Tetrahedron Letters No. 21, pp 1827 - 1830, 1977. Pergamon Press. Printed in Great Britain.

THALLIUM IN ORGANIC SYNTHESIS. 47. REGIOSELECTIVE RING EXPANSION OF CYCLIC ARALKYL KETONES VIA WITTIG-DERIVED OLEFINS WITH THALLIUM(III) NITRATE (TTN)[1,2]

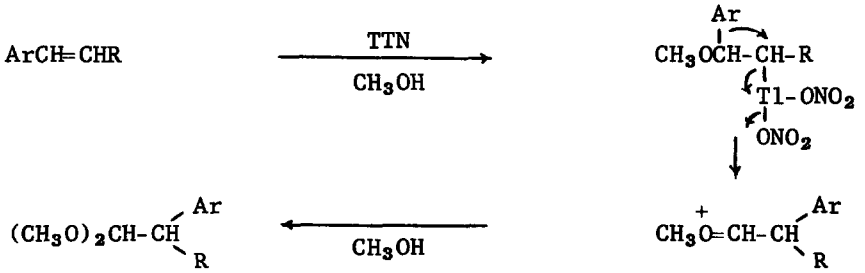
Edward C. Taylor* and Chih-Shu Chiang
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

and

Alexander McKillop
School of Chemical Sciences, University of East Anglia
Norwich NR4 7TJ, Norfolk, England

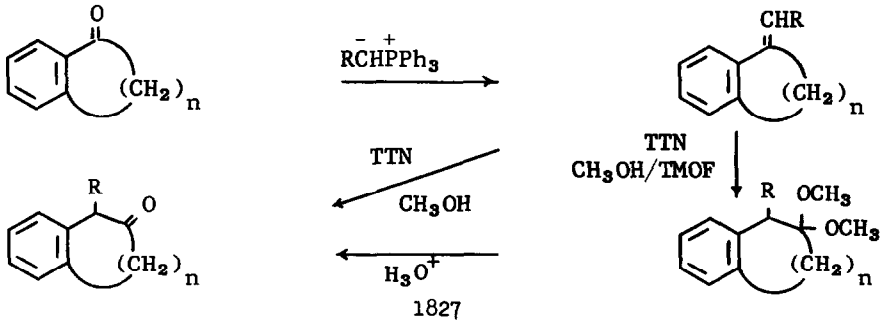
(Received in UK 28 March 1977; accepted for publication 12 April 1977)

We have recently described[3-5] a number of TTN-mediated oxidations of styrene derivatives which proceed extremely rapidly at room temperature to give high yields of carbonyl compounds. The overall transformation is initiated by oxythallation[6] of the double bond, followed by a 1,2-rearrangement of the aryl group; the carbon atom to which the aryl group was originally attached emerges as a (protected) carbonyl in the final product (eq. 1).



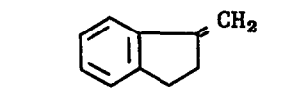
eq. 1

We now report a simple extrapolation of this oxidative rearrangement which provides a general method for ring expansion of cyclic aralkyl ketones whereby a methylene carbon (which may be substituted) is inserted selectively between the aromatic ring and the carbonyl group (eq. 2).

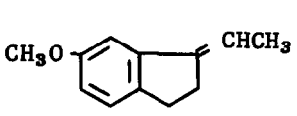


eq. 2

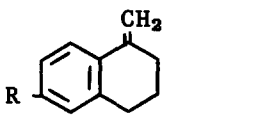
The overall transformation is effected in two steps: (i) conversion of the cyclic aralkyl ketone to an exomethylene derivative by reaction with an appropriate Wittig reagent,[7] and (ii) oxidative rearrangement of the latter with TTN.[8] The use of a mixture of methanol and trimethyl orthoformate as solvent (Method (a)) leads to the formation of the dimethylketal of the ring-expanded product (from which the parent carbonyl compound may be obtained in quantitative yield by acid hydrolysis), while the use of methanol alone as solvent (Method (b)) leads directly to the ring-expanded ketone. Typical conversions are summarized in eq. 3-11.



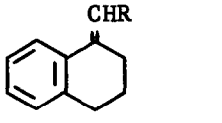
eq. 3



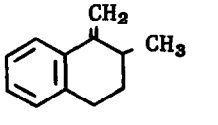
eq. 4



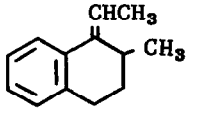
eq. 5



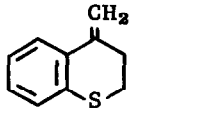
eq. 6



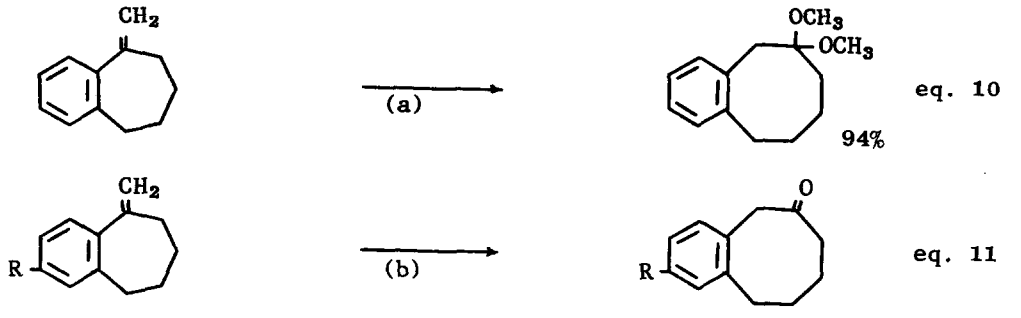
eq. 7



eq. 8



eq. 9



(a) TTN/TMOF/CH_3OH (b) TTN/CH_3OH

It should be noted in particular that this TTN-mediated ring expansion constitutes an unequivocal method for the preparation of products specifically substituted α and/or α' to the carbonyl group. Thus, 1-methyl-2-benzsuberone is obtained by TTN oxidation of the ethylidene derivative prepared from 1-tetralone (eq. 6), while the isomeric 3-methyl derivative results from oxidative rearrangement of the methylene derivative prepared from 2-methyl-1-tetralone and methylenetriphenylphosphorane (eq. 7). A combination of these two procedures leads to unequivocal 1,3-disubstitution (eq. 8). Sulfur-containing substrates may also be utilized (eq. 9).

This TTN-mediated ring expansion appears to be much superior to both classical (Wagner-Meerwein, Demjanov and diazomethane rearrangements[12]), and more recently introduced procedures which utilize dihalocarbenes[13] or cyanogen azide.[14] It also appears to be superior to methods for the preparation of benz-fused β-carbonyl compounds which involve carbonyl group transpositions.[15,16]

Method (a): To a solution of 4.5 g (10 mmol) of TTN.$3H_2O$ in a mixture of 20 ml of trimethyl orthoformate and 20 ml of methanol was added, in one portion with stirring, 1.62 g (10 mmol) of 4-methylene-1-thia-2,3-dihydronaphthalene. Reaction was instantaneous, as evidenced by the immediate separation of a voluminous precipitate of white thallium(I) nitrate. After 1 min of stirring, the reaction mixture was diluted with 30 ml of chloroform and filtered. The filtrate was neutralized with aqueous sodium bicarbonate, washed with water, dried (anhy. $MgSO_4$) and concentrated under reduced pressure to give 2.7 g of a crude product which was distilled (b.p. 105°/0.01 mm) to give 2.1 g (93%) of 1,2-benz-7-thiacyclohepten-4-one dimethylketal.

Method (b): To a solution of 4.5 g (10 mmol) of TTN.$3H_2O$ in 40 ml of methanol was added, in one portion with stirring, 1.72 g (10 mmol) of 1-propylidenetetralin. After 1 min, the reaction mixture was diluted with 30 ml of chloroform, filtered, and the filtrate worked up as described above. The crude product was distilled (b.p. 84-86°/0.01 mm) to give 1.8 g (96%) of 1-ethyl-2-benzsuberone.

REFERENCES AND NOTES

1. For the previous paper in this series, see A. McKillop, A. G. Turrell and E. C. Taylor, J. Org. Chem., 42, 362 (1977).

2. We are indebted to the National Science Foundation (Grant # MPS 72-00427) and to Eli Lilly and Company, Indianapolis, Indiana, for support of this work.

3. A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, J. Am. Chem. Soc., 95, 3635 (1973).

4. E. C. Taylor, R. L. Robey, K.-T. Liu, B. Favre, H. T. Bozimo, R. A. Conley, C.-S. Chiang, A. McKillop, and M. E. Ford, J. Am. Chem. Soc., 98, 3037 (1976).

5. E. C. Taylor, C.-S. Chiang, A. McKillop, and J. F. White, J. Am. Chem. Soc., 98, 6750 (1976).

6. See footnote 2 of reference 5.

7. I. H. Sadler, J. Chem. Soc. B, 1024 (1969).

8. Application of this principle to the preparation of 10,11-dihydrobenzo(b,f)thiepins in low yield has been described by Protiva et al.[9-11]

9. K. Sindelar, B. Kakac, J. Metysova, and M. Protiva, Farmaco. Ed. Sc., 28, 256 (1973).

10. J. O. Jilek, K. Sindelar, J. Pomykacek, O. Horesovsky, K. Pelz, E. Svatek, B. Kakac, J. Holubek, J. Metysova, and M. Protiva, Coll. Czechoslov. Chem. Commun., 38, 115 (1973).

11. K. Sindelar, B. Kakac, E. Svatek, J. Holubek, M. Rajsner, J. Metysova, and M. Protiva, Coll. Czechoslov. Chem. Commun., 39, 333 (1974).

12. C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions", Academic Press, New York, N.Y. 1968.

13. M. Sato, T. Tanaka, J. Tsunetsugu, and S. Ebine, Bull. Chem. Soc. Japan, 48(8), 2395 (1975).

14. J. E. McMurry and A. P. Coppolino, J. Org. Chem., 38, 16, 2821 (1973).

15. G. Fontaine, Ann. Chim. (Paris), 3, 469 (1968).

16. J. W. Lewis and A. A. Pearce, Tet. Lett., 2039 (1964).