9 g. (0.15 mole) of di-*n*-butylphosphine was added at a rate such that a temperature of 90° was maintained without external heating or cooling (1 hr.). After heating on the steam bath for 1 additional hr., the solution was poured onto a mixture of 100 g. of ice and 30 ml. of concentrated hydrochloric acid. The mixture was extracted with ether a number of times and the extracts were combined, dried with sodium sulfate, and then evaporated. The residue was distilled to give two fractions, b.p. 80°/0.5 mm. (6.9 g.) and 180–220°/0.5 mm. (15.2 g.), respectively. The first furnished 4.4 g. of p-thiocresol, m.p. 40–41°, upon recrystallization from ethanol. The second gave 11.6 g. of di-*n*-butylphosphinic acid, m.p. 64–66°, after recrystallization from hexane.

(b) In the same apparatus, 14.6 g. (0.1 mole) of the phosphine was added to a solution of 19.1 g. (0.1 mole) of p-toluenesulfonyl chloride, 25 ml. of dioxane, and 7.9 g. (0.1 mole) of pyridine. The temperature was kept at 0–10° during the 1-hr. addition period. The mixture was warmed to room temperature, allowed to stand for 5 hr., and then poured onto a mixture of ice and hydrochloric acid. The products were isolated using ether and then separated into two fractions by distillation, b.p. 75–100°/0.5 mm. and 170–198°/0.5 mm. The first fraction furnished 1.2 g. of p-thiocresol, m.p. 40–41°, upon recrystallization from ethanol. The second was separated into acidic and neutral fractions by extraction with alkali. The neutral fraction gave 5.0 g. of p-tolyl disulfide, m.p. 44–46° and the alkaline extracts deposited 10.2 g. of di-*n*-butylphosphinic acid, m.p. 67–68°, upon acidification.

Reaction of p-toluenesulfonyl chloride with bis(2-cyanoethyl)phosphine. (a) Using the apparatus described above, 14.0 g. (0.1 mole) of bis(2-cyanoethyl)phosphine[15] was added to a solution of 19.0 g. (0.1 mole) of p-toluenesulfonyl chloride in 25 ml. of pyridine. The temperature was maintained at 70° during the addition and the mixture was then heated for 1 hr. on the steam bath. The resulting solution was poured on a mixture of ice and hydrochloric acid and the precipitated solid was recrystallized from isopropyl alcohol to furnish 11.4 g. of di-p-tolyl disulfide, m.p. 44–46°.

(b) This experiment was repeated using a mixture of 25 ml. of dioxane and 7.9 g. (0.1 mole) of pyridine as solvent. Upon adding the resulting solution to ice and hydrochloric acid, 22 g. of a white solid was precipitated which upon repeated recrystallization from isopropyl alcohol gave 10.0 g. of *S*-p-tolyl bis(2-cyanoethyl)phosphinothioate, m.p. 120–122°.

(14) A. Michaelis and G. L. Linke, *Ber.*, 40, 3419 (1907).

(15) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Am. Chem. Soc.*, 81, 1103 (1959).

Anal. Calcd. for $C_{13}H_{15}N_2OPS$: C, 56.10; H, 5.43; N, 10.07; P, 11.13; S, 11.52. Found: C, 56.04; H, 5.56; N, 10.05; P, 11.44; S, 11.36.

Reaction of benzenesulfonyl chloride with bis(2-cyanoethyl)-phosphine. Experiment (b) above was repeated using 17.7 g. (0.1 mole) of benzenesulfonyl chloride in place of the *p*-toluenesulfonyl chloride. Following the same work up procedure there was obtained after recrystallization from isopropyl alcohol, 8.0 g. of *S*-phenyl bis(2-cyanoethyl)-phosphinothioate, m.p. 86–88°.

Anal. Calcd. for $C_{12}H_{12}N_2OPS$: C, 55.53; H, 4.96; P, 11.90; S, 12.13. Found: C, 55.44; H, 5.03; P, 12.03; S, 12.17.

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STAMFORD, CONN.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

α-Amino Acid Amides. A Convenient Synthesis[1]

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Investigation of the reaction of α-aminonitriles with alcoholic hydrogen chloride has led to a convenient high-yield synthesis of α-amino acid amide hydrochlorides.

$$R_1R_2CHCHCN + R_3OH + 2HCl \longrightarrow R_1R_2CHCHCONH_2 + R_3Cl$$
$$\quad\;\; | \qquad\qquad\qquad\qquad\quad |$$
$$\quad NH_2 \qquad\qquad\qquad\qquad NH_2\cdot HCl$$

The course of the reaction is critically dependent upon the alcohol that is used for solvent. If $R_1 = H$ and $R_2 = H$ or alkyl then the alcohol R_3OH must be secondary; otherwise ester formation results. When R_1 and R_2 are both alkyl, R_3OH must be primary in order for any reaction to take place. These and related effects as well as the probable reaction mechanism are discussed.

During an investigation of the chemistry of α-aminonitriles, it became of interest to define their reaction with alcohols in the presence of anhydrous hydrogen chloride. The reaction of nitriles with alcohols and hydrogen chloride is, of course, well known; in general, imido esters are formed when equivalent amounts of alcohol are used and ortho esters result when the alcohol is present in excess.[2] Nitriles having α-substituents other than carbon have not been as extensively investigated. Steinkopf and Malinowski[3] investigated a series of α-substituted acetonitriles and observed that imido esters and/or amides were produced upon reaction with alcoholic hydrogen chloride and that amides were more readily formed when the α-substituent was a strong electron-attracting group. McElvain *et al.*,[4] observed the formation of both amides and carboxylic esters in addition to the desired ortho esters upon treatment of α-substituted nitriles with alcoholic hydrogen chloride and concluded that these by-products were due to the presence of at least two α-substituents.

Imido esters of α-aminonitriles and their sulfonyl and acyl derivatives have also been prepared.[5–8] In contrast, α-aminophenylacetonitrile is reported to give only the amide upon reaction with methanolic hydrogen chloride and the imido ester dihydrochloride of glycine to be transformed into glycinamide hydrochloride upon storage at ambient temperatures.[7] The possible general synthetic usefulness of this formation of α-amino amides, however, apparently was not recognized.

In the present investigation, treatment of a benzene solution of α-aminoisovaleronitrile (I; $R_1 = R_2 = CH_3$) with one or two equivalents of ethanol and hydrogen chloride resulted only in the precipitation of the corresponding hydrochloride. However, when the reaction was conducted in saturated ethanolic hydrogen chloride, valinamide hydrochloride (II; $R_1 = R_2 = CH_3$) precipitated in 75% yield upon refluxing the reaction mixture, and ethyl chloride was evolved.

$$R_1R_2CHCHCN + R_3OH + 2HCl \longrightarrow R_1R_2CHCHCONH_2 + R_3Cl$$
$$\quad\;\; | \qquad\qquad\qquad\qquad\quad |$$
$$\quad NH_2 \qquad\qquad\qquad\qquad NH_2\cdot HCl$$
$$\quad \text{I} \qquad\qquad\qquad\qquad\quad \text{II}$$

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