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REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH TETRACYANOETHYLENE AND 7,7,8,8-TETRACYANOQUINODIMETHANE

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Summary

Alkylaluminium compounds undergo 1,2-addition to the C=C bond in tetracyanoethylene and 1,6-addition to the conjugated unsaturated carbon–carbon bond system in 7,7,8,8-tetracyanoquinodimethane. The relative activities of various organoaluminium compounds, the effects of complexing agents, and ESR observations indicate that the organoaluminium compound acts as a single electron donor towards the tetracyanoolefin.

Introduction

The addition of organoaluminium compounds to unsaturated bonds in organic substrates is usually discussed in terms of a polar mechanism involving a four or six centre transition state. There are only a few examples of reactions for which a radical mechanism of addition has been proposed. An uncatalyzed radical addition was observed in reactions of various alkylaluminium compounds with quinones [1,2] and of Me_3Al with dimesityl ketone and mesityl phenyl ketone [3]. The 1,4- and 1,6-addition of $EtAlCl_2$ to benzophenone and acetophenone [4] as well as the 1,4-addition of i-Pr_3Al to unsaturated ketones [5] were induced by UV radiation or traces of oxygen. All those carbonyl compounds contain a conjugated system of unsaturated bonds and their LUMO energy is relatively low. This energy is further lowered when the carbonyl groups are complexed by the organoaluminium compounds in the first step of the reaction. Because of this, a single electron transfer (SET) from the organoaluminium compound to the organic part of the complex can occur, and homolytic cleavage of the Al–C bond may compete with the polar reaction.

It could be expected that the SET process would proceed especially readily in

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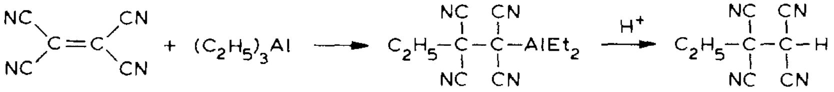
reactions with polycyanoolefins, which exhibit much stronger electron acceptor properties than ketones and most quinones. The purpose of this work was to investigate the reaction of alkylaluminium compounds with tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ = 2,2(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile)). The results obtained provide the first example of a reaction in which the organoaluminium compound does not attack the polar groups but adds to the carbon–carbon bonds solely as a result of a SET.

Results and discussion

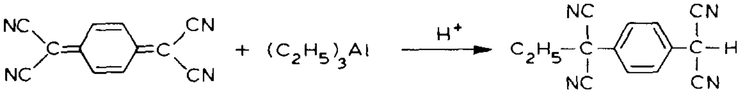
Et_3Al reacts with TCNE at −78°C in toluene or polar solvents to give a highly coloured mixture, which after acidification affords 1,1,2,2-tetracyanobutane in high yield (Table 1). The formation of that product indicates that 1,2-addition to the C=C bond occurs.



(1)

When an excess of TCNE is used, more than one Al–C bond takes part in the addition.

In reaction with TCNQ, Et_3Al undergoes 1,6-addition to the conjugated system of carbon–carbon bonds (Table 2).



(2)

In reactions in toluene $EtAlCl_2$ undergoes 1,2- and 1,6-addition only at higher temperatures (~ 0°C) and with much lower yields than Et_3Al. Complexation of the

TABLE 1

YIELD OF 1,2-ADDITION OF ORGANOALUMINIUM COMPOUNDS TO TCNE [a]

Organoaluminium compound	Molar ratio organoaluminium compound/TCNE	Solvent	Temp. (°C)	Yield [b] (%)
Me_3Al	1	THF	−78	64
Et_3Al	1	THF	−78	76
$EtAlCl_2$	1	THF	−78	60
$EtAlCl_3^-[C_2H_5(N)CH_3]_3^+$	1	THF	−78	82
i-Bu_3Al	1	THF	−78	70
i-Bu_2AlH	1	THF	−78	42
Et_3Al	1/2	THF	−78	143
Et_3Al	1/3	THF	−78	199
Et_3Al	1	THF	25	0
Et_3Al	1	Pyridine	−40	55
Et_3Al	1	Acrylonitrile	−78	65
Et_3Al	1	Toluene	−78	65
$EtAlCl_2$	1	Toluene	−78	0
$EtAlCl_2$	1	Toluene	0	36

[a] TCNE 1 g; solvent 100 cm^3; time 4 h. [b] Calculated to 1 mol of the organoaluminium compound.

TABLE 2

YIELD OF 1,6-ADDITION OF ORGANOALUMINIUM COMPOUNDS TO TCNQ[a]

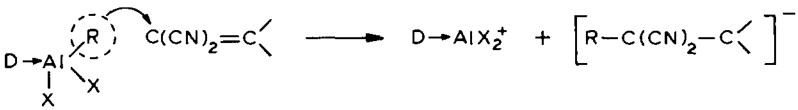
Organoaluminium compound	Solvent	Temp. (°C)	Yield (%)
Et_3Al	Toluene	−78	78
$EtAlCl_2$	Toluene	−78	traces
$EtAlCl_2$	Toluene	0	11
$EtAlCl_2$	THF	−78	74
Me_3Al	Toluene	−78	traces
Me_3Al	Toluene	0	67
Me_3Al	THF	−78	30

[a] Molar ratio organometallic compound/TCNQ = 1; saturated solutions of TCNQ (~ 5%); time 4 h.

$EtAlCl_2$ by a polar solvent or quaternary ammonium salt causes a marked increase in the yield. The greater activity of Et_3Al than of $EtAlCl_2$ and the increased activity of $EtAlCl_2$ after complexation shows that the addition occurs more easily the greater the electron density in the Al–C bond. The 1,6-addition cannot occur by the concerted mechanism because the distance between the C(7) and C(8) atoms in TCNQ is too great. This mechanism is also very unlikely in reactions of TCNE, since the approach of an olefin to the aluminium atom is blocked by strong Lewis bases. Furthermore, in concerted addition reactions the nitrile groups are markedly more reactive than the C=C bonds [6].

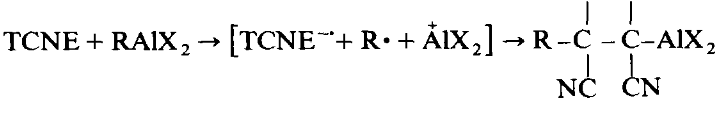
Insertion of TCNE into various metal–carbon bonds has already been studied [7,9,13]. The two principal mechanisms involve TCNE behaving either as an electrophile or as a single electron acceptor. Electrophilic cleavage of a metal–carbon bond is a common mechanistic pathway proposed for the insertion into some transition metal alkyls [7]; it is assumed that the olefinic carbons of TCNE attack the metal atom in the initial reaction step. Electrostatic molecular potential analysis of electron density distribution in aluminium compounds and their complexes [8] shows that the electrophile can react only with substituents attached to aluminium. Thus a hypothetic polar addition of organoaluminium compounds to tetracyanoolefins can be schematically represented in the following way:

(3)



(4)

The set process followed by recombination in cage was proposed for the reactions of TCNE with alkyl-lead, -tin and -mercury compounds [9]. An example of such a reaction is shown in eq. 5.



$$TCNE + RAlX_2 \rightarrow [TCNE^{-\cdot} + R\cdot + \overset{+}{A}lX_2] \rightarrow R-\underset{NC}{\overset{NC}{C}}-\underset{CN}{\overset{CN}{C}}-AlX_2 \qquad (5)$$

Various observations indicated that in reactions of organoaluminium compounds the radical mechanism of addition is more probable than the electrophilic one.

Competitive addition reactions with TCNE (Table 3) showed that the reactivity of various alkyl–aluminium bonds decreases in the order Et–Al > i-Bu–Al > Me–Al. Me_3Al is also much less active than Et_3Al in the 1,6-addition reactions (Table 2). The lower activity of methyl compounds than of higher alkylmetals is typical for processes in which SET is postulated [9,10], and can be attributed to the higher ionization potentials of the metal–methyl bonds. Furthermore, we found that in reactions of Me_3Al with TCNQ large quantities of methane (in THF 0.5 mol of CH_4 from one mol of Me_3Al) and TCNQ oligomers are formed along with the adduct. No gas evolution was observed in reactions of ethyl derivatives. This observation cannot easily be explained in terms of an electrophilic mechanism, whereas methyl radicals would be expected to diffuse from the cage more rapidly than ethyl radicals.

A further important feature favouring the radical mechanism of addition is the formation, in reactions of TCNE with diisobutylaluminium hydride, of the product of insertion into the Al–C and not the Al–H bond. In known polar reactions of this hydride the Al–H bond reacts selectively [6], since it is much more polarized than the Al–C bond. On the other hand in homolytic cleavage the Al–C bond should be more active than the Al–H bond, in accord with the lower dissociation energy [10].

Although the ESR spectra by themselves do not indicate the direct involvement of anion radicals in the insertion pathway, it is noteworthy that during the reactions between organoaluminium compound and tetracyanoolefins signals of $TCNE^{\cdot-}$ or $TCNQ^{\cdot-}$ are observed.

As was already mentioned, at low temperature no reactions involving the nitrile group take place. If the reaction of TCNE with alkylaluminium compounds is carried out at temperatures above −40°C, some tarry products containing carbonyl groups are formed after hydrolysis. In the presence of $EtAlCl_2$ at 0°C TCNE also reacts with toluene to give a small amount of 1-methyl-4-tricyanovinylbenzene. This product is formed also when $AlCl_3$ is used as catalyst [12], probably as a result of Friedel–Crafts reactions and then HCN elimination.

The above results indicate the possibility of formation of complexes between organoaluminium compounds and the nitrile groups of TCNE, the generation of addition products, and further reaction of these initial products at progressively higher temperature. However, Raman, IR, UV and ^{13}C NMR spectral studies of TCNE and $AlCl_3$ mixtures did not show any of the typical effects accompanying the

TABLE 3

RELATIVE REACTIVITIES OF ORGANOALUMINIUM COMPOUNDS IN COMPETITIVE ADDITIONS TO TCNE [a]

Organoaluminium compound		Addition to bonds [b] (mol %)		
1	2	Me–Al	Et–Al	i-Bu–Al
Me_3Al	Et_3Al	traces	~ 100	–
Me_3Al	$i\text{-}Bu_3Al$	35	–	65
Et_3Al	$i\text{-}Bu_3Al$	–	90	10

[a] TCNE 0.5 g in 50 cm^3 of solvent; molar ratio organometallic compound 1/organometallic compound 2/TCNE = 1/1/1; solvent THF; temp. −78°C; time 2 h. [b] Based on NMR spectra of crude products.

complexation of nitrile groups, and thus the formation constants of the complexes formed via those groups are probably small.

Experimental

Materials

Organoaluminium compounds were purified by distillation. TCNE was sublimed twice before use. TCNQ (pure) and tetra-n-butylammonium bromide (pure - Fluka) were used without purification. All solvents were dried and purified by known methods.

Procedure

All reactions were carried out under nitrogen in a glass vessel equipped with a stirrer and connected through a liquid seal to a glass burette. The organoaluminium compounds (4–8 mmol) were dissolved in an appropriate solvent in the reaction vessel. The solution of TCNE or TCNQ in the same solvent was then introduced with vigorous stirring. In some reactions $(n\text{-Bu})_4N^+Br^-$ was added to liquid $EtAlCl_2$ and the complex formed was then dissolved. After the reaction was complete trifluoroacetic acid or 1 *M* HCl was added to the cold solution. The solvents were removed under reduced pressure and the residue was extracted with $CHCl_3$ and water. The precipitate insoluble in water or $CHCl_3$ was filtered off, and the organic layer was separated, dried and concentrated to give the products.

Identification and isolation of products

1,1,2,2-Tetracyanopropane, M.p. 105–106°C (lit. [13] 97–98°C). Anal. Found: C, 58.90; H, 2.52; N, 38.56. $C_7H_4N_4$ calcd.: C, 58.33; H, 2.80; N, 38.87%. ^1H NMR (CF_3COOH): $\delta(CH_3)$ 2.13(s); $CH(CN)_2$, 5.20(s) ppm.

1,1,2,2-Tetracyanobutane, M.p. 68–69°C (lit. [13] 63–64°C). Anal. Found: C, 60.31; H, 3.76; N, 35.65. $C_8H_6N_4$ calcd.: C, 60.75; H, 3.82; N, 35.42%. ^1H NMR (CF_3COOH): $\delta(CH_3)$ 1.42(t); CH_2, 2.35(q); $CH(CN)_2$, 4.27(s) ppm.

4-Methyl-1,1,2,2-tetracyanopentane. M.p. 46–48°C. Anal. Found: C, 64.02; H, 5.22; N, 29.99. $C_{10}H_{10}N_4$ calcd.: C, 64.52; H, 5.22; N, 30.10%. ^1H NMR (CF_3COOH): $\delta(CH_3)$ 1.21(d); $CH_2 + CH$, 2.11; $CH(CN)_2$, 4.66(s) ppm.

The IR spectra (KBr) of the above compounds exhibit sharp strong bands at around 2910 and 740 cm^{-1}, which are characteristic for a $CH(CN)_2$ moiety [13]. No band assignable to the nitrile stretching vibrations was observed.

1-(1,1-Dicyanoethyl)-4-(1,1-dicyanomethyl)benzene. M.p. 100–103°C. Anal. Found: C, 70.34; H, 3.86; N, 25.01. $C_{13}H_8N_4$ calcd.: C, 70.91; H, 3.64; N, 25.45%. ^1H NMR (CF_3COOH): $\delta(CH_3)$ 2.11(s); $CH(CN)_2$, 5.12(s); H aromatic 7.75(s) ppm. IR (KBr): $\nu(C{\equiv}N)$ 2243, 2210(sh), ν(CC aromatic) 1503 cm^{-1}.

1-(1,1-Dicyanomethyl)-4-(1,1-dicyanopropyl)benzene. M.p. 119–121°C. Anal. Found: C, 71.48; H, 4.47; N, 23.47. $C_{14}H_{10}N_4$ calcd.: C, 71.79; H, 4.27; N, 23.93%. ^1H NMR: $\delta(CH_3)$ 1.30(t); CH_2, 2.42(q); $CH(CN)_2$, 5.57(s); H aromatic, 7.82(s) ppm. IR (KBr): $\nu(C{\equiv}N)$ 2240, 2210(sh), ν(CC aromatic) 1497 cm^{-1}.

The compounds listed were isolated by crystallization of the organic residues from $CHCl_3$/hexane (or pentane) mixtures. Analytic samples were crystallized twice.

1-Methyl-4-tricyanovinylbenzene. M.p. 117–118°C (lit. [12] 115–117°C). Anal.

Found: C, 74.41; H, 3.83; N, 21.74. $C_{12}H_7N_3$ calcd.: C, 74.61; H, 3.63; N, 21.76%. ^{1}H NMR (CF_3COOH): $\delta(CH_3)$ 2.20(s); H aromatic, ~ 6.5 ppm (doublet of doublets). IR (KBr): $\nu(C{\equiv}N)$ 2249, ν(CC aromatic and olefinic) 1570, 1540, 1510 cm^{-1}. Molecular weight (MS) = 193. The compound was isolated by column chromatography (Al_2O_3 acidic, benzene) from a tar formed from reactions of $EtAlCl_2$ with TCNE at 0°C and recrystallized from a $CHCl_3$/hexane mixture.

Tars, when formed in reactions of TCNE, contained from 5–23% of oxygen (by elemental analysis). Their IR spectra exhibit strong carbonyl stretching vibration bands in the region 1650–1680 cm^{-1}. TCNQ oligomers. Fraction soluble in boiling benzene. M.p. ~ 290°C (dec.). Anal. Found: C, 70.48; H, 2.41; N, 27.09. $C_{12}H_4N_4$ calcd.: C, 70.58; H, 1.96; N, 27.45%. ^{1}H NMR (CF_3COOH): δ(H) aromatic, 7.29, 7.68(s) ppm. Fraction insoluble in boiling benzene. M.p. ~ 310°C (dec.). Anal. Found: C, 70.60; H, 2.76; N, 26.49%. ^{1}H NMR (CF_3COOH): δ(H) aromatic, 7.70(s) ppm. IR (KBr): $\nu(C{\equiv}N)$ 2210, ν(CC aromatic) 1527 cm^{-1}. The oligomers precipitate out during the reactions and are insoluble in $CHCl_3$.

Spectroscopy

The ESR spectra were recorded on a JEOL JES MR-3X spectrometer. The toluene or THF solutions of organoaluminium compounds were introduced at −80°C into a Suprasil silica tube containing TCNE or TCNQ in the same solvent. The signals were rather weak and poorly resolved in toluene, whereas clear spectra of the anion radicals are observed in THF, and their parameters are very close to those reported in the literature for $\text{TCNE}^{\overline{\cdot}}$ [14] and $\text{TCNQ}^{\overline{\cdot}}$ [15].

IR, ^{1}H NMR, ^{13}C NMR and UV spectra were recorded on Zeiss UR, Varian NV-14, Varian NFF-20 and Specord UV-VIS spectrometers, respectively.

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