CONCLUSIONS

1. The MINDO/2 method was used to carry out a quantum-chemical study of the addition of acetals to vinyl ethers in the presence of an acid catalyst, and it was shown that despite the previously proposed mechanism, the reaction does not proceed via a step of carbocation formation.

2. A reaction mechanism has been proposed with intermediate participation of an acetal-catalyst-vinyl ether reaction complex.

LITERATURE CITED


REACTIONS OF CARBONYL COMPOUNDS IN THE PRESENCE OF PHASE-TRANSITION CATALYSTS.

4. STUDY OF THE REACTION OF ACETOACETIC ESTER WITH 1-CHLORO-3-METHYL-2-BUTENE IN THE PRESENCE OF VARIOUS ALKALINE AGENTS

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The alkylation of carbonyl compounds with alkyl halides proceeds through a step involving deprotonation. This reaction is usually carried out in anhydrous media in the presence of alkali metals or their hydrides or alkoxides [1]. Extractive alkylation [2] and alkylation in a two-phase catalytic system [3-5] are other methods. The latter method makes it possible to alkylate carbonyl compounds at high rates and does not require anhydrous solvents or large amounts of quaternary ammonium salts. In the present research we studied the reaction of acetoacetic ester (AAE) with 1-chloro-3-methyl-2-butenen [prenyl chloride (PC)] in the presence of various alkaline agents and triethylbenzylammonium (TEBA) chloride (QCl) under heterogeneous conditions.

EXPERIMENTAL

According to the results of gas-liquid chromatography (GLC), the PC contained 83.5% 1-chloro-3-methyl-2-butene and 16.5% 3-chloro-3-methyl-1-butene; it was obtained in 60% yield by the method in [6] by hydrochlorination of isoprene and had bp 59-60°C (110 mm). The AAE was distilled prior to the experiments and had bp 62-63°C (14 mm) and nD 1.4200. The benzene was purified thoroughly by the method in [7], the KOH was granulated analytical-grade material, the K2CO3 was analytical-grade material, and the water was distilled. The TEBA chloride was obtained in 75% yield from triethylamine and PhCH2Cl [8] and had mp 188°C. Monoprenyl- (I) and diprenyl-substituted (II) AAE were synthesized by the method in [9]. Compound I had bp 140°C (50 mm) and nD 1.4431. PMR spectrum (CCL4, δ, ppm): 1.19 t (CH3CH2), 1.58 br s [(CH3)2C-], 2.065 s [CH2C(O)], 2.38 br t (=CHCH2CH2), 3.23 t (=CH), 4.06 q (CH2C in COOEt), and 4.92 t (C-CH). Compound II had bp 197°C (70 mm) and nD 1.4671. PMR spectrum (CCL4, δ, ppm): 1.15 t (CH3CH2), 1.6 br d [(CH3)2C =], 1.955 s [CH3C(O)], 2.405 d (≡CHCH2CH2),...
4.08 q (CH2C in COOEt), and 4.8 t (C=CH). Compounds I and II were used to identify the peaks on the chromatograms of the reaction mixtures.

The formation of I, II, and 2-methylhept-2-en-6-one (MH) was observed during the reaction of AAE with PC in the presence of alkaline condensing agents:

\[
H_2C_2OOCCH_2CCH_2 \rightarrow H_2C_2OOCCHC=CH_2 + H_2C_2OOCCHR_2CCH_3 + RCH_2COCH_3
\]

The reaction products were analyzed by GLC with a Khrom-4 chromatograph under conditions with temperature programming at 6 deg/min from 50 to 230°C with 2.4 m by 0.5 cm glass columns filled with Chromaton N-AM-DMCS (0.2-0.25 mm) (treated with hexamethyldisiloxane) and 15% Reoplex. The following components of the reaction mixture were separated: ether, acetone, 3-chloro-3-methyl-1-butene, C6H5OH, C6H6, PC, C13H28, MH, AAE, I, and II.

The internal-standard method was used for the quantitative calculation of the chromatograms. The calibration coefficients for the principal components of the reaction mixture were first determined: MH [molecular weight (mol. wt.) 126] 1.3, I (mol. wt. 198) 1.83, and II (mol. wt. 266) 1.31. Tridecane (C13H28) served as the standard for GLC. The error in GLC analysis was ±5%.

The effect of various condensing systems was studied: A) solid K2CO3 and TEBA chloride; B) solid KOH; C) solid KOH and TEBA chloride; D) 50% aqueous K2CO3; E) 50% aqueous K2CO3 and TEBA chloride; F) 50% aqueous KOH; G) 50% aqueous KOH and TEBA chloride. A 5-g sample of K2CO3 or KOH and 0.23 g of TEBA chloride were used.

The use of solid condensing systems (A, B, and C) leads to the formation of a heterogeneous two-phase solid-liquid system, while the use of aqueous alkaline phases leads to the formation of a heterogeneous two-phase liquid-liquid system. Potassium carbonate, the potassium salt of prenylacetoacetic acid, and potassium derivatives of AAE and I, which precipitate to give a solid phase, are formed during the alkylation and decarboxylation reactions. The compositions of the organic and aqueous phases also change during the reaction due to the liberation of water and acetone, as well as I, II, and MH.

Condensing system D is an aqueous solution of K2CO3 and KOH, which is formed during hydrolysis of the salt. In conformity with \( K_D = K_{H_2O}/K_{H_2CO_3} \) = 2.26*10^-4 [10], the OH^- concentration in 50% aqueous K2CO3 solution is 0.035 g-ion/liter. The principal properties of system D are determined by the presence in it of CO3^- and OH^- ions. Our thermodynamic calculation of reactions (I) and (II) shows that \( K_{eq}(I) = 117,000 \), and \( K_{eq}(II) = 0.178 \):

\[
\begin{align*}
OH^- + HA &\rightleftharpoons H_2O + A^- \quad K_{eq}(I) = K_{H_2O}/K_{HCO_3^-} \\
CO_3^- + HA &\rightleftharpoons HCO_3^- + A^- \quad K_{eq}(II) = K_{H_2O}/K_{HCO_3^-}
\end{align*}
\]

where HA is AAE, A^- is the AAE anion, \( K_{H_2O} = 1.80*10^{-16} \) is the dissociation constant of H2O [10], \( K_{HCO_3^-} = 5.6*10^{-11} \) is the second dissociation constant of H2CO3 [10], and \( K_{HA} = 2.1*10^{-11} \) is the dissociation constant of AAE [11]. The differences in the catalytic properties of systems D and F are due to the low OH^- concentration in system D and the enormous difference in the \( K_{eq}(I) \) and \( K_{eq}(II) \) values in these systems.

Condensing system E is system D with the addition of 0.23 g of TEBA chloride. Potassium carbonate dissolves and a new upper organic layer is formed when 5 g of solid K2CO3 is added to a solution of 0.23 g of TEBA chloride in 5 ml of water:

\[
K_2CO_3 + H_2O \rightleftharpoons KHCO_3 + KOH \\
KOH + QCI \rightleftharpoons Q^+OH^- + KCl
\]

In conformity with the general concepts of the possible pathways of conversion of K2CO3, KOH, and TEBA chloride, as well as the data in [12], the upper layer is the TEBA base (Q^+OH^-). It has alkaline properties, a weak amine odor, and a yellowish color. The TEBA base is quite soluble in water, alcohol, and acetone but is insoluble in benzene, PC, and a mixture of AAE with benzene. The organic base is also formed in the reaction of TEBA chloride with aqueous solutions of alkalies and is liberated from 25-30% aqueous solutions of KOH,