RADICAL ADDITION OF LACTONES TO 1-ALKENES INITIATED BY CUPRIC OXIDE*

Milan HÁJEK, Božena ŠPIRKOVÁ and Jaroslav MÁLEK

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

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γ-Butyrolactone and γ-valerolactone react with 1-alkenes such as 1-octene and 1-decene, in the presence of cupric oxide as initiator to form the corresponding 2-n-alkyl-γ-butyrolactone and 2-n-alkyl-γ-valerolactone. Yields of these 1 : 1 adducts vary between 41 and 82% and depend on the lactone to 1-alkene molar ratio and on the procedure used for preparation of the metal oxide. The most efficient is the cupric oxide obtained by oxidation of copper powder in a stream of oxygen at 300°C or by a similar oxidation of a $CuO-Cu_2O-Cu$ mixture resulting from cupric oxide during the radical addition reaction.

Lactones can add to alkenes under the action of light and UV irradiation or in the presence of organic peroxides[1]. Di-tert-butyl peroxide (DTBP) proved to be suitable initiator for the addition of γ-butyrolactone to 1-alkenes (155 – 160°C; 5 h) producing the corresponding 2-n-alkyl-γ-butyrolactones in 50 – 80% yields[2]; UV irradiation and light were less effective and the yields of 1 : 1 adducts varied between 42 and 52% (ref.[3]).

In the preceding communications of this series, we reported addition reactions of nitriles[4], dicarboxylic acid esters and β-diketones[5] to 1-alkenes in the presence of metal oxides as initiators; the corresponding 1 : 1 adducts were obtained in good to excellent yields. In this work we summarize the results of investigation of the initiating activity of metal oxides in the addition of lactones to 1-alkenes.

We have found that γ-butyrolactone reacts with 1-alkenes such as 1-octene and 1-decene, best in the presence of cupric oxide (sample A, see Experimental), to form the corresponding 2-n-alkyl-γ-butyrolactone (Scheme 1, R = H, R^1 = n-C_6H_{13}, n-C_8H_{17}) in yields amounting up to 82% (Fig. 1). Other metal oxides such as MnO_2, Ag_2O, AgO and nickel peroxide exhibited very low initiating activity and selectivity and the yield of 1 : 1 adducts did not exceed 15%; the use of PbO_2 resulted in decomposition of γ-butyrolactone. As it is obvious from Fig. 1, the yield of 2-n-decyl-γ-butyrolactone produced by the reaction of γ-butyrolactone with 1-decene (Sche-

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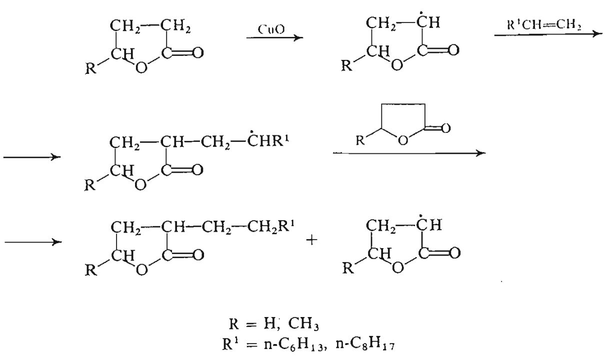

SCHEME 1

me 1, R = H; $R^1 = n\text{-}C_8H_{17}$) depends strongly on the lactone to alkene molar ratio; by changing the molar ratio of both reactants from 10 : 1 to 100 : 1, the yield of the 1 : 1 adduct could be increased from 16 to 82%. Addition reactions of γ-butyrolactone to alkenes are known to yield the corresponding 2-n-alkyl-γ-butyrolactone as the major product along with a smaller amount of the corresponding 4-n-alkyl derivative[1]. Gas chromatographic analysis of our product and comparison with the mixture containing known amounts of authentic samples of 2-n-decyl-γ-butyrolactone and 4-n-decyl-γ-butyrolactone revealed that the 1 : 1 adduct prepared by an addition

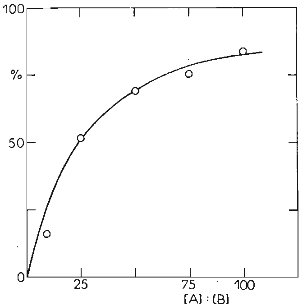

FIG. 1

Effect of the γ-Butyrolactone (A) to 1-Decene (B) Molar Ratio upon the Yield of 2-n-Decyl-γ-butyrolactone (including 4-n-decyl-γ-butyrolactone present in ≦2·7% by weight) in the Reaction Initiated by Cupric Oxide Prepared by Oxidation of Copper Powder

The 1-decene to cupric oxide molar ratio = 1 : 3; final conversion of 1-decene 93–97% temperature 198–200°C; reaction on a 9 mmol 1-decene scale.

reaction initiated with cupric oxide (sample A) was contaminated by only 2·7% of 4-n-decyl-γ-butyrolactone, as compared to 5·4% of the same compound which was formed in the presence of DTBP (the molar ratio γ-butyrolactone to 1-decene and DTBP = 10 : 1 : 0·2; 150°C, 1 h). In the cupric oxide (sample A) initiated addition reaction, γ-valerolactone was less reactive than γ-butyrolactone and afforded the 1 : 1 adduct (Scheme 1; $R = CH_3$; $R^1 = n\text{-}C_8H_{17}$) in 41% yield.

In accordance with an earlier observation[6], already preliminary experiments showed that the rate of addition of lactones to 1-alkenes depends on the origin of cupric oxide samples. Special attention has therefore been paid to the determination of the initiating activity of cupric oxide in dependence on the procedure employed for its preparation. As inferred from comparison of the initial rates for the addition of γ-butyrolactone to 1-decene which was followed by 1-decene consumption (Fig. 2), the cupric oxide (sample A; surface area 1·7 m^2/g) prepared by direct oxidation of copper powder (surface area 1·2 m^2/g) in a stream of oxygen (240 ml/h) at 300°C was twice as active as the oxide (sample B, surface area 44 m^2/g) obtained from copper sulphate by precipitation with potassium hydroxide. The cupric oxide (sample A) prepared by the oxidation of metallic copper exhibits increased activity, despite of its 37fold smaller surface area; this indicates that surface reactions do not play a significant role or that other more important effects apply overshadowing the effect of participation of the oxide surface on the overall addition reaction. Preliminary spectroscopic measurements indicated that cupric oxide (sample B) prepared by precipitation contains trace amounts of sulphate ions which could not be obviously removed even by a most careful washing of the hydrated cupric oxide so formed; one of the possible explanations for the reduced activity of cupric oxide of this type can thus be the presence of sulphate ions which may function as trappers of the starting radicals.

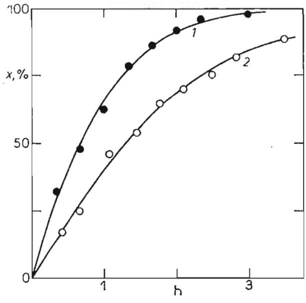

FIG. 2

Time Dependence of 1-Decene Conversion in the Reaction with γ-Butyrolactone Initiated by Cupric Oxide Prepared by Oxidation of Copper Powder *1* and by Alkaline Precipitation from a Copper Sulphate Solution *2*

Molar ratio of γ-butyrolactone to 1-decene and to CuO = 50 : 1 : 3; temperature 198 to 200°C; reaction on a 9 mmol 1-decene scale.

A relatively high molar concentration of cupric oxide in relation to 1-octene or 1-decene (3 : 1) was necessary to achieve high conversions of 1-alkenes. This fact can be explained by the difference between homogeneous (DTBP) and heterogeneous (CuO) initiation system and by a short kinetic chain of the radical addition of lactones to 1-alkenes initiated by cupric oxide. A similar situation was already encountered by us in the addition reactions of nitriles[4]. During the reaction of lactones with 1-alkenes, approximately the half amount of cupric oxide is reduced to cuprous oxide and partially also to metallic copper. The advantage of this new initiating system is the easy regeneration of the initiator which comprises oxidation of a $CuO–Cu_2O–Cu$ mixture in a stream of oxygen or air as well as the possibility of the reuse of the so formed cupric oxide in the next and subsequent reaction cycles. By this, cupric oxide initiation differs significantly from that effected by DTBP known to decompose irreversibly to form the tert-butoxy and methyl radicals starting the initiation step.

EXPERIMENTAL

Chemicals. Cupric oxide (sample A; surface area 1·7 m^2/g) was prepared by careful oxidation of copper powder (surface area 1·2 m^2/g) in a stream of oxygen (240 ml/h) at 300°C. The second sample of the oxide (sample B; surface area 44 m^2/g) was obtained by gradual addition of an aqueous copper sulphate solution to a hot (95°C) aqueous solution of potassium hydroxide. The dark brown hydrated cupric oxide was filtered off, washed with water until disappearance of K^+ and SO_4^{2-} ions and then dried *in vacuo* at 90°C. 1-Octene, 1-decene, γ-butyrolactone and γ-valerolactone were commercial products (Fluka A. G., Buchs, Switzerland) which were redistilled before use; their purity was checked by gas chromatography. 4-Decyl-γ-butyrolactone was prepared by a radical addition of acetic acid to 1-dodecene and simultaneous lactonisation in the presence of manganese(III) acetate[7]. Di-tert-butyl peroxide was a commercial product (Koch-Light, Ltd., London) and was used without further purification.

Analytical methods. Gas chromatographic analyses were made on Chrom 31 instrument (Laboratorní přístroje, Prague) equipped with a flame ionisation detector and a stainless steel column (1·7 m × 3 mm) packed with 7% Silicone OV-17 on Gas-Chrom Q (80—100 mesh). Separation of a mixture of 2-decyl-γ-butyrolactone and 4-decyl-γ-butyrolactone was effected using a column packed with 5% GE XE 1150 phase on Chromaton N. ^1H-NMR and IR spectra were recorded on Tesla BS 467—60 MHz spectrometer and Zeiss (Jena), Model UR 20, spectrophotometer, respectively.

Addition of lactones to 1-*alkenes.* Addition reactions were carried out in a 50 ml glass flask equipped with a magnetic stirrer, a thermometer, a reflux condenser and a neck for sample removal. The course of the reaction taking place under normal pressure and in an atmosphere of nitrogen was followed by determining time consumption of 1-octene and 1-decene by gas chromatographic analysis of the samples withdrawn at given time intervals from the reaction mixture. Yields of 1 : 1 adducts were determined by gas chromatographic analysis using n-octadecane as the internal standard; because of its limited solubility, the reaction mixture was homogenised by adding acetone before analysis. The preparation and isolation of 1 : 1 adducts are illustrated by the following typical experiments.

2-n-*Decyl-γ-butyrolactone.* A mixture containing 25·8 g (0·3 mol) of γ-butyrolactone, 0·84 g (6 mmol) of 1-decene and 1·44 g (18 mmol) of cupric oxide (sample A) was stirred and refluxed

(191—203°C) under nitrogen for 6 h. When 1-decene conversion attained 97% and the yield of the 1 : 1 adduct corresponded to 69% (GLC), the reaction mixture was cooled to ambient temperature; the partially reduced cupric oxide was filtered off, washed with acetone and thus isolated it contained after drying CuO 41%, Cu_2O 52% and Cu 7%. Solvent evaporation from combined filtrates and distillation *in vacuo* gave 0·72 g of a white product with b.p. 138—140°C/1 Torr and m.p. 34°C(ref.[2] b.p. 138—140°C/1 Torr, m.p. 36°C) which contained 97·3% of 2-n-decyl-γ-butyrolactone and 2·7% of 4-n-decyl-γ-butyrolactone. The yield of isolated mixture of both isomers was 53%. For $C_{14}H_{26}O_2$ (226·3) calculated: 74·3% C, 11·6% H; found: 74·0% C, 11·6% H. IR spectrum (neat): $\nu(C{=}O)$ 1 782 cm^{-1}. ^1H-NMR spectrum was identical with that reported earlier[3].

2-n-*Decyl-γ-valerolactone.* A mixture of 30 g (0·3 mol) of γ-valerolactone, 0·84 g (6 mmol) of 1-decene and 1·4 g (18 mmol) of cupric oxide (sample A) was stirred and refluxed (189—203°C) under nitrogen for 10 h. When the 1-decene conversion equaled to 80% and the yield of the 1 : 1 adduct corresponded to 41% (GLC), the reaction mixture was cooled to ambient temperature, the partially reduced cupric oxide was filtered off and washed with 10 ml of acetone. Solvent evaporation from combined filtrates followed by vacuum distillation of the residue gave 0·48 g of a colourless liquid which, according to gas chromatographic analysis, was 2-n-decyl-γ-valerolactone, b.p. 143—145°C/1 Torr; the yield of the isolated product was 33%. The amount of the 4-n-decyl derivative that could be eventually present in the product was not determined. For $C_{15}H_{28}O_2$ (240·4) calculated: 74·9% C, 11·7% H; found: 74·7% C, 11·6% H. IR spectrum (neat): $\nu(C{=}O)$ 1 776 cm^{-1}.

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