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REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH BENZONITRILE

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SUMMARY

Reactions of methylaluminium compounds $(CH_3)_nAlCl_{3-n}$ ($n=1, 2, 3$) with benzonitrile have been studied at reactant mole ratios of 1/1 and 1/2. The reactions afforded acetophenone (upon hydrolysis), 3,5-diphenyl-2-pyrazoline hydrochloride or tris(1,3-diphenylpropane-1,3-dionato)aluminium (according to the hydrolysis procedure applied), 2,4,6-triphenylpyrimidine, triphenyl-*s*-triazine, and methane. Product yields have been determined in relation to the nature of the methylaluminium compound and the reactant mole ratio. Reaction mechanisms are postulated and discussed in terms of the results obtained.

Earlier studies[1,2] on reactions of methylaluminium compounds $(CH_3)_n$-$AlCl_{3-n}$ (I) with benzonitrile at reactant mole ratios of 1/1 and 2/1 have shown that the major products are aluminium ketimine derivatives (II), which on hydrolysis [Scheme 1, (1)] yield acetophenone (VII). The use of trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride, respectively as starting materials leads to a successive decrease in the yield of acetophenone. In addition to acetophenone, a crystalline solid, m.p. (EtOH)[1] 184–185°, identified as 2,4,6-triphenylpyrimidine (VI) was obtained from these reactions.

The present work has been undertaken in an attempt to determine the nature of the reactions affording 2,4,6-triphenylpyrimidine and other reaction products.

RESULTS

The reactions of trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride with benzonitrile have been investigated at a reactant mole ratio of 1/2 and at temperatures of 140° and 170°. The yields obtained are listed in Table 1. In addition to acetophenone (VII), the reactions afforded 2,4,6-triphenylpyrimidine (VI), triphenyl-*s*-triazine (IV) and, according to the conditions of hydrolysis of the reaction mixture, either 3,5-diphenyl-2-pyrazoline hydrochloride (VIIIa) or tris(1,3-diphenyl-1,3-propanedionato)aluminium (VIIIb). Yields of (VIIIa), (VIIIb) and (IV) were not determined. When further hydrolyzed, (VIIIa) and (VIIIb) yielded dibenzoylmethane (1,3-diphenylpropane-1,3-dione) (IX).

The yields obtained from the reaction of (I) and benzonitrile in a 1/1 and 1/2

TABLE 1

YIELD OF ACETOPHENONE (VII), 2,4,6-TRIPHENYLPYRIMIDINE (VI) AND CH_4 IN THE REACTION OF $(CH_3)_nAlCl_{3-n}$ (I) WITH $C_6H_5CN^a$

(I) (n)	Reaction temp. (°C)	Yield (%)		
		(VII)[b]	(VI)[c]	CH_4[d]
3	140	52.5 (84.1)	2.7	27
2	140	0.9 (49.8)	15.4	43
1	140	(1.0)		
3	170	56.5	12.7	46
2	170	13.9 (71.0)	39.5	98
1	170	1.8 (30.2)	26.0	32

[a] Reaction time 8 h, (I)/C_6H_5CN 1/2. [b] Based on (I). In brackets based on C_6H_5CN, (I)/C_6H_5CN 1.1/1 (see ref. 1). [c] Based on C_6H_5CN. [d] Based on (I) (per single methyl group).

TABLE 2

YIELD OF ACETOPHENONE (VII), 2,4,6-TRIPHENYLPYRIMIDINE (VI), 3,5-DIPHENYL-2-PYRAZOLINE HYDROCHLORIDE (VIIIa) AND CH_4 IN THE REACTION OF $(CH_3)_nAlCl_{3-n}$ (I) WITH $C_6H_5CN^a$

(I) (n)	(I)/C_6H_5CN (mole ratio)	Yield (%)			
		(VII)[b]	(VI)[c]	(VIIIa)[c]	CH_4[d]
3	1/1	91.0		~1	
3	1/2	63.0	3.6	8.0	
3	1/2.8[e]	16.0	6.0	50.2 (70.2[b])	
2	1/1	49.7	6.3		10
2	1/2	0.7	34.1	16.7	71
2	1/2	0.9	36.0	16.5[f]	74
2	1/2[g]	1.2	39.7	33.0	80
1	1/1	5.7	10.6	Traces	12
1	1/2	2.6	6.2	Traces	8

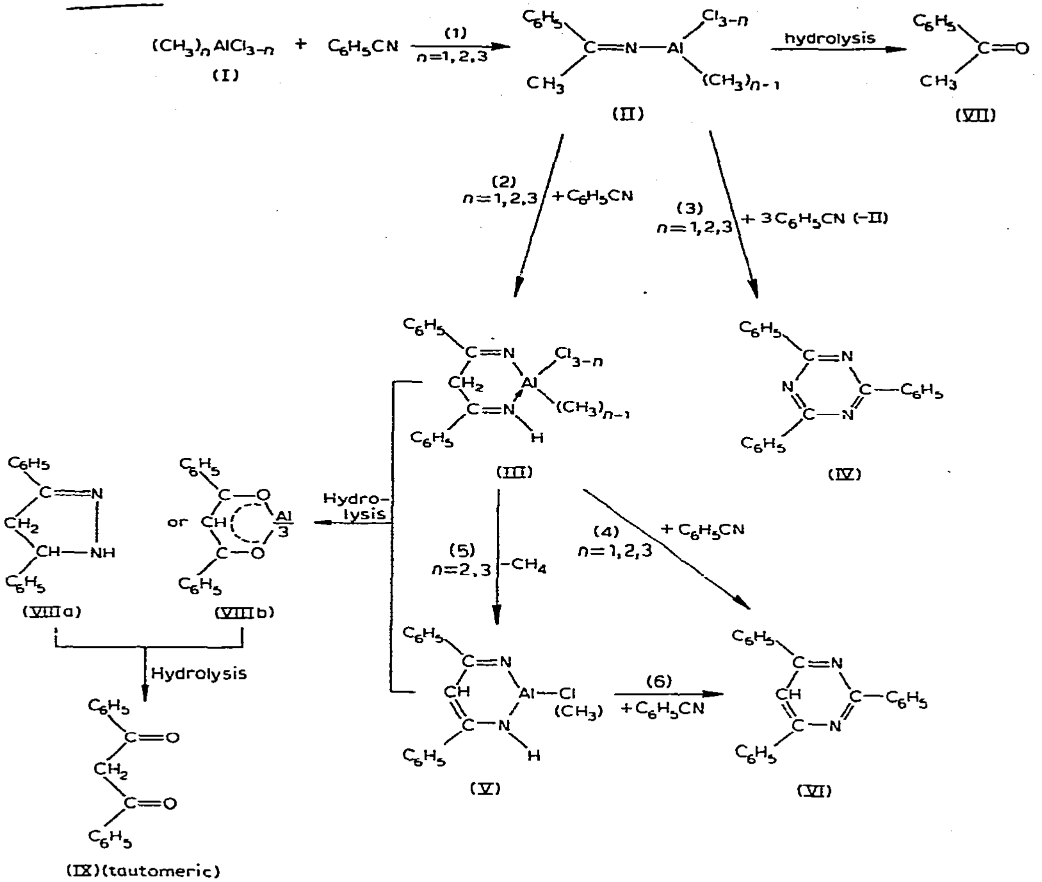
[a] Reaction temp. 150°, time 8 h. [b] Based on (I). [c] Based on C_6H_5CN. [d] Based on (I) (per single methyl group). [e] Reaction was carried out in two steps: 1st, (I)/C_6H_5CN 1/1, time 8 h, 2nd, C_6H_5CN was added (the amount being equal to 1.8 times the amount introduced in the 1st step), time 8 h. [f] Tris(1,3-diphenyl-1,3-propanedionato)aluminium (VIIIb) was obtained. [g] Reaction was carried out in two steps: 1st, (I)/C_6H_5CN 1/1, time 8 h, 2nd, C_6H_5CN was added (the amount being equal to that of C_6H_5CN introduced in the 1st step), time 8 h.

molar ratio at 150° (Table 2) demonstrate that the mole ratio of reactants is an important factor in the reaction. After treating methylaluminium dichloride with benzonitrile, triphenyl-s-triazine (IV) was obtained in 2% yield, whereas the yields of this material with other methylaluminium compounds were even smaller. When heated with aluminium trichloride, benzonitrile also yielded (IV) (2% at reactant mole ratio 1/3, 170°, 24 h).

In addition to the major products, benzoic acid and dibenzamide were detected in the reaction mixture in very slight amounts, having presumably been formed through secondary reactions.

Investigation of a dimethylaluminium chloride/benzonitrile reaction mixture prior to hydrolysis indicated the presence of compound (V), which on hydrolysis gave

SCHEME 1



(VIIIa). When heated with benzonitrile, (V) (Cl) gave (VI) (Scheme 1, reaction 6), a reactant mole ratio of 1 mole (V) (Cl) to 4 moles PhCN yielding (VI) in 40% yield at 170°, (8 h) and 30% yield at 150°, (5 h). Complexation of benzonitrile with aluminium trichloride only slightly affected the yield of (VI) obtained in this reaction.

DISCUSSION

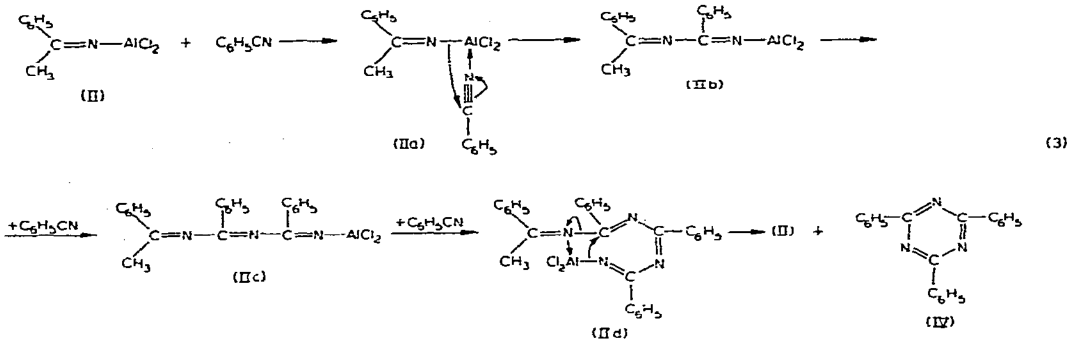
Scheme 1 is suggested as an explanation for the various reactions of methylaluminium compounds (I) with benzonitrile. A successive decrease in the yield of products from reaction (1) was found to occur with trimethylaluminium, dimethylaluminium chloride, and methylaluminium dichloride. It has been suggested[1,2] that this reaction involves intramolecular rearrangement of donor–acceptor complexes (Ia) through the addition of one of the methyl groups attached to the Al atom to the carbon atom of the nitrile group.

$$C_6H_5\text{–}C{\equiv}N{\rightarrow}Al(CH_3)_nCl_{3-n}$$

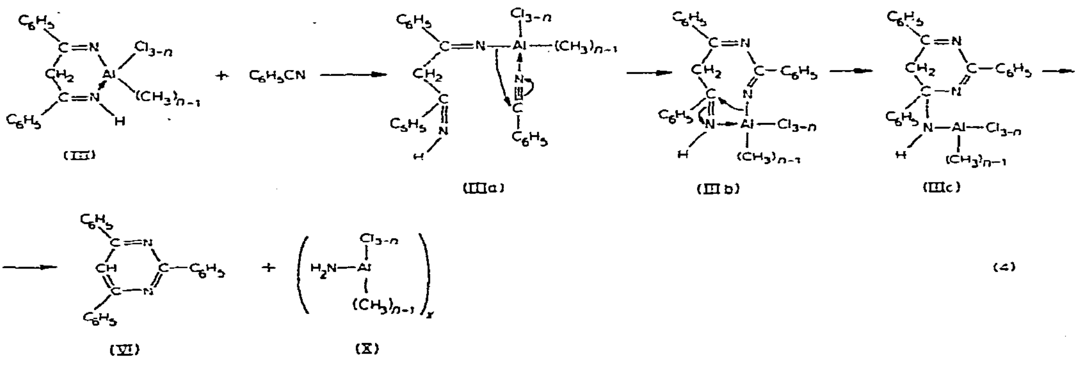
(Ia)

The resulting aluminium ketimine derivatives (II) react further with benzonitrile to add either the C_α–H (reaction 2) or the N–Al bond (reaction 3) to the nitrile group. The former type of addition predominates in the reactions under study. Reaction (2) with compounds (II) ($n=2$) and (II) ($n=3$) proceeds readily, provided the molar ratio of (I) to the benzonitrile is 1/2. When the molar ratio is 1/1, reaction (2) proceeds much less readily. In reaction (2), compound (II) ($n=2$) is much more reactive than compound (II) ($n=3$), because of the increased mobility of its H(C_α) atom. However, compound (II) ($n=1$) (formed from CH_3AlCl_2) which has the most mobile H(C_α) atom is less reactive than is compound (II) ($n=2$). One possible reason is that benzonitrile interacts with compound (II) to yield an intermediate donor–acceptor complex the H(C_α) atom would be much less mobile than the one in uncomplexed (II).

SCHEME 2



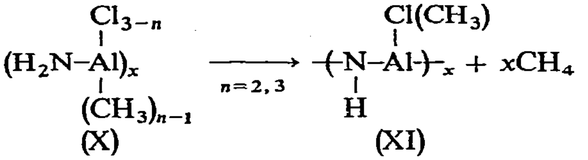
SCHEME 3



In the (IIa) complex (Scheme 2), the ketimine group can add to the carbon atom of the nitrile group to yield compound (IIb). This can then react with further benzonitrile to yield the products (IIc) and (IId). Owing to its favourable geometric structure, (IId) can form an internal complex. Such a complex would cyclize to yield (IV) and eliminate (II) (regeneration of the catalyst for trimerization of benzonitrile). Triphenyl-s-triazine is also formed in small amounts in the reactions of benzonitrile with other organometallic compounds such as dimethylzinc[3], diethylzinc[4], trimethylgallium[5], and triethylindium[6]. Under modified conditions, s-triazine derivatives are also feasible in reactions of nitriles with organomagnesium compounds[7].

Compounds (III) which are formed in reaction (2) can react further with benzonitrile (reaction 4) to yield (VI). This reaction presumably involves addition of the N–Al bond to the nitrile group of the benzonitrile (Scheme 3).

Benzonitrile attacks the aluminium atom in compound (III) to form an intermediate complex (IIIa). This rearranges intramolecularly into (IIIb) which, in turn, cyclizes to yield (IIIc), and this, by eliminating an aluminium amide compound (X), gives (VI). Tautomerization of compound (IIIb) with simultaneous elimination of (X) and cyclization to give (VI) cannot be ruled out as an alternative possibility. Compound (X) ($n = 1$) occurs as an associated molecule[8] which can react with unconverted methylaluminium dichloride to yield methane. This reaction will explain the evolution of methane on heating of benzonitrile with methylaluminium dichloride. Compounds (X) ($n = 2$ and 3) eliminate methane (reaction 7):



$$\overset{\text{Cl}_{3-n}}{\underset{(\text{CH}_3)_{n-1}}{(\text{H}_2\text{N–Al})_x}} \xrightarrow[n=2,3]{} \overset{\text{Cl(CH}_3)}{\underset{\text{H}}{\text{–(N–Al)–}_x}} + x\text{CH}_4 \qquad (7)$$

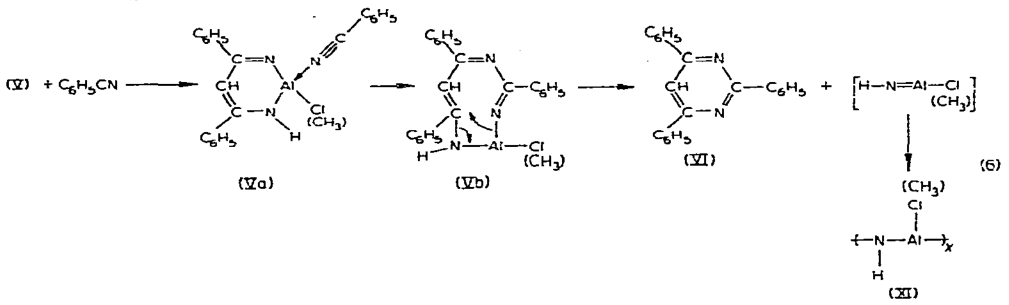
(X) (XI)

and the resulting compounds (XI) are presumably oligomers[8].

Reaction (4) proceeds most easily with compound (III) ($n = 1$). In addition to reaction (4) with benzonitrile, compounds (III) ($n = 2$ and 3) which still have methyl groups attached to the aluminium atom, undergo reaction (5) to eliminate methane and to yield (V).

Compounds (V) are insoluble in benzene, and for this reason may exist as dimers. Compounds (V) (with the Al atom attached to Cl or CH_3) react to yield (VI) (Scheme 4).

SCHEME 4



Reaction (6) involves addition of the N–Al bond to the nitrile group and cyclization of the intermediate product to (VI). With (V)(Cl), the yield of reaction (6) is higher than with (V)(CH_3).

All reactions in which the N–Al bond adds to the nitrile group of benzonitrile, *viz.*, reactions (3), (4), and (6), proceed more readily the greater the number of Cl atoms attached to the Al atom, *i.e.* as the ability of the Al atom to accept electrons increases. The same trend has been described[9] for reactions of aluminium amide compounds with benzonitrile.

Recently reactions of aluminium chloride propiophenimine derivatives, $C_6H_5(C_2H_5)C{=}N{-}AlCl_{3-n}(C_2H_5)_{n-1}$ ($n=1,2$), with nitriles, *e.g.* benzonitrile[10], have been reported. Two mechanisms have been suggested to explain reactions proceeding between benzonitrile and compounds similar in structure to (III) and (V). One mechanism involves addition of the N–Al bond to the nitrile group and subsequent cyclization to yield a pyrimidine group; the other suggests a Diels–Alder addition. The present data appears to favour the former mechanism.

EXPERIMENTAL

Materials

Methylaluminium dichloride and dimethylaluminium chloride were prepared from methylaluminium sesquichloride by conventional methods. Trimethylaluminium was prepared from dimethylaluminium chloride[11]. Aluminium trichloride was purified by sublimation. Benzonitrile and organic solvents were dried and distilled in a nitrogen atmosphere.

Procedure

Reactions were carried out in a nitrogen atmosphere in a 150 ml three-necked flask equipped with a stirrer and connected to a cold trap and, through a liquid seal, to a gas burette. The methylaluminium compound, 3–15 g, was placed in the flask and benzonitrile added with simultaneous mixing and cooling, whereupon the mixture was heated. The methane evolved was collected in the burette. After the reaction had been allowed to proceed to completion, the mixture was cooled and first benzene and then aqueous 12% hydrochloric acid added. The acid was added until the evolution of methane ceased (the basic aluminium oxides formed on hydrolysis remaining undissolved) or until no basic aluminium oxides remained undissolved. Upon hydrolysis the sediment was filtered and washed with benzene, and the resulting aqueous and organic phases separated. The aqueous phase was extracted with benzene and the extract combined with the organic phase. The combined phases were washed with aqueous sodium bicarbonate and dried.

Identification and determination of products

Methane was identified by gas chromatography and determined volumetrically through the use of a gas burette.

Acetophenone was identified as the 2,4-dinitrophenylhydrazone, m.p. 242–243°, and determined gravimetrically as the hydrazone from an aliquot of the benzene solution of the hydrolysed reaction mixture. The technique used has been described earlier[1], a correction being employed to allow for the co-precipitation of some 2,4,6-triphenylpyrimidine together with the hydrazone.

2,4,6-*Triphenylpyrimidine* (*VI*), m.p. (EtOH) 184–186° (lit.[62] m.p. 185–186°) was analyzed by NMR spectroscopy, the compound producing one singlet at τ 2.04 and three multiplets at τ 1.32, 1.77, and 2.45 with an intensity ratio 1/2/4/9 (a similar spectrum[12] has been reported). (Found: C, 85.80; H, 5.25; N, 8.95. $C_{22}H_{16}N_2$ calc.: C, 85.69; H, 5.23; N, 9.09%.) The pyrimidine dissolves in concentrated sulphuric acid and may be precipitated through dilution with water (m.p. 182–184°). It was determined gravimetrically from aliquots of the benzene solution of the hydrolyzed reaction mixture.

3.5-Diphenyl-2-pyrazoline hydrochloride (VIIIa), m.p. (EtOH) 218–220° (dec.) (lit.[13] m.p. 219–221° or [14] 205°) was analyzed by NMR spectroscopy the benzene ring protons giving two multiplets at τ 2.04 and 2.50 at a ratio of 1/4. (Found: C, 69.79; H, 5.98; N, 10.71. $C_{15}H_{15}N_2Cl$ calcd.: C, 69.39; H, 6.20; N, 11.17%.) When stored in air, compound (VIIIa) was oxidized (m.p. and NMR spectrum were measured on a partially oxidized compound). When treated with aqueous sodium hydroxide, the compound gave 3,5-diphenyl-2-pyrazoline, m.p. 85° (lit.[13] m.p. 88°), which on treatment with aqueous hydrochloric acid reverted to (VIIIa). When (VIIIa) was heated with aqueous 20% sodium hydroxide acetophenone (VII) and benzoic acid (as the sodium salt) were obtained. When treated with cold concentrated sulphuric acid or with hot concentrated hydrochloric acid, (VIIIa) gave dibenzoylmethane (IX) (precipitating on dilution of the mixture with water). (VIIIa) was determined gravimetrically as the sediment remaining in the hydrolysed solution obtained when the basic aluminium oxides were dissolved in hydrochloric acid.

Tris(1,3-diphenyl-1,3-propanedionato)aluminium (VIIIb) had a m.p. (EtOH) 279–284° (lit.[15] m.p. >270°). Its NMR spectrum consisted of one singlet at τ 3.13 and two multiplets at τ 2.03 and 2.57 in the ratio 1/4/6 (a similar chemical shift and a singlet at τ 3.09 have been reported[16] for a heterocyclic ring proton). (Found: C, 77.30; H, 5.02; Al, 3.80. $C_{45}H_{33}O_6Al$ calcd.: C, 77.57; H, 4.77; Al, 3.86%.) Compound (VIIIb) hydrolyzed in concentrated sulphuric acid to yield (IX) which precipitated on dilution of the mixture. On heating with aquous 20% sodium hydroxide, (VIIIb) gave (VII) and benzoic acid (as the sodium salt). (VIIIb) was determined gravimetrically as the residual sediment in the hydrolysed solution obtained when the basic aluminium oxides remained undissolved in hydrochloric acid (a portion of (VIIIb) dissolved in benzene together with other products and was separated from the solution). (VIIIb) was extracted with boiling benzene from the undissolved aluminium oxides.

Triphenyl-s-triazine(IV), m.p. (EtOH) 227–230° (lit.[6] m.p. 229°) had an NMR spectrum consisting of two multiplets at τ 1.35 and 2.51 in the ratio 1.8/3. Its IR spectrum was similar to that reported in the literature[17].

Dibenzoylmethane (1,3-diphenylpropane-1,3-dione) (IX), m.p. (EtOH) 77.3–78.5° exhibited one singlet at τ 3.18 and two multiplets at τ 2.07 and 2.51 in the ratios 1.17/4/6 in its NMR spectrum (chemical shift due to OH (enol) was not measured).

Benzoic acid and *dibenzamide* were recrystallized from water and identified by their m.p., 121.5–122.5° and 145.5–147.5°, respectively.

Aluminium chloride diimine derivative [(V)(Cl)]. Benzonitrile, 11.2 g, was added to 5 g $(CH_3)_2AlCl$ [(I), $n=2$] and the resulting complex (Ia) ($n=2$) was heated 4 h at 170° resulting in the formation of 1152 ml of methane. The mixture was allowed to cool and 60 ml of benzene was added. The undissolved products were filtered off, washed with three 10 ml aliquots of benzene and dried *in vacuo* to obtain 5.7 g of a yellowish solid [(V)(Cl)] m.p. ~195–220° (dec.). (Found: Cl, 13.2; Al, 10.3. $C_{15}H_{12}N_2ClAl$ calcd.: Cl, 12.54; Al, 9.54%.) With aqueous 12% hydrochloric acid, (V)(Cl) hydrolyzed to yield (VIIIa) or (VIIIb); with concentrated sulphuric acid, it gave (IX) upon dilution.

NMR studies

All NMR spectra were recorded with *s*-tetrachloroethane solutions on a JEOL JNM C-60H spectrometer with TMS as an internal standard.

REFERENCES

1 S. Pasynkiewicz, W. Kuran and E. Soszyńska, *Rocz. Chem.*, 38 (1964) 1285.
2 S. Pasynkiewicz and W. Kuran, *Rocz. Chem.*, 39 (1965) 979, 1199.
3 G. E. Coates and D. Ridley, *J. Chem. Soc. A*, (1966) 1064.
4 J. Pattison and K. Wade, *J. Chem. Soc. A*, (1968) 57.
5 J. R. Jennings and K. Wade, *J. Chem. Soc. A*, (1967) 1222.
6 H. Tada, K. Yasudo and R. Okawara, *J. Organometal. Chem.*, 16 (1969) 215.
7 J. D. Citron and E. J. Becker, *Can. J. Chem.*, 41 (1963) 1260.
8 M. Cohen, J. K. Gilbert and J. D. Smith, *J. Chem. Soc.*, (1965) 1092.
9 H. Hoberg and J. Barluenga Mur, *Justus Liebigs Ann. Chem.*, 733 (1970) 131; *J. Organometal. Chem.*, 17 (1969) P30.
10 H. Hoberg and J. Barluenga Mur, *Synthesis*, (1970) 142, 363.
11 S. Pasynkiewicz and M. Boleslawski, *J. Organometal. Chem.*, 25 (1970) 29.
12 T. Bacchetti, T. Salvatori and N. Palladino, *Chim. Ind. (Milan)*, 46 (1964) 1337.
13 N. Kishner, *J. Russ. Phys.-Chem. Ges.*, 47 (1915) 1102; *Chem. Zentr.*, (1916) I 1063.
14 J. L. Aubagnac, P. Bouchet, J. Elguero, R. Jacquier and C. Marzin, *J. Chim. Phys.*, 64 (1967) 1649.
15 H. Kaneyuki, *Bull. Chem. Soc. Jap.*, 35 (1962) 519.
16 J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, (1966) 1749.
17 V. A. Kabanov, V. P. Zubov, V. P. Kovaleva and V. A. Kargin, *J. Polym. Sci., Part C*, 4 (1964) 1009.