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FREE–RADICAL ADDITION REACTIONS INITIATED BY METAL OXIDES, VI

THERMALLY INITIATED AND COPPER(II) OXIDE CATALYZED ADDITION OF CYANOACETIC ACID ESTERS TO A TERMINAL CARBON-CARBON DOUBLE BOND

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CuO catalyzed additons of ethyl cyanoacetate, initiated thermally and by di-tert-butyl peroxide, to 1-decene and ethyl 10-undecylenoate were investigated. The CuO catalyzed reaction proceeds already at 80 °C at a high rate, produces 1:1 adducts in high yields and represents the first example of catalysis in radical addition reactions of non-halogenated compounds.

Было исследовано присоединение этилцианоацетата к 1-децену и этил 10-ундециленоату, катализированное CuO, термически и ди-трет.-бутилперекисью. Реакция, катализированная CuO, протекает с высокой скоростью уже при 80 °C, давая аддукты с составом 1 : 1 с высоким выходом. Эта реакция представляет собой первый пример катализа в реакциях радикального присоединения негалогенированных соединений.

Ethyl cyanoacetate (1) has been reported to give no EPR signal when heated in the spectrometer cavity at temperatures up to 200 °C. It has also been stated that the thermally initiated addition of 1 to methyl 10-undecylenoate does not occur and only the photochemically or di-tert-butyl peroxide (DTBP) initiated reaction gives the expected 1:1 adduct in an acceptable yield /1,2/.

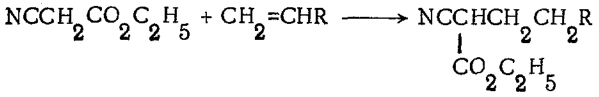
We now report a successful thermally initiated and copper(II) oxide catalyzed addition of 1 to 1-decene (2) and to ethyl 10-undecylenoate (3) chosen as model compounds.

EXPERIMENTAL

Reactions on a 2 mmol scale of 2 or 3, monitored by GLC, were carried out in the dark in a stirred 50 ml glass reactor, under normal pressure, in an atmosphere of nitrogen and at 50–180 °C. The reactants (Fluka, Switzerland) were carefully degassed, 2 and 3 were freed of peroxides and distilled before use.

RESULTS

As confirmed by analytical and spectral data /3/, the product resulting from the thermally initiated addition of 1 to 2 at 150 °C (6 hrs, mole ratio of 1 to 2 = 50:1; conversion of 2: 95%) is ethyl α-cyanododecanoate (4) (59%). A similar reaction of 1 with 3 at 160 °C (14 hrs, mole ratio of 1 to 3 = 10:1; conversion of 3: 86%) gave 43% of the new diethyl α-cyanotridecanedioate (5) (Bp. 189 °C/0.3 Torr; IR (neat): $\nu_{C=O}$ 1740(vs), $\nu_{C\equiv N}$ 2255(w), ν_{CH_3} 1370(m) cm^{-1}; ^{1}H NMR (in CDCl$_3$; TMS): methine triplet (1 H) centered at 3.4 ppm).



$$\mathrm{NCCH_2CO_2C_2H_5 + CH_2{=}CHR \longrightarrow NC\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{C}HCH_2CH_2R}$$

4 $R = (CH_2)_7CH_3$

5 $R = (CH_2)_8CO_2C_2H_5$

The addition of 1 to 3 in the presence of CuO (5.7 wt.% of 3) at 85 °C (4 hrs, mole ratio of 1 to 3 and CuO = 10:1:0.1; conversion of 3: 98%) yielded 73% of the 1:1 adduct 5. From a comparison of the initial rates for the conversion of 2 (Fig. 1), it follows that the addition of 1 to 2 catalyzed by CuO (5.7 wt.% of 2) proceeds about fifteen times, and the DTBP initiated reaction /4–6/ about five times, faster than the thermally initiated reaction. The thermally initiated addition of 1 to 2 producing adduct 4, which starts above 120 °C and attains its maximum (62%) at 180 °C (Fig. 2), is accompanied by substantial telomer and resinous product forma-

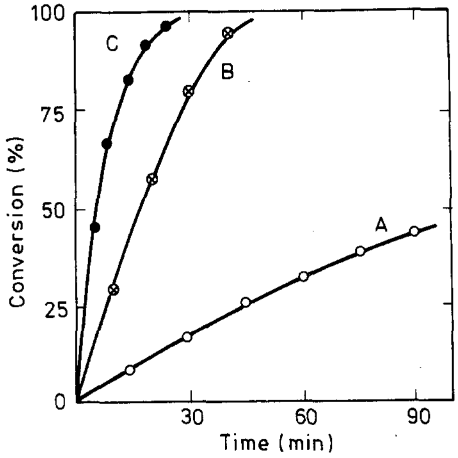


Fig. 1. Time dependence of the conversion of 1-decene (2) in a thermally initiated (A), DTBP initiated (B) and CuO catalyzed (C) addition reaction with ethyl cyanoacetate (1) at 140 °C. Initial mole ratios of the reaction components: (A) $[\underline{1}]_0 : [\underline{2}]_0 = 50{:}1$, (B) $[\underline{1}]_0 : [\underline{2}]_0 : [\mathrm{DTBP}]_0 = 50{:}1{:}0.1$, (C) $[\underline{1}]_0 : [\underline{2}]_0 : [\mathrm{CuO}] = 50{:}1{:}0.1$

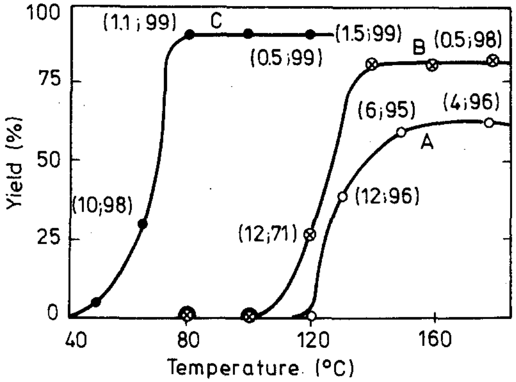


Fig. 2. Temperature dependence of the yield of ethyl α-cyanododecanoate (4) in a thermally initiated (A), DTBP initiated (B) and CuO catalyzed (C) addition of ethyl cyanoacetate (1) to 1-decene (2) at 50–180 °C. The numbers in parentheses denote reaction time (hr) and total conversion of 2 (%). For reaction conditions, see legend to Fig. 1

tion. The temperature dependence of the peroxide initiated addition (Fig. 2) is in accordance with the known half-lives of DTBP at 100–145 °C /7/. Thermal initiation contributes, however, to an appreciable extent to the overall conversion of 2 in the DTBP initiated reaction (Fig. 1). The addition of 1 to 2 in the presence of a catalytic amount of CuO (Fig. 2) proceeds already at 80–85 °C at a high rate, with high selectivity, without participation of thermal initiation and gives 1:1 adduct 4 in 90% yield (GLC). Copper(II) oxide used in this work, and prepared by heating metallic copper in a stream of oxygen (240 ml hr^{-1}), exhibits a markedly higher activity and selectivity than the oxide obtained by precipitation from an aqueous $CuSO_4$ solution /3,8/. Unlike DTBP, which disintegrates completely while generating the starting tert-butoxy and methyl radicals, CuO is not consumed significantly during the addition reactions and its activity remains essentially unchanged after the first and following cycles. To our knowledge, this is the first example of catalysis in radical addition reactions of non-halogenated compounds.

Thermolysis of carboxylic acid esters is generally assumed to follow a unimolecular cyclic /9/ or free-radical mechanism /10/. Detection of traces of CH_3CN, C_2H_5OH and CO_2 in the product of our thermally initiated addition reactions indicates the intermediacy of $NC\dot{C}H_2$ radicals. Presumably, these radicals as well as the radicals $NCCHCO_2C_2H_5$ starting the propagation step cannot be detected directly in situ; their involvement is, however, clearly evidenced by: a) complete inhibition of the addition reactions by traces of α-naphthol; b) disappearance of the EPR signal exhibited by a solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) ($4x10^{-4}$ mol l^{-1}) in 1 and simultaneous discoloration of the solution at 130 ° after 120 s in the absence and immediately in the presence of CuO ($2x10^{-2}$ mol l^{-1}). As confirmed by a parallel experiment, CuO alone does not interact with DPPH.

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