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REACTION OF ADAMANTANE-1-CARBOXAMIDES WITH OXALYL CHLORIDE: A NOVEL REARRANGEMENT OF ADAMANTANE SKELETON TO SPIROHOMOADAMANTANE (1)

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A new spiro-formation of oxazolidine-4,5-dione has been reported by us in the reaction of chrysanthemamide with oxalyl chloride (2). In the present communication, we wish to describe the results of the similar reactions of adamantane-1-carboxamide (Ia) and -carboxanilide (Ib) with oxalyl chloride, both of which resulted in the rearrangement to spirohomoadamantane oxazolidine-4,5-dione (Va and b) by the treatment of the primary adducts (IIIa and b) with ethanol.

Dropwise addition of excess oxalyl chloride to a stirred, ice-cooled suspension of Ia in methylene chloride caused immediate evolution of hydrogen chloride gas and simultaneous clarification of the reaction mixture. While being stirred for about 2 hr at room temperature (ca 20°), the clear solution became turbid and white precipitates, mp 98-100° (dec.), separated in 55-78% yields. The precipitates were very sensitive to moisture, heat and light, and the elemental analysis was consistent with a formula $C_{13}H_{16}O_3NCl$ (Found: C, 57.82; H, 5.72; N, 5.16. Calcd: C, 57.89; H, 5.98; N, 5.20.), to which four possible structure, IIa, IIIa, IVa, and Va (X=Cl), might be assignable. Since the spectral data of the precipitates were not reliable because of its instability, the direct ethanolysis and ammonolysis were carried out; treatment of the precipitates with absolute ethanol at room temperature afforded very insoluble white crystals, mp 194-195° (dec.), in 62% yield, the structure of which was characterized as 1-ethoxyhomoadamantane-2-spiro-2'-oxazolidine-4',5'-dione Va ($X=OC_2H_5$) by its analytical (Found: C, 64.12; H, 7.47; N, 4.79. Calcd for $C_{15}H_{21}O_4N$: C, 64.49; H, 7.58; N, 5.01.) and spectral

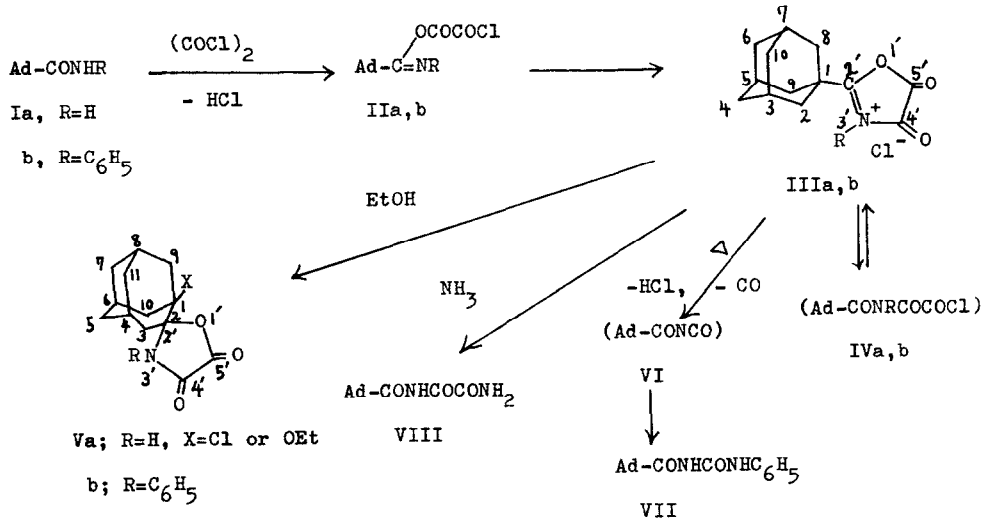
data; the infrared absorption bands (KBr) at 3200, 3090 (NH), 1815 and 1750 (C=O) cm^{-1} were similar to those of oxazolidine-4,5-dione (2) but perfectly different from those of acyl oxamate (3) and the ultraviolet absorption (EtOH) at 222 mμ (ε 5310) indicated the presence of -N-CO-CO- chromophore (2). In the nmr spectrum (4), the signals appeared at τ -1.04 (1 H, broad s, NH), 6.53 (2 H, q, J=7.2 Hz, OCH_2CH_3), 8.84 (3 H, t, J=7.2 Hz, OCH_2CH_3), 8.00 (3 H, broad s, methine protons at C-4, -6, and -8), 8.36 and 8.40 (12 H, methylene protons at C-3, -5, -7, -9, -10, and -11), all of which were in good accordance with those of Va. Similarly, the ammonolysis of the precipitates with conc. aqueous ammonia gave N-(1-adamantanoyl)oxalamide VIII, mp 219-220°. This structure was assigned on the basis of the elemental analysis (Found: C, 58.18; H, 7.84; N, 10.25. Calcd for $C_{13}H_{18}O_3N_2 \cdot H_2O$: C, 58.19; H, 7.51; N, 10.44.) and the following infrared data: 3320, 3220, 3040 (NH, NH_2), 1755, 1695, 1655 and 1635 (C=O) cm^{-1} bands support its acyl oxamate structure (3). All these results of the ammonolysis and ethanolysis indicate that the above precipitates should be characterized as 2'-(1-adamantyl)-oxazoline-4',5'-dione hydrochloride IIIa and its very complicated infrared absorption bands at 2800-2300 (NH^+), 1835 (C=O), 1760 (very strong and broad, C=O), and 1680 ($C=NH^+$) cm^{-1} were originated from the oxazoline-4,5-dione hydrochloride moiety, though the weak bands at 3180, 3090 (NH), and 1720 (shoulder, C=O) cm^{-1} might come from the mixed decomposed materials.

Since the acylisocyanate-formation from carboxamides and oxalyl chloride has been investigated extensively (5), IIIa was refluxed in methylene chloride for 28 hr and the formation of adamantanoylisocyanate VI was confirmed by the infrared inspection (by the presence of a band at 2260 cm^{-1} due to -N=C=O), which was not isolated but directly converted to the corresponding phenylurea derivative VII, mp 192-194°, in 48% yield, by the routine procedure. VII showed a satisfactory analysis (Found: C, 72.24; H, 7.72; N, 9.50. Calcd for $C_{18}H_{22}O_2N_2$: C, 72.45; H, 7.43; N, 9.39.), and the infrared (KBr) absorption bands at 3320, 3220, 3040 (NH), 1755, 1695 (weak) and 1655 (shoulder, C=O) cm^{-1} and nmr signals (4) at τ 8.03 (6 H, s), 8.07 and 7.98 (9 H, s, protons of 1-adamantyl group), 2.34 (5 H, phenyl protons), -0.77 and -0.05 (each 1 H, s, NH) were compatible with this structure VII.

The reaction mechanism of Ia with oxalyl chloride could be visualized as shown in Scheme 1: the first step, oxalyl chloride might attack the amide oxygen of Ia to afford an O-acylated derivative IIa under simultaneous evolution of hydrogen chloride gas and

the intramolecular acylation of the imino nitrogen of IIa could give an oxazoline-4,5-dione IIIa, which was assumed to be a key intermediate for Va (X=Cl or OC_2H_5), VI, and/or IVa, although the direct rearrangement of Ia to Va (X= Cl) could not be observed in its reaction with oxalyl chloride, presumably because of the low solubility of the intermediate IIIa. The high yield of Va ($X=OC_2H_5$) from IIIa indicates that the equilibrium between IIIa and IVa tautomers, if present, as observed in the similar cases (3), might be favored in IIIa and the formation of VI and VIII from IIIa could be reasonably explained (5). The facile rearrangement of IIIa to Va might be ascribable to the strong carbonium ion character of the 2'-carbon attached to adamantane skeleton of IIIa and a well known fact that the tertiary 1-homoadamantyl carbonium ion is much more stable than the primary 1-adamantylmethyl carbonium ion. Several examples of the rearrangement of adamantane skeleton to homoadamantane have been reported (6). However, the rearrangement caused by an iminium cation of adamantane to spirohomoadamantane has never been reported and therefore, this is the first example of it.

The similar reaction could be extended further to N-monosubstituted adamantane-1-carboxamide; treatment of adamantane-1-carboxanilide Ib with excess oxalyl chloride in 1,2-dichloroethane at 60° for 4 days gave an oil after evaporation of the excess oxalyl chloride and the solvent. The infrared spectrum showed no NH bands but two strong



Scheme 1

carbonyls at 1830 and 1760, and a weak band at 1680 ($C=N^+$) cm^{-1}, supporting the structure IIIb rather than IVb. This oil was heated in ethanol and cooling of the mixture afforded colorless crystals, mp 202-208° (dec.), in 56% yield. Its structure was confirmed as 1-ethoxyhomoadamantane-2-spiro-2'-N-phenyloxazolidine-4',5'-dione Vb ($X=OC_2H_5$) on the basis of the analytical (Found: C, 70.71; H, 6.91; N, 4.13. Calcd for $C_{21}H_{25}O_4N$: C, 70.96; H, 7.09; N, 3.94.) and spectral data; the infrared absorption bands at 1815 and 1740 cm^{-1} indicate the presence of an oxazolidine-4,5-dione ring and phenyl absorption bands at 1600, 740, and 690 cm^{-1} with no NH bands support Vb structure, while methyl N-chloroacetyloxanilate is shown to have three carbonyl bands at such lower frequencies as 1768, 1748 and 1720 cm^{-1}(3).

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