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THERMAL FRAGMENTATION OF SULFOXIMINES OF N-AMINOOXAZOLIDONES. A NOVEL OLEFIN SYNTHESIS

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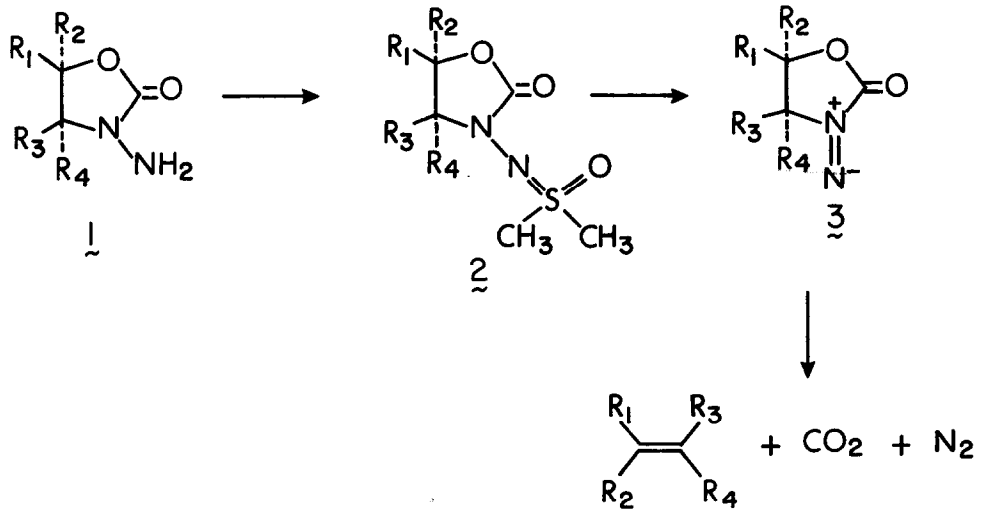
The sulfoximine function,[1] is a convenient progenitor of nitrenoid nitrogen by dissociation under either thermal or photochemical conditions.[2] It therefore seemed plausible that the sulfoximine 2 of an N-amino-2-oxazolidone 1 would yield a diazene 3[3] and that a subsequent cycloelimination, with extrusion of N_2 and CO_2 would liberate an olefin (Scheme I). We wish to report that diazenes (3) generated in this way undergo a very efficient and stereospecific, thermal fragmentation to the corresponding alkene.

Sulfoximines 2a-f were obtained in good yield by oxidation of the corresponding 3-amino-2-oxazolidones with lead tetraacetate in methylene chloride-dimethylsulfoxide (1:4) at 5° (Table).[4] These sulfoximines are stable compounds below 90° and are readily purified by crystallization. They exhibit a characteristic C=O frequency at 1750-1760 cm^{-1} and nmr signals for the dimethylsulfoximino protons at ca δ 3.2.[5] In the temperature range 110-130° they undergo smooth decomposition during 0.5 hr in dimethyl sulfoxide solution with vigorous gas evolution and formation of the olefin in high yield. In the case of 2a and 2b, the reaction mixture was swept with a stream of nitrogen into a trap containing a solution of bromine in methylene chloride, and ethylene and propylene were identified as 1,2-dibromoethane and 1,2-dibromopropane respectively. Cis and trans 4,5-diphenyloxazolidone sulfoximines (2d and 2e) gave cis and trans stilbenes respectively with > 98% stereoselectivity, indicating virtually complete retention of stereochemistry in the cycloelimination step. Sulfoximine 2f gave methylenecyclopentane with no trace of the endocyclic C=C isomer. In each case, the nmr spectrum of the reaction mixture in DMSO after decompostion of sulfoximines was complete showed essentially pure olefin.

Scheme I



Two general routes to N-amino-2-oxazolidones are available. In the first (Scheme II), an epoxide is heated with hydrazine hydrate in ethanol[6] to give a hydrazino alcohol (75-95%), which is then subjected to diethyl carbonate in the presence of sodium methoxide to yield the aminooxazolidone directly.[7] The crystalline aminooxazolidones (3300, 1740-1750 cm^{-1}) obtained in this way are stereochemically homogeneous. The further conversion of these aminooxazolidones to sulfoximines, followed by thermal decomposition, represents a useful and highly stereoselective synthesis of olefins from epoxides.[8] Moreover, in conjunction with olefin epoxidation, the process constitutes an effective means for inversion of olefin stereochemistry.

Scheme II

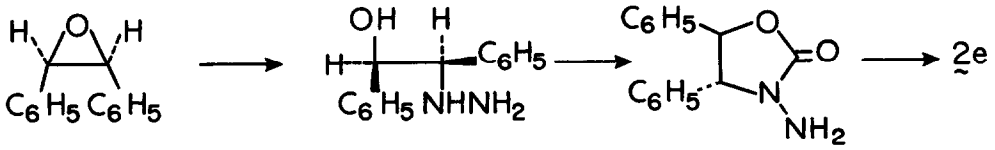


Table. Olefins from Thermal Decomposition of Sulfoximines of N-Amino-2-oxazolidones

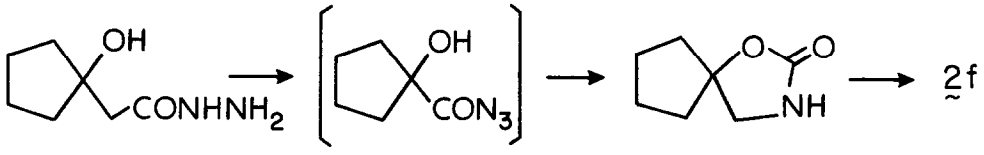
	Sulfoximine				Olefin (%)
	R_1	R_2	R_3	R_4	
2a	H	H	H	H	Ethylene (92)[a]
b	CH_3	H	H	H	Propylene (94)[a]
c	C_6H_5	H	H	H	Styrene (>97)[b]
d	C_6H_5	H	C_6H_5	H	cis-Stilbene (>97)[b]
e	C_6H_5	H	H	C_6H_5	trans-Stilbene (91)[b]
f	$-(CH_2)_4-$		H	H	Methylenecyclopentane (>97)[b]

[a]Based upon gas chromatography of dibromide derivative

[b]Based upon nmr analysis

An alternate route to N-aminooxazolidones (Scheme III) involves amination of a 2-oxazolidone via its lithium salt (BuLi, THF, -60°) with O-(2,4-dinitrophenyl)hydroxylamine[9] (30-40%). 2-Oxazolidones are readily available via diazotization of β-hydroxycarbohydrazides according to the method of Newman.[10]

Scheme III



The fragmentation process described here should provide a useful olefin synthesis in cases where mild, neutral reaction conditions are required and where contaminating byproducts are to be avoided. Moreover the high yields, regioselectivity, and stereoselectivity make this an attractive alternative to other cycloeliminative olefin synthesis.[11]

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