RADICAL ADDITION OF NITRILES TO 1-ALKENES INITIATED BY METAL OXIDES*

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The radical addition of acetonitrile, propionitrile, and phenylacetonitrile to terminal alkenes in the presence of silver(I), silver(II), manganese(IV), lead(IV) and copper(II) oxides or nickel and cobalt peroxides has been studied at 81—200°C. The reaction of acetonitrile and propionitrile with 1-decene initiated by lead(IV) oxide at 205—220°C produced dodecanenitrile and α-methyldodecanenitrile, respectively, in 59—77% yields. The other metal oxides were substantially less effective. The yield of the 1 : 1 adducts formed by the addition reaction of acetonitrile depended strongly upon the initial concentration of 1-alkenes. Phenylacetonitrile underwent, similarly as in reactions initiated by di-tert-butyl peroxide, preferentially dimerisation and polymerisation reactions.

Radical addition of acetonitrile to 1-alkenes provides a valuable homologation reaction for straight-chain nitriles[1]. Organic peroxides[1-3] and γ-irradiation[4] are known to initiate this reaction. Maximum yields of about 62% of the corresponding 1 : 1 adducts are achieved using di-tert-butyl peroxide as the most efficient initiator and acetonitrile in large excess[2]; benzoyl peroxide[3] and γ-irradiation[4] initiate these reactions in general less effectively. Propionitrile undergoes, similarly as other higher primary aliphatic nitriles, the addition reaction more readily and with higher selectivity than does acetonitrile and gives the corresponding α-methyl nitriles as main products[1,5]. For example, when propionitrile in excess is allowed to react with β-pinene in the presence of di-tert-butyl peroxide, the 1 : 1 adduct, *i.e.* α-methyl-β-
-(4-isopropylcyclohex-1-ene)propionitrile, is produced in 77% yield[1,6]. In the previous works[7-9] we have demonstrated the high efficiency of some metal oxides in the initiation of the anti-Markovnikov type addition of aliphatic and alicyclic ketones to terminal alkenes.

On investigating further the ability of metal oxides to generate radicals in reactions of alkenes with compounds possessing activated C—H bond, we have studied the radical addition of acetonitrile, propionitrile and phenylacetonitrile to terminal alkenes. We have found that acetonitrile can be added to 1-octene, 1-decene or β-pine-

ne to give the corresponding 1 : 1 adducts *IIa*, *IIb* (Scheme 1) or β-(4-isopropylcyclo-hex-1-ene)propionitrile, respectively, at best in the presence of lead(IV) oxide as initiator[10]. As it is illustrated by the addition of acetonitrile to 1-decene (Fig. 1), the formation of the anti-Markovnikov product is strongly influenced by the initial concentration of the alkene in the reaction mixture; a similar dependence was found in analogous reactions initiated by di-tert-butyl peroxide. At the initial molar ratio of acetonitrile to 1-decene and lead(IV) oxide equaling to $100-200 : 1 : 2-4$ and at 205°C, the corresponding 1 : 1 adduct, dodecanenitrile, was obtained in $59-65\%$ yield under essentially complete consumption of 1-decene ($\geqq 99\%$ after 7 h). Silver(I) oxide or silver(II) oxide may also be used to initiate this reaction. Because of the lower thermal stability of these oxides[8], the addition had to be carried out at temperatures below 100°C; however, telomerisation reaction are taking place preferentially under these conditions. When acetonitrile, 1-decene and silver(I) oxide or silver(II) oxide were allowed to react at an initial molar ratio of 50 : 1 : 4, dodecanenitrile has been obtained in only 31 to 37% yield under essentially complete consumption of the alkene ($> 99\%$ after $39-45$ h at 81°C). The other metal oxides such as manganese(IV) oxide, copper(II) oxide, Pb_3O_4, "nickel peroxide" ($Ni(III, IV)O_x(OH)_y$) or "cobalt peroxide" ($Co(III, IV)O_x(OH)_y$) were even less efficient, and the yields of the 1 : 1 adducts did not surpass 10%.

In the radical addition reactions of propionitrile and other higher aliphatic terminal nitriles with 1-alkenes, only lead(IV) oxide exhibits sufficiently high initiating capability. The yield of the 1 : 1 adducts depends substantially less upon the intial concentration of 1-alkene compared to the addition reactions of acetonitrile. At the initial molar ratio of propionitrile to 1-decene and lead(IV) oxide equaling to 50 to $100 : 1 : 4$, 77% yield of α-methyldodecanenitrile has been achieved at $97-99\%$ conversion of 1-decene (after $9-10$ h at 220°C). The preferential addition to the
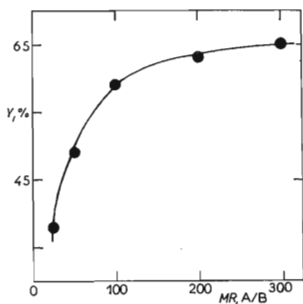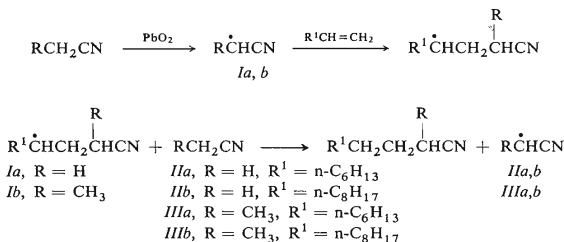

FIG. 1

Dependence of the Yield (Y) of Dodecane-nitrile upon the Initial Molar Ratio (MR) of Acetonitrile (A) to 1-Decene (B) in the Addition Reaction Initiated by Lead(IV) Oxide (C)

The A : B : C initial molar ratio = 25 to 300 : 1 : 4, temperature 205°C, reaction time 7 h, the conversion of B $\geqq$ 99%, reactions on $1-4$ mmol 1-decene scale.

α-position with respect to the nitrile group is documented by the absence of the isomeric tridecanenitrile.

As follows from the above results, the homologous terminal aliphatic nitriles such as dodecanenitrile (*IIb*) or α-methyldodecanenitrile (*IIIb*) can be prepared by addition reactions initiated by lead(IV) oxide in $59-77\%$ yields; these yields which were obtained under optimal conditions and at essentially complete consumption of 1-alkene are comparable to or higher than maximum yields achieved with di-tert-butyl peroxide as initiator. The course of these addition reactions, which is analogous to that generally accepted for the organic peroxide initiated addition reactions[1], is described in simplified manner in Scheme 1.

$$RCH_2CN \xrightarrow{PbO_2} \overset{\cdot}{R}CHCN \xrightarrow{R^1CH=CH_2} R^1\overset{\cdot}{C}HCH_2\overset{\overset{\displaystyle R}{|}}{C}HCN$$

$$\overset{\overset{\displaystyle R}{|}}{R^1\overset{\cdot}{C}HCH_2}CHCN + RCH_2CN \longrightarrow R^1CH_2CH_2\overset{\overset{\displaystyle R}{|}}{C}HCN + \overset{\cdot}{R}CHCN$$

Ia, R = H   *IIa*, R = H, R^1 = n-C_6H_{13} *IIa,b*

Ib, R = CH_3 *IIb*, R = H, R^1 = n-C_8H_{17} *IIIa,b*

                            IIIa, R = CH_3, R^1 = n-C_6H_{13}

                            IIIb, R = CH_3, R^1 = n-C_8H_{17}

SCHEME 1

Our results as well as those obtained with organic peroxides indicate that the homolytic cleavage of the α-C—H bond in primary aliphatic nitriles proceeding during the addition reactions with 1-alkenes is more difficult than in aliphatic ketones; the generally lower selectivity and higher formation of telomers is characteristic for the anti-Markovnikov addition of primary aliphatic nitriles to 1-alkenes[7,11].

No products of dimerisation of transiently formed radical *Ia* or *Ib*, *i.e.* succinonitrile or *meso-* and D,L-α,α'-dimethylsuccinonitrile, have been detected in the reaction mixtures. The reactions described in Scheme 1 were accompanied by the formation of acetamide or propionamide in amounts corresponding to 1 part per $1-8$ parts by weight of the product *IIa*, *IIb*, *IIIa* and *IIIb*; acetamide and propionamide are practically insoluble in the 1 : 1 adducts *IIa*, *IIb*, *IIIa* and *IIIb* and may be easily separated. Acetamide was formed in trace amounts ($\sim$0·01 g) also on heating neat acetonitrile with carefully dried lead(IV) oxide under identical conditions. Apparently, water adsorbed on the oxide surface[12,13], which cannot be removed completely by drying *in vacuo* at $25-90°C$, and water formed during the initiation step of the addition reaction[8] participates on the partial hydrolysis of acetonitrile and propionitrile to the corresponding amides.

The large excess of the starting nitriles, which is necessary to supress the telomeri-sation reaction and to obtain good yields of 1 : 1 adducts, can be substantially reduced by continuous addition of the 1-alkene to the reaction mixture; if the 1-alkene is being continuously added to the starting mixture containing the nitrile, 1-alkene and lead(IV) oxide in the initial molar ratio of 50 : 1 : 2−4 at such a rate as to maintain the 300 : 1 : 2−4 molar ratio during the reaction, the 1 : 1 adducts are obtained in a yield comparable with that obtained at high dilution.

The high concentration of the metal oxide relative to that of the alkene seems to indicate that in this case the formation of the 1 : 1 adduct is not a chain process. The two- to fourfold molar excess of metal oxides needed to secure sufficient supply of the start radicals is not surprising with regard to the expected heterogeneous nature of the initiation step. In fact, only about 30 and 60% of the available oxygen in lead(IV) oxide and silver(II) oxide, respectively, is consumed during the addition reaction. A light brown-red inorganic precipitate resulting from the lead(IV) oxide initiated reactions is a mixture of lead(II) oxide, hydrated lead(II) oxide, Pb_3O_4 and the unreacted lead(IV) oxide; silver(II) oxide is converted to a mixture of silver(I) oxide and metallic silver.

The addition of phenylacetonitrile to 1-hexene, 1-octene and 1-decene in the pre-sence of lead(IV) oxide, silver(I) oxide, silver(II) oxide, copper(II) oxide, "nickel peroxide" or "cobalt peroxide" as initiators at 27−170°C failed to give the 1 : 1 adducts in measurable yields. Instead, dimeric and mainly polymeric products were formed. The high capability of phenylacetonitrile to undergo dehydrodimerisa-tion and polymerisation reactions has been already observed in the preparation of *meso*- and D,L-α,α′-diphenylsuccinonitrile by the di-tert-butyl peroxide[14] or "nickel peroxide"[15] assisted dehydrodimerisation of phenylacetonitrile.

EXPERIMENTAL

AgO (ref.[16]) (98·6%) and Ag_2O (ref.[17]) were prepared by standard procedures. PbO_2, a commercial product (British Drug Houses, Ltd., London) of analytical grade purity was dried *in vacuo* at 90°C and stored in desiccator over KOH under reduced pressure; the content of active oxygen was 96·8%. "Nickel peroxide"[18,19] and "cobalt peroxide"[19] were prepared by reported proce-dures; the content of active oxygen in these peroxides equaled to $3\cdot4 \cdot 10^{-3}$ mol/g and $4\cdot5 \cdot 10^{-3}$ mol/g, respectively. CuO was prepared by the procedure described in the previous work[9] and dried similarly as PbO_2. Pb_3O_4 and MnO_2 were commercial products (Lachema, Brno) of analyti-cal grade purity. 1-Hexene, 1-octene, 1-decene, β-pinene and tetradecane (internal standard) of 98−99% purity (with the exception of β-pinene: 80−90%) were commercial products (Fluka A. G., Buchs); these hydrocarbons were fractionated until chromatographically pure and re-distilled before use. Authentic samples of dodecanenitrile and α-methyldodecanenitrile, which were needed for identification of our products, were prepared by the known procedure using di-tert-butyl peroxide as initiator[3]. Acetonitrile of analytical grade purity (Koch-Light, Ltd., London) and the pure propionitrile (Koch-Light, Ltd., London) were distilled successively over P_2O_5 and K_2CO_3 until they contained only 0·05 and 0·04% water, respectively, (by Fischer method) and stored under nitrogen.

Gas chromatographic analyses were made on Chrom-31 instrument (Laboratorní přístroje, Prague) equipped with a flame-ionisation detector, using a steel column (1·5 m × 0·3 mm) packed with 3% SE 30 silicone elastomer +3% Apiezon on Chromaton N-AW-HMDS. IR spectra were recorded with Zeiss, Model UR 20 spectrophotometer (Jena). ^{1}H-NMR spectra were measured on Tesla BS 467—60 MHz spectrometer.

Addition reactions of acetonitrile initiated by Ag_2O and AgO were carried out under normal pressure in an atmosphere of nitrogen using a 50 ml glass flask provided with a magnetic stirrer, a thermometer and a reflux condenser; the reaction temperature was 81°C. The alkene has been continuously added by means of a thin glass ballon provided with a capillary tube reaching to the neck of the flask. Experiments at 205 and 220°C were carried out in nitrogen atmosphere using sealed 25 ml Pyrex ampoules which were vibrationally mixed and heated in a thermostatted oil bath. The yields of 1 : 1 adducts were determined by gas chromatographic analysis with the use of tetradecane as internal standard and relate to the amount of the alkene charged. The reaction was monitored by chromatographic analysis of the reaction mixture (consumption of the alkene). A typical procedure used in experiments carried out in ampoules and the isolation of products are illustrated by the following examples.

Dodecanenitrile (IIb). Acetonitrile (10·2 g, 250 mmol), 1-decene (0·7 g, 5 mmol), and lead(IV) oxide (2·4 g, 10 mmol) were weighed into a 25 ml Pyrex ampoule purged with nitrogen. the ampoule was sealed and the mixture was vibrationally mixed and heated in an oil bath at 205°C for 7 h. After this reaction time, 99% of 1-decene has reacted (by g.l.c. analysis) to give the nitrile *IIb* in 49% yield (by g.l.c.). The mixture was cooled to room temperature, filtered and the inorganic precipitate was washed thrice with 5 ml of acetone. The combined organic materials were freed from acetone by evaporation and from the unreacted acetonitrile by distillation under reduced pressure. Short-path distillation of the liquid residue *in vacuo* afforded a fraction boiling at 60 to 100°C/2 Torr and undistillable telomers. The collected fraction was cooled to 10°C and the crystalline crude acetamide was filtered off. Short-path distillation of the filtrate *in vacuo* gave the pure dodecanenitrile (0·38 g) in 42% yield as a colourless liquid boiling at 99—101°C/1·5 Torr (ref.[20] b.p. 107·3°C/2 Torr). For $C_{12}H_{23}N$ (181·3) calculated: 79·5% C, 12·8% H; found: 79·7% C, 12·6% H. IR spectrum (neat): $\nu(C\equiv N)$ 2253 ± 2 cm^{-1}. ^{1}H-NMR spectrum (in CCl_4 with respect to hexamethyldisiloxane): terminal CH_3 (3 H) 1·23 (s) ppm. Recrystallisation of the crude acetamide (0·05 g) from benzene–ethyl acetate (3 : 1) gave the pure acetamide, m.p. 81°C (ref.[21] m.p. 80·0—80·1°C).

α-Methyldodecanenitrile (IIIb). Propionitrile (11·2 g, 200 mmol), 1-decene (0·56 g, 4 mmol), and lead(IV) oxide (3·8 g, 16 mmol) were weighed into a 25 ml Pyrex ampoule purged with nitrogen, the ampoule was sealed and the mixture was vibrationally mixed and heated in an oil bath at 220°C for 10 h. After this reaction time, 99% of 1-decene has reacted to give the nitrile *IIIb* in 76% yield (by g.l.c.). The mixture was cooled to room temperature and the inorganic precipitate was washed thrice with 5 ml of acetone. Combined organic materials were freed from acetone by evaporation and from the unreacted propionitrile by distillation *in vacuo*. Short-path distillation of the liquid residue under reduced pressure afforded a fraction boiling at 67—110°C / / 4 Torr; the fraction was cooled to 10°C and the crystalline crude propionamide was filtered off. Short-path distillation of the filtrate under reduced pressure yielded 0·41 g (52%) of the pure α-methyldodecanenitrile, b.p. 109—110°C/4 Torr (ref.[22] b.p. 146·3°C/12 Torr). For $C_{13}H_{25}N$ (195·3) calculated: 79·9% C, 12·9% H; found: 80·0% C, 12·7% H. IR spectrum (neat): $\nu(C\equiv N)$ 2243 ± 2 cm^{-1}. ^{1}H-NMR spectrum (in CCl_4 with respect to hexamethyldisilane): terminal CH_3 (3 H) 1·23 (s) ppm; α-CH_3CH (3 H) 1·28, 1·18 (d) ppm; α-CHCH_3 (1 H) 2·23—2·87 (m) ppm. Recrystallisation of the crude propionamide (0·31 g) from benzene–ethyl acetate (3 : 1) yielded the pure amide, m.p. 80°C (ref.[23] m.p. 79·5°C).

IR and ^{1}H-NMR spectra of the nitriles *IIb* and *IIIb* were identical with the spectra of authentic samples of *IIb* and *IIIb* which were prepared by the di-tert-butyl peroxide initiated reaction of 1-decene with acetonitrile and propionitrile, respectively, according to reported procedures[2].

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