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ALKYL N-PHOSPHORYLATED IMIDATES[1]

K. D. BERLIN and M. A. R. KHAYAT[2]
Department of Chemistry, Oklahoma State University,
Stillwater, Oklahoma, U.S.A.

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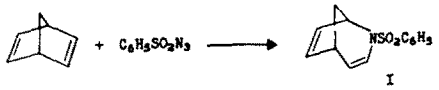
Abstract—Vinyl ethers react with phosphorus azides to give N-phosphorylated imidates in moderate yields. These previously unknown compounds undergo hydrolysis under mild conditions to give formylphosphoramidates and the corresponding alcohols. Treatment of the phosphorylated imidate (XIVh) with sodium borohydride effected carbon–oxygen bond scission and afforded dibutyl N-methylphosphoramidate. Possible mechanisms are offered to explain the transformations.

THE reactions of organic azides with compounds containing olefinic bonds have been studied under a variety of conditions by several workers.[3] The products of some of the condensations are Δ^2-1,2,3-triazolines while others give aziridines, anils, or enamines. Ease of the reaction is very much influenced by the nature of the azide and the reactivity of the olefinic bond.

In a recent kinetic study,[4] a number of substituted phenyl azides were treated with norbornene to give Δ^2-1,2,3-triazolines. The reaction is greatly facilitated when X is an electron-withdrawing group (such as *p*-Br, *m*-Br, *p*-NO_2, *m*-NO_2).

Azides having sulfonyl[5] or carbonyl[6,7] groups adjacent to the azide function react with alkenes, in some cases with the immediate evolution of nitrogen. For example, benzenesulphonyl azide and norbornadiene give, after loss of nitrogen, an amine which is believed to have the structure I.[8,9] A rapid evolution of nitrogen is also



I

[1] We gratefully acknowledge support by the Public Health Service under grant CA-07202-02 and CA-07202-03. We thank Dr. K. Loening of Chemical Abstracts for help in naming these compounds.

[2] Research Associate 1964–65.

[3] [a] L. Wolff, *Liebigs Ann.* **394**, 23–108 (1912); [b] C. S. Rondestvedt and P. K. Chang, *J. Amer. Chem. Soc.* **77**, 6532 (1955); [c] R. A. Abramovitch and B. A. Davis, *Chem. Revs.* **64**, 149 (1964); [d] L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.* **28**, 3303 (1963); [e] P. Scheiner, *Ibid.* **30**, 7 (1965).

[4] P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey and G. P. Nowack, *J. Amer. Chem. Soc.* **87**, 306 (1965).

[5] R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, *Gazz. Chim. Ital.* **92**, 1040 (1962).

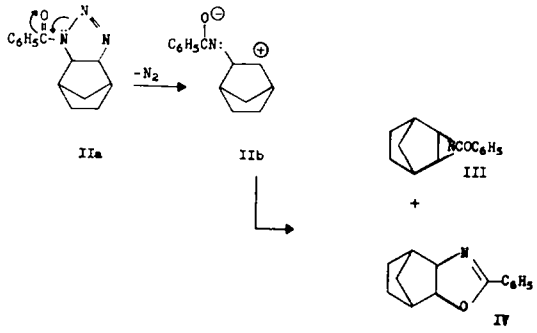
[6] S. J. Davis and C. S. Rondestvedt, *Chem. & Ind.* 845, 848 (1956).

[7] E. Fanghänel, *Z. Chem.* **3**, 309 (1963).

[8] J. E. Franz and C. Osuch, *Chem. & Ind.* 2058 (1964).

[9] A. C. Oehlschlager and L. H. Zalkow, *Chem. Comm.* No. **4**, 70 (1965).

observed in the example of benzoyl azide and norbornene.[10] The aziridine III and the oxazoline IV are isolable. It has been pointed out that withdrawal of electrons (see IIa) would weaken the triazene mesomerism and hence the decomposition of the triazoline



occurs, perhaps *via* IIb, to give III and IV.[10] Ring contraction and hydride shift have also been demonstrated in the reaction of aryl azides with some enamines.[11] Migration of a hydride ion has been observed in the formation of phosphorylated amidines by treatment of dimethyl isobutenylamine with phosphorus azides.[12]

$$R_2P(O)N_3 + (CH_3)_2C{=}CHN(CH_3)_2 \rightarrow (CH_3)_2CHC(N(CH_3)_2){=}NP(O)R_2$$

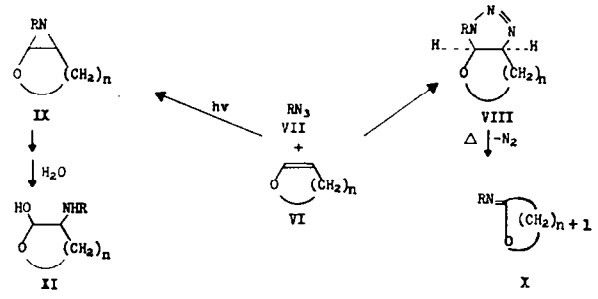
The reactivity of the olefinic bond has significant influence on the rate and the nature of products in this class of reactions. Among the factors which increase the reactivity of olefinic bond towards the azide function are: steric strain,[13] conjugation with an aryl group,[10,14] an adjacent carbonyl group,[15] a nitrogen atom in an enamine,[11,14] and an oxygen atom in a vinyl ether.[10,17,18] A rather unusual reaction occurs when tosyl azide is allowed to react with certain enamines of the general formula IV(R = H, —C(O)R′, —CO_2R′, —C(O)NHR′).[19] The products are amidines V and a diazo compound.

$$TosN_3 + R'C(N){=}CHR \rightarrow R'C(N){=}NTos + RCHN_2$$

IV V

The data reported herein are concerned with the reactions of vinyl ethers with phosphorus azides. A vinyl ether (VI, n = 2) is known to react with *p*-nitrophenyl azide (VIIa) at 20° to give the Δ^2-1,2,3-triazoline VIIIa in almost quantitative yield.[10] Furthermore, whereas the photochemical reaction of 1,2-dihydropyran (VII, n = 3)

[10] R. Huisgen, *Angew. Chem.* (Internat. Edition) **2**, 562 (1963).
[11] R. Fusco, G. Bianchetti and D. Pocar, *Gazz. Chim. Ital.* **91**, 849, 933 (1961).
[13] K. D. Berlin and L. A. Wilson, *Chem. & Ind.* 1522 (1965).
[15] K. Alder and G. Stein, *Liebigs Ann.* **501**, 1 (1933).
[14] G. Bianchetti, *Gazz. Chim. Ital.* **94**, 340 (1964).
[16] W. I. Awad, S. M. A. R. Omran and F. Nagieb, *Tetrahedron* **19**, 1591 (1963).
[18] M. E. Munk and Y. K. Kin, *J. Amer. Chem. Soc.* **86**, 2213 (1964).
[17] J. E. Franz and C. Osuch, *Tetrahedron Letters* 837 (1963).
[18] I. Brown and O. E. Edwards, *Canad. J. Chem.* **43**, 1266 (1965).
[19] R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, *Chem. Ber.* **96**, 802 (1963).



(a) R = *p*-$C_6H_4NO_2$, n = 2; (b) R = —$CO_2C_2H_5$, n = 3.

and ethyl azidoformate (VIIb) gives an aziridine (IXb), the thermal reaction of the former two compounds follows a completely different course to give the reactive intermediate (Xb)[18]. A Δ^2-1,2,3-triazoline(VIIIb) has been proposed as an intermediate in the latter reaction. Heating the aziridine (IXb) and subsequent treatment with water yields XIb.

Norbornene and diethyl phosphorazidate were reported from this laboratory to give a triazoline.[20] Evidence in support of the structure was afforded by NMR analysis. Consequently, the possibility existed that vinyl ethers and phosphorus azides might lead to a new class of phosphorylated triazolines. In addition, with a simple ether structure a mechanistic evaluation of the transformation appeared more assailable. Thus, diethyl (XIIa) and dibutyl phosphorazidate (XIIb) were treated with isobutyl vinyl ether while XIIa and XIIc were allowed to condense with XIIId. The reaction proceeded very slowly (2–4 days) at the boiling temperature of the corresponding vinyl ether which served as solvent. Slow evolution of diazomethane occurred and consequently, a substituted Δ^2-1,2,3-triazoline was not isolated. The

$$\underset{\text{XII}}{R_2P(O)N_3} + \underset{\text{XIII}}{CH_2{=}CHOR'} \rightarrow \underset{\text{XIV}}{HCOR'(NP(O)R_2)} + CH_2N_2$$

(a) R = C_2H_5O
(b) R = C_4H_9O
(c) R = C_6H_5
(d) R′ = $(CH_3)_2CH$
(e) R′ = $(CH_3)_2CHCH_2$
(f) R = C_2H_5O, R′ = $(CH_3)_2CH$
(g) R = C_2H_5O, R′ = $(CH_3)_2CHCH_2$
(h) R = C_4H_9O, R′ = $(CH_3)_2CHCH_2$
(i) R = C_6H_5, R′ = $(CH_3)_2CH$

products (average yields were 50–80%) are believed to have the structure shown in XIV which fall in the general class of N-phosphorylated imidates (Table 1). Diazomethane formed and was characterized by reaction with benzoic acid to produce methyl benzoate. The common chemical and spectroscopic features of compounds XIV as well as the specific properties of each compound will be considered in the following sections.

Hydrolytic cleavage of the alkyl N-*phosphorylated imidates* (XIV). A rather unusual property of these phosphorus compounds is the ease with which hydrolysis can be effected to give formylphosphoramidates (XV) and alcohols. Exposure to the atmosphere or treatment with hot water was sufficient to promote hydrolytic carbon-oxygen bond severance.

[20] K. D. Berlin and L. A. Wilson, *Chem. Comm.*, No. 13, 280 (1965).

TABLE 1. SOME PHYSICAL PROPERTIES OF THE N-PHOSPHORYLATED IMIDATES

Compound	Yield %	B.p./mm	n_D (°C)	Found (Calculated)[b]				Formula
				C	H	N	P	
$(C_2H_5O)_2P(O)N{=}CHOCH(CH_3)_2$ XIVf	60	109–111°/2	1·4290 (31)	43·25 (43·0)	8·1 (8·06)	6·4 (6·3)	13·86 (13·9)	$C_8H_{18}NO_4P$
$(C_2H_5O)_2P(O)N{=}CHOCH_2CH(CH_3)_2$ XIVg	50	118–9°/2·5	1·4358 (22)	46·1 (45·6)	8·7 (8·4)	5·9 (5·9)	12·8 (12·8)	$C_9H_{20}NO_4P$
$(C_4H_9O)_2P(O)N{=}CHOCH_2CH(CH_3)_2$ XIVh	86 and 72	146–7°/2	1·4369 (32)	52·79 (53·2)	9·4 (9·6)	5·65 (4·8)	10·6 (10·6)	$C_{13}H_{28}NO_4P$
$(C_6H_5)_2P(O)N{=}CHOCH(CH_3)_2$[a] XIVi	15	190–3°/2·6						$C_{16}H_{18}NO_2P$

[a] No refractive index measurement or elemental analysis was done on this compound due to its extreme sensitivity to moisture and the presence of a small amount of impurity $[(C_6H_5)_2P(O)N_3]$ which was not removable by repeated distillation.

[b] The analyses of XIVg and h were difficult to obtain because of the hygroscopic nature of the compounds.

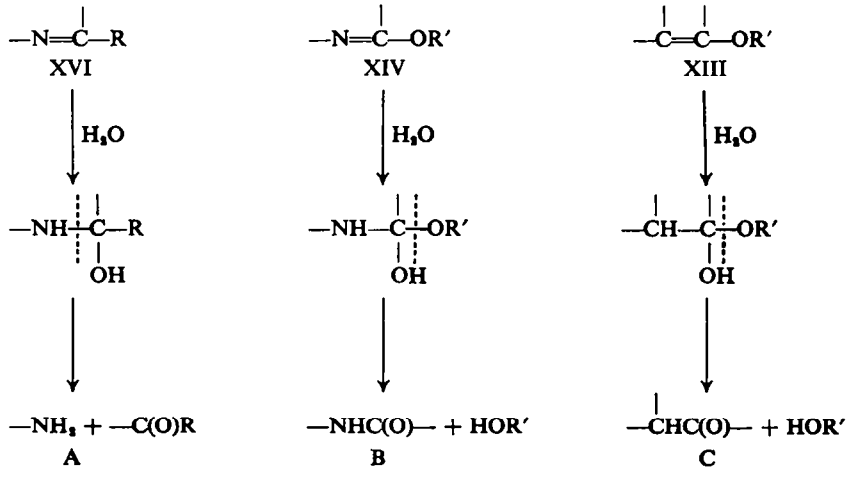
$$\underset{\text{XIV}}{HC(=NP(O)R_2)OR'} + H_2O \rightarrow \underset{\text{XV}}{R_2P(O)NHCHO} + R'OH$$

The ease of hydrolysis appeared to decrease in the order shown below.

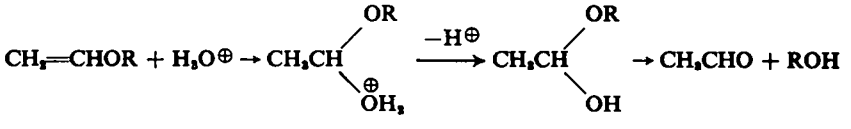
$$\text{XIVi} > \text{XIVf} > \text{XIVg} > \text{XIVh}$$

Characterization of the formylphosphoramidates (XV) will be treated separately.[21] Authentication of the alcohols was by means of IR and GLC analyses.

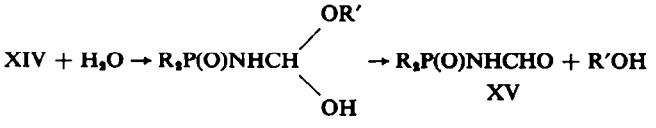
The hydrolysis of anils, such as XVI, usually yields primary amines and carbonyl compounds.[22] The fact that the N-phosphorylated imidates (XIV) gave XXI and R'OH and not $R_2P(O)NH_2$ and an alkyl formate, suggests that the behavior pattern is more like that found in hydrolysis of vinyl ethers (see schemes A, B, and C for comparison).



The acid-catalysed hydrolysis of straight-chain vinyl ethers has been described[23,24] to proceed *via* the intermediate formation of hemiacetals with the subsequent fission of the original vinyllic carbon-oxygen bond to yield aldehydes and alcohols.

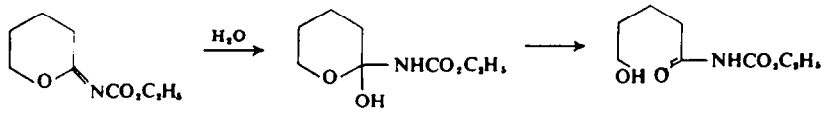


Hydrolysis of compounds XIV can be envisioned to occur in an analogous fashion.



[21] K. D. Berlin and M. A. R. Khayat, *Tetrahedron* **22**, 987 (1966).
[22] E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.* **85**, 2843 (1963).
[23] T. M. Fife, *J. Amer. Chem. Soc.* **87**, 1084 (1965).
[24] L. A. Kiprianova and A. F. Rekasheva, *Proc. Acad. Sci. U.S.S.R. (Chem. Section)* **142**, 56 (1962).

Additional support for the above mentioned reaction is found in the analogy involving hydrolysis of Xb to give XVIII *via* XVII.[18] The mode of hydrolysis apparently is characteristic of the system —O—C(=N—R)— when R has a phosphoryl group (as in XIV) or a carbonyl group (as in Xb) adjacent to the nitrogen atom.



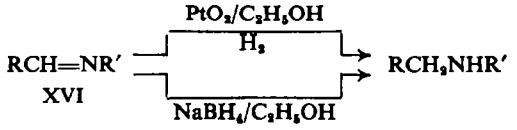
Xb XVII XVIII

Treatment of XIVh with dilute potassium hydroxide resulted in an extensive disproportionation of the molecule. *n*-Butanol and isobutyl alcohol were isolated and identified. Phosphate ion and formic acid were also detected in the mixture.

$$\text{XIVh} \xrightarrow[H_2O]{KOH} C_4H_9OH + (CH_3)_2CHCHOH + PO_4^{\equiv} + HCO_2H$$

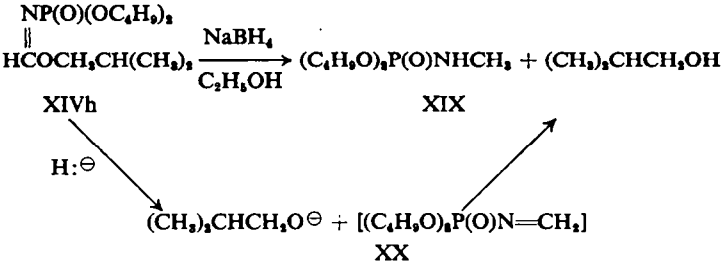
Similarly, when XIVf was subjected to the action of dilute base, ethanol, isopropyl alcohol, formic acid and phosphate ion were obtained and authenticated.

Reductive cleavage of XIV. Anils are easily hydrogenated to amines over metal catalysts or with metal hydrides as illustrated with XVI.[25,26] Two representative



members of the N-phosphorylated imidates in our series (XIVf and XIVh) were subjected to catalytic hydrogenation under strenuous conditions (Experimental). No appreciable amount of hydrogen uptake was observed. IR analysis of the recovered materials indicated the starting material was virtually unaffected. The resistance of the double bond in the system ≥P—N=C(—O—) towards catalytic reduction is not clear.

In contrast, the action of sodium borohydride on compound XIVh was smooth and provided XIX and the alcohol rather than the phosphorylated amine, $R_2P(O)NHCH_2CH_2OR'$. The mechanism of reduction may involve initial attack of the hydride ion on XIVh to displace isobutoxide ion. A logical intermediate XX[26]



[25] A. Roe and J. A. Montgomery, *J. Amer. Chem. Soc.* **75**, 910 (1953).
[26] Z. Horii, T. Sakai and T. Inoi, *J. Pharm. Soc. Japan* **75**, 1161 (1955); *Chem. Abstr.* **50**, 7756 (1956).

could be further reduced to the amidate but the presence of the former compound has not been definitely established.

The thermal stability of XIVh was surprising. The compound was recovered unchanged after it had been heated in boiling toluene for 45 hr under a dry and inert atmosphere.

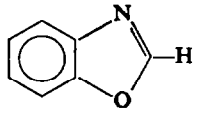
Spectral properties of XX. The freshly distilled compounds (XIVf–i) displayed characteristic bands in the IR spectra (Table 2). Strong absorption at 1639 cm^{-1} was

TABLE 2. IR SPECTRAL DATA FOR THE N-PHOSPHORYLATED IMIDATES

Compound	Assignment (cm^{-1})		
	N=C	P → 0	Misc. Bands
XIVf	1639	1250	1058, 1031, 980, 962
XIVg	1639	1250	1058, 1031, 980, 962
XIVh	1639	1250	1064, 1031, 980, 962
XIVi	1639	1250, 1212	1439(P–C_6H_5)

common to all members and was assigned to the N=C bond. Vinyl ethers[27] and anils[27,28] usually have strong bands in the region 1613–1667 cm^{-1}. The P → O band appeared at 1250 cm^{-1} while the P—O—C band was not clearly observable in the range 962–1064 cm^{-1} because of the overlap with C—O bands from ether linkage.[27]

The NMR spectra had characteristic doublets at low field (δ 8·10–8·35) which integrated for one proton in each case and was assigned to the vinyllic proton in XIVf–i. The coupling constants were in the range 15–17·5 c/s. The chemical shifts observed are consistent with that of a vinyl proton situated in a similar environment, e.g., the proton signal in XXI appears as a singlet at δ 8·07 in the same solvent.[29] The splitting of the proton signal in the system $\rangle$P—N=CH—O— is apparently



XXI

caused by the phosphorus atom and the value of the coupling constant is consistent with reported cases of J_{P-H} coupling[30] in structurally similar molecules. It is noteworthy that the signal at δ 4·0 (in XIVf) due to the methylene group in CH_3CH_2O—P, appeared as a quintet instead of a quartet. It has been suggested that the actual quartet in triethyl phosphite is further split by phosphorus and that the quintet is a

[27] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley, New York (1958).

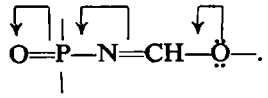
[28] V. Rosnati and D. Misiti, *Gazz. Chim. Ital.* **90**, 584 (1960); A. R. Katritzky and A. P. Ambler, *Physical Methods in Heterocyclic Chemistry* Vol. 2; pp. 186 and 218. Academic Press, New York (1963).

[29] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectral Catalog* spectrum number 147. Varian Associates, Palo Alto, California (1962).

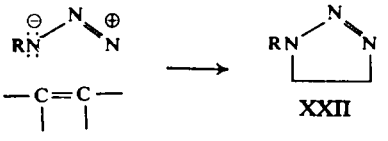
[30] G. Martin and A. Besnard, *C. R. Acad. Sci., Paris* **257**, 929 (1963).

result of the superimposition of the two quartets.[31] Signals corresponding to the other protons in the imidates are assembled in Table 3. A signal at approximately δ 2·3 was apparently due to a small amount of impurity since repeated distillation reduced its intensity (no change in the other peak heights) but did not remove it entirely.

The UV absorption spectra of the imidates (in ethanol or cyclohexane) did not reveal any significant absorption bands in the region 230–400 mμ. A poorly defined shoulder was observed at 222·5 mμ (ε = 6000). This suggests weak conjugation in the system



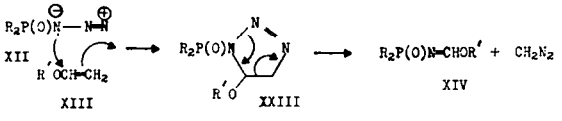
On the mechanism of formation of XIV. Several mechanisms have been put forward to explain the various results obtained by several investigators concerning the reactions of organic azides and alkenes.[8,10,11,19,32,33] A 1,3-dipolar addition of the azide group to the double bond can result in formation of Δ^2-1,2,3-triazoline represented by XXII. The stability and the course of the decomposition of the triazoline depends on various factors some of which have been mentioned earlier. Loss of nitrogen from XXII could give rise to an aziridine. Ring-opening and rearrangement of the



XXII

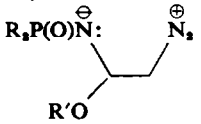
aziridine to give an anil or an enamine, are also conceivable.[34] An alternative route is a concerted loss of nitrogen and addition to the double bond to yield aziridine or, after rearrangement, an anil or an enamine.

In the reaction discussed in the present paper the azide (XII) and the vinyl ether (XIII) may give rise to the intermediate Δ^2-1,2,3-triazoline (XXIII). Immediate



XIII XXIII XIV

decomposition of the latter could result in formation of the imidates (XIV) and diazomethane. This is reminiscent of the reaction of tosyl azides with certain enamines cited previously.[19] Whether the decomposition is concerted as illustrated in XXIII or occurs *via* the zwitterion (XXIV) cannot be decided with the present evidence.



XXIV

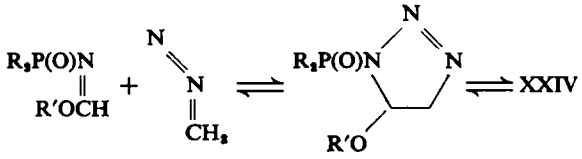
[31] J. D. Baldeschwieler and E. W. Randall, *Chem. Revs.* **63**, 81 (1963); Ref. 95.
[32] P. Walker and W. A. Waters, *J. Chem. Soc.* 1632 (1962).
[33] A. L. Logothetis, *J. Amer. Chem. Soc.* **87**, 749 (1965).
[34] The aziridine formed from norbornadiene and benzenesulfonyl azide rearranges on standing to a bicyclic enamine; see Refs 8 and 9.

TABLE 3. THE NMR DATA FOR THE N-PHOSPHORYLATED IMIDATES[a]

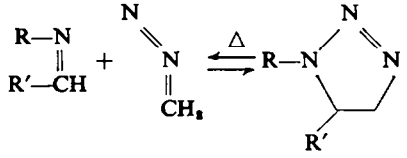
Compound	Chemical shift parameters (δ in ppm; J, c/s)							
	N=CH—O	C_6H_5	>CH—O	CH_2O	—CH<	CH_2CH_3	CH_3	$<^{CH_3}_{CH_3}$
XIVf	8·10 (d, J = 16)		5·22 (h, J = 6)	4·02 (q, J = 7)			1·29 (t, J = 7)	1·32 (d, J = 6)
XIVg	8·25 (d, J = 15·5)			4·05 (m)	2·0 (h, J = 7)		1·3 (t, J = 7)	0·97 (d, J = 6·5)
XIVh	8·15 (d, J = 15)			4·0 (m)	2·0 (h, J = 6·5)	1·55 (m)	1·0 (m)	1·0 (m)
XIVi	8·35 (d, J = 17·5)	7·41 and 7·92 (m)	5·28 (h, J = 6)					1·23 (d, J = 6)

[a] In CCl_4 with TMS as an internal reference; d, doublet; h, heptet; m, multiplet; q, quintet; t, triplet.

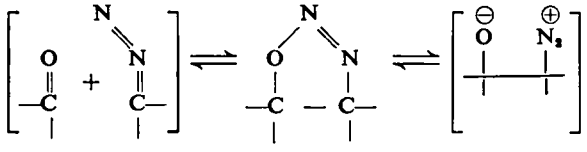
Furthermore, the possibility that a reversible process, of the type shown below, exists



cannot be ruled out. This situation is similar to the addition of diazomethane to anils which can be reversed upon heating,[35] and the addition of diazo compounds to alde-



hydes or ketones in which a reversible sequence (XXV ⇋ XXVI) has been suggested.[36]



XXV XXVI

In view of the products identified, it is logical that with the extended reaction times and the ease by which a phosphorylated triazoline may decompose below 100°,[20] an accumulation of a triazoline intermediate in the present system is unlikely or at least has escaped isolation and detection by the methods employed. Courtauld models do not imply the phosphorylated triazoline system should be geometrically distorted. The tentative conclusion is that powerful electron-withdrawing groups of which the P → O function is a member, inherently reduce the stability of attached triazoline systems probably by bond weaking through induction.

EXPERIMENTAL

All b.ps are uncorrected. The IR spectra were recorded as liquid films on a Beckman IR-5 spectrophotometer. The UV spectra were recorded on a Cary-14 spectrophotometer. The NMR spectra were taken (unless otherwise stated) in CCl_4 using a Varian instrument, Model A-60 spectrometer. The line positions were given in δ-values with TMS as an internal reference. GLC analysis was carried out on an A-550 Hy-Fi H_2-flame unit (produced by Wilkens Instrument, Inc., Walnut Creek, California). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Material. The azides were prepared from the corresponding disubstituted phosphorochloridates and sodium azide in acetone.[37] Diphenylphosphinic azide (from American Potash and Chemical Corporation) was employed without further purification. The vinyl ethers (from Matheson, Coleman and Bell) were freshly distilled before use.

[35] P. K. Kodaba and J. O. Edwards, *J. Org. Chem.* **26**, 2331 (1961).
[36] F. S. Brisdon-Jones, G. D. Buckley, L. H. Cross and A. P. Driver, *J. Chem. Soc.* 2999 (1951), F. Arndt and B. Eistert, *Ber. Detsch. Chem. Ges.* **68**, 193 (1935).
[37] F. L. Scott, R. Riordan and P. D. Morton, *J. Org. Chem.* **27**, 4255 (1962).

Dibutyl(isobutoxymethylene)phosphoramidate (XIVh)

The imidates XIVf–i (Table 1) were prepared by a general procedure as described below for XIVh.

The freshly distilled XIIb (24 g, 0·105 mole) was mixed with a large excess of the freshly distilled XIIIe (180 ml) and the solution was placed in a flask fitted with an efficient condenser. A continuous stream of N_2 was passed through the reaction mixture in order to sweep out diazomethane. The exit gases were passed through a solution of benzoic acid (15 g) in ether (250 ml). The reactants were heated at the b.p. of the vinyl ether (ca. 85°) until nearly all of the azide was consumed (50–60 hr). During these preparations, a white polymeric material (probably from a polymerization involving diazomethane) was always formed in a small amount and was discarded.

After the reaction was complete, the vinyl ether was distilled under normal press. and the remaining oil was fractionated under red. press. Distillation afforded XIVh (22 g; 72% yield based on the azide). A small amount of the azide was always recovered as the first fraction. The diazomethane thus obtained was characterized by reaction with benzoic acid and gave methyl benzoate (5·4 g; 38% yield).

Attempted catalytic hydrogenation of the imidates

(i) The imidate XIVf (2 g) in benzene (30 cc) was shaken with PtO_2 (0·2 g) under H_2 (3 atm.) at room temp for 4 hr. No H_2 was absorbed after the catalyst had been reduced and IR analysis showed the presence of unreacted starting material.

(ii) A solution of XIVh (1·2 g) in benzene (10 cc) was mixed with a suspension of Pd–C (5%; 0·2 g) in benzene (10 cc) and the mixture was shaken under 4 atm. of H_2 for 4 hr. No appreciable consumption of H_2 took place, and the imidate was recovered.

(iii) The previous experiment was repeated using H_2 under a press of 500–1000 psi and a temp of 80–100°. No hydrogenation occurred after 18 hr. The same result was obtained when rhodium on alumina (5%) was used as the catalyst and a H_2 press of 1000 psi and a temp of 100–120° were maintained for 4 hr.

Reductive cleavage of XIVh *with sodium borohydride*

Sodium borohydride (1·5 g, 0·04 mole) was added, in small portions, to a stirred solution of XIVh (8·5 g, 0·03 mole) in EtOH (15 ml). An exothermic reaction occurred with evolution of a gas. Stirring was continued for 9 hr; a white semi-solid material was formed and was decomposed with water. The aqueous solution was extracted several times with ether and the combined organic extracts were dried ($MgSO_4$). The volatile matter was distilled under red. press. and collected in a trap immersed in a dry ice–acetone bath. GLC analysis of the volatile mixture indicated the presence of isobutyl alcohol. The residual oil (6·4 ml; 95% yield) was distilled under red. press. giving XIX (5·5 g; 83% yield), b.p. 130–132°/0·25 mm, reported b.p. 116–119°/0·5 mm.

The identity of XIX was further confirmed by synthesis from dibutyl phosphorochloridate and methylamine.[38] The IR spectrum had bands at 3226(NH), 1235(P → O), and 1070–980 cm^{-1} (P–O–C); NMR, δ 5·40(NH), 4·16(CH_2O), 2·65(N–CH_3, a quartet as a result of splitting by H and P atoms in $\geq$P—NH—CH_3), 1·50(CH_2CH_2), and 0·90(CH_3).

The action of dilute base on the imidates

The XIVg (25 g, 0·1 mole) was mixed with a solution of KOH (21 g, 0·4 mole) in MeOH (100 ml). An exothermic reaction ensued (a rise of 20° in the temp of the mixture was observed). The mixture was heated at reflux for 1 hr. The solvent was distilled and the viscous residue thus obtained was brought to dryness by distilling the remaining liquid under red. press. The liquid collected (16 ml; Calc. 18·5 ml) was shown by IR and GLC analyses to contain EtOH and isobutanol. The solid (a mixture of KOH and K-salts) was dissolved in the minimum amount of water, made acidic, and extracted with ether. The ethereal layer was found to contain formic acid.[39] The presence of the phosphate ion was confirmed by testing the aqueous solution with ammonium molybdate.[40] The aqueous layer was warmed for several minutes and was made basic; ammonia vapours were immediately detected.

[38] A. C. Poshkus and J. E. Herweh, *J. Amer. Chem. Soc.* 79, 6127 (1957).
[39] F. Feigel, *Spot Tests in Organic Analysis* (5th English Edition) p. 34. Elsevier, New York (1956).
[40] J. Nordmann, *Qualitative Testing and Inorganic Chemistry* p. 392. J. Wiley, New York (1957).

The imidates XIVf and XIVh were treated with dilute base in a similar manner as that indicated above. The corresponding alcohols, ammonia, formic acid, and the phosphate ion thus obtained were identified as described above.

By employing aqueous, instead of methanolic, KOH, the same results were obtained.

Hydrolytic cleavage of XIVf

Compound XIVf (20 g; 0·08 mole) was shaken with warm water (60 ml) until the reaction was complete (1–2 hr), judged by examining the IR spectrum of the product in the complete disappearance of the band at 1639 cm^{-1} (due to N=C) and the appearance of a strong band at 1709 cm^{-1} (due to C=O). The reaction mixture was extracted with ether several times and the combined organic extracts dried ($MgSO_4$). The volatile matter was distilled and was found to contain isopropyl alcohol (by GLC analysis). The residual oil was fractionated under red. press. and gave XVa, b.p. 134·5–135°/0·25 mm; yield, 8·5 g (56%).[21]

The other two imidates XIVh and XIVg were similarly hydrolyzed to give XVb[21] and XVa,[21] respectively. Isobutanol, the other hydrolysis product from these two imidates, was identified by GLC.