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 ACETYLAMINOADAMANTANES 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 alkoxycarbonylaminoadamantanes (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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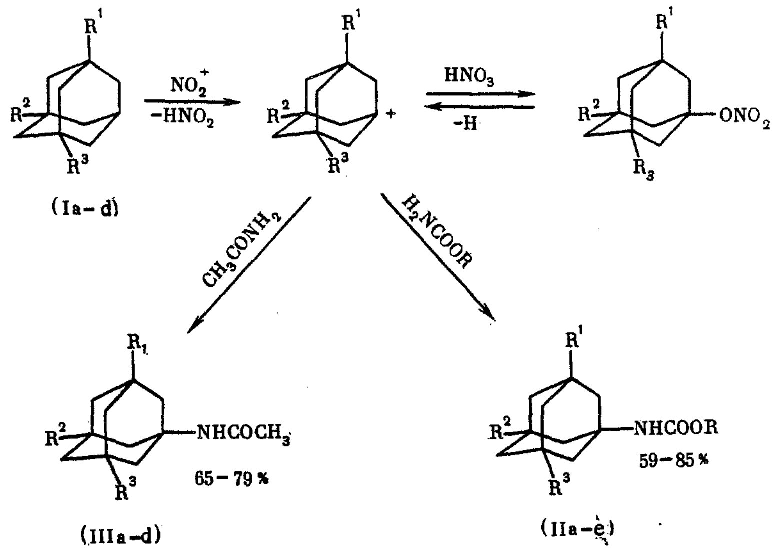

(I)–(III): $R = C_2H_5$, $R^1 = R^2 = R^3 = H$(a); $R = C_2H_5$, $R^1 = CH_3$, $R^2 = R^3 = H$(b); $R = C_2H_5$, $R^1 = R^2 = CH_3$, $R^3 = H$(c); $R = C_2H_5$, $R^1 = R^2 = R^3 = CH_3$(d); $R = CH_3$, $R^1 = R^2 = R^3 = H$(e).

Acetylaminoadamantanes (IIIa)-(IIId) are formed by the reaction of adamantanes (Ia)-(Id) with nitric acid and then with a six-fold excess of acetamide at 120°C. This reaction does not proceed without heating, apparently due to the significant protonation of acetamide in nitric acid.

The corresponding N-adamantylation products are not formed with 1-X-adamantanes (X = CO_2H, CH_2CO_2H, and ONO_2) as the starting compounds. This failure is apparently related to the lower rate of adamantylation in comparison with the rates of nitrosation, nitration, and hydrolysis of urethanes and acetamide under the reaction conditions. This may also be used to explain the failure of N-substituted urethanes and amides to undergo adamantylation in nitric acid medium.

EXPERIMENTAL

The IR spectra were taken neat and in KBr pellets on an IKS-29 spectrophotometer. The PMR spectra were taken on a Bruker WP-80DS at 80 MHz in DMSO-d_6 with HMDS as the internal standard.

1-Methoxycarbonylaminoadamantane (IIe). A sample of 7 g (0.052 mole) adamantane was added to 20 ml (0.48 mole) nitric acid (d 1.5) at 25°C, maintained for 15 min, and 15 g (0.2 mole) methyl carbamate was added at 30°C. This reaction mixture was maintained for 1 h and poured onto ice. The precipitate formed was filtered off, washed with water, dried, and recrystallized from hexane to give 4.5 g (84%) (IIe), mp 119°C [6]. IR spectrum (ν, cm^{-1}): 3310 (NH), 1720 (C=O), 1525 (C–N + δNH). Analogous procedures gave (IIa)-(IId).

1-Ethoxycarbonylaminoadamantane (IIa) was obtained in 81% yield, mp 90.5-91.0°C (from hexane). IR spectrum (ν, cm^{-1}): 3340 (NH), 1705 (C=O), 1535 (C–N + δNH). PMR spectrum (δ, ppm): 1.08 t (CH_3), 1.40-2.05 m (Ad), 3.87 q (CH_2), 6.54 s (NH). Found: N 6.10%. Calculated for $C_{13}H_{21}NO_2$: N 6.28%.

1-Ethoxycarbonylamino-3-methyladamantane (IIb) was obtained in 65% yield, bp 164°C (15 mm), n_D^{20} 1.4488. IR spectrum (ν, cm^{-1}): 3365 (NH), 1715 (C=O), 1525 (C–N + δNH). PMR spectrum (δ, ppm): 0.74 s (CH_3), 1.08 t (ethyl CH_3), 1.12-2.14 m (Ad), 3.86 q (CH_2), 6.52 s (NH). Found: N 5.80%. Calculated for $C_{14}H_{23}NO_2$: N 5.91%.

1-Ethoxycarbonylamino-3,5-dimethyladamantane (IIc) was obtained in 85% yield, bp 156°C (9 mm), n_D^{20} 1.4914. IR spectrum (ν, cm^{-1}): 3355 (NH), 1710 (C=O), 1530 (C–N + δNH). PMR spectrum (δ, ppm): 0.75 s ($2CH_3$) 0.80-1.84 m (Ad + ethyl CH_3), 3.83 q (CH_2), 6.54 s (NH). Found: N 5.40%. Calculated for $C_{15}H_{25}NO_2$: N 5.58%.

1-Ethoxycarbonylamino-3,5,7-trimethyladamantane (IId) was obtained in 59% yield, bp 154°C (7 mm), n_D^{20} 1.4945. IR spectrum (ν, cm^{-1}): 3380 (NH), 1720 (C=O), 1530 (C–N + δNH). PMR spectrum (δ, ppm): 0.77 s ($3CH_3$), 0.95-1.38 m (Ad + ethyl CH_3), 3.87 q (CH_2), 6.53 s (NH). Found: N 5.30%. Calculated for $C_{16}H_{27}NO_2$: N 5.28%.

1-Acetylaminoadamantane (IIIa). A sample of 6.5 g (0.048 mole) adamantane was added to 20 ml (0.48 mole) nitric acid (d 1.5) at 25°C and maintained for 15 min. Then, 17 g (0.288 mole) acetamide was added at <30°C, maintained for 2 h at 120°C, and poured onto ice. The precipitate formed was filtered off, washed with water, dried, and recrystallized from hexane to give 6.7 g (73%) (IIIa), mp 149-151°C. IR spectrum (ν, cm^{-1}): 3220 (NH), 1645 (C=O), 1550 (C—N + δNH). Analogous procedures gave (IIIb)-(IIId).

1-Acetylamino-3-methyladamantane (IIIb) was obtained in 70% yield, mp 112.0-112.5°C (from hexane) [7]. IR spectrum (ν, cm^{-1}): 3220 (NH), 1640 (C=O) 1550 (C—N + δNH).

1-Acetylamino-3,5-dimethyladamantane (IIIc) was obtained in 79% yield, mp 110°C (from hexane) [7]. IR spectrum (ν, cm^{-1}): 3210 (NH), 1640 (C=O), 1550 (C—N + δNH).

1-Acetylamino-3,5,7-trimethyladamantane (IIId) was obtained in 65% yield, mp 194-195°C (from hexane) [7]. IR spectrum (ν, cm^{-1}): 3215 (NH), 1640 (C=O), 1545 (C—N + δNH).

CONCLUSIONS

The reaction of adamantanes with nitric acid and urethanes or acetamide gave 1-alkoxycarbonylaminoadamantane and 1-acetylaminoadamantane derivatives, respectively.

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