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OXIDATIVE DIMERIZATION OF ALLYLIC SULFONES WITH IODINE AND WITH FERRIC CHLORIDE

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Dedicated to Professor Harry H. Wasserman
on the occasion of his 65*th* birthday.

Abstract: *Lithium salts of allylic sulfones are oxidized with ferric chloride-dimethylformamide complex mainly to 1,6-disulfones by 3-3' coupling. Products resulting from coupling of 3,3-disubstituted sulfones undergo Cope rearrangements affording vicinal disulfones with threo-configuration. Coupling with iodine results in mixtures containing mainly vicinal disulfones, again with threo-configuration.*

During work on the conversion of vitamin A to β-carotene[1,2] we had occasion to examine the oxidative dimerization of allylic sulfones. At the time the oxidative coupling of the potassium salt of 2,4-dinitrophenylmethyl-p-tolyl sulfone with iodine appeared to be the only example published.[3] M. Julia[4,5] later found that lithium salts of sulfones can be coupled efficiently with cupric trifluoromethanesulfonate in isobutyronitrile. Allylic sulfones afforded mainly 1,6-disulfones by 3-3' coupling.

In our experience iodine and a complex of ferric chloride with DMF[6] turned out to be the most useful reagents for allylic sulfones. The procedure consisted of generating the lithium salt of the sulfone in tetrahydrofuran at low temperature by adding one equivalent of n-butyllithium, followed, after ten minutes, by the addition of the required amount of oxidant in the same solvent. Dimerizations using iodine were performed at -50°C because complex mixtures were produced at room temperature. Oxidations with ferric chloride-DMF complex were found to proceed equally well at -50° or 0°C. The most interesting and potentially useful results were obtained with 3,3-disubstituted allyl sulfones. Data in Table I illustrate that the dimerizations proceeded with considerable regioselectivity, and that preference for coupling at either α- or γ-position could be controlled by the choice of oxidant. Additionally the 1,6-disulfones could be converted to vicinal disulfones by Cope rearrangement which were single diastereomers regardless of the method of preparation (Table II).

Table I. Oxidative Coupling of Allylic Sulfones.

Sulfone	Oxidant	Products (% yield of disulfones)		
		1,2	1,4	1,6
1a	Fe^{3+}	2a (6)	4a (16)	5a (68)
1a	I_2	2a (71)[a]	4a (5)	5a (11)
1b	Fe^{3+}	2b (6)	4b (16)	5b (45)
1c	Fe^{3+}	b	b	5c (40)[c]
1c	I_2	2c (63)[a,d]	b	5c (13)[c]
6d	Fe^{3+}	0	7d (43)[c]	8d (42)[c]
6e	Fe^{3+}	0	7e (25)	8e (47)

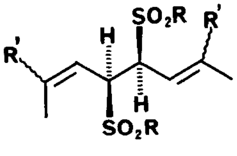
[a] Total of 1,2-disulfone plus minor amounts of 3 formed by elimination of sulfinic acid; [b] not isolated; [c] mixture of diastereomers; [d] mixture of isomers.

Table II. Cope Rearrangement of 1,6-Disulfones to 1,2-Disulfones.

1,6-Disulfone	1,2-Disulfone	% Yield	Solvent[a]	(time in hrs)
5a	2a	81	Xylene	47
5b	2b	82	"	24
5c[b]	2c[c]	92	"	21
8d	recovered starting material		Decalin	14
8e	recovered starting material		"	34

[a] All rearrangements were done at reflux; [b] higher melting diastereomer; [c] Lower melting isomer.

Crotyl 6d and allyl 6e p-tolylsulfones were dimerized with ferric chloride to mixtures of diastereomeric 1,4 (7d,e) and 1,6-(8d,c) disulfones. These two 1,6-disulfones were found to be thermally stable. Coupling 6d,e with iodine afforded complex mixtures of products. Oxidation of sulfonyl anions with ferric salts leads to radicals[6,7,8] and a polar effect seems to be responsible for preferential 3-3'-coupling of the corresponding allyl radicals. A different mechanism is operative when oxidations are performed with iodine. An intermediate α-iodosulfone appears to react with the original carbanion to produce a dimer. In support of this hypothesis alkylation of prenyl-p-tolylsulfone with methyl iodide occurred exclusively at the α-position and an α-iodosulfone was isolated from the reaction of benzyl p-tolyl sulfone and iodine. Nucleophilic substitution adjacent to sulfonyl groups are chronically difficult[9] but a good leaving group (I^-), next to a double bond, in a protic solvent should facilitate processes. SN_2' Reactions appear to be



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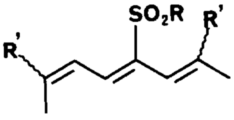

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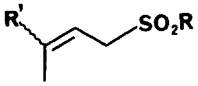

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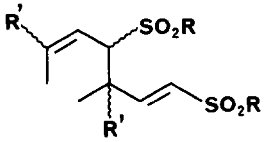

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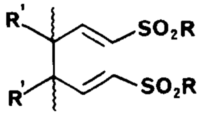

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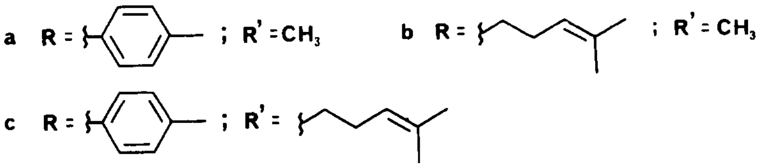

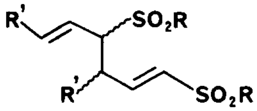

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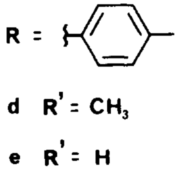

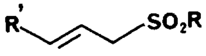

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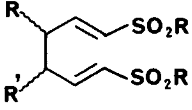

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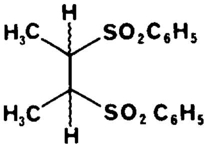

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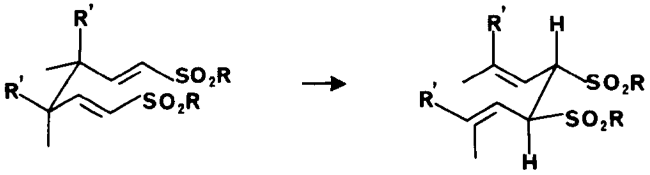

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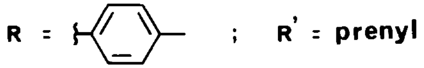

unimportant, a finding that agrees with observations made with γ-halo-α,β-unsaturated sulfones.[10] Vicinal disulfones **2a,b** were obtained as single diastereomers by either coupling procedure or thermal rearrangement. Concerted Cope rearrangement proceeding via a chair like conformation in the transition state would lead to disulfones **2a,b** with racemic configuration. Absence of vicinal proton coupling in **2a,b** agreed with this conclusion and was previously observed with the racemic modification of disulfone **9**.[11] Disulfone **2c** was produced as a mixture of geometric isomers and NMR evidence[2] indicates major (mp 109-111°) and minor (mp 92-99°) isomers to have (±)-*E,E*, and the threo-*E,Z*-configuration respectively. Thus all three vicinal sulfones **2a,b,c** possess the same configuration at the α-sulfonyl carbons. Cope rearrangement of the higher melting diastereomer (mp 166-168°) of the 1,6-disulfone **10** produced *threo*-(*E,Z*) disulfone **11** indicating *meso*-configuration in the starting material, and consequently racemic configuration for the lower melting 1,6-disulfone **5c**. The exclusive formation of racemic diastereomers **2a,b,c** in the oxidative coupling with iodine lacks precedence and theoretical interpretation.[12]

Reference and Notes

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