Filtration of the copper sulfide followed by evaporation of the methanol afforded pure hydroxamic acid.

Acknowledgment

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Hydrazinophosphorus Compounds. 5. Reaction of 1,3-Dicarbonyl Compounds with Diarylphosphoro- and Diphenylthiophosphinohydrazides

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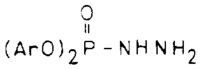
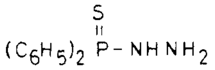
1,3-Dicarbonyl compounds (III) reacted with the phosphorus hydrazides to give the corresponding hydrazones. When the hydrazones of ethylacetoacetate were heated at their melting points, they were converted to the corresponding pyrazolin-5-ones. The spectral characteristics of these pyrazolinones were studied.

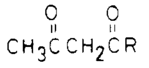
As the result of an effort (*1*, *2*) to further expand the field of organophosphorus hydrazide chemistry, we report in this paper the reaction of 1,3-dicarbonyl compounds with diarylphosphorohydrazides (I) and diphenylthiophosphinohydrazide (II).


$(\mathrm{ArO})_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{-NHNH_2}$

(I)


$(\mathrm{C_6H_5})_2\overset{\mathrm{S}}{\overset{\|}{\mathrm{P}}}\mathrm{-NHNH_2}$

(II)


$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$

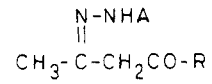
(III)

a, Ar = C_6H_5
b, Ar = $p\text{-}CH_3C_6H_4$

a, R = CH_3
b, R = C_6H_5
c, R = OC_2H_5

The 1,3-dicarbonyl compounds used (III) were acetylacetone, benzoylacetone, and ethylacetoacetate.

The hydrazinophosphorus compounds (I and II) behave as a typical hydrazide and react with an equimolar amount of the dicarbonyl compounds (III) to yield the corresponding hydrazones (IV) (cf. Table I).

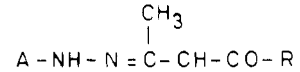

$\mathrm{CH_3\text{-}}\overset{\mathrm{N\text{-}NHA}}{\overset{\|}{\mathrm{C}}}\mathrm{\text{-}CH_2CO\text{-}R}$

(IV)

A = $(C_6H_5O)_2P=O$, $(p\text{-}CH_3C_6H_4O)_2P=O$, $(C_6H_5)_2P=S$
R = CH_3, OC_2H_5, C_6H_5

Correct analytical data were in support of the structures of these hydrazones (IV). Besides, the IR measurements showed absorption bands around 1600 cm^{-1} attributed to the C=N stretching. The P=O absorption of the phosphorohydrazones (IVa–f) appeared around 1200 cm^{-1} (*3a*) while the P=S absorption appeared at 700 cm^{-1} (*3b*).

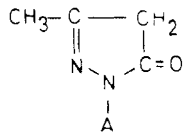
Table I. Physical Data


$\mathrm{A\text{-}NH\text{-}N=}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{\text{-}CH\text{-}CO\text{-}R}$

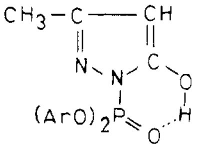
compd	A^a	R	mp, °C
IVa	A_1	CH_3	82-84
IVb	A_1	C_6H_5	102-103
IVc	A_1	OC_2H_5	79-80
IVd	A_2	CH_3	89-90
IVe	A_2	C_6H_5	140-142
IVf	A_2	OC_2H_5	69-71
IVg	A_3	CH_3	200-202
IVh	A_3	C_6H_5	134-135
IVk	A_3	OC_2H_5	111-112

^{a} $A_1 = (C_6H_5O)_2P=O$, $A_2 = (p\text{-}CH_3C_6H_4O)_2P=O$, $A_3 = (C_6H_5)_2P=S$.

In 1968, Abramov et al. (*4*) reported the synthesis of phosphorylated pyrazolin-5-one (Va) from the corresponding hydrazone (IVc). However, Abramov gave no real proof of structure, stating only that the IR spectrum confirmed the structure. In the present study, we have studied the cyclization of the hydrazones (IVc,f,k), and the structures of the corresponding



(V)



(V')

a, A = $(C_6H_5O)_2P=O$
b, A = $(p\text{-}CH_3C_6H_4O)_2P=O$
c, A = $(C_6H_5)_2P=S$

a, Ar = C_6H_5
b, Ar = $p\text{-}CH_3C_6H_4$

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Table II. IR and NMR Spectral Data

compd	IR absorption spectra, cm^{-1}	NMR chemical shifts, δ	
		^{31}P	^{1}H
Ia	3310 (N-H) 1190 (P=O) 995 (P-OAr)	−1.61	3.25 (s, NNH_2, 2 H) 5.25 (d, J_{NH} = 35 Hz, NH, 1 H) 7.26 (m, ArH, 10 H)
Ib	3310 (N-H) 1200 (P=O) 990 (P-OAr)	−0.06	2.26 (s, CH_3, 6 H) 3.40 (s, broad, NNH, 2 H) 5.26 (d, J_{PNH} = 35 Hz, 1 H) 7.10 (s, ArH, 8 H)
IVc	1600 (C=N) 1180 (P=O) 985 (P-OAr)	−11.5	1.30 (t, CH_3 (ester), 3 H) 1.80 (s, CH_3C=N, 3 H) 3.30 (s, CH_2, 2 H) 4.20 (qt, CH_2 (ester), 2 H) 7.30 (m, ArH and NH, 11 H)
IVf	1600 (C=N) 1190 (P=O) 985 (P-OAr)	−5.7	1.30 (t, CH_3 (ester), 3 H) 1.80 (s, CH_3C=N, 3 H) 2.30 (s, CH_3Ph, 6 H) 3.35 (s, CH_2, 2 H) 4.20 (qt, CH_2 (ester), 2 H) 7.16 (s, ArH, 8 H) 7.25 (d, J_{PNH} = 35 Hz, P-NH, 1 H)
Va	3250 (OH) 1180 (P=O) 980 (P-OAr)	−18.2	1.94 (d, CH_3, 3 H) 5.44 (d, CH=, 1 H) 7.10 (m, ArH, 10 H) 13.62 (s, broad, OH, 1 H)
Vb	3250 (OH) 1185 (P=O) 970 (P-OAr)	−17.3	2.10 (s, CH_3, 3 H) 2.20 (s, CH_3Ph, 6 H) 5.72 (s, CH=, 1 H) 7.10 (s, ArH, 8 H) 10.35 (s, broad, OH, 1 H)

pyrazolin-5-ones were determined.

Heating the hydrazones (IVc,f,k) at their melting points for 1 h without solvent yielded a colorless viscous oil which solidified slowly when kept at room temperature after trituration with petroleum ether. Comparing the ^{1}H NMR spectra (Figure 1) of the product pyrazolin-5-ones (Va,b) with those of the parent hydrazones (IVc,e) revealed the absence of the ethyl alcohol moiety from the spectra of the pyrazolinones (Va,b). Besides, ^{31}P NMR chemical shifts, IR, and analytical data (cf. Table II) support compounds V. Pyrazolin-5-one Vc could not be isolated in analytically pure form.

Interestingly, pyrazolin-5-ones (Va,b) exist predominantly in the OH tautomeric form (V′) which is stabilized by a hydrogen-bonded chelated ring. This is supported by the absence of the C═O absorption in the IR spectra and the appearance of a band at ~1485 cm^{-1} due to the group C═C—OH. The ^{1}H NMR also shows signals at δ 11 and 13 for Va and Vb due to the OH, respectively.

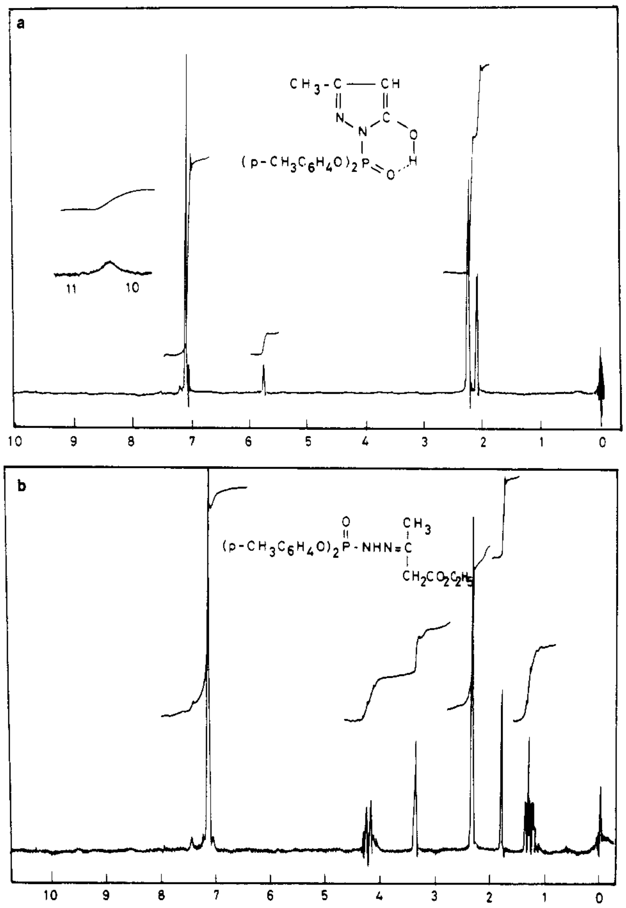


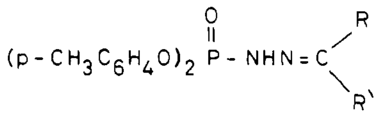
Figure 1. ^{1}H NMR spectra.

Di-*p*-tolylphosphorohydrazide (Ib) was prepared by the reaction of the corresponding chloride with a benzene suspension of hydrazine hydrate and was characterized as a hydrazide by conversion into a number of aldehyde and ketone derivatives (VI), $(p\text{-}CH_3C_6H_5O)_2P(O)NHN{=}CRR'$ (cf. Table III).

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-5A unit as KBr pellets. ^{1}H NMR spectra were obtained with JEOL-100 and EM-390 spectrometers in $DCCl_3$. ^{31}P NMR spectra were measured on a JEOL JNM-FX 60 Fourier transform NMR spectrometer, and shifts are given in ppm. Positive values are downfield from the reference (85% H_3PO_4).

Table III. Physical and Chemical Data



$$(p\text{-}CH_3C_6H_4O)_2\overset{O}{\overset{\|}{P}}\text{-}NHN{=}C\begin{matrix}R\\R'\end{matrix}$$

compd	R	R′	mp, °C	formula	analysis			
					%N		%P	
					calcd	found	calcd	found
VIa	C_6H_5	H	132–133	$C_{21}H_{21}N_2O_3P$	7.36	7.11	8.15	8.10
VIb	*p*-ClC_6H_4	H	158–159	$C_{21}H_{20}N_2O_3PCl$	6.76	6.79	7.47	7.44
VIc	*m*-$NO_2C_6H_4$	H	150–151	$C_{21}H_{20}N_3O_5P$	9.88	9.92	7.29	7.40
VId	*p*-$NO_2C_6H_4$	H	161–162	$C_{21}H_{20}N_3O_5P$	9.88	9.89	7.29	7.45
VIe	*o*-HOC_6H_4	H	178–180	$C_{21}H_{21}N_2O_4P$	7.07	6.91	7.83	8.01
VIf	*p*-HOC_6H_4	H	170–171	$C_{21}H_{21}N_2O_4P$	7.07	6.90	7.83	8.05
VIg	*p*-$CH_3OC_6H_4$	H	182–184	$C_{22}H_{23}N_2O_4P$	6.83	6.93	7.56	7.30
VIh	$C_{10}H_7$	H	124–125	$C_{25}H_{23}N_2O_3P$	6.51	6.33	7.20	6.99
VIi	$C_{14}H_9$	H	158–159	$C_{29}H_{25}N_2O_3P$	5.83	5.90	6.46	6.60
VIk	CH_3	CH_3	154–155	$C_{17}H_{21}N_2O_3P$	8.43	8.54	8.20	8.30

***Di-p-tolylphosphorohydrazide* (*Ib*).** Over a 2-h period, 0.1 mol of di-*p*-tolylphosphorochloride in 25 mL of benzene was added with stirring to a suspension of (0.25 mol) 95% hydrazine in 100 mL of benzene. The mixture then was refluxed for 3 h, cooled, and filtered. The colorless solid was washed with water and then crystallized from ethanol: mp 125 °C.

In the preparation of the hydrazones (IV and VI), the hydrazides (0.01 mol) were 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 recrystallized from ethanol. Analysis and IR spectral data supported the structures Ib, IV, and VI.

***Preparation of the Pyrazolin-5-ones* (*V*).** Acetylacetone hydrazones (IVc,f,k) (1 g) were heated at their melting points for 1 h and then allowed to cool. The viscous oil was triturated with petroleum ether and left for 12 h, whereby a crystalline precipitate was formed. It was removed by filtration and crystallized from ethanol. The pyrazolin-5-one of compound IVk did not crystallize out, and all of the trials to isolate it in analytically pure form failed (melting points (°C): Va, 114–115; Vb, 123–124).

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Reactions with (Arylmethylene)cycloalkanones. 5.[†] Synthesis of 2-Acetyl-5-aryl-5,6,7,8,9,10-hexahydrocyclohepta[*d*]thiazolo[3,2-*a*]pyrimidin-3(2*H*)-ones of Probable Biological Activity

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Cyclohepta[*d*]pyrimidine-2-thiones (III) were prepared by heating 2-(arylmethylene)cycloheptanones with thiourea in ethanolic potassium hydroxide. Compounds III reacted with chloroacetic acid in acetic anhydride to yield the title compounds (IV). Compounds IV condensed with the aromatic aldehydes to yield the 2-(arylmethylene) derivatives V. Also, the 2-(arylhydrazono) derivatives VI were prepared.

In continuation of our previous work on cyclooctanone (*4*), we now report on the synthesis of an analogous series involving the 2-(arylmethylene)cycloheptanone (*1*, *2*). (See Scheme I.) The structures of III–VI are substantiated by IR, UV, MS, and NMR.

Experimental Section

***2-(Arylmethylene)cycloheptanone* (*II*).** The 2-(arylmethylene) derivatives (IIa) are known in the literature (*2*). In this work the arylmethylene derivatives are prepared in ~80% yield as follows.

To a mixture of 11 g (0.1 mol) of cycloheptanone and 10.6 g (0.066 mol) of the appropriate aldehyde was added aqueous potassium hydroxide (4 g of KOH in 70 mL of H_2O). The mixture was refluxed for 12 h, allowed to cool, and then acidified with dilute HCl. The 2-(arylmethylene) derivatives were extracted with methylene chloride. The extract was dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude pale yellow oil (~80%) was used as such.

***4-Aryl-9H-1,2,3,4,5,6,7,8-octahydrocyclohepta[d]pyrimidine-2-thiones* (*III*).** A mixture of 0.02 mol of the crude 2-(arylmethylene)cycloheptanone (II), 1.5 g of thiourea, and 2 g of potassium hydroxide in 100 mL of ethanol and refluxed for 3 h. The mixture was allowed to cool, and then 50 mL of water was added, whereupon a white precipitate appeared. The product was filtered, washed with water, and crystallized from the proper solvent (see Table I).

Table I. 4-Aryl-9*H*-1,2,3,4,5,6,7,8-octahydrohepta[*d*]pyrimidine-2-thiones (III)[a]

compd	mp, °C	solvent[b]	yield, %
IIIa	190	M	70
b	191	M	68
c	188	M	72
d	200	M	75
e	190	P	70

[a] Elemental analyses in agreement with theoretical values were obtained. [b] Solvent key: A = acetic acid, E = ethanol, M = methanol, P = petroleum ether 60/80, NH = normal hexane.

Table II. 2-Acetyl-5-aryl-5,6,7,8,9,10-hexahydrohepta[*d*]thiazolo[3,2-*a*]pyrimidin-3(2*H*)-ones (IV)[a]

compd	mp, °C	solvent	yield, %
IVa	200	M	78
b	130	M	70
c	240	M	65
d	175	M	65
e	160	M	70

[a] See footnotes of Table I.

The infrared spectra of compounds III show bands assignable to NH (3250 cm^{-1}) and N—C═S (1640 cm^{-1}). The mass spectrum of compound IIIa showed the molecular ion peak (M^+) at *m*/*e* 258 (10%) and the base peak at *m*/*e* 181. The ^{1}H NMR spectrum of compound IIIa (in $CDCl_3$) showed the protons of the cycloheptene ring (10 H) as a multiplet in the δ 0.75–2.45 region, and the methine proton (a) as a singlet at δ

[†] For part 4, see ref *4*.

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