Hydrazinophosphorus Compounds. 1. Synthesis of Phosphoro- and Phosphinohydrazones of Substituted 1-Tetralones

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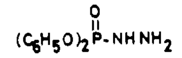
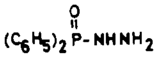
The diphenylphosphorohydrazones (IV) and diphenylphosphinohydrazones (V) of methoxy-1-tetralones (IIIa–d) have been prepared and characterized. Infrared and NMR data on these new compounds are included.

Recent interest in the chemistry of hydrazinophosphorus compounds (*2*, *3*, *5–7*, *9*) prompts this study. The investigation described in this publication is concerned with the reactions of diphenylphosphorohydrazidate (I) and diphenylphosphinohydrazidate (II).

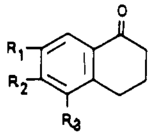

$(C_6H_5O)_2P(=O)\text{-}NHNH_2$

(I)


$(C_6H_5)_2P(=O)\text{-}NHNH_2$

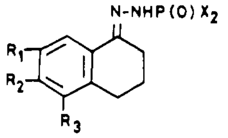
(II)

These compounds behave as a typical hydrazide and react with 1-tetralones (IIIa–d) to yield the corresponding hydrazones (IVa–d and Va–d).



(III)

	R_1	R_2	R_3
a-	H	H	H
b-	H	CH_3O	H
c-	CH_3O	CH_3O	H
d-	CH_3O	CH_3O	CH_3O



IV, $X = C_6H_5O$

V, $X = C_6H_5$

The structure of these hydrazones was confirmed by infrared and proton magnetic resonance (Table I). In the infrared spectra the phosphorohydrazones (IVa–d) showed a strong band in the region 1220–1250 cm^{-1} arising from the P=O stretching vibration whereas the P=O absorption for the phosphinohydrazones (Va–d) has shifted to lower frequencies 1195–2000 cm^{-1}.

The NMR spectra of these hydrazones were consistent with the assigned structures. A comparison of the NMR spectra (Figure 1) of the phosphorohydrazones (IVa–d) with those of the analogous phosphinohydrazones (Va–d) showed that in compounds Va–d two CH_2 triplet peak groups coalesce in one large triplet peak, i.e., one CH_2 group shifted downfield. Also, in the aromatic region of the spectra there are downfield shifts of the protons in the ortho positions of the phenyl groups which are attached directly to phosphorus and coalesce on the doublet of the H–N–P proton. The aromatic region of the spectra of compounds Va–d is, therefore, complicated. However, in phosphorohydrazones (IVa–d) the observed coupling constants (J_{PNH}) between the phosphorus atom and the α proton of the hydrazino group were high (30 Hz). It was of slightly higher order (5 Hz) to that recorded (*3*) for the phosphoramidic hydrazones.

All the hydrazones, IVa–d and Va–d, are new crystalline compounds. The ease by which they obtained may be used for the identification of the substituted methoxy-1-tetralones (IIIa–d). A comparison of their melting points (Table II) reveals that the phosphinohydrazones (Va–d) have higher melting points than the corresponding phosphorohydrazones (IVa–d).

Table I. IR and NMR Spectral Data for the Hydrazones

	IR absorption spectra in KBr, cm^{-1}			
compd	ν-(P=O)	ν-(C=N)	ν(NH)	^{1}H NMR spectral assignments, chemical shifts, δ
IVa	1257	1582	3125	1.77 (qt, CH_2, 2 H) 2.32 (t, CH_2, 2 H) 2.64 (t, CH_2, 2 H) 6.94-7.44 (m, Ar-H, 13) 8.04 (s, ArH, 1 H) 8.17 (d, J_{PNH} = 30 Hz, NH, 1 H)
IVb	1250	1582	3086	1.80 (qt, CH_2, 2 H) 2.30 (t, CH_2, 2 H) 2.69 (t, CH_2, 2 H) 3.86 (s, OCH_3, 3 H) 6.56 (s, ArH, 1 H) 7.00-7.36 (m, ArH, 11 H) 7.56 (s, ArH, 1 H) 7.55 (d, J_{PHN} = 30 Hz, NH, 1 H)
IVc	1250	1582	3106	1.80 (qt, CH_2, 2 H) 2.29 (t, CH_2, 2 H) 2.69 (t, CH_2, 2 H) 3.86 (s, OCH_3, 6 H) 6.56 (s, ArH, 1 H) 7.00-7.36 (m, ArH, 10 H) 7.56 (s, ArH, 1 H) 7.65 (d, J_{PHN} = 30 Hz, 1 H)
IVd	1269	1592	3155	1.76 (qt, CH_2, 2 H) 2.29 (t, CH_2, 2 H) 2.63 (t, CH_2, 2 H) 3.82 (s, OCH_3, 3 H) 3.86 (s, OCH_3, 3 H) 3.89 (s, OCH_3, 3 H) 6.98-7.34 (m, ArH, 10 H) 7.42 (s, ArH, 1 H) 7.71 (d, J_{PNH} = 30 Hz, NH, 1 H)
Va	1197	1602	3067	1.80 (qt, CH_2, 2 H) 2.60 (qt, CH_2, 4 H) 6.80-7.12 (m, ArH, 3 H) 7.20-7.54 (m, ArH, 6 H) 7.60-8.06 (m, ArH and NHP, 6 H)
Vb	1193	1597	3030	1.85 (qt, CH_2, 2 H) 2.59 (qt, CH_2, 4 H) 3.70 (s, OCH_3, 3 H) 6.48-6.62 (m, ArH, 1 H) 7.14-7.60 (m, ArH, 7 H) 7.62-8.08 (m, ArH and NHP, 6 H)
Vc	1199	1602	3030	1.87 (qt, CH_2, 2 H) 2.56 (qt, CH_2, 4 H) 3.62 (s, OCH_3, 3 H) 3.80 (s, OCH_3, 3 H) 6.46 (s, ArH, 1 H) 7.18 (s, ArH, 1 H) 7.22-7.66 (m, ArH, 7 H) 7.76-8.08 (m, ArH and NHP, 4 H)
Vd	1199	1577	3067	1.83 (qt, CH_2, 2 H) 2.59 (qt, CH_2, 4 H) 3.62 (s, OCH_3, 3 H) 3.78 (s, OCH_3, 3 H) 3.84 (s, OCH_3, 3 H) 7.06 (s, ArH, 2 H) 7.28-7.48 (m, ArH, 6 H) 7.68-8.06 (m, ArH and NHP, 4 H)

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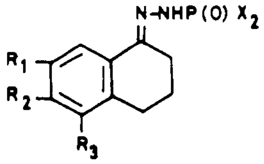
Table II. Physical and Chemical Data



compd	R_1	R_2	R_3	X	mp, °C	formula	analysis, % N calcd	analysis, % N found
IVa	H	H	H	C_6H_5O	170-172	$C_{22}H_{21}N_2O_3P$	7.14	6.98
IVb	H	CH_3O	H	C_6H_5O	148-149	$C_{23}H_{23}N_2O_4P$	6.63	6.45
IVc	CH_3O	CH_3O	H	C_6H_5O	138-140	$C_{24}H_{25}N_2O_5P$	6.19	5.97
IVd	CH_3O	CH_3O	CH_3O	C_6H_5O	162-163	$C_{25}H_{27}N_2O_6P$	5.81	5.84
Va	H	H	H	C_6H_5	195-196	$C_{22}H_{21}N_2OP$	7.77	7.58
Vb	H	CH_3O	H	C_6H_5	210-211	$C_{23}H_{23}N_2O_2P$	7.17	7.01
Vc	CH_3O	CH_3O	H	C_6H_5	260-262	$C_{24}H_{25}N_2O_3P$	6.66	6.49
Vd	CH_3O	CH_3O	CH_3O	C_6H_5	216-218	$C_{25}H_{27}N_2O_4P$	6.22	6.06

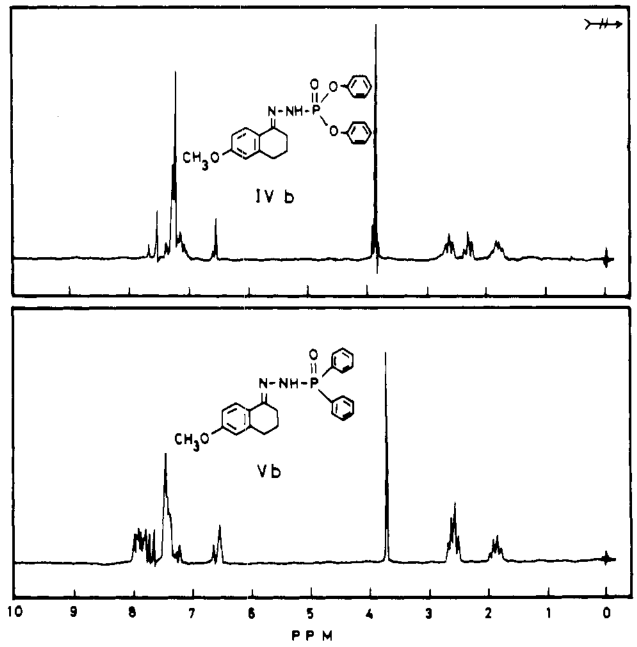


Figure 1. ^1H NMR spectra of compounds IVb and Vb.

Experimental Section

Melting points (Table II) were obtained with a Thomas Hoover melting point apparatus and were uncorrected. Infrared spectra were recorded on a Beckman IR-5A unit as KBr pellets. NMR spectra were obtained with a XL-100 (*15*) Varian spectrometer in $DCCl_3$. The methoxy-1-tetralones required for this investigation were synthesized by the method reported earlier (*8*). Phosphor- and phosphinohydrazides were prepared by condensation of the corresponding chloridate with hydrazine hydrate as previously described (*1*, *4*).

In the preparation of the hydrazones, the hydrazide (0.01 mol) was boiled under reflux with the appropriate carbonyl compound (0.01 mol) in ethanol (50 mL) for 2 h. The hydrazones generally separated from the cool concentrated solution and were collected and recrystallized from ethanol.

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