2-(N,N-Bis-2'-hydroxyethylamino)ethylidene-1,1-diphosphonic Acid (X). A mixture of 2.86 g (10 mmole) of (I) disodium salt trihydrate, 3.15 g (30 mmole) of diethanolamine, 3.0 ml (52 mmole) of acetic acid, and 4 ml of water was boiled for 11 h. Following treatment with cation exchange resin and evaporation of the eluate in vacuo to 5 ml, methanol (40 ml) was added slowly. The crystals were filtered off and washed with methanol to give 2.50 g (85%) of (X). The product was reprecipitated from water with methanol, and dried in vacuo at 80°C.

2-N-Piperidinoethylidene-1,1-diphosphonic Acid (XI). A mixture of 2.86 g (10 mmole) of (I) disodium salt trihydrate, 3.0 ml (30 mmole) of piperidine, 1.5 ml (26 mmole) of acetic acid, and 5 ml of water was boiled for 5 h, and worked up as described for (X) to give 2.60 g (95%) of (XI). The product was reprecipitated from water with methanol, and dried in vacuo at 80°C.

2-N-Morpholinoethylidene-1,1-diphosphonic Acid (XII). A mixture of 2.06 g (8.1 mmole) of the anhydrous trisodium salt of (I), 3.00 g (34.5 mmole) of morpholine, and 12 ml of acetic acid was heated for 2 h at 100°C, then worked up as described for (X) to give 2.20 g of (XII), yield quantitative. The product was reprecipitated from water with methanol, and dried in vacuo at 100°C.

CONCLUSIONS

The reaction of vinylidenediphosphonic acid with aliphatic amines gives N-substituted 2-aminoethylidene-1,1-diphosphonic acids.

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SYNTHESIS AND PROPERTIES OF PHENYL-α-HYDROXYCYCLOHEXYLTHIOPHOSPHINIC ACID

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E. I. Matrosov, and M. I. Kabachnik

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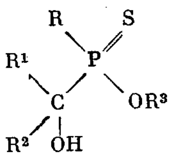
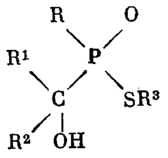
Synthetic routes to the O-alkyl esters of α-hydroxyalkylthiophosphinic acids (I) and the corresponding S-alkyl esters (II) [1-4]


(I)


(II)

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2806-2809, December, 1983. Original article submitted February 11, 1983.

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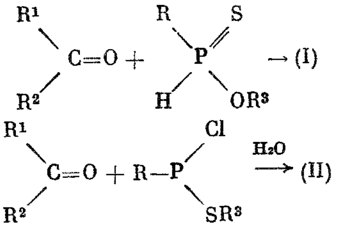
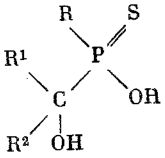
are based on the formation of the C—P bond by reacting aldehydes or ketones with thioorganophosphorus compounds containing the P(S)OR or PSR fragment (the Abramov reaction)



However, there have been no reports of the free α-hydroxyalkylmonothiophosphinic acids (III). It was therefore of interest to synthesize and examine acids of type (III)

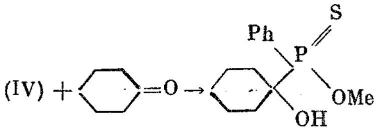


(III)

To prepare the acids (III) (R = Ph, $R^1 + R^2 = (CH_2)_5$), we used O-methyl phenylthiophosphonite (IV) [5] as starting material. Addition of this to cyclohexanone, by analogy with the known method [1], gave O-methyl phenyl-α-hydroxycyclohexylthiophosphate (V)

$$PhP(OMe)_2 + H_2S \xrightarrow{PhNEt_2} Ph(MeO)P(S)H + MeOH$$

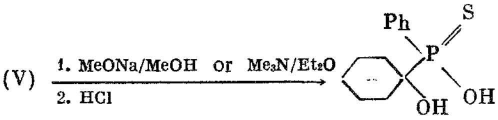
(IV)



(V)

The IR spectrum of the ester (V) contained a band at 3420 cm^{-1} characteristic of the OH group involved in weak hydrogen bonding. The strong absorption at 1045 and 790 cm^{-1} corresponded to the POMe group [6], and that at 1440 and 1115 cm^{-1} to the Ph—P group [7, 8]. The $^{31}P—\{^1H\}$ spectrum of (V) showed a singlet at δP 100 ppm, typical of thionosphosphinates [9].

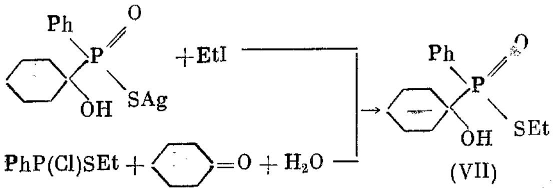
Dealkylation of the ester (V) with sodium methoxide in methanol, or triethylamine in ether followed by treatment with HCl, gave phenyl-α-hydroxycyclohexylthiophosphinic acid (VI)



(VI)

Compound (VI) was also obtained by hydrolysis of (V). This product was obtained by treatment with aqueous-alcoholic KOH. The yield of (VI) was 25-33%.

The acid (VI) was a colorless crystalline solid, which was purified by crystallization from benzene. The structure of (VI) was confirmed by its IR spectrum. There was a narrow band in the OH stretching region at 3420 cm^{-1} (alcoholic), and a broad band with a maximum at 2900 cm^{-1} (acidic). The assignment of the latter band was confirmed by comparison with the spectrum of diphenylmonothiophosphinic acid, which also contains a broad OH stretching band at 3000 cm^{-1}. The strong band at 930 cm^{-1} is related to P—O(H) vibrations, since it disappears in the spectrum of the potassium salt and is replaced by a strong band at 1080 cm^{-1} typical of salts of phosphorus monothioacids [10]. The presence of the PhP group is shown by the strong bands at 1440 and 1120 cm^{-1} [7, 8]. In the ^{31}P NMR spectrum of (VI), there occurs a signal at δP 87.6 ppm, characteristic of monothiophosphinic acids [9]. The structure of the acid (VI) was also confirmed by its chemical reactions, since alkylation of the silver salt of (VI) with ethyl iodide in methanol gave S-ethyl phenyl-α-hydroxycyclohexylthiophosphinate (VII), which from its constants, mixed melting point, and spectral characteristics was identical to the ester (VII) obtained by reacting S-ethyl phenylchlorothiophosphonite with cyclohexanone and water [3].



The dissociation constant of the acid (VI) was obtained by potentiometric titration in $MeNO_2$ [11]: $pK_a = 10.04 \pm 0.1$. This value is in good agreement with the correlational dependence of the dissociation constants of monothioacids on $\Sigma\sigma^{\Phi}$ in $MeNO_2$ [12]: $pK_a = 10.3$ (calculated).

EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument as suspensions in vaseline oil, and ^{31}P NMR spectra on a Bruker HX-90 (36.43 MHz) from 85% H_3PO_4.

O-Methyl Phenylthiophosphonite (IV) [5]. A mixture of 30 g (0.18 mole) of dimethyl phenylphosphonite, 7.2 g (0.21 mole) of H_2S, and 10.8 g (0.09 mole) of $PhNEt_2$ was heated in an autoclave at 50°C for 24 h. The pressure in the autoclave fell from 20 to 10 atm. Vacuum distillation of the mixture gave 24.8 g (80%) of (IV), bp 100°C (1 mm) (cf. [5]), n_D^{20} 1.5830. NMR spectrum: δP 67.8 ppm. $^1J_{PH} = 540$, $^3J_{PH} = 13$ Hz (no solvent).

O-Methyl Phenyl-α-hydroxycyclohexylthiophosphinate (V). To a mixture of 1.72 g (0.01 mole) of O-methyl phenylthiophosphinite and 0.98 g (0.01 mole) of cyclohexanone was added a few drops of a solution of MeONa in MeOH. On the following day, the crystalline solid which had separated was filtered off and recrystallized from hexane to give 2.27 g (84%) of (V), mp 74-75°C (hexane). Found: C 58.2; H 7.1; P 11.5; S 11.9%. $C_{13}H_{19}O_2PS$. Calculated: C 57.7; H 7.1; P 11.5; S 11.9%. NMR spectrum: δP 100 ppm (acetone).

Phenyl-α-hydroxycyclohexylthiophosphinic Acid (VI). a) A solution of 0.38 g (1.4 mmole) of O-methyl phenyl-α-hydroxycyclohexylthiophosphinate and sodium methoxide obtained from 0.032 g (1.4 mmole) of sodium in 15 ml of dry methanol was heated for 3 h on the water bath. The solvent was then removed, and the residual oil dissolved in water and acidified to give 0.1 g (28%) of (VI), mp 141°C (benzene). Found: C 55.8; H 6.8; P 12.3; S 12.7%. $C_{12}H_{17}O_2PS$. Calculated: C 56.2; H 6.7; P 12.1; S 12.5%. NMR spectrum: δP 87.6 ppm (benzene). Neutralization equivalent: found, 260.0, calculated, 256.3.

b) A solution of 0.5 g (2 mmole) of O-methyl phenyl-α-hydroxycyclohexylthiophosphinate and 1 ml of Me_3N in 5 ml of dry ether was heated in a sealed ampul for 4 h at 70°C. The resulting solid was filtered off, dissolved in water, and acidified to give 0.13 g (25%) of the acid (VI), identical to that obtained by method a) in its spectral and physicochemical properties.

c) To a solution of 0.33 g (1.3 mmole) of O-methyl phenyl-α-hydroxycyclohexylthiophosphinate in 5 ml of dry methanol was added a solution of 0.07 g of KOH in a mixture of 1 ml of water and 5 ml of dry methanol. The mixture was boiled for 4.5 h, and the oil remaining after removal of the methanol was dissolved in water and acidified with hydrochloric acid to give 0.1 g (33%) of the acid (VI), identical to that obtained by method a) in its physicochemical and spectral properties.

Silver Phenyl-α-hydroxycyclohexylthiophosphinate. To a solution of 1 g (3.9 mmole) of this acid (VI) and two drops of phenolphthalein in 30 ml of methanol was added MeONa until a pink coloration was obtained, followed by 0.66 g (3.9 mmole) of silver nitrate. The mixture was stirred for 1 h, and 30 ml of water added. The resulting solid was filtered off, and washed with water and acetone to give 0.87 g (58%) of silver phenyl-α-hydroxycyclohexylthiophosphinate, mp 124-125°C. Found: C 39.5; H 4.2%. $C_{12}H_{16}O_2PSAg$. Calculated: C 39.6; H 4.4%. IR spectrum: νOH 3400 cm^{-1}.

S-Ethyl Phenyl-α-hydroxycyclohexylthiophosphinate (VII). a) To a suspension of 0.8 g (2.2 mmole) of silver phenyl-α-hydroxycyclohexylthiophosphinate in 20 ml of dry methanol was added 1 ml of ethyl iodide, and the mixture boiled for 4 h. The precipitate of AgI was filtered off, and the methanol removed from the filtrate to give 0.31 g (50%) of (VII), mp 115-116°C (acetone) (cf. [3]); IR spectrum: $\nu P{=}O$ 1160, νOH 3240 cm^{-1}.

b) Reaction of 2.48 g (12 mmole) of S-ethyl phenylchlorothiophosphinite with 1.185 g (12 mmole) of cyclohexanone and 0.218 g (12 mmole) of water in 20 ml of dry ether at 10-15°C gave 2.18 g (64%) of (VII), mp 115-116°C (acetone).

CONCLUSIONS

Phenyl-α-hydroxycyclohexylthiophosphinic acid has been prepared, and some of its properties studied.

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PREPARATION OF FREE STABILIZED ALLYL CATIONS, STABILIZED BY THE η^5-C_5H_5-3-Fe^{II}-η^5-1,2-$C_2B_9H_{10}$-1 GROUP

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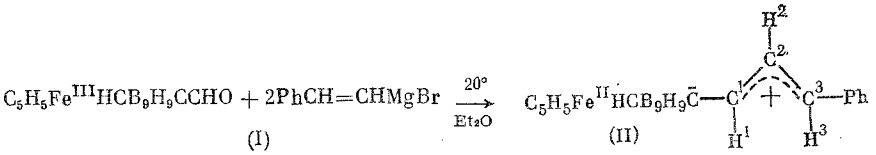
1-Ferrocenyl-3-arylallyl cations are known which are stabilized both by the ferrocenyl and aryl groups [1, 2]. The existence of these allyl cations has been demonstrated by PMR spectra and chemical reactions. 1-Ferrocenylallyl cations containing other substituents in the allylcation group have not been obtained. We have previously shown that the η^5-C_5H_5-3-Fe^{II}-η^5-1,2-$C_2B_9H_{10}$-1 group stabilizes the carbocationic center bonded to the η^5-dicarbollyl ligand [3-7]. It was of interest to obtain an allyl cationic system stabilized by this group. For this purpose, the aldehyde (I) was treated with an excess of β-styrylmagnesium bromide in ether, in order to obtain the allyl carbinol for conversion by protonation into its allyl cation (II). However, instead of the expected carbinol, the allyl cation (II) was obtained directly in a yield of 28%.



$$\underset{(I)}{C_5H_5Fe^{III}HCB_9H_9CCHO} + 2PhCH{=}CHMgBr \xrightarrow[Et_2O]{20^\circ} \underset{(II)}{C_5H_5Fe^{II}HCB_9H_9\bar{C}}-\underset{H^1}{C^1}\overset{H^2 - C^2}{\cdots+\cdots}\underset{H^3}{C^3}-Ph$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2809-2814, December, 1983. Original article submitted February 8, 1983.

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