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Oxidation of trans-Decahydronaphthalene in Acetic Anhydride

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The oxidation of trans-decahydronaphthalene (1) was carried out in acetic anhydride with oxygen in the presence of $Co(OAc)_2$, $Ce(OAc)_3$, and NH_4Br. Decahydronaphthyl acetates were obtained as main oxidation products in a selectivity of 81 mol% at 120 °C. In addition, relative reactivities of hydrogen atoms of 1 were determined at temperatures from 90 to 120 °C.

trans-Decahydronaphthalene (1) is one of hydrogenated compounds of naphthalene which is a main component of polynuclear aromatic hydrocarbons in coal tar and coal liquids expected as attractive hydrocarbon resources. Therefore, conversion of 1 into valuable chemicals by oxidation is meaningful for a new utilization of naphthalene. The oxidation of decahydronaphthalene is a well known reaction.1)-9) But there are few studies on its oxidation products because they consist of many isomers which resemble closely one another and are difficult to analyze. The oxidation of 1 didn't proceed smoothly in acetic acid. Meanwhile, it is known that oxidations in acetic anhydride usually proceed more rapidly than those in acetic acid and, what is more, the oxidation products have high selectivities in ester formation.10) On the basis of minute analyses, we wish to report in this communication the oxidation of 1 in acetic anhydride with oxygen in the presence of transition metal acetates and bromides.

In a typical procedure, an acetic anhydride solution (50 ml) of 1 (0.05 mol) was prepared with $Co(OAc)_2 \cdot 4H_2O$ (1.0 mmol), $Ce(OAc)_3 \cdot H_2O$ (1.0 mmol), and NH_4Br (2.0 mmol) as catalysts in a glass flask and oxidation was carried out by flowing oxygen (100 ml/min) under atmospheric pressure at 100 °C. The oxidation products were analyzed by gas chromatography (GC) with a packed column (FFAP 5%, Chromosorb W (AW-DMCS), 3 mm x 2 m) and a capillary column (PEG-20M, 0.25 mm x 50 m) for determining the conversion of 1 and the ratio of mono-substituted oxidation

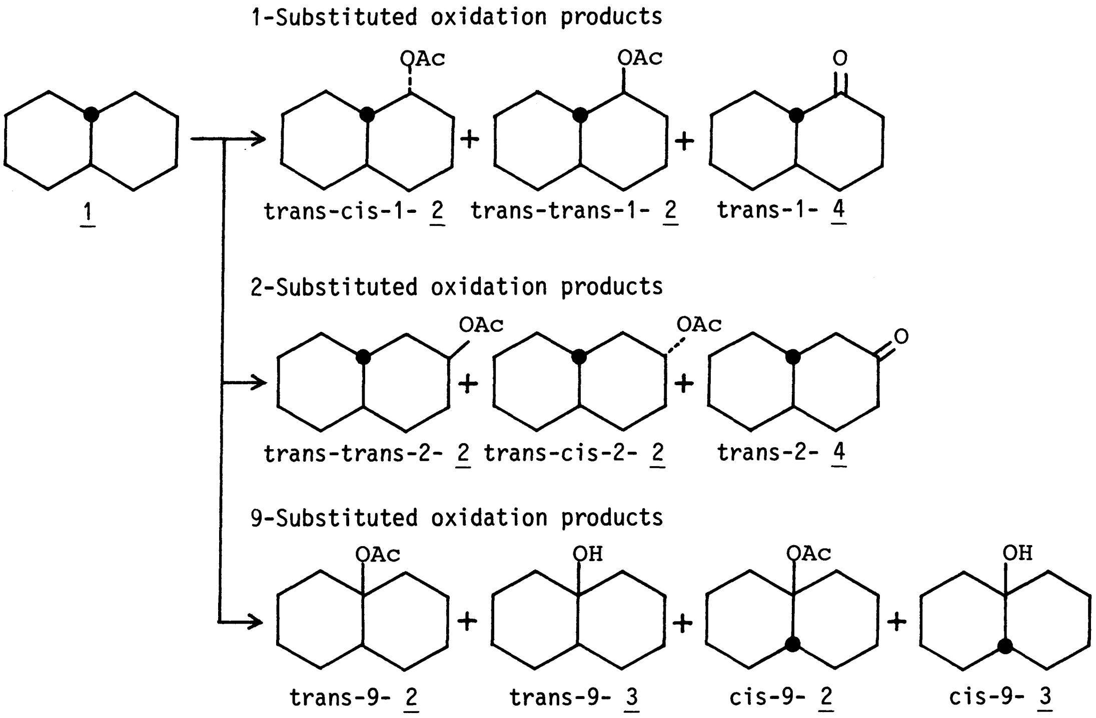


Fig. 1. Mono-substituted oxidation products of 1 in acetic anhydride.a)-c)

a) 2: Decahydronaphthyl acetate; 3: Decahydronaphthyl alcohol;
4: Decahydronaphthalenone.
b) The conformational designations are those proposed by Dauben et al.12)
c) Dots at 9-positions indicate that the hydrogen atoms are above the rings.

products (Fig. 1), respectively. The identifications of oxidation products were achieved with GC by comparing their peaks with those of standard samples which were either synthesized or obtained commercially.

The most active catalyst system was Co-Ce-NH_4Br similarly to that of oxidation of alkylbenzenes in acetic anhydride.10,11) The proper ranges of Co/Ce ratio, Br/(Co+Ce) ratio, and total metal concentration were 0.005 - 1.0, 1.0 - 2.0, and 3.5 - 7.0 x 10^{-2} (mol/l), respectively. The oxidation of 1 in acetic anhydride proceeded favorably in the presence of Co-Ce-NH_4Br and the initial oxidation rate, calculated from the conversion, was 1.4 x 10^{-3} mol/l•min at 100 °C. The conversions at 1, 3, and 5 hours were 8.7, 16.3, and 20.4 mol% at 100 °C, respectively.

The results of oxidation of 1 at various temperatures are summarized in Table 1. The main oxidation products were decahydronaphthyl acetates (2) whose selectivity was 81 mol% at 120 °C. 1- and 2-Decahydronaphthyl alcohols (3) were found wholly as 2. The selectivities of 2 of 1- and 2-positions increased with the

Table 1. Oxidation of 1 in acetic anhydride at various temperatures

Reaction temperature /°C	90	95	100	110	120
Conversion /mol% : Reaction time /min	5.0:120	6.4:60	4.9:30	5.4:30	6.3:30
Composition of initial oxidation products /mol%					
1-Subst. oxid. prod.	12.3	12.1	14.0	19.6	26.6
trans-cis-1- 2	3.0	2.7	3.0	4.9	7.8
trans-trans-1- 2	7.5	7.5	8.6	12.8	17.9
trans-1- 4	1.8	1.9	2.4	1.9	0.9
2-Subst. oxid. prod.	55.4	54.1	55.2	54.7	53.1
trans-trans-2- 2	13.4	12.6	14.1	16.9	20.8
trans-cis-2- 2	26.1	26.1	27.7	29.7	29.6
trans-2- 4	15.9	15.4	13.4	8.1	2.7
9-Subst. oxid. prod.	22.7	20.8	18.0	12.2	5.5
trans-9- 2	5.2	3.8	5.7	6.7	3.8
cis-9- 2	2.6	2.2	2.8	1.7	0.8
trans-9- 3	12.4	11.9	7.8	3.0	0.6
cis-9- 3	2.5	2.9	1.7	0.8	0.3
Others	9.6	13.0	12.8	13.5	14.8
Selectivity of 2 /mol%					
Total	58	55	62	73	81
1-Subst. oxid. prod.	85	84	83	90	97
2- "	71	72	76	85	95
9- "	34	29	47	69	83
Trans/cis ratio at 9-positions	78/22	75/25	75/25	80/20	80/20

increase of temperature and reached a value of about 95 mol% at 120 °C. At 9-positions, however, formation of 3 were found with that of 2 because of low reactivities in esterification. The selectivities of 2 of 9-positions also increased with the increase of temperature.

Among mono-substituted oxidation products, the selectivity of 2-ones was the highest of all (about 55 mol%), though 9-ones was expected to be obtained mainly. The selectivity of 1-ones increased with the increase of temperature but that of 9-ones decreased. On the other hand, the selectivity of 2-ones were kept almost constant at all temperatures by cancellation between those of 1- and 9-ones.

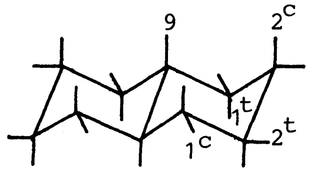
Considerable amounts of cis-9-substituted oxidation products were found in this study in accordance with the result of Ref. 7. They were formed through the inversion of 9-decahydronaphthyl radical and trans/cis ratios at the initial oxidation stage were 75/25 - 80/20 which are alike to 76/24 calculated from the values of Ref. 7.

The effect of reaction temperature on relative reactivities of hydrogen atoms

Table 2. Relative reactivities of hydrogen atoms of 1 at various temperatures[a),b)]

Reaction temperature /°C	90	95	100	110	120
2^t-Hydrogen atoms	103	114	99	64	39
2^c- "	53	55	51	37	27
1^c- "	25	28	28	26	23
1^t- "	10	10	10	10	10
9 - "	128	130	98	45	14

a)



b) Relative reactivities are calculated from the compositions of initial oxidation products (those of 1^t-hydrogen atoms: 10). The ratios of 4 of 1- and 2-positions are divided into those of 2 of corresponding positions respectively based on the compositions of 2.

of 1 are shown in Table 2. Differences in relative reactivities decreased with the increase of temperature. Relative reactivities of secondary hydrogen atoms are in order as follows: $2^t > 2^c > 1^c > 1^t$. This result can be explained in terms of steric effect. It is considered that 9-positions of 1 have large steric hindrances, because the reactivity of tertiary 9-hydrogen atoms is almost equal to that of secondary 2^t-ones even at 90 °C although tertiary hydrogen atoms are generally much more reactive than secondary ones. This is supported by low reactivities of 9-alcohols in esterification.

It is an attractive finding that decahydronaphthyl acetates can be obtained selectively by the oxidation of trans-decahydronaphthalene in acetic anhydride from the viewpoint of a new utilization technology of naphthalene.

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