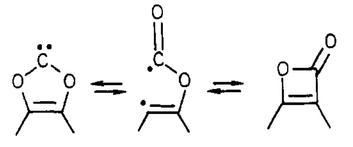
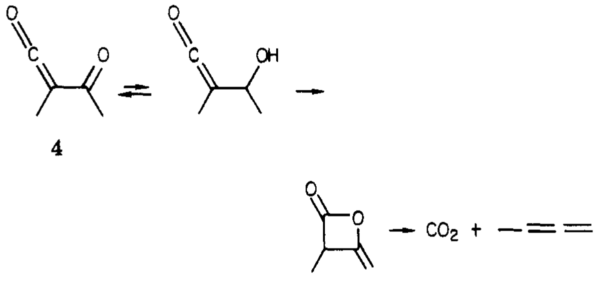
2 and 3 for the formation of the 2-butyne. This system is complicated by the fact that 5 could convert to 4 by the pathway in Scheme I and that interconversion of the dioxalenylidene, 6, and the unsaturated lactone 12 is possible via the sequence in eq 6. The formation of 6 in a single



6 12 (6)

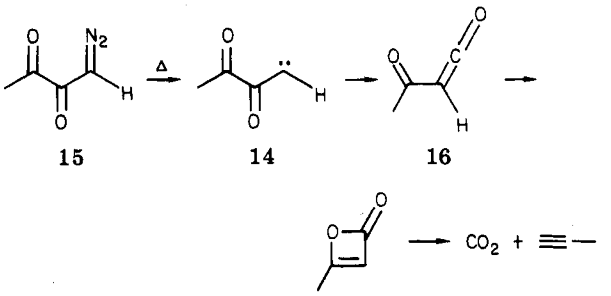
step by the reaction of C with 3 appears unlikely as very little of 3 is expected to be in the cisoid conformation.[10]

Since the product ratios in eq 4 demonstrate that considerably more CO$_2$ than 2-butyne is formed, there must be additional cleavage products corresponding to the CO$_2$. An obvious candidate is an isomer of 2-butyne, 1,2-butadiene, which could arise from cleavage of 13 (eq 7) or by stepwise bond rupture of one of the intermediates in eq 2 and 3.



4 13 (7)

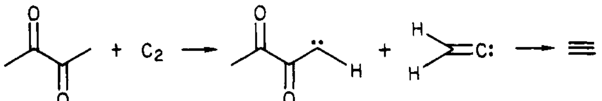
In order to test the possibility that a keto ketene will undergo an intramolecular cyclization of the type shown in eq 2 under the reaction conditions, we have generated pyruvylmethylidene, 14, by pyrolysis of the corresponding diazo compound 15 at 250 °C.[11] When 15 (12.2 mmol) is pyrolyzed and the products condensed at −196 °C under dynamic vacuum, both CO$_2$ (2.2 mmol) and propyne (2.9 mmol) are generated. Wolff rearrangement of carbene 14 (or its precursor) is expected to generate keto ketene 16. Cyclization of this species to an unsaturated lactone is followed by cleavage to CO$_2$ and propyne as shown in eq 8.



15 14 16 (8)

This result demonstrates that cyclization of keto ketenes and subsequent loss of CO$_2$ is possible under the conditions of the carbon atom reaction and nicely rationalizes the formation of 2-butyne and CO$_2$ in the deoxygenation of 3.

The reaction in eq 8 also serves to explain the formation of propyne and the additional CO$_2$ in the reaction of carbon vapor with 3. Skell and Plonka have demonstrated that C$_2$, a species always generated in the carbon arc, can abstract two hydrogens from the same carbon to generate a carbene and ethenylidene, 17.[12] An analogous process, involving abstraction of two hydrogens from the 1-carbon of 3, would generate 14 and 17 (eq 9). Carbene 14 then reacts as shown in eq 8 to generate CO$_2$ and propyne.



3 14 17 (9)

These investigations demonstrate that the removal of two oxygens from an α,β-diketone by atomic carbon is competitive with monodeoxygenation and that the second carbonyl group most probably serves as a trap for an intermediate in the deoxygenation of carbonyl compounds by atomic carbon.

Acknowledgment. Financial support by the National Science Foundation under Grant CHE-8103034 is gratefully acknowledged.

---

[10] (a) Durig, J. R.; Hannum, S. E.; Brown, S. C. *J. Phys. Chem.* **1971**, *75*, 1946. (b) Danielson, D. D.; Hedberg, K. *J. Am. Chem. Soc.* **1979**, *101*, 3730. (c) Tyrrell, J. *Ibid.* **1979**, *101*, 3766.

[11] The diazo compound was prepared by the reaction of diazomethane with pryuvyl chloride by a procedure adapted from ref 8.

[12] Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 5620.

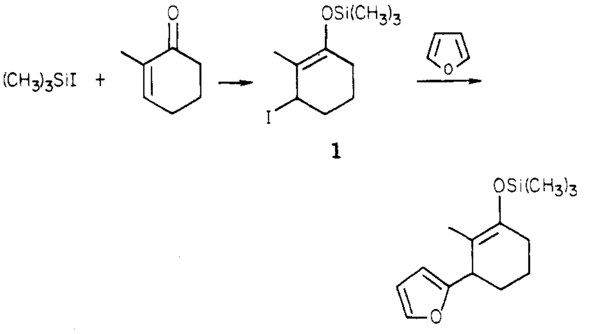
Keith A. Biesiada, Philip B. Shevlin*
Department of Chemistry
Auburn University, Alabama 36849

Received December 20, 1983

Iodotrimethylsilane-Mediated Additions of Dienol Silyl Ethers to α,β-Unsaturated Ketones

Summary: (Trimethylsilyl)oxy-substituted dienes react with 1 at low temperatures to afford annulated products.

Sir: While examining methods for the construction of the quassinoid diterpenes, we recently discovered a direct and mild method (eq 1) for the conjugate addition of furans



1 (1)

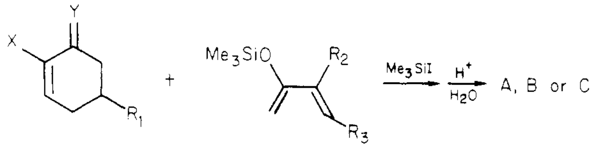
and enol silyl ethers to enones.[1] Notably the reaction produced a regiospecific enol silyl ether. In the course of studying the scope of this novel reaction, we encountered the transformation depicted in eq 2. We believe that the allylic carbocation generated by the reaction of the dienol silyl ether with 1 is intramolecularly trapped to produce 3. As evidenced by the entries in Table I, the trapping step is surprisingly stereoselective. Analysis of molecular models suggests that nonbonded interactions between R (in 2) and the methyl group attached to the enol silyl ether

---

[1] Kraus, G. A.; Gottschalk, P. *Tetrahedron Lett.* **1983**, *24*, 2727.

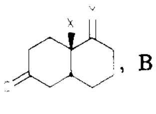
0022-3263/84/1949-1153$01.50/0 © 1984 American Chemical Society

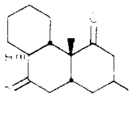
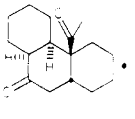
Table I. Iodotrimethylsilane-Mediated Annulations



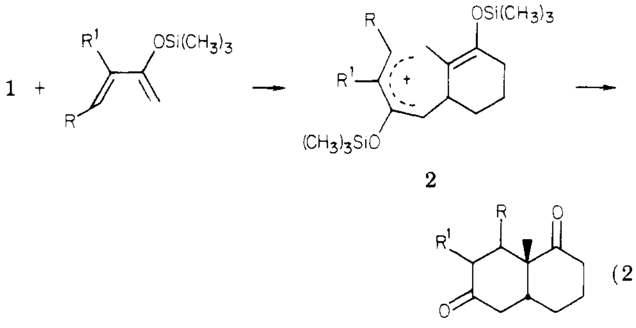
entry	X	Y	R_1	R_2	R_3	% yield[a]	product[e]
1	CH_3	O	H	H	H	40	A
2	$COCH_3$	H_2	H	H	H	45	A
3	CH_3	O	$C(CH_3)CH_2$	$(CH_2)_4$		59[b]	B
4	CH_3	O	H	$(CH_2)_4$		35	B
5	Br	O	H	H	H		
6	$COCH_3$	H_2	H	$(CH_2)_4$		77	C
7	CH_3	O	H	H	OCH_3	*c*	
8	CHO	H_2	$C(CH_3)CH_2$	$(CH_2)_4$		50[d]	

[a] Isolated, chromatographed yield. The structures of the products from entries 3, 4, and 6 were determined by X-ray crystallography for ^1H and ^{13}C NMR data, see ref 5. This represents the combined yield of two diastereomers. The major diastereomer was crystalline. Its structure was determined by X-ray crystallography. [c] Despite the low temperatures, a rapid reaction ensued and afforded only tarry residues. [d] In this case the aldol product was isolated.

[e] A = 

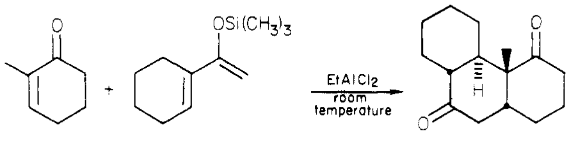
, B = 
; C = 
.

may be responsible for the selectivity. Both the regio- and stereoselectivity parallel that of the Diels–Alder reaction.



(2)

One advantage of the stepwise[2] reaction depicted above is that it is conducted at low temperature. In contrast, Diels–Alder reactions of cyclic enones often require either Lewis acid catalysis[3,4] or prolonged reaction times. Although Lewis acid catalysis does accelerate the Diels–Alder reaction, it can produce unexpected stereochemical results. A case in point is the ethylaluminum dichloride catalyzed reaction shown below. In this case only the product derived from an exo transition state is obtained. The structure of 4 was determined by X-ray crystallography (eq 3).



(3)

4 (38%)

As evidenced in Table I, several bicyclic and tricyclic ring systems can be generated. Both exocyclic and endocyclic unsaturated ketones can be used. The reaction with an unsaturated aldehyde (entry 8) produces only the β-hydroxy ketone. A typical procedure is as follows: To a solution of enone (1 equiv, 0.5 M in CH_2Cl_2) at −78 °C was added $(CH_3)_3SiI$ (1.1 equiv). After 45 min at −78 °C, a solution of the silyl dienol ether (1.1 equiv, 1 M in CH_2Cl_2) was added. The reaction was stirred for 1 h at −78 °C, quenched with Et_3N, and warmed to 0 °C. An aqueous workup provided the crude product, which was chromatographed on silica gel.[5]

Acknowledgment. We thank the National Institutes of Health (Grant CA30623) for generous financial support.

Registry No. 3 (R = R^1 = H), 4707-05-5; 4, 89016-45-5; A (X = $COCH_3$, Y = H_2), 88981-10-6; B (R_1 = $C(CH_3)CH_2$) (isomer 1), 88981-11-7; B (R_1 = $C(CH_3)CH_2$) (isomer 2), 88981-15-1; B (R_1 = H), 88981-12-8; C, 88981-13-9; Me_3SiI, 16029-98-4; 2-methyl-2-cyclohexen-1-one, 1121-18-2; 1-(1-cyclohexen-1-yl)ethanone, 932-66-1; 2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-one, 99-49-0; 2-bromo-2-cyclohexen-1-one, 50870-61-6; 4-(1-methylethenyl)-1-cyclohexenecarboxaldehyde, 2111-75-3; trimethyl[(1-methylene-2-propenyl)oxy]silane, 38053-91-7; [[1-(cyclohexen-1-yl)ethenyl]oxy]trimethylsilane, 54781-35-0; [(1-methoxy-1,3-butadien-3-yl)oxy]trimethylsilane, 59414-23-2; 1-cyclohexen-1-yl-3-hydroxy-3-[4-(1-methylethenyl)cyclohexen-1-yl]-1-propanone, 88981-14-0.

George A. Kraus,* Peter Gottschalk

Department of Chemistry
Iowa State University
Ames, Iowa 50011

Received November 28, 1983

---

(2) We have isolated the $(CH_3)_3SiI$ addition product. See also: Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1979**, 2305.

(3) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802 and references therein.

(4) For a recent example with a substituted diene and a cyclic enone, see: Trost, B. M.; Caldwell, C. G.; Murayama, E.; Heissler, D. *J. Org. Chem.* **1983**, *48*, 3252.

(5) Entry 1: ^1H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 1.40–2.70 (7, 13 H); ^{13}C NMR ($CDCl_3$) 22.70, 23.61, 26.47, 33.36, 37.20, 38.11, 43.44, 45.78, 48.25, 210.83, 213.76 ppm; mp 66–67 °C. Entry 2: ^1H NMR ($CDCl_3$) δ 1.10–1.80 (m, 8 H), 1.85–2.80 (m, 10 H, 2.22 (s, 3 H); ^{13}C NMR ($CDCl_3$) 21.07, 24.00, 24.65, 27.38, 28.29, 32.23, 37.78, 38.17, 44.94, 51.63, 210.57, 212.26 ppm. Entry 3, main fraction: mp 91.5–92.5 °C; ^1H NMR ($CDCl_3$) δ 1.00–2.90 (m, 18 H), 1.40 (s, 3 H), 1.76 (br s, 3 H), 4.70 (br s, 2 H). Minor fraction: ^1H NMR ($CDCl_3$) δ 0.90–3.00 (m, 18 H), 1.43 (s, 3 H), 1.72 (br s, 3 H), 4.73 (d, 2 H). Entry 4: ^1H NMR ($CDCl_3$) δ 1.49 (s, 3 H); ^{13}C NMR ($CDCl_3$) 21.46, 21.85, 25.43, 26.01, 27.05, 29.52, 40.38, 43.83, 43.96, 45.26, 50.20, 50.85, 211.54, 215.58. Entry 6: ^1H NMR ($CDCl_3$) δ 0.90–2.10 (m, 14 H), 2.16 n(s, 3 H), 2.30–3.00 (m, 7 H). ^{13}C NMR ($CDCl_3$) 19.96, 21.59, 23.80, 25.36, 26.08, 27.05, 28.35, 32.00, 42.27, 44.81, 47.80, 55.60, 114.51, 211.28, 211.74 ppm.