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ORGANOBORON COMPOUNDS.

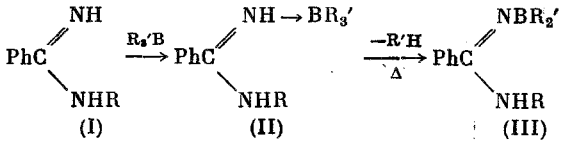
375. N^2-DIALKYLBORYL-N^1-ALKYLBENZAMIDINES

V. A. Dorokhov, I. P. Yakovlev, and B. M. Mikhailov

UDC 542.91:547.1'127

We had previously investigated certain dialkylborylamidines that were synthesized from N,N- or N,N'-dialkylamidines [1-3]. From N-monosubstituted amidines, it is also possible to obtain dialkylboryl derivatives [1] that are regarded as intermediates in the synthesis of chelate compounds of boron from amidines and organoboranes [4]. Here we are reporting on a more detailed study of the synthesis of dialkylborylamidines from N-alkylbenzamidines, and also the structure and certain chemical properties of these compounds.

Trialkylboranes react smoothly with N-alkylbenzamidines (I) upon refluxing in THF, benzene, or other aprotic solvents with boiling points in the 50-60° range or higher. The complexes (II) that are formed upon mixing the reactants [5] decompose upon heating to form N^2-dialkylboryl-N^1-alkylbenzamidines (III) and saturated hydrocarbons.

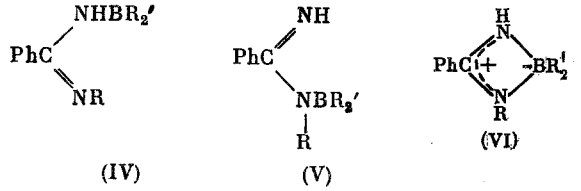


The isolation of some of the compounds (III) in pure form proved to be difficult, as they are thermally unstable. For example, when the product from the reaction of N-methylbenzamidine with Bu_3B was distilled, it decomposed to a considerable degree. It had been noted previously that thermal instability is also typical for dialkylboryl derivatives of amidines without any N-substitution [4].

Therefore, in order to obtain compounds (III) that would be thermally stable, we used certain N-alkylbenzamidines and trialkylboranes with branched substituents (i-Pr, i-Bu, t-Bu, etc.). The synthesized N^2-dialkylboryl-N^1-alkylbenzamidines (IIIa-IIIe) can be vacuum-distilled without decomposition and can be isolated in pure form (Table 1). One of these, (IIIb), was described in an earlier communication [1].

The freshly distilled compounds (IIIa-IIIc) are colorless, rather mobile liquids, whereas (IIId) and especially (IIIe) are viscous substances. In the presence of traces of moisture (IIIa-IIIe) are readily hydrolyzed to the original N-alkylbenzamidines.

In establishing the structure of the dialkylborylalkylbenzamidines (DABAB) that we have synthesized, we must consider not only the structure (III), but also the possible isomeric structures (IV)-(VI):



The prototropic [6] and metallotropic [7] rearrangements that are characteristic of amidines should be taken into account. Determination of the DABAB structure is difficult be-

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 663-669, March, 1980. Original article submitted January 4, 1979.

0568-5230/80/2903-0485$07.50

TABLE 1. N^2-Dialkylboryl-N^1-alkylbenzamidines (III)

Compound	R	R′	Yield, %	bp, °C (p, mm Hg)	IR spectrum,* ν, cm^{-1}		^{11}B NMR spectrum in THF, δ, ppm	Empirical formula	Found / Calculated, %			
					NH	C=N			C	H	B	N
(IIIa)†	*t*-Bu	*i*-Pr	82	116–120 (0,6)	3442	1795	−42±1	$C_{17}H_{29}BN_2$	74,97 / 74,99	10,65 / 10,74	3,85 / 3,98	10,65 / 10,29
(IIIb) [1]	*i*-Pr	*i*-Pr	87	103–105 (0,5)	3445 (3405)	1798 (1650)	−41±2‡	$C_{16}H_{27}BN_2$	74,41 / 74,42	10,51 / 10,54	3,81 / 4,19	10,71 / 10,85
(IIIc)	*i*-Pr	*i*-Bu	78	106–110 (0,5)	3440 (3395)	1794 (1640)	−40±1	$C_{18}H_{31}BN_2$	75,89 / 75,52	10,95 / 10,92	3,51 / 3,78	9,95 / 9,79
(IIId)	*i*-Pr	*n*-Pr	86	132–136 (1,5)	3430 (3402)	1798 (1644)	−41±5	$C_{16}H_{27}BN_2$	74,39 / 74,42	10,52 / 10,54	4,01 / 4,19	10,98 / 10,85
(IIIe)	cis-C_6H_{11}	*n*-Pr	72	160–162 (1,5)	3430 (3408)	1790 (1641)	**	$C_{19}H_{31}BN_2$	76,60 / 76,50	10,15 / 10,48	3,33 / 3,62	— / 9,39

*Values are for freshly distilled (III) without solvent. Values in parentheses are frequencies for dimeric form.

†PMR spectrum of (IIIa) in CCl_4 (δ, ppm): 7.03-7.58 m (Ph), 4.23 br s (NH), 1.35 s (Me_3C), 0.72-1.22 m ($2Me_2CH$). Mass spectrum of (IIIa) (m/e): 229 $(M - 43)^+$.

‡Spectrum without solvent at 120°.

**Has a very weak signal in region of about −40 ppm and an intense signal of the dimer at −3.5 ppm.

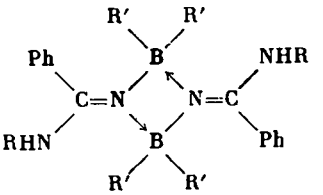
cause of the tendency of these compounds to dimerize, either partially or completely. Upon standing, crystals of the dimer (stable in air) separate out slowly from (IIIc) and more rapidly from (IIId) and (IIIe). Only (IIIa), obtained from i-Pr_3B and N-tert-butylbenzamidine, does not dimerize even after extended storage. This substance is monomeric as demonstrated by the molecular weight determined cryoscopically in benzene, and it does not contain any dimeric impurity as determined by mass spectrometry and ^{11}B NMR. Therefore, this compound (IIIa) is a convenient object of investigation. The ^{11}B chemical shift of about −40 ppm eliminates the structure (VI) and corresponds to (III) with the dialkylboryl group on the imine nitrogen. A signal is given in this same region by N^2-dialkylboryl-N^1,N^1-dialkylamidines [2], whereas amidines with the R_2B group on the amine nitrogen characteristically give a signal in the weaker-field region (about −50 ppm) [3]. Strong evidence for the structure (III) is obtained from the IR spectrum, in which intense absorption is observed in the 1800 cm^{-1} region, typical of nonassociated compounds with the fragment $R_2B - N = C$ [8, 9], including the N^2-dialkylboryl-N^1,N^1-dialkylamidines that were mentioned above [2]. At the same time, there are no spectral bands in the region of C =N stretching vibrations, which would correspond to the isomers (IV) and (V).

Investigation of the other DABAB compounds also showed that, in the monomeric state, they have the structure (III), and the isomers (IV)-(VI) could not be detected. In the IR spectra of freshly distilled (IIIb) [1] or (IIIc), the predominant, intense absorption is at 1800 cm^{-1}, but along with this there is a medium-intensity band at 1645 cm^{-1}. Simultaneously, in the region of NH stretching vibrations, there is a weak band at 3405 cm^{-1} in addition to the band at 3440 cm^{-1} that is also characteristic for (IIIa). However, the bands at 1645 and 3405 cm^{-1} pertain to the dimeric form of these DABAB compounds, not to the isomer (IV) or (V) as was suggested for (IIIb) in an earlier communication [1]. The presence of the dimer in freshly distilled (IIIb) and (IIIc) has been demonstrated by mass spectrometry. Moreover, when these substances are stored, the equilibrium shifts toward the dimeric form, so that we were able to isolate the crystalline dimer of the amidine (IIIc) in pure form. In its IR spectrum, the above-indicated 1645 and 3405 cm^{-1} bands are observed, and there is no absorption whatever at 1800 or 3440 cm^{-1}. Conversely, when the liquid (IIIc) is heated, the equilibrium shifts back toward the monomer, and the intensity of the 1645 and 3405 cm^{-1} bands decreases, but then again increases upon cooling.

In (IIId) and (IIIe), which have less-branched groups (n-Pr) on the B atom, the content of the dimeric form in the freshly distilled compounds is substantially greater than in (IIIb) or (IIIc), as can be readily seen from the IR, ^{11}B NMR, and mass spectra. For example, in the IR spectrum of (IIId), the 1645 cm^{-1} band is more intense than the 1800 cm^{-1} band; also, in the NH stretching vibration region, the band of the monomer is manifested only as a shoulder at 3435 cm^{-1} on the 3410 cm^{-1} dimer band. Heating of these substances produces an increase in the monomer content in the equilibrium mixture and an increase in intensity of the monomer bands in the IR spectra and the intensity of the signal in the −40 ppm region in the ^{11}B NMR spectra. The increasing susceptibility to dimerization in the series (IIIa) → (IIIe) is apparently explained by the decrease in steric hindrance by the substituents on the B and N atoms.

In accordance with the general trend, greater stability is shown by tautomers with an alkyl group on the amine nitrogen and an aryl group on the imine nitrogen [10]. The existence of the DABAB compounds in the monomeric state in the form of the dialkylborylimino isomers (III) corresponds to this relationship. We should also regard in this same light the structure of dialkylboryl derivatives of N-phenylbenzamidine, for which the dialkylborylamino isomer is apparently the most energetically favorable [1].

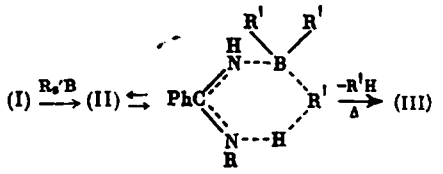
The crystalline dimers of the amidines (IIIc-IIIe), when isolated in pure form, are insoluble in alcohols but are readily soluble in most other organic solvents. Cryoscopic molecular weight determinations have confirmed that these substances are dimeric. Their mass spectra typically show intense peaks for $(2M - R')^+$, and in the ^{11}B NMR spectra there are signals in the region of 4-coordinated boron, at about −3 to −4 ppm. The DABAB dimers are distinguished by high stability in air, and are not decomposed by boiling methanol. Their structure,



(VII)

by analogy with the readily dimerized iminodialkylboranes [8, 9], can be represented by the formula (VII). The alternative eight-membered cyclic associates are less characteristic for borazo compounds, and are not distinguished by high chemical or thermal stability (see [11], for example, on the dimerization of dialkylborylamides). Further studies will be required for a final resolution of the structure of the DABAB dimers.

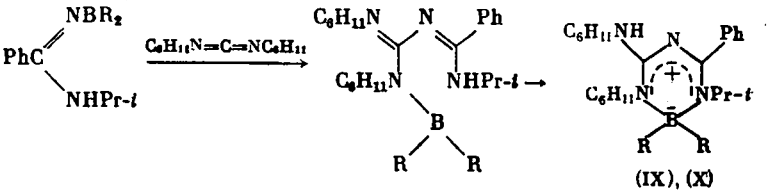
The formation of the dialkylborylamidines (III) from trialkylboranes and (I) can be represented by the scheme



The thermal stability of (III) is comparatively high. For example, the ^{11}B NMR spectrum of (IIIa) does not change when it is heated to 150°. Examination of the IR spectra of (IIIc) over a range of 30-175° showed that only above 150° does the 2230 cm^{-1} band of benzonitrile appear.

The N^2-dialkylboryl-N^1-alkylbenzamidines are highly reactive. Of the greatest interest is their ability to add to certain unsaturated systems, forming cyclic compounds with a 4-coordinated B atom in the ring. They can be used without isolation or purification in reactions with benzonitrile for the synthesis of dialkylboryl-(N-alkyl)benzimidoylbenzamidinates [4]. By the action of tributylborane and N-methylbenzamidine on dicyclohexylcarbodiimide, without isolation of the corresponding (III), dibutylboryl-[N-(N,N'-dicyclohexylamidino)-N'-methylbenzamidinate] has been obtained [12].

The exothermic reaction of addition of (III) at a C =N bond of dicyclohexylcarbodiimide has been used in synthesizing other chelates of this series. From (IIIc) or (IIId), this route has been used in obtaining the crystalline dialkylboryl-[N-(N,N'-dicyclohexylamidino)-N'-isopropylbenzamidines] (IX) and (X), which are stable in air and are not decomposed by water or alcohols.



(IX), (X)

R=Pr (IX); R=*i*-Bu (X)

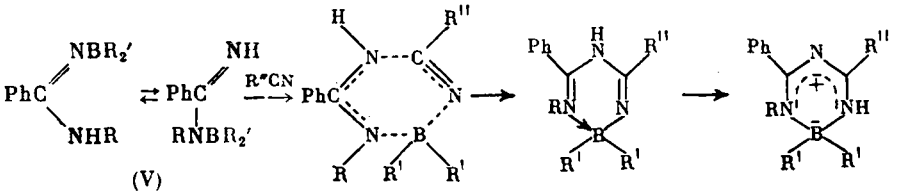
In contrast to the aminoborylation of carbodiimides with the participation of ordinary aminoboranes [13], here the addition products are stabilized as a result of prototropic rearrangements and intramolecular coordination.

The mechanism is similar in the reaction of 2-pyridylaminodialkylboranes with dicyclohexylcarbodiimide, leading to the formation of chelates with an analogous structure [12, 14]. The (IX) and (X) are similar to these latter compounds, and also to the dialkylborylimidoylamidinates [4], in that in the six-membered chelate ring of these compounds, the 6 π-electrons are delocalized in five orbitals. Correspondingly, in the IR spectra of (IX) and (X), we observe intense bands in the 1590-1610 and 1430-1470 cm^{-1} regions, and there is no absorption in the 1610-1800 cm^{-1} range. The mass spectra of (IX) and (X) are characterized by in-

tense peaks (about 25% of the total ion flux) for the ions $(M - R)^+$, which have an aromatic nature (see mass spectra of dialkylborylimidoylamidinates [15]).

It is interesting that the dialkylboryl derivatives of N,N'-dialkylamidines do not react with dicyclohexylcarbodiimide; for example, N-dibutylboryl-N,N'-diisopropylbenzamidine does not add to dicyclohexylcarbodiimide, even at 100°. In this case, it is easy to see, the formation of a chelate ring with a delocalized system of π electrons is impossible, so that addition is evidently not energetically favorable.

In comparing the reactivity of (III) with that of the related 2-alkylborylaminopyridines [16], we must note that the latter, in contrast to (III), do not react with nitriles under these same conditions, even though they tend to add to other reactants at multiple bonds (aldehydes, ketones, isocyanates, carbodiimides, etc.) [12, 14, 16, 17]. The difference in behavior of these compounds with respect to nitriles apparently indicates that (III) reacts with nitriles in the tautomeric form (V). We have proposed the following scheme, which includes tautomeric conversions, to explain the formation of dialkylborylacylamidinates from dialkylborylamides and nitriles [18]:



(V)

It is obvious that a similar isomerization in the series of 2-dialkylborylaminopyridines is energetically unfavorable, since such isomerization would destroy the aromaticity of the pyridine ring.

Thus we see that the dialkylboryl derivatives of N-alkylamidines not only equal the corresponding derivatives of N,N'-disubstituted amidines and 2-aminopyridine in reactivity, but are even somewhat more reactive. Further investigation of the structure and reactivity of these compounds is of undoubted interest.

EXPERIMENTAL

All operations were carried out in a dry argon atmosphere. The ^{11}B NMR spectra were measured in RS 56/19 and Bruker SXP 4-100 spectrometers with $Et_2O \cdot BF_3$ as an external standard. The PMR spectra were recorded in a Varian DA-60-IL instrument with TMS as an internal standard. The IR spectra were taken in UR-20 and Perkin–Elmer 577 spectrometers. The measurements of the spectra at elevated temperatures were performed in a thermostated cuvette, the temperatures being measured by means of a thermocouple. The mass spectra were recorded in a Varian MAT CH-6 instrument.

The N-alkylbenzamidines were prepared by known methods (see literature references given in [5]). The synthesis of the N^2-diisopropylboryl-N^1-isopropylbenzamidine (IIIb) was described in [1].

N^2-Dialkylboryl-N^1-alkylbenzamidines (IIIa), (IIIc), (IIId), and (IIIe). A mixture of 0.05-0.1 mole of the N-alkylbenzamidine and 0.07-0.14 mole of the trialkylborane in 25-40 ml of THF or benzene was refluxed until gas evolution ceased (3-8 h). The solvent was removed under vacuum, and the compounds (III) were segregated by vacuum distillation; these compounds are characterized in Table 1.

Dimers (IIIc), (IIId), and (IIIe). The distilled compounds (III) were stored under argon for periods from 3 days to 3 months. The completely or partially crystallized substances were treated with absolute methanol and filtered, and the crystals on the filter were washed with methanol.

Dimer of N^2-dipropylboryl-N^1-isopropylbenzamidine, mp 131-135°. Found: C 74.30; H 10.59; B 4.07; N 10.54%; mol. wt. (cryoscopic, in benzene) 505. $C_{32}H_{54}B_2N_4$. Calculated: C 74.42; H 10.54; B 4.19; N 10.85%; mol. wt. 516.42. ^{11}B NMR spectrum in THF (δ, ppm): −3 ±1. Mass spectrum (m/e): 473. IR spectrum (in KBr, ν, cm^{-1}): 702 s, 725 w, 740 m, 791 s, 910 m, 925 m, 947 w, 1012 m, 1082 s, 1128 w, 1150 w, 1186 m, 1235 m, 1330 m, 1370 sh, 1390 s, 1450 m, 1500 m, 1582 sh, 1600 s, 1640 vs (C =N), 2800 m, 2868 s, 2902 m, 2925 m, 2952 s, 2978 m, 3035 w, 3065 w, 3090 w, 3112 vw, 3405 m (NH).

Dimer of N^2-diisobutylboryl-N^1-isopropylbenzamidine, mp 118-122°. Found: C 75.69; H 10.92; B 3.74; N 9.76%. $C_{36}H_{62}B_2N_4$. Calculated: C 75.52; H 10.92; B 3.78; N 9.7%. Mass spectrum (m/e): 515.

Dimer of N^2-diisopropylboryl-N^1-cyclohexylbenzamidine, mp 129-133°. Found: C 76.68; H 10.55; B 3.65; N 10.25%. $C_{38}H_{62}B_2N_4$. Calculated: C 76.50; H 10.48; B 3.62; N 9.39%. ^{11}B NMR spectrum in THF (δ, ppm): −3.5 ±1. Mass spectrum (m/e): 553.

Dipropylboryl-[N-(N,N'-dicyclohexylamidino)-N'-isopropylbenzamidinate] (IX). To 3.8 g of freshly distilled (IIId), 3.0 g of fused dicyclohexylcarbodiimide was added; after stirring, the mixture was allowed to stand for 48 h. The solidified reaction mass was treated with absolute mathanol, and the crystals were filtered off. Obtained 4.6 g (67%) of the chelate (IX), mp 114-117° (from hexane). Found: C 75.30; H 10.80; B 2.21; N 12.21%. $C_{29}H_{49}BN_4$. Calculated: C 74.98; H 10.63; B 2.33; N 12.06%. ^{11}B NMR spectrum in THF (δ, ppm): −2.6. Mass spectrum (m/e): 407. IR spectrum (in KBr, ν, cm^{-1}): 700 m, 757 m, 788 w, 825 w, 842 m, 870 w, 893 w, 940 w, 980 m, 1012 m, 1030 m, 1050 m, 1080 m, 1090 m, 1120 m, 1142 m, 1198 s, 1245 m, 1260 w, 1290 w, 1329 m, 1349 m, 1362 s, 1376 sh, 1435 sh, 1452 vs, 1463 sh, 1495 m, 1532 m, 1595 vs, 1610 sh, 2860 s, 2925 sh, 2945 s, 3010 w, 3030 w, 3065 w, 3090 vw, 3115 vw, 3483 m.

Diisobutylboryl-[N-(N,N'-dicyclohexylamidino)-N'-isopropylbenzamidinate] (X). Analogously, from (IIIc), compound (X) was obtained in yield of 64%, mp 71-76° (from hexane). Found: C 75.77; H 10.93; B 2.09; N 11.47%. $C_{31}H_{53}BN_4$. Calculated: C 76.58; H. 10.85; B 2.19; N 11.38%. Mass spectrum (m/e): 435.

SUMMARY

1. By the action of trialkylboranes on N-alkylbenzamidines, N^2-dialkylboryl-N^1-alkylbenzamidines (III) have been synthesized.

2. The compounds (III) tend to dimerize, this tendency being more pronounced for the compounds with less highly branched alkyl radicals on the B and N atoms.

3. By the addition of (III) at a C =N bond of dicyclohexylcarbodiimide, heterocyclic compounds of the chelate type, dialkylboryl[N-(N,N'-dicyclohexylamidino)-N'-alkylbenzamidinates], have been obtained.

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SYNTHESIS OF CHLOROMETHYLPHOSPHINE OXIDES

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UDC 542.91:547.1'118

Chloromethylphosphine oxides are intermediates in the synthesis of various substituted phosphine oxides. They are mainly prepared from hydroxymethylphosphine oxides by substitution of the hydroxyl group by Cl using PCl_5 [1, 2], halogenophosphoranes [1], $SOCl_2$ [2-4], $COCl_2$, ClCOCOCl [5], or HCl [6, 7]. Other methods are also known, such as the reaction of chlorophosphines with CH_2O [8] or the oxidation of tris(chloromethyl)phosphine with HNO_3 [9], Br_2 [1], or H_2O_2 [2].

We have converted acetoxymethyl to chloromethyl by hydrolysis to hydroxymethyl and conversion of this to chloromethyl with PCl_5 [10]. Attempts at the direct conversion of acetoxymethyl to chloromethyl with $SOCl_2$ were not entirely successful [11] (yields of 18-50%). However, this method is necessary because acetoxymethylphosphine oxides are comparatively accessible and can be purified more easily than the hydroxymethyl compounds [10].

We have developed a method for the direct conversion of acetoxymethylphosphine oxides to chloromethylphosphine oxides (I)-(III) by gaseous HCl with removal of AcOH by distillation [12]:

$$(Me)_nP(O)(CH_2OAc)_{3-n} \xrightarrow[180-200^\circ]{HCl\ (gas)} (Me)_nP(O)(CH_2Cl)_{3-n} + AcOH$$

(I) — (III)

$n = 0$ (I), 1 (II), 2 (III)

We prepared the acetoxymethylphosphine oxides from tris(acetoxymethyl)phosphines, which were converted to the oxides by oxidation [10], pseudoallylic rearrangement [13], or other methods [10]. Pure tris(acetoxymethyl)phosphine oxide need not be isolated to prepare tris(chloromethyl)phosphine oxide (I) by this method. The synthesis can be carried out directly from tetrakis(hydroxymethyl)phosphonium chloride without isolating the intermediates:

$$(HOCH_2)_4\overset{+}{P}Cl^- \xrightarrow[H_2O_2]{NaOH} (HOCH_2)_3PO \xrightarrow{Ac_2O} (AcOCH_2)_3PO \xrightarrow[180-200^\circ]{HCl\ (gas)} (ClCH_2)_3PO + AcOH$$

(I)

The acetylation stage can even be omitted. However, the yield of oxide (I) from the direct reaction of HCl with tris(hydroxymethyl)phosphine oxide is much lower.

An attempt to use this method for the substitution of the acetoxy group by Cl to prepare diphenyl(chloromethyl)phosphine oxide was unsuccessful. The acetoxy group of diphenyl(acetoxymethyl)phosphine was not cleaved by gaseous HCl at 180-200°C. We were able to carry out the substitution only at 250°C, but considerable resinification of the reaction mixture occurred under forcing conditions, depriving the method of any preparative value.

Another route to chloromethylphosphine oxides involves the use of the pseudoallylic rearrangement [14] of α-substituted phosphines. We have found that tris(acetoxymethyl)phosphine is converted to methylbis(acetoxymethyl)phosphine oxide by heating in AcOH in the presence of acid catalysts [13]. The reaction of gaseous HCl with tris(acetoxymethyl)phosphine involves both rearrangement and substitution of the acetoxy group by Cl [15]:

$$(AcOCH_2)_3P \xrightarrow[160-180^\circ]{HCl\ (gas)} MeP(O)(CH_2Cl)_2$$

(II)

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 669-672, March, 1980. Original article submitted January 29, 1979.

0568-5230/80/2903-0491$07.50