

The carbonylation was carried out in glass ampules placed in a 0.15-liter steel autoclave at 170°C with 100 atm initial CO pressure (at 20°C) and α -C₆H₁₂:AcOH:H₂O:HI mole ratio = 1:1:1:0.2. In the experiment, we took 4.2 g (0.05 mole) 1-hexene, 3 ml o-xylene, 3 g acetic acid, 2.4 g (0.01 mole) 47% HI, and 0.9 g (0.05 mole) water. The reaction products were analyzed by gas-liquid chromatography on an LKhM-8MD chromatograph on 2.75 m × 3 mm steel column packed with 15% polyethylene glycol adipinate with 3% H₃PO₄ on Chromosorb G (60-80 mesh) at 175°C. The sample inlet temperature was 250°C. A flame ionization detector was used. The helium carrier gas flow velocity was 30 ml/min.

The authors express their gratitude to A. L. Tarasov for taking and discussing the ESR spectra and to P. I. Slyunyaev for determining the palladium content in the catalysts on the Saturn-2 spectrophotometer.

CONCLUSIONS

A catalyst obtained by the deposition of palladium(II) on weakly basic anion-exchange resins displays high efficiency in the carbonylation of 1-hexene with the formation of a mixture of enanthoic and 2-methylcaproic acids.

LITERATURE CITED

1. A. L. Lapidus, S. D. Pirozhkov, A. R. Sharipova, and K. V. Puzitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 371 (1979).
2. A. L. Lapidus, S. D. Pirozhkov, A. Vellekov, V. I. Garanin, P. I. Slyunyaev, and Kh. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2304 (1982).
3. K. M. Saldadze and V. D. Kopylova-Valova, *Complexing Ion-Exchange Resins* [in Russian], *Izd. Khimiya, Moscow* (1980).
4. G. Charlot, *Analytical Chemistry* [Russian translation], *Khimiya, Moscow* (1969).

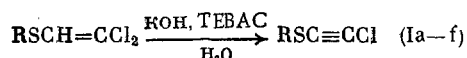
SYNTHESIS AND REACTIONS OF ORGANYL CHLOROETHYNYL SULFIDES WITH PHOSPHORUS-CONTAINING NUCLEOPHILES

A. N. Mirskova, S. G. Seredkina, I. D. Kalikhman,
and M. G. Voronkov

UDC 542.91:547.379'131:547.1'118

Organyl chloroethynyl sulfides $\text{RSC}\equiv\text{CCl}$ (I) were previously obtained by the dehydrochlorination of organyl β,β -dichlorovinyl sulfides upon heating with KOH in vacuum without solvent in 40-50% yield [1] and in DMSO at 5-10°C and normal pressure with yields up to 80% [2].

In the present work, we used phase-transfer catalysis to simplify the preparation of these compounds and avoid the use of organic solvents. The yields were raised to 90-95%. The reaction was carried out in water using triethylbenzylammonium chloride (TEBAC) as the phase-transfer catalyst:



The optimal reaction conditions include a sulfide:alkali:TEBAC ratio of 1:2:0.1, 50% alkali concentration in water, 5-6 h reaction time, and 20-22°C. Heating to 30-35°C led to the partial polymerization of the desired product, while cooling to 10-15°C led to a marked decrease in the reaction rate.

The physicochemical characteristics and yields of (Ia)-(If) are given in Table 1. The IR spectra of the chloroacetylenes show a medium-intensity band at 2150-2170 cm⁻¹ in the

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2818-2821, December, 1985. Original article submitted March 4, 1985.

region close to that for chloroethynylphosphonates [3].

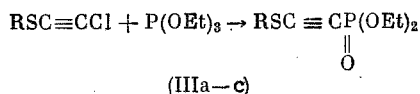
^{13}C NMR spectroscopy was used to study the polarization of the triple bond of sulfides (I). Comparison of the chemical shifts of the acetylenic carbon atoms of sulfides (Ia) and (Ib) (Table 2) with the analogous shifts in ethylthioacetylene ($\text{C}_2\text{H}_5\text{SC}\equiv\text{CH}$, $\delta\text{C}^1 = 72.8$, $\delta\text{C}^2 = 81.6$ ppm) reveals the significant role of back electron polarization [4].

We have previously shown that organyl chloroethynyl sulfides react with secondary and tertiary amines [5, 6] in ether and with thiolates in DMSO [2] to give the chlorine substitution products. Products of the addition of amines and thiols at the triple bond were not observed.

In a further investigation of the chemical properties of sulfides (I), we studied the reactions of these compounds with phosphorus-containing nucleophiles. Thus, the reaction of phenyl chloroethynyl sulfide with PPh_3 in abs. ether leads to triphenyl(phenylthioethynyl) phosphonium chloride (II), which is a yellow crystalline compound soluble in water, alcohols, acetone, and acetonitrile. The structure and composition of (II) were confirmed by elemental analysis, ^{13}C and ^{31}P NMR, and IR spectroscopy. The IR spectrum of (II) shows a band for stretching of the $\text{C}\equiv\text{C}$ bond at 2100 cm^{-1} . The acetylenic carbon atom signals in the ^{13}C NMR spectra of (II) are downfield relative to the starting sulfide (I) (see Table 2). The spin-spin coupling constants of the ^{31}P atom with the acetylenic carbon atoms ($^{31}\text{P}-^{13}\text{C}_\alpha-180.7$, $^{31}\text{P}-^{13}\text{C}_\beta-28$ Hz) and the phenyl carbon atoms ($^{31}\text{P}-^{13}\text{C}^1-100.1$ Hz, $^{31}\text{P}-^{13}\text{C}^2-12.2$, $^{31}\text{P}-^{13}\text{C}^3-13.4$, $^{31}\text{P}-^{13}\text{C}^4-3.7$ Hz) are characteristic for triphenylphosphonium chlorides.

Halocetylenes have three sites susceptible for nucleophilic attack, namely, the halogen atom and both acetylenic carbon atoms. In order to elucidate the direction of the nucleophilic attack on the organyl chloroethynyl sulfide molecule, we carried out the reaction of phenyl chloroethynyl sulfide with PPh_3 in aqueous acetonitrile. However, in contrast to the reaction of phenylethynyl bromide with PPh_3 in aqueous acetonitrile described by Hofman and Forster [7], the terminal acetylene (phenylthioacetylene) is not formed. The only reaction product was phosphonium salt (II) obtained in aprotic solvents. This indicates preferential attack of PPh_3 on the sp-hybridized carbon adjacent to the chlorine atom. Phosphonium salt (II) is recovered unaltered after heating at reflux for 3 h in aqueous solution.

The only products of the reaction of organyl chloroethynyl sulfides with trialkyl phosphites are organylthioethynylphosphonates (IIIa-c), which are the Arbuzov rearrangement products:



The structures of (III) were shown by IR and ^{13}C and ^{31}P NMR spectroscopy and confirmed by elemental analysis. The physicochemical indices and yields of (IIIa-c) are given in Table 1. The IR spectrum of (IIIa-c) have strong bands for the stretching vibrations of the $\text{C}\equiv\text{C}$ bonds ($2115-2120\text{ cm}^{-1}$) and $\text{P}=\text{O}$ bonds (1265 cm^{-1}). The chemical shifts and coupling constants in the ^{31}P and ^{13}C NMR spectra of these phosphonates are close to those found for $\text{R}-\text{C}\equiv\text{C}-\text{P}(\text{O})(\text{OEt})_2$, where $\text{R} = \text{Alk}$ [3], and indicate a slight polarizing effect of the organylthio group.

EXPERIMENTAL

The IR spectra were taken neat and in Vaseline mull on a UR-20 spectrometer, while the ^1H , ^{13}C , and ^{31}P NMR spectra were taken on a Jeol-90 Q spectrometer.

Ethyl Chloroethynyl Sulfide (Ia). A mixture of 15.7 g ethyl β , β -dichlorovinyl sulfide, 22.4 g 50% aq. KOH, and 2.27 TEAC was stirred at $20-22^\circ\text{C}$ for 6 and extracted in ether. The extract was washed with water and dried over CaCl_2 . Ether was distilled off, and the product was distilled in vacuum to yield 11.7 g (Ia), bp 44°C (12 mm), n_D^{20} 1.5105, d_4^{20} 1.1063. IR spectrum (ν , cm^{-1}): 2170 ($\text{C}\equiv\text{C}$). Found: Cl 28.92; S 26.65%. Calculated for $\text{C}_4\text{H}_5\text{Cl}$: Cl 29.46; S 26.55%. Sulfides (Ib)-(If) were obtained by analogous procedures.

(Phenylthioethynyl)triphenylphosphonium Chloride (II). A sample of 1.68 g (If) was added to a solution of 2.62 g PPh_3 in abs. ether at $20-22^\circ\text{C}$, maintained for 12 h, and then filtered to yield 3.56 g (83%) (II), mp $50-52^\circ\text{C}$. IR spectrum (ν , cm^{-1}): 2100 ($\text{C}\equiv\text{C}$). Found: C 72.48; H 4.55; Cl 8.97; P 7.54; S 6.40%. Calculated for $\text{C}_{26}\text{H}_{20}\text{ClPS}$: C 72.46; H 4.69; Cl 8.22; P 7.18; S 7.43%.

TABLE 1. Characteristics and Yields of $\text{RSC}\equiv\text{Cl}$ (I) and $\text{RSC}\equiv\text{CP(O)}(\text{OC}_2\text{H}_5)_2$ (III)

Compound	R	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %			Chemical formula	Calculated, %		
						Cl	P	S		Cl	P	S
(Ia)	Et	92	44(12)	1.5105	1.1063	28.92	—	26.65	$\text{C}_4\text{H}_9\text{ClS}$	29.46	—	26.55
(Ib)	Pr	94	49(12)	1.4913	1.1075	26.40	—	23.75	$\text{C}_5\text{H}_9\text{ClS}$	26.35	—	23.81
(Ic)	n-Bu	95	62(11)	1.5050	1.0823	24.00	—	21.72	$\text{C}_6\text{H}_9\text{ClS}$	23.90	—	21.54
(Id)	t-Bu	90	65(14)	1.5020	1.0684	24.01	—	21.03	$\text{C}_6\text{H}_9\text{ClS}$	23.90	—	21.54
(Ie)	t-Bu	92	23(3)	1.5000	1.0777	24.02	—	21.36	$\text{C}_6\text{H}_9\text{ClS}$	23.90	—	21.54
(If)	Ph	94	78-80(1)	1.6118	1.1095	21.10	—	19.25	$\text{C}_8\text{H}_9\text{ClS}$	21.92	—	19.25
(IIIa)	Et	57	432(2)	1.4775	1.0950	—	43.00	43.50	$\text{C}_8\text{H}_{15}\text{O}_3\text{PS}$	—	43.47	43.90
(IIIb)	Pr	60	433(2)	1.5020	1.1050	—	42.62	43.37	$\text{C}_9\text{H}_{17}\text{O}_3\text{PS}$	—	43.10	43.57
(IIIc)	n-Bu	72	435(1)	1.5034	1.0862	—	43.65	43.65	$\text{C}_{10}\text{H}_{19}\text{O}_3\text{PS}$	—	43.37	42.81

TABLE 2. IR and ^{13}C and ^{31}P NMR Data for (I)-(III)

Compound	δ , ppm, (J, Hz)			ν , cm^{-1}
	$^{13}\text{C}^1$	$^{13}\text{C}^2$	^{31}P from H_3PO_4	
$\text{C}_2\text{H}_5\text{SC}\equiv\text{C}^1\text{Cl}$ (Ia)	69,57	59,71	—	2170
$\text{C}_2\text{H}_5\text{SC}\equiv\text{CCl}$ (Ib)	68,65	59,71	—	2150
$(\text{C}_2\text{H}_5\text{SC}\equiv\text{CP}^+\text{Ph}_3)\text{Cl}^-$ (II)	76,97d ($^1J=180,7$)	112,3d ($^2J=28,1$)	-6,35	2100
$\text{C}_2\text{H}_5\text{SC}\equiv\text{CP}(\text{O})(\text{OC}_2\text{H}_5)_2$ (IIIa)	86,15 ($^1J=29,30$)	93,71 ($^2J=50,4$)	6,00	2115
$\text{C}_2\text{H}_5\text{SC}\equiv\text{CP}(\text{O})(\text{OC}_2\text{H}_5)_2$ (IIIb)	86,74 ($^1J=300,3$)	93,30 ($^2J=50,5$)	8,0	2115
$n\text{-C}_4\text{H}_9\text{SC}\equiv\text{CP}(\text{O})(\text{OC}_2\text{H}_5)_2$ (IIIc)	85,87d ($^1J=300,3$)	93,68d ($^2J=57,4$)	10,6	2120

(Ethylthioethynyl)diethylphosphonate (IIIa). A sample of 16.6 g triethyl phosphite was added dropwise with rapid stirring to 12.5 g (Ia). The mixture warmed spontaneously to 60-65°C and was then stirred for an additional 2 h at 20-22°C. Vacuum distillation gave 12.65% (57%) (IIIa). Phosphonates (IIIb) and (IIIc) were obtained by analogous procedures.

CONCLUSIONS

1. A method was proposed for the preparation of organyl chloroethynyl sulfides by the dehydrochlorination of organyl β , β -dichlorovinyl sulfide by alkali under phase-transfer catalysis conditions.

2. The reactions of organyl chloroethynyl sulfides with triphenylphosphine and triethyl phosphite lead to the products of the normal substitution of halogen in chloroacetylene, namely to organylthioethynylphosphonium chlorides and organylthioethynylphosphonates.

LITERATURE CITED

1. A. S. Atavin, A. N. Mirskova, and É. F. Zorina, USSR Inventor's Certificate No. 416,351 (1973); Byull. Izobret., No. 7 (1974).
2. S. G. Seredkina, V. E. Kolbina, V. G. Rozinov, A. N. Mirskova, and M. G. Voronkov, Zh. Obshch. Khim., **52**, 2694 (1982).
3. A. A. Petrov, A. V. Dogadina, B. I. Ionin, V. A. Garibina, and A. A. Leonov, Usp. Khim., **52**, 1793 (1983).
4. G. A. Kalabin, Dissertation, Irkutsk (1982).
5. A. N. Mirskova, S. G. Seredkina, and M. G. Voronkov, USSR Inventor's Certificate No. 1,097,616 (1984); Byull. Izobret., No. 22 (1984).
6. A. N. Mirskova, S. G. Seredkina, I. D. Kalikhman, O. B. Bannikova, and M. G. Voronkov, Zh. Org. Khim., **20**, 657 (1984).
7. H. Hofman and H. Forster, Tetrahedron Lett., 983 (1964).