REACTION OF 1-ACETYLADAMANTANE WITH THIONYL CHLORIDE

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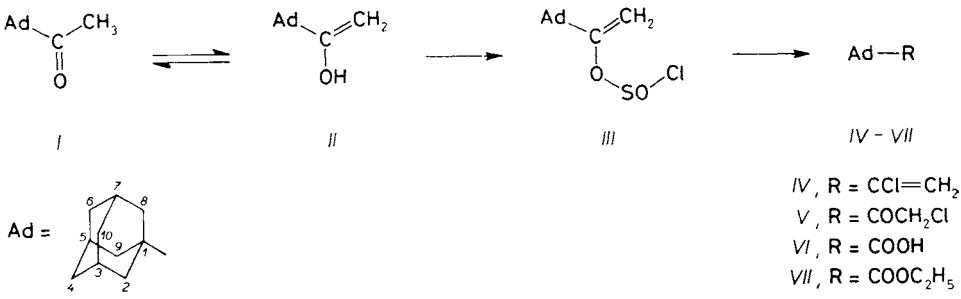
1-Acetyladamantane (*I*) reacts with thionyl chloride in the presence of pyridine to give 1-(1'-chloroethenyl)adamantane (*IV*). In the absence of pyridine, the same reaction affords a more complex mixture containing 1-adamantanecarboxylic acid (*VI*), its ethyl ester (*VII*), and 1-chloroacetyladamantane (*V*).

In our previous paper[1] we described the reaction of substituted adamantanones and diamantanones with thionyl chloride. The first reaction step consists probably in addition of hydrogen chloride to the carbonyl group leading to a chlorohydrin which reacts further with thionyl chloride by the same mechanism as alcohols, the final product being a geminal dichloro derivative. In contrast to adamantanone or diamantanone, 1-acetyladamantane (*I*) can exist in the enol form (*II*). Probably, compound *I* reacts in this form with thionyl chloride (Scheme 1) giving rise to the chlorosulfite *III* which, in the presence of pyridine, decomposes into sulfur dioxide and 1-(1'-chloroethenyl)adamantane (*IV*). On the other hand, in the absence of pyridine, the reaction is complex and its mechanism is so far not clear. The product mixture contains 1-chloroacetyladamantane (*V*) as well as compounds arising by cleavage of the double bond in the side chain of *III*, such as 1-adamantanecarboxylic acid (*VI*) and its ethyl ester *VII*.



SCHEME 1

The principal components were isolated from the reaction mixture by chromatography on silica gel and their structure was determined by mass, infrared, and ^1H and ^{13}C NMR spectroscopy. In the mass spectra (electron impact) of all the isolated compounds the peak of m/z 135 (Ad^+) is the most abundant whereas peaks due to molecular ions are either weak or entirely absent. The chemical ionization mass spectra of most compounds display the relatively abundant $(M + 1)^+$ ions. The ^1H and ^{13}C NMR spectra are in accord with the assumption that all the compounds are monosubstituted derivatives with the substituent attached to the tertiary carbon atom of the adamantane skeleton. The proton spectra exhibit three separated signals in the ratio 1 : 2 : 2, corresponding to protons on the three tertiary carbon atoms (C-3, C-5, C-7; Scheme 1) and on two types of secondary carbon atoms (C-2, C-8, C-9 and C-4, C-6, C-10). For the individual compounds there are only small differences in the chemical shifts of protons on the more distant carbon atoms (C-3 and C-4). The shift of the proton at C-2 depends strongly on the substituent. ^{13}C NMR spectra invariably exhibit one signal of quaternary (C-1), one signal of tertiary (C-3, C-5, C-7), and two signals of secondary (C-2, C-8, C-9 and C-4, C-6, C-10) carbon atoms. Also here the positions of the C-3 and C-4 signals in the spectra of individual compounds differ very little and the chemical shifts of C-1 and C-2 signals are markedly affected by the substituent. The final structural assignment was done on the basis of the remaining ^1H and ^{13}C NMR signals, the M^+ or $(M + 1)^+$ values and fragment ions higher than 135 in the mass spectra and characteristic bands in the IR spectra (CO, COO, CCl). All these data, together with the assignment are given in the Experimental.

EXPERIMENTAL

Analytical Techniques

Gas liquid chromatographic analyses were performed on a Chrom 5 chromatograph combined with a CI 100 integrator (Laboratorní přístroje, Prague); 1 200 mm glass column, internal diameter 3 mm, packed with 3% XF 1 150 on Chromaton N-AW-DMCS 0·10—0·16 mm, carrier gas nitrogen, column temperature 150°C, flame ionization detector. The elution data are given as relative retention times (t_r) related to the retention time of 1-acetyladamantane (*I*).

Mass spectra were measured on a JEOL DX 303 spectrometer (electron impact, 75 eV, or chemical ionization, CH_4), using the GLC–MS technique; carrier gas helium. Infrared spectra were recorded on a Perkin–Elmer 325 spectrometer in KBr pellets. NMR spectra were obtained with a Bruker AM-400 instrument (FT mode) in deuteriochloroform with tetramethylsilane as internal standard at 35°C. The respective frequencies for the ^1H and ^{13}C NMR spectra were 400·13 MHz and 100·62 MHz.

Reaction of 1-Acetyladamantane (*I*) with $SOCl_2$

A) A mixture of *I* (0·53 g; 3 mmol), thionyl chloride (8·3 g; 70 mmol), and dry pyridine (1 ml) was refluxed for 4 h. The excess thionyl chloride was distilled off in vacuo and the residue

was partitioned between hexane and water. The hexane layer was separated and the aqueous one was extracted twice with hexane. The combined organic extracts were washed with water, dried and taken down to afford 0·55 g of the crude product which was analysed by gas–liquid chromatography (for results see Table I). The crude product was purified by chromatography on silica gel. Elution with hexane afforded 0·53 g (90%) of 1-(1′-chloroethenyl)adamantane (*IV*). For $C_{12}H_{17}Cl$ (196·7) calculated: 73·27% C, 8·71% H, 18·02% Cl; found: 73·31% C, 8·82% H, 17·83% Cl. IR spectrum (cm^{-1}): 876 (=CH_2); 665, 733 (CCl). ^{1}H NMR spectrum: 5·11, 5·10, 5·08, 5·07, 2 H (=CH_2); 2·03, 3 H (H-3, H-5, H-7); 1·79, 1·78, 6 H (H-4, H-6, H-10); 1·74, 1·71, 1·67, 1·64, 6 H (H-2, H-8, H-9). ^{13}C NMR spectrum: 153·35 (C-1′), 108·77 (C-2′), 40·65 (C-2, C-8, C-9), 40·01 (C-1), 36·6B (C-4, C-6, C-10), 28·42 (C-3, C-5, C-7).

B) A mixture of *I* (1·78 g; 10 mmol) and thionyl chloride (27 g; 227 mmol) was refluxed for 4 h and the reaction mixture was worked up as described under *A*). The obtained product (2·02 g; for composition see Table I) was chromatographed on a column of silica gel. Elution with hexane, hexane–ether (gradient), ether, ether–methanol (gradient) afforded successively: 0·06 g of olefin *IV*, 0·13 g of ethyl ester *VII*, 0·42 g of chloroketone *V*, 0·31 g of acetyladamantane *I*, 0·38 g of acid *VI*, and 0·68 g of intermediate fractions.

1-*Chloroacetyladamantane* (V), m.p. 95–96°C. For $C_{12}H_{17}ClO$ (212·7) calculated: 67·76% C, 8·06% H, 16·67% Cl; found: 67·59% C, 7·97% H, 16·41% Cl. IR spectrum (cm^{-1}): 1 715 (CO); 1 303, 1 405 (CH_2Cl); 663, 727 (CCl). Mass spectrum (*m/z*), electron impact: 212 (0·4%, M), 163 (9%, M—CH_2Cl), 135 (100%); chemical ionization: 213 (86%, M + 1), 179 (100%), 135 (32%). ^{1}H NMR spectrum: 4·35, 2 H (CH_2Cl); 2·07, 3 H (H-3, H-5, H-7); 1·86, 1·87, 6 H (H-4, H-6, H-10); 1·79, 1·76, 1·72, 1·69, 6 H (H-2, H-8, H-9). ^{13}C NMR spectrum: 179·78 (CO), 46·32 (C-1), 45·63 (CH_2Cl), 38·36 (C-2, C-8, C-9), 36·37 (C-4, C-6, C-10), 27·82 (C-3, C-5, C-7).

1-*Adamantanecarboxylic acid* (VI), m.p. 179·5–180·5°C (reported[2] m.p. 181·0°C). For $C_{11}H_{16}O_2$ (180·2) calculated: 73·30% C, 8·95% H; found: 73·22% C, 8·79% H. ^{13}C NMR spectrum agrees with the published one[3].

TABLE I

Product composition (% rel.) in the reaction of 1-acetyladamantane (*I*) with thionyl chloride

t_r	Compound	A^a	B^b
0·35	unidentified	<0·1	2·5
0·53	1-(1′-chloroethenyl)adamantane (*IV*)	98·5	4·6
0·67	unidentified	<0·1	0·6
0·78	ethyl 1-adamantanecarboxylate (*VII*)	<0·1	7·8
1·00	1-acetyladamantane (*I*)	0·4	25·5
3·03	unidentified	<0·1	3·4
3·61	unidentified	<0·1	11·0
5·88	1-chloroacetyladamantane (*V*)	1·1	40·7
6·25	unidentified	<0·1	3·8

[a] With pyridine; [b] without pyridine.

Ethyl 1-*adamantanecarboxylate* (VII). For $C_{13}H_{20}O_2$ (208·3) calculated: 74·96% C, 9·68% H; found: 75·04% C, 9·72% H. IR spectrum (cm^{-1}): 1 729, 1 235 (COO). Mass spectrum (*m/z*), electron impact: 208 (12%, M), 180 (5%, M—CH_2CH_2), 135 (100%); chemical ionization: 209 (100%, M + 1), 181 (10%), 135 (36%). ^{1}H NMR spectrum: 4·13, 4·11, 4·09, 4·07, 2 H (OCH_2); 2·01, 3 H (H-3, H-5, H-7); 1·89, 1·88, 6 H (H-4, H-6, H-10); 1·75, 1·71, 6 H (H-2, H-8, H-9); 1·25, 1·24, 1·21, 3 H (CH_3). ^{13}C NMR spectrum: 177·73 (COO), 59·99 (OCH_2), 40·58 (C-1), 38·89 (C-2, C-8, C-9), 36·60 (C-4, C-6, C-10), 28·06 (C-3, C-5, C-7), 14·20 (CH_3). Elution time identical with that of a standard[4].

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