

ON REACTIONS OF 2-METHYLADAMANTANE IN CONCENTRATED SULFURIC ACID*

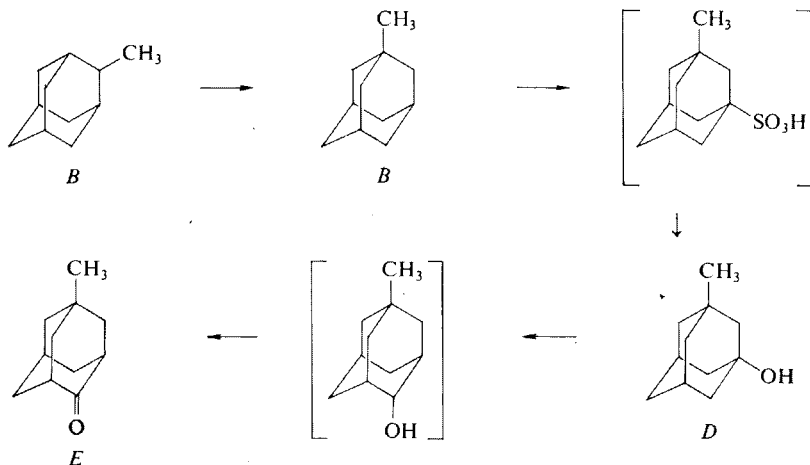
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The behaviour of 2-methyladamantane in 96% sulfuric acid has been examined at 45, 75, and 100°C. Over less than 5 minutes, a lesser shift of the methyl group has been observed from the secondary carbon atom to the tertiary one. The content of oxygenous compounds in the solution increases with the increasing time; 3-methyl-1-adamantanol is transformed by a slower reaction into 5-methyl-2-adamantanone. Dark brown tars are mostly formed. As determined by parallel experiments with 1- and 2-methyladamantane, the concentration of 1-methyladamantane in sulfuric acid (especially during the first 30 minutes) is higher than in the case of the 2-methyl isomer.

Reactions of adamantane and derivatives in concentrated sulfuric acid have been examined by several authors. Reactions of 1-methyladamantane have been investigated by Geluk and Schlattmann¹. The behaviour of 2-methyladamantane in concentrated sulfuric acid has not been reported so far while some observations on the behaviour of 2-methyl-2-hydroxyadamantane have been reported by Geluk and Schlattmann¹ as well as McKervey and coworkers².



SCHEME 1

* Part XXX in the series Adamantane and its Derivatives; Part XXIX: This Journal 39, 1083 (1974).

In order to elucidate the course of the oxidation of 2-methyladamantane in sulfuric acid, we have now examined the formation of reaction products at various temperatures and have been interested in the time effect on the yields of particular products. For purposes of comparison with findings of Geluk and Schlatmann¹, we have also performed the oxidation of 1-methyladamantane under the same conditions as in the case of 2-methyladamantane, *i.e.*, in 96% sulfuric acid at 75°C. When the 1- and 2-methyladamantanes are added into 96% sulfuric acid and heated, the resulting

TABLE I
Analysis of Products Formed from 2-Methyladamantane by Reaction with 96% Sulfuric Acid

Assay No	Temperature °C	Time min	Resins %	Products determined by GC ^a , %				
				A	B	C	D	E
1	45	30	—	2.1	0.4	1.3	89.5	6.7
2	45	60	—	4.2	0.8	2.1	84.6	8.3
3	45	180	—	3.0	0.4	2.9	79.4	14.3
4	45	240	—	3.0	0.2	3.1	78.9	14.8
5	45	360	—	1.9	—	3.9	75.5	18.7
6	45	480	—	0.6	—	8.7	70.7	20.0
7	45	600	71.6	0.9	—	10.5	66.3	22.3
8	60	60	—	2.7	1.0	0.2	59.8	36.3
9	60	180	67.5	5.3	1.1	0.9	45.5	47.2
10	60	240	80.6	6.5	1.4	1.3	26.2	64.6
11	75	5	—	5.9	3.0	0.5	78.9	11.7
12	75	15	—	4.4	2.1	1.0	76.2	17.3
13	75	30	—	3.6	0.7	5.3	64.5	25.9
14	75	60	—	6.4	2.1	3.0	36.5	52.0
15	75	120	—	5.3	2.8	2.2	22.6	67.1
16	75	180	—	3.8	2.0	2.0	1.5	90.7
17	75	240	81.8	2.8	2.1	2.2	—	92.9
18	100	5	—	4.0	1.1	1.0	54.5	39.4
19	100	15	—	6.2	1.4	1.3	31.3	59.8
20	100	30	79.4	11.0	2.6	2.2	3.3	80.9

^a GC, gas chromatography; A, a volatile oxygen-containing substance, the presence of which was detected by GC only but which was neither isolated nor identified; B, methyladamantanes; C, a volatile oxygen-containing substance (heavier than A), the presence of which was detected by GC only but which was neither isolated nor identified; D, 3-methyl-1-adamantanol; E, 5-methyl-2-adamantanone.

solution becomes yellow, brown, and dark-brown and there also may be observed evolution of sulfur dioxide. In addition to volatile reaction products, there are formed dark condensation products which finally predominate.

EXPERIMENTAL

2-Methyladamantane was prepared according to Schleyer and Nicholas³ from adamantanone and methylmagnesium iodide, dehydration of 2-methyl-2-hydroxyadamantane, and hydrogenation of 2-methyleneadamantane in 96% yield. M.p. 145.5–147.0°C; reported³, 143.8–146.0°C.

1-Methyladamantane was obtained by the procedure of Schleyer and coworkers⁴ from 1-bromo-adamantane and excess methylmagnesium iodide in a sealed ampoule at 100°C; yield, 62%. M.p. 102–103°C; reported⁴, m.p. 102–103°C.

Chromatographical analyses were performed at 140°C and 175°C on Chrom II and Chrom III apparatus with the use of 50 m long capillary columns packed with Chromosorb W; SE-30 or Carbowax 20 M (in the case of hydroxylic compounds) served as stationary phases.

NMR spectra were taken on a Tesla BS 477 (60 MHz) apparatus with the use of hexamethyl-disiloxane or tetramethylsilane as standards.

Mass spectra were measured on a combined Gas Chromatograph-Mass Spectrometer LKB 9000. The ionic source of the mass spectrometer was charged with samples by means of a reservoir.

Procedure. To 0.5 g (3.3 mmol) of 2-methyladamantane or 1-methyladamantane there was added 10 ml (187 mmol) of 96% sulfuric acid, the mixture vigorously stirred, and heated. Samples were pipetted in time intervals shown in Tables I and II, poured into ice-cold water, and the whole extracted with ether. The ethereal extracts were dried over anhydrous sodium sulfate and evaporated. The residue was subjected to gas chromatography at 140°C. For the results see Table I. The reaction of 96% sulfuric acid with 1-methyladamantane at 75°C was performed analogously to that of 2-methyladamantane and the results were summarised in Table II.

RESULTS AND DISCUSSION

As it may be seen from data of Table I, numerous compounds are formed from 2-methyladamantane in 96% sulfuric acid. The reaction mechanism is not known and only approximate reaction rates can be estimated. Notwithstanding, withdrawal of samples in relatively brief time intervals and at various temperatures made possible to examine to a considerable extent the course of reactions. In addition to coloured polymeric products, there was observed 1-methyladamantane and a great amount of 3-methyl-1-adamantanol even shortly after the addition of 2-methyladamantane into sulfuric acid (see particularly experiments 1 to 7, 11, and 17). Longer reaction periods of time lead to a decrease of 3-methyl-1-adamantanol and to the proportional increase of 5-methyl-2-adamantanone. From the formation of particular products in certain time intervals, the reaction sequence shown in Scheme 1 could be inferred.

The shift of the methyl group in 2-methyladamantane from the secondary carbon atom to the tertiary carbon atom is very rapid, almost instantaneous, similar to the

TABLE II

Analysis of Products Formed from 1-Methyladamantane by Reaction with 96% Sulfuric Acid at 75°C

Time min	Resins %	Products determined by GC ^a , %			
		A	B	D	E
5	—	—	14.7	75.2	10.1
15	—	—	13.5	71.1	15.4
30	—	0.5	5.0	55.3	39.2
60	—	1.6	1.0	41.8	55.6
120	—	2.9	—	8.4	88.7
180	61.1	1.7	—	—	98.3

^a For abbreviations see Table I.

sulfonation and replacement of the sulfo group by the hydroxylic function. When compared with this rapid conversion, the transformation of 3-methyl-1-adamantanol to 5-methyl-2-adamantanone is very slow. The behaviour of 2-methyladamantane in 96% sulfuric acid is different from that of 1-methyladamantane. Thus, the solution contains after 15 min at 75°C about 12% of 1-methyladamantane and is almost free of 1-methyladamantane after 1 hour. On the other hand, the content of 2-methyladamantane in the reaction mixture decreases over 5 min to a value (about 2%) which then remains almost constant during the whole experiment.

The temperature considerably affects the reaction mechanism and the ratio of reaction products. The ionic reactions occur at about 0°C while at temperatures round 40°C, the radical reactions begin to assert themselves, particularly by an increased and rapid formation of tars and ketones. After one hour, the content of 5-methyl-2-adamantanone was 8.2% at 45°C and 52% at 75°C while after 30 minutes at 100°C, the content was 80.9%. The amount of tars was 71.6% after 10 hours at 45°C and 79.4% after 30 minutes at 100°C.

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