

THALLIC ION OXIDATION OF CYCLOHEXANONE¹

Kenneth B. Wiberg and Werner Koch

Department of Chemistry, Yale University

New Haven, Conn.

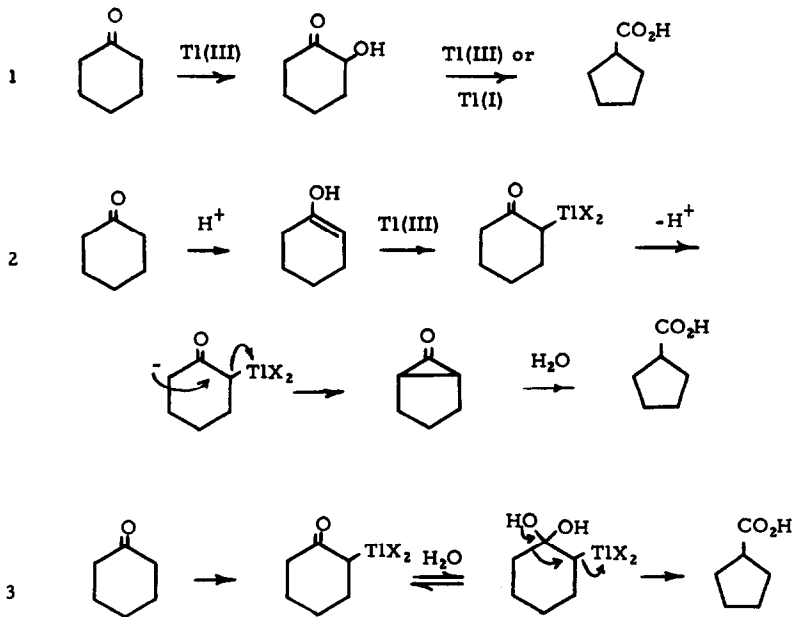
(Received 14 February 1966)

Thallic ion is of particular interest as an oxidant because unlike most other metal ion oxidants, it appears capable only of effecting a two electron change.² The reaction of thallic ion with cyclohexanone in aqueous perchloric acid solution has been reported by Littler³ to proceed via rate determining enolization leading to α -hydroxycyclohexanone as the product in analogy with the results of Kabbe⁴ on the oxidation of cyclohexanone with thallic acetate in acetic acid solution.

In hopes of learning more about the details of the reaction, we also have investigated the oxidation in aqueous perchloric acid solution. In contrast to the report of Littler, we find the products to be cyclopentanecarboxylic acid (75%) along with a trace (0-3%) of α -hydroxycyclohexanone and some recovered cyclohexanone (22-25%).

Cyclopentanecarboxylic acid could be formed by one or more of three general routes. First, α -hydroxycyclohexanone could be an intermediate, and be converted to the acid by Tl(III) or Tl(I); second, an α -thallium derivative could be formed from the enol, and this undergoes a Favorskii rearrangement via a cyclopropanone intermediate;⁵ and third, the α -thallium derivative could be formed and undergo a Favorskii rearrangement via attack of water at

the carbonyl function followed by rearrangement in a fashion similar to that for α -bromocyclobutanone.⁶



The first possibility was shown to be incorrect since α -hydroxycyclohexanone was not converted to the acid under the reaction conditions. The second and third possibilities could be distinguished by deuterium labeling. Using cyclohexanone-2, 2, 6, 6- d_4 , mechanism 2 would give the acid containing a maximum of two deuterium whereas mechanism 3 could lead to acid having three deuterium. The reaction was carried out as usual in 35% perchloric acid, the reaction mixture was quickly extracted with pentane, and the pentane solution immediately treated with lithium

aluminum hydride. The cyclohexanol had the composition 4% d_4 , 19% d_3 , 33% d_2 , and 45% d_1 , and the cyclopentylcarbinol had the composition 60% d_3 , 25% d_2 , and 15% d_1 , as determined mass spectrometrically. The high deuterium content of the cyclohexanol indicates that oxidation is competitive with return of the enol to the keto form, as suggested by Littler's kinetic data. The high deuterium content of the product demonstrates that the third mechanism is correct.

The oxidation of 2-methylcyclohexanone gave a mixture of products consisting of 78% 2-methylcyclohexen-2-one and 22% 2-methyl-2-hydroxycyclohexanone. The lack of ring contraction in this case might be expected since enolization will occur toward the methyl group, and loss of T1(I) from the intermediate will give a better stabilized α -keto carbonium ion, decreasing the driving force for rearrangement. Under the same conditions, 3-methylcyclohexanone gives mainly 2-methylcyclopentanecarboxylic acid; 4-methylcyclohexanone gives 3-methylcyclopentanecarboxylic acid; and 2,2-dimethylcyclohexanone gives 2,2-dimethylcyclopentanecarboxylic acid. cis- and trans- β -Decalones also undergo the ring contraction. The stereochemistry of the products is under investigation so that the stereochemistry of the reaction may be determined.

The ring contraction did not occur with cyclopentanone, cycloheptanone or cyclooctanone. The products from some of these appear to contain thallium; the structures are under investigation. The relationship between the present reaction and the ring contraction with selenium dioxide and hydrogen peroxide observed by Payne and Smith⁷ is also being studied.

References

1. This work was supported by a grant from the National Science Foundation.
2. A. G. Sykes, J. Chem. Soc., 5549 (1961); H. N. Halvorson and J. Halpern, J. Am. Chem. Soc., 78, 5562 (1956).
3. J. S. Littler, J. Chem. Soc., 827 (1962).
4. H. J. Kabbe, Ann., 565, 204 (1962).
5. R. B. Loftfield, J. Am. Chem. Soc., 73, 4707 (1951).
6. J. M. Conia and J. Salaun, Bull. soc. chim. France, 1957 (1964).
7. G. B. Payne and C. W. Smith, J. Org. Chem., 22, 1680 (1957).