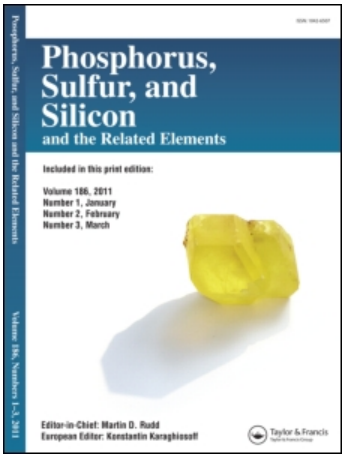

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TRIACIDIC SALTS OF TRIS(AMINOMETHYL)PHOSPHINES AND THEIR OXIDES

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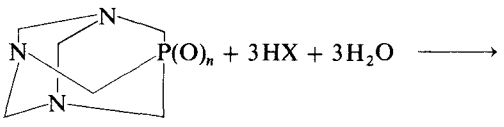
Tris(aminomethyl)phosphines and their oxides form triacidic salts that, unlike the free bases, are air-stable and non-hygroscopic. The salts of the unsubstituted compounds, $(NH_3^+CH_2)_3P(O)_n3X^-$(**3b**: $n = O$, X = Br; **4a–c**: $n = 1$, X = Cl, Br, or I), may be prepared directly from 1,3,5-triaza-7-phosphaadamantane (**1**) or its oxide (**2**) or from tris(N-carbomethoxylaminomethyl)phosphine oxide (**9**) by hydrolysis with the appropriate acid. The behaviour of the compounds towards acids and nucleophilic reagents is discussed.

INTRODUCTION

The phosphaadamantanes **1** and **2** react with methyl iodide to form 1:1 adducts that are ammonium rather than phosphonium salts.[2,3] Similar products are obtained from **1** and **2** and formaldehyde in the presence of strong acids such as hydrochloric acid or picric acid.[4] We now wish to report the hydrolysis of these and other PCH_2N compounds[5] to salts of tris(aminomethyl)phosphines and their oxides, and to describe some interesting and unusual properties of the salts.

RESULTS AND DISCUSSION

Hydrolysis of 1,3,5-triaza-7-phosphaadamantane (**1**) with hydrobromic acid at room temperature gave tris(aminomethyl)phosphine trihydrobromide (**3b**), isolated as a crystalline solid, dec 214°C, in 74% yield (Eq. 1).



$$+ P(O)_n + 3HX + 3H_2O \longrightarrow$$

1, $n = 0$
2, $n = 1$

$$(NH_3^+CH_2)_3P(O)_n3X^- + 3CH_2O \quad (1)$$

3b, $n = 0$, X = Br
4a, $n = 1$, X = Cl
4b, $n = 1$, X = Br

The product was a triacidic salt, despite the use of excess acid. Its NMR spectrum (Table I) showed a singlet for the methylene groups at δ 3.63 ppm, whereas **1** shows a doublet at δ 3.9 (J = 9 Hz) for the methylene groups adjacent to phosphorus.[2] The salt-free base corresponding to **3b** is unknown.

Hydrolysis of 1,3,5-triaza-7-phosphaadamantane 7-oxide (**2**) with excess hydrobromic acid under the same conditions gave tris(aminomethyl-phosphine oxide trihydrobromide (**4b**), dec 233°C, in 73% yield. The trihydrochloride (**4a**), dec 239°C, was prepared similarly in 60% yield. The NMR spectra of both salts (Table I) exhibited a doublet for the methylene groups in the same region as **2**.[2]

Neutralization of the trihydrobromide **4b** with sodium hydroxide gave tris(aminomethyl)phosphine oxide (**5**), isolated as a hydrate in 98% yield. The separation of the product from the sodium bromide was difficult because of the solubility of sodium bromide in organic solvents. Attempts at vacuum sublimation or recrystallization from various solvents failed, but the **5** was finally isolated by continuous extraction in a Soxhlet extractor with 2-propanol, in which **5** is slightly soluble. The trihydrochloride **4a** yielded **5** quantitatively, with no separation problem provided that the stoichiometric amount of sodium hydroxide was used. The product is not salted out by excess alkali.

The triamine (**5**) has hitherto been accessible only from tris(chloromethyl)phosphine oxide by

TABLE I

Physical properties of the triamines and their salts

Compound	Composition (β = triamine)	Mp, °C	IR $\nu P = 0$, cm^{-1}	^1H NMR (D_2O) δCH_2 (J, Hz)[a]	δCH_3[b]
		Tris(aminomethyl)phosphines			
3b	β-3 HBr	dec 214	—	3.63[b]	—
10	β	oil	—	[c]	—
12a	β-3 HCl	209–210 dec	—	3.95 (1.5)	3.10
		Tris(aminomethyl)phosphine oxides			
4a	β-3 HCl	dec 239	1170	3.95 (7.5)	—
4b	β-3 HBr	dec 233	1180	4.10 (7.5)	—
4c	β-3 HI	dec 213	1170	4.01 (7.0)	—
4d	β-3 CF_3CO_2H[d]	—	—	4.44 (7.0)	—
4e	β-2 H_2SO_4	dec 224	1180	3.92 (7.5)	—
4f	2β-3$(CO_2H)_2$	dec 242	1175	3.75 (7.0)	—
4g	β-citric acid[d]	—	1170	3.74 (7.0)[e]	—
5	β	oil	1140	3.22 (6.0)	—
11	β	150–152	1130, 1165	3.00 (6.0)	2.38[f]
13a	β-3 HCl	234–235 dec	1180	4.31 (7.0)	3.21
13d	β-3 CF_3CO_2H[d]	—	—	4.40 (6.5)	3.36

(a) Doublet, (b) Singlet. (c) Lit[19] (no solvent given) δ2.25 (s, CH_3) and 2.47 (d, CH_2, J = 3.5 Hz). (d) Identified only by their spectra. (e) The citrate CH_2 protons were an AB quartet, $\delta_B = 2.58$, $\delta_B = 2.72$, $J_{AB} = 15.0$ Hz, upfield of citric acid like other citrates. (f) Lit[19] (C_6H_5CN) δ 2.32 (s, CH_3) and 2.72 (d, CH_2, J = 7.0 Hz).

the Gabriel synthesis. The anhydrous product was described as a white, hygroscopic solid, mp 40°C after sublimation or recrystallization from dimethylformamide.[6] In our hands, the hydrate was a colorless, hygroscopic oil that resisted vacuum sublimation or recrystallization and gave a neutral pH when dissolved in water. The product was reported[6] to form a white, nonhygroscopic, crystalline *mono*hydrochloride, mp above 320°C; we obtained only the *tri*hydrochloride **4a**.

The triamine **5** readily formed crystalline salts with other monobasic acids such as hydriodic acid and trifluoroacetic acid, dibasic acids such as sulfuric acid and oxalic acid, and tribasic acids such as citric acid. The physical properties of the products (**4c–g**) are given in Table I. All products had the correct stoichiometry except the sulfuric acid salt (**4e**). It unexpectedly analyzed as a bis(dihydrogen sulfate), $(NH_2CH_2)_3PO \cdot 2H_2SO_4$, and was unaffected by excess sulfuric acid.

Because of our interest in the salts **4a–g** as potential flame retardants for cotton, we explored some alternative methods of preparation.

Hydrolysis of tris(N-carbomethoxylaminomethyl)phosphine (**6**) with 48% hydrobromic acid under the conditions employed with **1** produced no reaction, but on heating to 105–110°C the tertiary phosphine underwent alkyl-nitrogen fission giving ammonium bromide (60.7%), bis(hydroxymethyl)methylphosphine oxide (**7**, 33.8%), and (bromomethyl)(hydroxymethyl)methylphosphine oxide (**8**, 46.3%). The initial phosphorus-containing product, tris(hydroxymethyl)phosphine, is known to undergo rearrangement and substitution in hot acidic media[7] (Eq. 2).

$$\underset{\mathbf{6}}{(CH_3O_2CNHCH_2)_3P} + 6HX + 3H_2O \longrightarrow \underset{\mathbf{7}}{CH_3P(O)(CH_2OH)_2} + 3NH_4X + 3CO_2 + 3CH_3X$$

$$\mathbf{7} \xrightarrow{HBr} \underset{\mathbf{8}}{CH_3P(O)(CH_2Br)CH_2OH} + H_2O \qquad (2)$$

Hydrolysis of tris(N-carbomethoxylaminomethyl)phosphine oxide (**9**) with 48% hydrobromic acid under the same conditions gave **4b** in 55% yield. The product separated in crystalline form during the reaction. Extending the reflux time from 3 h to 7 h increased the yield to 73%.

Clearly, the tertiary phosphine oxide **9**, unlike the tertiary phosphine **6** and the corresponding phosphonium salt,[8] underwent predominantly acyl-nitrogen fission (Eq. 3).

$$\underset{\mathbf{9}}{(CH_3O_2CNHCH_2)_3PO} + 6HX \longrightarrow \underset{\mathbf{4}}{(NH_3^+CH_2)_3PO\,3X^-} + 3CO_2 + 3CH_3X \quad (3)$$

Hydrolysis of **9** with constant-boiling (19%) hydrochloric acid yielded only 8% of **4a**, even after prolonged refluxing. None of the **9** was recovered. Hydrolysis with constant-boiling (49%) hydriodic acid gave an 11% yield of **4c** after 2 h refluxing, but none after 5 h refluxing. The product, which did not separate during the reaction, was apparently destroyed. Hydrolysis with 36% sulfuric acid gave no **4e**, though little ester remained.

Hydrolysis of the urea derivatives tris(ureidomethyl)phosphine oxide[9] and tris(1,3-dimethylureidomethyl)phosphine oxide[9] with constant-boiling hydrobromic (or hydrochloric) acid gave no identifiable products other than the HBr (or HCl) salts of ammonia and methylamine, respectively.

The reaction of tetrakis(hydroxymethyl)phosphonium chloride with 1,1,3-trimethylurea, carried out under conditions that usually yield tetrakis(ureidomethyl)phosphonium salts,[9] gave a degradation product that appeared to be tris(dimethylaminomethyl)phosphine trihydrochloride (**12a**), based on its IR and NMR spectra and elemental analysis. The IR spectrum showed strong NH^+ absorption in the 2300 or 2600 cm^{-1} region but no absorption in the C=O region. The NMR spectrum showed a singlet at δ 3.10 ppm for the six methyl groups and a doublet at δ 3.95 ppm ($J = 1.5$ Hz) for the three methylene groups (Table I). The degradation could be averted by carrying out the reaction under milder conditions.[9]

The identity of the product was confirmed by direct synthesis. Tris(dimethylaminomethyl)phosphine (**10**) gave a quantitative yield of the crystalline trihydrochloride (**12a**), mp 209–210°C dec, when treated in an inert atmosphere with excess hydrochloric acid at room temperature (Eq. 4).

$$[(CH_3)_2NCH_2]_3P(O)_n + 3HX \longrightarrow [(CH_3)_2NH^+CH_2]_3P(O)_n3X^- \quad (4)$$

10, $n = 0$ — **12a**, $n = 0$, X = Cl

11, $n = 1$ — **13a**, $n = 1$, X = Cl

Tris(dimethylaminomethyl)phosphine oxide (**11**) also formed a trihydrochloride when treated with hydrochloric acid at room temperature. The product (**13a**) was a crystalline solid, mp 234–235°C dec.

Efforts to determine the coupling between CH_2 and NH in the triamines and their salts were unsuccessful. Trifluoroacetic acid, which is often used to detect such coupling,[10,11] shifted the CH_2 doublet of **5** and **11** further downfield than any of the other salts (Table I), but the signal remained a doublet even when the probe temperature was reduced to −20°C. The N-methyl singlet in **13d** remained a singlet. Another technique, in which the acidity of the medium is increased by the addition of DCl,[12] shifted the CH_2 doublet of the trihydriodide **4c** from δ 4.01 to 4.08 ppm, but the signal remained a doublet. The trihydrochloride **4a** was too insoluble to produce any signal at all.

We believe that the behaviour of the salts is the consequence of an electron-withdrawing effect exerted by the ammonium groups on the phosphorus atom:

$$\left[R_2\overset{+}{N}HCH_2 \longleftarrow \ddot{P} \longrightarrow CH_2\overset{+}{N}HR_2 \;\Big|\; CH_2\overset{+}{N}HR_2\right] 3X^-$$

In the tertiary phosphines, the inductive effect tends to disperse the phosphorus lone pair electrons over the three adjacent bonds, leaving the phosphorus less susceptible to bonding with oxygen, water, and other electrophilic reagents. Tertiary phosphines containing 2-aminoethyl groups exhibit the same behavior.[13]

In the tertiary phosphine oxides, the inductive effect is manifested by nonhygroscopicity and by the shift of the P=O stretching vibration to higher frequency in their infrared spectra (Table I). The behavior of **2**[2] and **11**[14] toward methyl iodide can be explained in the same manner, for the effects of HBr and CH_3Br on νP=O are identical.[15]

EXPERIMENTAL[16]

Melting points were corrected. Elemental analyses, all performed by Galbraith Laboratories, Inc., Knoxville, Tenn., are reported in Table II.

Reagents The tertiary phosphines **1**, **6**, and **10** were prepared from tetrakis(hydroxymethyl)phosphonium chloride as de-

TABLE II

Analytical data for new compounds

Compound	Found, %					Calcd., %				
	C	H	N	P	Cl	C	H	N	P	Cl
3b	10.00	4.24	11.37	8.62	65.51[a]	9.89	4.18	11.54	8.51	65.87[a]
4a	14.59	6.11	17.46	12.45	43.29	14.60	6.13	17.04	12.56	43.14
4b	9.68	4.02	10.97	8.26	62.90[a]	9.49	3.98	11.06	8.16	63.10[a]
4c	7.16	3.19	8.31	6.26	73.37[b]	6.92	2.90	8.07	5.95	73.09[b]
4e	10.82	4.97	12.58	9.40	19.02[c]	10.81	4.84	12.61	9.29	19.24[c]
4f	26.31	5.56	15.35	11.40	—	26.48	5.56	15.44	11.38	—
5	23.47	9.16	27.12	20.30	—	23.22	9.10	27.09	19.96	—
12a	33.77	8.63	13.22	—	33.20	34.35	8.65	13.36	—	33.80
13a	32.82	8.46	12.57	9.49	32.15	32.69	8.23	12.71	9.37	32.16

(a) Bromine. (b) Iodine. (c) Sulfur.

scribed previously[3,8,17] and oxidized to the tertiary phosphine oxides **2**, **9**, and **11**, respectively, with air[18] or hydrogen peroxide.[2,8]

Spectra IR spectra were taken on a Perkin–Elmer Model 137B instrument with NaCl optics (m = medium, s = strong, vs = very strong, br = broad). NMR spectra were taken either on a Varian A-60A or a Varian EM360L, with DSS as an internal reference. Interaction of the triamine salts with the DSS produced a series of low-level signals in the 0 to 100 Hz region, whose identity could be verified by omitting the DSS.

Hydrolysis of 1,3,5-Triaza-7-phosphaadamantane (**1**) *and its 7-Oxide* (**2**) A solution of **1** (3.14 g, 0.02 mol), 48% hydrobromic acid (25 g, 0.15 mol), and water (40 g) was poured onto a watch glass and allowed to evaporate. After three days at room temperature, the product was collected on a filter, rinsed twice with hot methanol (100 ml), and air-dried, giving 5.40 g (74%) of **3b** as a white, crystalline solid, dec 214°C without melting; IR (KBr) 1550 (s, NH_3^+) cm^{-1}.

Hydrolysis of **2** with hydrochloric acid under the same conditions gave a 60% yield of **4a** as a white, crystalline solid, dec 239°C without melting; IR (KBr) 830 (vs), 1170 (vs, P=O), 1560 and 1580 (both s, NH_3^+), and 2580 (s, NH_3^+) cm^{-1}.

Hydrolysis of **2** with hydrobromic acid under the same conditions gave **4b** (IR same as below) in 73% yield.

Hydrolysis of Tris(N-carbomethoxylaminomethyl)phosphine (**6**) *and its Oxide* (**9**) A solution of **9** (31.12 g, 0.1 mol) in 48% hydrobromic acid (100 ml) was heated to reflux with constant stirring. Solids started to separate after a few minutes. The mixture was heated at 105–110°C for 3 h, cooled, and filtered. The filter cake was rinsed with ethanol and air-dried, giving 20.80 g (55%) of **6** as a white, crystalline solid, dec 233°C. The filtrate, stripped of ethanol and heated another 4 h with fresh hydrobromic acid (50 ml), yielded an additional 6.95 g (18%) of **4b**. Two recrystallizations from 90% ethanol (50 ml/g) afforded pure **4b**, dec 233°C (reddening) without melting; IR (Nujol) 825 (vs), 1180 (vs, P=O), 1540 and 1565 (both s, NH_3^+), and 2530–2600 (s, NH_3^+) cm^{-1}.

Hydrolysis of **6** with hydrobromic acid under the same conditions, but under argon, produced no solids even after cooling. The solution was stripped, shaken with ethanol and filtered, giving 17.84 g (60.7%) of ammonium bromide, identified by IR, NMR, and by the liberation of ammonia upon treatment with 10% NaOH solution. The filtrate yielded 26.36 g of colorless oil identified by NMR as a mixture of **7** (33.8%), **8** (46.3%), and other impurities. No **3b** was found in either fraction.

Ion Exhange A solution of the trihydrobromide **4b** (11.40 g, 0.03 mol) in water (40 ml) was passed onto a chromatographic column containing 50 g of Bio-Rad AG50W-X4 cation exchange resin[12] and eluted with water until bromide-free. A small quantity (0.83 g, 7%) of the **4b** passed through the resin. The column was then eluted with 3*N* HCl to displace the trihydrochloride **4a**. (The product separates on the column if 6*N* HCl is used). After being stripped, the residue was rinsed with ethanol and dried, giving 7.19 g (97%) of **4a** as a white, crystalline solid, identical (IR, NMR) to the product described above.

Tris(aminomethyl)phosphine Oxide (**5**) A solution of **4a** (9.86 g, 0.04 mol) in water (50 ml) was neutralized with a solution of sodium hydroxide (4.80 g, 0.12 mol) in water (25 ml) and stripped to dryness on a rotary evaporator. The residue was shaken with ethanol, filtered to remove sodium chloride, and stripped again, giving 6.10 g (98%) of **5**, $n^{20}D$ 1.5628; IR (neat) 830 (s, br), 1140 (vs, P=O) 1580 (m, NH) and 3300 (vs, NH) cm^{-1}. The product analyzed as a hydrate, $(NH_2CH_2)_3PO \cdot H_2O$.

Other Salts of Tris(aminomethyl)phosphine Oxide (**4c–f**) A solution of **5** (3.10 g, 0.02 mol) in water (50 ml) was treated with 49% hydriodic acid (15.65 g, 0.06 mol), allowed to stand overnight, and stripped to dryness. The residue was rinsed with ethanol and air-dried, giving 10.46 g (100%) of the trihydriodide **4c** as a white, crystalline solid. A portion of the product was recrystallized from ethanol/water, giving pure **4c**, dec 213°C (reddening) without melting; IR (Nujol) 812 (s), 1170 (vs, P=O), 1600 (m, NH_3^+), and 2600–2700 (s, NH_3^+) cm^{-1}.

The bis(dihydrogen sulfate) **4e**, which separated on standing, was a white, crystalline solid, dec 224°C after recrystallization from water (7 ml/g); IR (Nujol) 820 (m), 1100 (s), 1180 (vs, P=O), 1600 (m, NH_3^+), and 2600–2700 (m, NH_3^+) cm^{-1}.

The sesquixolate **4f**, which separated almost at once, was a white, crystalline solid, dec 242°C after recrystallization from water (10 ml/g); IR (Nujol) 764 (m), 845 (m), 1175 (s, P=O), 1600 (vs, br, NH_3^+), and 2600–2700 (s, NH_3^+) cm^{-1}.

The solubility of the salts in water decreases in the order HI, citric acid $\gg$ HCl, HBr > H_2SO_4 > oxalic acid. The NMR

signal of **4f** in D_2O is barely detectable. The salts becomes less soluble as the acidity of the solution increases, resembling in this respect the inorganic salts such as sodium chloride. All are anhydrous, nonhygroscopic solids except for **4f**, which crystallizes with 4 equiv of water. The salts are insoluble in the common organic solvents, but some such as **4a–c** are soluble in hot dimethylsulfoxide.

Tris(dimethylaminomethyl)phosphine Trihydrochloride (**12a**) A rubber-capped serum bottle was purged with argon and charged by means of a syringe with **10** (2.31 g, 11.25 mmol), ethanol (25 ml), and 6*N* hydrochloric acid (7.00 ml, 42.0 mmol). The mixture fumed but remained clear. After being shaken for 30 min, it was stripped under vacuum, giving 3.55 g (100%) of **12a** as a white, crystalline solid. One recrystallization from ethanol (50 ml/g) gave pure **12a**, mp 209–210°C dec; IR (Nujol) 965 (m), 1005 (m), 1120 (m), 1270 (m), and 2300–2600 (vs, NH^+) cm^{-1}.

The salt **12a** is soluble in water, methanol, hot ethanol, and hot dimethylsulfoxide, and insoluble in other common organic solvents. In contrast to **10**, which fumes and oxidizes when exposed even momentarily to air, **12a** is air-stable and nonhygroscopic. No precautions were taken to exclude air during the recrystallization, yet there was no evidence of oxidation.

Tris(dimethylaminomethyl)phosphine Oxide Trihydrochloride (**13a**) A mixture of **11**(2.21 g. 0.01 mol) and 6*N* hydrochloric acid (5.00 ml, 0.03 mol) was shaken until the fuming and exotherming subsided, allowed to stand 30 min, and stripped of water under vacuum, giving 3.32 g (100%) of **13a** as a white, crystalline solid. A portion of the product was recrystallized from methanol (50 ml/g), giving pure **13a**, mp 234-235°C (reddening); IR (Nujol) 827 (m), 897 (m), 980 (m), 1005 (m), 1150 (s), 1180 (vs, P=O), 1260 (m), and 2400–2470 (vs, NH^+) cm^{-1}.

The salt **13a** is soluble in water, hot methanol, and hot dimethylsulfoxide, and insoluble in other common organic solvents. Unlike **11**, it is not hygroscopic.

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REFERENCES AND NOTES

1. One of the facilities of the Southern Region, Science and Education Administration, U.S. Department of Agriculture.
2. D. J. Daigle, A. B. Pepperman, Jr., and S. L. Vail, *J. Heterocycl. Chem.*, **11**, 407 (1974).
3. D. J. Daigle and A. B. Pepperman, Jr., *J. Heterocycl. Chem.*, **12**, 579 (1975).
4. D. J. Daigle, G. J. Boudreaux, and S. L. Vail, *J. Chem. Eng. Data*, **21**, 240 1976).
5. For a general review of the chemistry of P—C—N systems, see D. Redmore, *Top. Phosphorus Chem.*, **8**, 515–585 (1976).
6. E. B. Trostyanskaya, E. S. Venkova, and Yu. A. Mikhailin, *Zh. Obshch. Khim.*, **37**, 1655 (1967).
7. A. W. Frank, *Phosphorus Sulfur*, **5**, 197 (1978).
8. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.*, **42**, 4040 (1977).
9. A. W. Frank, *Phosphorus Sulfur*, **5**, 19 (1978).
10. W. R. Anderson, Jr. and R. M. Silverstein, *Anal. Chem.*, **37**, 1417 (1965).
11. J. C. N. Ma and E. W. Warnhoff, *Can. J. Chem.*, **43**, 1849 (1965).
12. J. D. Roberts, *Nuclear Magnetic Resonance: Applications to Organic Chemistry*, (McGraw-Hill Book Co., Inc., New York, 1959), p. 78.
13. K. Issleib, R. Kümmel, H. Oehme and I. Meissner, *Chem. Ber.*, **101**, 3612 (1968).
14. L. Maier, *Helv. Chim. Acta*, **51**, 1608 (1968).
15. G. Aksnes and J. Songstad, *Acta Chem. Scand.*, **19**, 888 (1965).
16. Mention of companies of commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.
17. H. Coates and P. A. T. Hoye, *Ger. Patent* 1,077,214 to Albright and Wilson (Mfg.) Ltd. (1960).
18. A. W. Frank and S. L. Vail, *Text. Res. J.*, **46**, 791 (1976).
19. Z. N. Mironova, E. N. Tsvetkov, L. I. Petrovskaya, V. V. Negrebetskii, A. V. Nikolaev, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **42**, 2152 (1972).