Rates of Oxidation of Some Bicyclic Alcohols with Silver Carbonate on Celite

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It is well known that silver carbonate is a powerful agent for the oxidation of both primary and secondary alcohols[1,2] Recently Fétizon introduced a convenient modification of this procedure by using silver carbonate precipitated on celite[3-5]. The presence of celite increases the useful reaction surface thus increasing the efficiency of the reagent. Such an oxidant, known as *the Fétizon Reagent,* has proved to be quite effective and very selective. Particularly, the synthetic utility of this procedure has been emphasized[5].

In this communication we wish to report our observations on the rates of oxidation of epimeric 2-norbornanols **1N** and **1E** and of *endo*-2-norbornenol (**3**) using silver carbonate on celite as oxidant. Also α-deuterium labeled bicyclic alcohols **2N** and **2E**[6] were subjected to oxidation under the same conditions in order to get some information about the mechanism of this reaction. The progress of the reaction was followed by glc using a Carbowax

| **1 N** | X = H |
| **1 N** | X = D |

| **1 E** | X = H |
| **2 E** | X = D |

3
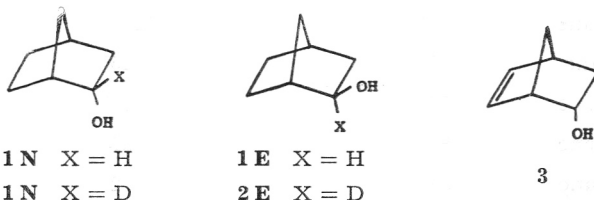
(20⁰/₀ on Chromosorb P) column operated at 150⁰. When benzene was used as a solvent and the reaction performed at 80⁰, the yields of the corresponding ketones were better than 90 per cent. The purity of the products was checked by glc, nmr, and infrared spectra. The reaction is characterized by an induction period when oxidation is extremely slow. After this sluggish period which varies with different solvents, good *pseudo* first order kinetics was observed. Rates could be reproduced within a few percent. The accuracy was limited by the experimental technique used because of the heterogeneity of the medium. Rate constants were determined between 25 and 80 per cent of the reaction completion. The results are summarized in Table I.

Silver carbonate oxidation exhibits similar effects on the oxidation of epimeric norborneols as chromic acid oxidation. The *endo/exo* rate ratio is about 4.5 and can be compared with the corresponding value (2.5) observed with chromic acid[7]. The primary isotope effect differs only slightly for the

TABLE I

Pseudo First Order Rate Constants for the Oxidation of Bicyclic Alcohols by the Fétizon Reagent in Benzene at 80° C[a]

Compound	$k \times 10^3$ sec^{-1}	k_H/k_D
1N	5.4	
2N	1.5	3.6
1E	1.2	
2E	0.39	3.1
3	0.1	

[a] 0.25 moles of Ag_2CO_3 for each 0.01 mole of alcohol.

two epimers and clearly demonstrates that α-hydrogen abstraction is the rate limiting step[8]. Some oxidations were also performed at different temperatures using benzene or *n*-alkanes as solvents. The results are summarized in Table II. These results show that not only temperature but also the choice of solvent

TABLE II

The Effect of Different Solvents and Temperature on the Oxidation Rate of endo-2-Norbornanol *(**1 N**)*

Solvent	Temp. (°C)	Reaction's completion time (min)
n-pentane	36[a]	1200
n-hexane	69[a]	15
benzene	70	80[b]
benzene	80[a]	22
n-heptane	98[a]	2

[a] reflux temperature.
[b] the oxidation of *exo*-norbornanol *(1E)* in benzene at 70° was about 15 times slower than for *1N*.

has a marked influence on the rate. It seems that the presence of double bonds which enables the formation of a π-complex with silver decreases the oxidation rate. Therefore, saturated hydrocarbons are better solvents for this reaction than benzene, and saturated alcohols are oxidized at a faster rate than unsaturated ones as shown by the *endo*-2-norbornanol/*endo*-2-norbornenol rate ratio (see Table I.).

General Procedure

In a typical experiment 2-norbornanol (**1N** or **1E**) (340 mg., 3 mM) was added to a stirred suspension of the reagent (4.145 g., corresponding to 15 mM of Ag_2CO_3) in the appropriate solvent (see Table II). The reagent was prepared following the original procedure[4] but prior to use dried by azeotropic distillation over benzene.

The reaction mixture was refluxed and the progress of reaction followed by inspecting filtered samples for the presence of alcohols either by glc or the infrared spectrum. After the completion of the reaction, the cooled mixture was filtered, and the solvent evaporated *in vacuo*. Sublimation of the residue yielded pure norcamphor (250 mg., 90%). For kinetic measurements the corresponding alcohol was added to a suspension of the reagent in benzene preheated to the boiling point. Also, a five times greater amount of the reagent was used than in the preparative runs.

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IZVOD

Brzine oksidacije nekih bicikličkih alkohola sa srebrnim karbonatom na celitu

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Ispitane su brzine oksidacije bicikličkih alkohola (*endo*- i *egzo*-2-norbornanol i *endo*-2-norbornenol) sa srebrnim karbonatom na celitu. Utvrđeno je da srebrni karbonat djeluje slično kao oksidacija s kromnom kiselinom, i utvrđen je odnos brzina oksidacije *endo/egzo* 4,5. Primarni izotopni efekt ukazuje da do apstrakcije α-vodika dolazi u sporom stupnju reakcije. Otapala ili supstrati koji mogu tvoriti π-komplekse sa srebrom znatno usporavaju brzinu reakcije.