closer structural resemblance to the natural substrate than do the acids. Consistent with this interpretation is the present observation that the rate of reduction of ε-N-(DL-lipoyl)-L-lysine by DPNH in the presence of *E. coli* dihydrolipoic dehydrogenase was 2 to 3 times as fast as the rate of reduction of DL-lipoamide.

It is to be noted that ε-N-lipoyl-L-lysine bears a striking structural resemblance to biocytin (ε-N-biotinyl-L-lysine) which was isolated previously from yeast autolysate.[44] Biotin is known to occur naturally in association with proteins[45] and protein-bound biotin has been reported to be involved in the synthesis of fatty acids from acetate.[46] Although the nature of the moiety to which biotin is bound has not been established, it seems highly probably that it is bound to the ε-amino group of a lysine residue. It would appear that comparative studies of the release of protein-bound biotin and the incorporation of biotin into protein are in order.

Acknowledgments.—We wish to express our appreciation to Dr. Joanne M. Ravel for microbiological lysine assays and to Mr. Jack Matthews for the manometric lipoic acid assays.

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(43) V. Massey, *Biochim. Biophys. Acta*, **30**, 205 (1958).

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE ST. LOUIS RESEARCH DEPARTMENT, ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO.]

Reactions of Phosphorus Compounds. II. A New Type of Oxidizing Agent—Trichloroacetamides

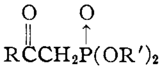
BY A. J. SPEZIALE AND R. C. FREEMAN

RECEIVED APRIL 6, 1959

Phosphites and phosphines react with N,N-disubstituted trichloroacetamides to give trichlorovinylamines (VIII) in 23–83% yield and the corresponding quadruply-connected phosphorus compound. This new reaction which appears to be general for trialkyl phosphites and tertiary phosphines entails the oxidation of phosphorus by an amide with concomitant migration of a chlorine atom. This reaction also represents a novel method for the preparation of a new class of vinylamines. The mechanism of the reaction leading to trichlorovinylamines may involve the same type of intermediate as that proposed in the Perkow rearrangement. The unique differences in these two reactions are discussed.

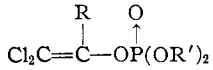
The reaction of 2-monohaloacetamides[1] and 2-monohaloacetates[1,2] with trialkyl phosphites has been shown to give phosphonates (I) (Michaelis–Arbuzov reaction[3]) and not vinyl phosphates (II Cl = H) (Perkow rearrangement[4]). Whetstone and Stiles,[5] however, have isolated vinyl phosphates (III) from the reaction of 2-chloro-N,N-dialkylacetoacetamides and trialkyl phosphites. Vinyl phosphates[2,4,6,7] (II, R = hydrogen, alkyl, aryl, alkoxyl) were also formed from the reaction of trialkyl phosphites with trihaloesters, aldehydes and ketones.

Allen and Johnson[7a,c] have reported that trichloroacetamides gave vinyl phosphates [II, R = $N(C_2H_5)_2$] in a manner analogous to trihaloesters and aldehydes. Because of the similarity of the reactions of esters and amides, one would have expected these haloamides to yield vinyl phosphates.



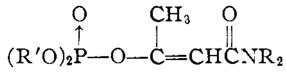
$R\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\uparrow}{P}}(OR')_2$

I



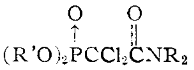
$Cl_2C{=}\overset{R}{\overset{|}{C}}{-}O\overset{O}{\overset{\uparrow}{P}}(OR')_2$

II



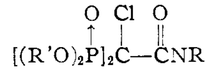
$(R'O)_2\overset{O}{\overset{\uparrow}{P}}{-}O{-}\overset{CH_3}{\overset{|}{C}}{=}CH\overset{O}{\overset{\|}{C}}NR_2$

III



$(R'O)_2\overset{O}{\overset{\uparrow}{P}}CCl_2\overset{O}{\overset{\|}{C}}NR_2$

IV



$[(R'O)_2\overset{O}{\overset{\uparrow}{P}}]_2\overset{Cl}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}NR_2$

V

We have found, however, that the reaction of trialkyl phosphites and α-trihaloacetamides yielded trichlorovinylamines (VIII). Attempts to isolate phosphates [II, R = $N(alkyl)_2$ or $N(aryl)_2$] and phosphonates IV and V were unsuccessful. These by-products may have been formed since varying amounts of alkyl chlorides were obtained in some of the reactions studied. The trialkyl phosphites were converted to trialkyl phosphates. Unlike the Perkow and Arbuzov reactions, this new rearrangement is not limited to phosphorous esters. Vinylamines (VIII) were also produced by the action of tertiary phosphines on trichloroacetamides.

The over-all transformation entailed the oxidation of a triply-connected phosphorus compound with concomitant migration of a chlorine atom.

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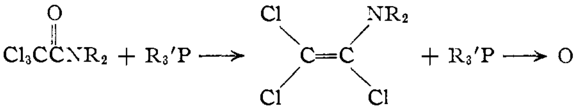
(6) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(7) (a) J. F. Allen and O. H. Johnson, THIS JOURNAL, **77**, 2871 (1955); (b) J. F. Allen, S. K. Reed, O. H. Johnson and N. J. Brunsvold, *ibid.*, **78**, 3715 (1956); (c) Allen and Johnson isolated an impure compound from the reaction of N,N-diethyl-2,2,2-trichloroacetamide with triethyl phosphite, which they assumed to be the vinyl phosphite, based on infrared absorption at 6.1 μ.

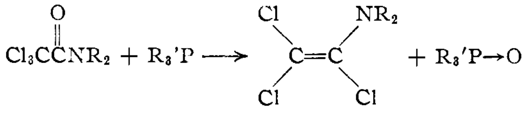
Table I

Reaction of Trivalent Phosphorus Compounds with 2,2,2-Trichloroacetamides


VI VII VIII IX

VI, R	VII, R′	Yield of IX, %	Yield, of VIII, %	M.p. or b.p. °C.	Mm.	$n^{25}D$	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Calcd. N	Found C	Found H	Found Cl	Found N
CH_3	C_2H_5O	72.3	52.7[a]	65–66	24	1.4948	27.53	3.47	60.97	8.03	27.56	3.55	60.27	7.76
CH_3	C_6H_5O	0	0[b]											
CH_3	n-C_4H_9	59.8	60.3											
C_2H_5	C_2H_5O	70.7	72.6[a]	66–67	6.2	1.4850	35.58	4.98	52.52	6.92	36.10	5.16	52.57	6.73
C_2H_5	i-C_3H_7O	14.9	31.5[c]											
C_2H_5	n-C_4H_9	72.6	82.5											
C_2H_5	C_6H_5	21.4	22.5[d]											
n-C_3H_7	CH_3O	51.8	51.8[a,e]			1.4705								
n-C_3H_7	C_2H_5O	39.5	33.4[f]											
C_6H_5	C_6H_5	69.6	55.4[g]	50.0–50.5			56.31	3.38	35.62	4.69	55.88	3.37	35.55	4.89
C_6H_5	C_6H_5O	0[h]	0											

[a] Small amounts of alkyl chlorides were isolated. [b] The amide was recovered in an 84.5% yield. [c] Isopropyl chloride was isolated in a 37% yield. [d] Based on the amount of amide recovered, 40.2%. [e] Calculated on the basis of a 48.2% recovery of amide. [f] Calculated from the amount of N,N-dipropyl-2,2-dichloroacetamide isolated on hydrolyzing the vinylamine–phosphate azeotrope. [g] Recrystallized from methanol. [h] Based on infrared analysis.

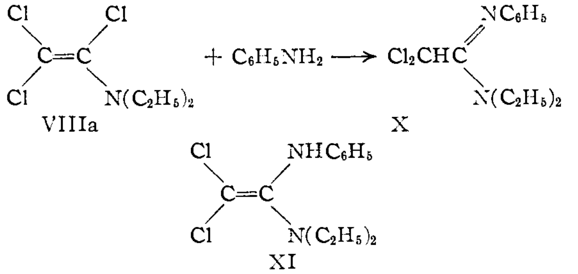

VI VII VIII IX

VI or VIII
a, R = C_2H_5
b, R = n-C_3H_7
c, R = CH_3
d, R = C_6H_5

VII or IX
a, R′ = C_2H_5O
b, R′ = CH_3O
c, R′ = i-C_3H_7O
d, R′ = C_6H_5O
e, R′ = n-C_4H_9
f, R′ = C_6H_5

From the reaction of triethyl phosphite (VIIa) with N,N-diethyl-2,2,2-trichloroacetamide (VIa), N,N-diethyl-1,2,2-trichlorovinylamine (VIIIa) was isolated in a 73% yield. The reaction products and yields were the same whether a 2:1 or 1:1 molar ratio of phosphite to amide was used. In contrast to the reaction of VIa with VIIa, which required heating to 145–155°, the reaction of VIa with tributylphosphine (VIIe) occurred exothermally at room temperature. The vinylamine (VIIIa) and tributylphosphine oxide (IXe) were isolated in 83 and 73% yields, respectively. In general, the trialkylphosphines gave higher yields and purer products than the phosphorous esters.

The structure of VIIIa was proved in the following manner: Its infrared spectrum indicated a carbon–carbon double bond (6.2 μ) flanked by electronegative groups. The presence of a double bond was substantiated by a positive test with bromine and potassium permanganate. Elemental analysis showed phosphorus and oxygen to be absent. Treatment with a saturated solution of sodium bicarbonate or water led to the displacement of one-third of the total amount of chlorine. N,N,-Diethyl-2,2-dichloroacetamide was isolated from the organic phase. Ott, *et al.*,[8] have shown that 1,2-dichlorovinylamines reacted similarly with water. Reaction of trichlorovinylamine (VIIIa) with aniline gave the amidine X and not its tautomer XI.


VIIIa X XI

The assignment of the amidine structure to the reaction product was made on the basis of the infrared spectrum which possessed a broad band at 6.25 μ characteristic for the C=NAr grouping. The NH– stretching and deformation frequencies were not present. The infrared spectrum of X from VIIIa and aniline was superimposable on that of an authentic sample of N,N-diethyl-N′-phenyl-2,2-dichloroacetamidine which was prepared from N-phenyl-2,2-dichloroacetimidoyl chloride and diethylamine.[9] The analyses and physical data of the amidine prepared by the two methods were in agreement.

All the vinylamines except the diphenyl derivative reacted exothermally with water and alcohols at room temperature and were handled under nitrogen to prevent attack by atmospheric moisture. The diphenylvinylamine (VIIId), on the other hand, was quite stable and was recrystallized from methanol.

The infrared data on the vinylamines are found in Table II. The carbon–carbon double bond frequency occurred at 6.19–6.29 μ (absorbancy 0.09 to 1.17) and C–N bond at 10.46–10.59 μ (absorbancy 0.40–1.20). The C–N bond was not observed in the spectra of the di- and trichloroacetamides. However, the latter compounds gave a very intense peak at 11.88–11.92 μ (absorbancy 0.61–1.50) which was due to the CCl_3 group. The carbonyl group of the di- and trichloroacetamides absorbed at 5.92–6.00 μ (absorbancy 1.18–1.80).

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[8] E. Ott, *et al.*, *Chem. Ber.*, **76B**, 80, 84, 88 (1943).

[9] R. L. Shriner and F. W. Newmann, *Chem. Revs.*, **35**, 351 (1944).

TABLE II

INFRARED DATA[a] OF DI- AND TRICHLOROACETAMIDES AND TRICHLOROVINYLAMINES

Compound	Frequencies in microns (absorbancy)			
	C=O	C=C	—CCl_3	C—N
$CCl_3CON(CH_3)_2$[b]	5.92 (1.65)		11.88 (1.50)	
$CCl_3CON(C_2H_5)_2$[c]	6.00 (1.27)		11.93 (0.82)	
$CCl_3CON(C_3H_7\text{-}n)_2$[c]	6.00 (1.18)		11.90 (0.61)	
$CCl_3CON(C_6H_5)_2$[d]	5.93 (1.40)		11.92 (0.85)	
$Cl_2C{=}C(Cl)N(CH_3)_2$[e]		6.19 (0.28)		10.48 (1.20)
$Cl_2C{=}C(Cl)N(C_2H_5)_2$[e]		6.20 (0.09)		10.59 (1.05)
$Cl_2C{=}C(Cl)N(C_3H_7\text{-}n)_2$[e]		6.2[f]		10.46[f]
$Cl_2C{=}C(Cl)N(C_6H_5)_2$[e]		6.29 (1.17)		10.44 (0.40)
$Cl_2CHCON(CH_3)_2$[e]	5.97 (1.80)			
$Cl_2CHCON(C_2H_5)_2$[d]	6.00 (1.67)			
$Cl_2CHCON(C_3H_7\text{-}n)_2$[c]	6.00 (1.26)			

[a] Taken in a 0.2-mm. sodium chloride cell using a Perkin–Elmer model 21 instrument. [b] 2% carbon disulfide solution. [c] 2% chloroform solution. [d] 3% chloroform solution. [e] Capillary film (0.01 mm.). [f] The intensity was about the same as that of the diethyl isomer.

The oxidation of trivalent phosphorus compounds by trichloroacetamides is a new and unique reaction. Previous methods[10] involved oxidizing agents such as nitric acids, peracids, permanganate, chromic acid, oxygen and ozone.[11] While these methods are generally useful for the oxidation of phosphines, they are not always applicable to the oxidation of the more hydrolytically unstable phosphites. Recently several investigators have shown that phosphites can be oxidized with alkyl hypochlorites,[12] epoxides,[13] dinitrogen tetroxide[14] and ozone.[15] Only the latter two methods are of preparative value. This paper presents a third method which should be generally applicable to trialkyl phosphites and tertiary phosphines.

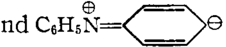
When phosphorous esters were allowed to react with trichloroacetamides, temperatures of 145–155° were required in order to obtain a moderate rate of reaction. Alkyl phosphites derived from primary alcohols produced higher yields of VII and IX than those derived from secondary alcohols. Triethyl phosphite and VIa gave a 73% yield of VIIIa compared to triisopropyl phosphite which gave only a 32% yield of VIIIa.

The competitive Perkow and Arbuzov reactions appeared to take place to a greater extent with triisopropyl phosphite than with triethyl phosphite since more isopropyl chloride (37%) was isolated than ethyl chloride (25%). A difference in the behavior of phosphites derived from primary alcohols from those derived from secondary alcohols has also been noted by Reetz and co-workers[16] in their study of the reaction of phosphites with haloquinones. Surprisingly, triphenyl phosphite did not react with VIc (or VId) even when heated eleven hours (normal time for alkyl phosphites, 2–3 hours) at 170–175°. Only starting materials were recovered.

The difference in reactivity of triisopropyl and triphenyl phosphites with trichloroacetamides, under the same conditions, indicated that electrical effects were more important than steric. A comparison of Catalin molecular models of these two phosphites showed that steric factors were about the same. The side of the phosphorus atom on which the unshared pair of electrons are located is available to attack the amide oxygen atom in all conformations. This unusual stability of triphenyl phosphite could be due to delocalization of the electrons of oxygen (resonance with ring) and phosphorus (inductive shift due to $\delta+$ on oxygen). The net result would be a decrease in the nucleophilic character of the phosphorus atom.

Since phosphines, in general, are more easily oxidized by oxygen[10] than are phosphites, trichloroacetamides were expected to react readily with tertiary phosphines. At room temperature tributylphosphine (VIIe) reacted exothermally with amides (VIa, c, d) in contrast to the phosphorous esters which required heating to about 150°. The yields of trichlorovinylamines were higher (60–83%) than in case of the phosphite esters (53–73%).

Triphenylphosphine reacted more sluggishly with amides than either alkylphosphines or phosphites. Contributions of resonance forms in which the electron density on phosphorus is dissipated through the three phenyl rings (thereby decreasing the nucleophilic character of phosphorus) would, in part, explain this behavior.

Triphenylphosphine with N,N-diphenyltrichloroacetamide (VId) gave a 55.4% yield of the vinylamine VIIId, whereas N,N-diethyltrichloroacetamide (VIa) afforded only a 22.5% yield of VIIIa. The yields of triphenylphosphine oxide were 69.6 and 21.0%, respectively. The higher yield in the first instance must be the result of an increase in electrophilic character of the carbonyl group of VId. Electrophilic or some peroxide[17] character imparted to the carbonyl oxygen atom by the inductive effects of the CCl_3 and  groups and resonance effect of $(C_6H_5)_2N-$ groups

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(10) See ref. 3, pp. 23, 98 and 231.

(11) L. Horner, H. Schaefer and W. Ludwig, *Chem. Ber.*, **91**, 75 (1958).

(12) K. A. Petrov and G. A. Sakolskii, *J. Gen. Chem. (USSR)*, **26**, 3377 (1956).

(13) C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957).

(14) J. R. Cox, Jr., and F. H. Westheimer, THIS JOURNAL, **80**, 5441 (1958).

(15) W. S. Knowles and Q. E. Thompson, *Chemistry & Industry*, 121 (1959).

(16) Th. Reetz, J. F. Powers and G. R. Graham, Abstracts of 134th Meeting of the American Chemical Soc., Chicago, Ill., Sept. 7–12, 1958, p. 86P.

(17) M. A. Greenbaum, D. B. Denny and A. K. Hoffman, THIS JOURNAL, **78**, 2563 (1956). Attack at an electrophilic oxygen atom as in peroxides by phosphines has been clearly demonstrated.

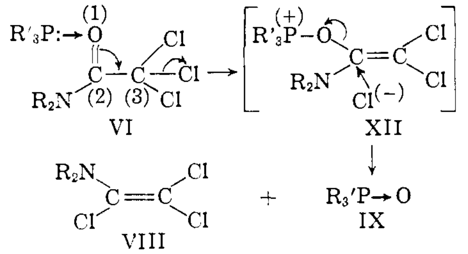
would facilitate the attack at oxygen by the nucleophilic phosphorus atom.

One important feature to be considered in a discussion of the mechanism of the reaction of trivalent phosphorus compounds with trichloroacetamides is that the oxygen atom of the amide becomes the phosphoryl oxygen of the oxidized phosphorus compound.

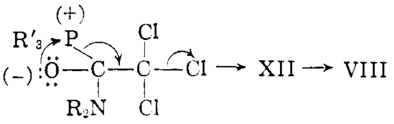
The reaction of trialkyl phosphites with certain 2-halocarbonyl compounds (Perkow reaction) resembles the present reaction only in that a phosphite is oxidized to a phosphate. In the Perkow reaction, an alkyl halide is one of the major reaction products and the halocarbonyl reagent becomes one of the ester groups of the phosphate. When the trichloroacetamides serve as halocarbonyl compounds, the products are the phosphates of the corresponding phosphites and trichlorovinylamines.

Ramirez and Dershowitz[18] reported the oxidation of triethyl and triphenyl phosphites to the corresponding phosphates by chloroquinones. Horner and Hoffmann[19] stated that triphenylphosphine was converted to triphenylphosphine oxide in the presence of dibenzoylethylene. A mechanism which amounts to an attack on the oxygen atom by phosphorus has been proposed for the oxidation process.

In the reaction of trialkyl phosphites with α-halocarbonyl compounds, the initial attack by the nucleophilic phosphorus atom has been postulated to occur at (1) the oxygen atom,[7a,19] (2) the carbonyl carbon atom[7a,20] or (3) the carbon alpha to the carbonyl group.[4] In the reaction of trialkyl phosphites with trichloroacetamides, we favor the initial direct attack of the phosphorus atom on the oxygen atom[21] to give XII. The attack on oxygen with simultaneous elimination of chloride ion would be aided by the strong inductive effect of the α-chlorine atoms. The second step would involve displacement of the trialkyl phosphate moiety by chloride ion to give VIII. The chloride ion is probably not expelled as a free species in XII but rather would remain within the sphere of the positively charged phosphorus atom (as an ion pair) and in a position stereochemically related to the π-electrons of the double bond. This geometry would facilitate the displacement of the phosphate (or phosphine oxide) group. This premise is supported by examination of a Catalin molecular model of XII.



Initial attack at position 2 of the amide by phosphite would give rise to the phosphonate intermediate XIII. The phosphorus atom could then undergo a carbon to oxygen migration[20,22–24] as indicated to form XII. Attack at position 3 should lead to phosphonates of the type IX and V. Attack at position 3 should lead to phosphonates of the type IV and V. These were not isolated. The absence of phosphonate type compounds in the phosphate fractions was shown by vapor phase chromatography and nuclear magnetic resonance spectra. Triethyl phosphate was the major phosphorus-containing compound detected. An attempt was made to obtain evidence for the incipient formation of C–P or C–O–P bonds in order to establish whether phosphorus atom attacked the carbonyl carbon or carbonyl oxygen of the amides. Periodic n.m.r. spectra (−145 to 20 p.p.m.) of a mixture of triethyl phosphite and N,N-diethyltrichloroacetamide were taken at room temperature. If C–O–P bond of the type in XII were formed, a chemical shift positive with respect to that of triethyl phosphate should have been observed. If the attack had occurred at position 2, this would have given rise to a phosphonate (P–C bond) compound (XIII). In this case a chemical shift[1,25] should have been found near −35 to −18 p.p.m. Between the 36th and 49th hour a weak chemical shift developed at +1 p.p.m. (relative to 85% phosphoric acid). This was the only chemical shift observed in the spectra other than that of triethyl phosphite (−139 p.p.m.). The +1 p.p.m. shift was due to triethyl phosphate. The conclusion was made that if trivalent phosphorus compounds attack either the amide oxygen or the carbonyl carbon, the half-life of XII or XIII is too short to be measured by n.m.r. That is, the concentrations of XII and XIII were too small to be detected by this method.



XIII

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[18] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957).

[19] L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

[20] I. S. Bengelsdorf, *J. Org. Chem.*, **21**, 475 (1956); A. N. Pudovik, *J. Gen. Chem.* (*USSR*), **26**, 2503 (1956).

[21] A. C. Poshkus and J. E. Herweh, THIS JOURNAL, **78**, 6127 (1956), proposed a similar attack on the oxygen of sulfuryl chloride by the phosphorus atom of triethyl phosphite. N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959), and also M. J. Boskin and D. B. Denny, *Chemistry and Industry*, 330 (1959), have shown that phosphites and phosphines react with episulfides via initial attack on the sulfur atom. Boskin and Denny, however, reported that epoxides react predominantly via an initial attack at the carbon atom. However, based on their yields of *cis*- and *trans*-2-butenes from either *cis*- or *trans*-2-butenes epoxides attacked at oxygen could have occurred to the extent of 17–26%. Whereas a direct correlation of the reaction of these phosphorus compounds with episulfides or epoxides and amides cannot be made, the data do show that an attack on the oxygen atom is possible. For additional references for other reactions of trivalent phosphorus compounds with epoxides and episulfides see: R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); R. D. Shuetz and R. L. Jacobs, *ibid.*, **23**, 1799 (1958); C. B. Scott, *ibid.*, **22**, 1118 (1957). After this paper was accepted for publication, we became aware of an article by V. A. Kykhtin, *Proc. Acad. Sci.* (*USSR*), 557 (1958), in which an initial attack on the oxygen atom by phosphorus in the Perkow reaction was considered.

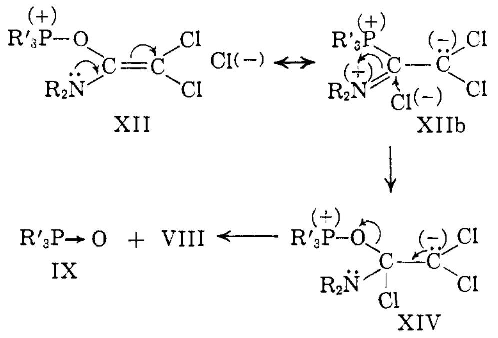
[22] W. Lorenz, A. Henglein and G. Schraeder, *ibid.*, **77**, 2554 (1955).

[23] W. F. Barthel, B. H. Alexander, P. A. Giang and S. A. Hall, *ibid.*, **77**, 2424 (1955).

[24] A. M. Mattson, J. L. Spillane and G. W. Pearce, *J. Agri. Food Chem.*, **3**, 319 (1955).

[25] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, **78**, 5715 (1956).

The fact that trichloroacetamides behaved differently from their aldehyde and ester counterparts could be rationalized on the basis that the intermediate XII would be stabilized through resonance to a greater degree by nitrogen than by oxygen.


XII XIIb

IX XIV

The chloride ion would attack the iminum carbon atom of XIIb to give XIV rather than the alkyl group of the phosphate ester to give alkyl chloride. The pair of electrons in XIV would assist in expelling the trialkyl phosphate moiety. This route is an alternative[26] to that already proposed (XII going directly to VIII) and also accounts for the absence of alkyl chloride.

Acknowledgment.—We are indebted to Dr. B. Katlafsky and Mr. O. Kinast for the infrared spectra, to Drs. E. M. Emery and W. E. Koerner for vapor phase chromatography spectra, to Drs. C. F. Callis and Dr. D. P. Ames of our Inorganic Division for the nuclear magnetic resonance and to Messrs. J. L. O'Sullivan and O. S. Kring for the analytical data.

Experimental[27]

N,N-Diethyl-1,2,2-trichorovinylamine (VIIIa). A. Trialkyl Phosphate Method. 1a. Triethyl Phosphite.—N,N-Diethyl-2,2,2-trichloroacetamide (218.5 g., 1 mole) was heated to 145°, with stirring. One mole (166.2 g.) of triethyl phosphite was added to the amide at such a rate that the temperature did not exceed 150°. The addition required 100 min. and the mixture was heated for an additional hour. During the addition period 6.05 g. of ethyl chloride was evolved. An additional 10 g. was caught in a cold trap during the distillation of the trichlorovinylamine. The total yield of ethyl chloride was 16.05 g. (0.249 mole, 25%) and therefore only 0.751 mole of amide was available for conversion to VIIIa. Distillation of the reaction mixture afforded 147.4 g. of N,N-diethyl-1,2,2-trichlorovinylamine (VIIIa), b.p. 67–71° (6.2 mm.), $n^{25}\text{D}$ 1.4779, 96.8% yield based on the amount of ethyl chloride isolated and 72.6% yield based on the amount of amide charged. Substances with higher boiling points were obtained in addition to a large amount of residue. The analytical sample of VIIIa distilled at 67° (6.2 mm.), $n^{25}\text{D}$ 1.4850. *Anal.* Calcd. for $C_6H_{10}Cl_3N$: C, 35.58; H, 4.98; Cl, 52.52; N, 6.92. Found: C, 36.10; H, 5.16; Cl, 52.57; N, 6.57.

1b. In another preparation of VIIIa using 2 moles of reagents there was obtained a 66.3% yield of VIIIa (b.p. 84–85° (22 mm.)) and a 70.7% yield of impure triethyl phosphate, b.p. 94–98° (14 mm.). Four cuts were made of the phosphate fraction which had the following indices of refraction at 25°; A, 1.4200; B, 1.4120; C, 1.4128; D, 1.4126.

Infrared analysis of the phosphate fractions showed absorption at 6.05 μ and the characteristic phosphate absorptions (P→O, 8.05 μ; P–O–C_2H_5, 8.65 μ; C–O–P, 9.9 μ). Vapor phase chromatography and nuclear magnetic resonance spectra showed that these fractions were triethyl phosphate containing about 5% of some phosphonate compounds.

The chemical shift for triethyl phosphate has been reported to occur at ±1 p.p.m. relative to orthophosphoric acid.[25] Fraction A showed chemical shifts at −32.1, −29.1, +0.7, +14.5 p.p.m. The shifts observed at −32.1 and −29.1 p.p.m. may be due to alkylphosphonates such as diethyl ethylphosphonates[25] (−32.5 p.p.m.), while that for +14.5 p.p.m. could be due to a vinyl phosphate. The peak at +0.7 p.p.m. was due to triethyl phosphate.

Fraction D was partially separated by vapor phase chromatography into two major components. One component by infrared analysis showed the presence of triethyl phosphate and the other component exhibited a carbonyl compound which was unreacted N,N-diethyltrichloroacetamide. The vapor phase chromatography separation was hindered by the decomposition of the trichloroacetamide.

The n.m.r. spectra of fraction D showed triethyl phosphate to be the only phosphorus compound present. Therefore, based on the data presented, the carbonyl absorption maximum in fraction D and others must be due to unreacted N,N-diethyltrichloroacetamide and the characteristic phosphorus absorption frequencies must be due to triethyl phosphate.

Samples of the reaction mixture before and after distillation of the trichlorovinylamine (VIIIa) fraction were submitted to n.m.r. analysis. Both samples exhibited identical chemical shifts at −9.0, +0.5, +13.0 and +24.9 p.p.m.

The reaction leading to the trichlorovinylamine was very fast since the major phosphorus component of these samples was triethyl phosphate (0.5 p.p.m). No unreacted triethyl phosphite was present since no maximum was observed in the −139 p.p.m. region.[25] The chemical shifts at −9.0, +13.0 and +24.9 were minor bands representing 5% of phosphorus impurities.

1c. **Two to One Molar Ratio of Phosphite to Amide.**—In a third preparation of VIIIa using the above procedure (1a), 65.5 g. (0.3 mole) of amide VIa and 99.6 g. (0.6 mole) of triethyl phosphite were allowed to react. There were isolated 32.7 g. (0.197 mole, 30.4%), of triethyl phosphite, b.p. 57–58° (22 mm.); 39.9 g. (65.7%) of VIIIa; and 46.6 g. (85.3%) of triethyl phosphate, b.p. 85–86° (8 mm.). The products were characterized by infrared analysis.

2. **Triisopropyl Phosphite.**—There were isolated from 109.3 g. (0.5 mole) of triisopropyl phosphite and 102.1 g. (0.5 mole) of N,N-diethyl-2,2,2-trichloroacetamide, according to a slight modification of the above procedure (1a), 31.5 g. (31%) of the vinylamine VIIIa and 16.7 g. (14.9%) of triisopropyl phosphate, b.p. 107–110° (12 mm.). The addition of the phosphite was shortened to 45 minutes. There was considerably more isopropyl chloride evolved during the reaction and especially at the end of the heating period (one hour). The total amount of isopropyl chloride isolated during the reaction and distillation period was 14.5 g. (0.185 mole, 37%).

B. **Trialkylphosphine Method. Tributylphosphine.**—The reaction must be conducted in an oxygen-free atmosphere. Tributylphosphine (40.5 g., 0.2 mole) was added to N,N-diethyl-2,2,2-trichloroacetamide (43.7 g., 0.2 mole) at 25° under nitrogen. The reaction temperature rose quickly to 50°. The addition was completed in 30 minutes by cooling with tap water. Heating was continued an additional four hours at 50–55°. Distillation through a 15 × 150 mm. Vigreux column afforded 33.4 g. (82.5%) of N,N-diethyl-1,2,2-trichlorovinylamine, b.p. 63–64° (7 mm.), $n^{25}\text{D}$ 1.4858, and 29.4 g. (72.6%) of tri-*n*-butylphosphine oxide,[28] b.p. 104° (0.04 mm.).

C. **Triarylphosphine Method. Triphenylphosphine.**—A mixture of 43.7 g. (0.2 mole) of N,N-diethyl-2,2,2-trichloroacetamide, 52.4 g. (0.2 mole) of triphenylphosphine

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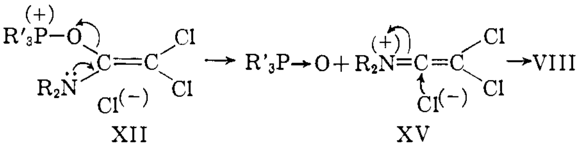
[26] A third alternative may involve the pair of electrons on the nitrogen atom of XII, displacing the phosphate to give XV, which could react with the chloride ion to yield VIII. The elimination of the stable trialkyl phosphate could be the driving force for the formation of XV.


XII XV

[27] The boiling points and melting points reported are uncorrected.

[28] G. M. Kosolapoff, THIS JOURNAL, **72**, 5508 (1950), reported b.p. 185–186° (18 mm.).

and 200 ml. of *o*-xylene was heated at 145–150° for three hours. After this time the reaction mixture was cooled and distilled through 15 × 150 mm. straight tubular column: A, b.p. 50–55° (20 mm.); B, 43–47° (2 mm)., $n^{25}\mathrm{D}$ 1.4864, 9.43 g.; C, 63–66° (0.3–0.35 mm.), $n^{25}\mathrm{D}$ 1.4900, 19.2 g.; D, residue, 23.3 g. Fraction A was *o*-xylene. Fraction B represented a 22.5% yield of the desired trichlorovinylamine VIIIa or a 40.2% yield based on the amount of trichloroamide consumed. Fraction C represented a 44.0% recovery of the starting amide. Fraction D was separated into triphenylphosphine oxide, 12.4 g. (21.4% yield), m.p. 156.4–157.2°, and triphenylphosphine, 8.9 g. (15.5% recovery), m.p. 80.6–80.8°. The phosphine oxide was precipitated by adding ether to fraction D and filtering. The residue was triphenylphosphine oxide. The filtrate was concentrated and the residual oily-solid mass was triturated with petroleum ether (b.p. 38–48°). The solid which remained was mixed with the phosphine oxide above and recrystallized from benzene. The petroleum ether solution was evaporated to dryness and the residue was recrystallized from methanol to give pure triphenylphosphine.

N,N-Dimethyl-1,2,2-trichlorovinylamine(VIIIc). **Triethyl Phosphite.**—There were isolated from 83.1 g. (0.5 mole) of triethyl phosphite and 95.2 g. (0.5 mole) of N,N-dimethyl-2,2,2-trichloroacetamide (VIc) according to procedure A, 1a, above, 25.9 g. (52.7%) of the trichlorovinylamine VIIIc, 65.7 g. (72.3%) of triethyl phosphate and 4.06 g. (0.063 mole) of ethyl chloride.

Triphenyl Phosphite.—Triphenyl phosphite (93.1 g., 0.3 mole) was not oxidized by the amide VIc (51.2 g., 0.3 mole) according to procedure A, 1a, above. Distillation of a small fraction of the reaction mixture through a 15 × 150 mm. glass helices packed column afforded amide VIc, b.p. 110° (30 mm.), as the first distillate. An infrared spectrum of the distillate was identical with the starting amide. The distillate was therefore returned to the reaction mixture which was then heated 9 hours between 170–175°. After this time there was obtained 48.3 g. (84.5% recovery) of the starting amide VIc, b.p. 85–88° (3.5–4 mm.), $n^{25}\mathrm{D}$ 1.5017.

Tributylphosphine.—Following procedure B described for the preparation of VIIIa there were obtained from 109.3 g. (0.5 mole) of N,N-dimethyl-2,2,2-trichloroacetamide and 101.0 g. (0.5 mole) of tri-*n*-butylphosphine, 52.6 g. (60.3%) of N,N,-dimethyl-1,2,2-trichlorovinylamine and 57.0 g. (59.2%) of tri-*n*-butylphosphine oxide.

N,N-Di-*n*-propyl-1,2,2-trichlorovinylamine (VIIIb).—There was added to 49.4 g. (0.2 mole) of N,N-di-*n*-propyl-2,2,2-trichloroacetamide, according to the procedure described in A, 1a, 66.4 g. (0.4 mole) of triethyl phosphite. There was obtained 60.2 g. of fraction A, b.p. 101–102° (20 mm.), $n^{25}\mathrm{D}$ 1.4370; fraction B, 26.9 g. (0.162 mole) of triethyl phosphite, b.p. 63–82° (20 mm.), $n^{25}\mathrm{D}$ 1.4120. Fraction A was redistilled, b.p. 98° (10 mm.), $n^{25}\mathrm{D}$ 1.4350–1.4368, and the middle cut (36.1 g., $n^{25}\mathrm{D}$ 1.4358) was treated with water. There was present in the aqueous layer an equal molar amount of acid and chloride ions (0.045 mole). The organic phase yielded 11.2 g. (0.0614 mole) of triethyl phosphate, b.p. 63° (1.2 mm.), $n^{25}\mathrm{D}$ 1.4040, and 11.1 g. (0.045 mole) of N,N-di-*n*-propyl-2,2-dichloroacetamide,[29] b.p. 93° (0.75 mm.), $n^{25}\mathrm{D}$ 1.4790, m.p. 32–33°.

Trimethyl Phosphite.—The above procedure A, 1a, was used except 49.3 g. (0.2 mole) of amide VIb and 24.8 g. (0.2 mole) of trimethyl phosphite were employed. Distillation of the residue gave fraction A, 31.5 g., b.p. 37–63° (0.08–1.6 mm.), and fraction B, 23.7 g. (48.2% of recovered amide VIb). Fraction A separated into two layers during distillation. The top layer ($n^{25}\mathrm{D}$ 1.4705) was hydrolyzed with water to N,N-di-*n*-propyl-2,2-dichloroacetamide, thus proving that the top layer to be the trichlorovinylamine VIIIb. The bottom layer was trimethyl phosphate ($n^{25}\mathrm{D}$ 1.4078).

N,N-Diphenyl-1,2,2-trichlorovinylamine. **Triphenylphosphine.**—To a solution consisting of 600 ml. of hexane and 68.6 g. (0.218 mole) of N,N-diphenyl-2,2,2-trichloroacetamide heated to 70°, there was added 200 ml. of hexane containing 78.7 g. (0.3 mole) of triphenylphosphine. The hexane–triphenylphosphine solution was warmed in order to maintain a homogeneous solution. The addition required one hour after which the reaction mixture was heated (70°) two hours. Triphenylphosphine oxide began precipitating immediately after the addition of triphenylphosphine was started. After the heating period the reaction mixture was filtered through a coarse fritted glass funnel. The residue (A) was washed with ether and the washings were added to the filtrate. The ether–hexane filtrates were concentrated *in vacuo* to a solid–oil residue which was triturated several times with boiling petroleum ether (b.p. 38–48°). The solid (B) which remained was mixed with the above residue (A) and dissolved in methanol. Triphenylphosphine oxide (m.p. 151–153°, 58.1 g., 69.6% of theory) was isolated from the methanolic solution by adding water.

A bright red oil (51.6 g.) was obtained from the petroleum solution after distilling the solvent *in vacuo*. There was isolated from this oil 35.7 g. (55.4% of theory) of N,N-diphenyl-1,2,2-trichlorovinylamine, m.p. 49–50°, on recrystallizing from methanol. The analytical sample melted at 50.0–50.5°.

Triphenyl Phosphite.—A solution consisting of 68.6 g. (0.218 mole) of amide VId, 93.1 g. (0.3 mole) of triphenyl phosphite and 600 ml. of heptane was heated at the reflux temperature (102°) 72 hours. Analysis by infrared showed that reaction had not taken place. The peak for the CCl_3 group (11.92 μ) was as intense at this time as at the start of the reaction. Also, the C–N band at 10.44 μ was not observed in the spectra of the samples taken. At this time the heptane was removed by distillation and replaced with *o*-xylene simultaneously. The reaction mixture was then heated at 150° for 26 hours. Infrared analysis indicated that no reaction had occcurred.

Hydrolysis of N,N-Diethyl-1,2,2-trichlorovinylamine (VIIIa).—Treatment of 19.8 g. (0.098 mole) of VIIIa with water at 50° for one hour resulted in the recovery of 17.5 g. (88%) of material. During this time 0.093 mole (31.6%) of chloride and an equivalent amount of acid (HCl) was liberated. Distillation of the organic phase afforded 15.0 g. (76%) of N,N-diethyl-2,2-dichloroacetamide, b.p. 76° (0.9 mm.), $n^{25}\mathrm{D}$ 1.4792. This amide was identical with an authentic sample[30] by infrared analysis. No other products were isolated.

Hydrolysis of N,N-Dimethyl-1,2,2-trichlorovinylamine.—Fifteen grams (0.086 mole) of the vinylamine; VIIIc, obtained from the amide by the tributyl phosphine method, was mixed cautiously with 30 ml. of ice-water and 30 ml. of acetone. Additional acetone was added in order to obtain a homogeneous solution and the reaction mixture was heated to refluxing for one hour. After this time the reaction mixture was made basic with solid sodium carbonate, diluted with water and extracted several times with ether. The ethereal mixture was dried with magnesium sulfate and filtered. The ether was distilled *in vacuo* and the residual oil was distilled through a 7 × 300 mm. spiral wire packed column. The N,N-dimethyl-2,2-dichloroacetamide[31] distilled at 57–58° (0.35 mm.), $n^{25}\mathrm{D}$ 1.4947, yield 9.4 g. (70.2%). The amide solidified after standing several days and melted at 39–40°.

N,N-Diethyl-N′-phenyl-2,2-dichloroacetamide.—A mixture of 18.5 g. (0.091 mole) of N,N-diethyl-1,2,2-trichlorovinylamine and 75 ml. of benzene was heated to 60° and then 8.47 g. (0.091 mole) of aniline dissolved in 25 ml. of benzene was added dropwise. The temperature rose quickly to 88°. After refluxing the mixture for 16 hours the benzene was distilled *in vacuo*. A mobile liquid was decanted from a tacky ether-insoluble residue. The tacky substance was washed with ether and the washings added to the decanted liquid. Triethylamine (4 ml.) was added to the ether solution from which was deposited 0.22 g. of triethylamine hydrochloride (m.p. 256–257°). The mixture melting point with an authentic sample was 256–257°. About 15 ml. of triethylamine and 30 ml. of ether was added to the tacky residue. The mixture was stirred vigorously for about 10 minutes and filtered. There was obtained an additional 5.58 g. of triethylamine hydrochloride (total yield 5.8 g., 42%). Therefore 58% of the theoretical amount of hydrogen chloride should have been evolved from the reaction mixture. The filtrate and the first ethereal solution was mixed. The ether and excess triethylamine were distilled *in vacuo*. The N,N-diethyl·N′-phenyl-2,2-dichloroacetamidine, b.p. 88° (0.02 mm.), $n^{25}\mathrm{D}$ 1.5649, d^{25} 1.1520, was distilled through a 15 × 150 mm. straight tubular column. The yield was 18.87 g. (77.7%).

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(29) A. D. Swensen and W. E. Weaver, This Journal, **70**, 4060 (1948). The authentic sample was prepared according to the reported procedure. These authors reported b.p. 87° (0.3 mm.), $n^{25}\mathrm{D}$ 1.4779.

(30) Ref. 29 reported b.p. 100° (4 mm.), $n^{25}\mathrm{D}$ 1.4813.

(31) Ref. 29 reported b.p. 97° (9 mm.), $n^{25}\mathrm{D}$ 1.4931.

The amidine was identical with that prepared from N-phenyl-2,2-dichloroacetimidoyl chloride as follows: To a solution consisting of 10.62 g. (0.048 mole) of N-phenyl-2,2-dichloroacetimidoyl chloride[32] and 25 ml. of benzene there was added 7.02 g. (0.096 mole) of diethylamine which was dissolved in 15 ml. of benzene. The benzene–amine solution was added at such a rate that the temperature rose slowly from 25 to 67°. The reaction mixture was then refluxed for 1.5 hours. Diethylamine hydrochloride, m.p. 227–228° (5.26 g., 100% yield), was filtered and washed with benzene after the reaction mixture was cooled to about 30°. The filtrate and washings were mixed and the benzene distilled *in vacuo*. N,N-Diethyl-N′-phenyl-2,2-dichloroacetamidine, b.p. 92° (0.05 mm.), n^{25}_D 1.5650, d^{25} 1.1605, was distilled through a 15 × 70 mm. Vigreux column. The yield was 10.68 g. (86.4%).

Anal. Calcd. for $C_{12}H_{16}Cl_2N_2$: C, 55.61; H, 6.22; Cl, 27.36; N, 10.81. Found: C, 55.52; H, 6.25; Cl, 27.37; N, 11.10.

N-Phenyl-2,2-dichloroacetimidoyl Chloride.[32]—A mixture of 61.23 g. (0.3 mole) of 2,2-dichloroacetanilide, 60 g. (0.288 mole) of phosphorus pentachloride and 100 ml. of benzene was heated at 45° for 0.5 hour and then refluxed 0.5 hour. The benzene and phosphorus oxychloride were co-distilled *in vacuo*. N-Phenyl-2,2-dichloro-acetimidoyl chloride, b.p. 115–117° (10 mm.), n^{25}_D 1.5723, was distilled through a 15 × 70 mm. Vigreux column. The yield was 44.63 g. (69.4%).

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[32] J. F. Braun, F. Jostes and W. Munch, *Ann.*, **453**, 133, 146 (1927).

[CONTRIBUTION FROM THE ST. LOUIS RESEARCH DEPARTMENT, ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO.]

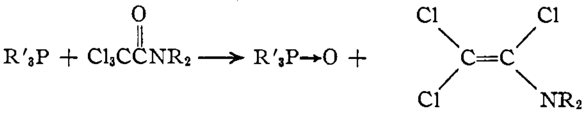
The Reactions of Enamines. I. N,N-Disubstituted-1,2,2-trichlorovinylamines

BY A. J. SPEZIALE AND R. C. FREEMAN

RECEIVED JULY 2, 1959

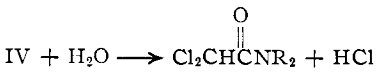
N,N-Diethyl-1,2,2-trichlorovinylamine (IVa) is an effective reagent for the replacement of hydroxyl groups by chloride. The yields are good in the cases of carboxylic acids and primary, secondary and tertiary alcohols. *d-sec*-Butyl alcohol is transformed to *l-sec*-butyl chloride in good yield and high optical purity. Amidines are formed from the reaction of IVa with amines. Stable salts are obtained from the reaction of IVa with halogen acids. The mechanisms for these reactions are discussed. The iminium ion $>CH\overset{|}{C}{=}\overset{+}{N}H—$ appears to be important in the reaction of IVa with acids, alcohols and amines.

Trivalent phosphorus compounds have been shown to undergo oxidation by trichloroacetamides to yield the corresponding phosphates or phosphine oxides and trichlorovinylamines.[1]



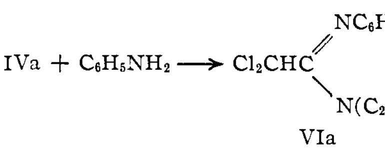
I II III IVa, R = C_2H_5

As part of the proof of structure of IVa, it was reported that upon reaction with water,[1,2] hydrogen chloride and the dichloroacetamide (Va) were formed. In addition, reaction of IVa with aniline yielded the amidine VIa.



$$IV + H_2O \longrightarrow Cl_2CH\overset{\overset{O}{\|}}{C}NR_2 + HCl$$

Va, R = C_2H_5



VIa

The reactions of these trichlorovinylamines have now been extended to alcohols, acids and to aliphatic and aromatic amines and their hydrochlorides.

N,N-Diethyl-1,2,2-trichlorovinylamine (IVa) reacted rapidly with alcohols and carboxylic acids[3] (see Table I) to give good yields of the corresponding alkyl and acid chlorides, respectively. In these reactions N,N-diethyl-2,2-dichloroacetamide was isolated in yields ranging from 67–95%. The conversion of trichloroamides to dichloroamides

TABLE I

REACTION OF N,N-DIETHYL-1,2,2-TRICHLOROVINYLAMINE (IVa) WITH WATER, ALCOHOLS AND ACIDS

ROH R =	Yield, % RCl, R =	Yield, % $Cl_2CHCON(C_2H_5)_2$	Reacn. temp., °C.
H	H, 95.5	76.0	25
C_2H_5	C_2H_5[a]	79.6	35–38
C_2H_5	C_2H_5, 82	86.5	55–60
dl-s-C_4H_9	*dl-s*-C_4H_9, 81[b]	91.8	40–50
dl-s-C_4H_9	*dl-s*-C_4H_9, 68.7[c]	83.5	60–75
d-s-C_4H_9	*l-s*-C_4H_9, 83.8[b]	94.5	40–50
t-C_4H_9	*t*-C_4H_9, 50.8[d]	61.8[e]	20–25
t-C_4H_9	*t*-C_4H_9, 56.2[f]	87.0	60–75
t-C_4H_9	*t*-C_4H_9, 23.1[g]	78.7[h]	75–80
CH_3CO	CH_3CO, 72.1	75.1	50–60
C_6H_5CO	C_6H_5CO, 72.3	66.6	85
2,4,6-$(NO_2)_3C_6H_2$	O[i]	0	65–70

[a] Ether was used as solvent; ethyl chloride was not isolated. [b] About 1% of hydrogen chloride and 2-butene were formed. [c] The amount of hydrogen chloride and 2-butene were not determined. [d] The yield was 60.8% based on the recovery of 16.9% of *t*-butyl alcohol. Only a trace of hydrogen chloride was detected. [e] The yield was 77.9% based on the recovery of 21% of IVa. [f] Isobutylene was formed. [g] Benzene was used as a solvent. The yield was 32.8% based on the recovery of 29.4% of *t*-butyl alcohol. [h] The yield was 92.3% based on the recovery of 14.8% of IVa. [i] 85.6% of the picric acid was recovered and 89.3% of IVa.

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(1) A. J. Speziale and R. C. Freeman, THIS JOURNAL, **81**, 903 (1959).

(2) E. Ott, *et al.*, *Chem. Ber.*, **76B**, 80, 84, 88 (1943). These authors reported the reaction: $ClCH{=}C(Cl)N(C_2H_5)_2 + H_2O \rightarrow ClCH_2CON(C_2H_5)_2$.

(3) Th. R. Rix and J. F. Arens, *Proc. Koninkel. Ned. Akad. Wetenschap.*, **56B**, 368,372 (1953); *C.A.*, **44**, 2300 (1955), reported that 1-chloro-1-ethoxyethylene reacted with alcohols and carboxylic acids to yield ethyl acetate and the corresponding alkyl chlorides and acid chlorides. Also see I. A. Smith, *J. Chem. Soc.*, 1099 (1927), and H. Crompton and P. L. Vanderstichele, *ibid.*, 691 (1920), who obtained similar results with 1,2-dihalo-1-alkoxyethylene.