Derivatives of *cis*-$NPCl_2(NSOCl)_2$ and $(NPCl_2)_2NSOCl$. Part XVIII*. Methoxy and Phenoxy Derivatives of *cis*-$NPCl_2(NSOCl)_2$ and *trans*-$NPCl_2(NSOPh)_2$

D. M. KOK, A. M. G. KOK-HETTINGA and J. C. VAN DE GRAMPEL**

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Nijenborgh 16, 9747 AG Groningen, The Netherlands

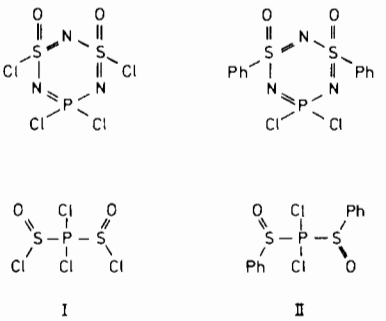
Received July 29, 1981

The reaction of sodium methoxide with cis-*$NPCl_2(NSOCl)_2$ (I) (molar ratio 2.2:1) in a methanol–diethyl ether mixture afforded the disubstituted product $NP(OMe)_2(NSOCl)_2$. The mono(methoxy) derivatives of I could be prepared using methylacetate as solvent. Reaction of sodium methoxide with* trans-*$NPCl_2(NSOPh)_2$ (II) did not lead to substitution of chlorine atoms. However, $NPCl(OMe)(NSOPh)_2$ and $NP(OMe)_2(NSOPh)_2$ could be prepared via a Friedel-Crafts arylation of their S-chloro-precursors. The interaction of sodium phenoxide and I (or II) in diethyl ether led to the formation of the corresponding P-phenoxy derivatives.*

Introduction

Several papers have dealt with the preparation of alkoxy and aryloxy derivatives of the cyclic system hexachlorotriazatriphosphorine $(NPCl_2)_3$ [1, 2]. Both the sodium salts of the alcohols (aliphatic or aromatic) and the free alcohols, combined with an hydrochloric acid acceptor, were used as reagents. During these studies it was found that the methoxy and ethoxy derivatives can undergo at elevated temperature a rearrangement of the type $-NP(OR)_2 \rightarrow -N(R)P(O)OR$ [1, 3, 4]. The phenoxy compounds are recovered unchanged, even after heating to 300 °C for 26 hr [3].

In the present study we report the methanolysis and phenolysis of two N,S,P ring systems, *viz. cis*-$NPCl_2(NSOCl)_2$ (I) and *trans*-$NPCl_2(NSOPh)_2$ (II) (Fig. 1). Similar to the reactions involving $(NPCl_2)_3$ [5–8] salts of methanol and phenol were used as reagents.



I II

Fig. 1. The systems *cis*-$NPCl_2(NSOCl)_2$ and *trans*-$NPCl_2(NSOPh)_2$ and their schematic representations.

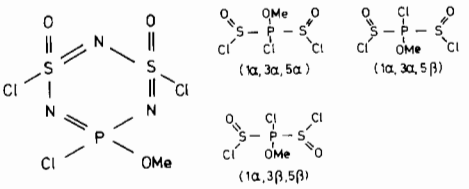


Fig. 2. Stereochemical nomenclature of the three isomers of 1,3,5-trichloro-5-methoxy-1λ^6,3λ^6,2,4,6,5λ^5-dithiatriazaphosphorine-1,3-dioxide.

Nomenclature

In this paper α- and β-descriptors (*Chem. Abstracts Nomenclature*, Index Guide 1977, Appendix IV) will be used in order to indicate the configuration of compounds having three 'stereogenic' centres. When two of these centres are present the prefixes *cis* and *trans* are used [9]. An example is given in Fig. 2.

Experimental

All experiments were carried out under dry nitrogen. *Cis*-$NPCl_2(NSOCl)_2$ and *trans*-$NPCl_2(NSOPh)_2$

*Part XVII: Barteld de Ruiter and Johan C. van de Grampel, submitted for publication.

**Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

were prepared as described elsewhere [10, 11].
Sodium methoxide (Merck, 98%) and phenol (Baker) were used without prior purification. $AlCl_3$ (Merck) was used after sublimation. All solvents were purified and dried by conventional methods. Elemental analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. Hamminga. Infrared spectra (4000–400 cm^{-1}) were recorded on a Hitachi EPI-G spectrophotometer, using KBr discs; calibration was performed by means of polystyrene film bands. Mass spectra were recorded on an AEI M.S. 9 mass spectrometer operating at 70 eV using an accelerating voltage of 8 kV. The samples were introduced directly by a conventional inlet system between 70 and 110 °C (Mr. A. Kiewiet, Department of Organic Chemistry, this University). The ^{31}P NMR spectra were recorded on a Varian XL-100 FT spectrometer at 40.5 MHz. Chemical shifts were determined relative to the external standard 85% H_3PO_4. The ^2H resonance of the solvent $CDCl_3$ was used for field frequency lock. The ^1H NMR spectra were taken on a Varian A60 spectrometer and standardized toward internal TMS.

Methanolysis

Preparation of isomers NPCl(OMe)(NSOCl)$_2$ (III and IV)

To a stirred solution of 3.22 mmol of I in 30 ml of methyl acetate 3.22 mmol of sodium methoxide was added at 0 °C. After stirring for 1 hour at 0 °C the solvent was evaporated. The residual white solid was extracted (three times) with n-hexane. Recrystallization of the residue from n-hexane afforded 44% of a mixture of III and IV (ratio 2.5:1), m.p. 42–60 °C.

Analysis: Calcd. C 3.92, H 0.99, N 13.71 S 20.92, Cl 34.70.

Found: C 4.05, H 1.08, N 13.93, S 21.17, Cl 34.26. Mass spectrum: m/e 305 $(M^{35}Cl)^+$ 4%; m/e 270 $(M^{35}Cl-{}^{35}Cl)^+$ 100%.

Preparation of cis-*NP(OMe)$_2$(NSOCl)$_2$ (V)*

3.22 mmol of I was added at −50 °C in small portions to a stirred solution of 7.09 mmol of sodium methoxide in 20 ml of diethyl ether and 20 ml of methanol. The solution was warmed slowly, showing a white precipitate at −20 °C. At −10 °C the solvent was evaporated, keeping the temperature below 0 °C. The residual white solid was extracted with n-hexane (three times). The resultant solid was recrystallized from n-hexane, yield 55% of pure V, m.p. 72.5–74 °C.

Analysis: Calcd. C 7.95, H 2.02, N 13.91, S 21.23, Cl, 23.48. Found: C 8.07, H 2.05, N 13.87 S, 21.36, Cl 23.60.

IR: 1335s, 1306s, 1217s, 1184s, 1142m, 1086m, 1054s, 1027s, 842m, 791s, 701m, 636s, 628s, 541m, 522m, 419m.

Mass spectrum: m/e 301 $(M^{35}Cl)^+ < 2\%$; m/e 266 $(M^{35}Cl-{}^{35}Cl)^+$ 100%.

Phenylation of Derivatives III, IV and V

Preparation of (1α, 3β, 5α)-NPCl(OMe)(NSOPh)$_2$ (VI)

A mixture of 3.35 mmol of III and IV and 6.70 mmol of $AlCl_3$ was boiled under reflux in 60 ml of benzene for 48 hours. The resulting dark purple solution was hydrolyzed with a hydrochloric acid/ice mixture. After washing of the benzene layer with water and drying over $CaCl_2$, the organic phase was evaporated to dryness yielding 43% of the crude product. The ^1H NMR spectrum showed the presence of only one isomer. Recrystallization from diethyl ether afforded 12% of pure VI, m.p. 67.5–69 °C.

Analysis: Calcd. C 40.06, H 3.36, N 10.78, S 16.45, Cl 9.09. Found C 40.10, H 3.38, N 10.85, S 16.47, Cl 9.27.

IR: 1483m, 1265s, 1183s, 1165vs, 1155vs, 1067s, 1050s, 873m, 850m, 803m, 746s, 725m, 683m, 650m, 570vs.

Mass spectrum: m/e 389 $(M^{35}Cl)^+$ 78%; m/e 221 $(M^{35}Cl-NPh_2)^+$ 100%.

Preparation of trans-*NP(OMe)$_2$(NSOPh)$_2$ (VII) and* cis-*NP(OMe)$_2$(NSOPh)$_2$ (VIII)*

The reaction was carried out as described above for the preparation of VI, using 1.66 mmol of V and 3.22 mmol of $AlCl_3$ in 30 ml of benzene. The crude product (86%) contained two isomers according to the ^1H NMR spectrum. Recrystallization from diethyl ether afforded 28% of pure VII, m.p. 87–89 °C. Further concentration and crystallization afforded 10% of pure VIII, m.p. 123–125 °C.

Analysis (for VII): Calcd. C 43.63, H 4.18, N 10.90, S 16.64. Found C 43.85, H 4.16, N 11.03, S 16.68.

IR: 1476m, 1446s, 1255s, 1202s, 1180s, 1160vs, 1050brvs, 995m, 880m, 868m, 842s, 793m, 746m, 729s, 713s, 683m, 570vs.

Mass spectrum: m/e 385 $(M^{35}Cl)^+$ 90%; m/e 217 $(M^{35}Cl-NPh_2 + 2H)$ 100%.

Analysis (for VIII): Calcd. C 43,63, H 4.18, N 10.90. Found C 43.84, H 4.24, N 11.33.

IR: 1478m, 1445s, 1276s, 1254s, 1200s, 1155s, 1100m, 1068s, 1038s, 998m, 870s, 850s, 795s, 768s, 748s, 729s, 712s, 685s, 610s, 552s, 505m.

Mass spectrum: m/e 385 $(M^{35}Cl)^+$ 100%.

Phenolysis

A solution of sodium phenoxide in diethyl ether was prepared by reaction of equimolar quantities of sodium phenoxide and of sodium in diethyl ether.

Method 1: The sodium phenoxide solution was added to a stirred solution of I or II in diethyl ether at room temperature.

Method 2: Compound I or II was added in portions to a stirred solution of sodium phenoxide at room temperature.

Preparation of (1α, 3α, 5α) – NPCl(OPh)(NSOCl)$_2$ (IX)

Reaction of 3.22 mmol of sodium phenoxide and 3.22 mmol of I according to Method 1. After stirring for 4 hours the NaCl was filtered off and the solvent evaporated. Recrystallization of the residue from n-hexane afforded 31% of pure IX, m.p. 66.5–68 °C.

Analysis: Calcd. C 19.55, H 1.37, N 11.40, S 17.40, Cl 28.86. Found C 19.63, H 1.44, N 11.48, S 17.34, Cl 28.86.

IR: 1334m, 1320s, 1210m, 1165s, 1144s, 712m, 657s, 571m, 543m, 539m, 531m, 521m.

Mass spectrum: m/e 367 $(M^{35}Cl)^+$ 50%; m/e 91 $(OPh-2H)^+$ 100%.

Preparation of cis-$NP(OPh)_2(NSOCl)_2$ *(X)*

Reaction of 9.65 mmol of sodium phenoxide and 3.22 mmol of I according to Method 2. After stirring for 20 hours the NaCl was filtered off and the solvent evaporated. Recrystallization of the residue from n-hexane afforded 28% pure X, m.p. 100–103 °C.

Analysis: Calcd. C 33.81, H 2.36, N 9.86, S 15.05, Cl 16.64. Found C 34.24, H 2.33, N 9.56, S 14.90, Cl 16.38.

IR: 1490m, 1329s, 1314s, 1232m, 1175s, 1155s, 1040s, 1024s, 996s, 857m, 689m, 641s, 581m, 554m, 526m, 485m.

Mass spectrum: m/e 425 $(M^{35}Cl)^+$ 40%; m/e 77 $(Ph)^+$ 100%.

Preparation of (1α, 3β, 5α)-NPCl(OPh)(NSOPh)$_2$ (XI)

Reaction of 1.91 mmol of sodium phenoxide and 1.91 mmol of II according to Method 1. After stirring for 20 hours the NaCl was filtered off and the solvent evaporated. Recrystallization of the residue from a diethyl ether/n-pentane mixture afforded 37% of pure XI, m.p. 77.5–79 °C.

Analysis: Calcd. C 47.84, H 3.35, N 9.30, S 14.19, Cl 7.85. Found C 47.74, H 3.33, N 9.36, S 14.21, Cl 7.92.

IR: 1580m, 1470m, 1440m, 1273vs, 1205s, 1183s, 1165vs, 1151vs, 1060m, 1024m, 979s, 909m, 841s, 833s, 781m, 755s, 750s, 736s, 715s, 688m, 681m, 654s, 584s, 564vs, 543m, 510m, 495m.

Mass spectrum: m/e 451 $(M^{35}Cl)^+$ 100%.

Preparation of trans-$NP(OPh)_2(NSOPh)_2$ *(XII)*

Reaction of 2.04 mmol of sodium phenoxide and 1.02 mmol of II according to Method 2. After stirring for 20 hours the solvent was evaporated and the residue extracted with diethyl ether (three times). Recrystallization of the residue, after evaporation of diethyl ether, yielded 64% of pure XII, m.p. 129–130 °C.

Analysis: Calcd. C 56.57, H 3.96, N 8.25, S 12.59. Found C 56.75, H 4.15, N 8.16, S 12.43.

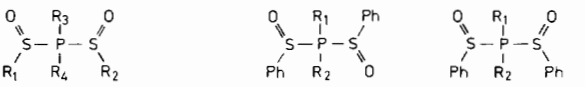
IR: 1580m, 1475s, 1435m, 1264s, 1252s, 1125m, 1184s, 1162vs, 1073m, 1039m, 1023m, 1012m, 984m, 964vs, 912m, 872s, 840m, 832m, 790s, 777s, 761s, 752s, 729m, 718s, 693m, 686s, 574vs, 555s, 515s.

Mass spectrum: m/e 510 M^+ 100%.

Discussion

As may be seen from the above, the first and second substitution step of the methanolysis of I take place at the phosphorus centre only. Reasonable yields of the mono methoxy derivatives III and IV are obtained using methyl acetate as a solvent. Isomer III, which is formed in preponderance, is supposed to have the (1α, 3α, 5α)-configuration in which the methoxy and the oxygen ligands are on the same side of the ring (see refs. [12] and [13], for arguments of structure assignment).

Methanolysis of *trans*-$NPCl_2(NSOPh)_2$ (II) did not lead to the expected results. Although small amounts of the mono methoxy derivative (δ ^{31}P = 17.9 ppm) could be detected in 1:1 molar ratio reactions (solvent methyl acetate/methanol), the major product resonates at a much higher field (δ ^{31}P = –2.4 ppm) pointing to a P(O)R moiety. Both the structure and mode of formation of this product (and related compounds) are still under investigation; and the results will be the subject of a separate paper. The synthesis of the methoxy derivatives of II in appreciable yields succeeded by Friedel-Crafts reaction in benzene starting from a mixture of the isomers III and IV and from *cis*-$NP(OMe)_2(NSOCl)_2$ (V), respectively. In the former case only one of the three possible isomers of $NPCl(OMe)(NSOPh)_2$ (VI) is formed, according to the ^1H NMR spectrum of the crude reaction product.



I $R_1 = R_2 = R_3 = R_4 = Cl$
III $R_1 = R_2 = R_4 = Cl$ $R_3 = OMe$
IV $R_1 = R_2 = R_3 = Cl$ $R_4 = OMe$
V $R_1 = R_2 = Cl$ $R_3 = R_4 = OMe$

II $R_1 = R_2 = Cl$
VI $R_1 = Cl$ $R_2 = OMe$
VII $R_1 = R_2 = OMe$

II' $R_1 = R_2 = Cl$
VIII $R_1 = R_2 = OMe$

The strong resemblance of the phenyl ^1H NMR multiplets of VI to that of II (Fig. 3) suggests a *trans* configuration of the phenyl groups. A similar example of stereospecific Friedel-Crafts phenylation is observed in the formation of the (1α, 3β, 5α)-isomer of $NPCl(NH_2)(NSOPh)_2$ from (1α, 3α, 5α)

TABLE I. NMR Data of the Methoxy and Phenoxy Derivatives of $NPCl_2(NSOR)_2$ (R = Cl, Ph).[a] Chemical shifts (δ) ($CDCl_3$ solution) are positive in low field direction.

		δ(^{31}P) [ppm]		δ(^{1}H) [ppm]	$^3J_{PH}$ [Hz]
		PCl(OR)	$P(OR)_2$		
(1α, 3α, 5α)-$NPCl(OMe)(NSOCl)_2$	(III)	17.9		4.05	15.0
(1α, 3α, 5β)-$NPCl(OMe)(NSOCl)_2$	(IV)	18.9		4.13	15.8
cis-$NP(OMe)_2(NSOCl)_2$	(V)		4.1	3.80,	13.5,
				4.02	12.6
(1α, 3β, 5α)-$NPCl(OMe)(NSOPh)_2$	(VI)	17.4		3.83	15.9
trans-$NP(OMe)_2(NSOPh)_2$	(VII)		5.9	3.63	13.4
cis-$NP(OPh)_2(NSOPh)_2$	(VIII)		10.5	3.89,	12.3,
				3.90	14.0
(1α, 3α, 5α)-$NPCl(OPh)(NSOCl)_2$	(IX)	13.0			
cis-$NP(OPh)_2(NSOCl)_2$	(X)		5.7		
(1α, 3β, 5α)-$NPCl(OPh)(NSOPh)_2$	(XI)	13.1			
trans-$NP(OPh)_2(NSOPh)_2$	(XII)		−3.4		

[a] δ ^{31}P values for I, II and II′ are 27.6 ppm (from *Z. Naturforsch., 33b,* 959 (1978)), 22.1 ppm (from *Z. Naturforsch., 31b,* 1216 (1976)) and 25.4 ppm (*ibid.*), respectively.

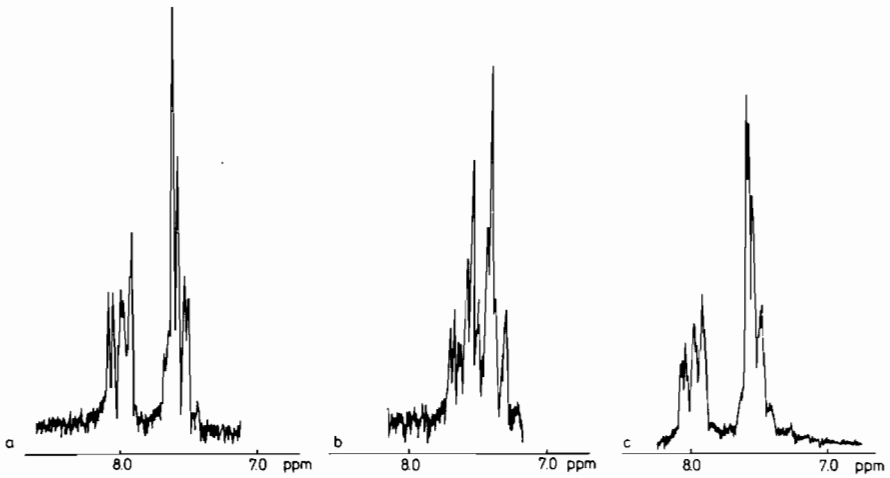


Fig. 3. The phenyl region of the ^{1}H NMR spectrum of a) *trans*-$NPCl_2(NSOPh)_2$ (II); b) *cis*-$NPCl_2(NSOPh)_2$ (II′); c) (1α, 3β, 5α)-$NPCl(OMe)(NSOPh)_2$ (VI).

–$NPCl(NH_2)(NSOCl)_2$ [14]. However, Friedel-Crafts phenylation of (1α, 3α, 5α)-$NPCl(HNBu)(NSOCl)_2$ leads to three isomers of $NPCl(HNBu)(NSOPh)_2$ [15]. No explanation can be given for these seemingly conflicting results. Phenylation of V yielded two isomers of $NP(OMe)_2(NSOPh)_2$ (VII and VIII). Structures can be assigned on the basis of their ^{1}H NMR spectra. The presence of one OMe doublet in the spectrum of VII points to a *trans*-configuration of the phenyl groups. Accordingly, VIII possesses a *cis*-configuration (two OMe doublets).

On using sodium phenoxide and I or II in a 1:1 molar ratio the replacement of chlorine resulted in the formation of the monophenoxy derivatives (1α, 3α, 5α)-$NPCl(OPh)(NSOCl)_2$ (IX) and (1α, 3β, 5α)-$NPCl(OPh)(NSOPh)_2$ (XI), respectively.

IX $R_1=R_2=R_4=Cl$ $R_3=OPh$ XI $R_1=Cl$ $R_2=OPh$
X $R_1=R_2=Cl$ $R_3=R_4=OPh$ XII $R_1=R_2=OPh$

The diphenoxy derivatives $NP(OPh)_2(NSOCl)_2$ (X) and $NP(OPh)_2(NSOPh)_2$ (XII) were obtained using a nucleophilic-ring compound ratio, equal to 3 in the case of compound I and equal to 2 in the case of compound II. It is noteworthy that monosubstitution by sodium phenoxide only leads to one isomer

$NPCl(OPh)(NSOCl)_2$, which contrasts with the comparable reaction of sodium methoxide giving two isomers. This difference might be caused by a steric effect of the closely packed chlorine atoms *trans* to the oxygen atoms in *cis*-$NPCl_2(NSOCl)_2$ [16], allowing only a nucleophilic attack of the more bulky phenoxide anion at the oxygen-side of the ring. From this reasoning, compound IX will possess a configuration in which the OPh-group and the oxygen ligands are in the *cis*-position (1α, 3α, 5α-configuration).

Both the methanolysis and phenolysis of I show a geminal substitution pattern of the chlorine atoms. It is concluded therefore that in these reactions the SOCl centre is less reactive in comparison with a PCl_2 or a PCl(OR) centre. A similar sequence of reactivity has been found in the aminolysis of I by small primary amines (methylamine, ethylamine [12], and butylamine [17]).

As shown in Table I the introduction of a OMe or OPh group results in an upfield shift of the ^{31}P resonance.

Except for the ^{31}P chemical shift of X, the influence of the second OR group is still more pronounced. In this respect the methoxy and phenoxy derivatives described here differ from the amino substituted compounds $NPCl_{2-n}(NHR)_n(NSOCl)_2$ (n = 1, 2; R = CH_3, C_2H_5), where a linear relationship is observed between n and the value of the ^{31}P chemical shift [12].

Acknowledgements

The authors wish to thank the NMR Department of the University of Amsterdam for performing the ^{31}P NMR spectroscopic measurements.

References

1 H. R. Allcock, 'Phosphorus Nitrogen Compounds, Cyclic Linear, and High Polymeric Systems', Academic Press, New York, London (1972).
2 R. Keat and R. A. Shaw, in 'Organic Phosphorus Compounds', Vol. 6, Chapter 17, Ed. G. M. Kosolapoff and L. Maier, Wiley–Interscience, New York, London, Sydney and Toronto (1973).
3 B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *J. Chem. Soc.*, 4459 (1964).
4 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *Inorg. Nucl. Chem. Letters, 15*, 109 (1979).
5 F. Heatley and S. M. Todd, *J. Chem. Soc. A*, 1152 (1966).
6 B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1735 (1964) and references therein.
7 D. Dell, B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 4070 (1965).
8 V. B. Tolstoguzov, V. V. Pisarenko and V. V. Kireev, *Russ. J. Inorg. Chem., 10*, 382 (1965).
9 For the determination of the order of preference of substituents the IUPAC sequence rule was used. *J. Org. Chem., 35*, 2849 (1970).
10 H. H. Baalmann, *Thesis*, University Groningen, The Netherlands, 1976.
11 J. B. van den Berg, B. de Ruiter and J. C. van de Grampel, *Z. Naturforsch., 31b*, 1276 (1976).
12 C. Cnossen-Voswijk and J. C. van de Grampel, *Z. Naturforsch., 34b*, 850 (1979).
13 F. van Bolhuis, C. Cnossen-Voswijk and J. C. van de Grampel, *Cryst. Struct. Comm., 10*, 69 (1981).
14 H. Winter and J. C. van de Grampel, to be published.
15 J. B. van den Berg and J. C. van de Grampel, *Z. Naturforsch., 34b*, 27 (1979).
16 J. C. van de Grampel and A. Vos, *Acta Cryst., B25*, 651 (1969).
17 J. B. van den Berg, E. Klei, B. de Ruiter, J. C. van de Grampel and C. Kruk, *Recl. Trav. Chim. Pays-Bas, 95*, 206 (1976).