187. The Ring Contraction of Cyclic Trimethylsilyl Enol Ethers with Arenesulfonyl Azides. Ring Expansion and Ring Contraction Reactions by Means of Diazonium Betaines. III [1]

Preliminary Communication[1]

by **Ronald A. Wohl**

School of Chemistry, Rutgers, The State University of New Jersey
New Brunswick, N. J. 08903 (U.S.A.)

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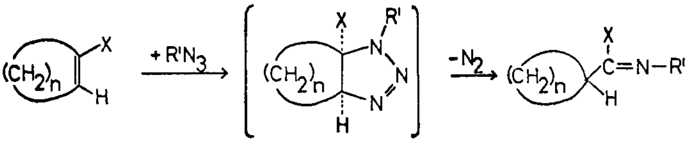
Organic azides react with olefins **1** in a 1,3-cycloaddition to form Δ^2-triazolines **2**, a reaction first reported by *Wolff* in 1912[2] [2] [3]. Strong electron withdrawing substituents (R′ = CN, ROCO, picryl, $ArSO_2$) on the azide, while facilitating the addition to (relatively) electron-rich olefins, cause the resulting triazolines to be relatively unstable and lose nitrogen easily [1] [3] [4]. The final product is then determined by subsequent reaction of the intermediate betaines formed (see below).



(1)

1 **2** **3**

a) X = H b) X = NR_2 c) X = OR, R′ = $ArSO_2$ d) X = $OSiMe_3$, R′ = $ArSO_2$

Fusco et al. have shown that enamines **1b** derived from cyclic ketones react with organic azides mainly under ring contraction with formation of the corresponding amidines **3b** (eq. 1(b)) [4]. In Part II of this series we have shown that enol ethers **1c** derived from cyclic ketones similarly react with arenesulfonyl azides *via* intermediate unstable Δ^2-triazolines **2c** to give mainly the ring contracted imidate esters **3c** according to eq. 1(c) [1].

In this paper we would like to demonstrate the analogous reaction of trimethylsilyl enol ethers **1d.** Trimethylsilyl enol ethers are useful synthetic analogs of alkyl enol ethers [5]. The reaction with azides proceeds in an analogous way to that of the alkyl enol ether except that the rate determining-step of the 1,3-dipolar addition is significantly slower. The reaction is best carried out by keeping equimolar amounts of the 2 reactants in a relatively polar anhydrous solvent such as acetonitrile either at room temperature or at temperatures up to 60° until an IR.-spectroscopic analysis shows, that the azide component has reacted completely.

It is very difficult to isolate the trimethylsilyl imidate esters **3d** because of their extreme sensitivity to moisture or protic solvents. With water or methanol attack at the silicon atom occurs with immediate formation of the corresponding amide or

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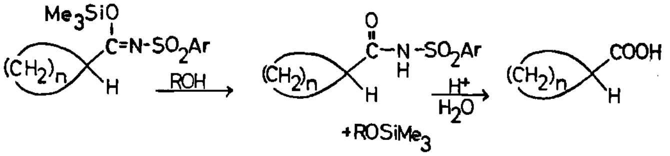
[1] The full details of this work will appear in this journal.

[2] For reviews of this reaction, see [3].

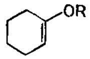
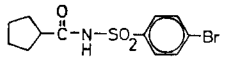
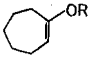
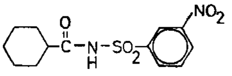
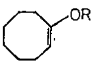
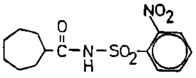
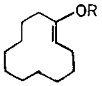
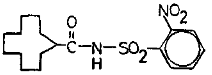
imide **4** (eq. 2). The imide can be hydrolyzed readily with 20% sulfuric acid to give the corresponding carboxylic acid **5**.



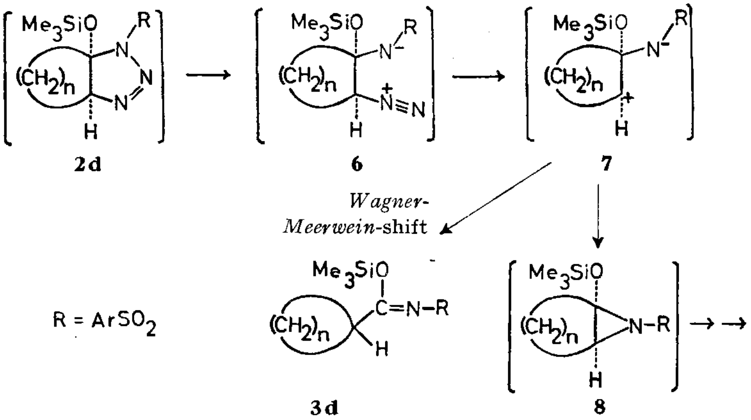
3d **4** **5** (2)

The major ring contractions carried out according to eq. 1(d) are summarized in the Table.

Table. *Physical Properties of Cycloalkanecarbonyl Arenesulfonimides obtained according to Eq. 1(d)*

Starting Trimethylsilyl Enol Ether (R = – SiMe$_3$)	Imide	m.p.	yield[a]	IR.[b] Amide I	IR.[b] Amide II	NMR.[c] $>\underset{H}{C}-C-\underset{H}{N}-$
		172 –172.5°	73	1720	1570	2.59 (*m*)
		118 –118.5°	50	1730	1540	2.14 (*m*)
		190.5–192.5°	58	1718	1565	2.42 (*m*)
		173 –174°	97	1725	1541	2.44 (*m*)

[a] Crude weight yield of relatively pure material after column chromatography on silica gel.
[b] In cm^{-1}. Spectra taken in CH_2Cl_2 solution.
[c] Chemical shifts δ with respect to tetramethylsilane as internal standard. Spectra were taken in $CDCl_3$.



(3)

The mechanism of the reaction may in agreement with the usual thermal (as opposed to photochemical) decomposition of Δ^2-triazolines be formulated according to eq. 3 [3]. The major pathway of the betaine **7** is the *Wagner-Meerwein* (or *Demjanov-Tiffeneau* type) rearrangement to the imidate ester **3d**. Side products are probably derived from the intermediate aziridine **8**, which being unstable undergoes further rearrangements.

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