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# SYNTHETIC APPLICATIONS OF PHENYLTRIMETHYLSILYLSELENIDE[1]

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The utility of bifunctional, neutral molecules which contain both hard acid and soft base components have received increased attention recently by synthetic chemists.[2] In particular, we were interested in adding mixed silicon-selenium reagents to unsaturated aldehydes and ketones to produce adducts which are potential enone β-anion equivalents. We wish to report some synthetic applications of one of these "mixed" reagents, phenyltrimethylsilylselenide, 1.[3]

The reagent is prepared as follows: To a solution of 2.75 g of benzeneselenol (17.5mmole) in dry ether (20 ml, 0°C under argon) is added 11.2 ml of 1.6 M $CH_3Li$ in ether (17.5 mmole) in a dropwise fashion. When methane evolution ceases, 2.85 g of freshly distilled $(CH_3)_3SiCl$ (26.3 mmole) is added in a dropwise fashion and the resulting mixture is allowed to stir for one hour at room temperature. Since 1 is both oxygen and moisture-sensitive, the most efficient work-up procedure involves filtration in a glove bag purged with argon,[4] followed by removal of the solvent and excess $(CH_3)_3SiCl$ *in vacuo*. Compound 1 can then be distilled (b.p. = 70°C, 1.9 torr) or used directly without purification. Unless the reagent is to be used immediately, we recommend preparing a standard solution and removing aliquots as needed.[5] Under these conditions solutions of 1 exhibit only a slight degree of decomposition with time (<5% in a month).[6]

$$PhSeH \xrightarrow[2)\ (CH_3)_3SiCl]{1)\ CH_3Li} PhSeSi(CH_3)_3 \quad 91\%$$

1

The results of reactions of 1 with a variety of aldehydes and ketones are shown in Table I. Compound 1 reacts slowly with saturated aldehydes 2 and 4 to produce hemiselenoacetals 3 and 5 in quantitative yield. Of the three catalysts studied ($BF_3$, $PPh_3$, and $ZnCl_2$), $ZnCl_2$ and $PPh_3$ effect reaction most efficiently. Attempts to produce the corresponding bis-selenoacetals of

TABLE I

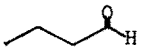
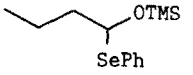
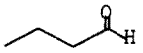
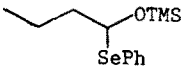
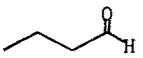
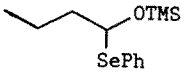
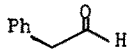
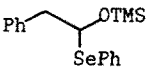
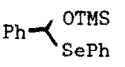
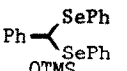
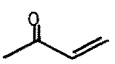
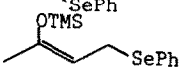
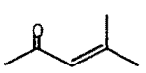
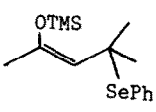
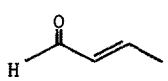
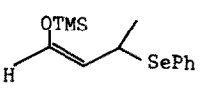
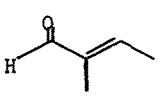
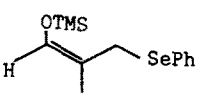
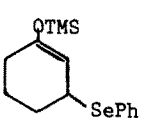
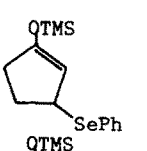
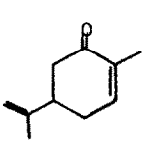
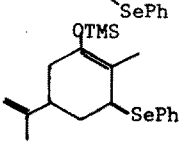
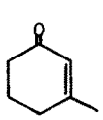
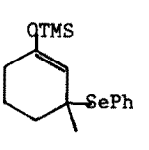
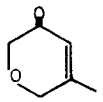
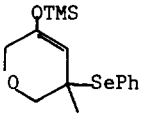
| Substrate | Compound Number | Catalyst[a] | Time/Temp. | Adduct[b] | Adduct Number | E/Z[c] | % Yield[e] |
|---|---|---|---|---|---|---|---|
|  | 2 | $BF_3$ B | 24h/55° |  | 3 | - | 100 |
|  | 2 | $PPh_3$ A | 14h/55° |  | 3 | - | 100 |
|  | 2 | $ZnCl_2$ A | 14h/55° |  | 3 | - | 100 |
|  | 4 | $ZnCl_2$ A | 14h/55° |  | 5 | - | 100 |
|  | 6 | - B | 9h/25° |  | 7 | - | 100 |
|  | 6 | $ZnCl_2$ A | 48h/55° |  | 8 | - | 99 |
|  | 9 | $PPh_3$ A | 14h/25° |  | 10 | 3/2 | 90 |
|  | 11 | $PPh_3$ A | 30m/25° |  | 12 | -[d] | 70[f] |
|  | 13 | $PPh_3$ A | 12hr/25° |  | 14 | 2/1 | 100 |
|  | 15 | $PPh_3$ A | 11hr/25° |  | 16 | 6/1 | 95 |
|  | 17 | $PPh_3$ A | 2-4h/25° |  | 18 | - | 100 |
|  | 19 | $PPh_3$ A | 2-4h/25° |  | 20 | - | 100 |
|  | 21 | $PPh_3$ A | 4h/25° |  | 22 | - | 100 |
|  | 23 | $PPh_3$ A | 30m/25° |  | 24 | - | 70[f] |

TABLE I. Continued

| Substrate | Compound Number | Catalyst | Time/Temp. | Adduct | Adduct Number | E/Z | % Yield |
|---|---|---|---|---|---|---|---|
|  | 25 | $PPh_3$ A | 8h/25° |  | 26 | - | 100 |

a) One crystal (or drop) of catalyst was used; A = $CH_3CN$ or $CD_3CN$; B = $CHCl_3$ or $CDCl_3$

b) All reactions were carried out using 1.0-1.1 equiv. of 1 and 1 equiv. of reactant. Products were identified by analysis of their ir and nmr spectra. The mass spectra of all stable compounds were also determined and found to be consistent with the assigned structure.

c) Assignments based on analyses of nmr coupling constants.

d) E-isomer was assumed to be present in the largest quantities.

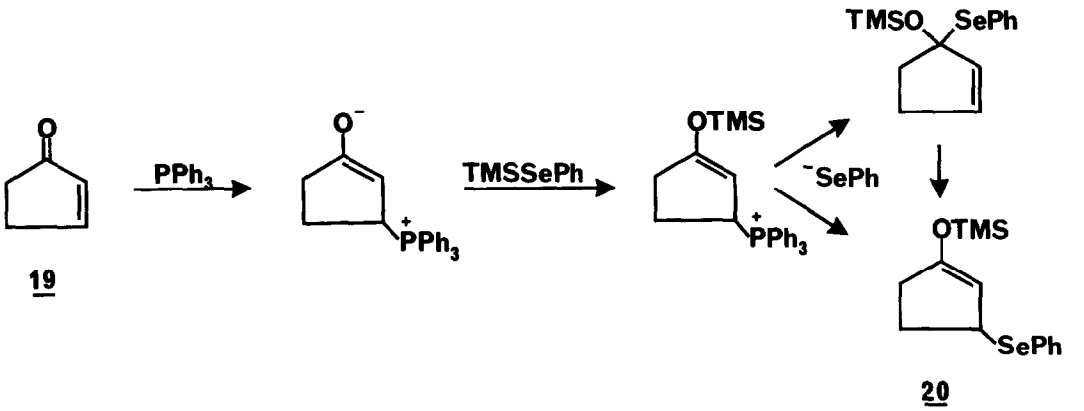
e) % yield represents the yield of isolated, undistilled product.

f) % yield determined by nmr.

2 and 4 gave disappointing mixtures of mono- (70-80%) and bis- (20-30%) addition products. In fact, the only bis-selenoacetal which we were able to efficiently prepare with our reagent was 8, the bis-selenoacetal of benzaldehyde.[7]

Unsaturated aldehydes react with 1 at a considerably faster rate than their saturated counterparts. Thus, compounds 9, 11, 13 and 15 yield 1,4-adducts 10, 12, 14 and 16, respectively, at room temperature in the indicated times. Interestingly, nmr studies of the reactions mixture 1 with 13 and 15 after relatively short reaction times (∿30 min) indicate the presence of both 1,2- and 1,4-adducts in an approximately 2:1 ratio.[8] With time, the relative amounts of 1,4-adducts of both aldehydes increase at the expense of the 1,2-adducts. Thus, the implication is that 1,2-adducts are kinetically-favored, while 1,4-adducts are thermodynamically more stable.

With unsaturated ketones no 1,2-adducts were observed, irrespective of the reaction times employed. Based on our data, we have no basis for differentiating between exclusive 1,4-addition and 1,2-addition followed by rapid rearrangement to the corresponding 1,4-adducts.[9] A plausible mechanism for reactions of 1 with unsaturated aldehydes and ketones is shown below:




19 20

With the exception of 12 and 24, all the adducts shown in Table I are relatively stable oils which survive vacuum distillation as well as washing with water and aqueous base.[10] Compounds 12 and 24 are somewhat unstable under the indicated reaction conditions and yield biproducts which are mixtures of dienol ethers (elimination of benzeneselenol).

Finally, it is worth mentioning that 1 reacts with saturated ketones at a rate which is substantially slower than any of the reactions given in Table I. This then strongly suggests the possibility of obtaining regioselective reactions of 1 with molecules which contain both saturated and unsaturated aldehydes and/or ketones. This and other applications of phenyltrimethylsilylselenide additions will be the subject of future reports.

References

1. We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for financial support. We also thank the National Science Foundation for funds for the purchase of our Finnigan 4000 GC-MS system.
2. For example, see (a) D. A. Evans, L. K. Truesdale, K. G. Grimm and S. L. Nesbitt, J. Amer. Chem. Soc., 99 5009 (1977); (b) M. E. Jung and M. A. Lyster, J. Amer. Chem. Soc., 99, 968 (1977); (c) M. E. Jung, W. A. Andrus and P. L. Ornstein, Tetrahedron Lett., 4175 (1977).
3. This reagent has been previously reported. See: N. Derkach, N. A. Pasmurtseva and E. S. Levchenko, Zh. Org. Khim., Eng. Ed., 7, 1600 (1971).
4. All attempts to use solutions of 1, which were prepared in situ and used without removal of residual lithium chloride, have yielded only recovered starting material.
5. Although we have typically used $CDCl_3$ or $CD_3C{\equiv}N$ as solvent, many other organic solvents can also be successfully used.
6. Solution decomposition can be easily monitored via nmr.
7. Bis-selenoacetals can be easily prepared by other methods. See: A. Krief, W. Dumont and P. Bayet, Angew. Chem., International Ed. Eng., 13, 804 (1974).
8. At this point, substantial quantities of starting material are present.
9. For another example of competitive 1,2- and 1,4-adducts to enones, see: W. C. Still and A. Mitra, Tetrahedron Lett., 2659 (1978).
10. All adducts are rapidly hydrolyzed by aqueous acid.

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