CATALYTIC ACTIVITY OF CUPRIC OXIDE IN ADDITION REACTIONS OF ALKYL CYANOACETATES WITH 1-ALKENES*

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Received January 24th, 1979

Dedicated to Professor E. Hála on the occasion of his 60th birthday.

In the presence of cupric oxide as the catalyst, ethyl cyanoacetate reacts with 1-alkenes to form 1 : 1 adducts in high yields. The active catalytic component was found to be a soluble copper species generated in the absence of oxygen in 10^{-3} to 10^{-5}M concentrations by a partial dissolution of cupric oxide in ethyl cyanoacetate. The homogeneous catalytic reaction proceeds already at temperatures about 80°C at a fast rate and with high selectivity. Results of inhibition experiments in the presence of α-naphthol and galvinoxyl support strongly the view on a free-radical mechanism of the addition reaction.

In the previous work of this series we reported the high initiating efficiency of cupric oxide in addition of cyanoacetates to the carbon–carbon double bond; it was found that the rate of formation of 1 : 1 adducts in the presence of cupric oxide is much faster than that in the thermal or di-tert-butyl peroxide-initiated reactions[1]. It was also shown that the initiating efficiency of cupric oxide exceeds substantially that of silver(II), manganese(IV) and lead(IV) oxides as well as that of nickel peroxide and that it is comparable only with the efficiency of cuprous oxide in the formation of anti-Markovnikov 1 : 1 adducts[2].

In this communication we summarize the results of experiments aimed at elucidating the nature of the high initiating efficiency of cupric oxide in radical addition reactions. The addition of ethyl cyanoacetate to 1-decene yielding ethyl α-cyanododecanoate has been chosen as a model reaction.

RESULTS AND DISCUSSION

At the first sight, the addition of an ester of cyanoacetic acid to a 1-alkene in the presence of cupric oxide as the initiating agent appears to be a typical heterogeneous reaction. Its rate could be therefore influenced by diffusion, the surface area of the

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* Part IX in the series Free-Radical Addition Reactions Initiated by Metal Oxides; Part VIII: This Journal *44*, 2393 (1979).

metal oxide and by the method of its preparation. Preliminary experiments showed that a vigorous stirring is necessary ($\geqq 500$ revs/min) to eliminate macrokinetic effects in the addition reaction. All measurements were carried out with an intensity of stirring corresponding to 500 revs/min, at 80°C and in a nitrogen atmosphere. From Fig. 1 it becomes evident that the rate of the addition reaction is essentially independent upon the metal oxide surface varying from 0·3 to 44 $m^2 g^{-1}$. On the other hand, Fig. 1 documents clearly the substantial dependence of the conversion of 1-decene on the origin of cupric oxide. The highest efficiency exhibited cupric oxide (sample CuO-1) prepared by oxidation of copper powder in a stream of oxygen at 300°C. As inferred from the initial rates of the 1-decene conversion (Fig. 1), the activity of cupric oxide (sample CuO-2) prepared by precipitation of a cupric sulphate solution with sodium hydroxide is 2·2-times lower than the activity of sample CuO-1. This decrease in activity is likely due to traces of sulphate ions which could not be removed even by a very careful washing. The presence of these

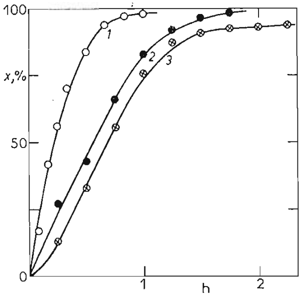


FIG. 1

Time Dependence of Conversion of 1-Decene in the Reaction with Ethyl Cyanoacetate in the Presence of Cupric Oxide as the Catalyst of Different Origin

1 CuO-1 prepared by the oxidation of copper powder in a stream of oxygen at 300°C, *2* CuO-2 obtained by alkaline precipitation of cupric sulphate solutions, *3* CuO-3 obtained by thermal decomposition of cupric nitrate trihydrate at 500°C. $[NCCH_2CO_2.C_2H_5]_0$: $[CH_2{=}CH(CH_2)_7CH_3]_0$: [CuO] = 50 : 1 : 0·1; temperature 80°C.

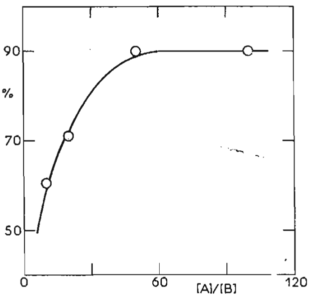


FIG. 2

Dependence of the Yield of Ethyl α-Cyanododecanoate on the Initial Molar Ratio of Ethyl Cyanoacetate (A) to 1-Decene (B) in the Heterogeneous Addition Reaction Catalysed by Cupric Oxide

$[CH_2{=}CH(CH_2)_7CH_3]_0$: [CuO] = 1 : 0·1; temperature 80°C.

ions, which may act as radical trappers, was proved by IR spectroscopy of cupric oxide. An efficiency similar to that exhibited by sample CuO-2 showed cupric oxide obtained by thermal decomposition of cupric nitrate trihydrate at 500°C (sample CuO-3); the only difference could be seen in the occurence of a slight induction period at the very beginning of the addition reaction (Fig. 1); the induction period might be due to a partial sintering of the metal oxide surface during preparation of the oxide at high temperatures. Samples CuO-1 and CuO-3 were spectroscopically pure and at present no explanation for the difference in their activity can be offered. Cupric oxide (CuO-1) prepared by the oxidation of metallic copper showed also greater selectivity and the yields of ethyl α-cyanododecanoate were by 7% higher (90%) than those obtained using the CuO-2 and CuO-3 samples.

Dependences of the reaction rate and of the product yield on the concentration of cupric oxide in a suspension of ethyl cyanoacetate and 1-decene were examined in the range from 0.14 to 3·50 g CuO/l; this corresponds to the following molar ratios of the components: ethyl cyanoacetate: 1-decene: CuO = 50 : 1 : 0·01 – 0·25. It was found that the initial reaction rate for the 1-decene conversion and the yields of the addition product increased with the cupric oxide concentration increasing from 0·14 to 0·7 g CuO/l; an oxide concentration higher than 0·7 g CuO/l did not affect the rate of the addition reaction. These results and the fact that the cupric oxide separated from the reaction mixture can be used in subsequent addition reactions without a significant loss of activity indicate that it behaves rather as a typical catalyst than an initiating agent[1,2].

The effect of the ester and alkene mutual concentrations in the reaction mixture on the yield of the addition product was investigated in a broad range of the molar ratios of both components: ethyl cyanoacetate: 1-decene: CuO = 10 – 100: 1 : 0·1. As the Fig. 2 shows, an increase in the ester to 1-decene molar ratio from 10 : 1 to 50 : 1 rises yields of ethyl α-cyanododecanoate from 61 to 90%; further increase in the molar ratio does not affect the formation of the 1 : 1 adduct.

Determination of the effect of the ester to alkene molar ratio on the rate of the addition reaction was prevented by a limited miscibility of both components; higher alkene concentrations in the ester led to two-phase mixtures.

If the higher catalytic efficiency of cupric oxide and its essential independence on the catalyst surface is taken into consideration, a question arises whether the metal oxide does not dissolve in the reaction mixture and, consequently, to which extent the addition of the ester to the alkene could proceed as a homogeneous catalytic reaction. The answer came from the following experiments. Heating a sample of cupric oxide ($1{\cdot}9 \,.\, 10^{-2}$M) suspended in ethyl cyanoacetate (the ester to CuO molar ratio = 50 : 0·1) to 80°C for 5 min and another for 2 h and separating the solid cupric oxide gave colourless solutions containing $2{\cdot}8 \,.\, 10^{-4}$M and $1{\cdot}44 \,.\, 10^{-3}$M, respectively, of a soluble copper species of unknown composition; the latter concentration corresponded to dissolution of 7% (by mass) of the solid cupric oxide.

The filtrate obtained by a 2-hour heating was mixed with 1-decene (the ester to alkene molar ratio = 50 : 1) and the course of the reaction at 80°C was followed by determining time changes in the 1-decene concentration. As follows from Fig. 3, the rate of the homogeneous addition reaction catalysed by a soluble copper species (curve *2*) was close to the rate of the heterogeneous catalysed reaction (curve *1*). At the same time, the concentration of the soluble copper species in the reaction mixture corresponded to 0·4% by mass (*i.e.* 0·7 mol.%) with respect to 1-decene and 0·01% by mass with respect to the reaction mixture. The high activity of the copper species is clearly seen from a comparison, *e.g.* with dibenzoyl peroxide (curve *7*) which was more than five times less active under comparable conditions. The addition of the cyano ester to 1-decene in the presence of the soluble copper species represents a new example of a highly effective homogeneous catalytic addition reaction. The yet known examples of homogeneous catalytic addition reactions initiated

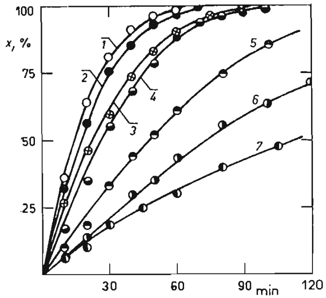


FIG. 3

Time Dependence of Conversion of 1-Decene in the Heterogeneous *1* and Homogeneous *2*—*7* Addition Reaction with Ethyl Cyanoacetate Catalysed by Cupric Oxide, CuO-1 *1*, Soluble Copper Species (Cu-S) *2*—*6* and Dibenzoyl Peroxide (DBP) *7*

$[NCCH_2CO_2C_2H_5]_0 : [CH_2{=}CH(CH_2)_7.CH_3]_0 = 50:1$; temperature 80°C; *1* [CuO-1] $= 1·9 . 10^{-2}$M; *2* [Cu-S] $= 1·44 . 10^{-3}$M; *3* [Cu-S] $= 0·72 . 10^{-3}$M; *4* [Cu-S] $= 0·36 . 10^{-3}$M; *5* [Cu-S] $= 0·14 . 10^{-3}$M; *6* [Cu-S] $= 0·07 . 10^{-3}$M; *7* [DBP] $= 2·0 . 10^{-3}$M.

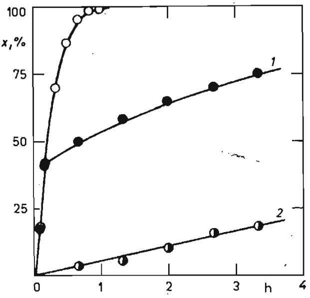


FIG. 4

Time Dependence of Conversion of 1-Decene in the Heterogeneous Addition Reaction with Ethyl Cyanoacetate Catalysed by Cupric Oxide (CuO-1) in the Absence and Presence of *1* Galvinoxyl and *2* α-Naphthol as Inhibitors

$[NCCH_2CO_2C_2H_5]_0 : [CH_2{=}CH(CH_2)_7.CH_3]_0 : [CuO\text{-}1] : [inhibitor]_0 = 50 : 1 : 0·1 : 0·01$; temperature 80°C.

by redox transfer and leading to anti-Markovnikov 1 : 1 adducts refer to the addition of aliphatic halogenated compounds to a terminal carbon-carbon double bond; the concentrations of homogeneous catalysts in these reactions correspond approximately to 1 mol.% (refs[3,4]).

The above results explain the independence of the rate of the cyano ester addition to 1-decene on the surface area of cupric oxide. Nearly identical values of conversions of 1-decene in the heterogeneous and homogeneous system, represented in Fig. 3 by curves *1* and *2*, might lead to the conclusion that also in the heterogeneous reaction the formation of the 1 : 1 adduct is catalysed almost exclusively by the soluble copper species. This conclusion is at variance, however, with the low initial rate of dissolution of cupric oxide in the cyano ester (*vide supra*). Involvement of the souble copper species only should therefore result in the occurrence of an induction period in the heterogeneous catalysed reaction. The absence of this induction period (Fig. 3, curve *1*) indicates that in the heterogeneous system, at least at the very beginning of the reaction, the surface of the suspended cupric oxide contributes to the overall catalytic effect.

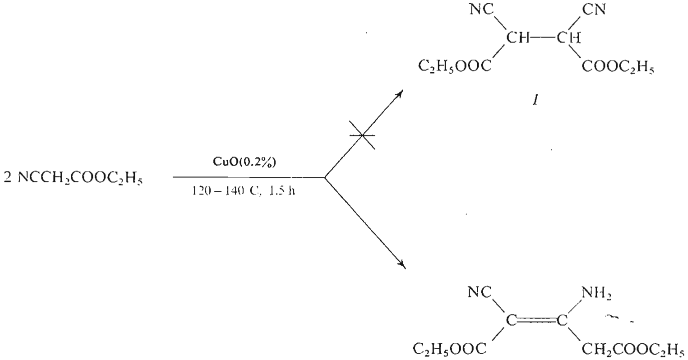
Noteworthy is also a relatively high sensitivity of the hot suspensions of cupric oxide in the cyano ester, and even more so of the hot solutions of the copper species, to air and oxygen; in contact with these gases at higher temperatures the initially colourless solutions turn immediately yellow and the colouration is accompanied by a considerable loss in activity. At present, no unambiguous explanation can be offered for this phenomenon.

As Fig. 4 shows, the reaction under study is also highly sensitive to radical inhibitors; the addition of α-naphthol or galvinoxyl suppresses nearly completely the 1 : 1 adduct formation. These results are in harmony with the inhibiting effect of 1,1-diphenyl-2-picrylhydrazyl on the reaction[1].

An attempt to gain evidence for the participation of radicals in the reaction of cyanoacetate with 1-decene in the presence of the soluble copper species as the catalyst and of nitrosodurene as the "spin-trapping" agent by EPR spectra at 50–80°C did not meet with success. Notwithstanding, we succeeded in generating the ethyl cyanoacetate radical by UV irradiation of a mixture of the ester, 1-decene and di-tert-butyl peroxide at −15°C; the radical was detected by "spin-trapping" technique with the use of nitrosodurene ($a^H = 3{\cdot}85$ G; $a^N = 12{\cdot}5$ G; $g = 2{\cdot}007$). At higher temperatures the spin adduct with nitrosodurene was not stable. This thermal instability was obviously the reason of the unsuccessful detection of the spin adduct in the reaction catalysed by the soluble copper species starting only at temperatures above 40°C (ref.[1]).

Sometimes, radical addition reactions are accompanied by formation of dimers arising from the dehydrodimerisation (termination) reaction. Formation of dimers was observed also by us in some addition reactions initiated by metal oxides[2,5].

It is of interest that the addition of ethyl cyanoacetate to 1-decene (80°C, 70 min) catalysed by cupric oxide does not produce even traces of the dimer *I* (Scheme 1). As verified by us, also the product resulting from the di-tert-butyl peroxide-initiated reaction does not contain the dimer *I*. On prolonged heating (5 h) of a mixture of ethyl cyanoacetate and cupric oxide or cupric acetate to 80°C or by rising the temperature above 100°C, a crystalline product was obtained which was identified as 1-cyano-1,3-diethoxycarbonyl-2-amino-1-propene (*II*), (Scheme 1). Compound *II* was prepared earlier from ethyl cyanoacetate in the presence of catalytic amounts of $Pt[P(C_6H_5)_3]_4$ or $Pd[P(C_6H_5)_3]_4$ acting as strong Lewis bases[6,7].



II

SCHEME 1

In an attempt to gain a deeper insight into the catalytic function of the soluble copper species, we examined the effect of its concentration on the rate of the reaction of ethyl cyanoacetate with 1-decene. The relationship between the reaction rate and the catalyst concentration (c_{cat}) in the range from $1{\cdot}44 \,.\, 10^{-3}$ to $7{\cdot}0 \,.\, 10^{-5}$M (0·03 to 0·7 mol.% with respect to 1-decene) was determined at a constant ester to alkene molar ratio equaling to 50 : 1 and at 80°C. Initial reaction rates (r^0, s^{-1}), which were read from curves *2–6* in Fig. 3 for the 1-decene conversions lower than 20% and at the given concentrations c_{cat} (mol l^{-1}) of the catalytically active soluble copper species, correspond to the following values:*

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* As it is seen from Fig. 3, the addition reaction initiated by dibenzoyl peroxide (curve 7) proceeds at a substantially slower rate; for a dibenzoyl peroxide concentration equal to $200 \,.\, 10^{-5}$ mol l^{-1}, and under otherwise identical conditions, the initial rate of the 1 : 1 adduct formation (r^0) (<10% conversion of 1-decene) corresponded to a value of $1{\cdot}04 \,.\, 10^{-4}$ s^{-1}.

$c_{cat} \cdot 10^5$	144	72	36	14	7
$r^0 \cdot 10^4$	5·4	3·6	3·0	1·67	1·11

The plot of log r^0 *vs* log c_{cat} gave a linear dependence with the correlation coefficient r corresponding to 0·9957 (Fig. 5). The slope of this dependence equals to 0·51, confirming that the homogeneous catalytic addition of ethyl cyanoacetate is one half-order in the soluble copper species in a broad range of concentrations. This result is in accordance with the kinetics of free-radical chain reactions which are known to be one half-order in the initiating agent, usually an organic peroxide[8].

The structure of the catalytically active soluble copper species is still unknown. The valence state of copper in this compound is not clear. It should be mentioned, however, that the addition reaction proceeds also in the presence of cuprous oxide[2] and that also metallic copper exhibits some, though very low activity. Attempts to isolate the copper species from its solutions in ethyl cyanoacetate were unsuccessful. By evaporating the ester at low temperatures and under high vacuum we obtained only a dark brown amorphous product which could not be purified by any of the known separation procedures. Considering the possible structures of the soluble copper species, one of the alternatives may be an organometallic copper compound; an unstable compound of this type was prepared by the reaction of phenylcopper with ethyl cyanoacetate[9]. The formation of such a compound under conditions of the reaction studied by us makes this alternative improbable. Another possibility may be a partial hydrolysis of ethyl cyanoacetate (with participation of traces of water always present in the ester) and subsequent formation of cupric or cuprous cyanoacetate; these salts are known to undergo easily decarboxylation[10,11]. Cupric cyanoacetate loses carbon dioxide already under mild conditions and pro-

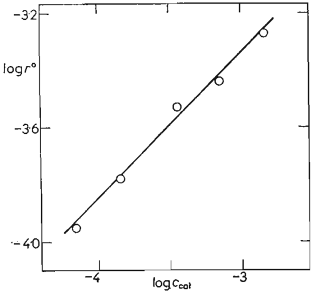
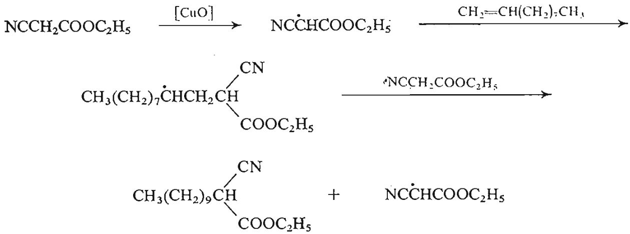


FIG. 5

Dependence of Logarithms of Initial Rates r^0 of the 1-Decene Conversion on Logarithms of Concentrations c_{cat} of the Catalytically Active Soluble Copper Species in the Addition Reaction with Ethyl Cyanoacetate duces cyanomethylcopper and the dinitrile of succinic acid[11]. This hypothesis is supported by the finding that the addition of 1% (by mass) of water (with respect to the ester) to a suspension of cupric oxide in the cyano ester and 1-decene increases 1·4-times the initial reaction rate of the addition reaction. A strong support comes from the experiment in which the dissolved cupric cyanoacetate ($4{\cdot}6 \,.\, 10^{-5}\text{M}$) was used as the catalyst in place of cupric oxide; the initial rate of the addition reaction was nearly identical with that read from the linear dependence in Fig. 5 for the same concentration of the soluble copper species. These experiments were limited by a low solubility of cupric cyanoacetate in the cyano ester (max. $4{\cdot}6 \,.\, 10^{-5}\text{M}$). Available methods allow to prepare this salt obviously only in a poorly soluble dimeric or polymeric form[12]; on the other hand, mild conditions of the addition reaction do not exclude formation of a more soluble form resulting from interaction of cupric oxide with the cyano ester. However, we have never been able to prove the presence of the dinitrile of succinic acid in the products of our addition reactions. These conflicting results do not allow to draw definite conclusions about the nature of the catalytically active, soluble copper species.

The remaining problem is a radical or nonradical character of the addition of ethyl cyanoacetate to 1-decene catalysed by cupric oxide. From the literature it is known that addition to 1,3-dienes of compounds having an activated methylene group can be catalysed by complexes $PdCl_2(P(C_6H_5)_3)_2$—C_6H_5ONa and $PtCl_2(P(C_6H_5)_3)_2$—C_6H_5ONa (refs[13,14]). These catalytic reactions produce also anti-Markovnikov 1 : 1 adducts, but according to a nonradical mechanism involving the activation of the conjugated diene by the metal complex[14]. In our case it seems likely that the majority of experimental results accumulated so far indicates rather a free radical mechanism of the addition of cyano esters to 1-alkenes in the presence of cupric oxide as the catalyst. This hypothesis is supported by the following facts: *a*) thermal and di-tert-butyl peroxide-initiated[1] as well as the cupric oxide catalysed addition of ethyl cyanoacetate to 1-decene yields the same product, ethyl α-cyanododecanoate; *b*) as a rule, an increase in the ester to 1-alkene molar ratio leads to a marked increase



$$NCCH_2COOC_2H_5 \xrightarrow{[CuO]} NC\dot{C}HCOOC_2H_5 \xrightarrow{CH_2{=}CH(CH_2)_7CH_3} CH_3(CH_2)_7\dot{C}HCH_2CH\begin{matrix}CN\\COOC_2H_5\end{matrix} \xrightarrow{NCCH_2COOC_2H_5} CH_3(CH_2)_9CH\begin{matrix}CN\\COOC_2H_5\end{matrix} + NC\dot{C}HCOOC_2H_5$$

SCHEME 2

in the yield of the 1 : 1 adduct and to suppression of telomer formation; *c*) the rate of the addition reaction is highly sensitive to the inhibitors of radical reactions; *d*) the addition reaction is one half-order in the catalytically active soluble copper species; *e*) the reaction of ethyl cyanoacetate with styrene catalysed by cupric oxide gives exclusively polymeric products; this is in accordance with the report[15] that a cupric salt-ethyl cyanoacetate system may initiate the radical polymerisation of styrene.

Even though the generation of starting radical is still unclear, it seems likely that the formation of the 1 : 1 adduct can be described by a general scheme (Scheme 2) involving the initiation and propagation step.

EXPERIMENTAL

Chemicals. Ethyl cyanoacetate (Fluka A.G., Buchs, Switzerland) of analytical purity was fractionated under reduced pressure until chromatographically pure; the water content was 0·02% (by mass). 1-Decene (Fluka A.G.) was freed from peroxides by passing through alumina activated by heating to 420–450°C, then redistilled and stored under nitrogen. Di-tert-butyl peroxide (Koch-Light Ltd., Colnbrook-Bucks, England) and dibenzoyl peroxide (Lachema, Brno) were used without further purification. n-Nonane, n-octadecane (internal standards) (Fluka, A.G.), α-naphthol (Ciech-Gliwice, Poland) and galvinoxyl (Aldrich-Europe, Beerse, Belgium), all of analytical purity, were used as obtained. Cupric oxide sample CuO-1 (specific surface 1·7 m^2/g) was prepared by a careful oxidation of copper powder (99·99%) (specific surface 1·2 m^2/g) in a stream of oxygen (240 ml/h) at 300°C. Sample CuO-2 (specific surface 44 m^2/g) was obtained by portionwise addition of cupric sulphate to a stirred hot (95°C) solution of sodium hydroxide; the dark brown oxide was filtered off, washed with water until negative test on SO_4^{2-} ions and dried *in vacuo* at 90°C. Sample CuO-3 (0·3 m^2/g) was obtained by thermal decomposition of cupric nitrate at 500°C. Cupric cyanoacetate was prepared from cyanoacetic acid and basic cupric carbonate according to the reported procedure[12].

Analytical methods. Gas chromatographic analysis was carried out on Chrom 31 instrument (Laboratorní přístroje, Prague) equipped with a flame-ionisation detector and a steel column (1·7 m × 3 mm) packed with 7% Silicone OV-17 on Gas-Chrom Q (80–100 mesh). EPR spectra were recorded on Jeol PE XXX spectrometer. The copper content in the filtrate obtained by dissolving cupric oxide in ethyl cyanoacetate was determined by the following method[16]: the pipetted amount of the sample (1 ml) was evaporated to dryness, the residue was calcinated and dissolved in 50 ml of dilute hydrochloric acid (1 : 1). Then 1 ml of a 5% solution of Komplexon III and 1 ml of a 1% polyvinyl alcohol solution were added. Ca. 0·1 g of morpholinium N,N-3-oxo-pentamethylenedithiocarbaminate was added to the mixture under stirring and the absorbance of the solution was measured at 430 nm. The copper content was calculated from the absorbances determined for calibration solutions.

Typical example of the heterogeneous addition reaction. Cupric oxide (0·016 g; $2 . 10^{-4}$ mol), ethyl cyanoacetate (11·3 g; 0·1 mol), 1-decene (0·28 g; $2 . 10^{-3}$ mol) and n-nonane (0·15 g, internal standard to 1-decene) were weighed into a 25 ml glass flask provided with a neck for sampling, a nitrogen inlet, a thermometer and a magnetic stirrer. The stirred reaction mixture (≧500 revs/min) was first purged with nitrogen for 10 min, the nitrogen stream was stopped, the flask was topped with a small resin ball and the reaction mixture content was warmed up to 80°C during 3 min; the temperature was maintained constant within ±1°C. The samples were removed at fixed time intervals and the content of 1-decene was determined by gas chromatographic analysis. When the 1-decene conversion attained ≧98%, the reaction mixture was cooled to an ambient temperature, the known amount of n-octadecane (internal standard) was added together with 20 ml of acetone to homogenise the mixture (n-octadecane is not miscible with the ester), and the content of ethyl α-cyanododecanoate was determined by gas chromatographic analysis. To determine the yield of the product, we used the method of the peak height ratios and of the calibration curve constructed according to analyses of n-octadecane and product mixtures of the known composition; the calibration curve was checked before each series of analytical measurements.

Homogeneous catalytic addition reaction. A suspension of cupric oxide in ethyl cyanoacetate containing both components in 1 : 50 molar ratio was heated at 80°C for 2 h in a nitrogen atmosphere. After cooling the mixture to room temperature, the cupric oxide was filtered off and the filtrate was used in the reaction with a given amount of 1-decene. Solutions containing the soluble copper compound in the lower concentration were prepared by diluting the stock solution ($1{\cdot}44 . 10^{-3}$M-Cu) with ethyl cyanoacetate.

Dimerisation of ethyl cyanoacetate. A mixture of ethyl cyanoacetate (11·3 g; 0·1 mol) and cupric oxide (16 mg; $2 . 10^{-4}$ mol; 0·2 mol.%) was heated at 140°C for 1·5 h in a nitrogen atmosphere; all the metal oxide dissolved during the reaction The reaction mixture was cooled to room temperature and the unreacted ethyl cyanoacetate was distilled off under reduced pressure. Distillation of the residue gave 0·8 g of a solid product (7%) boiling at 150—152°C/66·7 Pa, which after crystallisation from ether had m.p. 55°C (ref.[6] gives m.p. 54–55°C). IR spectrum of the product agreed with that reported[6] for 1-cyano-1,3-diethoxycarbonyl-2-amino-1-propene. For $C_{10}H_{14}N_2O_4$ (226·2) calculated: 53·09% C, 6·24% H; found: 53·44% C, 6·22% H.

The authors are grateful to Dr L. H. Sutcliffe, University of Liverpool, for a kind gift of a sample of nitrosodurene, Dr Pilař, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, for EPR *spectra measurements and Mrs P. Valentová, this Institute, for analytical determinations of copper.*

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Translated by J. Hetflejš.