

PHOTOCHEMICAL OXIDATION AND AUTOXIDATION OF SOME CYCLOALKANES

PROMOTED BY CERIC AMMONIUM NITRATE IN ACETONITRILE

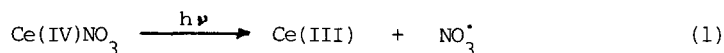
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Summary: The oxidation and autoxidation of adamantane, norbornane and cyclohexane can be photochemically promoted by ceric ammonium nitrate in acetonitrile at room temperature, both processes being extremely efficient and selective with adamantane.

Our recent work has shown that the photolysis of cerium(IV) ammonium nitrate (CAN) in acetonitrile leads to the formation of NO_3^{\bullet} radicals (eq. 1) which efficiently promote side-chain substitution reactions of alkylaromatics under very mild conditions and with good selectivity^{1,2}. When the photolysis is carried out in the presence of dioxygen autoxidation of alkylaromatics can be performed using catalytic amounts of CAN³.



As an extension of this work to aliphatic hydrocarbons we now report on the CAN-promoted photochemical oxidation of adamantane, norbornane and cyclohexane under both stoichiometric and catalytic conditions.

Stoichiometric Reactions. A solution of CAN (16 mmol) and the hydrocarbon (16 mmol) in 100 ml of CH_3CN has been photolyzed (125 W high pressure mercury lamp with pyrex filter) for 2-5 h at room temperature. After the usual work up procedure a reaction product has been obtained whose composition has been determined by VPC or NMR after reduction of the formed nitrates to alcohols by LiAlH_4 . In the case of adamantane, N-(1-adamantyl)- and N-(2-adamantyl)acetamide were also formed, presumably due to the solvolysis of the first formed nitrates. The acetamides were determined by VPC of the crude product before reduction.

The results, reported in Table 1, indicate that the reaction is particularly efficient with adamantane and norbornane which are functionalized in a practically quantitative yield. Lower yield is obtained with cyclohexane, but the reaction can be still considered satisfactory in view of the very mild experimental conditions.

Worth noting is the high reaction selectivity. With adamantane a strong preference for attack at the tertiary carbon is observed (30:1 after statistical correction); with norbornane the exo : endo reactivity ratio is 10 and no attack at the bridgehead position takes place.

Table 1. Photochemical Oxidation of Some Cycloalkanes Promoted by Cerium(IV) Ammonium Nitrate in Acetonitrile at Room Temperature.

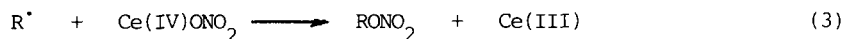
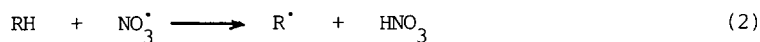
Substrate ^a	Products (yield) ^b
Adamantane	1-adamantyl nitrate (35%) ^c N-(1-adamantyl)acetamide (56%) ^d 2-adamantyl nitrate (5%) ^c N-(2-adamantyl)acetamide (4%) ^d
Norbornane	2-exo-norbornyl nitrate (80%) ^e 2-endo-norbornyl nitrate (8%) ^e
Cyclohexane	Cyclohexyl nitrate (30%) ^{e,f}

^a Substrate, 16 mmol, and CAN, 16 mmol, in 100 ml of CH₃CN. Irradiation was performed by a 125 W Helios-Italquartz high pressure mercury immersion lamp with pyrex filter. ^b With respect to the CAN used, assuming a CAN:hydrocarbon 2:1 stoichiometry. ^c Determined as the corresponding alcohol (VPC, comparison with authentic specimens in the presence of *p*-dibromobenzene) after reduction of the reaction product by LiAlH₄. ^d Determined by VPC before reduction with LiAlH₄. ^e Determined as the corresponding alcohol (NMR, comparison with authentic specimens in the presence of *p*-dibromobenzene) after reduction of the reaction product by LiAlH₄. ^f 52% of cyclohexane has been recovered unchanged.

It has been suggested that the reaction of NO₃[•] with alkylaromatics takes place by an electron transfer mechanism^{2,4}. To test if this mechanism may also hold for the saturated substrates we studied the photochemical reaction of CAN with 1-*t*-butyladamantane under the same experimental conditions than above. No evidence for the formation of products derived from C-C cleavage was obtained, but only N-(3-*t*-butyl-1-adamantyl)acetamide and 3-*t*-butyl-1-adamantyl nitrate were observed⁵. In contrast, substantial C-C cleavage with formation of N-(1-adamantyl)acetamide occurs in the anodic oxidation of 1-*t*-butyladamantane in acetonitrile, a reaction certainly involving the intermediacy of a radical cation⁶.

Thus, the reaction of saturated hydrocarbons with NO₃[•] is most probably a hydrogen atom transfer process leading to an alkyl radical which is further oxidized by CAN to the final

product (eqs. 2 and 3).



Autoxidation Reactions. Dioxygen was bubbled through a solution of the hydrocarbon (4 mmol), CAN (0.08 mmol), HNO₃ (0.8 mmol), in 100 ml of CH₃CN, irradiated for ca. 5 h under the same conditions than above. In the case of adamantane reactions substantial amounts of peroxidic materials were formed, which were decomposed by refluxing the crude product for 1 h with KI in 25 ml of isopropyl alcohol and 1 ml of acetic acid.

With cyclohexane and norbornane there was no evidence for the formation of peroxidic material; carbonyl compounds and alcohols were formed and the crude product was reduced with LiAlH₄, before analysis, to convert the former into the second. The results are in Table 2.

Table 2. Photochemical Autoxidation of Some Cycloalkanes Catalyzed by Cerium(IV) Ammonium Nitrate in Acetonitrile at Room Temperature.

Substrate ^a	Products (yield) ^b
Adamantane	1-adamantanol (85%) ^c 2-adamantanol (5%) ^c 2-adamantanone (5%) ^c
Norbornane	2-exo-norborneol (10%) ^{d,e} 2-endo-norborneol (10%) ^{d,e}
Cyclohexane	Cyclohexanol (10%) ^{d,e}

^aFor the reaction conditions see text. ^bWith respect to the hydrocarbon. ^cDetermined by VPC after reflux of the crude reaction product with KI (see text). ^dDetermined by NMR after treatment of the crude reaction product with LiAlH₄. ^eThe percent of unreacted hydrocarbon cannot be given since blank experiments showed that it is slowly lost during the bubbling of dioxygen.

The data show that also the photochemical autoxidation of adamantane catalyzed by CAN is an extremely efficient and very selective process. Conversion is around 95% and the

selectivity in 1-adamantanol is 90%, to our knowledge the highest value among those reported in the literature for catalyzed autoxidations of adamantane⁷. The relative reactivity of tertiary to secondary carbon (C^3/C^2 ratio) is 25 after statistical correction.

Less good results are obtained with norbornane and cyclohexane. Probably this is due to the lower reactivity of the secondary hydrogen atoms of these substrates with respect to the tertiary ones of adamantane, which makes possible the competition of other reaction pathways in the former case.

The CAN-promoted photochemical autoxidation of alkylbenzenes has been suggested to occur by a mechanism involving regeneration of Ce(IV) from Ce(III) by alkylperoxy radicals³. The formed Ce(IV) oxidizes NO_3^- to NO_3^{\cdot} which propagates the chain. The same mechanism probably also holds in the reactions of cycloalkanes as the selectivity of the catalytic reaction of adamantane is quite close to that of the stoichiometric one, which suggests the same hydrogen abstracting species (NO_3^{\cdot}) in the two processes⁹. Moreover, a selectivity lower than that found here is observed in autoxidation reactions of adamantane where chain propagation is exclusively due to hydrogen abstraction by adamantylperoxy radicals¹⁰.

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References and Notes

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4. E.Baclocchi, T.Del Giacco, S.M.Murgia, and G.V.Sebastiani, paper submitted for publication.
5. A specific search for the presence of products of attack at the secondary center was not carried out. In the light of results with adamantane the formation of small amounts of these products is probable.
6. G.J.Edwards, S.R.Jones, and J.M.Mellor, J.Chem.Soc.Perkin Trans. II, 505 (1977).
7. For example, in the autoxidation reaction of adamantane catalyzed by azoisobutyronitrile conversion is 13% and the yield in 1-adamantanol is 11%⁸.
8. T.Muto, C.Urano, T.Hayashi, T.Miura, and M.Kimura, Chem.Pharm.Bull., 31, 1166 (1983).
9. The comparison for the case of norbornane is not significant since, in the autoxidation, alcohols derive also from 2-norbornanone.
10. To our knowledge the highest value of C^3/C^2 ratio in the literature for this kind of reaction is 16.5⁸.

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