

## OXIDATION OF TRIAMANTANE

Zdeněk KAFKA and Luděk VODIČKA

*Laboratory of Synthetic Fuels, Prague Institute of Chemical Technology, 166 28 Prague 6*

Received November 18th, 1985

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Oxidation of triamantane by various oxidation procedures was studied. Besides minor amounts of monosubstituted derivatives, the oxidation afforded mainly disubstituted derivatives, particularly hydroxytriamantanone and triamantanedione. The reactions were monitored by gas-liquid chromatography and the products were identified by mass spectrometry.

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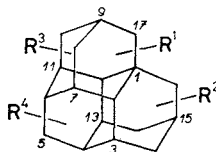
Oxidation of diamantoid hydrocarbons with concentrated sulfuric acid represents the method of choice for preparation of derivatives substituted at the secondary carbon atoms. Therefore, this reaction has been thoroughly investigated with both adamantane and diamantane<sup>1,2</sup>. Triamantane contains one quaternary carbon atom, four non-equivalent types of tertiary carbon atoms and three non-equivalent secondary carbon atoms in positions 5, 8 and 16 which are oxidized less readily. Oxidation of triamantane with concentrated sulfuric acid<sup>3</sup> at 75°C affords 8-triamantanone (the position of the keto group was determined by <sup>13</sup>C NMR spectroscopy<sup>4</sup>). In addition to this monosubstituted derivative, the reaction also gives disubstituted derivatives, 8,16-triamantanedione and 15-hydroxy-8-triamantanone; the amount of the disubstituted derivatives increases with increasing temperature and longer reaction time. Oxidation with other reagents gives preponderantly hydroxy derivatives. Hollowood<sup>5</sup> oxidized triamantane with lead(IV) benzoate in molten benzoic acid and obtained 3-triamantanol as the principal product. Tetraalkylammonium, tetraalkylphosphonium and tetraalkylarsonium permanganate<sup>6</sup> oxidize triamantane under mild conditions to the four possible triamantanols, the composition of the reaction mixture depending on the permanganate used.

This paper concerns the oxidation of triamantane with some other oxidation reagents. The aim of our investigation was to determine the types of the oxidation products (see formulae I–V; the position of the substituents has not been determined, R<sup>1</sup> and R<sup>2</sup> are substituents on tertiary carbon atoms, R<sup>3</sup> and R<sup>4</sup> on secondary carbon atoms) with regard to the possible preparation of triamantane derivatives containing oxygen functionalities.

Oxidation of triamantane with chromium trioxide in concentrated acetic acid led only to hydroxy derivatives (besides the starting compound). The composition of the reaction mixture depended on the temperature and reaction time. After 5 hours at 25°C the product contained only traces of hydroxy and dihydroxy derivatives,

most of the compound being unreacted. The amount of the unreacted compound decreased to a half when the reaction time was doubled. At 50°C all triamantane reacted and after 5 hours the mixture contained almost 80% of dihydroxy derivatives. Longer reaction time led to compounds of higher molecular weight: thus after 10 h the reaction mixture contained, in addition to hydroxy and dihydroxy derivatives, almost 50% of compounds of higher molecular weight, mainly trihydroxy derivatives.

When sulfuric acid was employed instead of acetic acid, the reaction afforded keto derivatives along with hydroxy compounds.



- I,  $R^1 = \text{OH}$ ;  $R^2 = \text{H}$ ;  $R^3 = \text{H}_2$ ;  $R^4 = \text{H}_2$   
 II,  $R^1 = \text{OH}$ ;  $R^2 = \text{OH}$ ;  $R^3 = \text{H}_2$ ;  $R^4 = \text{H}_2$   
 III,  $R^1 = \text{H}$ ;  $R^2 = \text{H}$ ;  $R^3 = \text{O}$ ;  $R^4 = \text{H}_2$   
 IV,  $R^1 = \text{OH}$ ;  $R^2 = \text{H}$ ;  $R^3 = \text{O}$ ;  $R^4 = \text{H}_2$   
 V,  $R^1 = \text{H}$ ;  $R^2 = \text{H}$ ;  $R^3 = \text{O}$ ;  $R^4 = \text{O}$

Similarly to the above-mentioned case, prolonged reaction time resulted in higher percentage of reacted triamantane and after 30 h no starting compound was detected. The principal part of the product consisted of disubstituted derivatives, particularly hydroxytriamantanone and triamantanedione. In the oxidation with 20% oleum all the triamantane reacted within 30 h and the solid residue after work-up of the reaction mixture contained predominantly hydroxytriamantanone and triamantanedione, together with minor amount of triamantanone. Oxidation with 65% nitric acid afforded only hydroxy derivatives. After 20 h we found mainly triamantanediol and small amount of compounds of higher molecular weight, probably higher substituted triamantane derivatives.

The described experiments show that oxidation of triamantane at 50–100°C with the systems employed by us affords predominantly disubstituted derivatives, mainly hydroxytriamantanone and triamantanedione whereas the monosubstituted derivatives, which are the main products in the oxidation with concentrated sulfuric acid, arise only in minor amounts (up to 10%).

## EXPERIMENTAL

Gas-liquid chromatographic analyses were carried out on a Chrom 5 instrument (Laboratorní přístroje, Prague), mass spectra were taken on an LKB 9000 spectrometer (LKB Produkter AB, Stockholm). Triamantane was prepared from 2,5-norbornadiene<sup>7</sup>.

## Oxidation of Triamantane with Chromium Trioxide in Acetic Acid

*A*) A solution of triamantane (1 g) in 98% acetic acid (10 ml) was added to a solution of chromium trioxide (5 g) in 98% acetic acid (10 ml). After stirring at 25°C for 10 h, the mixture was treated with 30% aqueous potassium hydrogen carbonate (100 ml) and extracted several times with chloroform. The chloroform extracts were combined, dried over sodium sulfate, filtered and the solvent was evaporated. According to gas-liquid chromatography and mass spectrum, the residue (0.6 g) contained triamantanol (*I*) ( $M^+ = 272$ , 30%) and starting triamantane (50%).  
*B*) The same mixture as in experiment *A* was heated to 50°C for 10 h and processed in the same way as described. The solid residue contained *I* (10%), *II* (40%) and compounds of higher molecular weight (50%).

## Oxidation of Triamantane with Chromium Trioxide in Sulfuric Acid

*A*) Triamantane (1 g) was stirred at 75°C with a solution of chromium trioxide (3 g) in 96% sulfuric acid (20 ml) for 30 h. After cooling, the mixture was neutralized with aqueous potassium carbonate and filtered. The filtrate was extracted several times with ether, the ethereal extracts were combined, washed with a solution of sodium hydroxide and water, dried over anhydrous sodium sulfate, and the solvent was evaporated. The solid residue (0.5 g) consisted of triamantanone (*III*) ( $M^+ = 254$ ; 10%), hydroxytriamantanone (*IV*) ( $M^+ = 270$ ; 55%), triamantanedione (*V*) ( $M^+ = 268$ ; 30%) and *II* (5%).

*B*) The same solution as described in experiment *A* was heated to 100°C for 10 h. The mixture was worked up as described under *A*. The solid residue contained 25% of *IV*, 65% of *V* and 10% of unreacted triamantane.

## Oxidation of Triamantane with Oleum

*A*) Triamantane (1 g) was stirred with 20% oleum (10 ml) at 75°C for 30 h. After cooling, the mixture was diluted with water and extracted several times with ether. The ethereal extracts were combined, washed with aqueous sodium hydroxide and water, dried over sodium sulfate, filtered and the solvent was removed *in vacuo*. The solid residue (0.5 g) contained 5% of *III*, 70% of *IV* and 25% of *V*.

*B*) The solution described in experiment *A* was stirred at 75°C for 20 h and worked up as described under *A*. The solid residue contained 5% of *III*, 55% of *IV*, 30% of *V* and 10% of unreacted triamantane.

## Oxidation of Triamantane with Nitric Acid

*A*) A stirred mixture of triamantane (1 g) and 65% nitric acid (10 ml) was heated to 100°C for 5 h, diluted with water and extracted several times with ether. The ethereal extracts were combined, washed with aqueous sodium hydroxide, water, dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The solid residue (0.6 g) contained 60% of *I*, 30% of unreacted triamantane and 10% of unspecified compounds.

*B*) The above-mentioned mixture was heated to 100°C for 20 h and processed in the same way as described under *A*. The solid residue contained 85% of *II* and 15% of unknown compounds

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Translated by M. Tichý.