Thermal Retro-Trimerization of Some 1,3,5,2,4,6-Trioxatriphosphorinanes to Phosphenites

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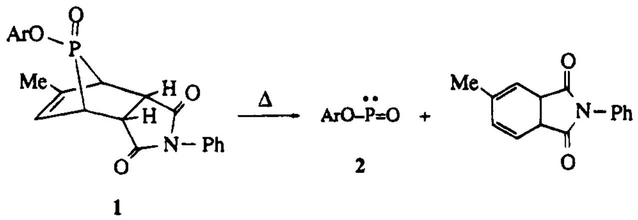
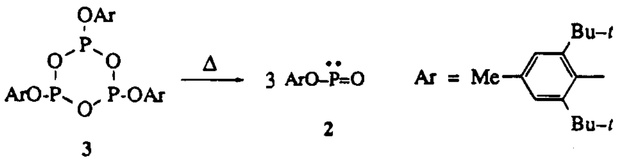
Pyrolysis in a packed tube of the vapor from three 2,4,6-tris(aryloxy)-1,3,5,2,4,6-trioxatriphosphorinanes was performed at 300–350 °C and 10^{-6} mm; the product was collected on a cold finger chilled by liquid nitrogen. The cracking of the trimer was complete, and the product at −195 °C appeared to consist only of the monomeric aryl phosphenite, ArOP=O. On warming, dimerization occurred, later followed by trimer formation. The weak ^{31}P NMR signal for the phosphenite (about δ 238 for three *O*-aryl derivatives) persisted in the solution for several weeks if water was rigorously excluded. Treatment of the phosphenite with water or alcohols at −195 °C gave a mixture of products; the major product (ArO-PH(O)OH) came from addition of the nucleophile to the P=O bond, but significant amounts (10–20%) of dialkyl H-phosphonates ($HP(O)(OR)_2$) were present, apparently from displacement of the *O*-aryl substituent of the phosphenite, followed by addition to the double bond.

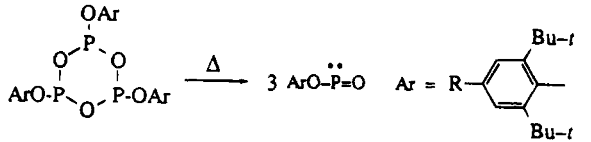
Two-coordinate phosphoryl compounds are of theoretical interest because they would represent the only true case of a $p_\pi-p_\pi$ double bond between phosphorus and oxygen and would not depend upon back-bonding from oxygen to phosphorus for establishing the multiplicity. In that sense, the bonding would be more like that between nitrogen and oxygen than is found in the common form of phosphoryl group, where phosphorus is four-coordinate (as in phosphates, phosphonates, phosphine oxides, etc.). However, the known forms of two-coordinate phosphoryl compounds are few and are characterized by great instability through rapid self-condensation reactions. Prior to 1992, the only known forms were inorganic and had the structure XP=O where X = OH, F, Cl, Br.[1] These species were preserved in argon matrices, and although their infrared and photoelectron spectra were recorded, little is known about their chemistry. The first organic derivative to be directly observed, the aryl phosphenite **2**, was generated in this laboratory in 1992 by the thermal fragmentation of two quite different compounds, the 7-phosphanorbornene derivative **1** and the 1,3,5,2,4,6-trioxatriphosphorinane derivative **3**.[2]





The latter, which is especially easily obtained,[3] is the preferred precursor of **2**. In fact, the discoverers of **3** had performed a pyrolysis that resulted in the collection of the dimer of **2** and had speculated on the possibility that the mechanism involved the retro-trimerization to **2** and its recombination to the dimer and trimer. We first[2] conducted the thermolysis at 10^{-6} mm in a Displex apparatus that allowed condensation of the pyrolysate on surfaces at 12 K for measurement of IR and UV spectra. Another thermolysis technique simply involved heating in a Kugelrohr apparatus (0.1 mm) where the vapor was condensed at −195 °C in a liquid nitrogen bath. By placing the condensed material in $CDCl_3$, the ^{31}P NMR spectrum could be recorded and a small signal at δ 238 was attributed to phosphenite **2**. This assignment was supported by theoretical calculations of the shift for phenyl phosphenite.[2] Under these experimental conditions, most of the product was the dimer **4**[4] and the trimer **3**, and only a few percent of the monomer **2** was present.

We describe here an improved technique for the thermal fragmentation of trimer **3** and for two related *O*-aryl derivatives **4** and **5**. The procedure allowed the trapping of sufficient amounts of the phosphenites so that the first chemical studies of these compounds could be initiated.



3, R = Me
4, R = Bu–*t*
5, R = MeO

Experimental Section

Synthesis of 2,4,6-Tris(aryloxy)-1,3,5,2,4,6-trioxatriphosphorinanes. Compounds **3**–**5** were prepared by partial

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[1] Quin, L. D.; Szewczyk, J. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; Part D, Chapter 11.

[2] Quin, L. D.; Jankowski, S.; Sommese, A. G.; Lahti, P. M.; Chesnut, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 11009.

[3] Chasar, D. W.; Fackler, J. F.; Mazany, A. M.; Komoroski, R. A.; Kroenke, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5956.

[4] Chasar, D. W.; Fackler, J. F.; Komoroski, R. A.; Kroenke, W. J.; Mazany, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 5690.

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hydrolysis of the corresponding aryl phosphorodichloridites as described by Chasar et al.[3] The ^{31}P NMR spectra matched those reported[3] and consisted of an upfield doublet and downfield triplet with $^{2}J_{PP} = 10$ Hz in all cases; shifts were **3**, δ 120.0 and 127.9; **4**, δ 119.7 and 128.1; **5**, δ 120.9 and 129.4.

Thermolysis of the Trioxatriphosphorinanes. The apparatus was similar to that described in the literature.[5] The reaction tube (10 mm i.d. by 43 cm) was mounted horizontally in a 15 in. tube furnace heated at 300–350 °C. It was packed with glass helices. The sample was placed in a small flask at one end of the tube. The other end was connected to a vertically-mounted dry ice type condenser, which was filled with liquid nitrogen and fitted with a small flask as a receiver. A vacuum of 10^{-5} to 10^{-6} mm was applied, and the sample was heated with a small flame to effect volatilization. No residue remained. The product was deposited as a solid at the point of impact on the cold finger.

Recovery of the Pyrolysate. The reaction tube was disconnected from the condenser, and a solvent (chloroform, 1,2-dichloroethane, *o*-dichlorobenzene, or carbon disulfide) was quickly sprayed from a syringe onto the cold finger. The liquid nitrogen was then removed from the condenser, and the melt collected in the receiver. All operations were conducted under dry argon. The ^{31}P NMR spectrum was taken immediately on this solution in sealed tubes, as well as at later times. For trimer **3**, the first measurement revealed only monomer **2** (δ 238) and dimer **6** (δ 176.5) to be present; the ratio of signal intensities was 6:94, respectively. After a few minutes, signals for the trimer **3** appeared. Similar results were obtained for the pyrolysis of trimers **4** and **5**; from **4**, signals at δ 237.9 and δ 176.6 were noted, and δ 238.2 and δ 177.2 from **5**. When the spectrum for the pyrolysate of **3** was taken after about 15 min at room temperature, the composition was found to be about 66–71% trimer, 27–32% dimer, and 1.5–1.8% monomer in repetitive experiments. The pyrolysates from **4** and **5** behaved similarly. After heating of such mixtures, only the signal for the trimer could be observed.

Hydrolysis of the Pyrolysate from Trimer 3. The reaction tube was disconnected from the liquid nitrogen condenser, and with a syringe a solution of water in acetone–chloroform (1:1) was sprayed directly on the deposit of solid pyrolysate on the cold finger. The material was slowly allowed to warm to room temperature, collecting the melt in the receiver. The ^{31}P NMR spectrum was then recorded. Signals and relative intensities were the following: δ 4.0 ($^{1}J_{PH}$ 708 Hz), 69%; δ 0.5 ($^{1}J_{PH}$ 679.5 Hz), 31%. The major[4] component was identical to a known sample of compound **7** prepared in earlier work[2] and was further characterized by conversion to the known methyl ester[2] with diazomethane, confirmed by ^{1}H and ^{31}P NMR and by GC-MS. The ^{31}P NMR properties of the minor product matched those reported for phosphorous acid[6] (δ 1.7, $^{1}J_{PH}$ 694 Hz).

Reaction of the Pyrolysate with Alcohols. Methyl alcohol was sprayed from a syringe onto the frozen pyrolysate as in the hydrolysis, and the temperature was allowed to rise slowly. The ^{31}P NMR spectrum at room temperature consisted of signals as follows: **11** (R = Me), δ 6.9 ($^{1}J_{PH}$ 720 Hz), 75% relative intensity; **13** (R = Me), δ 11.5 ($^{1}J_{PH}$ 712.1 Hz, $^{3}J_{PH}$ 12.2 Hz, septet), 20%; H_3PO_3, δ 1.3 ($^{1}J_{PH}$ 699 Hz), 5%. The signals for **13** (R = Me) matched those of a commercial sample of dimethyl H-phosphonate. The identity of **11** was established by comparison to the product from the reaction of diazomethane with acid **7**.[7]

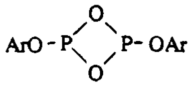
A similar product mixture was obtained on reacting the pyrolysate at −175 °C with ethanol: **11** (R = Et) δ 3.89 ($^{1}J_{PH}$ 712.1 Hz, $^{3}J_{PH}$ 8.1 Hz, t), 75%; **13** (R = Et) δ 6.7 ($^{1}J_{PH}$ 692.6 Hz, $^{3}J_{PH}$ 8.4 Hz), 20%.

The reaction with *tert*-butyl and neopentyl alcohols was slower, and some of the phosphenite persisted in the presence of these alcohols at room temperature for 5 min. From *tert*-butyl alcohol: **11** (R = *t*-Bu) δ 0.7 ($^{1}J_{PH}$ 691.8 Hz), 75%; **13** (R = *t*-Bu) 7.85 ($^{1}J_{PH}$ 689.4 Hz), 20%. From neopentyl alcohol: **11** (R = Np) δ 4.16 ($^{1}J_{PH}$ 708.0 Hz, $^{3}J_{PH}$ 8.1 Hz), 75%; **13** (R = Np) δ 7.75 ($^{1}J_{PH}$ 699.9 Hz, $^{3}J_{PH}$ 8.14 Hz, t), 20%. In confirmation of **13**, commercial dineopentyl H-phosphonate had δ 8.2 ($^{1}J_{PH}$ 687 Hz, $^{3}J_{PH}$ 8.1 Hz, t).

Reaction of the Dimer 6 with Water. Dimer **6** was prepared by thermolysis of trimer **3** at 220 °C and 20 mm, as described by Chasar et al.[4] The sublimate was purified by washing with ether to remove trimer **3**; the residue had the expected ^{31}P NMR signal at δ 176.5, but still contained a few percent of **3** and 1–2% of monomer **2**. The sample was dissolved in CS_2 (undried) and after a few minutes the ^{31}P NMR spectrum was recorded. Aside from that for the originally present trimer **3**, the only signal was that for the pyro compound **8** at δ −8.0 ($^{1}J_{PH}$ 760 Hz), as reported earlier.[7] Addition of water then led rapidly to the H-phosphonate **7** (δ 3.3, $^{1}J_{PH}$ 712.0 Hz), reported earlier.[7] The reaction in chloroform was much slower, requiring overnight standing for hydrolysis to **7**. In neither solvent was any hydrolysis to phosphorous acid noted.

Results and Discussion

The three trioxatriphosphorinanes **3–5** were completely volatilized under the conditions used and successfully passed through the reaction tube at 300–350 °C. Each deposited a white solid on impinging on the liquid nitrogen chilled finger. Ideally, to prove that the solid is the desired phosphenite, spectral measurements should be made at this temperature to avoid dimerization. In our initial study,[2] this was accomplished by both IR and UV spectroscopy on thin films deposited in a Displex apparatus. In our new experiments, we have not yet been successful in recording NMR spectra before extensive dimerization to **6** took place.



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However, each of the samples removed from the cold finger gave a phosphenite signal around δ +238, though only accounting for 3–5% of signal intensity. Apparently, the ^{31}P NMR shift is not noticeably influenced by changes in the substituent in the para position of the aryloxy group. This had also been observed[3] for the signals for the trimer of the phosphenites; our measurements confirmed this and also showed the same to be true for the dimers. It is therefore necessary to prove that the phosphenite was the product of the thermolysis by indirect means.

According to the IR and UV spectra of the films in the Displex apparatus,[2] phosphenite **2** is stable at −195 °C, the temperature at which it is collected in our new procedure. Dimer formation occurs on allowing the temperature to rise. We assume, then, that our samples deposited on the cold finger at −195 °C are the monomeric phosphenites. Significantly, no trimer is present when the samples are washed from the cold finger and immediately observed by ^{31}P NMR. This clearly establishes that the cracking of the trimer was complete in the pyrolysis tube. However, signals for the trimer do begin to appear after a few minutes of standing at room temperature, and after 15 min, the ratio of ^{31}P signals in the product from thermolysis of **4** was typically 2% monomer, 30% dimer, and 68% trimer. Similar compositions were recorded for products from **4** and **5**.

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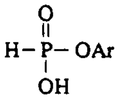
(5) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980; p 31.

(6) Gallagher, M. J. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; CRC Press: Boca Raton, FL, 1991; p 289.

(7) Quin, L. D.; Ionkin, A. S. *Phosphorus Sulfur Silicon*, in press.

Further information on the identity of the frozen pyrolysate came from studies of its behavior with water. The hydrolysis was accomplished by spraying a solution of water in acetone–chloroform directly on the pyrolysate while still on the liquid nitrogen cold finger. The temperature was then allowed to rise slowly to that of the room, and the material on the finger was washed into an NMR tube with chloroform. As will be discussed, the major product detected by ^{31}P NMR was the H-phosphonate **7**. The ^{31}P NMR spectrum was of value also in showing that no trimer was present at this point; this compound is known[3,7] to be stable to water, and had any been present in the pyrolysate it would have been detected. As expected, the hydrolysis mixture contained no signal for the dimer, for this compound was observed to react with water and form compound **8**, which resists further hydrolysis for short periods. However, there was no signal at δ −8.0 for **8** in the hydrolysis product, implying that no dimer existed in the pyrolysate at −195 °C.



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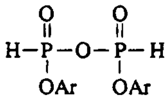

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By these indirect means, we feel we have demonstrated that the pyrolysate when maintained at −195 °C consists almost entirely of the monomeric phosphenite **2**, and that with properly designed experiments the chemical character of the phosphenite can now receive study. We can comment on two aspects of its chemistry at this time, its thermal stability and its behavior with water and alcohols.

As noted, the monomer **2** rapidly forms the dimer **6** as the temperature is raised. However, in the solution of the pyrolysate in various solvents (chloroform, *o*-dichlorobenzene, 1,2-dichloroethane, carbon disulfide) at room temperature, a small but detectable amount (3–5% of ^{31}P NMR signal intensity) of monomer always remained. Basic materials such as pyridine, triethylamine, and tributylamine caused rapid and complete conversion of monomer and dimer to the trimer; this behavior of the dimer has been previously observed.[4] In our first experiments,[2] we had noted that the δ +238 signal disappeared after a few hours, but we have now observed that if the solution is carefully protected from water and stored in a freezer the signal is still present after two months of standing. However, when such a solution is heated for 30 min at 80 °C, all monomer and dimer are converted to the trimer, which persists at room temperature. The best explanation for the persistence of the δ +238 signal is that an equilibrium is established between monomer and dimer, and that the monomer therefore does indeed have a finite existence at room temperature. As the solution ages, trimer begins to form, but the ^{31}P NMR signal of the monomer is detectable as long as there is also some dimer present. It is known that pure trimer is stable and forms neither the monomer nor the dimer in solutions; therefore trimer formation represents a disruption of the monomer–dimer equilibrium. The mechanism of the formation of the trimer is uncertain. It could be created directly from the monomer according to eq 1, it could be a product of reaction of the monomer with the dimer as in eq 2, or it could be formed from the dimer with accompanying formation of the monomer, eq 3.

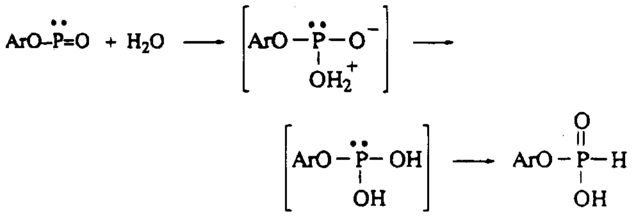
$$3\,\mathrm{ArOP{=}O} \longrightarrow (\mathrm{ArOPO})_3 \qquad (1)$$

$$\mathrm{ArOP{=}O} + (\mathrm{ArOPO})_2 \longrightarrow (\mathrm{ArOPO})_3 \qquad (2)$$

$$2\,(\mathrm{ArOPO})_2 \longrightarrow \mathrm{ArOP{=}O} + (\mathrm{ArOPO})_3 \qquad (3)$$

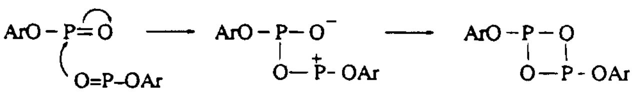
We have attempted to confirm the existence of the monomer–dimer equilibrium by preparing a sample of pure dimer according to the literature[4] and determining if the same equilibrium composition was approached. In fact, we were never able to prepare a sample of dimer that did not immediately display a signal for trace amounts of the monomer when placed in chloroform solution. The intensity was the usual 3–5% of total signals. It is not clear if this indicates a very rapid establishment of the suspected equilibrium, or if the monomer was present in the dimer from the synthesis, which also involves a pyrolysis procedure.[4]

In the earlier discussion, the hydrolysis of the pyrolysate was put in terms of proof of its composition, indicating the absence of both dimer and trimer. Important information on the reactivity of the monomeric phosphenite also resulted from this study. The main product (about 70%) was the known[3,7] H-phosphonate **7**, which was isolated and fully characterized by analysis, spectroscopy, and conversion to its methyl ester with diazomethane. The phosphenite signal at δ +238 was absent in the hydrolysate. Since neither the dimer nor the trimer hydrolyze to compound **7** under these conditions, **7** must be the major product from reaction of the monomer with water; its formation can be accounted for on the assumption that the phosphorus atom is an electrophilic center undergoing addition of a nucleophile to form a phosphite (**9**) which undergoes the usual tautomeric H-shift:

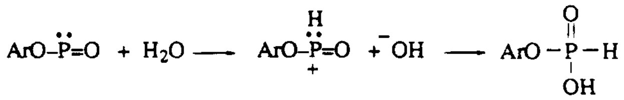


9 **7**

The dimerization of the monomer is of course also a consequence of this electrophilicity:



A less likely pathway for the hydrolysis would involve protonation at the phosphorus lone pair, followed by addition of the nucleophile:



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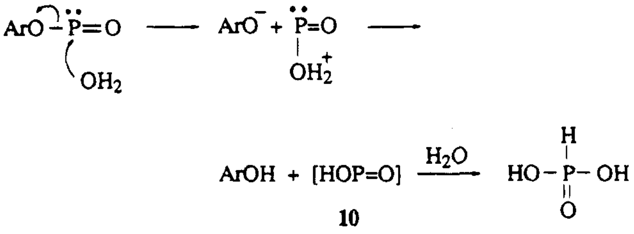
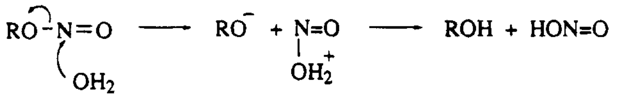
However, in other two-coordinate species, such as phosphaalkenes and phosphineimines, the lone pair is not reactive and appears to have an energy level below that of the π system. This may be true also in the phosphenites, as discussed by Chasar et al.[4]

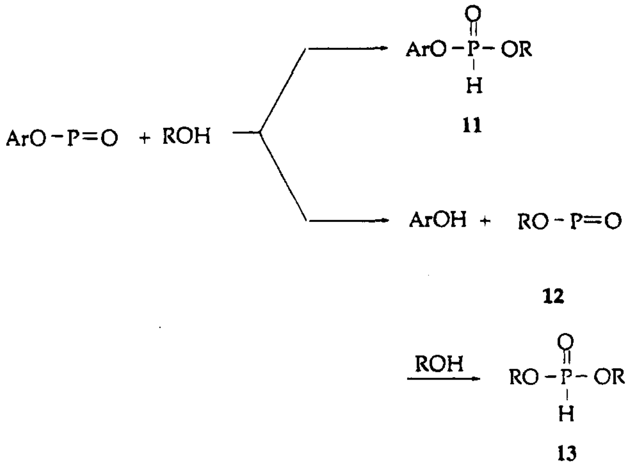
Also of importance was the observation that the hydrolysis product contained some 30% of phosphorous acid, identified by its characteristic ^{31}P NMR shift of δ 1.9 and P–H coupling constant of 694 Hz.[6] Again, neither the dimer, the trimer, nor compound **7** give this product under these conditions, and it possibly is formed from the monomer by displacement of the aryloxy group to form phosphenous acid (**10**), followed by hydration.



This is quite an unexpected reaction, since the implication is that displacement on phosphorus competes with the addition of the nucleophile to the P=O group that forms the H-phosphonate. In that sense, the phosphenite is behaving like its nitrogen counterpart, an ester of nitrous acid, which undergoes facile displacement of the oxy grouping:[8]

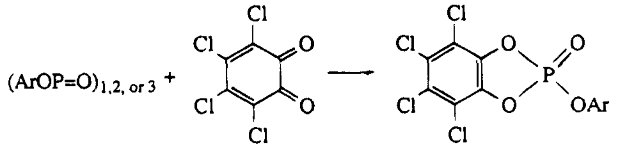


Confirmation of the displacement process came from the behavior of the frozen pyrolysate when sprayed with an alcohol. With ethanol or methanol, the solution obtained after warming to room temperature contained ^{31}P NMR signals for the alkyl aryl H-phosphonate (**11**) as the major product (75–80%), consistent with the behavior on hydrolysis, but also contained signals for the dialkyl H-phosphonate (**13**, 10–20%). A small amount of phosphorous acid (3–5%) was also present. The dialkyl H-phosphonate can only be accounted for as arising from an initial displacement process on phosphorus in competition with nucleophilic addition, followed by ROH addition to the alkyl phosphenite intermediate **12**.



The hindered alcohols *tert*-butyl and neopentyl were also sprayed onto the frozen pyrolysate, but were less reactive than methyl or ethyl alcohols. In these cases, the solution contained the usual few percent of monomer, which persisted overnight. Only after about 2–3 days did the monomer disappear. Dimer also formed in this process and this can be taken to mean that the hindered alcohols are not as effective as traps for the monomeric phosphenite as are the unhindered alcohols.

We have also studied the behavior of the pyrolysate at −195 °C with tetrachloro-*o*-quinone, well known to form adducts with trivalent phosphorus compounds. All phosphorus was found to be incorporated in the adduct **14**, which we had prepared earlier[7] from the trimer **3**. Since the trimer and the dimer rapidly gave this adduct, it cannot be concluded that the phosphenite has undergone the cycloaddition; it remains possible that **14** is formed from the dimer and that the disappearance of the signal for the monomer is simply due to its conversion to the dimer in the equilibrium process. This ambiguity is absent in the studies of the pyrolysis with water and alcohols, since the trimer is unreactive under the conditions used and the dimer gives different products.



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[8] Smith, P. A. S. *The Chemistry of Open Chain Organic Nitrogen Compounds*; Benjamin: New York, 1966; Vol II, pp 467–468.