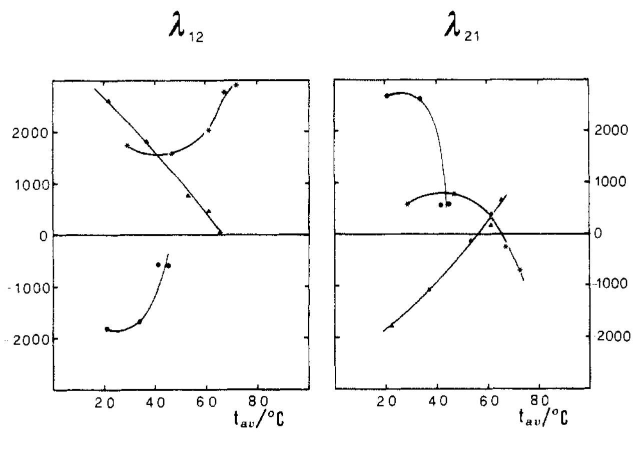

Figure 2. Values of the parameters λ_{12} and λ_{21} of the Wilson equation as a function of the average temperature in the isobaric groups of the vapor-liquid data for the binary mixtures of 1,3-dioxolane with (●) dichloroethylene, (▲) trichloroethylene, and (*) tetrachloroethylene.

7.7597, $B = -1754.4$; tetrachloroethylene, $A = 7.5966$, $B = -1855.3$. The vapor pressure of 1,3-dioxolane is given in ref *1*. The values of parameters λ_{12} and λ_{21} appear in Tables V–VII together with their estimated standard errors and the root-mean-square deviation $\sigma = [\Phi/(N-2)]^{0.5}$ evaluated at the minimum of the objective function Φ. The estimation of the standard errors of the parameters is obtained with the procedure outlined in ref *2*. Moreover, Tables V–VII give the values of the activity coefficients γ_1 and γ_2 calculated from eq 2 and 3 with the parameters λ_{12} and λ_{21}. The values of the activity coefficients lead to the conclusion that the binary mixtures of 1,3-dioxolane with 1,2-*trans*-dichloroethylene and trichloroethylene are nearly ideal in the liquid phase, whereas the mixture with tetrachloroethylene shows a notable departure from ideality with activity coefficients up to ~2. Parameters λ_{12} and λ_{21} are strongly dependent on the temperature, as can be seen in Figure 2, which shows the parameters as a function of the average values of the temperature in each isobaric group of the data. Thus, the mixtures of chloro compounds with 1,3-dioxolane exhibit a behavior exactly opposite to that of the mixture 1,3-dioxolane–water, where the parameters are fairly independent of temperature, whereas the activity coefficients of components are very large—up to 15 (*1*).

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NEW COMPOUNDS

Synthesis of Cycloalkylhydroxamic Acids and Their N-Substituted Derivatives

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The preparation of a series of cycloalkylhydroxamic acids (C_3–C_7 rings) and their *N*-methyl and *N*-cyclohexyl derivatives are reported. Some of their copper complexes are also prepared and characterized. The IR and NMR spectral results are tabulated and discussed.

Hydroxamic acids of the general formula RCONHOH have been known earlier and considered to be good complexing agents with a number of metal ions (*1*). They have been used widely for the colorimeteric determination of trace metals (*2*). Although a large number of these ligands have been prepared for these purposes, they were mainly aromatic and to a lesser extent alicyclic hydroxamic acids (*3*). The aim of the present work is to prepare a number of small-sized cycloalkylhydroxamic acids and their N-substituted derivatives (I–XV) (see Table I).

Some of the prepared hydroxamic acids that could not be purified by the usual methods were purified through their copper chelates. The physical and spectral data of I–XV are given in Table II.

Table I

$$\underset{\text{I-XV}}{\text{RCOCl} + \text{R'NHOH} \rightarrow \text{RCONR'OH} + \text{HCl}}$$

	R′		
R (cycloalkyl)	H	CH_3	C_6H_{11}
C_3H_5	I	II	III
C_4H_7	IV	V	VI
C_5H_9	VII	VIII	IX
C_6H_{11}	X	XI	XII
C_7H_{13}	XIII	XIV	XV

Experimental Section

Infrared spectra were recorded on an IR 10 Beckman infrared spectrophotometer, and ^1H NMR spectra with a Varian T 60 A spectrometer using Me_4Si as internal standard. CHN elementary analyses were obtained by using a 185 HP analyzer. Melting points were obtained on a Kofler block and were uncorrected. The purities of different products were checked by TLC using glass plates coated with silica.

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Table II. Physical and Spectral Data of Cycloalkylhydroxamic Acids and Some of Their Cu Complexes

					copper hydroxamate[d]	
compd	mp, °C (solvent)[a]	yield, %	IR,[b] cm^{-1}	NMR,[c] δ	mp, °C (solvent)[a]	IR $\nu_{C=O}$,[g] cm^{-1}
I	117-120[e] (B)	15.1	3200 (OH, NH)[g] 3030 (OH, NH)[g] 1605 (C=O)	0.65 (d, 4 H, C_2H_4)[i] 1.5 (m, 1 H, CHCO) 9.2 (s, 1 H, OH, NH)[j] 11.2 (s, 1 H, OH, NH)[j]	138 (B)	1530
II	74-76 (E)	20.5	3150 (OH)[g] 1590 (C=O)	1.0 (m, 4 H, C_2H_4)[k] 2.2 (m, 1 H, CHCO) 3.6 (s, 3 H, NCH_3) 9.4 (s, 1 H, OH)[j]	183 (E)	1590
III	105-107 (PE)	33.5	3120 (OH)[g] 1585 (C=O)	0.3-2.2 (m, 15 H, C_3H_5, C_5H_{10})[k] 4.4 (s, 1 H, CHN) 8.8 (s, 1 H, OH)[j]		
IV	oil (crude)	30.0			220 decomp	1525
V	oil[e]	20.0	3180 (OH)[g] 1600 (C=O)	1.6-2.6 (m, 6 H, C_3H_6)[k] 3.4 (s, 3 H, NCH_3) 3.8 (m, 1 H, CHCO) 9.8 (s, 1 H, OH)[j]	142	1590
VI	117 (PE)	18.0	3300 (free OH)[g] 3120 (bonded OH) 1590 (C=O)	0.8-2.4 (m, 16 H, C_3H_6, C_5H_{10})[k] 3.7 (br, 2 H, CHN, CHCO) 8.5 (s, 1 H, OH)[j]		
VII	110-112 (A-B)	98.0	3190 (br, OH, NH)[g] 3020 (sh, OH, NH)[g] 1625 (C=O)			
VIII	oil	97.0	3160 (br, OH)[h] 1605 (C=O)	0.6-2.4 (m, 9 H, C_5H_9)[i] 3.34 (s, 3 H, NCH_3) 8.84 (s, 1 H, OH)[j]		
IX	135-136 (A)	56.0	3250 (br, OH)[h] 1600 (C=O)	0.6-2.4 (m, 18 H, C_4H_8, C_5H_{10})[k] 3.06 (m, 1 H, CHCO) 4.13 (m, 1 H, CHN) 8.8 (br, 1 H, OH)[j]		
X	134-136[f] (E-A)	61.4	3190 (br, OH, NH)[g] 3020 (sh, OH, NH)[g] 1625 (C=O)			
XI	103-104 (A)	81.0	3160 (br, OH)[h] 1590 (C=O)	0.6-2.4 (m, 10 H, C_5H_{10})[l] 3.0 (br, 1 H, CHCO) 3.5 (s, 3 H, NCH_3) 10.0 (br, 1 H, OH)[j]	191	1590
XII	175-177 (A)	62.6	3190 (br, OH)[h] 1595 (C=O)	0.6-2.6 (m, 20 H, $2C_5H_{10}$)[k] 2.6 (m, 1 H, CHCO) 4.13 (m, 1 H, CHN) 6.8 (br, 1 H, OH)[j]	245 (M)	1560
XIII	129-131 (B)	90.7	3230 (br, OH, NH)[h] 3420 (sh, OH, NH)[h] 1660 (C=O)			
XIV	71-73 (PE)	92.2	3180 (br, OH)[h] 1600 (C=O)	1.0-2.33 (s, 12 H, C_6H_{12})[l] 3.26 (m, 1 H, CHCO) 3.46 (s, 3 H, NCH_3) 10.2 (br, 1 H, OH)[j]		
XV	131-133 (A)	68.5	3220 (br, OH)[h] 1595 (C=O)	0.6-2.4 (m, 22 H, C_6H_{12}, C_5H_{10})[l] 2.8 (m, 1 H, CHCO) 4.06 (m, 1 H, CHN) 8.8 (br, 1 H, OH)[j]		

[a] A = acetone, B = benzene, E = ether, M = methanol, PE = petroleum ether (30–50 °C). [b] A decrease of ~20 cm^{-1} of the $\nu_{C=O}$ due to N-substitution is observed (*6, 7*). [c] s = singlet, d = doublet, m = multiplet, br = broad, sh = shoulder. [d] The ligand/metal ratio for the Cu complexes of V, XI, and XII is 1:2, while it is 1:1 for IV (the latter value may be attributed to the formation of polymeric complex (*5*)). [e] Obtained from Cu complexes. [f] Reported 131–132 °C (*4*). [g] KBr disk. [h] Chloroform solution. [i] Deuteriodimethyl sulfoxide solution. [j] Exchangeable with D_2O. [k] Deuteriochloroform solution. [l] Carbon tetrachloride solution.

Preparation of Unsubstituted and N-Methyl-Substituted Hydroxamic Acids. In a 1-L round-bottomed flask, a suspension of *N*-methylhydroxylamine hydrochloride (0.2 mol) and sodium bicarbonate (0.6 mol) in water (100 mL) and ether (350 mL) was placed. The stirred reaction mixture was cooled to -5 °C, and the appropriate acid chloride (0.1 mol) in ether (150 mL) was added over 1 h at this temperature. After the addition was completed, the reaction mixture was stirred at room temperature for 2 h and then worked out to give the crude hydroxamic acids. Purification of the latter by recrystallization or through their copper complexes gave the pure hydroxamic acids in relatively good yields (Table II).

Preparation of N-Cyclohexylhydroxamic Acids. The above procedure used was followed here except that the molar proportions of the reactants used in this case were 1:1:2 of the acid chloride–*N*-cyclohexylhydroxylamine–sodium bicarbonate, respectively. The products were purified as mentioned above to give the pure hydroxamic acids (Table II).

Preparation of Copper Complexes of Hydroxamic Acids. A saturated solution of copper acetate was added to the hydroxamic acid dissolved in chloroform. After shaking, the greenish blue copper complex which was formed in the chloroform layer was dried and the solvent evaporated in vacuo to give a pure greenish blue complex of hydroxamic acid (Table II).

Purification of Hydroxamic Acids through Their Copper Complexes. Hydrogen sulfide was passed through a suspension of the copper complex of hydroxamic acid in methanol.

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

Acknowledgment

We thank Mr. A. M. Raoof for his assistance during the preparation of some of the compounds.

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

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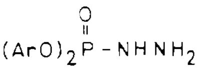
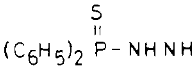
1,3-Dicarbonyl compounds (III) reacted with the phosphorus hydrazides to give the corresponding hydrazones. When the hydrazones of ethylacetoacetate were heated at their melting points, they were converted to the corresponding pyrazolin-5-ones. The spectral characteristics of these pyrazolinones were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



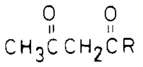
$(ArO)_2\overset{O}{\overset{\|}{P}}-NHNH_2$

(I)



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

(II)



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

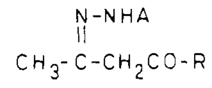
(III)

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).



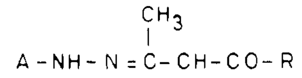
$CH_3-\overset{N-NHA}{\overset{\|}{C}}-CH_2CO-R$

(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

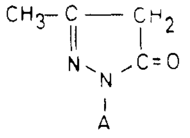


$A-NH-N=\overset{CH_3}{\overset{|}{C}}-CH-CO-R$

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

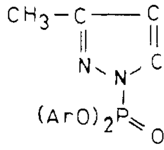
[a] $A_1 = (C_6H_5O)_2P{=}O$, $A_2 = (p\text{-}CH_3C_6H_4O)_2P{=}O$, $A_3 = (C_6H_5)_2P{=}S$.

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)

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



(V')

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

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