When crystallized, desolvated phosphorane was heated for 20 min under vacuum at 250–260°, very little distillate collected in a dry ice–acetone trap. However, triphenylphosphine oxide (identical ir spectrum) was recovered by extracting the dark, solid residue in the reaction flask with cold dry benzene and evaporating. The solid which remained after the benzene extraction could be recrystallized from a large volume of dry benzene to give prisms melting at 242.5–243.5 °C. The infrared spectrum (Nujol) was different than that of the above bisphosphorane and showed either both CN and C≡C or two kinds of CN (2210 and 2190 cm^{-1}); the acyl carbonyl was shifted to 1640 cm^{-1}. The elemental analyses suggest a benzene solvate of $(C_6H_5)_3P^+-{}^-C(CN)CO(CF_2)_3C{\equiv}CCN\cdot\frac{1}{3}C_6H_6$.

1,7-Bis(triphenylphosphoranylidene)-1,7-bis(carboethoxy)-3,3,4,4,5,5-hexafluoro-2,6-dioxoheptane. After recrystallization from dry benzene:cyclohexane (2:1) the melting point of this compound (obtained in quantitative yield) was 194–195 °C.

Although the pyrolysis of the bisphosphorane under the usual conditions furnished triphenylphosphine oxide, the desired acetylenic ester was not recovered. A GLC on liquid distillate revealed a complex mixture (15 peaks).

2,2,2-Trifluoroethyltriphenylphosphonium Iodide. Triphenylphosphine (52.5 g, 0.02 mol) in 250 ml of dry benzene was treated with 42.0 g (0.02 mol) of 2,2,2-trifluoroethyl iodide. The solution stood in a stoppered, Pyrex flask on a window sill with northern exposure for 9 months. White crystals very gradually formed; although the solution was initially pale yellow colored, it became quite dark. The solid was removed, washed with benzene and dried; 8.7 g (9.2%), mp 160–165 °C. (Attempts to recover more crystalline compound by further standing or by adding more trifluoroethyl iodide and allowing to stand were generally not very successful; some solid might form, but if allowed to stand too long the solid would redissolve.) The compound was slightly soluble in hot water but decomposed upon prolonged heating. Two grams were recrystallized by solution in 30 ml of absolute ethanol, adding 100 ml of ether and seeding; mp 162–167 °C. The white-to-pale-yellow crystals rapidly darken in the light.

No crystalline solid separated when the above quantities of reactants were refluxed in the dark for 8 h.

Acknowledgment

The interest of Dr. Arnold Adicoff is appreciated.

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Trialkylacetohydroxamic Acids as Selective Extractants. The Synthesis and Properties of the Symmetrical Derivatives

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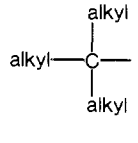
A series of new trialkylacetohydroxamic acids with the general structure $(R)_3CCONHOH$ (where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_4H_9, n-C_5H_{11}) has been prepared. Their solubility, chemical stability with mineral acids, and extractive capacity have been examined.

Hydroxamic acids can easily form stable complexes with a great number of metal ions such as Fe^{3+}, V^{5+}, Zr^{4+}, Nb^{4+}, Mo^{5+}, and Cu^{2+} and generally with actinides and lantanides (*3, 5, 7*).

Unfortunately the hydroxamic function exhibits an elevated solubility in water and an insufficient solubility in nonpolar solvents as well as a poor stability with respect to acidic and oxidant solutions; the increase of the straight aliphatic chain bounded to the hydroxamic group only reduces the solubility in water.

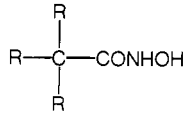
Recent investigations carried out in our laboratory have shown that neotridecanohydroxamic acids can be conveniently used as a novel extracting agent for analytical as well as for industrial purposes (*2*).

The increase and the branching of the aliphatic chain in the "neo" structure seems to transmit to the hydroxamic acids different physical and chemical properties with respect to the corresponding straight chain isomers; they have a higher solubility in organic solvents and a lower solubility in water. The steric hindrance of the substitutions at the hydroxamic group increases the chemical stability with regard to oxidative or acid attack as well as the radiolytic stability.



This fact has suggested the application of this kind of hydroxamic acid in the extraction of metal in aqueous reprocessing of irradiated nuclear fuels (*1*) and has induced us to start a study on the influence of a branched alkyl structure on the properties of these compounds.

In the present work we report the result of the preparation and the evaluation of a series of symmetrical trialkylated acetohydroxamic acids with the general structure:



where R = CH_3, C_2H_5, C_3H_7, n-C_4H_9, i-C_4H_9, or n-C_5H_{11}.

The hydroxamic acids have been prepared from the corresponding carboxylic derivative with two different procedures according to their solubility or insolubility in water. The data concerning the preparation of the hydroxamic acids and of their corresponding intermediates are reported in Table I.

The purity tests by potentiometric or colorimetric methods have been reported in Table II. The higher values of potentio-

Table I. The Preparation of Trialkylacetohydroxamic Acids and Its Intermediates[a]

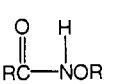
R	Molecular weight	Bp, °C (mm Hg), or mp, °C (cryst solv)	% yield	General formula
		Trialkylacetonitriles R_3CCN		
n-C_3H_7	167.30	90 (5)	64	$C_{11}H_{21}N$
n-C_4H_9	209.38	107–110 (1.5)	66	$C_{14}H_{27}N$
i-C_4H_9	209.38	—	50	$C_{14}H_{27}N$
n-C_5H_{11}	251.46	153–156 (8)	75	$C_{17}H_{33}N$
		Trialkylacetamides R_3CCONH_2		
n-C_3H_7	185.31	140 (1.5)	71	$C_{11}H_{23}ON$
n-C_4H_9	227.39	153–155 (1.5)	69	$C_{14}H_{28}ON$
i-C_4H_9	227.39	140–170 (5)	80	$C_{14}H_{28}ON$
n-C_5H_{11}	269.47	179–182 (3)	86	$C_{17}H_{35}ON$
		Trialkylacetic Acids R_3CCOOH		
n-C_2H_5	144.22	128–133	—	$C_8H_{16}O_2$
n-C_3H_7	186.30	114–117 (5)	97	$C_{11}H_{22}O_2$
n-C_4H_9	228.38	166–167 (2)	70	$C_{14}H_{28}O_2$
i-C_4H_9	228.38	—	45	$C_{14}H_{28}O_2$
n-C_5H_{11}	270.46	167–168 (2)	70	$C_{17}H_{34}O_2$
		Trialkylaceto Chlorides R_3CCOCl		
n-CH_3	120.48	105–106 (760)	—	C_5H_9OCl
n-C_2H_5	162.67	193–195 (51)	90	C_8H_5OCl
n-C_3H_7	204.75	117–125 (38)	98	$C_{11}H_{21}OCl$
n-C_4H_9	246.83	160 (35)	93	$C_{14}H_{27}OCl$
i-C_4H_9	246.83	100–105 (8)	80	$C_{14}H_{27}OCl$
n-C_5H_{11}	288.91	150–160 (40)	92	$C_{17}H_{33}OCl$
		Trialkylacetohydroxamic Acids $R_3CCONHOH$		
n-CH_3	117.15	mp 164–165 (et. acet.)	98	$C_5H_{11}NO_2$
n-C_2H_5	159.23	mp 134–135 (n-hexane)	92	$C_8H_{17}NO_2$
n-C_3H_7	201.31	mp 110–111 (benzene)	81	$C_{11}H_{23}NO_2$
n-C_4H_9	243.40	mp 132–133 (n-hexane)	82	$C_{14}H_{29}NO_2$
i-C_4H_9	243.40	mp 100–101 (benzene)	70	$C_{14}H_{29}NO_2$
n-C_5H_{11}	285.47	mp 125–126 (n-hexane)	84	$C_{17}H_{35}NO_2$

[a] Elemental analyses (C, H, N) in agreement with theoretical value were obtained and submitted for review.

Table II. Purity Determinations of Hydroxamic Acids by Potentiometry and Colorimetry

	% by potentiometry	% by colorimetry
$(CH_3)_3C-$	99	95
$(C_2H_5)_3C-$	98	91
$(C_3H_7)_3C-$	98	92
$(C_4H_9)_3C-$	97	92
i-$(C_4H_9)_3C-$	100	93
$(C_5H_{11})_3C-$	99	96

metric determination may be attributed to the presence of an alkyl hydroxamate:



a secondary weak acid compound, which does not give the colorimetric reaction with Fe^{3+}; its presence may be ascribed to the excessive amount of acid chloride during the reaction with hydroxylamine.

Uv and ir spectra of these hydroxamic acids have been obtained. In Table III the wavelength at maximum absorption (λ_{max}) and the molar extinction coefficient (ϵ_{max}) are reported.

The ir absorption bands of hydroxamic acids occur in the region of 3500–2800 cm^{-1} (OH and NH stretching) and 1700–1500 cm^{-1} (CO stretching). The limited solubility in CCl_4 and the structure of these compounds do not generally permit the obtaining of good ir spectra.

Table III. Uv Spectrophotometry of Trialkylacetohydroxamic Acids

Compound	Diluent	λ_{max}, mμ	ϵ_{max}
$(CH_3)_3CCONHOH$	Water	193	5770
	Ethanol	203	2840
	n-Heptane	214	890
$(n$-$C_4H_9)_3CCONHOH$	Ethanol	204	4200
	n-Heptane	215	2150
HX 70	Water	190	5800
(neotridecanohydroxamic	Ethanol	203	3000
acid)	n-Heptane	222	400

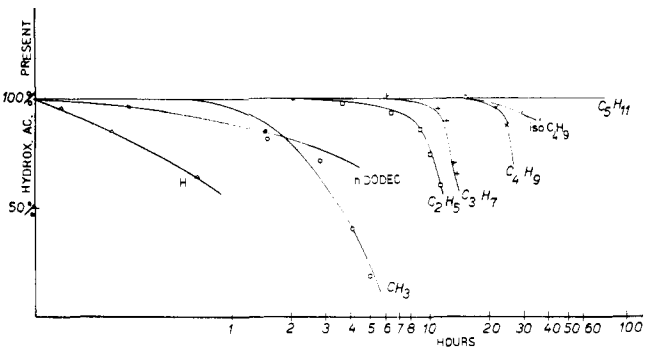


Figure 1. Thermal stability of trialkylacetohydroxamic acids at 80 °C.

A comparison of the chemical and physical properties of these hindered hydroxamic acids has been carried out with regard to their solubility, their stability as well as their complexing capacity at the equilibrium, and their extraction kinetics; n-dodecanohydroxamic acid and acetohydroxamic acid have been chosen as a standard to compare the new products.

Solubility data, compared with those of straight chain compounds, are reported in Table IV with regard to the dielectric coefficient of solvents. The solubility in nonpolar solvents, which is related to the loading capacity of the extractant, is better than that of normal dodecanohydroxamic acid but lower than that of HX 70, a mixture of branched hydroxamic acids obtained from a commercial mixture of carboxilic acids named neotridecanoic acid (*2*). The best performances are achieved only when chains bounded to the quaternary carbon atom are completely branched (triisobutylhydroxamic acid). The higher values are obtained with chlorinated diluents. The solubilities in hydrocarbons, the usual diluents in reprocessing plants, are insufficient. The solubility in water, which gives an idea of the extractant's losses during an extraction cycle, is sufficiently low for compounds with a molecular weight higher than 200. A very high solubility in alcohol is useful for all cleaning or recuperation operations.

All these tertiary hydroxamic acids show a diffused capacity to give gel solutions which is higher for the tripropyl derivative; experiments to correlate this feature, by osmometric pressure measures of molecular weight, seem to exclude massive aggregation phenomena.

The thermal stability tests (Figure 1) show that these hydroxamic acids are more stable than the linear compounds.

The different solubility features of these new products do not make it easy to obtain significant and homogeneous data on chemical stability (Figure 2–6). However, it has been confirmed that the "neo" alkyl structure confers an evident stability to the hydroxamic function.

Results on the degration rate make it possible to suppose that the reactions with 1 M HNO_3, 5 M HCl, and 5 M $HClO_4$ have a first-order kinetics and probably are simple hydrolysis reactions; the degradation with 3 M HNO_3 is a second-order reaction and that with 5 M HNO_3 is of higher order, probably more complex

Table IV. Solubility of Trialkylacetohydroxamic Acids at 25 °C; mmol/l. (g/l.) R—CONHOH

	ϵ dielectric constant	$(CH_3)_3C-$ mol wt = 117.15	$(C_2H_5)_3C-$ mol wt = 159.23	$(C_3H_7)_3C-$ mol wt = 201.31	$(n\text{-}C_6H_9)_3C-$ mol wt = 243.40	$(i\text{-}C_4H_9)_3C-$ mol wt = 243.40	$(C_5H_{11})_3C-$ mol wt = 285.47	$n\text{-}C_{12}H_{25}-$ mol wt = 229.22	HX 70 mol wt = 232
Ethanol	24.3	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	314 (72)	$>10^3$
Chloroform	4.8	34 (3.98)	150 (23.8)	800 (161.1)	440 (107.1)	$>10^3$	370 (105.7)	19.2 (4.4)	$>10^3$
Carbon tetrachloride	2.23	0.54 (0.06)	4.0 (0.64)	54 (10.87)	43 (10.47)	—	22.8 (6.51)	0.075 (0.02)	$>10^3$
Benzene	2.28	2.5 (0.29)	18 (2.9)	80 (16.08)	76 (18.45)	370 (90)	49 (14)	1.6 (0.37)	$>10^3$
Xylene	2.3–2.4	1.16 (0.23)	9 (1.4)	75 (15.07)	62 (15.01)	—	22.4 (6.4)	1.0 (0.23)	$>10^3$
Mesitylene	2.27	1.0 (0.12)	8.2 (1.3)	37 (7.44)	32 (7.8)	190 (46.25)	19.2 (5.5)	0.92 (0.21)	$>10^3$
n-Heptane	1.92	0.1 (0.01)	0.23 (0.03)	3.0 (0.6)	2.1 (0.5)	150 (36.51)	1.66 (0.47)	—	$>10^3$
Water	80.37	356 (41.7)	50 (7.9)	2.05 (0.4)	0.07 (0.02)	0.4 (9.74)	Insol	Insol	2.8
1 M HNO_3	—	—	59 (9.4)	0.21 (0.04)	Insol	—	Insol	Insol	—

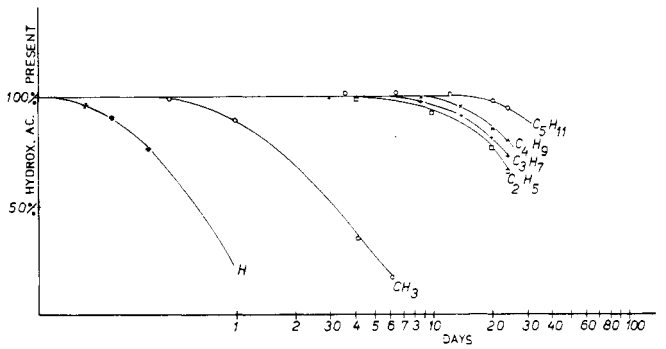


Figure 2. Chemical stability of 0.1 M trialkylacetohydroxamic acids with 10 M $HClO_4$ in CH_3COOH at 50 °C.

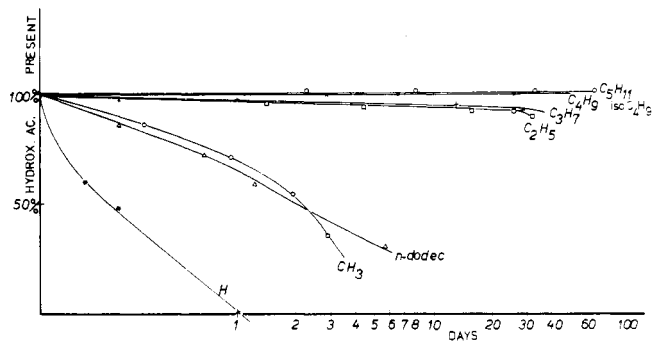


Figure 3. Chemical stability of 0.1 M trialkylacetohydroxamic acids with 3 M HNO_3.

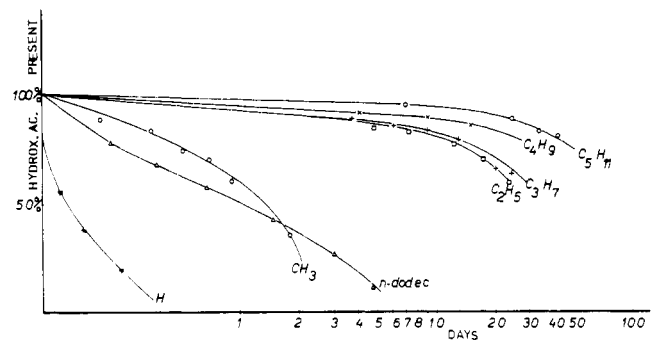


Figure 4. Chemical stability of 0.1 M trialkylacetohydroxamic acids with 5 M HNO_3.

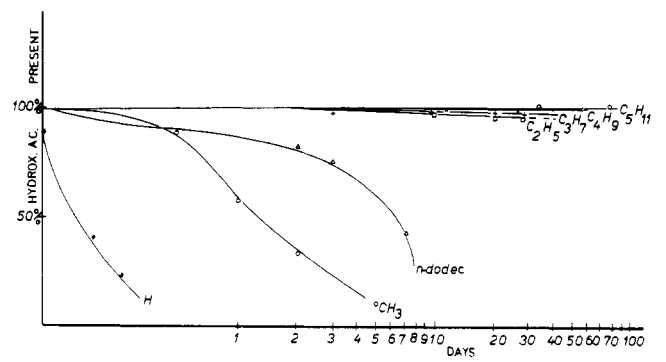


Figure 5. Chemical stability of 0.1 M trialkylacetohydroxamic acids with 5 M HCl.

reactions as oxidation or nitration begin to start at higher concentrations of HNO_3.

The particularly hindered structure of these acids may introduce some differences in the kinetics of the complex formation. The extraction rate with Fe^{3+} is reported in Figure 7.

The branching of the alkyl chain does not seem to introduce modifications as the extraction of Fe^{3+} is as fast as that with the

Table V. Extraction of Fe(III) and Pu(IV) by Trialkylacetohydroxamic Acids

	Concn mol/l.	Fe(III) aqueous ph. *c/m*	Fe(III) organic ph. *c/m*	$E_{o/a}$ (Fe)	Pu(IV) aqueous ph. *c/m*	Pu(IV) organic ph. *c/m*	$E_{o/a}$ (Pu)	$E_{o/a}$ (Fe) concn 10^{-2} M	$E_{o/a}$ (Pu)	*E*(Fe)/ *E*(Pu) sep factor
$(CH_3)_3C-$	8.5×10^{-3}	35 000	0	0.00	5790	0.00	0.00	10^{-4}	10^{-4}	—
$(C_2H_5)_3C-$	9.1×10^{-3}	37 600	180	0.004	5280	10	0.002	6×10^{-3}	10^{-3}	6
$(C_3H_7)_3C-$	8.2×10^{-3}	35 720	3340	0.093	1730	5810	3.36	1.6×10^{-1}	7.0	0.023
$(C_4H_9)_3C-$	9.6×10^{-3}	35 300	2250	0.062	1980	5510	2.78	8.0×10^{-2}	3.8	0.021
$(C_5H_{11})_3C-$	9.6×10^{-3}	36 300	1735	0.048	4045	2084	0.52	5.5×10^{-2}	0.6	0.092
HX 70	8.8×10^{-3}	37 500	1500	0.040	5670	337	0.06	6.0×10^{-2}	0.1	0.6

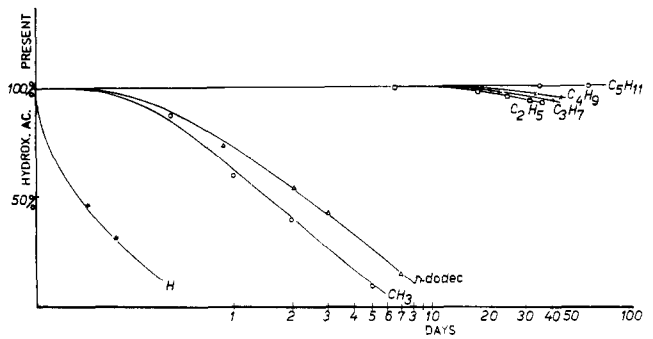


Figure 6. Chemical stability of 0.1 M trialkylacetohydroxamic acids with 5 M $HClO_4$.

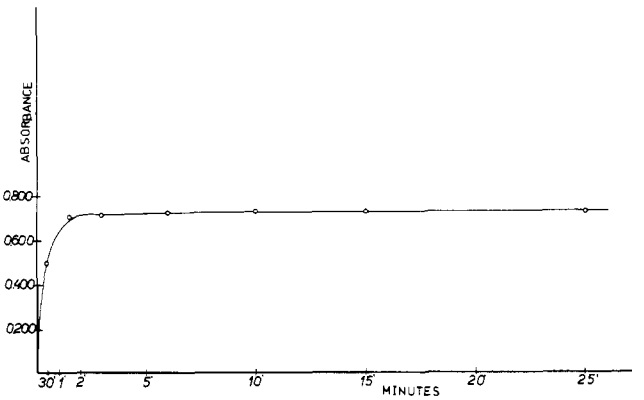


Figure 7. Extraction kinetics of Fe(III) with 0.1 M tributylacetohydroxamic acid in $CHCl_3$; 0.01 M Fe in 2 M HNO_3 (*o/a* ratio 1/1).

simpler hydroxamic acids. An extraction test of Pu and of Fe shows that the extraction capacity of these acids is very high and that, in this series, there is an evident difference of the extracting capacity between the different compounds (Table V).

Experimental Section

Preparative Procedure. The preparation of these kind of hydroxamic acids has, as obligatory intermediates, the corresponding trialkylacetic acids, which react as esters or as acid chlorides with hydroxylamine to obtain the desired hydroxamic acid.

Symmetrical trialkyl acetic acids may be synthesized as follows: (a) by addition of carbon dioxide on *tert*-alkylmagnesium chlorides (*8*), limited to the simpler compounds as trimethyl and triethyl derivatives:

$$(C_2H_5)_3C\text{-}MgCl + CO_2 \rightarrow (C_2H_5)_3CCOOH$$

(b) by alkylation of a nitrile and hydrolysis to amide and acid (*6*):

$$CH_3CN \xrightarrow[NaNH_2]{BuBr} (C_4H_9)_3CCN \xrightarrow{H_2SO_4\ 80\%} (C_4H_9)_3CCONH_2$$

$$\xrightarrow[HCl]{BuONO} (C_4H_9)_3CCOOH$$

for the other compounds.

Care must be taken in separating trialkylacetic acids because the potassium salts of tributyl and triamyl derivatives are partially soluble in ethyl ether; for their complete washing the etheral solutions must be treated several times with 10% KOH and water alternatively.

Hydroxamic acids which are insoluble in water (triethyl, tripropyl, tributyl, and triamyl derivatives) have been prepared by the reaction of the acid chloride with hydroxilamine in pyridine. Hydroxamic acids soluble in water (trimethyl, and straight chain hydroxamic acids) have been prepared by the reaction on the methyl ester with hydroxilamine (*4, 9*).

For the preparation of *hydroxamic acids insoluble in water,* 0.5 mol of acid chloride has been added dropwise under vigorous stirring to 1 mol of hydroxylamine hydrochloride in 600 ml of pyridine into an ice bath. After the introduction of the acid chloride, the mixture was stirred at room temperature 48 h. The largest part of pyridine was then removed by distillation under vacuum at not more than 40–45 °C in order to avoid any decomposition or transformation of the hydroxamic acid. The residue, dissolved in ethyl ether, was washed repeatedly with aliquots of 1 M HCl to remove the last traces of pyridine. The etheral phase was finally dried by anhydrous Na_2SO_4 and the solvent completely removed at reduced pressure taking care that the temperature did not rise above 40–45 °C. The solid obtained was crystallized several times.

For the preparation of *hydroxamic acids soluble in water* were prepared two separate solutions of 0.2 mol of hydroxylamine hydrochloride in 100 ml of methyl alcohol and 0.3 mol of KOH in 50 ml of methyl alcohol: both were cooled to 30–40 °C and the alkaline solution was added to the hydroxylamine solution, with shaking cooling the reaction vessel in an ice bath. After 10 min 0.1 mol of the methyl ester of the carboxilic acid was added and after shaking the mixture was immediately filtered by suction. The residue was washed with cold methyl alcohol and the resulting liquid added to the filtrate. This solution was allowed to stand at room temperature for 48 h. In order to obtain the free hydroxamic acid from its salt, a carboxilic cation exchange resin (H^+ form) equilibrated in methyl alcohol was utilized. The resultant mixture was mixed with the resin and allowed to stand for 0.5 h. If the solution was not yet acidic, more cation resin was added. The resin was filtered by suction and then washed. Methyl alcohol was eliminated, the crude free hydroxamic acid dried by vacuum and purified by repeated crystallizations with a suitable solvent.

Comparative Tests. The *potentiometric titrations* of hydroxamic acids were performed with an automatic recording titrator Metrhom E 436 at the following conditions: *titrant,* $(C_4H_9)_4N^+OH^-$ 0.1 M in isopropyl alcohol–benzene 1:1 controlled with benzoic acid; *solvent,* 150 ml of pyridine with 5% of saturated KCl in methanol; *electrodes,* (I) a calomel electrode with a saturated solution of KCl in methanol, (II) a glass electrode

conditioned for several hours in pyridine; sample, about a milliequivalent; delivery rate: 1 ml/min with vigorous stirring.

Colorimetric tests: the well known colored reaction which takes place between ferric ions and hydroxamic function in acidic medium was adopted; for the iron solution 10 g of $Fe(ClO_4)_3 \cdot 9H_2O$ was dissolved in 95% ethyl alcohol into a 1 l. volumetric flask cautiously adding 250 ml of 70% perchloric acid and finally diluting with ethyl alcohol. Procedure: pipet a carefully measured volume of an hydroxamic acid solution (1–10 mmol) into a 25-ml volumetric flask. Add 5 ml of the iron perchlorate alcoholic solution and dilute with ethyl alcohol. Measure the absorbance at 520 mμ against the reagent blank. The concentration of hydroxamic acid may be deduced from a standard calibration curve.

For the *solubility* test saturated solutions of hydroxamic acids in different solvents were put in a thermostat at 26 °C for 2 h into glass tubes. On the centrifuged solution the amount of hydroxamic acid was determined by iron colorimetry.

The *thermal stability* was determined as follows: 250 μl of a 0.1 M solution of hydroxamic acid in chloroform was put into ten 25-ml volumetric flasks. After evaporation of chloroform by vacuum, the flasks were put into a thermostatic oven. At regular intervals the remaining hydroxamic acid was determined by iron colorimetry in order to control the variation of hydroxamic acid concentration as a function of the contact time.

The *chemical stability* was determined under different conditions. (a) In the same phase with 10 M $HClO_4$ in CH_3COOH at 50 °C: 0.1 M solutions of hydroxamic acids in 10 M $HClO_4$ in CH_3COOH were put into a thermostatic oven at 50 °C. At regular intervals the remaining hydroxamic acid was determined by iron colorimetry. (b) In the same phase in HNO_3, $HClO_4$, and HCl aqueous solutions: aqueous solutions contained hydroxamic acid (0.1 M) were maintained at 22 °C in glass tubes. At regular intervals colorimetric tests for hydroxamic acids were performed. (c) With HNO_3, $HClO_4$, and HCl in two phases: 20 ml of 0.1 M hydroxamic acid solution in chloroform were mechanically shaken with an equal volume of various acidic solutions in glass tubes. At regular intervals aliquots of the organic phases were submitted to colorimetric analysis in order to control the variation of hydroxamic acid concentration as a function of the contact time.

In all tests, urea (0.01 M) was added to HNO_3 to destroy nitrous acid. For *the extraction of* Fe^{3+} several 25-ml plastic stoppered tubes containing 10 ml of 2 M HNO_3, 10 ml of 0.1 M tributylacetohydroxamic acid chloroformic solution, and 250 μl of 0.01 M ferric nitrate aqueous solution were mechanically shaken. At regular intervals the optical density at 440 mμ of every solution was read against a reference of a chloroformic solution of 0.1 M hydroxamic acid equilibrated with the same volume of 2 M HNO_3.

The *extraction coefficients of* ^{59}Fe *and of* ^{239}Pu were determined as follow: 1 ml of 1 M HNO_3 (treated with urea), 2 ml of a 0.01 M hydroxamic acid choloformic solution and 250 μl of a 1 M nitric solution, containing ^{59}Fe and ^{239}Pu as tracers, were introduced in a plastic stoppered tube. The two phases were separated after 15 min of mechanical shaking and centrifugation. From every phase samples were prepared for α solid counting for ^{239}Pu and for liquid γ counting for ^{59}Fe (250/nl).

For α counting a Zn scintillation detector and for γ counting a NaI well detector were used.

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Potential Antituberculous Agents. 3. *N*-Aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides

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Various *N*-aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides have been synthesized by the condensation of corresponding 2-amino-4-phenyl-5-arylazothiazoles with different arylisothiocyanates. The intermediates required in these syntheses were prepared according to the methods given in the literature.

There has been a growing interest, during the last few years, in the synthesis and biological evaluation of compounds containing the N*–N*–S* or O*–N*–S* tridentate ligand system (*3, 6–9*) or arylazo grouping (*10, 12*). This interest stems mainly from certain interesting antituberculous activities of disubstituted thiocarbamides (*1, 11*). As a part of a general study directed towards the development of antituberculous agents, the above mentioned rationale led to the examination of the synthesis and biological properties of *N*-aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides having N*–N*–S* ligand and arylazo grouping and a modified azomethine linkage. Hopefully these potential antituberculous agents might afford compounds that would be less toxic to normal cells and have a better chemotherapeutic index. These compounds have been submitted for biological screening and the results will be reported elsewhere.

The present communication deals with the syntheses of *N*-aryl-*N'*-2-(4-phenyl-5-phenylazothiazolyl)-, *N*-aryl-*N'*-2-(4-phenyl-5-*o*-tolylazothiazolyl)-, *N*-aryl-*N'*-2-(4-phenyl-5-*m*-tolylazothiazolyl)-, and *N*-aryl-*N'*-2-(4-phenyl-5-*p*-tolylazothiazolyl)thiocarbamides by the condensation of corresponding 2-amino-4-phenyl-5-arylazothiazoles (II) with appropriate arylisothiocyanates.

The precursor 2-amino-4-phenylthiazole (I) was obtained by the condensation of acetophenone and thiourea in the presence