OXIDATION OF TRIAMANTANE BY SULPHURIC ACID

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The oxidation of triamantane by sulphuric acid was studied in various reaction conditions. 8-Triamantanone, 8,16-triamantanedione, and 15-hydroxy-8-triamantanone were isolated and identified as reaction products. The reaction was monitored and the purity of the compounds prepared was checked by gas chromatography and mass spectrometry, the position of the functional groups was determined by ^{13}C NMR spectrometry.

Similarly as adamantane and diamantane, triamantane contains in its molecule secondary carbon atoms, the reactivity of which is considerably lower than that of the tertiary carbon atoms present[1]; and so while a number of derivatives have been synthesized with substituents at the tertiary carbon atoms[2], no triamantane derivative substituted at a secondary carbon atom has been as yet reported. Therefore, as part of our wider study of polycyclic hydrocarbons, we have concerned ourselves with the preparation of some triamantane derivatives of this kind.

For adamantane and diamantane, derivatives with substituents at secondary carbon atoms are best prepared by oxidation with concentrated sulphuric acid; this reaction has been studied in detail for adamantane by Geluk and Schlatmann[3]. Sulphuric acid acts on adamantane to transform it first into a hydroxy derivative substituted at a tertiary carbon atom, and by additional oxidation, possibly associated with disproportionation, adamantanone is formed in a high yield as the final product. Diamantanone has been obtained similarly in a high yield from a reaction of diamantane with concentrated sulphuric acid[4], and nowadays this substance is the only starting material available for the preparation of derivatives substituted at secondary carbon atoms.

We attempted to oxidize triamantane in the same manner, although the situation is more complicated in this case owing to the more complex structure of the molecule. Triamantane is the first member of the adamantane-analogue series in which a quaternary carbon atom is present. Owing to the occurrence of three non-equivalent carbon atoms in positions 5, 8, and 16, three isomeric ketones can be formed, that with the keto group in position 8 being statistically most favoured. This derivative was actually isolated from the product of oxidation of triamantane; the position of the keto group was determined by ^{13}C NMR spectroscopy making use of the additive rule[5]. A disubstituted derivative containing a keto group in position 8 and another keto group in position 16 was also isolated from the reaction mixture. Only small
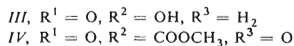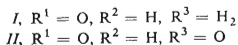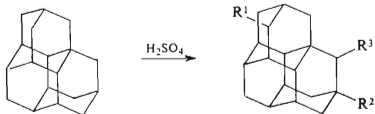
quantities of this derivative are formed at the reaction temperature of 75°C, but it is obtained in higher amounts at elevated temperatures and prolonged reaction periods. In addition to these substances, a derivative involving a keto group and a hydroxy group was also isolated. The presence of the hydroxy group indicates that similarly as with adamantane, oxidation of triamantane proceeds *via* a hydroxy derivative, which after a rearrangement of the hydroxy group from the tertiary to a secondary carbon atom is transformed, on additional oxidation and, possibly, disproportionation, into the keto derivative.

The composition of the reaction mixture from the oxidation of triamantane by sulphuric acid was investigated in dependence on temperature. At 50°C the reaction did not take place. On the other hand, when the temperature was raised to 100°C, disubstituted derivatives were formed besides a variety of side products, probably higher molecular mass compounds. A temperature of 75°C emerged as a suitable compromise for the preparation of monosubstituted derivatives, at which the yield of the ketone was highest.

The composition of the system was also examined in dependence on time. In 10 h, only several per cent triamantane had reacted, but the yield increased with time up to 40% in 40 h. Additional lengthening of the reaction time had no favourable effect on the yield of the ketone, unidentified side products being formed during that time.

Thus, comparing the composition of the reaction mixture for triamantane with that for diamantane under identical conditions we find that while for diamantane the monosubstituted derivatives are formed readily in a yield higher than 80%, the oxidation products of triamantane contain, in addition to the monosubstituted derivatives and a small amount of the unreacted starting substance, also disubstituted derivatives and higher molecular mass compounds.

To facilitate the isolation of the products from the reaction mixture we finished the procedure with the Koch–Haaf carboxylation, consisting in a transformation of the hydroxy derivatives present into the corresponding carboxylic acids. The carboxylation was, however, incomplete, so that a small amount of the hydroxy derivative was isolated, besides the keto derivative, also from the ethereal extracts. The carboxylic acids were transformed with diazomethane into the esters to facilitate the gas chromatographic analysis.

I, $R^1 = O$, $R^2 = H$, $R^3 = H_2$
II, $R^1 = O$, $R^2 = H$, $R^3 = O$

III, $R^1 = O$, $R^2 = OH$, $R^3 = H_2$
IV, $R^1 = O$, $R^2 = COOCH_3$, $R^3 = O$

EXPERIMENTAL

The melting points have not been corrected. The purity of the substances was checked gas chromatographically on a Chrom 4 apparatus, mass spectrometrically on an LKB 9000 instrument, and ^{13}C NMR spectroscopically on a Tesla BS 567 spectrometer.

Triamantane was prepared from 2,5-norbornadiene by a five-stage synthesis[6,7]; m.p. 218 to 219°C (ref.[6] 221—221·5°C).

Oxidation of triamantane with sulphuric acid. Triamantane (1 g) was heated[8] with constantly stirred 96% sulphuric acid (10 ml) at 75°C for 40 h. The mixture was allowed to cool down to room temperature, 99% formic acid (2 ml) was added, and the whole was filtered over a glass filter and poured into cooled water. The product separated was multiply extracted with ether, the combined extracts were washed with 5% aqueous solution of potassium hydroxide and water and dried with sodium sulphate, and ether was removed by distillation to give a solid residue (0·4 g, yield 40%).

The residue (0·8 g) was dissolved in benzene and chromatographed on an Al_2O_3 column (Brockmann II neutral, 32 g) using benzene, ether, and acetone as eluents. The residue from the benzene fraction obtained on evaporating the solvent was recrystallized from hexane to give a substance, m.p. 218—219°C. For $C_{18}H_{22}O$ (254·4) calculated: 84·98% C, 8·73% H; found: 84·76% C, 8·62% H; IR spectrum: ν_{max} 1 700 cm^{-1}; M$^+$ = 254; ^{13}C NMR spectrum: 217·7; 55·8; 47·4; 46·0; 45·7; 45·6; 43·6; 38·5; 47·6; 37·3; 37·1; 36·9; 36·2; 34·8; 33·4; 27·4 ppm. The substance was identified to be 8-triamantanone (*I*).

The ethereal fraction was evaporated to give a residue which furnished a substance with m.p. 240—242°C on recrystallization from a hexane–acetone mixture (1 : 1). For $C_{18}H_{20}O_2$ (268·4) calculated: 80·56% C, 7·52% H; found: 80·26% C, 7·40% H; M$^+$ = 268; ^{13}C NMR spectrum: 215·5; 78·8; 78·4; 77·1; 76·3; 75·9; 54·9; 46·5; 46·2; 45·3; 45·0; 44·7; 44·2; 37·3; 36·8; 36·2; 35·2; 33·2 ppm. The substance was identified as 8,16-triamantanedione (*II*).

The residue obtained by evaporating the solvent from the acetone fraction was recrystallized from a hexane–acetone mixture (1 : 1) and a substance with m.p. 171—173°C was obtained. For $C_{18}H_{22}O_2$ (270·4) calculated: 79·95% C, 8·21% H; found: 79·71% C, 8·38% H; M$^+$ = 270; ^{13}C NMR spectrum: 78·4; 77·1; 75·8; 68·0; 55·0; 50·9; 46·2; 45·1; 44·7; 44·6; 39·7; 39·3; 38·3; 37·0; 36·4; 35·9; 33·6 ppm. The substance was identified to be 15-hydroxy-8-triamantanone (*III*).

The aqueous layer after the separation of the ethereal layer was neutralized with hydrochloric acid (1 : 1), extracted with ether and dried with sodium sulphate, and ether was distilled off. The distillation residue constituted by the corresponding acid (M$^+$ = 298) was converted to the ester by means of diazomethane. A substance m.p. 48—51°C was obtained, M$^+$ = 312; ^{13}C NMR spectrum: 55·3; 51·7; 46·4; 45·4; 45·3; 44·8; 39·1; 38·6; 38·2; 37·1; 37·0; 36·9; 36·7; 36·3; 33·8; 33·3 ppm. The substance was identified to be methyl ester of 8-triamantanone-15-carboxylic acid (*IV*).

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