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SOME OBSERVATIONS ON BAEYER-VILLIGER OXIDATION OF ALICYCLIC KETONES WITH MAGNESIUM MONOPEROXYPHTHALTE IN APROTIC SOLVENT IN THE PRESENCE OF BENTONITE CLAY

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ABSTRACT: Magnesium monoperoxyphthalate oxidation of unsubstituted and substituted cyclohexanones has been carried out in acetonitrile in the presence of bentonite clay, affording the corresponding ϵ -caprolactones in fairly good yields.

Lactones occur in nature and are also important reaction intermediates in organic syntheses. Accordingly, the formation of lactones has attracted significant attention, as evident by the wide range of reagents and reaction conditions that have been employed

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for their preparations; *viz.*, oxidation, reduction, cyclisation, carbonylation, rearrangement, *etc.* Among a variety of methodologies, oxidative procedures have been generally accepted because of easy accessibility; striking examples are those by the *Baeyer-Villiger* reaction of cyclic ketones,¹) *Fetizon* oxidation of diols and lactols using silver carbonate on celite,²) manganese(III) acetate oxidation of olefins in carboxylic acids,³) oxidation of diols with aqueous sodium bromite,⁴) and so on.

In connection with one of our ongoing projects, we have recently investigated the oxidation of sulphides with a newly developed peroxy acid derivative,⁵) MMPP [short for magnesium monoperoxyphthalate hexahydrate⁶)], in an aprotic solvent,⁷) since MMPP chemistry in a water-free medium has been hardly explored so far, as compared with the conventional oxidations under aqueous conditions⁸) owing to negligible solubility of MMPP in organic solvents except for lower alcohols. We have observed that a sulphide having an oxo-functionality undergoes smooth reaction, but leads to appreciable formation of unknown products in addition to the anticipated sulphoxide, suggesting competitive operation of sulphoxidation and Baeyer-Villiger oxidation. In continuation of our research on MMPP chemistry, it might be incumbent on us to provide some information concerning the latter oxidation under our conditions and, moreover, in the field of peroxy acids chemistry reaction of ketones bearing functional groups often presents a challenging task.⁹) In this article, we would like to describe an alternative approach for lactone synthesis from cyclohexanones in an aprotic solvent in the presence of a bentonite clay as well as the remarkable aspects of the reactions.



Attempted reaction was initiated by simply mixing cyclohexanone (1) as a representative substrate, a slight excess of *MMPP*, and the moist bentonite (vide infra) in acetonitrile at 303K, the standard reaction conditions under which the previous sulphide oxidation⁷) had been carried out. However, serious problems were experienced in attaining high conversion of the ketone and in yielding ε -caprolactone (2) in synthetically acceptable yield (Scheme; R¹- R⁴= H). For example, upon treating 1 with MMPP ([MMPP]/[1]= 0.52; mole ratio) significant quantity of the starting ketone (48% by GC) remained even after 15 hours and resulted only in poor formation of ε -caprolactone (51%), rendering this method impractical. Repetition of the reaction with an increasing amount of MMPP, at an elevated temperature, and/or for a prolonged period also failed to accomplish satisfactory conversion of the ketone. Supposing that the main reason for the low conversion of the ketone was associated with the thermal lability of MMPP under the reaction conditions, some means must be found of repressing its unproductive decomposition. We therefore sought to improve conversion of the ketone to the lactone by deliberately adding a given amount of MMPP "in portions" to the heterogeneous mixture of the ketone and the bentonite in acetonitrile at 333K thus maintaining a constant but "high" MMPP concentration available for the oxidation. This modification was met with immediate success in a beneficial reduction in reaction time. Indeed, when was cyclohexanone subjected to the action of MMPP added by portions (total three equivalents), a rapid consumption of the ketone ensured which permited virtually exclusive formation of ε caprolactone in good yield within a two-hours period (Entry 1).

The results of MMPP oxidation of alkyl-, dialkyl, and aryl-substituted cyclohexanones are set up in the Table. The tabulated ketones were successfully converted into the lactones. The regiochemical outcomes of the present Baeyer-Villiger oxidation, the relative proportions of the isomeric lactones derived from unsymmetrical cyclohexanones (Entries 2, 3, 5, and 6), are well in accord with the generally accepted migratory aptitudes of the skeleton-carbons. It is worthy of mention that 2-tert-butylcyclohexanone sounds unattractive for the present lactonisation, since the ketone recovered essentially unchanged upon the reaction under the "standard" conditions indicated in the Table. This unexpected failure in combination with the results in Entries 2, 5, and 6 might suggest that the oxidative feasibility of a ketone is influenced strongly by an electrosteric requirement around the migrating sheleton-The MMPP/Bentonite/MeCN system was carbon. also effective for ring enlargement of cyclopentanone giving δ -valerolactone in 82% yield, but cyclic ketones of large ring size (seven- or more membered) were found to resist oxidation.

In summary, cyclohexanones underwent **smo**oth oxidation with *MMPP* in acetonitrile with the aid of the bentonite under neutral and relatively mild conditions,

Entry		<pre>&-Caprolactones</pre>	Yields
No.	Cyclohexanones	(Products ratios) ^{b)}	
1			88
2	o Me Me	Me Me	88
3	Me	(96:4)	95
4	° 	Me (50 : 50)	89
5	Me o iPr	Me Me ⁱ Pr	94
6	Ph	O Ph	65

Table. Oxidation of Cyclohexanones with MMPPa)

a) At 333K for 2 hrs; 2 mmol of ketone, 3 mmol of MMPP, 2 g of the moist bentonite clay, and 10 mL of acetonitrile were used in every run. b) Determined by 1 H NMR. c) Isolated yields based on the ketones consumed.

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affording the corresponding *e*-caprolactones in fairly good yields within a reasonable period of time. The products were stable during both the reaction and workup stages, and were therefore amenable to ready purification (vide infra). MMPP as a laboratory peroxy has progressively found extensive use acid in transformation of various functional groups, 8,10) being comparable with mCPBA, but considerably easier and safer Thus, we hope that the present results to handle. coupled with those of the previous work⁷) might contribute to extend the domain of the MMPP chemistry and the reagent's oxidative capability.

Experimental Section

Proton NMR spectra were measured with a Generals: JEOL JNM-60SI or JNM-FX200 spectrometer for solutions in carbon tetrachloride or deuteriochloroform using TMS as internal standard. IR spectra were recorded for thin disks JASCO films (neat) or KBr οn A-100 spectrophotometer. GC was performed on a Shimadzu GC-4CM instrument with a 2 m glass column packed with 5% PEG-20M on Chromosorb WAW-DMCS, with temperature programming.

MMPP was purchased from Tokyo Chemical Industry Co., Ltd. [JAPAN]; its purity was determined on the basis of iodometry (ca. 86%). The moist bentonite clay was prepared by adding distilled water (2.7 g) to the bentonite (*Kukita Yakuhin Kogyo Co., Ltd.* [*JAPAN*]; 18 g), carcined at *ca.* 620K for several hours, in portions followed by vigorous shaking of the mixture on every addition until a free-flowing powder was obtained (It should be done within a few minutes). All the ketones were commercial chemicals and were used without further purification; their purities were checked by GC analyses just befor use.

Oxidation Procedure: typical A oxidation procedure was as follows. Cyclohexanone (2 mmol), the moist bentonite clay (2 g), acetonitrile (10 mL), and a Teflon-coated magnetic stirring bar were placed in a 30 mL, round-bottom, two-necked flask equipped with a glass stopper and ca. 25cm long reflux condenser. The resultant cloudy mixture was heated in a thermostatic oil-bath at 333K with stirring. To the reaction mixture was added MMPP (3 mmol) in six portions at ten minute intervals; loose replacement of the glass stopper followed every addition. After completing the addition of MMPP, the heterogeneous mixture was continuously stirred for an additional hour vigorously. After cooling to room temperature, the whole mixture was transferred onto a sintered glass funnel, and the

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residue was thoroughly washed with *ca.* 100 mL of dichloromethane. Condensation of the combined filtrate on a rotary evaporator under reduced pressure followed by chromatographic separation on silica gel column (*Merk Silica Gel 60*; hexane: ethyl acetate= 3:2 by volume) afforded ε -caprolactone contaminated with a faint trace of an oxidant residue. Repeated column chromatography eluting with ethyl acetate gave the satisfactorily pure (by GC, NMR, and TLC) lactone in 84% isolated yield at 95% conversion (88% based on cyclohexane consumed).

The oxidation of the other ketones was performed as above, and the structure proof for each lactone was provided by proton NMR and IR. Since the complete separation by GC of the lactone isomers in Entries 2 and 3 were not attainable, their relative proportions were determined by ¹H NMR. In the cases of Entries 5 and 6, no spectroscopic evidence could be found for the formation of the isomers, accounting for the exclusive "methine migration".

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