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(1) (a) K. Kondo and M. Matsumoto, *J. Chem. Soc., Chem. Commun.*, 1332 (1972); (b) E. Demole, C. Demole, and D. Berthet, *Helv. Chim. Acta*, **56**, 265 (1973).
(2) R. L. Kenney and G. S. Fisher, *J. Am. Chem. Soc.*, **81**, 4288 (1959).
(3) Monoterpenes **1** and **11** were commercially available.
(4) All the peroxides obtained in this work were colorless oils, unless otherwise stated, and gave satisfactory analytical data.
(5) When the sensitized photooxygenation of **2** and **3** were carried out in dichloromethane–methanol mixed solvent, the peroxides **4** and **5** were also obtained, although the reaction was slow and the yield was low.
(6) G. V. Piglevskii and Z. Enebish, *Zh. Obshch. Khim.*, **30**, 1051 (1960).
(7) The epoxide **9** was prepared from **1** via the corresponding bromohydrin by a modification of the reported method: E. E. van Tamelen and T. J. Curphey, *Tetrahedron Lett.*, 121 (1962), 67%, bp 76–80° (13 mm) [lit. bp 73–75° (14 mm) reported by G. V. Pigulevskii and N. L. Prokudina, *Dokl. Akad. Nauk. SSSR*, **67**, 511 (1949)].
(8) The epoxide **12** was prepared from **11** by oxidation with *m*-chloroperbenzoic acid in dichloromethane in 48% yield: bp 78–81° (11 mm); NMR (CCl_4) δ 6.26 (d, J = 17.0 Hz, 1 H), 5.62 (d of t, J = 17.0 and 6.0 Hz, 1 H), 2.88 (q, J = 5.8 Hz, 1 H), 2.34 (br d, J = 6.0 Hz, 2 H), 1.83 (s with fine coupling, 3 H), 1.31 (d, J = 5.8 Hz, 3 H), and 1.17 (s, 3 H).
(9) The mixture (68% yield) was comprised of at least two hydroperoxides which could be assigned as 2,6-dimethyl-6-hydroperoxy-1,3,7-octatriene and 7-hydroperoxy-2-methyl-6-methylene-1,3-octadiene based on the NMR spectrum.
(10) M. Mitzner, E. T. Theimer, L. Steinbach, and J. Wolt, *J. Org. Chem.*, **30**, 646 (1965).
(11) The 1,2-disubstituted monoolefin might also be less reactive than the 1,3-diene toward $^1O_2$, as the 1,2-dioxin **5** was selectively formed from **3**.

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1,3-Dipolar Cycloadditions of Azomethine Imines and Sulfenes

Summary: The first examples of a new heterocyclic ring system (**2**) have been prepared by the 1,3-dipolar cycloaddition of azomethine imines **1** and sulfenes.

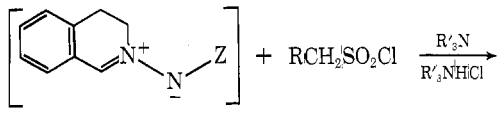
Sir: Although numerous examples of 1,2 and 1,4 cycloaddition reactions of sulfenes to yield four- and six-membered-ring heterocycles, respectively, are known,[1] only two examples of the formation of five-membered rings by cycloaddition reactions of sulfenes have been reported.[2,3] Reactions of other 1,3 dipoles under sulfene-generating conditions have led to products other than those expected from 1,3-dipolar cycloaddition reactions.[1] To further define the reactivity of sulfenes and dipolarophiles, the reactions of sulfenes with highly reactive azomethine imines of the 3,4-dihydroisoquinoline type (**1**)[4] have been explored.

The brightly-colored dipoles **1** were prepared in situ by the thermal dissociation of their respective dimers[4–6] in aromatic hydrocarbon solvents. Dropwise addition of a solution of the alkanesulfonyl chloride to the hot mixture containing the azomethine imine and an excess of trialkylamine led to the formation of adducts **2** (Table I; also, see supplementary material). Derivatives of this ring system have not previously been described. The structural assignments of **2** were based primarily on spectral and elemental analysis data. Further support for these assignments was obtained through the dehydrogenation of three of the adducts (**2a, 2b,** and **2i**) to compounds **3** by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

Table I
Preparation of 1,2,3-Thiadiazolidine Derivatives

2[a]	Z	R	R′	Conditions[b]	Yield,[c] %
a	C_6H_5	H	Et	A	92
b	C_6H_5	C_6H_5	Et	A	77
c	C_6H_5	Cl	Et	A	29
d	C_6H_5	C_6H_5CO	Et	A	31
e	*p*-$NO_2C_6H_4$	H	*n*-Pr	B	86
f	*p*-$NO_2C_6H_4$	C_6H_5	*n*-Pr	B	88
g	EtO_2C	H	*n*-Pr	C	51
h	EtO_2C	C_6H_5	*n*-Pr	C	61
i	C_6H_5CO	H	Et	D	43
j	C_6H_5CO	C_6H_5	Et	D	57
k	*p*-$CH_3C_6H_4SO_2$	H	*n*-Pr	B	29
l	*p*-$CH_3C_6H_4SO_2$	C_6H_5	*n*-Pr	B	58

[a] Satisfactory elemental analysis data were obtained for compounds **2a** through **2l** (see supplementary material). [b] (A) In benzene at 70°; (B) in toluene at 100°; (C) in mesitylene at 155°; (D) in benzene at 80°. [c] Isolated yields of purified product.



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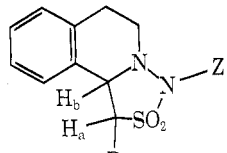

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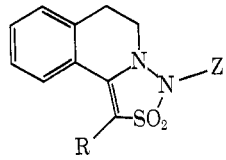

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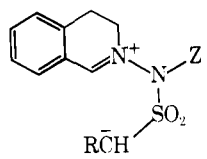
The reactions of substituted sulfenes with the dipoles **1** could lead to the formation of two possible stereoisomers of **2** (i.e., H_a and H_b may be cis or trans). The stereoselectivity with which adducts **2b, 2h, 2j,** and **2l** were formed was studied in some detail by observing the splitting patterns of H_a and H_b in the δ 6.5–4.5 region of their NMR spectra.[7] The NMR spectrum of the crude product isolated from the reaction in which **2b** was formed indicated that the two possible isomers were present in approximately equal amounts.[8] These two isomers were separated by column chromatography and were shown to be noninterconvertible under the conditions leading to their formation.

In contrast to **2b,** adduct **2f** was formed with a high degree of stereoselectivity. Within the limits of detection of the NMR spectrometer, only one isomer of **2f** was observed in the crude product. The NMR spectra of crude adducts **2j** and **2l** showed a great preponderance of one isomer, although small amounts (<10% and <20%, respectively) of the second isomers may have been formed.[10] Purification of crude adducts **2f, 2j,** and **2l** led to the isolation of a single isomer of each adduct.

The most likely mechanisms for the formation of products **2** are either (a) a concerted $[_\pi4_s + _\pi2_s]$ cycloaddition process or (b) a stepwise addition of sulfene to **1**, leading to **2** by the ring closure of zwitterion **4**. Since it was observed



4

that under identical conditions of temperature (80°) and concentration (8 mmol of the dipole in 60 ml of benzene) adduct **2b** was produced with a complete lack of stereoselectivity, while **2j** was formed with a high degree of stereoselectivity, the intermediacy of zwitterion **4** in these reactions seems unlikely; the effect of the "Z" group on the stereochemical outcome of the ring closure of **4** is expected to be minimal. On the other hand, if it is assumed that the azomethine imines and sulfenes undergo a concerted $[_\pi2_s + _\pi4_s]$ cycloaddition,[11] the differences in the stereoselectivities with which **2b** and **2j** were formed may be rationalized by considering the reactivity of the dipoles **1**. Those azomethine imines in which the charge on the anionic nitrogen is stabilized by a carbonyl or a sulfonyl group may be less reactive and more selective than those in which the anionic charge is stabilized by a phenyl group. The more selective dipoles may discriminate between the two possible orientations of phenyl sulfene leading to the transition state and therefore may lead stereoselectively to the observed product.[14] The more reactive, less selective dipole **1** (Z = C_6H_5) may react indiscriminantly with phenyl sulfene to yield a mixture of two isomers.

A more complete evaluation of the scope and utility of these reactions is underway and will be reported at a later date.

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Supplementary Material Available. Procedures for the preparation of all compounds **2** and **3**, along with spectral data for each, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2260.

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(5) We wish to thank Professor R. Huisgen and Dr. R. Grashey for providing directions for the preparation of certain of the dimers of dipoles **1**.
(6) D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).
(7) The NMR spectra of the crude products **2c** and **2d** indicated that both isomers had been formed in each case. Owing to the low yield of these reactions, detailed stereochemical investigations were not carried out. The low solubility of **2f** in organic solvents precluded the use of NMR spectroscopy as a means of determining the stereoselectivity with which it was formed.
(8) Because J_{ab} was 9.5 Hz for one isomer of **2b** and 10.5 Hz for the other, it was not possible to use the Karplus relationship[9] to assign absolute stereochemistries to these adducts.
(9) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963).
(10) Peaks which may have been due to a small amount of a second isomer may also have been caused by impurities in the crude products.
(11) Recent molecular orbital calculations on the frontier orbitals of azomethine imine **1** (Z = C_6H_5)[12] and of sulfene[13] suggest that the orbital symmetries of these two species are compatible with a $[_\pi4_s + _\pi2_s]$ cycloaddition.
(12) K. N. Houk et al., *J. Am. Chem. Soc.*, **95**, 7287, 7301 (1973).
(13) J. P. Snyder, *J. Org. Chem.*, **37**, 3965 (1972).
(14) This argument suggests that the isolated isomers of **2h, 2j,** and **2l** are those in which H_a and H_b are trans. However, the absolute stereochemistry of these adducts has not yet been determined.

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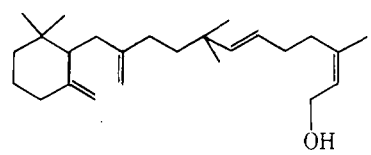
The Total Synthesis of (±)-Diumycinol

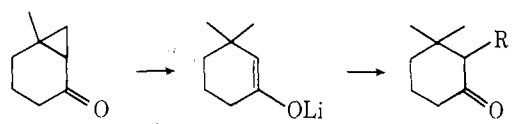
Summary: The first synthesis of the sesterterpene (±)-diumycinol (**1**) is reported featuring the reductive opening of a cyclopropyl ketone (**2**) which regiospecifically generates the β,β-disubstituted lithium enolate **3** and undergoes alkylation exclusively at C-2 with no loss of regiospecificity.

Sir: Diumycinol, the nonisoprenoid C_{25} lipid obtained by acid hydrolysis of the antibiotic diumycin, has been shown to possess structure **1**.[1] Diumycinol became of interest to



1

us, not only because of its polyolefinic nonisoprenoid nature, but also because it allowed us the opportunity to generate regiospecifically an enolate ion (e.g., from a cyclopropyl ketone[2]) which in principle should be capable of being alkylated without loss of structural integrity (cf. **2** → **3** → **4**).[2-5] We wish to report the first synthesis of (±)-diumycinol and demonstrate that the specifically generated β,β-disubstituted lithium enolate **3** undergoes alkylation as the exclusive process with no loss of regiospecificity.[5]



2 3 4

The synthesis of diumycinol outlined below involves the combination of two synthetic pieces, the six-membered-ring building block **7** and the sulfone moiety **12**.[7] The required intermediate **7**[8] was prepared from cyclopropyl ketone **2**[10] in the following manner. The β,β-disubstituted lithium enolate **3** formed during the metal–ammonia cleavage of cyclopropyl ketone **2** underwent exclusive C-2 alkylation (70%) with allyl bromide in 1,2-dimethoxyethane (glyme).[11] Oxidative cleavage of the double bond of **4** (R = allyl) in a two-phase system [benzene–water (1:1)] contain-