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CLAY-SUPPORTED REAGENTS, III(1)
THE INTERMEDIACY OF NITROUS ESTERS IN THE OXIDATION OF ALCOHOLS BY CLAY-SUPPORTED FERRIC NITRATE

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Abstract Stereospecific intermediate nitrite formation occurs in the title reaction.

QUANTITATIVE conversion of alcohols into carbonyl compounds can be effected conveniently, under mild reaction conditions, using ferric nitrate impregnated on K 10 bentonite clay. This reagent ("clayfen" for short) is obtained easily and cheaply from addition of the clay to a suspension of ferric nitrate in acetone and evaporation of the solvent To perform the oxidation, clayfen is added to a pentane or hexane solution of the alcohol, followed by reflux till evolution of nitrogen oxides stops One then filters off the reagent and evaporates the solvent (2).

The overall reaction is best formulated as

$$3\ R_1R_2\ CHOH + 2\ H^+ + 2\ NO_3^- \xrightarrow[\text{clay}]{\text{FeIII}} 3\ R_1R_2C = O + 2\ NO + 4\ H_2O$$

with subsequent air oxidation of NO to NO_2.

What is the mechanism ? We report here the key experimental finding that, quite unexpectedly, nitrous esters, and not nitric esters, are intermediates in this new oxidation reaction.

A convenient clayfen oxidation to study is that of cyclohexanol into cyclohexanone It is slow enough (24 h in refluxing hexane) to be followed by vpc besides reactant and product, an intermediate builds up to a maximum of 50% of the starting molecules after 3/4 h and then slowly decays.

Isolation (filtration, solvent evaporation, and treatment with 85% orthophosphoric acid in order to separate nitric and nitrous compounds from their mixture with an alcohol and a ketone(3)) yields a compound $C_6H_{11}NO_2$, with ir absorptions at 780(m), 825(s), 1600(m) and 1635(s) cm^{-1}, diagnostic (4) of a nitrite RONO. Preparation of an authentic sample of cyclohexyl nitrite (5) showed its identity (vpc, ir) with the isolated substance.

Cyclohexyl nitrite is indeed an intermediate in the oxidation of cyclohexanol into cyclohexanone

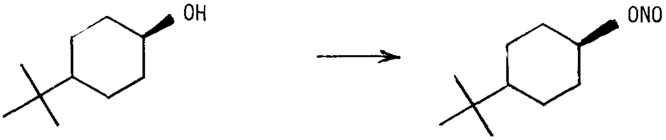
(i) under the reaction conditions (clayfen in hexane), it gives rise to a mixture of product and starting material,

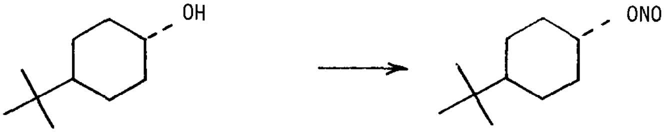
(ii) it is formed from clayfen ferric nitrate, in the absence of the bentonite clay, is a poor cyclohexanol oxidant, other nitrates ($NaNO_3$, NH_4NO_3) dispersed on the clay give no reaction,

(iii) in the presence of the bentonite K 10, with no ferric nitrate present, cyclohexyl nitrite is also converted into a mixture of cyclohexanone and cyclohexanol

Likewise, we were able to prove the intermediacy of a nitrite in the clayfen oxidations of benzyl alcohol, of 2-octanol, and of a mixture of 4-*t*-butyl-cyclohexanols (*cis* and *trans*)

Stereochemically, the nitrite is formed from the alcohol with retention of configuration at the oxygen-bearing carbon .





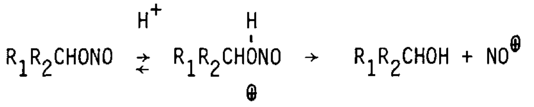
Two questions remain

A How does the alcohol go to the nitrite ?

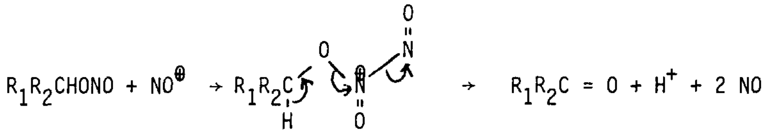
B How does the nitrite transform into the ketone ?

With respect to the former, we could rule out an organic nitrate as precursor an equimolar mixture of cyclohexyl nitrate and of cyclohexanol-d_4, in the presence of the clay does not lead to cyclohexyl nitrite. The only reaction observed is a slow dehydration of the alcohol. Furthermore, cyclohexyl nitrate is stable under the reaction conditions (Clayfen in refluxing hexane)

As to question B, a plausible mechanism for decomposition of the nitrite would be, following Barton$^{(6)}$



$$R_1R_2CHONO \overset{H^+}{\rightleftarrows} R_1R_2CH\overset{H}{\underset{\oplus}{O}}NO \rightarrow R_1R_2CHOH + NO^{\oplus} \qquad (1)$$



(2)

Coupling of reactions (1) and (2) will lead to formation of the ketone (or aldehyde) and NO products

The one pending question is thus A it is somewhat paradoxical that an inorganic nitrate will combine with an alcohol to form a nitrite. This could however very well occur in the following manner

$$R_1R_2CHOH + NO_3^- \rightarrow R_1R_2C = O + NO_2^- + H_2O \qquad (3)$$

$$R_1R_2CHOH + NO_2^- + H^+ \rightleftarrows R_1R_2CHONO + H_2O \qquad (4)$$

Also, the role of the metal remains enigmatic our initial choice of Fe(III) was based upon its complexing of oxygenated ligands and its redox properties

Nitrite preparation has recently raised a renewal of interest $^{(7)}$ Among the potential developments of our easy and economical access to this functionality, the photochemical quenching of the nitrous ester by a Barton reaction $^{(8,9)}$ is obviously a prime candidate.

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