126. Organic Phosphorus Compounds 60 The Direct Synthesis of Tris(N-Substituted Carbamoylethyl) Phosphine Oxides[1])

by **Ludwig Maier**

Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich, Switzerland

(13. III. 73)

Summary. The reaction of elemental white phosphorus with N-alkyl acrylamides and N,N-dialkyl acrylamides in the presence of a base is described and the physical properties of 8 new tertiary phosphine oxides of general formula $(R_2NCOCH_2CH_2)_3P{=}O$ (R = H, CH_3, C_2H_5, $-(CH_2)_4-$, $-(CH_2)_5-$, and $-C_2H_4OC_2H_4-$, $CH_2{=}CHCH_2$) are reported. Interaction of white phosphorus with RNCS, RNCO, azo-bis-isobutyronitrile, $Ph_2N{-}NPh_2$, vinyl acetate, vinyl ethyl ether, and epoxides has also been investigated.

Previously we have reported on the reaction of elemental phosphorus with alkyl halides [2], with *Mannich*-bases [3], and with formaldehyde under basic conditions [4]. Several other reactions of elemental phosphorus with organic substrates which led to the direct synthesis of organic phosphorus compounds, were recently reviewed by us [5]. Continuing our studies we have now investigated the reaction of elemental phosphorus with N-alkyl-acrylamides and N,N-dialkyl-acrylamides. It was hoped to obtain in this way tris(N-alkyl-carbamoylethyl)phosphine oxides and tris(N,N-dialkyl-carbamoylethyl)phosphine oxides according to (1):

$$P_4 + 2\,KOH + 4\,H_2O + 9\,CH_2{=}CH\overset{\overset{O}{\|}}{C}NR_2 \longrightarrow 3\,(R_2N\overset{\overset{O}{\|}}{C}CH_2CH_2)_3P{=}O + K_2HPO_3 \quad (1)$$

Several years ago *Rauhut, Bernheimer & Semsel* described the direct synthesis of tertiary phosphine oxides by reaction of white phosphorus with activated olefins such as $CH_2{=}CHX$, X = CN, H_2NCO, and RO_2C [6]. Whether N-substituted acrylamides would also be suitable in this reaction was not indicated. Since it was hoped that phosphine oxides prepared with substituted acrylamides would be more useful as antistatic agents, the reaction of white phosphorus with several N-substituted acrylamides was investigated, although we are aware that by substituting alkyl for hydrogen in the amido group, the electrophilicity of the double bond is decreased and thus makes the reaction less readily to occur.

In fact, when we attempted to prepare tris(N-alkylcarbamoylethyl)phosphine oxide from white phosphorus, N-alkylacrylamides and a base using alcohol/water as the reaction medium, no reaction was observed. All the phosphorus was recovered.

On the other hand, when N,N-dialkyl substituted acrylamides were treated with white phosphorus in alcoholic solution in the presence of KOH, a ready reaction was observed – although the electrophilicity in these disubstituted acrylamides is even lower than that of the monosubstituted acrylamides – and the tris(dialkylcarbamoylethyl)phosphine oxides were obtained in yields between 30 and 87% (see Table 1).

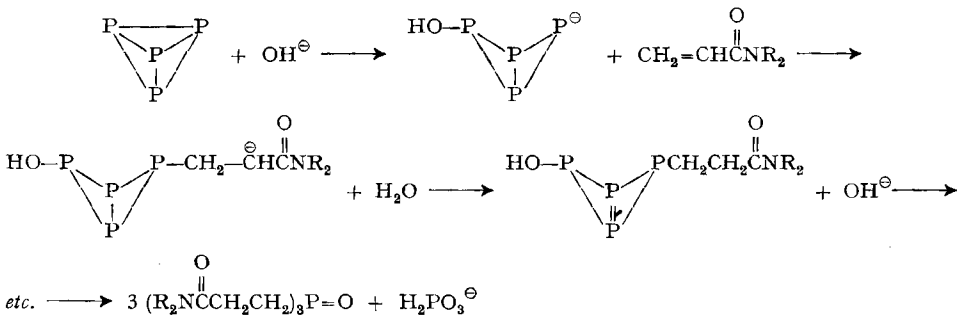
[1]) Part 59, see [1].

Table I. *Physical properties of tris(N,N-dialkyl-carbamoylethyl)phosphine oxides,* $(R_2NCOCH_2CH_2)_3P{=}O$

R	m.p. °C	yield (%)	^{31}P-chem. shift (85proz. H_3PO_4 as ref.)
CH_3	100–101	36.2	– 53.5 (CCl_4/CH_3OH)
C_2H_5	104–105	87.0	– 52.5 ± 0.5 (CCl_4/CH_3OH)
$-(CH_2)_4-$	130–132	75.4	– 56.5 (in H_2O)
$-(CH_2)_5-$	173–175	84.0	– 56 (in CH_3OH)
$-C_2H_4OC_2H_4-$	215–218	30.2	– 55.5 (in CH_3OH/H_2O)
$-CH_2CH{=}CH_2$	oil	72.0	– 48.5 (in $CHCl_3$)

Subsequently it was found that N-alkyl acrylamides do react with white phosphorus when acetonitrile is used as solvent or when the reaction in alcohol is carried out at a higher pH by using three times as much base.

Since in the experiments with dialkyl substituted acrylamides potassium phosphite was also isolated, the mechanism of the reaction seems to be the same as that proposed by *Rauhut et al.* [6] for the $P/CH_2{=}CHX$ reaction:



Extension of this reaction to other electrophilic olefins is being attempted.

Unsuccessfull reactions of elemental phosphorus with organic substrates. – a) White phosphorus and radical forming compounds. Previously we reported that the alkylation of phosphorus with alkyl halides follows a radical mechanism. Since alkyl halides are rather stable, this reaction requires a catalyst and a high temperature [2] [5]. However, irradiation with Co^{60}-γ-rays of solutions of phosphorus in CCl_4, $CHBr_3$, CCl_3Br, CH_3SSCH_3, C_6H_{12}/CCl_4 produces organic phosphorus compounds of the type CCl_3PCl_2, $CHBr_2PBr_2$, $CCl_3(Br)P{-}P(Br)CCl_3$, $(CH_3S)_3P$ and $C_6H_{11}PCl_2$, respectively, at much lower temperature [5]. It would therefore seem reasonable to assume that white phosphorus would react with other radical forming compounds also.

a_1) P_w + *azo-bis-isobutyronitrile* (*AIBN*) (ratio 1:4). Treatment of diphenylphosphine with azo-bis-isobutyronitrile or $Ph_2N{-}NPh_2$ produced in a radical chain reaction $Ph_2PC(CN)Me_2$ and Ph_2PNPh_2, respectively [7], *e.g.*

When a mixture of azo-bis-isobutyronitrile and white phosphorus in toluene solution was heated to 90°, a homogeneous solution was obtained. Work-up gave isobutyronitrile, Me_2CHCN, and the dimer, tetramethylsuccinic acid dinitrile, $Me_2C(CN)(CN)CMe_2$ m.p. 166–168.5°, ^{1}H-NMR. (in $CDCl_3$): CH_3 at 1.93 (*s*). White phosphorus was recovered unchanged. When the reaction was run without a solvent, the same result was obtained.

a$_2$) P_w+ Ph_2N–NPh_2 (ratio 1:1.5). Whereas tetramethylbiphosphine interacts with tetraphenylhydrazine with UV. irraditaion or heating (130–200°) to give diphenylamino-dimethyl-

$$Me_2P{-}PMe_2 + Ph_2N{-}NPh_2 \xrightarrow{UV.} 2\ Me_2PNPh_2$$

phosphine [8], elemental phosphorus did not enter into a reaction when a mixture of tetraphenylhydrazine and white phosphorus was heated with (toluene) or without a solvent up to 150° in a bomb tube. Only decomposition products of tetraphenylhydrazine were isolated.

b) P_w+ *RNCS*(*RNCO*) *and ROH* (ratio 1:6:10). Biphosphines of the type $R_2P{-}PR_2$ are readily cleaved by isothiocyanates in the presence of alcohol [9] to produce phosphinites and tertiary phosphines. White phosphorus did, however, not react under the same conditions with

$$R_2P{-}PR_2 + R'OH + RNCS \longrightarrow R_2PCSNHR + R'OPR_2$$

PhNCS (with or without catalytic amounts of sodium, the only products isolated were PhNHC(S)-OEt, m.p. 66–68°, and starting material), C_4H_9NCS (P_w dissolves well on heating and crystallizes on cooling nicely), or PhNCO.

c) P_w+ RS_2R (ratio 1:1.5). Biphosphines [8] [10] as well as elemental phosphorus [5] interact with disulfides with UV. irradiation or heat to give thiophosphinites and trithiophosphites, respectively *e.g.*,

$$P_4 + 6\ RSSR \longrightarrow 4\ P(SR)_3$$

d) P_w+*epoxides* (ratio 1:3). In contrast to a patent which claimed the formation of organic phosphorus compounds when P_w in CH_3OH was treated with sodium and ethylene oxide (or propylene oxide) [11] we observed no reaction under the conditions given in the patent.

e) P_w+*vinyl acetate* (ratio 1:2.2). When a mixture of white phosphorus, vinyl acetate and alcohol in the presence of KOH as catalyst was heated to 30°, white phosphorus was rapidly consumed. The final product contained however, no phosphorus. All the phosphorus was present as inorganic salts.

f) P_w+ CH_3CN (ratio 1:2). An attempt was made to synthesize aminoethylidene diphosphonic acid, $H_2O_3PC(NH_2)(CH_3)PO_3H_2$, an excellent sequestering agent, directly from white phosphorus and acetonitrile in alkaline solution. When a mixture of white phosphorus and acetonitrile with NaOH (ratio 1:2:0.8) in CH_3OH/H_2O was heated to 55°, a black-brown solution was obtained and white phosphorus was completely consumed after 3 h. Filtration over celite and evaporation of the filtrate gave 27.3 g of a slightly brown solid which after passing through an acidic ion exchanger gave a clear yellow oil consisting of 70% H_3PO_2 and 30% H_3PO_3. No phosphoric acid was detected.

g) P_w+ $CH_2{=}CHOC_2H_5$ (ratio 1:3). When a mixture of white phosphorus and vinyl ethyl ether in alcoholic solution in the presence of KOH was heated to 30° a dark red suspension was obtained which turned dark-brown after 1.5 h at 30°. Filtration and distillation of the filtrate gave no $(EtOCH_2CH_2)_2P{=}O$, which should be a liquid with b.p. 105–106°/0.001 Torr [12]. Most of the white phosphorus was recovered.

Preparation of N-substituted acrylamides. – N-substituted acrylamides were prepared by reaction of acrylic acid chloride with two equivalents of amine in benzene solutions with the addition of a few crystals of hydroquinone to prevent polymerization (when in the case of $CH_2{=}CHCON(CH_3)_2$ no hydroquinone was added, the product polymerized on attempted distillation).

Experimental Part

with Miss *H. Muntwyler* and Mr. *M. Rötheli*[2])

1. $[(CH_3)_2\overset{c}{N}\overset{O}{\overset{\|}{C}}\overset{b}{C}H_2\overset{a}{C}H_2]_3P{=}O$ (**1**). To 5.17 g (0.167 g-at.) of P_w, and 37.3 g (0.377 mol) $CH_2{=}CHCON(CH_3)_2$ in 100 ml ethanol is added at 30–35° in 1 h a solution of 8.3 ml 10N (= 0.083 mol) KOH in 32.2 ml ethanol. Then the

[2]) Microanalyses were carried out by *W. Manser*/ETH, Zürich. ^{31}P- and ^1H-NMR. spectra were run on an HA 60 IL *Varian* spectrometer using H_3PO_4 or TMS as reference. Shifts are given in ppm.

mixture is kept for 1.5 h at this temperature, cooled to 5°, and the precipitated inorganic salt (K_2HPO_3) filtered. The filtrate is evaporated at reduced pressure. Recrystallization of the residue from benzene gives 21.0 g (36.2%) **1**, m.p. 62–93°, which after recrystallization from benzene melts at 100–101° (very hygroscopic). ^{31}P −53.5 ppm (in CCl_4/CH_3OH); ^1H—NMR. (in CCl_4/CD_3OD): a) 2.06 (*m*); b) 2.58 (*m*); a + b = 4H; c) 2.90 and 3.05 (*s*, 6H).

2. $[(CH_3CH_2)_2\underset{a\ d}{N}\overset{O}{\overset{\|}{C}}\underset{c}{C}\underset{b}{H_2CH_2}]_3P{=}O$ (**2**). From 5.17 g (0.167 g-at.) of P_w, 48 g (0.377 mol) $CH_2{=}CHCONEt_2$ in 100 ml EtOH, 8.3 ml 10N KOH (0.083 mol) and 33.2 ml EtOH as under 1. The filtrate is evaporated under reduced pressure to give 68.7 g of an yellow oil which contains still some N,N-diethyl acrylamide. The latter (5.8 g) is distilled in the vacuum. The residue crystallized on standing (63 g = 87%). **2** is a waxy and very hygroscopic solid, m.p. 70–95°. For the analysis a small sample is sublimed in the vacuum (1.5 g) to give (0.55 g) **2**, white-green crystals, m.p. 70–95° which after recrystallization from C_6H_6 melt at 104–105°. ^{31}P −52.0 (−53.0) ppm (in CCl_4/CH_3OH). ^1H-NMR. (in CCl_4/CD_3OD): a) 1.09 (*t*) and 1.20 (*t*, 18.2 H); b) 2.05 (*m*); c) 2.58 (*m*); b + c 11.8 H; d) 3.35 and 3.37 (*qu*, 12H).

$C_{21}H_{42}N_3O_4P$ (431.58) Calc. C 58.44 H 9.81 N 9.74% Found C 57.62 H 9.75 N 8.83%

3. $\left(\underset{a\ c}{\square}\overset{O}{\overset{\|}{N}}\underset{b}{CCH_2CH_2}\right)_3P{=}O$ (**3**). From 1.76 g (0.05 g-at.) P_w, 16 g (0.128 mol) $CH_2{=}CHCONC_4H_8$, 50 ml EtOH, 2.85 ml 10N (= 0.0285 mol) KOH in 15 ml EtOH as under 1. Evaporation of the filtrate gave 18.3 g (75.4%) **3**, a white-yellow mass, which is dissolved in 2-propanol, small amounts of insoluble material filtered and the filtrate evaporated to give **3**, a white solid, m.p. 130–132°. ^{31}P −56.5 ppm (in H_2O). ^1H-NMR. (in D_2O): a) 1.93 (*m*, 4H); b) 2.0–2.9 (*m*, 4H); c) 3.47 (*m*, 4H).

$C_{21}H_{36}N_3O_4P$ (467.6) Calc. C 59.27 H 8.52 N 9.87% Found C 58.92 H 8.45 N 9.79%

4. $\left(\underset{a\ c}{\text{a}\square}\overset{O}{\overset{\|}{N}}\underset{b}{CCH_2CH_2}\right)_3P{=}O$ (**4**). From 4.5 g (0.144 g-at.) P_w, 45 g (0.323 mol) $CH_2{=}CHCONC_5H_{10}$ in 100 ml EtOH, 7.2 ml 10N (0.072 mol) KOH in 27.5 ml EtOH as under 1. Then the solution was cooled to −5° and the inorganic salts filtered. Evaporation of the filtrate gave 57 g (84%) white brown, hygroscopic mass. For the analysis a part was chromatographed on weakly acidic alumina to give a beige solid compound, m.p. 142–160°, which when washed with acetone gave white solid **4**, m.p. 167–173°, recrystallized from CH_3CN, m.p. 173–175°. **4** is soluble in all common solvents and in water. ^{31}P −56 ppm (in CH_3OH): ^1H-NMR. (in CD_3OD): a) 1.62 (br., 5.94 H); b) 1.9–2.95 (*m*, 4.04 H); c) 3.5 (br., 4.04 H).

$C_{24}H_{42}N_3O_4P$ (467.6) Calc. C 61.64 H 9.05 N 8.98% Found C 61.59 H 9.03 N 8.96%

5. $\left(\underset{b}{O\square}\overset{O}{\overset{\|}{N}}\underset{a}{CCH_2CH_2}\right)_3P{=}O$ (**5**). From 6.32 g (0.204 g-at.) P_w, 65 g (0.46 mol) $CH_2{=}CHCONC_4H_8O$ in 100 ml EtOH, 10.2 ml 10N (0.102 mol) KOH in 40 ml EtOH as under 1. The reaction mixture is filtered to remove unreacted P_w. The filtrate on standing deposits white crystals. 29.2 g (30.2%), m.p. 215–219°. Recrystallized from propanol m.p. 219–222. ^{31}P −55.5 ppm (CH_3OH/H_2O), ^1H-NMR. (in CD_3OD): a) 1.9–2.95 (*m*, 4H); b) 3.58 (*s*, 8H).

$C_{21}H_{36}N_3O_7P$ (473.5) Calc. C 53.26 H 7.66 N 8.87% Found C 53.18 H 7.62 N 8.87%

The mother liquor gave on evaporation 46.1 g of a viscous brown oil.

6. $(\underset{a\ c\ d}{CH_3CH_2NH}\overset{O}{\overset{\|}{C}}\underset{b}{CH_2CH_2})_3P{=}O$ (**6**). From 3.038 g (0.098 g-at.) P_w, 21.9 g (0.22 mol) $CH_2{=}CHCONHEt$ in 30 ml CH_3CN and 7.05 ml 10N (0.07 mol) KOH as under 1. A white solid precipitates. This is dissolved by adding water, then the solution is neutralized with HCl, small amounts of unreacted P_w filtered off and the filtrate evaporated to dryness. The residue is extracted with isopropanol to give 15.7 g crude **6**,

which is recrystallized from CH_3CN to give 6.1 g (42%) **6**, white crystals, m.p. 196–199°, ^{31}P -56 ± 0.5 ppm (in H_2O). ^1H-NMR. (in D_2O): a) 1.1 (*t*, 9.08 H); b) 1.8–2.8 (*m*, 12.08 H); c) 3.2 (*qu*, 5.84 H); d) 4.7 (*s*, 3H).

$C_{15}H_{30}N_3O_4P$ (347.39) Calc. C 51.86 H 8.70 N 12.09% Found C 50.89 H 8.40 N 11.63

7. $(CH_3NHC(=O)CH_2CH_2)_3P{=}O$ (**7**) (labels: b, c, a). From 5.6 g (0.182 g-at.) P_w, 35 g (0.411 mol) $CH_2{=}CHCONHCH_3$, 150 ml EtOH and 9.1 ml 10 N KOH as under 1. Since no reaction was observed, another 20 ml 10 N KOH were added and the mixture stirred at 35° for 10 h. Evaporation to dryness and extraction with CH_3CN yields after recrystallization from CH_3CN/EtO_2 and then from CH_3CN 25 g (45%) **7**, white needles, m.p. 171–173°. ^{31}P -57.0 ppm (in H_2O). ^1H-NMR. (in D_2O): a) 2.35–3.2 (*m*, 12.15 H); b) 3.18 (*s*, 8.95 H); c) 5.2 (*s*, 2.8 H); (in CCl_4/CD_3OD): a) 1.7–2.5 (*m*, 12.0 H); b) 2.68 (*s*, 9.0 H); c) 4.46 (*s*, 3H).

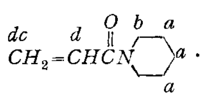
$C_{12}H_{24}N_3O_4P$ (305.34) Calc. C 47.20 H 7.92 N 13.76% Found C 47.16 H 7.87 N 13.41%

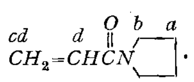
N-substituted acrylamides. – N, N-substituted dialkylaminoacrylamides were prepared by reaction of $CH_2{=}CHCOCl$ with 2 eq. HNR_2 in benzene solution with the addition of a few crystals of hydroquinone. (When in the case of $CH_2{=}CHCON(CH_3)_2$ no hydroquinone was added, the product polymerized on attempted distillation.

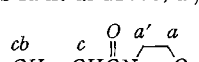
$CH_2{=}CHC(=O)N(CH_3)_2$. B.p. 79–80°/20 Torr, $n_D^{20} = 1.4745$, (yield 87.2%). Lit. [13] b.p. 83–84.5°/21 Torr, $n_D^{20} = 1.4738$ ^1H-NMR, ($CDCl_3$): CH_3 at 3.03 (br *s*), 6H; HC*H* at 5.62 (1 H) ($J_{gem.} = 3.5$, $J_{trans} = 9.5$); CH=CH at 6.50; 2H.

C_5H_9NO (99.12) Calc. C 60.58 H 9.15 N 14.13% Found C 61.49 H 9.16 N 13.66%

Later fractions showed the presence of $(CH_3)_2NCH_2CH_2C(=O)N(CH_3)_2$. ^1H-NMR. ($CDCl_3$): CH_3 3.03; CH_2 2.8 (*t*, $J = 7$ Hz); $COCH_2$ 3.8 (*t*, J = 7 Hz).


B.p. 86–89°/5.6 Torr, $n_D^{20} = 1.5070$ (yield 85.0%). ^1H-NMR. (in CCl_4): a) 1.6 (*m*, 6H); b) 3.46 (*m*, 4H); c) 3.50 (2*d*, $J_{gem.} = 3.5$, $J_{trans} = 9.6$, 1H); d) 5.9–6.8 (*m*, 2H). The last small fraction showed the presence of $C_5H_{10}NCH_2CH_2CONC_5H_{10}$ (a′, b′): a+b as above, a′) 2.7 (*t*, $J = 7$), b′), 3.7 (*t*, $J = 7$).


B.p. 86–90°/5.8 Torr, $n_D^{20} = 1.5065$ (yield 75.1%). ^1H-NMR. (in CCl_4): a) 1.89 (b, 3.88 H); b) 3.45 (b, 4.06 H); c) 5.5 (2*d*, $J_{cis} = 4$, $J_{trans} = 9$, 1.0 H); d) 6.0–6.67 (*m*, 2.05 H). The last fraction showed the presence of $C_4H_8NCH_2CH_2CONC_4H_8$ (a′, b′), a+b same as above; a′) 2.65 (*t*, $J = 7$); b′) 3.7 (*t*, $J = 7$).


B.p. 112–116°/5 Torr, $n_D^{20} = 1.5105$ (yield 83.3%). ^1H-NMR. (in CCl_4): a, a′) 3.55 (*s*, 8.01 H); b) 5.57 ($J_{gem.} = 3.6$, $J_{trans} = 9.5$ Hz, 1.02 H); c) 6.0–6.8 (*m*, 1.97 H). By adding Eu $(DPM)_3$ a′ and a are separated and furthermore coupling constants change.

a) 4.65 (b); a′) 5.3 and 6.0 (b); b) 7 ($J_{cis} = 2$, $J_{trans} = 10$); c) 9.28 ($J_{cis} = 2$, $J_{trans} = 10$, $J_{gem.} = 16.5$). The last fraction showed the presence of $OC_4H_8NCH_2CH_2CONC_4H_8O$ (a′, b′) with C_4H_8 at 3.55 (*s*); a′) 2.73 (*t*, $J = 7$); b′) 3.72 (*t*, $J = 7$).

$CH_2{=}CHC(=O)N(CH_2CH_3)_2$ (labels: cd, d, b, a). B.p. 83°/9 Torr, or 77–78°/5 Torr (Lit. [14] b.p. 85–86°/10 Torr). ^1H-NMR. (in $CDCl_3$): a) 1.17 (*t*, 5.83 H); b) 3.43 (*qu*, 4.08 H); c) 5.62 ($J_{gem.} = 4$, $J_{trans} = 9$, 0.9 H); d) 6.35–6.82 (*m*, 2.11 H).

$CH_2{=}CHC(=O)N(CH_2C_7H_{15})_2$ (labels: cd, d, b, a). Oil, which decomposed on attempted distillation. ^1H-NMR. (in $CDCl_3$): a) 0.9–1.3 (*m*, 31 H); b) 3.30 (br, 4.1 H); c) 5.6 ($J_{gem.} = 4$, $J_{trans} = 9$, 06 H); d) 6.1–6.8 (*m*, 1.21 H).

bc c O *d a* B.p. 70–75°/0.3 Torr (contain 9 mol-% $CH_3NHCH_2CH_2CONHCH_3$
$CH_2{=}CHCNHCH_3$. (Lit. [14] b.p. 86–87°/3 Torr). ^{1}H-NMR. (in CCl_4): a) 2.78 and 2.86 (*s*, 2.87H); b) 5.50 ($J_{gem.} = 4$, $J_{trans} = 8$, 1H); c) 6.18–6.33 (*m*, 2H); d) 8.33 (br, 0.9H).

c d d e b a B.p. 68–70°/0.033 Torr (Lit. [14] b.p. 85–86°/10 Torr).
$CH_2{=}CHCNHCH_2CH_3$. ^{1}H-NMR. (in CCl_4): a) 1.15 (*t*, 3.09H); b) 3.25 and 3.37 (2*qu*, 2.03H); c) 5.47 ($J_{gem.} = 4.7$, $J_{trans} = 8$, 0.88H); d) 6.18–6.31 (*m*, 2.03H); e) 8.2 (br 0.97H).

REFERENCES

[1] *L. Maier*, Helv. *56*, 492 (1973).
[2] *L. Maier*, Helv. *46*, 2026 (1963); Angew. Chem. *71*, 574 (1959); *L. Maier*, Helv. *49*, 2459 (1966).
[3] *L. Maier*, Helv. *50*, 1723 (1967); Angew. Chem. *77*, 549 (1965).
[4] *L. Maier*, Z. anorg. allg. Chem. *394*, 117 (1972).
[5] *L. Maier*, in «Fortschritte der chemischen Forschung» *19*, 1–60 (1971).
[6] *M. M. Rauhut, R. Bernheimer & A. M. Semsel*, J. org. Chemistry *28*, 478 (1963); U.S. Pat. 3067251 (1962).
[7] *H. Low & P. Tavs*, Tetrahedron Letters *1966*, 1357.
[8] *Yu. N. Shluk, G. M. Bogoyubov & A. A. Petrov*, Zh. Obshch. Khim. *38*, 193 (1968).
[9] *K. Issleib & G. Harzfeld*, Z. anorg. allg. Chem. *351*, 18 (1967).
[10] *Yu. N. Shluk, G. M. Bogolyubov & A. A. Petrov*, Dokl. Akad. Nauk, SSSR, *176*, 1327 (1967).
[11] *Union & Carbide Co.*, DAS 1913644 (1969).
[12] *L. Maier*, Helv. *53*, 2069 (1970).
[13] *W. P. Ratchford & C. H. Fisher*, J. Amer. chem. Soc. *69*, 1911 (1947).
[14] *M. M. Koton, A. Sokolova, M. N. Savitskaya & T. M. Kiseleva*, Zh. Obshch. Khim. *27*, 2239 (1957); Chem. Abstr. *52*, 6228g (1958).

---

127. Organic Phosphorus Compounds 61

Esterification and Chlorination of Nitrilo-tri(methylenephosphonic acid), $N(CH_2PO_3H_2)_3$, and Hydroxyethylidenediphosphonic Acid, $H_2O_3PC(OH)(CH_3)PO_3H_2$, and the Corresponding Esters[1])

by **Ludwig Maier**

Monsanto Research S.A., Eggbühlstrasse 36, 8050 Zürich, Switzerland

(13. III. 73)

Summary. Nitrilo-tri(methylenephosphonic acid) and hydroxyethylidenediphosphonic acid are esterified in high yield when treated with excess orthoformic acid ester under reflux. Because of the high temperature necessary to effect esterification a partial isomerization of hydroxyethylidenediphosphonate to the phosphate-phosphonate isomer V takes place. Chlorination of $N(CH_2PO_3H_2)_3$ or a mixture of the ester and the acid with PCl_5 yields tris(chloromethyl)amine, $N(CH_2Cl)_3$. Interaction of $N(CH_2Cl)_3$ and $(EtO)_3P$ yields nitrilo-tri(methylenephosphonate), which on hydrolysis with HCl conc. produces $N(CH_2PO_3H_2)_3$. Chlorination of a mixture of hydroxyethylidene-diphosphonic acid and the corresponding ethyl ester IV which contained the phosphate-phosphonate isomer V gave the products VII to XI. Chlorination of the acid III with PCl_5 gave 4 products, *i.e.* VIII, IX, XI and $Cl_2(O)POP(O)Cl_2$. The ^{1}H- and ^{31}P-NMR. spectra of the products are discussed.

---

[1]) Part 60, see [1].