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THE REACTION OF CYCLIC ENOL ETHERS WITH ARENESULFONYL AZIDES. A NEW RING CONTRACTION REACTION. RING EXPANSION AND RING CONTRACTION REACTIONS BY MEANS OF DIAZONIUM BETAINES. II.

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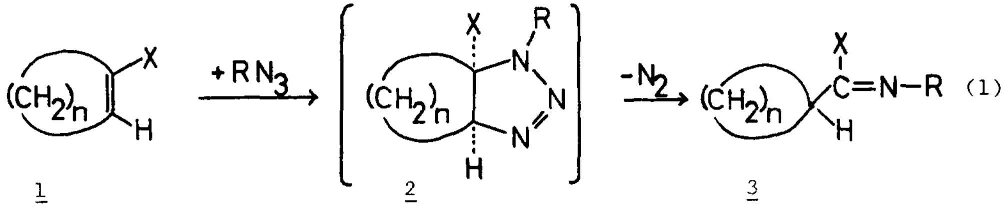
We would like to report a new general ring contraction reaction according to the following scheme (eq. 1(a), R = $ArSO_2$): The enol ether 1a derived from a cyclic ketone is reacted with a suitable azide leading via an intermediate unstable Δ^2-triazoline 2a to the ring-contracted imidate ester 3a.



a) X = OR' b) X = H c) X = NR'$_2$

Organic azides react with olefins 1 in a 1,3-cyclo-addition to form Δ^2-triazolines 2, a reaction first reported by Wolff in 1912.[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 reactions of the intermediate betaines formed (see below).

Fusco and coworkers have shown that enamines derived from cyclic ketones 1c react with such azides mainly under ring contraction with formation of the corresponding amidines 3c (eq. 1(c)). Although azides have been added to enol ethers[5], the ring contraction sequence of eq. 1(a) has not been reported to date.

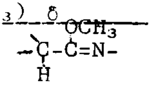
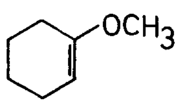
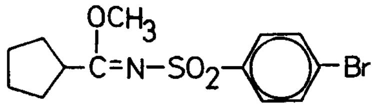
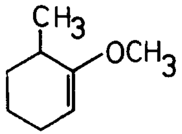
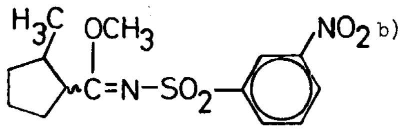
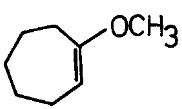
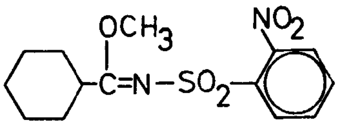
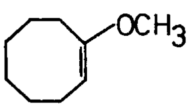
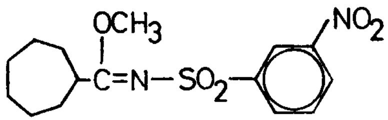
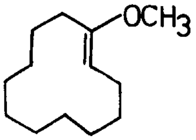
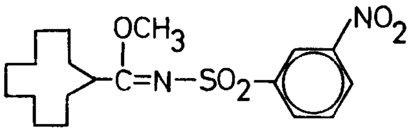
Our results are summarized in Table I. All enol ethers derived from cyclic ketones with six- or higher membered rings reacted smoothly to give the ring contracted imidate ester 3a as the major product. The structure of the imidate esters is supported by their IR and NMR-spectra the most important features of which are included in Table I.

The reactions were carried out by keeping a equimolar mixture of the reactants in a relatively polar solvent, preferably abs. acetonitrile, for several days or weeks until the IR spectrum showed that the azide component had disappeared completely. The imidate esters 3a were isolated by column chromatography on silica gel and/or recrystallization. A particularly convenient work-up for the crude reaction mixture, which includes partial hydrolysis, consists in percolating the mixture after evaporation of the original solvent through a column of activated alumina in a petroleum ether/benzene mixture. This treatment results in hydrolysis of the imide bond only and the corresponding methyl cycloalkanecarboxylate is eluted as the sole product. The imidate esters are also hydrolyzed readily to the corresponding cycloalkanecarboxylic acids by refluxing with 20% sulfuric acid.

1-Methoxy-1-cyclopentene although reacting readily with arenesulfonyl azides under evolution of nitrogen failed to give any ring-contracted product in analogy to the corresponding enamine reaction.[4]

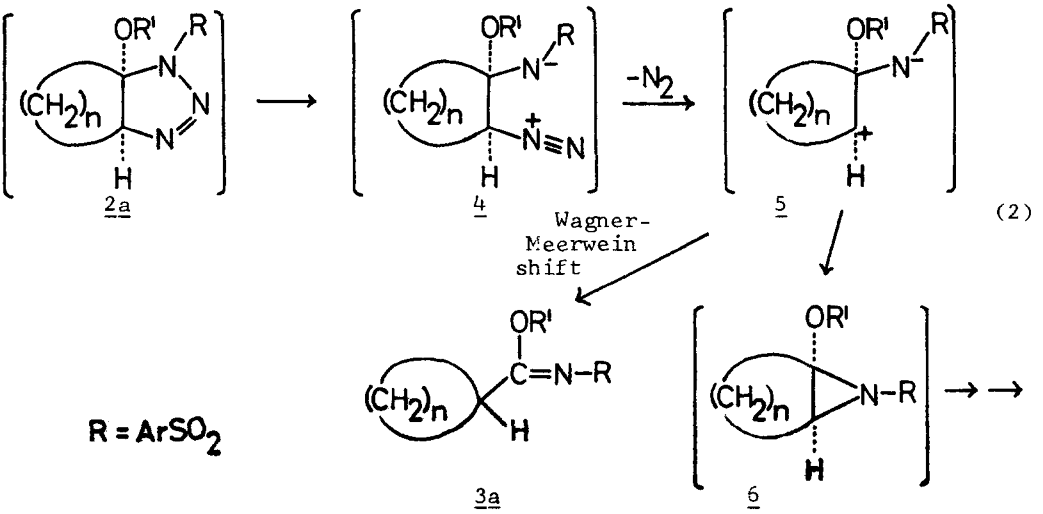
The mechanism of the reaction may in agreement with the usual thermal (as opposed to photochemical) decomposition of Δ^2-triazolines be formulated according to eq. 2. The major pathway of the betaines 5 is the Wagner-Meerwein (or Demjanov-Tiffeneau type)rearrangement to the imidate ester 3a. Side products as well as the products from 1-methoxy-1-cyclopentene are probably derived from the intermediate aziridine 6, which being unstable undergoes further rearrangements.

Table I.

Enol ether	Imidate ester[a]	Yield %	mp	IR(CH_2Cl_2) cm^{-1}	NMR($CDCl_3$) δ -OCH_3	NMR($CDCl_3$) δ  $>\underset{H}{C}-\overset{OCH_3}{C}=N-$
		87	-	1593	3.70(s)	3.78(m)
		89	(70 - 70.5°)[b)]	1592	3.78	3.33(m) 3.77(m)
		61	76.5 - 77°	1593	3.74(s)	3.38(m)
		58	120 - 120.5°	1593	3.77(s)	3.63(m)
		75	64 - 65°	1593	3.77(s)	3.75(m)

a) All new compounds gave satisfactory elemental analyses. We are indebted to Hoffmann-LaRoche Corp., Nutley, N. J., for the execution of the elemental analyses.

b) Approx. 50:50 mixture of <u>cis</u> and <u>trans</u> compound as based upon the NMR spectrum.



(2)

Full details of this work will be described elsewhere.

References

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3. For reviews of this reaction see: G. L'Abbé, *Chem. Rev.*, **69**, 345 (1969); T. Sheradsky in "The Chemistry of the Azido Group", S. Patai, ed., Interscience, New York, 1971, p. 359ff, 373ff; W. Lwowski, *ibid.*, p. 529; and references cited therein.

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5. R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, **100**, 2494 (1967), and references cited therein.

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Acknowledgement

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