Tetrahedron Letters,Vol.25,No.45,pp 5147-5150,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

# REACTIONS OF 1,1,3,3-TETRAMETHYLINDANE-2-SELONE WITH GRIGNARD AND ORGANOLITHIUM REAGENTS

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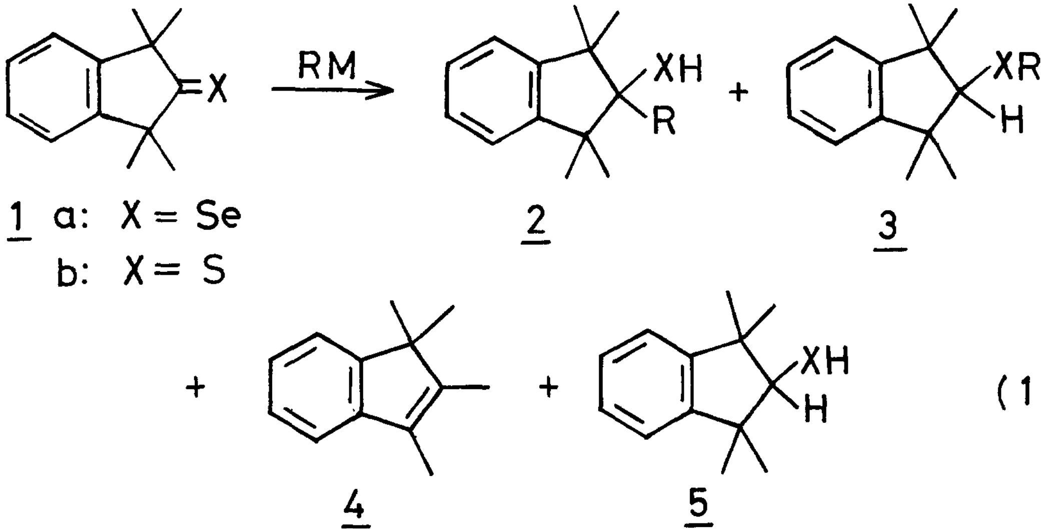
Summary: The title reaction afforded selenophilic, carbophilic, and reduction products depending on the kinds of the organometallic reagents and the heterophilic nature of the reaction was more conspicuous in the reaction with the selenoketone than with the corresponding thioketone.

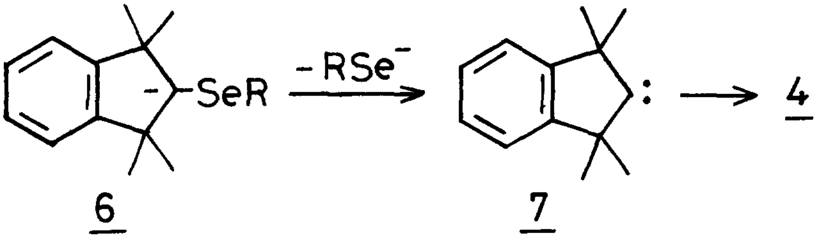
Organoselenium chemistry is of current interest.[1-3] We have recently reported a novel synthesis of selenoketones (selones) from ketone hydrazones.[4] We now delineate here the first example of the reaction of the selenoketones with Grignard and organolithium reagents. Although the reactions of Grignard and organolithium reagents with thioketones have been attracting considerable attention in recent years because of its unique heterophilic nature,[5-7] there has been no report on the reaction of selenoketones with such organometallic compounds which is considered to be an important reaction to reveal the reactivity of the carbon-selenium double bond.

When 1,1,3,3-tetramethylindane-2-selone (1a)[4] was allowed to react with Grignard and organolithium reagents in ether at room temperature, four types of compounds were produced depending upon the reagents used, i.e., carbophilic (2a), selenophilic (3a), reduction products (5a), and 1,1,2,3-tetramethylindene (4) [equation (1) and Table 1].[8] For comparison, the reactions of ogranolithium compounds with the corresponding thioketone (1b) were also carried out and similar types of products were obtained. The results are included in Table 1.

The formation of 4 can be accounted for in terms of equation (2) involving selenophilic intermediate (6) and carbene (7). Although there are some precedents of such carbene-forming reactions for sulfur-stabilized carbanions,[9] this is, to our knowledge, the first example for selenium analogs.



(1)



(2)

The results obtained here indicate that the reactions of organometallic reagents with slenoketones are very unique in that the heterophilic nature is much more conspicuous than those with thioketones. Thus, both selenophilic and carbophilic products are formed in the reactions of methyllithium with 1a whereas only the carbophilic product is found in the reaction with 1b (entry 1). In the reaction with t-butyllithium (entry 3) some selenophilic product (3a) was formed from 1a, while no thiophilic product was obtained from 1b. In the reaction with phenyllithium (entry 6) the preference of the heterophilic attack is even more obvious; the selenophilic product (3a) is a sole product in the reaction with 1a whereas the carbophilic product (2b) is a main product in the reaction with 1b.

Table 1. Reactions of selenoketone (1a) and thioketone (1b) with Grignard and organolithium reagents[a]

| Entry | RM | Yield (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 2a | 2b | 3a | 3b | 4 | 5a | 5b |
| 1 | MeLi | 73 | 91 | 10 | | | | |
| 2 | MeMgI | 69 | | | | | | |
| 3 | t-BuLi | | | 9 | | | 66 | 57 |
| 4 | t-BuMgCl | | | 15 | | 20 | 44 | |
| 5 | $PhCH_2Li$ | 86 | 95 | | | | | |
| 6 | PhLi | | 56 | 47 | 24 | | | |
| 7 | PhMgBr | | | 3 | | 14 | | |

[a] The reactions were carried out using 3 mole equivalents of the organometallic reagents except entries 3 and 7 where the reaction was slow and 4.5 and 6 mole equivalents were used respectively.

## References and Notes

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8. The reaction product had the following spectral data [NMR (δ, $CDCl_3$); IR (ν, KBr)]. 2a (R= $CH_3$): δ -0.45 (SeH, s, 1H), 1.29 (s, 6H), 1.39 (s, 3H), 1.44 (s, 6H), 7.16 (s, 4H); 2a (R= $PhCH_2$): δ -0.61 (SeH, s, 1H), 1.45 (s, 6H), 1.55 (s, 6H), 3.26 (s, 2H), 6.9-7.7 (m, 9H); 2b (R= $CH_3$): δ 1.22 (s, 3H), 1.28 (s, 6H), 1.39 (s, 6H), 7.1-7.2 (m, 4H); ν(SH) 2585 $cm^{-1}$; 2b (R= Ph): δ 0.96 (s, 6H), 1.55 (s, 6H), 1.61 (s, 1H), 7.0-7.4 (m, 9H), ν (SH) 2610 $cm^{-1}$; 2b (R= $PhCH_2$): δ 1.14 (SH, s, 1H) (disappeared in $CD_3OD$-$C_6D_6$), 1.38 (s, 6H), 1.57 (s, 6H), 3.20 (s, 2H), 7.05-7.68 (m, 9H); 3a (R= $CH_3$) δ 1.25 (s, 6H), 1.40 (s, 6H), 2.11 (s, 3H), 3.03 (s, 1H), 7.18 (s, 4H); 3a (R= t-Bu) δ 1.21 (s, 6H), 1.38 (s, 6H), 1.50 (s, 9H), 3.04 (s, 1H), 7.19 (s, 4H); 3a (R= Ph) δ 1.31 (s, 6H), 1.32 (s, 6H), 3.49 (s, 1H), 7.1-7.8 (m, 9H); 3b (R= Ph) δ 1.31 (s, 12H), 3.46 (s, 1H), 7.0-7.7 (m, 9H); δ ($C_6D_6$) 1.27 (s, 6H), 1.36 (s, 6H), 3.49 (s, 1H), 6.9-7.6 (m, 9H); 5a δ -0.76 (d, J= 8 Hz, 1H), 1.21 (s, 6H), 1.31 (s, 6H), 3.28 (d, J= 8 Hz, 1H), 7.17 (s, 4H); 5b δ 1.16 (d, J= 11 Hz, 1H), 1.19 (s, 6H), 1.35 (s, 6H), 3.03 (d, J= 11 Hz, 1H), 7.20 (s, 4H); ν(SH) 2580 $cm^{-1}$.
   The indene 4 was identified by comparison of the NMR spectral data with those reported (J. Buddrus, Chem. Ber., 101, 4152 (1968)).
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(Received in Japan 19 July 1984)