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REACTIONS OF TRIMETHYL- AND TRIETHYLALUMINIUM WITH 2,4,6-TRI-t-BUTYLNITROSOBENZENE

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Summary

Me_3Al and Et_3Al undergo 1,2-, 1,4- and 1,6-addition to 2,4,6-tri-t-butylnitrosobenzene to give after hydrolysis the corresponding nitrones and oximes. In systems containing Et_3Al the addition products partly undergo further reduction to aromatic amines bearing an ethyl group on the nitrogen atom or the ring. Reduction processes, leading to 2,4,6-tri-t-butylaniline, take place along with the addition reactions.

Introduction

A number of reactions are known in which the aluminium–carbon bond undergoes homolytic cleavage as a result of a single electron transfer to strong organic electron acceptors such as quinones [1–3], tetracyanoolefins [4] or aromatic ketones [5,6]. The radicals formed in these systems can react in a cage or dissociate to give reactive alkyl radicals and long living paramagnetic species which have been characterized by means of ESR spectroscopy. The ESR spectra have also been reported for the product of the reaction of alkylaluminium compounds with some nitroso [7,8] and nitro compounds [9]. However, the origin of these radicals is often uncertain, and it is possible that side processes are responsible for their formation [8,9]. The main reaction pathways are well understood only for some systems comprising α-chloronitroso compounds and aluminium trialkyls [8]. In the reactions of aromatic nitroso or nitro compounds with organoaluminium compounds, however, the formation of a mixture of many reduction products was usually observed, which precluded studies of the mechanism of the processes.

We describe here a study of the products of the reaction between organoaluminium compounds and 2,4,6-tri-t-butylnitrosobenzene. It has been possible to confirm for the first time some intermediate steps of the reduction of aromatic nitroso compounds by organometallic reagents.

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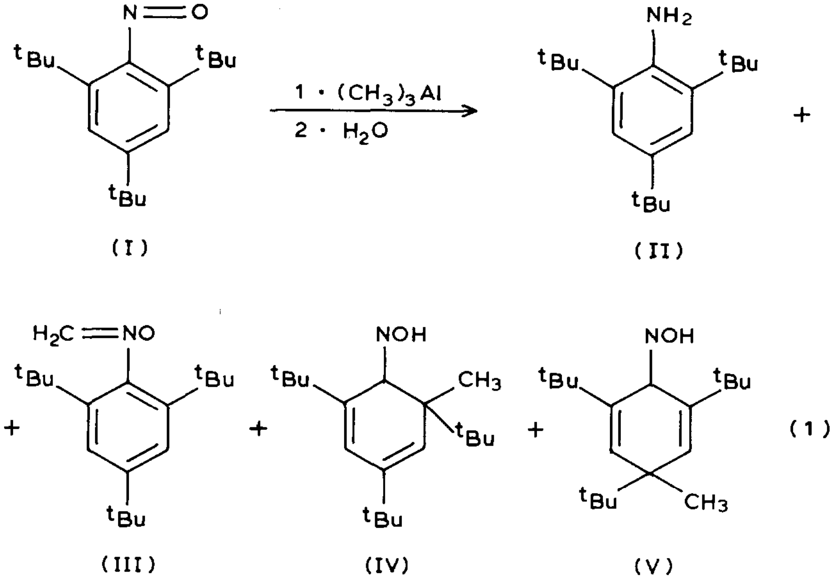
Results and discussion

2,4,6-Tri-t-butylnitrosobenzene (I) reacts with Me_3Al at room temperature in toluene to give a deep brown mixture. When the reactions are carried out with an excess of Me_3Al evolution of methane and ethane (mol ratio 94/6) is observed. After hydrolysis, 2,4,6-tri-t-butylaniline (II), methylene-*N*-2,4,6-tri-t-butylbenzene nitrone (III), 2,4,6-tri-t-butyl-2-methyl-2,4-cyclohexadiene oxime (IV) and 2,4,6-tri-t-butyl-4-methyl-2,5-cyclohexadiene oxime (V) are the main products (eq. 1, Table 1).



In the reactions of I with Et_3Al the dark-brown colour of the reaction mixture turns to yellow with time. The evolution of gaseous products containing mainly ethylene and ethane (mol ratio 70/29) and traces of n-butane and isobutene is observed irrespective of the mole ratio of reactants. Analogous products as in the reactions with Me_3Al are formed after hydrolysis, i.e. amine II, nitrone VI and oximes VII and VIII. Considerable amounts of *N*-ethyl-2,4,6-tri-t-butylaniline (IX),

TABLE 1

YIELDS OF THE MAIN PRODUCTS OF THE REACTION OF Me_3Al WITH 2,4,6-TRI-t-BUTYLNITROSOBENZENE (I) OBTAINED AFTER HYDROLYSIS [a]

Mol ratio Me_3Al/I	Yield (mol%) [b]			
	II	III	IV	V
0.5	10	9	9	4
2	14	20	15	7
4	20	25	28	18

[a] I 1–5 g; solvent toluene 10–50 cm^3; T −80 up to 25°C; time 2 h. [b] Based on eq. 1; yields determined by ^1H NMR spectroscopy with CH_3NO_2 as internal standard.

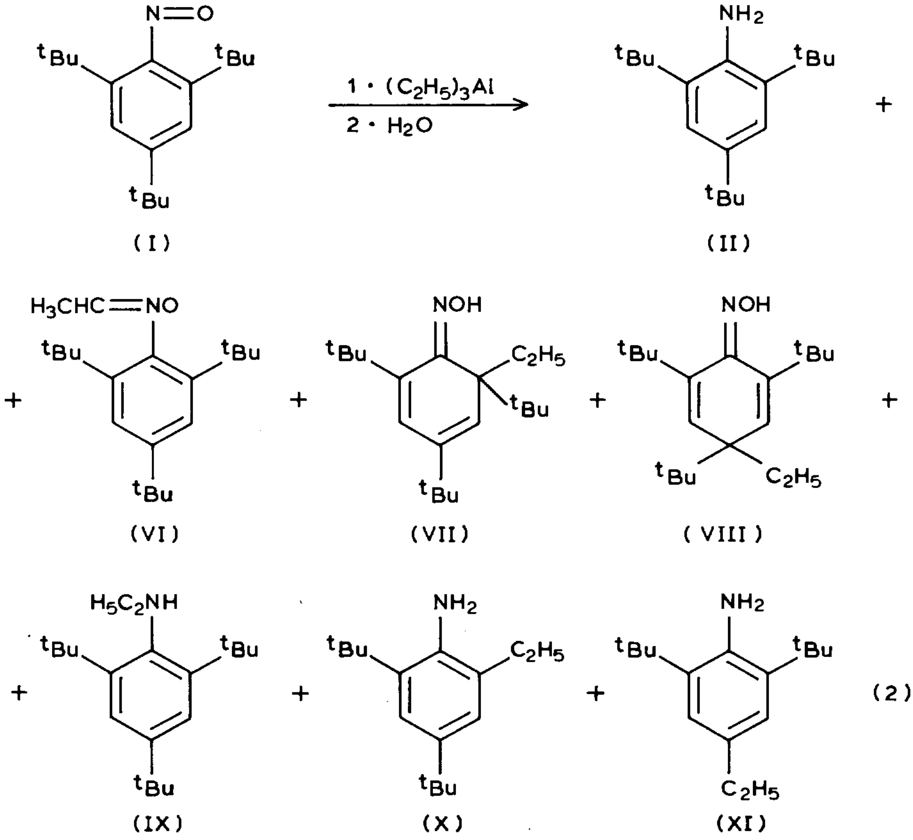
TABLE 2

YIELDS OF THE MAIN PRODUCTS OF THE REACTION OF Et_3Al WITH 2,4,6-TRI-t-BUTYLNITROSOBENZENE (I) OBTAINED AFTER HYDROLYSIS [a]

Mol ratio Et_3Al/I	Yield (mol%) [b]					
	II	VI	VII	VIII	IX	X+XI
0.5	15	3	7	9	9	11
1	20	11	7	10	11	15
2	29	4	5	12	12	19
4	46	0	0	0	12	36
2 [c]	13	5	20	20	10	6

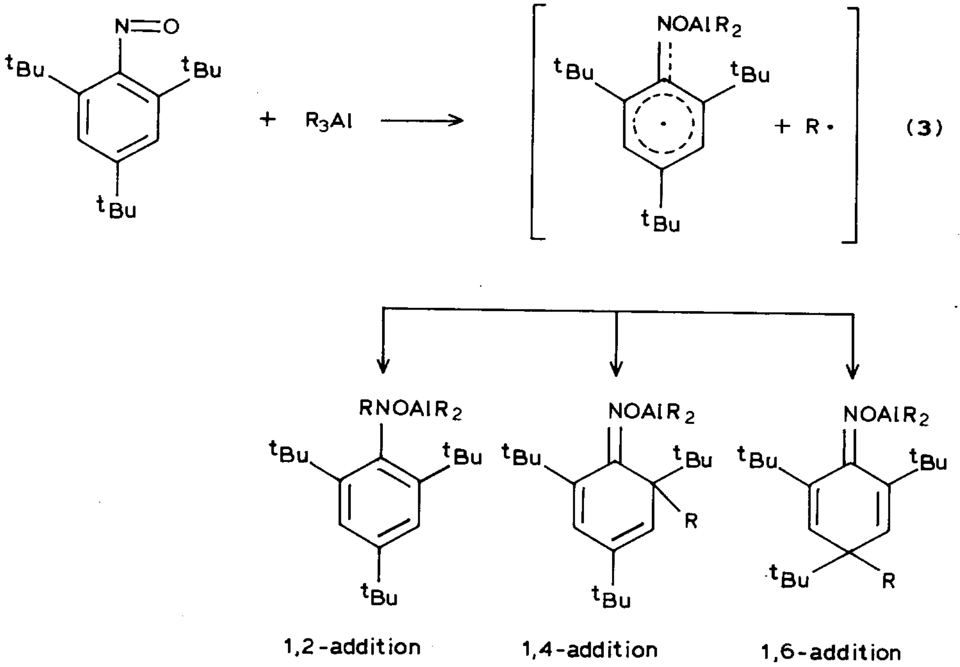
[a] I 1–5 g; solvent toluene 10–50 cm^3; T −80 up to 25°C; time 2 h. [b] Based on eq. 4; yields were determined by ^1H NMR spectroscopy with CH_3NO_2 as internal standard. [c] Et_3Al was complexed by ethyl acetate and the reaction was carried out in 1/1 toluene ethyl acetate.

2,4,6-di-t-butyl-6-ethylaniline (X) and 2,6-di-t-butyl-4-ethylaniline (XI) are also formed (eq. 2, Table 2).



(2)

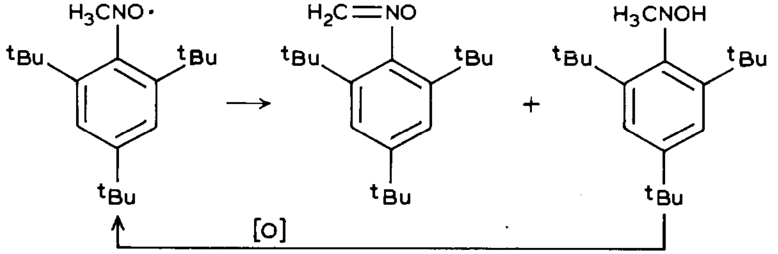
The formation of nitrones and oximes indicates the course of 1,2-, 1,4- and 1,6-addition. In reactions of organometallic compounds with strong organic π-acceptors such additions are often the result of a single electron transfer and recombination within a cage of the paramagnetic products, as e.g. in eq. 3.



However, there is no evidence which would enable us to exclude the polar mechanism of addition (e.g. concerted 1,2-addition and further isomerization) in the systems studied.

After the hydrolysis of the 1,2-addition products, *N*-alkylhydroxylamines should be formed, but these compounds are not stable, and are known to undergo oxidation to nitroxide radicals. A rapid increase in the concentration of nitroxides was observed during the hydrolysis when the reactions were carried out in the cavity of an ESR spectrometer.

The nitroxide radicals disproportionate to yield a nitrone as a stable product, and *N*-alkylhydroxylamine, which is again oxidized [12].

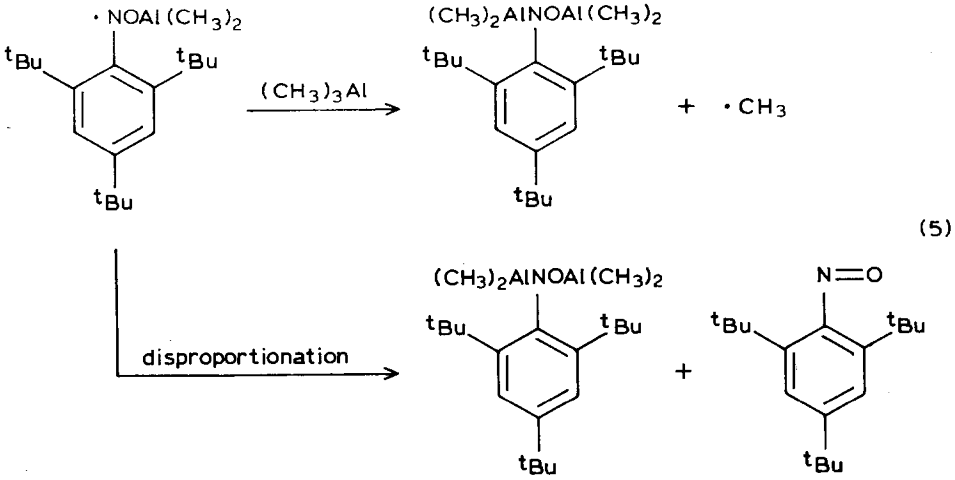


(4)

In reactions involving participation of Et_3Al a significant proportion of the product of the 1,2-addition undergoes further reduction to amine IX. In systems with Me_3Al such reduction occurs only to a small extent, and only traces of *N*-methyl-2,4,6-tri-t-butylaniline are formed after hydrolysis.

It was found that the reaction of oxime VIII with Et_3Al in toluene at room temperature gave amine XI and isobutene oligomers after hydrolysis (during the reaction ethane and trace amounts of ethylene and n-butane were evolved). Thus, it is very probable that under the influence of an excess of Et_3Al the 1,4- and 1,6-addition products undergo further reactions to give amines X and XI. This is indicated by a high yield of oximes in the reactions in which Et_3Al is complexed by ethyl acetate, and a systematic decrease of the yield of oximes in comparison to those of amines X and XI with an increase in the Et_3Al/I ratio (Table 2).

The reduction reactions, of which amines II are the final products, compete with the addition reactions. In the reactions with Me_3Al the first step of reduction to a hydroxylamine derivative is probably the result of diffusion from the cage of the radicals formed in reaction 3 and further reactions of the aniline-type radical.



(5)

In systems with Et_3Al the hydrogen transfer from the carbon of the ethyl group plays an essential role in the reduction, as indicated by the formation of a considerable excess of ethylene over ethane in the gaseous products as well as by the presence of signals of protons bonded to nitrogen ($\delta - 3.62$ ppm) in ^1H NMR spectra of the product mixture before hydrolysis.

The alkyl radicals which diffuse from the cage or are formed from the homolytic substitution (eq. 5) by reaction with I, give nitroxide radicals, the spectra of which have been described earlier [7]. Formation of nitroxide radicals is not observed when a large excess of the organoaluminium compound is used, and the alkyl radicals form the corresponding hydrocarbons.

In previous studies of the reaction of aromatic nitroso and nitro compounds with organoaluminium compounds [9–11], only products of complete reduction were isolated, mainly mixtures of amines substituted at the nitrogen atom or in the ring. In view of the results now obtained it can be presumed that these reactions proceed via the corresponding hydroxylamine and oxime derivatives. Studies on the mechanism of the further reduction of these derivatives are being carried out.

Experimental

Materials

Organoaluminium compounds (commercial grade) were purified by distillation. 2,4,6-Tri-t-butylnitrosobenzene was obtained by a published method [13]. Toluene and ethyl acetate were dried and purified by distillation under nitrogen.

Procedure

All reactions were carried out under nitrogen in a glass vessel equipped with a stirrer and connected through a liquid seal to a gas burette. 2,4,6-Tri-t-butylnitrosobenzene (5–15 mmol) was dissolved in an appropriate solvent in the reaction vessel. The solution of organoaluminium compound in toluene or ethyl acetate was then added dropwise at −78°C with vigorous stirring and the temperature was then slowly raised up to 25°C. When the reaction was complete, the mixture was treated with water, and the organic layer was concentrated and its ^1H NMR spectrum used to determine the yields of the products. The samples of pure products were isolated by column chromatography using silica gel and hexane, hexane/methylene chloride, and methylene chloride as eluents. They were crystallized from methanol or a methanol/water mixture. In some experiments, before the chromatography, the amines II, XII and XIII were removed by treatments with gaseous HCl.

Identification of products

Amines

2,4,6-Tri-t-butylaniline (II). M.p. 142–145°C (lit. [14] 147–148°C). Anal. Found: C, 82.73; H, 12.04; N, 5.30. $C_{18}H_{31}N$ calcd.: C, 82.75; H, 11.87; N, 5.36%. ^1H NMR (CCl_4): δ(($CH_3)_3C$) 1.21(s), 1.42(s); NH_2 3.69; $H_{aromatic}$ 6.98(s) ppm.

N-Methyl-2,4,6-tri-t-butylaniline. M.p. (CH_3OH/H_2O) 102–110°C (lit. [12] 111–112°C). Anal. Found: C, 82.30; H, 12.02; N, 4.80. $C_{19}H_{33}N$ calcd.: C, 82.84; H, 12.07; N, 5.08%. ^1H NMR (CCl_4) δ(($CH_3)_3C$) 1.23(s), 1.43(s); NCH_3 2.60(s); $H_{aromatic}$ 7.07(s) ppm. Molecular weight (MS) 275.

N-Ethyl-2,4,6-tri-t-butylaniline (IX). M.p. 73–76°C. Anal. Found: C, 82.28; H, 12.21; N, 5.07. $C_{20}H_{35}N$ calcd.: C, 82.97; H, 12.19; N, 4.84%. ^1H NMR (CCl_4): δ(CH_3(CH_2)) 1.15, $C(CH_3)_3$ 1.25, 1.42, NCH_2 2.72, $H_{aromatic}$ 7.11 ppm.

2,4-Di-t-butyl-6-ethylaniline (X). M.p. (CH_3OH/H_2O) 39–41°C. Anal. Found: C, 82.46; H, 11.66; N, 5.36. $C_{16}H_{27}N$ calcd.: C, 82.40; H, 11.58; N, 6.0%. ^1H NMR (CCl_4): δ(CH_3(CH_2)) 1.18(t), $(CH_3)_3C$ 1.26(s), 1.38(s), CH_2 2.44 (q), NH_2 3.52, $H_{aromatic}$ 6.94(d), 7.12(d) ppm.

2,6-Di-t-butyl-4-ethylaniline (XI). M.p. 94–95°C. Anal. Found: C, 82.47; H, 11.60; N, 5.84. $C_{16}H_{27}N$ calcd.: C, 82.40; H, 11.58; N, 6.00%. ^1H NMR (CCl_4): δ(CH_3(CH_2)) 1.13(t), $(CH_3)_3C$ 1.40(s), CH_2 2.44 (q), NH_2 3.79, $H_{aromatic}$ 6.81(s) ppm.

Oximes

2,4,6-Tri-t-butyl-2-methyl-2,4-cyclohexadiene oxime (IV). M.p. 161–162°C. Anal. Found: C, 78.24; H, 11.66; N, 4.70. $C_{19}H_{33}NO$ calcd.: C, 78.29; H, 11.41; N, 4.81%. ^1H NMR (CCl_4) δ(CH_3) 1.06, $(CH_3)_3C$ 0.95, 1.07, 1.30, CH= 5.29(d), 6.02(d), NOH 10.01 ppm. IR (KBr): ν(O-H) 3270, C=C 1640, 1620, C=N 1473 cm^{-1}.

2,4,6-Tri-t-butyl-4-methyl-2,5-cyclohexadiene oxime (V). M.p. 118–119°C. Anal. Found: C, 78.32; H, 11.61; N, 4.81. $C_{19}H_{33}NO$ calcd.: C, 78.29; H, 11.41; N, 4.81%. ^1H NMR (CCl_4) δ(CH_3) 1.06, $(CH_3)_3C$ 0.83, 1.19, 1.21, CH= 5.73(d), 5.84(d), NOH 7.70 ppm.

2,4,6-Tri-t-butyl-2-ethyl-2,4-cyclohexadiene oxime (VII). M.p. 137–139°C. Anal. Found: C, 78.57; H, 11.77; N, 4.50. $C_{20}H_{35}NO$ calcd.: C, 78.63; H, 11.54; N, 4.50%.

^{1}H NMR (CCl_4) δ $CH_3(CH_2)$ 0.71, $(CH_3)_3C$ 0.88, 1.06, 1.25, CH_2 1.54, CH= 5.32(d), 6.30(d), NOH 10.22 ppm.

2,4,6-Tri-t-butyl-4-ethyl-2,5-cyclohexadiene oxime (VIII). M.p. 117–118°C. Anal. Found: C, 78.42; H, 11.63; N, 4.53. $C_{20}H_{35}NO$ calcd.: C, 78.63; H, 11.54; N, 4.53%. ^{1}H NMR (CCl_4) δ $CH_3(CH_2)$ 0.65, $(CH_3)_3C$ 0.83, 1.20, 1.23, CH_2 1.62, CH= 5.62(d), 5.74(d), NOH 8.59 ppm.

Nitrones

Methylene-N-2,4,6-tri-t-butylbenzene nitrone (III). M.p. 193–196°C (lit. [12] 194–195°C). Anal. Found: C, 78.87; H, 11.13; N, 4.35. $C_{19}H_{31}NO$ calcd.: C, 78.83; H, 10.79; N, 4.83%. ^{1}H NMR (CCl_4): $\delta(CH_3)_3C$ 1.23, 1.42, CH_2= 6.86, 6.80, 6.65, 6.56, $H_{aromatic}$ 7.36 ppm. MS m/e 289.

Ethylene-N-2,4,6-tri--t-butylbenzene nitrone (VI). M.p. 160–162°C. Anal. Found: C, 78.39; H, 10.90; N, 4.64. $C_{20}H_{33}NO$ calcd.: C, 79.15; H, 10.96; N, 4.61%. ^{1}H NMR (CCl_4) $\delta(CH_3)_3C$ 1.30, 1.39, CH_3(CH=) 1.96(d), CH=N 6.88(q), $H_{aromatic}$ 7.32 ppm.

Gas samples were analyzed by means of GLC.

Acknowledgement

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References

1 Z. Florjańczyk, W. Kuran, S. Pasynkiewicz and J. Kwas, J. Organomet. Chem., 112 (1976) 21; Z. Florjańczyk, W. Kuran, S. Pasynkiewicz and A. Kraśnicka, ibid., 145 (1978) 21; Z. Florjańczyk and E. Szymańska-Zachara, ibid., 259 (1983) 127.
2 G.A. Razuvaev, G.A. Abakumov, E.S. Klimov, E.N. Gladyshev and P.Ya. Bayshkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1128.
3 A. Alberola, A.M. Gonzalez Nogal and R. Pedrosa, An. Quim., 74 (1978) 1147.
4 Z. Florjańczyk and U. Iwaniak, J. Organomet. Chem., 252 (1983) 275.
5 J. Furukawa, K. Omura and K. Ishikawa, Tetrahedron Lett., (1973) 3119.
6 E.C. Ashby and A.B. Goel, J. Organomet. Chem., 221 (1981) C15.
7 Z. Florjańczyk and J. Sitkowska, J. Organomet. Chem., 251 (1983) 1.
8 J. Lub, Thesis, Amsterdam, 1977, chapter 2.
9 Z. Florjańczyk, E. Lusztyk and J. Korenik, Makromol. Chem., 186 (1985) 2268.
10 A. Alberola, A.M. Gonzales Nogal and R. Pedrosa, An. Quim., 74 (1978) 1104; 74 (1978) 1108.
11 Z. Florjańczyk, Homolytical reactions of alkylaluminium compounds, Warsaw Technical University Publications, Chemistry 32 (1984).
12 J. Martinie-Hombrouck and A. Rassat, Tetrahedron, 30 (1974) 433.
13 R. Okazaki, T. Hosogai, E. Iwadare, M. Hasimoto and M. Inamoto, Bull. Chem. Soc. Japan, 42 (1969) 3611.
14 J. Burgess, M.A. Hoefnagel, P.E. Verkade, H. Visser and B.M. Wepster, Rec. Trav. Chim., 77 (1958) 491.