CONDENSATION OF α-ETHOXYACROLEIN WITH SECONDARY AMINES

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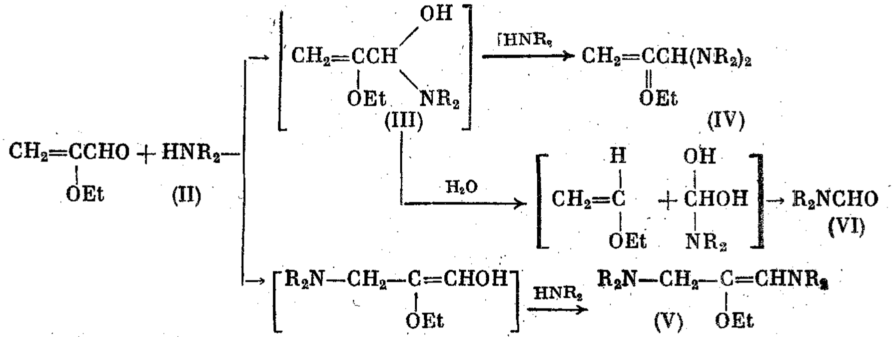
Secondary amines add to α,β-unsaturated aldehydes [1] and ketones [2] at the 1,4 positions. In the case of acrolein, subsequent condensation of the adduct occurs with a second amine molecule to form enediamines [1]. The presence of an α-alkoxy group in the acrylic system leads to the addition of a number of nucleophiles only at the 1,2 positions [3, 4].

We have found that, in contrast to primary amines, which react with α-ethoxyacrolein to give Schiff bases [3], piperidine and morpholine undergo 1,2 and 1,4 addition to form a mixture of 3,3- (IV) and 1,3-diamino-2-ethoxy-1-propenes (V) in 80-90% yields.

Propene (V) is obtained as a result of the condensation of the product of 1,4 addition with a second amine molecule. The ratio of these two pathways depends significantly on the nature of the amine: 1,2 addition predominates in the case of morpholine, while the 1,4 adducts are mainly formed in the case of more basic piperidine and dibutylamine.

In all cases, N-formylamine (VI) formed in about 3% yield was an additional unexpected reaction product. The formation of this product apparently is the result of intramolecular or hydrolytic cleavage of the C^2—C^3 bond in intermediate 3-amino-2-ethoxy-1-propen-3-ol (III). The alternative scheme involving the direct N-formylation is unlikely in light of the high stability of the C^2—C^3 bond. The N-formylamine yields are increased to 10% upon prolonged heating of the reaction mixture at reflux without removal of the water produced in the condensation. N-Formyldiethylamine is the major product (10-30% yield) in the reaction of diethylamine with α-ethoxyacrolein. The products of 1,2 and 1,4 addition are not formed, and the conversion of the starting aldehyde did not exceed 45-65%. This may be attributed to the low rate of the addition reaction since it was carried out at the boiling point of dimethylamine (55°C). However, upon carrying out the reaction at 95°C in a sealed ampul or using H_2CO_3 as a catalyst and water acceptor, the major product was again N-formyldiethylamine obtained in yields of 30% and 5%, respectively.



$NR_2 = NC_4H_8O$ (a); NC_5H_{10} (b); NBu_2 (c).

Thus, the reaction of secondary amines with α-ethoxyacrolein gives the formation of 1,2 addition products as well as nucleophilic 1,4 addition, which is rarely encountered for this type of system, with subsequent anhydrocondensation with a second amine molecule. The accompanying unexpected formation of N-formylamines is attributed to the weakness of the C^2—C^3 bond in the product of the addition of the amine at the carbonyl group. Such facile C—CHO bond cleavage has been reported previously only for aldehydes with highly electronegative groups in the α position such as chloral [5].

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EXPERIMENTAL

The PMR spectra were taken on a Jeol FX-90Q spectrometer at 89.95 MHz in $CDCl_3$, and the IR spectra were taken neat on a UR-20 spectrophotometer.

Condensation of α-Ethoxyacrolein (I) with Morpholine. a) A mixture of 5.0 g (50 mmoles) (I) and 8.7 ml (100 mmoles) morpholine in 20 ml benzene was heated at reflux for 2 h until no further water was liberated. A total of 0.7 ml (78%) water was distilled off. Removal of the solvent and the remaining starting reagents gave 11.4 g (89%) of a mixture of 3,3-dimorpholino-2-ethoxy-1-propene (IVa) and 1,3-dimorpholino-2-ethoxy-1-propene (Va). PMR spectroscopy indicated that the (IVa):(Va) ratio was 60:40. Vacuum distillation gave 9.2 g of a mixture of (IVa) and (Va) with bp 120-126°C (1 mm), n_D^{20} 1.4940. IR spectrum (ν, cm^{-1}): (IVa) 1620 (C=C), (Va) 1670 (C=C). PMR spectrum (δ, ppm): (Va) 1.22 t (CH_3), (IVa) 1.32 t (CH_3, $^3J \sim 7$ Hz), 2.45 m, 2.92 m [morpholine $N(CH_2)_2$], 2.70 s (CH_2N), 3.62 m (OCH_2), 3.97 d, 4.10 d (CH_2=, $^2J = 1.7$ Hz), 4.03 s (CH), 4.83 s (CH=). Found: C 61.19; H 9.42; N 11.06%. Calculated for $C_{13}H_{24}N_2O_3$: C 60.94; H 9.37; N 10.94%. N-Formylmorpholine (3% yield) was indicated by gas—liquid chromatography with 5% XE-60 silicone on Chromaton N-AW or 15% Carbowax 20M on Chromaton N-AW-DMCS.

b) A mixture of 5.0 g (50 mmoles) (I) and 8.7 ml (100 mmoles) morpholine in 25 ml benzene was heated at reflux without distilling off the water formed. Vacuum distillation gave 7.9 g of a mixture of (IVa), (Va), and N-formylmorpholine, bp 76-121°C (1 mm). The yield of N-formylmorpholine was about 10%, as indicated by gas—liquid chromatography.

The condensation of (I) with piperidine was carried out analogously to procedure *a* from 5.0 g (50 mmoles) (I) and 10 ml (100 mmoles) piperidine. Evaporation of the solvent and of the unreacted starting reagents gave 11.8 g (94%) of a 15:85 mixture of (IVb) and (Vb), as indicated by PMR spectroscopy. Vacuum distillation gave 9.6 g of this mixture with bp 110-117°C (1 mm), n_D^{20} 1.4945. IR spectrum (ν, cm^{-1}): (IVb) 1620 (C=C), (Vb) 1670 (C=C). PMR spectrum (δ, ppm): (Vb) 1.20 t (CH_3), (IVb) 1.27 t (CH_3, $^3J \sim 7$ Hz), 1.48 m [$(CH_2)_3$], 2.39 m, 2.88 [piperidine $N(CH_2)_2$], 2.77 s (CH_2N), (IVb) 3.65 q (OCH_2), (Vb) 3.85 q (OCH_2, $^3J \sim 7$ Hz), 3.94 m (CH_2=, CH), 4.87 s (CH=). Found: C 71.44; H 11.24; N 10.96%. Calculated for $C_{15}H_{28}N_2O$: C 71.43; H 11.15; N 11.15%. Gas—liquid chromatography of the reaction mixture indicated the formation of about 1% N-formylpiperidine.

Condensation of (I) with Dibutylamine. A mixture of 5.0 g (50 mmoles) (I) and 12.9 g (100 mmoles) dibutylamine in 25 ml benzene was heated at reflux for 4 h until there was no further water formation; 0.55 ml (61%) water was distilled off. Removal of the solvent and the unreacted starting reagents gave 11.6 g (68%) 1,3-bis(dibutylamino)-2-ethoxy-1-propene (Vc). Vacuum distillation gave 8.3 g (Vc) with bp 82-142°C (1.5 mm), n_D^{19} 1.4560. IR spectrum (ν, cm^{-1}) (Vc) 1680 (C=C), 1620 sh. PMR spectrum (δ, ppm) 0.86 t (butyl CH_3, $^3J \sim 7$ Hz), 1.26 m [butyl $(CH_2)_2$ and ethyl CH_3], 2.37 m, 2.78 m [butyl $N(CH_2)_2$], 2.85 s (CH_2N), 3.83 q (OCH_2, $^3J \sim 7$ Hz), 4.86 s (CH=). Found: C 73.42; H 12.90; N 7.95%. Calculated for $C_{21}H_{44}N_2O$: C 74.12; H 12.94; N 8.24%. A yield of about 1% N-formyldibutylamine was indicated in the reaction mixture by gas—liquid chromatography.

Reaction of (I) with Diethylamine. a) A mixture of 5.0 g (50 mmoles) (I) and 10.3 ml (100 mmoles) diethylamine in 15 ml benzene was maintained in a sealed ampul for 5 h at 95°C. Gas—liquid chromatography on columns packed with 15% Carbowax 20M on Chromaton N-AW-DMCS and SKTFT-50 on Chromaton N-AW-HMDS indicated that the conversion of (I) was 45% and the yield of N-formyldiethylamine was 10%. Tar formation was observed during the reaction.

b) A mixture of 5.0 g (50 mmoles) (I) and 10.3 ml (100 mmoles) diethylamine in 15 ml benzene was heated at reflux for 5 h at 70°C and then, in light of the incomplete conversion of (I), the mixture was left for 3 months at about 20°C. Gas—liquid chromatography indicated that the conversion of (I) was 65% and the yield of N-formyldiethylamine was 30%.

c) A suspension of 5.0 g (50 mmoles) (I), 10.3 ml (100 mmoles) diethylamine, and 3.5 g (25 mmoles) K_2CO_3 in 15 ml benzene was maintained for 5 h at 70°C. Gas—liquid chromatography indicated that the conversion of (I) was 40% and the yield of N-formylethylamine was 5%.

CONCLUSIONS

Morpholine, piperidine, and dibutylamine undergo both 1,2 and 1,4 addition to α-ethoxyacrolein to form a mixture of 3,3- and 1,3-diamino-2-ethoxy-1-propenes. The N-formyl derivative of the starting amine is a side product. The reaction of α-ethoxyacrolein with diethylamine gives only splitting of the C—C bond and formation of N-formyldiethylamine.

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INNER-SPHERE MECHANISM FOR THE REDUCTION OF Co(III) COMPLEXES WITH α-HYDROXYLAMINOOXIMES ON A MERCURY ELECTRODE

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Criteria have been developed for distinguishing between inner-sphere and outer-sphere mechanisms for electron transfer from an electrode to metal complexes in aqueous media [1-3]. In the case of an inner-sphere mechanism, the structure of the internal layer of solvent molecules directly adjacent to the electrode (the electrode "coordination sphere") is destroyed by the reacting species in the transition state. Such ligands as Cl^-, Br^- and SCN^- are capable of acting as bridging groups due to specific adsorption on the electrode—water boundary surface. In the outer-sphere mechanism, electron transfer occurs without the participation of bridging groups.

A study of the electrochemical reduction of Co(III) complexes with α-hydroxylaminooximes (α-HAO) in dimethylformamide and anionic ligands capable of forming a bridging bond with the electrode showed that the transfer of the first electron is quasireversible. In a continuation of this work, we attempted to clarify whether the first electron transfer in the electrochemical reduction of Co(III) complexes with α-HAO in nonaqueous media occurs by an inner-sphere or outer-sphere mechanism.

EXPERIMENTAL

The Co(III) complexes with α-HAO $[Co(L'-H)_2X]$, where L' is the ligand form dehydrogenated at the N—H bond, X = Cl^-, Br^-, I^- and NO_3 were described by D'yachenko et al. [5]. The starting α-HAO have the formula $Me_2C(NHOH)C({=}NOH)R$, where R = Ph and Me.

The electrochemical measurements were carried out in anhydrous DMF with 0.1 M $(Et)_4NClO_4$ as the base electrolyte. The DMF sample was dried over K_2CO_3 and distilled with absolute benzene (10 vol.%). The base electrolyte was purified by crystallization thrice from ethanol. The cyclic volt—amperograms were taken on a dropping mercury electrode according to Kemule and on a platinum electrode. The depolarizer concentration was $1 \cdot 10^{-3}$ M. Oxygen was removed by flushing with a helium stream for 20 min.

RESULTS AND DISCUSSION

The chelates of Co(III) ions with α-HAO and anionic ligands capable of serving as bridges in electrode reactions (Cl^-, Br^-, I^-, and NO_3^-) studied in our previous work [4] give anodic and cathodic peaks on Kemule cyclic volt—ampere curves. However, Weaver's criterion based on the change in k_S at different concentrations of added iodide ion is inapplicable in this case. The addition of the corresponding Cl^- or Br^- ion as their tetraalkylammonium salts to solutions of $[Co(L'{-}H)_2CCl]$, R = Me (I), and $[Co(L'{-}H)_2Br]$, R = Ph (III), in DMF containing $(Et)_4NClO_4$ (at constant solution ionic strength) led to the disappearance of the anodic peaks even at $1 \cdot 10^{-5}$ M halide ion concentration. Hence, k_S cannot be found by a method in which the difference in the potentials of the cathodic and anodic peaks on a mercury electrode is used [6],

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