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REACTION OF DIACETYL DIANIL WITH METHYL- AND ETHYL-ALUMINIUM COMPOUNDS

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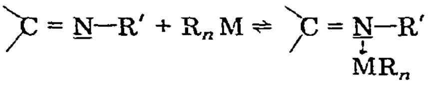
Summary

The reaction of diacetyl dianil (DAD) with methyl- and ethyl-aluminium compounds was investigated: with methylaluminium dichloride, a donor—acceptor complex DAD·$MeAlCl_2$ was obtained, and with trialkylaluminium an organoaluminium product of the addition of the alkyl group R_3Al to one of the two DAD azomethine bonds. Subsequent hydrolysis gives 2-(*N*-phenylamine)-2-alkylbuta-3-none anil, in each case. The yield of anil depends on the type (acidity) of organoaluminium compound and decreases in the order $R_3Al > R_2AlCl > RAlCl_2$.

A reaction mechanism is proposed.

Introduction

Organometallic compounds readily react with azomethines to form donor—acceptor complexes:

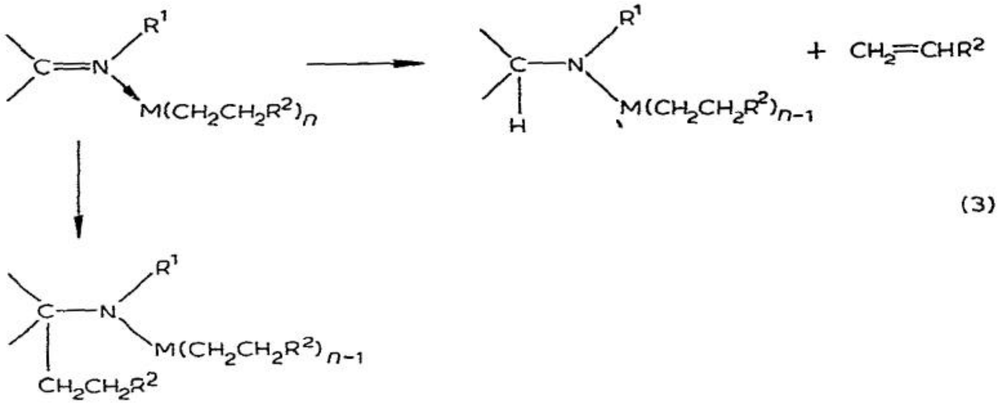


$$>C=\underline{N}-R' + R_nM \rightleftharpoons >C=\underset{\underset{\displaystyle MR_n}{\downarrow}}{\underline{N}}-R' \qquad (R = \text{alkyl, H}) \tag{1}$$

Complexes in which R = alkyl are usually stable. Trimethylaluminium complexes with *N*-isopropylidenemethylamine and with many *O*-methyl ketoximes [1] have been isolated. The azomethine bond is preserved also in the reaction of metal alkyls with ketimines [2]:

$$>C=N-H + R_nM \rightarrow >C=N-MR_{n-1} + RH \tag{2}$$

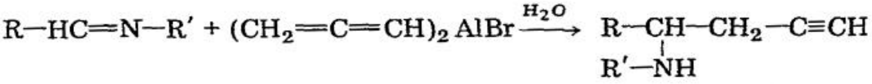
In many cases the C=N bond after complexation undergoes addition (*C*-alkylation) and reduction reactions:



(3)

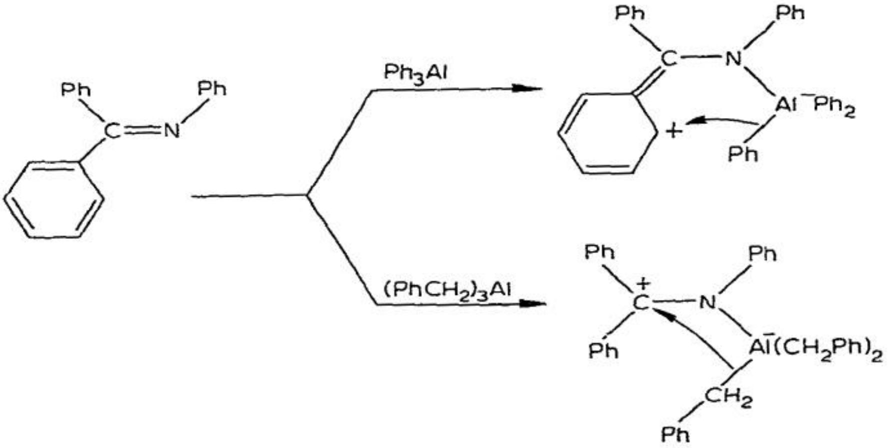
Azomethines react in this way with organomagnesium compounds [3], organocadmium and organozinc compounds [4]. Besides the product of 1,2-addition (reaction 3) the α,β-unsaturated azomethines can also give 1,4-addition [5]. The result of the reaction with organoaluminium compounds (which readily undergo complexation) is determined by the structure of the organoaluminium compounds, the structure of azomethine, and the reaction conditions [6,7]. The rearrangement of the complex, leading to alkylation or reduction of the C=N bond has high activation energy in most cases and requires drastic conditions.

The *C*-alkylation reaction (eqn. 3) proceeds when azomethine is mixed with diallenealuminium bromide [8]:



$$R{-}HC{=}N{-}R' + (CH_2{=}C{=}CH)_2AlBr \xrightarrow{H_2O} R{-}\underset{\textstyle R'{-}NH}{\underset{|}{CH}}{-}CH_2{-}C{\equiv}CH \qquad (4)$$

Phenyl—aluminium bonds add only in 1,4-fashion to benzophenone anil*, while benzyl—aluminium bonds add only in a 1,2-manner [9]:



(5)

(6)

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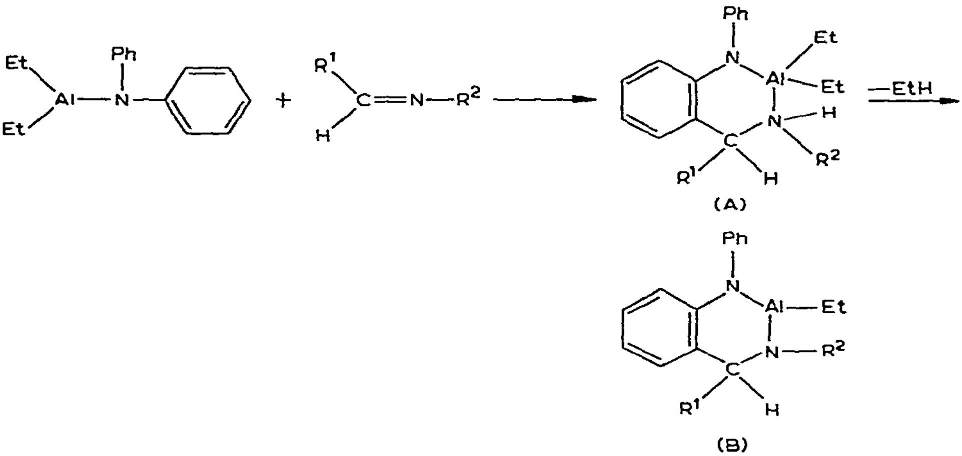
* Organomagnesium compounds react identically with benzophenone anil [9a].

The alkylation of benzophenone anil requires drastic conditions (140°, 120h) and proceeds with a low yield.

The reaction of *N*-diethylaluminium *N,N*-diphenylamide with aldimines [10] has an interesting and unexpected course:



(7)

Instead of the expected addition of the ethyl group to the C=N bond, the addition of an *ortho* C—H bond of the diphenylamino group to the imino group occurs (A), which then eliminates ethane and produces the Al-heterocycle (B).

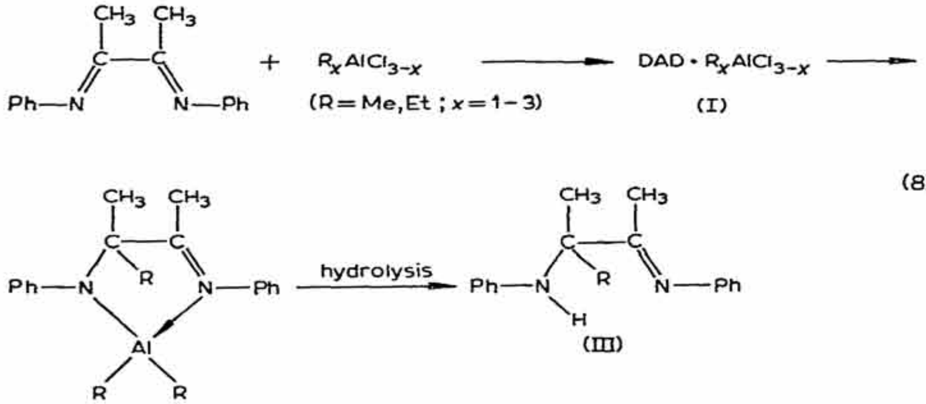
Pyridine, 2,2′-bipyridine and their derivatives, that can be treated formally as azomethines, do not undergo the *C*-alkylation reaction by organometallic compounds [11 - 13]. Nevertheless, in the case of the reaction of bipyridine and triethylaluminium there may well be a small quantity of the alkylation product that has not yet been isolated [12].

There are no published data relating to the reaction of organometallic compounds with diazomethines containing a conjugated, chain-like system of C=N double bonds. The presence of two azomethine bonds creates a possibility of forming complexes with the molar ratio 1/1 or 1/2 having a chelate, linear polymeric or cyclic structure. There exists a possibility of alkylation of both the azomethine bonds. For checking the course of change of linear, conjugated azomethines, we tested the reaction of diacetyl dianil (DAD) with organoaluminium compounds.

Results and discussion

The reaction of diacetyl dianil (DAD) with organoaluminium compounds may be represented by a general equation (eqn. 8).

In the case of the reaction of the DAD with trialkylaluminium, the donor—acceptor complex (I) that is formed in the first stage of the reaction cannot be isolated. This compound was obtained by using methylaluminium dichloride instead of trialkylaluminium. Further details about this complex will be the subject of a future publication.

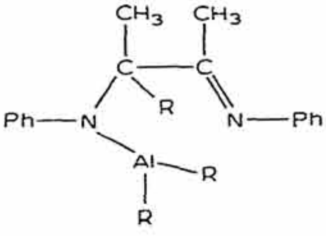


(8)

(II)

In the reaction of DAD with trimethylaluminium, an organometallic compound *N*-dimethylaluminium *N*-phenyl-*N*-[2-(2-methyl)buta-3-none anil] amide (II) was isolated. It is the product of the addition of the organoaluminium compound to one of the azomethine bonds. Complex II occurs as yellow crystals, is slightly soluble in aromatic hydrocarbons and chlorinated hydrocarbons and is insoluble in aliphatic hydrocarbons. The similar diethyl complex is slightly more soluble in aromatic hydrocarbons.

II is comparatively stable, even in air for some tens of seconds without any visible changes. It is decomposed readily by water and alcohols, with formation of methane (or ethane) and III, the alkyl derivative of DAD. IR, NMR, elemental analysis, and alkane gas measurement confirm that the compound is a product of addition reaction and not a complex of the substrates. Cryoscopy indicates that both the methyl and ethyl compound are monomers. The proposed chelate structure of II is monomeric with the aluminium being 4-coordinated. The depression of ν(C=N) in the IR confirms the complexation of nitrogen from the azomethine group by the aluminium atom. ν(C=N) is displaced from 1660 cm^{-1} (III) to 1635 cm^{-1} (II). The results obtained exclude the chain-like structure IV:



(IV)

The result of hydrolysis of compound II is 2-(*N*-phenylamino)-2-alkylbuta-3-none anil (III). This compound is the main product of the reaction, irrespective of temperature (− 50° to 111°C), duration time (2 to 440 min), concentration of reactants and molar ratio of DAD/ organoaluminium compound (1/4 to 3/1) (Tables 1,2). Certain by-products are also formed: unidenti-

TABLE 1

THE ALKYLATION REACTION OF DAD BY METHYLALUMINIUM COMPOUNDS. MOLAR RATIO DAD/Al IS 1/1 AND THE SOLVENT IS TOLUENE EXCEPT WHERE STATED

Organoaluminium	[DAD] (mol/l)	Reaction temp. (°C)	Reaction time (min)	Yield Me-DAD[a] (%)
Me_3Al	0.073	−50	2—3	73.0
	0.250	room tem.	2—3	74.5
	0.685[b]	42	120	88.8
	0.357[c]	70—80	440	90.0
	0.500[d]	111	60	90.0
	1.000	111	60	100.0
Me_2AlCl	0.250	50	60	26.2
	0.125	30	180	12.7
	0.125	50	300	36.0
$MeAlCl_2$	0.250	50	60	9.5
	0.250	50	60	8.0
	0.125	50	300	8.7

[a] Me-DAD is 2-(*N*-phenylamine)-2-methylbuta-3-none anil. [b] Solvent CH_2Cl_2. [c] Solvent benzene. [d] DAD/Al = 1/4. [e] DAD/Al = 3/1.

fied low molecular weight condensation compounds of pitchy composition are formed in minute quantity. In the reaction of DAD with ethylaluminium compounds there were detected small amounts of the product of reduction of one of the azomethine bonds, 2-(*N*-phenylamino)-buta-3-none anil, although a considerable part of the product of the reduction reaction could be expected as it takes place in the reaction of ketones with ethylaluminium compounds [14].

The type of organoaluminium compound has a material influence on the conversion of DAD. The yield of reaction (see Tables 1 and 2) decreases in the order $R_3Al > R_2AlCl > RAlCl_2$ (R = Me, Et) in the same order as Lewis acidity of these compounds [14] rises.

The alkylation of DAD by trialkylaluminium proceeds rapidly. This facility of reaction suggests that the reaction of DAD with R_xAlCl_{3-x} must proceed by another mechanism than the known and described [8 - 10] reactions

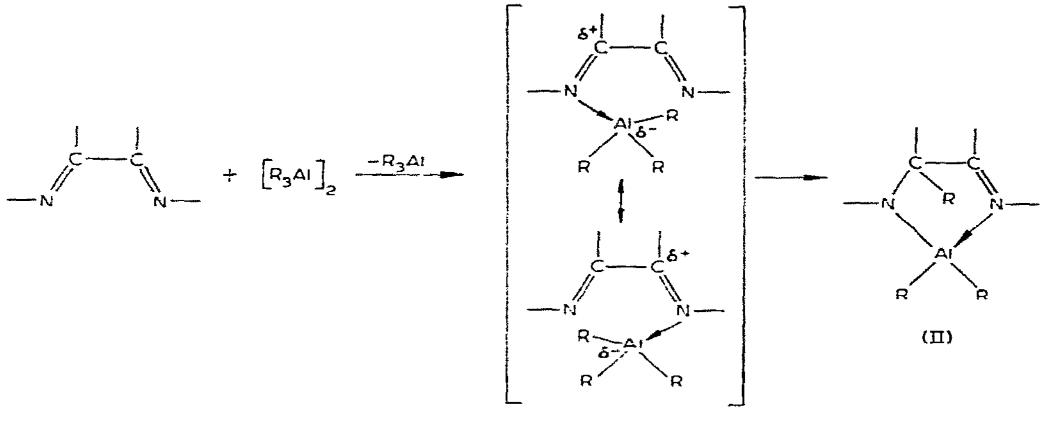
TABLE 2

THE REACTION OF DIACETYL DIANIL (DAD) WITH ETHYLALUMINIUM COMPOUNDS. MOLAR RATIO OF DAD/Al IS 1/1 AND THE SOLVENT IS TOLUENE EXCEPT WHERE STATED

Organoaluminium	[DAD] (mol/l)	Reaction temp. (°C)	Reaction time (min)	Yield Et-DAD[a] (%)
Et_3Al	0.273	−10	4	84
	0.405	room temp.	2—3	94
	0.520[b]	80	150	95
	0.273[c]	111	4	93
	0.273[d]	111	3	95
	0.500[e]	111	60	95
Et_2AlCl	0.250	50	60	90
$EtAlCl_2$	0.250	50	60	10

[a] Et-DAD is 2-(*N*-phenylamine)-2-ethylbuta-3-none anil. [b] Solvent benzene. [c] Order DAD then Et_3Al. [d] Order Et_3Al then DAD. [e] DAD/Al = 1/4.

of compounds containing one C=N bond in a molecule with organometallic compounds. On the basis of the results we propose the following mechanism:



(I)

The simultaneous influence of two nitrogen atoms (I) forming a chelate increases the electron density on the aluminium atom and makes possible the rearrangement of the alkyl anion from aluminium to the carbon atom of the azomethine bond. In the reactions of monoazomethines known up to now, the lack of the chelating effect is probably the reason for the low yields of addition of reduction of C=N bond. The chelation of aluminium in II excludes the possibility of alkylation of the free DAD (reaction with an excess of diacetyl dianil, Table 1) by an organoaluminium compound complexed in such a way. The nitrogen electron pair from the C=N arrangement in chelate II is utilized for forming a firm bond with the aluminium. The decrease of basicity of nitrogen and the generally low reactivity of the monoazomethine resulting from that, makes the addition of free organoaluminium compound to the chelate C=N bond impossible (reaction with an excess of Me_3Al, Table 1).

Experimental

All the experiments were carried out in a dry, deoxidized nitrogen atmosphere. The solvents were dried by heating with a sodium—potassium alloy.

Infrared spectra were recorded on a Zeiss spectrophotometer model UR-10; mass spectra with LKB-9000 and NMR spectra with JEOL model 60 CH. The chemical shifts are given on the τ scale. The gas chromatographic analysis was carried out by Willy Giede G.C.H.F. 18.3 apparatus (liquid phase SE 30 or OV-17).

Diacetyl dianil (DAD)

Diacetyl dianil was obtained from 2,3-butadione and aniline and was purified by crystallization with toluene. The yellow crystals of DAD melted at 136° (uncorr.). NMR in CCl_4 : 2.5 multiplet; 7.85 singlet. IR in KBr : 3060w, 3030w, 2975w, 1940w, 1860w, 1735w, 1640s, 1595m, 1580m, 1485s, 1450m, 1430w, 1370m, 1360s, 1210s, 1170m, 1150m, 1120s, 1080m, 1030w, 905m, 810s, 805m, 770s, 700s, 535w, 505m and 480w cm^{-1}.

Reaction of organoaluminium compounds with DAD. General procedure

A non-saturated DAD solution in benzene or toluene at the required temperature was prepared in a thermostatted reactor with a mixer and the tested organoaluminium solution was injected by a syringe into it. For an experiment proceeding above room temperature, the reactor contents were cooled to stop reaction, and the organoaluminium compounds were decomposed by methanol, or in the case of organoaluminium chloride, by using sodium methylate solution in methanol. The post-reaction mixture was filtered and the aluminium alcoholate precipitate obtained was extracted several times by heating to boiling point with benzene. The filtrate and extracts were combined, and the anil contents in solution were determined by GLC.

2-(N-phenylamino)-2-methylbuta-3-none anil (III)

This was obtained by distilling off the solvent from the filtrate and by crystallization of the residue from petroleum. The colourless crystals of anil melted at 65.5 - 67.5° (uncorr.). NMR in CCl_4 : 2.8 - 3.4, 1OH, multiplet; 6.03, 1H, singlet; 8.18, 3H, singlet; 8.43, 6H, singlet. IR in KBr : 3400m, 3055w, 2990w, 2975m, 2940w, 1935w, 1660s, 1600s, 1580m, 1510s, 1490s, 1430w, 1385s, 1365w, 1320s, 1295w, 1270s, 1230w, 1200w, 1185w, 1160w, 1135s, 1070w, 1055w, 1000w, 905w, 883w, 820w, 785s, 755s, 718m, 700s, 635w, 550w and 500w cm^{-1}.

Mass spectrum (relative intensities in parentheses): *m/e* 252(1.92) $C_6H_5NHC(CH_3)_2C(CH_3)NC_6H_5$; 135(13.0)134 + H; 134(100.0)$C_6H_5NHC(CH_3)_2$; 133 (10.0)134 — H; 132(8.9)134 — 2H; 119(3.5)118 + H; 118(21.8) $C_6H_5NC(CH_3)$; 91(3.6) C_6H_5NH; 78(3.6)C_6H_5 + H; 77(34.9) C_6H_5; 42(6.5) $C(CH_3)_2$; 41(4.7)42 — H.

2-(N-phenylamino)-2 ethylbuta-3-none anil

This was isolated analogously to III and recrystallized from methanol. The white, fine-crystalline solid melts at 83 - 84° (uncorr.). NMR in CCl_4: 2.9 - 3.4, 10H, multiplet; 5.75, 1H, singlet; 8.06, 2H, quartet; 8.20, 3H, singlet; 8.48, 3H, singlet; 9.10, 3H, triplet. IR in KBr: 3400m, 3080w, 3050w, 3020w, 2990m, 2940m, 2860w, 1935w, 1660s, 1600s, 1510s, 1490s, 1465m, 1440m, 1390w, 1365m, 1320m, 1300m, 1260m, 1230m, 1183w, 1170w, 1140m, 1070m, 1030w, 1000w, 900w, 880w, 820w, 790m, 760s, 708m, 700s, 625w, 530m and 490m cm^{-1}.

Preparation of N-dimethylaluminium N-phenyl-N-[2-(2-methyl)-buta-3-none anil] amide

30 mmoles (7.08g) of DAD was dissolved in 30 ml of benzene at 40° and then 30 mmoles (2.06g) of Me_3Al was added. The yellow solution of the substrate changed to a dark brown colour and the pale yellow compound which precipitated, was filtered off, washed several times with benzene and dried under reduced pressure. Pale yellow crystals were obtained (6.4g, 70% yield). Analysis: Found C, 76.92%; H, 6.59%; Al, 8.55%. $C_{19}H_{25}N_2Al$ calcd.: C, 74.02%; H, 8.11%; Al, 8.82%. Ratio methyl/aluminium = 1.93 ($\approx$ 2.00). NMR in CH_2Cl_2: 2.8 - 3.3, 10H, multiplet; 7.94, 3H, singlet; 8.26, 6H, singlet; 10.80, 6H, singlet. The chemical shift was measured in relation to the protons of

solvent signal (4.70). IR in KBr: 3060w, 2995w, 2930w, 2880w, 2820w, 1660m, 1635s, 1597s, 1565m, 1510m, 1495s, 1458m, 1370w, 1350w, 1320s, 1285m, 1273m, 1235m, 1190m, 1180s, 1160w, 1140m, 1100m, 1077w, 1044w, 1030w, 1000w, 990w, 885w, 850m, 795m, 760s, 700s, 665s, 657s, 645m, 575m, 510m, 467w and 435w cm^{-1}.

References

1 M. Bender, Z. Buczkowski and J. Plenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 17(1969)637.
2 K. Wade, R. Snaith and B.K. Wyatt, J. Chem. Soc. A, (1970) 380; ibid., (1967) 1339; B. Samuel and K. Wade, ibid., (1969) 1742; J.R. Jennings, J.E. Lloyd and K. Wade, ibid., (1965) 5083; J.E. Lloyd and K. Wade, ibid., (1965) 2662.
3 R.E. Dessy, J.H. Wotiz and C.A. Hollingsworth, J. Amer. Chem. Soc., 77(1955)103.
4 J. Thomas, E. Henry-Basch and P. Freon, C.R. Acad. Sci. Ser. C., 267 (1968) 176; J. Thomas, P. Freon, ibid., 267 (1968) 1850, Bull. Soc. Chim. Fr., 3 (1973) 1078; ibid., 3 (1973) 1082.
5 B. Mauze and L. Miginiac, Bull. Soc. Chim. Fr. 3(1973)1078; ibid., 3(1973)1082.
6 E. Bonitz, Chem. Ber., 88(1955)742.
7 W.P. Neumann, Angew. Chem., 69 (1965) 730; Justus Liebigs Ann. Chem., 629 (1960) 23; ibid., 667 (1963) 1; ibid., 667 (1963) 12.
8 J.L. Moreau and M. Gaudemar, Bull. Soc. Chim. Fr., (1971)3071.
9 J.J. Eisch and J.M. Biedermann, J. Organometal. Chem., 30(1971)167.
9a H. Gilman, J.E. Kirby and C.R. Kinney, J. Amer. Chem. Soc., 51(1929)2252; R.C. Fuson, R.J. Lokken, R.L. Pedrotti, *ibid.*, 78 (1958) 6064.
10 H. Hoberg and A. Milchereit, Justus Liebigs Ann. Chem., 766(1972)146.
11 K.H. Thiele and W. Bruser, Z. Anorg. Allg. Chem., 348(1966)179; ibid 349(1967)33.
12 H. Lehmkuhl and H.D. Kobs, Justus Liebigs Ann. Chem., 719(1968)11.
13 D. Giurgiu, A. Ciobanu, M. Bostan and I. Popescu, Rev. Rumaine Chim., 13(1968)943.
14 S. Pasynkiewicz, Pure Appl. Chem., 30(1972)509.