ELECTROCHEMICAL CHLORINATION OF ETHYL ACETOACETATE AND THE FORMATION OF ETHYL 2,2,4-TRICHLOROACETOACETATE

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Ethyl acetoacetate (I) reacts under mild conditions with chlorinating agents to give 2-chloro derivatives. Virtually quantitative preparations of $CH_3COCHClCO_2C_2H_5$ (II) [1] and $CH_3COCCl_2CO_2C_2H_5$ (III) [2, 3] have been described by the reaction of (I) with sulfuryl chloride. The reaction with molecular chlorine proceeds just as smoothly [4]. The formation of 4-chloro derivatives has not been observed in the chlorination of (I).

The electrochemical chlorination of (I) in aqueous medium at $12-60^{\circ}C$ gave about 3% ethyl 2,2,4-trichloroacetoacetate (IV) in addition to the major product, (III). Our volt-amperometric measurements have shown that (I) is electrochemically inactive under chlorination conditions. Only chlorine generation takes place on the anode. Thus, the formation of chloro derivatives (I) is the result not of an electrode reaction, but rather subsequent chemical reactions. Under the electrochlorination conditions, (III) is not further chlorinated. Thus, there are only two variants possible for the formation of (IV), namely, by rearrangement of (II) or (III) similar to that reported for $CH_3COCHBrCO_2C_2H_5$ [5, 6] or the competitive chlorination of (I) at C⁴.

Product (IV) is not formed upon heating (II) and (III) or maintaining these compounds for a prolonged period at 12-60°C in the electrolyte with the passage of current. Thus, rearrangement of the 2-chloro derivatives does not occur under these conditions. This is in accord with the results of Srendsen and Boll [5]. Comparison of the results of the electrochemical chlorination of (I) and (II) obtained independently according to a standard procedure [1] showed that (IV) is formed in the former case in much greater amounts. The chlorination of (I) by electrochemically generated chlorine could not be stopped at the step involving the formation of the monochloro product. Even when the reaction was carried out with a five-fold excess of starting (I) at 0-5°C, (III), (IV), $CH_2ClCOCH_2CO_2C_2H_5$ (V), and $CH_2ClCOCHClCO_2C_2H_5$ (VI) were detected in addition to (II). These results unequivocally indicate, in our opinion, that this reaction is characterized by competitive chlorination.

EXPERIMENTAL

The identification of the products of the chlorination of (I) and analysis of the reaction mixtures were carried out using PMR spectroscopy on a Tesla BS-467 spectrometer at 60 MHz with TMS as the internal standard in CCl₄ and by gas-liquid chromatography on an LKhM-80 chromatograph using a 3 m \times 3-mm column packed with 5% SE-30 on Chromaton N-AW-DMCS (0.16-0.3 mm). Standard samples of (V) and (VI) were prepared according to reported procedures [7, 8].

The electrolyzer had separate cathodic and anodic spaces with a $100-cm^2$ rutheniumtitanium oxide anode, $40-cm^2$ cathode, and ceramic diaphragm. The anolyte was 600 ml of a solution of 117 g (2 moles) sodium chloride and 65.1 g (0.5 mole) (I). The catholyte was 80 ml 20% hydrochloric acid. A current of 7 A was passed with strong stirring of the anolyte at 22-25°C for 8.5 h (the total electricity passed was 59 A•h) until chlorine appeared at the electrolyzer outlet. The reaction mixture was stirred without current for an additional 40 min. The anloyte was neutralized to pH 7 by the addition of calcium carbonate and cooled to 10°C. The organic layer was separated. The aqueous layer was extracted with 200 ml CH₂Cl₂. The combined organic layer and the extract were dried over Na₂SO₄ and CH₂Cl₂ was distilled off. PMR spectroscopy and gas-liquid chromatography showed that the residue (97.2 g) consisted of (III) with a minor amount of (IV) and traces of (II). Distillation gave 91.3 g (92%) (III), bp 92-94°C (12 mm) [2] and 3.5 g (3%) (IV), bp 90-91°C (3 mm), n_D^{2°} 1.4730. PMR spectrum (δ , ppm): 4.65 s (2H, CH₂Cl), 4.33 q (2H, OCH₂), 1.28 t (3H, CH₃). Found: C, 31.28; H 3.10; Cl 45.10%. Calculated for C₆H₇Cl₃O₃: C 30.87; H 3.02; Cl 45.55%.

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CONCLUSIONS

The electrochemical chlorination of ethyl acetoacetate in aqueous media proceeds at C^2 and, partially, at C^4 to give ethyl 2,2-dichloroacetoacetate and small amounts of ethyl 2,2,4-trichloroacetoacetate.

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SYNTHESIS OF ALKOXYCARBONYLAMINOADAMANTANES AND ACETYLAMINO-

ADAMANTANES IN NITRIC ACID

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Adamantane [1] and alkyladamantanes [2] react with 96-100% nitric acid to undergo oxinitration. In previous work [3], we proposed a likely mechanism for this reaction involving the formation of an adamantyl cation with its subsequent stabilization by the predominant nucleophilic species in the reaction medium, which leads to the corresponding nitroxy derivatives. Thus, there is a possibility for the reaction of the carbenium ion with other nucleophiles in the nitric acid medium.

In order to check this proposal, we studied the reaction of nitroxyadamantanes with carbamate esters and acetamide in nitric acid.

The reaction of adamantanes (Ia)-(Id) with a 10-25-fold molar excess of nitric acid with the subsequent addition of methyl(ethyl)urethane to the solution obtained gives alkoxycarbon-ylaminoadamantanes (IIa)-(IIe), which are the products of the corresponding carbenium ions with carbamate esters. Competition of other nucleophilic species (nitric acid or nitrate ion) in this case does not play a significant role since nitroxyadamantanes are protonated in nitric acid with the equilibrium formation of an adamantyl cation (for 100% nitric acid, $pH_0 = -6.3$ [4]).

We should note the formal contradiction between the synthesis of (IIa)-(IIe) in nitric acid and the finding of the replacement of the urethane group by the nitrate group in the same medium [5]. The sharp drop in the acidity of the reaction mixture upon the addition of urethane due to its partial decomposition in nitrosation and nitration reactions serves here as an explanation.

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