conversion can be visually monitored as the orange dansyl chloride converts to the yellow dansyl fluoride.

The mild reaction conditions, excellent yields, simple isolation and purification of products, and scalability[18] are advantages of this procedure over prior arts that require energy input, sophisticated equipment, and expensive, noncommercially available reagents.

Experimental Section

Reactions were carried out in Pyrex equipment. Sulfonyl chlorides were commercially available (Eastman Kodak Co.). Potassium fluoride was commercially available (MCB) in anhydrous form and was not dried prior to use. 18-Crown-6 ether was prepared according to a known literature procedure.[19]

Preparation of *p*-Acetamidobenzenesulfonyl Fluoride (6). Acetonitrile Method. To a mixture of *p*-acetamidobenzenesulfonyl chloride (117.0 g, 0.5 mol) and potassium fluoride (58.0 g, 1.0 mol) in 200 mL of acetonitrile was added a solution of 18-crown-6 ether/acetonitrile complex (5 g) in 100 mL of acetonitrile at room temperature (20 °C). The reaction mixture was allowed to stir overnight. It was then drowned out in 5 volumes of water. The off-white solid was collected, washed with water, and dried to provide 105.0 g of *p*-acetamidobenzenesulfonyl fluoride, mp 175–177 °C, 96% yield.

Preparation of Benzenesulfonyl Fluoride (3). Neat Method. To a solution of 18-crown-6 ether/acetonitrile complex (5 g) and benzenesulfonyl chloride (340 g, 1.93 mol) was added portionwise potassium fluoride (130 g, 2.24 mol). The reaction mixture was allowed to stir overnight after completion of the exothermic addition. One liter of water was then added, and the organic layer was separated, dried over anhydrous magnesium sulfate, and vacuum distilled to give 285.0 g of benzenesulfonyl fluoride, bp 84–85 °C (8 mmHg), 92.5% yield.

Registry No.—1 chloride derivative, 124-63-0; 2 chloride derivative, 1939-99-7; 3 chloride derivative, 98-09-9; 4 chloride derivative, 98-59-9; 5 chloride derivative, 98-58-8; 6 chloride derivative, 121-60-8; 7 chloride derivative, 605-65-2.

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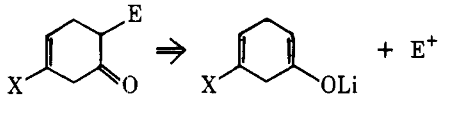
(14) 1,4,7,10,13,16-Hexaoxacyclooctadecane.
(15) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
(16) C. L. Liotta, private communication.
(17) Diethyl ether has been successfully used as a solvent.
(18) Compound 3 has been prepared on a 16-kg (68.4 mol) scale, using 280 g (0.81 mol) of 18-crown-6 ether/acetonitrile complex.
(19) G. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974).

Communications

α'-Functionalization of β,γ-Unsaturated Cyclohexenones. Utilization of Silyl Enol Ethers Produced from the Lithium/Ammonia Reduction of Silyl Aryl Ethers

Summary: Lithium/ammonia reduction of isopropyldimethyl- and *tert*-butyldimethylsilyl aryl ethers provides a high-yield synthesis of 1,4-dihydroaryl silyl ethers which may be regiospecifically elaborated to nonconjugated ketones.

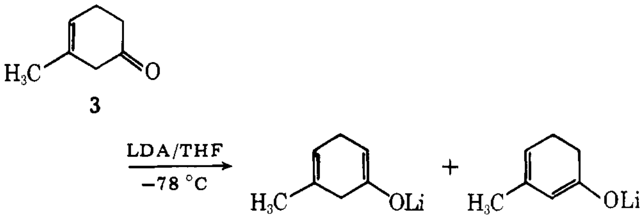
Sir: We have been faced with the need for a general method for synthesis of nonconjugated enones of the type **1a,b**. Analysis of this problem suggested that one conceptually simple solution might be via the reaction of enolate **2a,b** with an electrophilic species, E$^+$.



1a, X = CH_3 2a, X = CH_3
b, X = OCH_3 b, X = OCH_3

Attempts to generate enolate **2a** by addition of ketone **3** to a solution of lithium diisopropyl amide (LDA) were precluded by preferential formation of conjugated enolate **4**.[1]

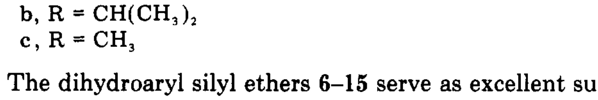
Since it has been established that silyl enol ethers can be regiospecifically functionalized under kinetic conditions either directly, by electrophilic substitution reactions,[2] or via prior conversion to an enolate,[3,4] it was felt that a similar expedient with dihydroaryl silyl ethers such as **6a–c** might provide an efficient synthesis for the desired class of nonconjugated enones.



3

2a (~20%) 4 (~80%)

Preparation of the requisite dihydroaryl silyl ethers can be conveniently achieved by lithium/ammonia reduction of the corresponding *tert*-butyldimethylsilyl or isopropyldimethylsilyl phenyl ethers **5a–b**[5] under carefully controlled conditions[6] (see Chart I). The corresponding trimethylsilyl aryl ether **5c** is hydrolytically unstable to the reaction conditions and provides only a very poor yield of dihydroaryl isomer **6c**.

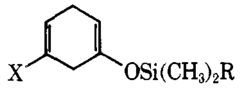


5a, R = $C(CH_3)_3$
b, R = $CH(CH_3)_2$
c, R = CH_3

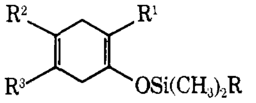
6a–c

The dihydroaryl silyl ethers **6–15** serve as excellent substrates for further functionalization; for example, reaction of isopropyldimethylsilyl enol ether of **7b** with methyllithium[3,13] cleanly generates enolate **2a** as demonstrated by reaction with acetic anhydride (inverse addition) to produce oxygen and carbon acylated products **16**[8,9] and **17**[8,9,14] which are uncontaminated by products which would have resulted from eno-

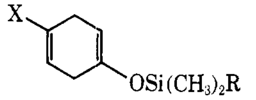
Chart I. Dihydroaryl Silyl Ethers Produced from Aryl Silyl Ethers[7-9]



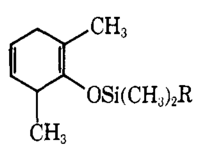
6a, X = H; R = *t*-Bu (95%)
b, X = H; R = *i*-Pr (90%)
7a, X = CH_3; R = *t*-Bu (92%)
b, X = CH_3; R = *i*-Pr (90%)
8a, X = OCH_3; R = *t*-Bu (95%)
b, X = OCH_3; R = *i*-Pr (90%)



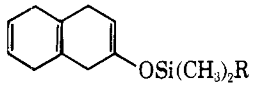
9a, R^1 = CH_3; R^2 = R^3 = H; R = *t*-Bu (96%)
b, R^1 = CH_3; R^2 = R^3 = H; R = *i*-Pr (89%)
10a, R^1 = R^2 = CH_3; R^3 = H; R = *t*-Bu (97%)
b, R^1 = R^2 = CH_3; R^3 = H; R = *i*-Pr (90%)
11a, R^1 = R^3 = CH_3; R^2 = H; R = *t*-Bu (95%)
b, R^1 = R^3 = CH_3; R^2 = H; R = *i*-Pr (93%)



12a, X = CH_3, R = *t*-Bu (95%)
b, X = CH_3, R = *i*-Pr (89%)
13a, X = OCH_3; R = *t*-Bu (85%[10])
b, X = OCH_3; R = *i*-Pr (80%[10])

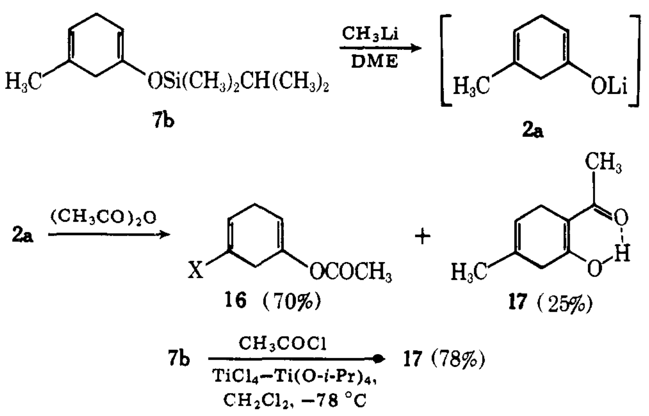


14a, R = *t*-Bu (60%[11])
b, R = *i*-Pr (54%[11])



15a, R = *t*-Bu (95%[12])
b, R = *i*-Pr (91%[12])

late equilibration.[15,16] The further versatility of dihydroaryl silyl ethers is shown by the *direct* production of **17** via the $TiCl_4$ catalyzed[2] reaction of **7b** with acetyl chloride.

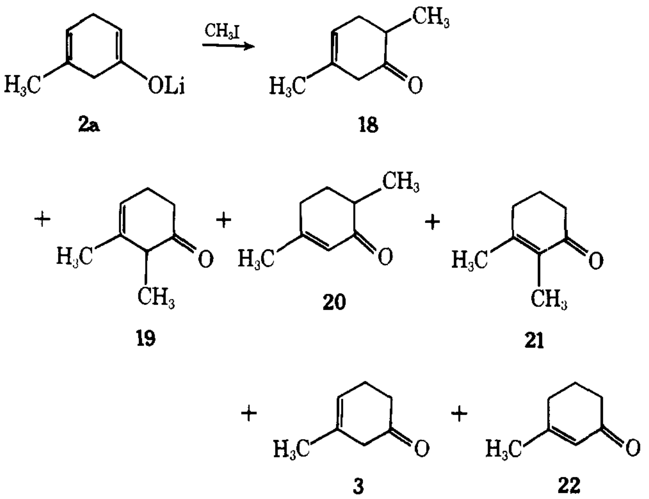


7b **2a**

2a **16** (70%) **17** (25%)

7b

Initial attempts at alkylation of enolate **2a** were disappointing. Addition of **2a** to excess methyl iodide (with or without HMPA) does not smoothly produce the desired ketone **18**. In addition to a poor yield of **18** (25%), the mixture contains nonconjugated ketone **19** (20%), conjugated isomers **20** (5%) and **21** (5%), nonmethylated ketones **3** (10%) and **22** (5%), as well as several polyalkylated products (30%). During the course of the alkylation reaction, the initially produced alkylated ketone **18** is apparently serving as an acid to allow enolate equilibration which fosters the observed plethora of products.[17]

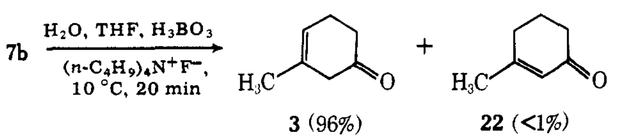


2a **18**

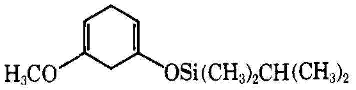
19 **20** **21**

3 **22**

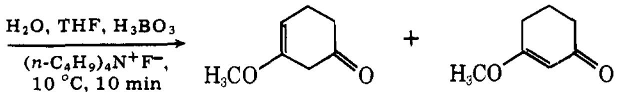
Dihydroaryl isopropyldimethylsilyl ethers also provide convenient substrates for the synthesis of nonconjugated ketones via tetraalkylammonium fluoride mediated hydrolysis.[18-20] Reaction of **7b** with a homogeneous solution of tetrabutylammonium fluoride[5] in aqueous tetrahydrofuran buffered with boric acid smoothly produces enone **3**. Hydrolysis of *mixed* siloxyalkoxy ethers **8b** and **13b** similarly yields the regiospecifically monoprotected diones **23** and **25**, respectively.[7-9]



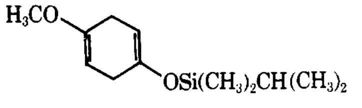
7b **3** (96%) **22** (<1%)



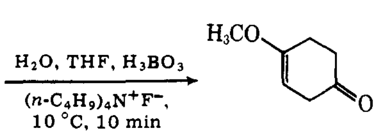
8b



23 (97%) **24** (1%)

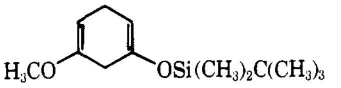


13b

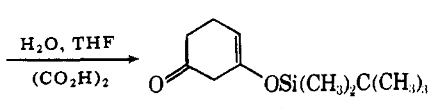


25 (96%)

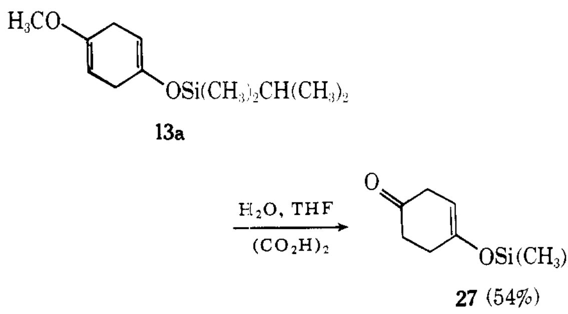
The complimentary hydrolysis of the alkyl enol ether moiety of *tert*-butyldimethyl silyl ethers **8a** and **13a** may be satisfactorily achieved under acidic conditions.[7-9,21,22]



8a



26 (55%)



13a

27 (54%)

Acknowledgment. This investigation was supported by Grant Number CA-19689-01, awarded by The National Cancer Institute, DHEW.

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(1) This ratio was obtained by NMR analysis of the mixture of oxygen and carbon acetylated products which result from quenching the **2a/4** reaction with acetic anhydride.

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(3) (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90,** 4462 (1968); (b) *ibid.*, 4464 (1968); (c) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34,** 2324 (1969); (d) G. Stork and J. d'Angelo, *J. Am. Chem. Soc.*, **96,** 7114 (1974); (e) M. E. Jung and C. A. McCombs, *Tetrahedron Lett.*, 2935 (1976), and references contained therein.

(4) I. Kuwajima and E. Nakamura, *J. Am. Chem. Soc.*, **97,** 3257 (1975).

(5) The phenyl silyl ethers were easily prepared (average 94% yield,[7-9] 20 cases) by reaction of the appropriate phenol with either *tert*-butyldimethylchlorosilane[5a] or isopropyldimethylchlorosilane[5b] in DMF with imidazole as catalyst.[5a] (a) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94,** 6190 (1972). (b) E. J. Corey and R. K. Varma, *ibid.*, **93,** 7319 (1971).

(6) The following experiment is typical of the procedure employed for the reduction of dimethyl-*tert*-butyl and dimethylisopropylsilyl aryl ethers. A 500-mL three-necked flask is fitted with a mechanical stirrer, dry ice condenser, a Claisen adaptor to allow for the use of a septum for introducing reagents, and a stopcock for introducing ammonia gas. The system is flame dried, flushed with N_2 gas, and, after cooling, 100 mL of THF [distilled from Na/$(C_6H_5)_2CO$] and 15.0 mL of *tert*-butyl alcohol (160 mmol, distilled from sodium) are introduced via a syringe. Ammonia (250 mL, distilled from lithium) is condensed into the flask and 25 cm of lithium–1% sodium wire (0.0423 g/cm, 150 mmol) is added with cooling. After the lithium has dissolved (~10 min) the silyl aryl ether is added (25.0 mmol) and the mixture is maintained at reflux (−33 °C). After 15 min, 7.5 additional mL of *tert*-butyl alcohol (80 mmol) is added to the reaction mixture. After an additional 30 min, the excess lithium is quenched with solid anhydrous NH_4Cl. (Caution! Cooling is necessary at this point to avoid bumping.) When the blue color has been discharged, the reaction mixture is poured carefully into a vigorously stirred mixture of 750 mL of hexane/750 mL of saturated aqueous NH_4Cl. The layers are separated and the aqueous layer is extracted with 300 mL of hexane. The hexane fractions are combined, dried ($MgSO_4$), and evaporated in vacuo. The product is then vacuum distilled. Kugelrohr distillation is usually sufficient. Similarly to the corresponding reductions of alkyl phenyl ethers [W. S. Johnson, B. Bannister, and R. Pappo, *J. Am. Chem. Soc.*, **78,** 6331 (1956); A. L. Wilds and N. A. Nelson, *ibid.*, **75,** 5360 (1953)], the reduction of 1,2,3-trisubstituted isomers **14a,b** requires more forcing conditions. This reduction can be realized by treating the substrate (25 mmol) with 50 cm of lithium–1% sodium wire (250 mmol) in 60 mL of THF/120 mL of NH_3/28 mL of *t*-BuOH (300 mmol) for 2 h at reflux (−33 °C) followed by the usual workup procedure. The dihydroaryl silyl ethers are modestly sensitive to oxidative rearomatization, especially in basic media, and are best kept cold under nitrogen for extended storage.

(7) Yields refer to isolated material of >95% purity.

(8) These compounds have spectral properties (IR, NMR, mass spectra) in accord with their assigned structures.

(9) These compounds exhibit analytical properties (exact mass and/or elemental analysis) in accord with their assigned structures.

(10) A lower boiling co-product (~10%) formed in the reductions of **13a,b** is the silyl enol ether of cyclohexanone. This product is formally derived via reductive cleavage[10a,b] of the conjugated isomer of dienes **13a,b** followed by further reduction. Control experiments suggest that **13b** is not the precursor of the observed reduction product—even with extended reaction times. (a) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **29,** 2102 (1964). (b) J. A. Marshall and N. H. Anderson, *ibid.*, **30,** 1292 (1965).

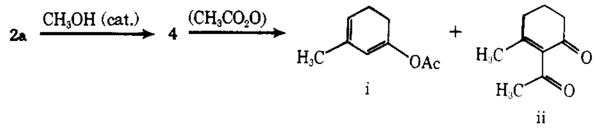
(11) Substantial (35–40%) amounts of an over-reduction product,[10] the silyl enol ether of 2,6-dimethylcyclohexanone, is also produced in this reaction, which is run under more vigorous conditions.[6]

(12) A lower boiling by-product (2–6%), 1,4,5,6,7,8-hexahydronaphthalene, is also produced in this reaction (cf. footnote 10).

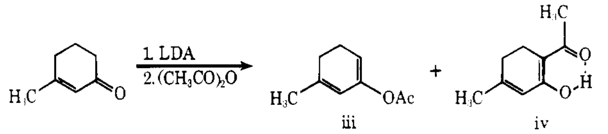
(13) Cleavage of the *tert*-butyldimethylsilyl substrate **7a** with methyllithium was far more sluggish (cf. ref 3a,b).

(14) The endocyclic structure of this enol is assigned on the basis of spectral similarity with previously studied acylcyclohexanones.[14a-c] (a) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **87,** 505 (1965). (b) S. Hunig and H. Hoch, *Justus Liebigs Ann. Chem.*, **716,** 68 (1968). (c) H. Sterk, *Monatsh. Chem.*, **100,** 1246 (1969).

(15) Samples of oxygen and carbon acetylated compounds i[8,9] and ii[8,9] were independently prepared via acylation of enolate **4** (obtained by methanol catalized equilibration of enolate **2a**) and were shown to be absent (<1%) from the crude **2a** acetylation reaction as judged by NMR, TLC, and VPC analyses.



(16) Samples of oxygen and carbon acetylated compounds iii[8,9] and iv[8,9,14] were independently prepared from 3-methyl-2-cyclohexen-1-one and were shown to be absent (<1%) from the crude **2a** acetylation reaction as judged by NMR, TLC, and VPC analysis.



(17) Alternate approaches for the direct alkylation of dihydroaryl silyl ethers are currently being evaluated.

(18) Since this reaction is run under relatively neutral conditions, it provides a useful compliment to the standard *acidic* hydrolysis of dihydroaryl alkyl ethers [cf. W. S. Jdhnson, J. A. Marshall, J. F. W. Keana, R. W. Franck, D. G. Martin, and V. J. Bauer, *Tetrahedron Suppl., No. 8,* Part 2, 541 (1966)].

(19) The corresponding hydrolysis of the *tert*-butyldimethyl silyl ethers **7a, 8a,** and **13a** is less satisfactory. The longer required reaction times allow several reactions to become competitive (particularly product isomerization).

(20) Treatment of silyl enol ethers **7b, 8b,** and **13b** (2.0 mmol) with 4.0 mmol of $(n\text{-}C_4H_9)_4N^+F^-$ and 2.0 mmol of H_3BO_3 in 5.0 mL of H_2O/32 mL of THF (homogeneous solution) at 10 °C for 10 min (**7b** requires longer reaction time, 20 min) gives the corresponding ketone. The reaction mixture is then added to a vigorously stirred mixture of 200 mL of H_2O/100 mL of $CHCl_3$ at 5 °C (emulsion removed by filtration). The aqueous layer is extracted with 50 mL of $CHCl_3$. The $CHCl_3$ fractions are combined, washed with 2 × 100 mL of H_2O, dried ($MgSO_4$), and evaporated at 15 mm. The product is vacuum distilled (Kugelrohr, 0.5 mm, 40 °C). In the purification of ketone **23,** temperatures must be kept below 40 °C during evaporation and distillation to prevent double-bond isomerization.

(21) The corresponding isopropyldimethyl silyl ethers **8b,** and **13b** give lower yields owing to competitive hydrolysis of both vinyl ether moieties.

(22) **8a** (5.0 mmol) is treated with a homogeneous solution of $(HO_2C)_2 \cdot 2H_2O$ (65 mmol, 8.2 g) in 20 mL of THF at 30 °C for exactly 10 min (cleavage of **13a** requires 7 min). The reaction mixture is quickly added to 200 mL of hexane/200 mL of 5% Na_2CO_3. (Caution! Foaming may occur.) The aqueous layer is extracted with 100 mL of hexane. The hexane fractions are combined, dried ($MgSO_4$), and evaporated in vacuo. The product is kept under vacuum (0.5 mm) for 4 h to remove *tert*-butyldimethylsilanol and is then distilled.

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Received February 17, 1977

Organoselenium Chemistry. Epoxidation of Olefins with Benzeneseleninic Acid and Hydrogen Peroxide ("Benzeneperoxyseleninic Acid")

Summary: Benzeneseleninic acid and hydrogen peroxide generate in situ "benzeneperoxyseleninic acid" which functions as an epoxidizing agent.

Sir: We have observed the formation of epoxides during the oxidation (50% aqueous hydrogen peroxide) and subsequent elimination of phenylseleno groups adjacent to carbonyls.[1]