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# A KETONE-ENONE CONVERSION VIA THE REACTION OF ENOL SILYL ETHERS WITH DDQ[1]

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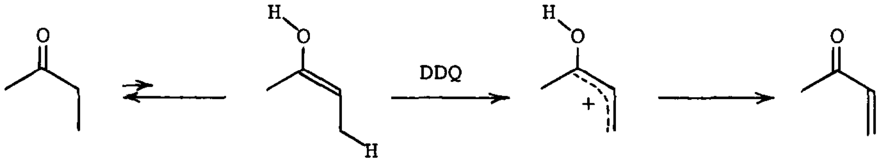
Development of a convenient method for introduction of α,β-unsaturation into saturated ketones is of current interest for synthetic organic chemists. Among a good many of accumulations of previous works, direct dehydrogenation of ketones by quinones seems one of the attractive approaches to enones and it has already found an extensive application in the dehydrogenation of steroidal ketones.[2]

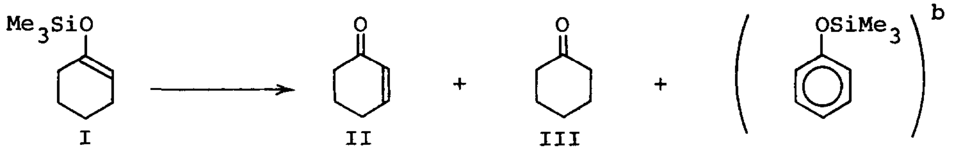
This approach, however, seems not applicable to simple saturated ketones, such as cyclohexanone, which are not easily enolizable.[3,4] All preceding data strongly suggest that the dehydrogenation of ketones by quinones is initiated by hydrogen abstraction from the allylic position of the corresponding enols (see the following scheme). This appears to place restriction on the starting ketones. For quinone-induced enone formation, the use of enol silyl ethers instead of ketones occurred to us.



We now wish to report an efficient method for the conversion of ketones to enones via the reaction of enol silyl ethers with DDQ (2,3-dichloro-5,6-dicyanoquinone).[2]

The reaction of 1-trimethylsiloxycyclohexene with DDQ at 15° proceeded smoothly and completed within 0.5-1 h.[5] Cyclohexanone itself did not react at all under the same reaction conditions. Several attempts for the synthesis of cyclohexenone are listed in the Table I.

Table I. Yields of Cyclohexenone from the Reaction of 1-Siloxycyclohexene with Quinones.[a]



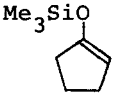
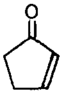
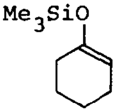
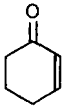
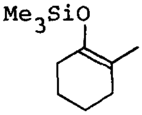
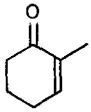
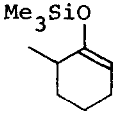
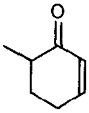
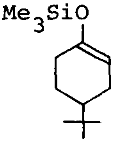
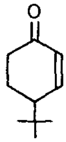
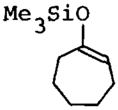
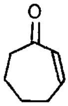
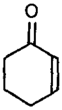
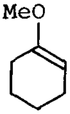
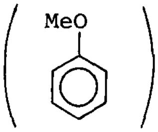
| Entry | Substrate | Reagent | Solvent | Time, Temp. | Yield of II [%] | (II:III)[c] |
|---|---|---|---|---|---|---|
| 1 | 1-Siloxycyclohexene | Chloranil | Benzene | 1h, 15° | 4 | ( 57 : 43 ) |
| 2 | | DDQ | Dioxane | 1h, 15° | 42 | ( 85 : 15 ) |
| 3 | | DDQ | Benzene | 1h, 15° | 51 | ( 80 : 20 ) |
| 4 | | DDQ +HMDS[d] | Benzene | 1h, 15° | 68 | ( 91 : 9 ) |
| 5 | | DDQ +BSA[e] | Benzene | 1h, 15° | 60 | ( 92 : 8 ) |
| 6 | Cyclohexanone | DDQ | Benzene | 1h, 15° | 0 | ( 0 :100) |

a) Reaction conditions: Under atmosphere of dry nitrogen, to a stirred solution of quinone (43 mmol) in 2.5 ml of solvent with or without silylating reagent was added enol silyl ether (0.25 mmol) in one portion at 15°, and then the stirring was continued for 1h. b) A few percents formation of phenyl silyl ether was observed in every case except entry 6. c) Estimated by GLC (DEGS / 3m / 100°). d) Hexamethyldisilazane (0.10 mmol) was added. e) Bis(trimethylsilyl)-acetamide (0.12 mmol) was added.

The use of chloranil (entry 1) was ineffective, while the use of DDQ showed better results (entries 2, 3). A drawback to be overcome in these procedures was contamination of considerable amounts of cyclohexanone in the products, which was very likely to arise from the side reaction of the starting enol silyl ether with the mono-silylated hydroquinone, a by-product of the reaction. The addition of silylating reagents to mask the hydroquinone gave improved results (entries 4, 5).

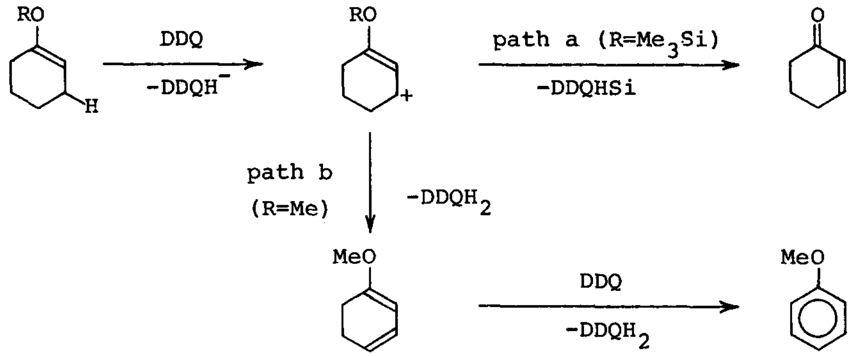
The results of the synthesis of α,β-unsaturated ketones employing DDQ-BSA were summerized in Table II. The results show that the present method is most suitable for the synthesis of cyclohexenones (entries 8, 9, 10, 11). Regioselective synthesis of 2- and 6-methylcyclohexenones was attained by employing the corresponding enol silyl ethers (entries 9, 10).[6] When 1-methoxycyclohexene was reacted under the same reaction conditions, anisole, in stead of cyclo-

Table II. Conversion of Enol Silyl Ethers to Enones by DDQ-BSA[a].

| Entry | Substrate | Enone | Yield of Enone[b,c] | (Yield of Ketone[b]) [%] |
|---|---|---|---|---|
| 7 |  |  | 20 | (32) |
| 8 |  |  | 60 | ( 5) |
| 9 |  |  | 50 | ( 3) |
| 10 |  |  | 53 | (11) |
| 11 |  |  | 84 | (14) |
| 12[d] |  |  | 14 | (24) |
| 13 |  | No reaction | ( - ) | ( - ) |
| 14[e] |  |  | (65) | ( 0) |

a) Reaction conditions are the same in entry 6 in the Table I. b) Analyzed by GLC (DEGS / 3m / 100°). c) Yields are not optimized. d) The reaction was conducted under refluxing conditions of benzene. e) 2.1 Molar excess of DDQ was used.

hexenone, was obtained in 65% yield (entry 14). The following scheme could account for the observed results. The trimethylsilyl group of I acts as a nice positive leaving group (path a) and the path competes successfully with deprotonation (path b). On the other hand, in case of methyl ether, deprotonation (path b : R=Me) overwhelms dealkylation.[7]



## References and Notes

(1) Synthesis via Silyl Alkenyl Ethers, Part XIV. Part XIII: I. Ryu, S. Murai, A. Shinonaga, T. Horiike, and N. Sonoda, J. Org. Chem., 43, 780 (1978).

(2) H.-D. Becker, "The Chemistry of Quinoid Compounds", S. Patai Ed., Wiley, New york, N. Y., 1974, Part 1, Chapter 7; H. O. House, "Modern Synthetic Reactions", 2nd Ed., Benjamin, Menlo Park, Calif., 1972. pp 37-44; D. Walker and J. D. Hiebert, Chem. Rev., 67, 153 (1967); A. B. Turner, "Synthetic Reagents", J.S. Pizey Ed., Ellis Horwood Ltd., England, 1977, Vol. 3, Chapter 2.

(3) The reaction of cyclohexanone with DDQ has previously been reported not to give cyclohexenone but a coupled product at α-position of carbonyl: H. B. Henbest and D. N. Jones, Chemistry and Industry, 1113 (1960).

(4) J. Carretto and M. Simalty reported the dehydrogenation of cyclohexyl phenyl ketone (enolizable) by DDQ to yield a mixture of cyclohexenyl phenyl ketone and benzophenone. See, Tetrahedron Lett., 3445 (1973).

(5) Very recently M. E. Jung and coworkers reported their finding in the same area: M. E. Jung, Y.-G. Pan, M. W. Rathke, D. F. Sullivan, and R. P. Woodbury, J. Org. Chem., 42, 3961 (1977). Ketone-enone conversion by other approaches employing enol silyl ethers has also been reported. The reaction with Pd(II), see Y. Ito, T. Hirao, and T. Saegusa, J. Org. Chem., 43, 1101 (1978). The reaction with singlet oxygen, see E. Friedrich and W. Lutz, Angew. Chem. Int. Ed. Eng., 16, 413 (1977).

(6) Usually dehydrogenation of ketones takes place in non-regioselective manner. For example, see B. Bierling, K. Kirschke, and H. Oberender, J. Prakt. Chem., 314, 170 (1972).

(7) Partial formation of phenyl silyl ether in case of 1-siloxycyclohexene (Table I, footnote b) may imply the presence of a leak to a small extent from the path b in the scheme.

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