Results and Discussion

The results are given in Table I. The liquid-phase composition is expressed in terms of weight percent; the solid phase is, in any investigated condition, anhydrous sodium formate. Three determinations were made at least for each data point and we have reported the significant digits of the averages.

Figure 1 is a semiquantitative description of the total phase diagram HCOONa–NaOH–H_2O based on the knowledge of binary systems (*1*, *2*). It is a triangle diagram in which the compositions on the coordinates are taken from literature data and the compositions at 21, 60, and 120 °C are experimental values. Similar to other phase diagrams (salt–strong base–water), a large range of pure solid HCOONa existence can be predicted.

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NEW COMPOUNDS

Hydrazinophosphorus Compounds. 2. Mass Spectra of Diphenylphosphino- and Diarylphosphorohydrazides

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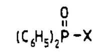
The mass spectra of diphenylphosphino- and diarylphosphorohydrazides have been examined. Diphenylphosphinohydrazide (Ia) behaves in a manner comparable to derivatives having the diphenylphosphinyl moiety (Ib–e). The molecular ion of diarylphosphorohydrazides (IIa,b), on the other hand, undergos fragmentation to give the corresponding phenol as a base peak.

Whereas the behavior of organophosphorus compounds under electron impact has been extensively investigated, this is clearly reflected in the recent review published by Granoth in this field (*3*), a general study on the hydrazinophosphorus compounds has not been reported hitherto.

As a corollary to our interest in the reactivity of hydrazinophosphorus compounds (*2*), we wish to report the behavior of diphenylphosphino- and diarylphosphorohydrazides under electron impact.

It has been well established (*4*) that although the phosphine oxides (Ib,c) and the phosphinate (Id) give ions of mass 201 as base peak, arising by the loss of group X (I), the spectrum of benzylphosphinate (Ie) has ions of mass 202 as base peak, arising by the elimination of benzaldehyde from the molecular ion and the 201 ion is of rather low intensity (15%).



$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}-X$$

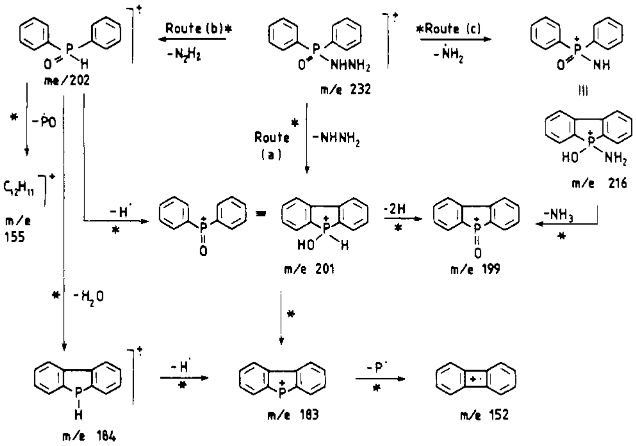
(I)

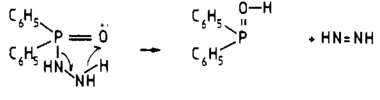
a; X = $NHNH_2$
b; X = H   d; X = OC_6H_5
c; X = $CH_2C_6H_5$ e; X = $OCH_2C_6H_5$

The most interesting feature of the mass spectrum of diphenylphosphinohydrazide (Ia) (Figure 1) is that it shows both ions 201 and 202, the former ions being the base peak and the latter the next most abundant (90%). Most of the peaks observed at the lower mass result from fragmentation of these two species (*7*).

A common feature between the hydrazide (Ia) and the ester (Ie) is the presence of hydrogens on an atom *β* to phosphorus. Both yield the *m*/*q* 202 ion as a base peak. Compounds without *β* hydrogens do not behave similarly. A possible mechanism for the formation of *m*/*q* 202 ion might be through a hydrogen transfer in the molecular ion via a five-membered cyclic transition state as follows:

Scheme I





The molecular ion of the hydrazide (Ia) undergoes fragmentation via three routes; the decomposition pathways which account for all the abundant ions and metastable transitions (marked with an *) are summarized in Scheme I.

Route (a) involves the formation of the phosphacylium ion (M − 31) by the loss of the hydrazine moiety. In this case it behaves like the benzylphosphine oxide (Ic) and the phenoxyphosphinate (Id). This route is supported by the appearance of a weak metastable peak at *m*/*q* 174.5. Route (b) involves the formation of 202 ion (M − 30), similar to the behavior of the benzyloxy ester (Ie). The appearance of a strong metastable ion at *m*/*q* 176.1 supports this route. This indicates that both 201 and 202 ions

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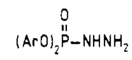
Figure 1. Mass spectrum of diphenylphosphinohydrazide (Ia).

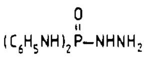
must certainly be quite stable and ions of *m/q* are produced from the loss of the hydrazine moiety from the molecular ion (route a). A second route to ions 201 is during the transition *m/q* 202 → 201, via loss of H. The latter process is established by an appropriate strong metastable peak at *m/q* 200. Route (c) involves the break of the N–N bond to give ions of mass 216 (19.5%) which lose a molecule of ammonia to give ions 199. The elimination of ammonia from ions of mass 216 is apparently preceded by rearrangement to the cyclic form. These steps are authenticated by the presence of metastable ions at 201.5 and 183.4, respectively.

The modes of dissociation of diphenylphosphinohydrazide (Ia) and diarylphosphorohydrazides (II) differ considerably from one another. While the base peak for the former is being formed by the extrusion of the hydrazide moiety, the base peak for the diarylphosphorohydrazides (II) is the corresponding phenol. This is formed by rearrangement of hydrogen and decomposition of the molecular ion. This process could be partially thermal decomposition in the source.



$$(ArO)_2P(=O)-NHNH_2$$

(II)



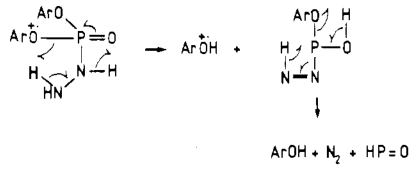
$$(C_6H_5NH)_2P(=O)-NHNH_2$$

(III)

a; Ar = C_6H_5

b; Ar = p-$CH_3C_6H_4$

The mass spectra of diphenyl- and di-*p*-tolylphosphorohydrazides are simple and show only two intense peaks, M^+ and $(ArOH)^+$, the latter being the base peak. The mass spectra of (IIa,b) are shown in Figure 2. Most of the peaks observed at lower mass result from fragmentation of the phenol ions. The fragmentation of molecular ions of IIa,b to the corresponding phenol is confirmed by the appearance of the relavent metastable peaks (m^+ obsd 33.5, calcd 33.48; (m^+ obsd 40.4, calcd 39.95). A possible mechanism for the main fragmentation of IIa,b to give mainly phenol might be:



The behavior of diarylphosphorohydrazides (II) under electron impact is similar to that of the hydrazido-nitrogen counterpart (III), *N*,*N*-diphenylphosphorodiamidic hydrazide, which showed aniline as a base peak (*6*).

Experimental Section

The preparation of diphenylphosphino- (Ia) and diphenylphosphorohydrazide (IIa) has been reported (*1*, *5*). Di-*p*-tolylphosphorohydrazide (IIb) was similarly prepared in (60%) yield by condensation of the corresponding phosphorochloridate with hydrazine hydrate; mp 125 °C. Anal. Calcd for $C_{14}H_{17}N_2O_3P$: N, 9.58. Found: N, 9.78. IR (KBr): 3340 (NH), 1200 (P=O), and 995 cm^{-1} (P-OAr). Mass spectrum *m/q* 292 (parent).

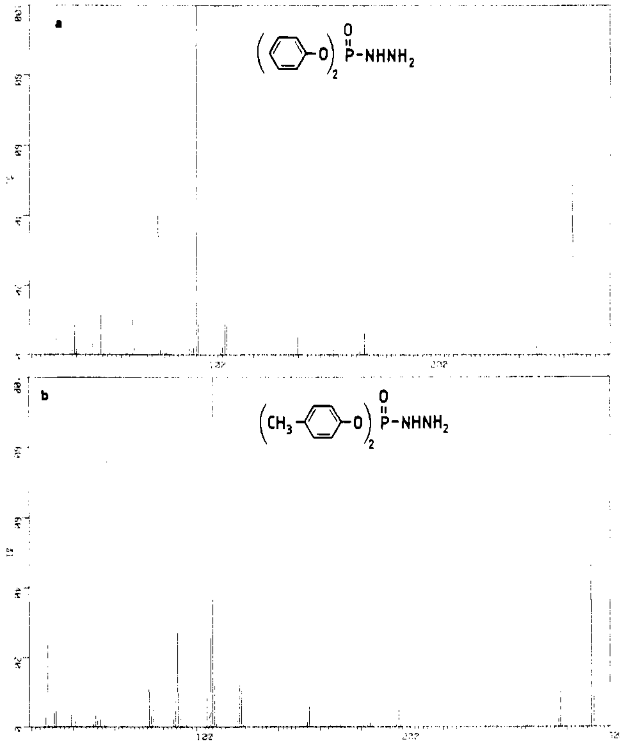


Figure 2. (a) Mass spectrum of diphenylphosophorohydrazide (IIIa). (b) Mass spectrum of di-*p*-tolylphosphorohydrazide (IIIb).

Mass spectra were obtained with a DuPont 21-492 B mass spectrometer. A 2–4 mg sample of the hydrazide was dissolved in 1.0 mL of methanol, and a suitable aliquot to allow 2–4 μg for analysis was taken. After the solvent was removed in vacuo, the samples were analyzed by direct probe and an ionizing voltage of 75 eV. Source temperature was 260 °C and the direct probe temperatures for compounds Ia, IIa, and IIb, were 170–190, 125–140, and 130–150 °C, respectively.

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