Addition of α,α-dichloropropionitrile to unsaturated compounds under conditions of metallocomplex initiation

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α,α-Dichloropropionitrile reacts with unsaturated compounds in the presence of complex initiating systems based on metal carbonyls. The systems based on iron pentacarbonyl are the most efficient.

Key words: dichloropropionitrile, metal carbonyls, iron pentacarbonyl.

Polyfunctional compounds including nitrile and CHCl or CCl_2 groups are promising synthons for synthesizing nitrogen-containing heterocycles.[1] At the same time, there are only a few examples of metallocomplex initiation of addition reactions involving CCl_2 groups.[2]

To study the possibilities of using both metallocomplex initiators and compounds containing the CCl_2 group in synthesis, the addition of α,α-dichloropropionitrile to unsaturated compounds in the presence of metal carbonyls (MC) or systems based on MC is studied in this work.

$$\underset{\mathbf{1}}{MeCCl_2CN} + \underset{\mathbf{2a-c}}{CH_2{=}CXR} \xrightarrow{MC} \underset{\mathbf{3a-c}}{RCXClCH_2C(Me)ClCN}$$

a: X = H, R = $SiMe_3$; **b**: X = H, R = Bu;
c: X = Cl, R = Me

Trimethylvinylsilane (**2a**), 1-hexene (**2b**), and 2-chloropropene (**2c**) were used as monomers.

The initiating abilities of iron, chromium, molybdenum, and tungsten carbonyls and $Fe(CO)_5$+cocatalyst (MeCN, Pr^iOH, Ph_3P) systems are compared in this work.

For this purpose the reaction between **1** and **2a**, which results in the formation of adduct **3a** in the form of two diastereomers in a ratio of 49 : 51, is chosen as a reference reaction. Initiators are divided into groups in terms of their activity in this reaction. *tert*-Butyl peroxide (TBP) and Mo, Cr, and W carbonyls are relatively inefficient (the yield of the adduct is 14 to 17 %), and the cocatalyst exerts no effect on the yield.

$Fe(CO)_5$ is the most efficient, and the yield of the adduct is 67 %. The addition of cocatalysts results in an unusual decrease in the yield in this case. In the majority of reactions studied, the efficiency of iron carbonyl increases when it is combined with cocatalyst.[3]

It can be assumed that in this case addend **1** itself plays the role of cocatalyst. Adducts **3b** (40 %) and **3c** (35 %) are obtained in the reaction of **1** with **2b** and **2c** in the presence of iron pentacarbonyl. The structures of all the adducts were confirmed by ^{13}C NMR spectroscopy (Table 1).

Experimental

GLC analysis of reaction mixtures was carried out on an LKhM-8MD chromatograph, a katharometer was used as the detector, and helium was the carrier gas, steel column 2 m×3 mm, 15 % SKTFT on Chromaton N-AW-HMDS (0.16 to 0.20 mm), temperature programmed from 50 to 250 °C (rate 8 °C min^{-1}) was used. A steel column 850 mm×8 mm with 15 % silicone E-301 on Chromaton N-AW (0.20 to 0.25 mm) was used for preparative GLC. ^{13}C NMR spectra were recorded on a Bruker WP-200SY spectrometer, and CCl_4 and $CHCl_3$ were used as references.

Experiments were carried out in glass tubes sealed in an argon atmosphere according to the "freezing—evacuating—thawing out" method.

Initial reagents: **1**, 7.5 mmol; **2a—c**, 5 mmol; MC, 5 to 10 mol. %; cocatalyst, 15 to 30 mol. %; T = 140 °C. Reaction mixtures were analyzed by GLC without preliminary treatment, and the yields of adducts were determined with respect to the internal standards. The following yields of **3a**

Table 1. ^{13}C NMR spectra of compounds **3a—c**

Compound	δ					
	CN	C-1	C-2	C-3	C-4	C-5
3a	118.11; 118.88	29.14; 31.07	56.18	46.15; 47.11	43.08; 44.54	−3.95
3b	117.94; 118.62	30.37; 31.45	50.63; 51.43	54.08; 54.24	56.73; 57.34	37.96; 38.68
3c	118.03	31.32	52.46	58.96	84.40	37.50

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were obtained in the reaction between **1** and **2a** with the initiators TBP, $Mo(CO)_6$, $W(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$, $Fe(CO)_5+Pr^iOH$, $Fe(CO)_5+MeCN$, and $Fe(CO)_5+Ph_3P$: 8, 14, 17, 15, 67, 57, 48, and 31 %, respectively. To isolate individual compounds, reaction mixtures of several similar experiments were united, unreacted initial compounds were distilled off, and adducts were isolated from the residue by GLC: (1,3-dichloro-3-cyanobutyl)trimethylsilane (**3a**), 2,4-dichloro-2-cyanooctane (**3b**), and 2,2,4-trichloro-4-cyanopentane (**3c**), whose structures were confirmed by ^{13}C NMR spectroscopy (see Table 1). Compound **3a** was isolated in pure form: n_D^{20} 1.4690, d_4^{20} = 1.0792 g cm^{-3}. Found (%): C, 42.18; H, 6.80; Cl, 30.82; Si, 12.28. $C_8H_{15}Cl_2NSi$. Calculated (%): C, 42.85; H, 6.74; Cl, 31.63; Si, 12.53.

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References

1. M.-G. A. Shvekhgeimer, K. I. Kobrakov, and S. S. Sychev, *Dokl. Akad. Nauk SSSR*, 1987, **294**, 893 [*Dokl. Chem.*, 1987, **294** (Engl. Transl.)].
2. L. N. Kiseleva and N. A. Rybakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2511 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2323 (Engl. Transl.)].
3. A. A. Kamyshova, V. I. Dostovalova, and E. Ts. Chukovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1174 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1087 (Engl. Transl.)].

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