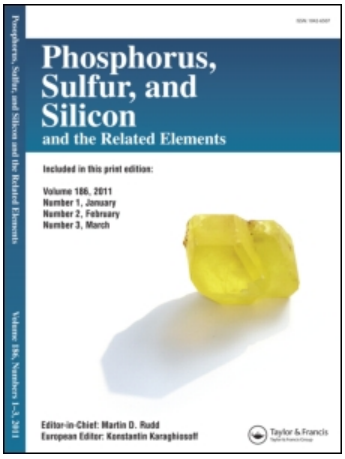

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DIMETHYL 3-CHLOROPROPENE-2-PHOSPHONATE 1. SYNTHESIS THROUGH OXIDATIVE CHLOROPHOSPHORYLATION OF ALLYL CHLORIDE

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To cite this Article Gurevich, Igor E. , Tebby, John C. , Dogadina, Alla V. and Ionin, Boris I.(1995) 'DIMETHYL 3-CHLOROPROPENE-2-PHOSPHONATE 1. SYNTHESIS THROUGH OXIDATIVE CHLOROPHOSPHORYLATION OF ALLYL CHLORIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 101: 1, 267 — 272
To link to this Article: DOI: 10.1080/10426509508042526
URL: http://dx.doi.org/10.1080/10426509508042526

Phosphorus, Sulfur, and Silicon, 1995, Vol. 101, pp. 267–272
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DIMETHYL 3-CHLOROPROPENE-2-PHOSPHONATE 1. SYNTHESIS THROUGH OXIDATIVE CHLOROPHOSPHORYLATION OF ALLYL CHLORIDE

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(Received November 28, 1994; in final form December 6, 1994)

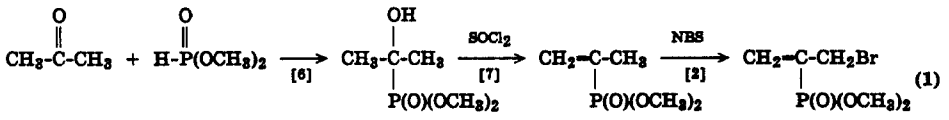
An effective method for the synthesis of dimethyl 3-chloropropene-2-phosphonate (**2**) in a overall yield of 25% has been developed. The method is based on oxidative chlorophosphorylation of 3-chloropropene followed by elimination of hydrochloric acid and esterification.

Key words: 3-chloropropene-2-phosphonate, oxidative chlorophosphorylation, ammonium salt.

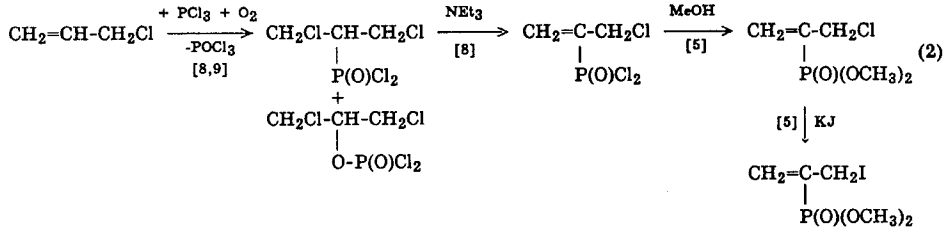
As a part of a programme on the synthesis of unsaturated compounds with a phosphonate group at the second atom of the carbon chain, we required dialkyl 3-halogeno-1-propene-2-phosphonate as an alkylating agent.

The chemistry of its carboxylic analogues alkyl-α-halogenomethylacrylates[1] are well established and have been investigated extensively. However, there have been only a limited number of studies of the chemical behaviour of 3-halogeno-1-propene-2-phosphonates. The reactions which have been investigated include their use as organozinc reagents,[2,3] as an alkylating agent,[4] and some selected reactions with iodide, sodium methoxide and diethylamine.[5] Three principally different methods for their synthesis have been reported. Benezra[2] first described the synthesis of 3-bromo-1-propene-2-phosphonate (**1**) by the bromination of dimethyl propene-2-phosphonate using N-bromosuccinimide (Scheme I).

Another approach to 3-halogen-1-alkene-2-phosphonates[5] has been based on the oxidative halophosphorylation of allyl chloride (3-chloropropene) followed by the elimination of hydrochloric acid and esterification (Scheme II). The synthesis of diethyl 3-chloro-1-propene-2-phosphonate by Michael-Arbusov reaction of 1,2,3-trichloropropene with triethyl phosphite has also been described.[10] However with respect to the last method we found that the dimethyl phosphonate (**2**) readily reacted with trimethyl phosphite at 70°C whereas no reaction of 1,2,3-tribromopropene with trimethyl phosphite was observed at this temperature. In our hands attempts to carry out the Michael-Arbusov reaction resulted only in isomerisation



SCHEME I Synthesis of 3-bromopropene-2-phosphonate by NBS-bromination method.

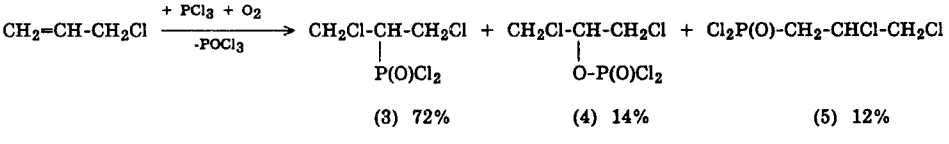


SCHEME II Synthesis of 3-chloro-1-propene-2-phosphonate via oxidative chlorophosphorylation.

of trimethyl phosphite. We were interested in a method which would give a good yield of pure 3-halogeno-1-propene-2-phosphonate without column separation. We report below an improved method for the synthesis of dimethyl 3-chloro-1-propene-2-phosphonate (**2**) based on Belykh's method.

RESULTS AND DISCUSSION

An NMR study of the crude product from the oxidative halophosphorylation of allyl chloride[8,9,11] showed that the reaction produced three organophosphorus products (**3–5**). A small amount (2%) of 1,2,3-trichloropropene from the chlorination of allyl chloride was also formed.



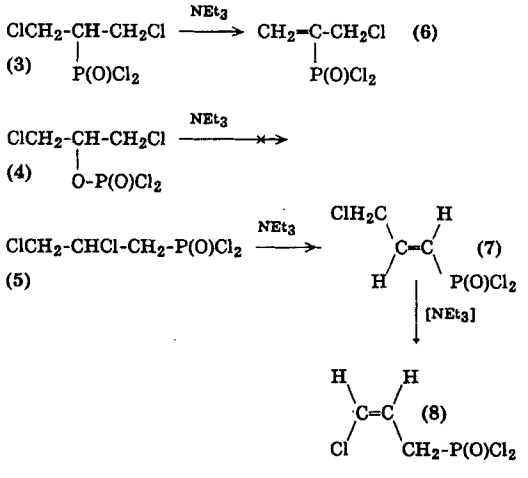
The ^{31}P NMR spectrum of the crude product showed three signals corresponding to organophosphorus products each of which could be assigned from the multiplicity of the proton coupled spectra (phosphonate (**3**) δ_p = 41.9, sextet; phosphate (**4**) δ = 7.8, doublet; phosphonate (**5**) δ = 40.1, quartet). The structure of the compounds were also confirmed by ^1H and ^{13}C NMR spectroscopy, and their further interconversions. Isolation of the individual compounds at this stage was not carried out. It is known,[12] that in the oxidative halophosphorylation of alkenes, the presence of a donor substituent on the double bond facilitates the formation of phosphonate. The chemoselectivity observed in the oxidative halophosphorylation of allyl chloride can be attributed to the nucleophilic character of the radical formed in the initial attack of the chloride atom on the terminal carbon of the allyl chloride.[13] The "philicity" of this radical[9] determines the preferential reaction of the radical with the PCl_3 molecule, which is more electrophilic than the oxygen mol-

ecule. The regioselectivity of the reaction can be explained by steric factors[9] and radical stability.

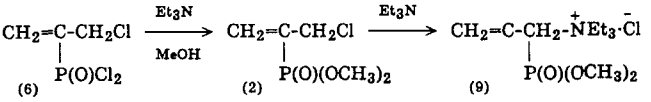
The crude product from the oxidative halophosphorylation of allyl chloride was distilled followed by treatment with triethylamine. The three organophosphorus compounds (**3–5**) still present in the distillate interacted with triethylamine in quite distinctive manners (Scheme III). The different reactivities can be explained by the following ease of proton removal by the base: $-CH(P(O)Cl_2)-$ >> $-CH_2-P(O)Cl_2$ >> $-CH(OP(O)Cl_2)-$.

Accordingly, upon the addition of triethylamine to the distilled reaction product while the phosphonate (**4**) did not react, all the phosphonyl dichloride (**3**) underwent elimination of hydrochloric acid. On the other hand only 22% of its isomer (**5**) eliminated HCl to produce the dichloride (**7**) and once formed 21% of 3-chloro-1-propene-1-phosphonic acid dichloride (**7**) underwent a prototropic isomerization under the catalytic action of triethylamine to form cis-3-chloro-2-propen-1-phosphonate (**8**).[14] A number of examples of the isomerization of vinyl phosphonates to allylic phosphonates including the above[14] had been described in the literature.[15–17] The distinctive character of the final compounds (**4–8**) permitted 3-chloro-1-propene-2-phosphonic acid dichloride (**6**) to be purified by fraction vacuum distillation.

Esterification of 3-chloro-1-propen-2-phosphonic acid dichloride (**6**) by methanol in the presence of triethylamine gave dimethyl 3-chloro-1-propene-2-phosphonate (**2**). The competitive reaction at this stage was the formation of the ammonium salt (**9**) by the reaction of the ester (**2**) with triethylamine (Scheme IV). Attempts at distilling the phosphonate (**2**) from the reaction mixture resulted in its rapid polymerisation and the isolation of the ester (**2**) in low yield (30%). The cause of polymerisation appeared to be the presence of the ammonium salt (**9**) (or a product of its thermal conversion). This was indicated by the observation that pure phosphonate (**2**) polymerises rapidly in the presence of a catalytic amount of triethylamine. Separation of ester (**2**) from its ammonium salt (**9**) was achieved by passage



SCHEME III Interaction of the distilled reaction mixture, from the oxidative halophosphorylation of allyl chloride, with triethylamine.



SCHEME IV Reaction of 3-chloro-1-propene-2-phosphonic acid dichloride with triethylamine.

of the reaction mixture through silica. After evaporation of the solvent, the residue was distilled in vacuum without polymerisation to give pure ester (**2**).

Thus, with a knowledge of the structures and properties of all the compounds (**3–9**), a simple and effective method for synthesis of the phosphonate (**2**) in an overall yield of 25% was developed. All compounds (**3–9**) were characterised by ^{1}H, ^{31}P, ^{13}C NMR spectroscopy followed by conversion to the corresponding dimethyl esters and their analysis by GC-MS.

EXPERIMENTAL

NMR spectra were determined on solutions in $CDCl_3$, with TMS as the standard, using JEOL FX90Q, GSX270 and Bruker AC200 instruments. GC-MS analysis was performed on a VG Trio 1000 HS linked to a Carlo Erba Mega GC using a DB 17 0.32 mm capillary column. The mass spectroscopy conditions were as follows: electron energy 70 eV, source temperature 200°C, resolution 1 a.m.u.

Oxidative Chlorophosphorylation of Allyl Chloride

A 1 litre reactor was charged with allyl chloride (80 g) and phosphorus trichloride (800 ml), and with vigorous stirring and cooling to maintain the temperature at 20°C, oxygen was bubbled in at a volume rate of 0.02 m^3/h until the exothermic reaction was complete (about 10 h). Phosphoryl trichloride was distilled off at reduced pressure (ca 15 mm) and the residue was vacuum distilled at ca 1 mm to give a colourless distillate (201 g, bp 80–100°C).

The relative amounts of the compounds (**3–5**) depended to a moderate extent (about 5%) on the rate of flow of the oxygen and the rate of stirring. Increasing the oxygen flow facilitated the formation of the phosphate (**5**) and 1,2,3-trichloropropane.

The NMR spectra were recorded on the distillate (bp 80–100°C 1 mm), which was a mixture of the compounds (**3–5**).

1,3-Dichloropropane-2-phosphonic acid dichloride (**3**) had ^{1}H-NMR spectrum, δ, ppm (J, Hz): 4.14 (H_A (CH_AH_BCl), J_{PA} = 22.46), 4.15 (H_B, J_{PB} = 22.46), 3.22 (CH, J_{PH} = 19.54, J_{AH} = 3.91, J_{BH} = 6.32). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 38.44 (CH_2Cl, J_{PC} = 1), 54.5 (CH, J_{PC} = 95.58). ^{31}P NMR spectrum, δ_p: 41.9.

1,3-Dichloropropane-2-phosphoric acid dichloride (**4**) had ^{1}H-NMR spectrum, δ, ppm (J, Hz): 5.07 (CH, J_{PH} = 11.72, J_{HH} = 4.88), 3.89 (CH_2Cl, J_{PH} = 1.46). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 42.29 (CH_2Cl, J_{PC} = 5.49), 80.06 (CH, J_{PC} = 8.79). ^{31}P NMR spectrum, δ_p: 7.8.

2,3-Dichloropropane-1-phosphonic acid dichloride (**5**) had ^{1}H-NMR spectrum, δ, ppm (J, Hz): 3.46 (H_A (CH_AH_B), J_{PA} = 15.6, J_{HA} = 4.88, J_{BA} = 15.6), 3.1 (H_B, J_{PB} = 14.6, J_{HB} = 7.8), 3.98 (H_E (CH_DH_ECl), J_{DE} = 19.8), 4.0 (H_D), 4.58 (CHCl, J_{PH} = 11.75, J_{EH} = 6.78, J_{DH} = 9.27). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 47.76 (CH_2, J_{PC} = 102.17), 53.11 (CHCl, J_{PC} = 3.8), 47.82 (CH_2Cl, J_{PC} = 16.48). ^{31}P NMR spectrum, δ_p: 40.1.

3-Chloro-1-propene-2-phosphonic Acid Dichloride

To a solution of the distillate (183.5 g) (from the oxidative chlorophosphorylation of allyl chloride) in absolute ether (700 ml), triethylamine (65 g) in absolute ether (300 ml) was added dropwise at 5°C. A higher temperature facilitated the formation of byproducts (**7**) and (**8**). When the addition was completed, the precipitated triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was vacuum distilled (1 mm). The product was redistilled twice using a Vigreux column (12 cm length). Each time the first fraction was collected (1 mm., b.p. 40–45°C, 102 g and 1 mm, b.p. 40–42°C, 83 g (75%) respectively). The phosphonic acid dichloride (**6**) had ^{1}H-NMR spectrum, δ, ppm (J,

Hz): 6.51 (H_A (CH_AH_B=), J_{PA}^{trans} = 62.01, J_{HA} = 2.5), 6.62 (H_B, J_{PB}^{cis} = 28.32, J_{HB} = 1.0), 4.37 (CH_2Cl, J_{PH} = 13.19). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 135.22 (CH_2=, J_{PC} = 9.88), 140.45 (=C—, J_{PC} = 148.43), 40.3 (CH_2Cl, J_{PC} = 26.37). ^{31}P NMR spectrum, δ_p: 30.2.

The NMR spectra of the residue showed it to be a mixture of the compounds (**4**), (**7**), and (**8**).

3-Chloro-1-propene-1-phosphonic acid dichloride (**7**) had ^1H-NMR spectrum, δ, ppm (J, Hz): 6.55 (P—CH_A = J_{PA} = 35.64 J_{AH} = 1.95, J_{AB} = 16.61), 7.06 (=CH_B—, J_{PB} = 28.81, J_{HB} = 4.39), 4.29 (CH_2Cl, J_{PH} = 2.93). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 125.48 (P—CH=, J_{PC} = 148.33), 147.00 (=CH—, J_{PC} = 6.59), 41.79 (CH_2Cl, J_{PC} = 30.76). ^{31}P NMR spectrum, δ_p: 30.2.

3-Chloro-2-propene-1-phosphonic acid dichloride (**8**) had ^1H-NMR spectrum, δ, ppm (J, Hz): 3.26 (CH_2, J_{PH} = 19.53 J_{AH} = 7.82, J_{BH} = 0.97), 5.92 (=CH_A—, J_{PA} = 7.82, J_{AB} = 7.82), 6.5 (=CH_BCl, J_{PB} = 7.82). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 40.25 (CH_2, J_{PC} = 100.0), 117.19 (=CH—, J_{PC} = 14.28), 124.77 (=CHCl, J_{PC} = 21.97). ^{31}P NMR spectrum, δ_p: 40.1.

3-Chloro-1-propene-2-phosphonic Acid Dimethyl Ester (**2**)

To a stirred solution of 3-chloro-1-propene-2-phosphonic acid dichloride (**6**) (58.2 g) in absolute benzene (400 ml), a solution of triethylamine (60.6 g) and methanol (19.2 g) in absolute benzene (150 ml) was added dropwise at 30–35°C. A lower temperature facilitated the formation of the ammonium salt (**9**). The triethylamine hydrochloride precipitate was filtered off, the solvent was distilled off at a reduced pressure, the residue was dissolved in ether and passed through a layer of silica (50 g). After evaporation of the solvent, vacuum distillation gave the dimethyl ester of 3-chloro-1-propen-2-phosphonic acid (**2**) (29.9 g, 54%), bp 60°C (1 mm). ^1H-NMR spectrum, δ, ppm (J, Hz): 6.27 (H_A (CH_AH_B=), J_{PA}^{trans} = 45.04 J_{AB} = 1.9), 6.3 (H_B, J_{PB}^{cis} = 21.51), 4.23 (CH_2Cl, J_{PH} = 10.1, J_{AH} = 1.54), J_{BH} = 1.9). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 132.82 (CH_2=, J_{PC} = 8.05), 133.93 (=C—, J_{PC} = 178.82), 42.17 (CH_2Cl, J_{PC} = 17.81), 52.04 (OCH_3, J_{PC} = 6.54). ^{31}P NMR spectrum, δ_p: 18.3. Mass spectrum, m/z (I_{rel}, %) 149 (100), 109 (97.65), 93 (92.55), 135 (92.16), 79 (91.76), 96 (64.71), 75 (60.39), 117 (48.63), 71 (47.06), 103 (36.86). $[C_5H_{10}O_3PCl]^+$ 184 (20.2), 186 (6.86).

Esterification of the Distilled Crude Product of Oxidative Chlorophosphorylation

To a stirred solution of the distilled crude product (2.2 g) from the oxidative chlorophosphorylation in absolute benzene (20 ml), a solution of triethylamine (2.9 g) and methanol (0.62 g) in absolute benzene (5 ml) was added dropwise at 15–20°C. The triethylamine hydrochloride precipitate was filtered off, the solvent was distilled off at a reduced pressure and the residue was analysed by GC-MS analysis, column chromatography on silica and NMR spectroscopy and shown to be a mixture of the compounds described below.

1,3-Dichloropropane-2-phosphoric acid dimethyl ester had ^1H-NMR spectrum, δ, ppm (J, Hz): 4.3 (CH, J_{PH} = 7.81, J_{HH} = 5.37), 3.4 (CH_2Cl, J_{PH} = 1.46), 3.41 (OCH_3, J_{PH} = 11.23). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 68.56 (CH_2Cl, J_{PC} = 5.5), 89.87 (CH, J_{PC} = 5.49), 57.35 (J_{PC} = 5.5). ^{31}P NMR spectrum, δ_p: −0.2. Mass spectrum, m/z (I_{rel}, %) 109 (100), 187 (90.18), 127 (74.11), 185 (29.91), 189 (27.23), 79 (21.65), 75 (13.95), 137 (13.06), 95 (9.65), 77 (5.97). $[C_5H_{11}O_4PCl_2]^+$ 237 (0.82), 239 (0.52), 241 (0.09).

3-Chloro-1-propene-1-phosphonic acid dimethyl ester had ^1H-NMR spectrum, δ, ppm (J, Hz): 5.66 (P—CH_A = J_{PA} = 15.13, J_{AH} = 1.95, J_{AB} = 16.6), 6.44 (=CH_B—, J_{PB} = 12.2, J_{HB} = 5.37), 3.78 (CH_2Cl, J_{PH} = 2.0), 3.33 (OCH_3, J_{PH} = 11.23). ^{13}C NMR spectrum, δ_c, ppm (J, Hz): 118.51 (P—CH=, J_{PC} = 178.97), 147.71 (=CH—, J_{PC} = 6.59), 44.06 (CH_2Cl, J_{PC} = 26.36), 53.05 (OCH_3, J_{PC} = 5.49). ^{31}P NMR spectrum, δ_p: 19.7. Mass spectrum, m/z (I_{rel}, %) 149 (100), 109 (85.88), 79 (78.43), 135 (78.04), 93 (77.25), 96 (28.24), 75 (26.27), 71 (19.61), 117 (18.33), 55 (16.47). $[C_5H_{10}O_3PCl]^+$ 184 (8.43), 186 (2.72).

3-Chloro-2-propene-1-phosphonic acid dimethyl ester had ^1H-NMR spectrum, δ, ppm (J, Hz): 2.43 (CH_2, J_{PH} = 21.98, J_{AH} = 7.33, J_{BH} = 1.47), 5.43 (=CH_A—, J_{PA} = 7.33, J_{AB} = 7.33), 5.83 (=CH_BCl, J_{PB} = 4.88), 3.36 (OCH_3, 11.23). ^{13}C spectrum, δ_c, ppm (J, Hz): 24.78 (CH_2, J_{PC} = 141.72), 121.63 (=CH—, J_{PC} = 10.99), 121.78 (=CHCl, J_{PC} = 37.35), 53.05 (OCH_3, J_{PC} = 5.49). ^{31}P NMR spectrum, δ_p: 28.2. Mass spectrum, m/z (I_{rel}, %) 149 (100), 109 (92.37), 79 (55.42), 93 (49.4), 75 (33.33), 77 (12.75), 150 (9.64), 63 (4.72), 73 (4.39), 51 (3.11). $[C_5H_{10}O_3PCl + 1H]^+$ 185 (0.25).

2,3-Dichloropropane-1-phosphonic acid dimethyl ester had ^1H-NMR spectrum, δ, ppm (J, Hz): 2.63 (H_A (—CH_AH_B—), J_{PA} = 15.63, J_{CA} = 5.37, J_{BA} = 18.06), 2.34 (H_B, J_{PB} = 15.62, J_{CB} = 7.81), 4.7 (CH_CCl), 3.8 (CH_2Cl), 3.8 (OCH_3). Mass spectrum, m/z (I_{rel}, %) 137 (100), 185 (46.53), 79 (42.13), 109 (30.32), 151 (19.91), 187 (15.97), 75 (11.75), 57 (11.69), 149 (8.8), 95 (8.51). $[C_5H_{11}O_3PCl_2]^+$ 221 (3.11), 223 (2.01), 225 (0.95).

ACKNOWLEDGEMENTS

We thank G. S. Evans at the University of Keele and V. Gindin at St.-Petersburg bureau of Bruker for the measurement of highfield NMR spectra, T. J. Barker for carrying out of the GC-MS analysis, Dr. A. W. G. Platt for valuable discussions and M. C. Salt for laboratory assistance.

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