

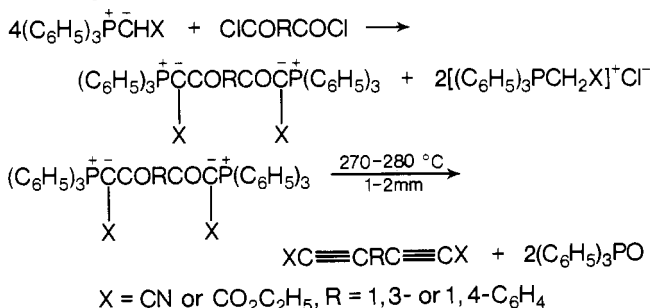
Bis(substituted-ethynyl)benzenes

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1,3-Bis(cyanoethynyl)benzene (mp 147–148°) and 1,3- and 1,4-bis(carboethoxyethynyl)benzenes (mp 52–53 and 90–91°, respectively) were obtained by pyrolyzing the requisite acylphosphoranes at 275–280°, 1–2 mm. A similar pyrolysis of 1,7-bis(triphenylphosphoranylidene)-1,7-dicyano-3,3,4,4,5,5-hexafluoro-2,6-dioxoheptane (mp 248–250°) or the analogous 1,7-dicarboethoxy compound (mp 194–195°) did not furnish bisacetylenes.

The versatile Diels–Alder reaction has been utilized for the preparation of polymers by condensing bisdienes with bisdienophiles (7, 4–8). For the latter component, bismaleimides, diacrylates, diacrylamides, *p*-benzoquinone, bistriazolones, etc., have been investigated. As part of a study to make and examine bisdienophiles which would have a wide range of reactivities toward 1,3-dienes, the new bis(substituted-ethynyl)benzenes described in Table I were prepared. These compounds were synthesized without difficulty in moderate yield by an extension of the method of Gough and Trippett (3) for making monoacetylenic compounds from suitable acyl phosphoranes. The following steps were involved:



Typical procedures are described in the Experimental Section. As expected, these bis(substituted-ethynyl)benzenes and benzylazide react readily to form 1,2,3-triazole derivatives (Table I).

Attempts to synthesize bisacetylenic compounds with R = –(CF₂)₃– by this same method were not successful. The desired bisacylphosphoranes were easily prepared from perfluoroglutaryl chloride, but the thermolysis of these intermediates failed to yield significant amounts of the acetylenes even though triphenylphosphine oxide was formed. The reasons for this failure were not examined.

Since –CF₃ is another electronegative group which activates an acetylenic bond (for example, hexafluorobutyne-2), the preparation of bisacetylenes, where X = CF₃, was also considered. However, the necessary starting ylide, (C₆H₅)₃P⁺–CHCF₃, could not be recovered from 2,2,2-trifluoroethyltriphenylphosphonium iodide by treatment with an equivalent amount of base. The latter salt was made in low yield by a photolytic reaction of 2,2,2-trifluoroethyl iodide and triphenylphosphine. The procedure of Gough and Trippett was successfully used by Filler and Heffern (2) in the synthesis of bis(pentafluorophenyl)acetylene and 2,3,4,5,6-pentafluorodiphenylacetylene.

Experimental Section

1,4-Di(carboethoxyethynyl)benzene. Terephthaloyl chloride (4.5 g, 0.022 mol) in 20 ml of dry benzene was added with stirring

during 2 h to 31.4 g (0.09 mol) of carboethoxymethylenetriphenylphosphorane (Aldrich) in 150 ml of dry benzene at 25 °C. After stirring overnight the solid was filtered, washed several times with benzene, and dried; 40.7 g. The cake was extracted with two 70-ml and two 35-ml portions of ice-cold water to leave, after vacuum drying, 17.2 g (quantitative) of acylphosphorane, mp 252–253 °C. (With isophthaloyl chloride, the acylphosphorane, which was never satisfactorily recrystallized, was soluble in the benzene and was recovered by evaporating the latter.) Some was recrystallized from dry xylene for analysis (Table I).

Eight grams of the above acylphosphorane was heated for 15 min at 1–2 mm pressure in a Wood's metal bath at 275–280 °C. The cooled mass was crushed and then extracted with three 50-ml portions of boiling *n*-hexane. The latter extract was cooled to 5 °C, filtered from a trace of triphenylphosphine oxide, and evaporated to leave 0.75 g (28%) of impure acetylenic ester. Another 1.0 g (39%) of less pure material was recovered by dissolving the hexane insoluble residue in 25 ml of benzene, filtering, adding 150 ml of *n*-hexane, chilling to 5 °C, refiltering, and evaporating the filtrate. Ester which had been recrystallized several times from absolute ethanol was free of phosphine oxide. Ir (Nujol): C≡C, 2210; C=O, 1700 cm⁻¹.

1,7-Bis(triphenylphosphoranylidene)-1,7-dicyano-3,3,4,4,5,5-hexafluoro-2,6-dioxoheptane. The title compound was prepared in 80% yield from perfluoroglutaryl chloride and cyanomethylene triphenylphosphorane (1:4 molar ratio). The short colorless needles obtained after recrystallization from dry benzene desolvated at 80–90 °C (the weight loss corresponds to a monobenzene solvate) and melted 248–250°. Ir (Nujol): CN, 2200; CO, 1605 cm⁻¹.

Table I. Disubstituted Benzenes^a

Position and substituents	Empirical formula	Mp, °C	Recryst solvent
1,3-(C ₆ H ₅) ₃ P ⁺ CCO– CN	C ₄₈ H ₃₄ N ₂ O ₂ P ₂ · 1.5CH ₃ C ₆ H ₅	255– 257	Toluene
1,3-NCC≡C–	C ₁₂ H ₄ N ₂	147– 148	Ethanol
1,4-(C ₆ H ₅) ₃ P ⁺ CCO– CO ₂ C ₂ H ₅	C ₅₂ H ₄₀ O ₆ P ₂	252– 253	Xylene
1,4-C ₂ H ₅ OCC≡C– O	C ₁₆ H ₁₄ O ₄	90– 91	Abs. ethanol
1,4-C ₂ H ₅ OCC=C– O N NCH ₂ C ₆ H ₅	C ₃₀ H ₂₈ N ₆ O ₄	193– 197	Ethanol
1,3-C ₂ H ₅ OCC≡C– O	C ₁₆ H ₁₄ O ₄	52– 53	<i>n</i> -Hexane
1,3-C ₂ H ₅ OCC=C– O N NCH ₂ C ₆ H ₅	C ₃₀ H ₂₈ N ₆ O ₄	102– 103	Ethanol

^a Elemental analysis (C, H, N, P) in agreement with theoretical values were obtained and submitted for review.

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 (C₆H₅)₃P⁺–⁻C(CN)CO(CF₂)₃C≡CCN· $\frac{1}{3}$ C₆H₆.

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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Received for review December 15, 1975. Accepted April 24, 1976.

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

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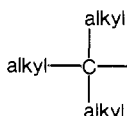
A series of new trialkylacetohydroxamic acids with the general structure (R)₃CCONHOH (where R = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉, *i*-C₄H₉, *n*-C₅H₁₁) has been prepared. Their solubility, chemical stability with mineral acids, and extractive capacity have been examined.

Hydroxamic acids can easily form stable complexes with a great number of metal ions such as Fe³⁺, V⁵⁺, Zr⁴⁺, Nb⁴⁺, Mo⁵⁺, and Cu²⁺ and generally with actinides and lanthanides (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).

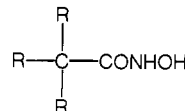
The increase and the branching of the aliphatic chain in the "neo" structure seems to transmit to the hydroxamic acids dif-



ferent 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 (7) 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 = CH₃, C₂H₅, C₃H₇, *n*-C₄H₉, *i*-C₄H₉, or *n*-C₅H₁₁.

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 potentiometric