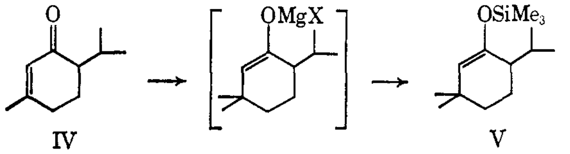
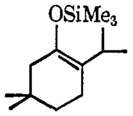
ether V (ir 1660 cm^{-1}; nmr δ 4.6 (broad singlet, 1 H)). The isomeric enol ether Va with a tetrasubstituted double bond could be obtained by anhydrous acid isomerization of V and has $\lambda_{\max}$ 1672 cm^{-1}.[9]



IV V



Va

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(9) The retention times of V and Va were 7.0 and 7.3 min, respectively, on 10-ft SE-30 columns at 140° (100 ml/min).

(10) We thank the National Science Foundation for the support of this work.

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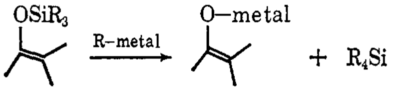
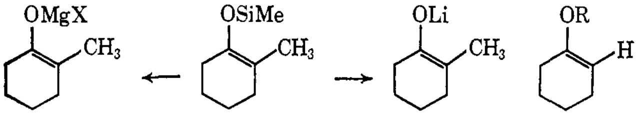
Generation, Nuclear Magnetic Resonance Spectra, and Alkylation of Enolates from Trialkylsilyl Enol Ethers

Sir:

We have found trialkylsilyl enol ethers[1] ideally suited to the generation of a variety of metal enolates *via* reaction with organometallic reagents. The major advantage of this method is that the only extraneous substance formed in the process is an inert tetraalkylsilane (*e.g.*, tetramethylsilane).



The rate of cleavage of silyl enol ethers is strongly dependent on the specific organometallic reagent, the solvent, and the nature of the trialkylsilyl group. For instance, at room temperature, methyllithium completely transforms the trimethylsilyl enol ether of 2-methylcyclohexanone (I) into the lithium enolate II within 6 min in glyme and in about 1 hr in ether, while in benzene, cleavage with butyllithium is only about 15% complete within 1 hr. Complete cleavage is achieved by refluxing for 1 hr. Transformation into the magnesium enolate III *via* methylmagnesium bromide requires refluxing in glyme for 24 hr. It is worth noting that hindered silyl ethers such as *t*-butyldimethylsilyl enol ethers are only cleaved to the extent of 1% in 24 hr by methylmagnesium bromide in refluxing glyme and are stable for 1 day to methyllithium in ether at room temperature. Cleavage may, however, be accomplished quantitatively in 20 hr at room temperature with methyllithium in glyme.



III I II IV

The generation of enolate ions from the corresponding silyl enol ethers allows determination of the effect of the metal ion and solvent composition on the nature of these species. We have now carried out an examination of some of the metal enolates of cyclohexanone with respect to the position of their vinyl protons in the nmr. In THF-d_8, the vinyl proton appeared as a triplet centered at δ 4.16 in the lithium enolate IV, R = Li, and at δ 4.78 for the magnesium enolate IV, R = MgBr. In glyme, in which the vinyl proton of the lithium enolate appears at δ 4.24, that of the potassium enolate IV, R = K, is at δ $\sim$3.9. For comparison, the proton in the trimethylsilyl enol ether IV, R = SiMe$_3$, is at 4.83 in THF-d_8 and 4.75 in CCl$_4$, a solvent in which the enol acetate, ethyl enol ether, and pyrrolidine enamine of cyclohexanone (IV, R = Ac, Et, pyrrolidinyl) show their vinyl protons at δ 5.27, 4.43, and 4.13, respectively.

This last sequence, in which the proton is progressively more shielded as electron availability on the double bond is increased, allows the reasonable assumption that the position of the vinyl proton absorption reflects electron availability at the β carbon of the enolate salt and that the chemical shift of that proton gives a rough indication of the looseness of the oxygen–metal bond. This last property should be related to the ability of the enolate to function as a base toward protons α to a carbonyl group, and thus, to participate in the proton transfer reactions which are responsible for the loss of structural specificity in enolate reactions, as well as for undesirable polyalkylation.

Fortunately, tightness of the oxygen–metal bond sufficient to prevent proton transfer is not prohibitive with respect to reaction with sufficiently active electrophilic agents, *e.g.*, methyl iodide. These were, of course, the considerations which had led us to introduce the use of lithium enolates, rather than their sodium or potassium analogs, in the alkylation of specifically generated enolates.[2]

The remarkable observation has been made that addition of hexamethylphosphoramide (HMP) has very little effect on the position of the vinyl proton absorption in these enolates. The lithium enolate of cyclohexanone shows practically no shift from THF-d_8 to THF-d_8 containing 40% HMP. The magnesium enolate shows some upfield shift from δ 4.78 to 4.62 with 50% HMP, and the vinyl proton of the potassium salt which absorbs at δ $\sim$3.9 in glyme shifts $\sim$3.72 in glyme–30% HMP.

We could not detect an appreciable solvent effect of HMP on the position of the olefinic proton of vinyl ethers, enamines, or enol silyl ethers, and since, in any event, the addition of HMP did not lead to the same position of the vinyl hydrogen starting with enolates from different metals, it is clear that most metal enolates are not transformed into free ions by this dipolar aprotic solvent.[3]

The preparation of lithium or magnesium enolates *via* silyl enol ethers has considerable synthetic utility, since they are produced free of substances (such as

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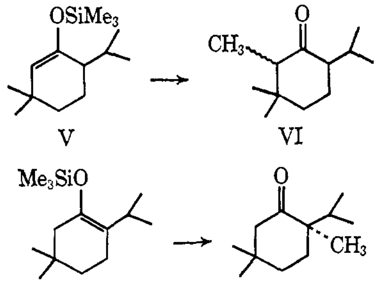
(1) G. Stork and P. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462 (1968).

(2) G. Stork, P. Rosen, and N. L. Goldman, *ibid.*, **83**, 2965 (1961); G. Stork, P. Rosen, N. L. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965).

(3) Compare H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965).

t-alkoxides present when enol acetates[4] are used as precursors) which can promote polyalkylation. The expected structural integrity of enolates from silyl ethers is illustrated by the alkylation[5] of the lithium enolates from the silyl ethers V and Va[1] to the respective methylated substances VI and VII[6] in 80% yield.[7]



V VI

Va VII

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[4] H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965).

[5] The alkylation of various cyclohexanone enolates is being studied more intensively by Dr. P. Tardella.

[6] VI was separable into two base-interconvertible components (*cis* and *trans*), the major isomer having a retention time of 15.4 min and the minor 14.1 min on 10-ft 20% LAC 2-R-446 columns at 140° (120 ml/min). The major component was characterized as the 3,5-dinitrobenzoate, mp 72–75°, of the corresponding alcohol (LAH). Both isomers of VI showed three methyls as doublets and two as singlets in the nmr, in contrast to VII (retention time 15.1 min) which showed three methyls as singlets and two as doublets. The main difference in the mass spectra of VI and of VII was the much larger peak at *m/e* 140 (loss of propylene) from the latter.

[7] We thank the National Science Foundation for the support of this work.

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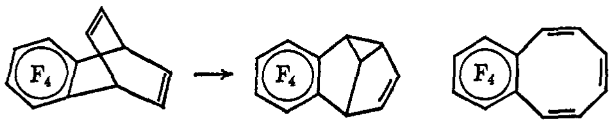
Photoisomerization of Mono- and Dibenzobarrelenes

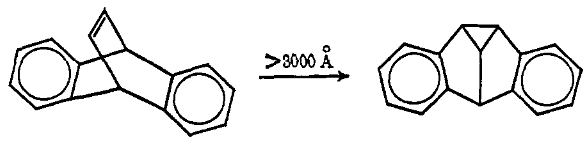
Sir:

It was recently reported[1] that the photosensitized (acetone) rearrangement of barrelene (bicyclo[2.2.2.]-octa-2,5,7-triene) yields semibullvalene (tricyclo[3.-3.0.0.^{2,8}]octa-3,6-diene). Similarly, tetrafluorobenzobarrelene[2] was converted to the corresponding semibullvalene derivative,[3] while direct irradiation reaction gave tetrafluorobenzocyclooctatetraene.



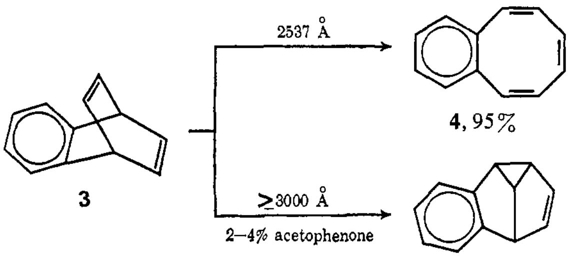
(pentane, quartz) 17% 56%
(4% acetone, quartz) 66% trace

However, the photolysis of dibenzobarrelene[4] (**1**) in acetone or benzene (Pyrex filter) is reported to give only dibenzosemibullvalene (**2**).



1 **2**, 85%

We now wish to report that direct irradiation (2537 Å) of benzobarrelene[5] (**3**) (in cyclohexane) leads to the exclusive formation of benzocyclooctatetraene (**4**) while photosensitization (acetophenone or acetone) produces benzosemibullvalene[6,7] with only a trace of **4**.



3

4, 95%

5, 99%

Contrary to the previous interpretation,[4] the unsensitized[8] photoisomerization of dibenzobarrelene (**1**)[9] leads to the formation of *sym*-dibenzocyclooctatetraene (**6**).[10] From the relative amounts of **6** (or **6a**) and **2** (or **2a**) obtained, it is concluded that photoisomerization of ^{1}**1*** proceeds more rapidly (10–20 times) than intersystem crossing.

Direct irradiation of **7**[11] in cyclohexane produced only **8**,[4] probably from ^{3}**7***. On the other hand, compound **9** (mp 105–107°) was smoothly converted to the cyclooctatetraene derivative **10** (mp 105–107°). It fol-

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[1] H. Zimmerman and G. Grunewald, *J. Am. Chem. Soc.*, **88**, 2882 (1966).

[2] J. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

[3] A single photoproduct was obtained in the photolysis of bis-(perfluoromethyl)benzobicyclo[2.2.2]octatriene. Unpublished results (H. Zimmerman) for the conversion of benzobarrelene to benzosemibullvalene are cited: R. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

[4] E. Ciganek, *ibid.*, **88**, 2882 (1966).

[5] Prepared in 20% yield from the reaction of benzyne and benzene: L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

[6] (a) All new products have satisfactory spectral data and microanalyses. (b) The nmr spectra of benzosemibullvalene showed multiplets centered at τ 2.92 (4), 4.52 (1), 4.97 (1), 6.28 (1), 7.18 (3).

[7] (a) A solution of 2% acetophenone in cyclohexane is five times more effective (20 min, using an immersed 100-W GE medium-pressure Hg lamp (H100A4/T), Pyrex glass filter) than neat acetone as the photosensitizer, and is easily removed from the reaction mixture by chromatography on alumina. Direct irradiation (>3000 Å) gave **5** very slowly (3% conversion, 2 days). (b) Benzosemibullvalene is unstable to continued irradiation at 2537 and >3000 Å with or without photosensitization. The products are benzocyclooctatetraene (~50%) and polymeric residues.

[8] In this study direct irradiation (nonsensitized) was effected in cyclohexane and tetrahydrofuran at 2537 Å (60 hr, Rayonette photochemical reactor) and is different from that described by Ciganek (Pyrex cutoff, in benzene).[4] Tetrahydrofuran is the preferred solvent since polymer formation is surpressed. The material balance is excellent (>90%) and essentially all **1** is consumed. **1a** (mp 123.5–124.5°) is converted to **6a** (mp 71–72°) and a mixture, **2a** (mp 74–82°, not resolved by glpc), more rapidly than **1** is. We find that direct irradiation at longer wavelengths (>3000 Å) slowly gives **2** (~1% conversion, 2–3 days) when conducted in benzene (*i.e.*, benzene photosensitization), while in cyclohexane **6** and **2** are slowly formed.

[9] Dibenzobarrelene can be prepared in 53% yield by the reaction of *cis*-acetylene dichloride and anthracene followed by dehalogenation: S. Cristol and R. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960). This material can also be made by the reaction of benzyne and naphthalene: 7% yield, R. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963); 20–30% yield by a modification in procedure, L. Friedman and P. W. Rabideau, unpublished results.

[10] This material is identical with that prepared by Wittig [G. Wittig, G. Koenig, and K. Clauss, *Ann.*, **593**, 127 (1955)] and Griffin [C. Griffin and J. Peters, *J. Org. Chem.*, **28**, 1715 (1963)] but different from that reported by Fieser [L. F. Fieser and M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946)], Cope [A. Cope and S. Fenton, *ibid.*, **73**, 1668 (1951)], Nenitzescu [M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **93**, 1789 (1960)], and Schroeder [G. Schroeder, W. Martin, and J. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 870 (1967)]. This discrepancy is under current investigation.

[11] W. Vaughan and K. Milton, *J. Am. Chem. Soc.*, 74, 5628 (1952).