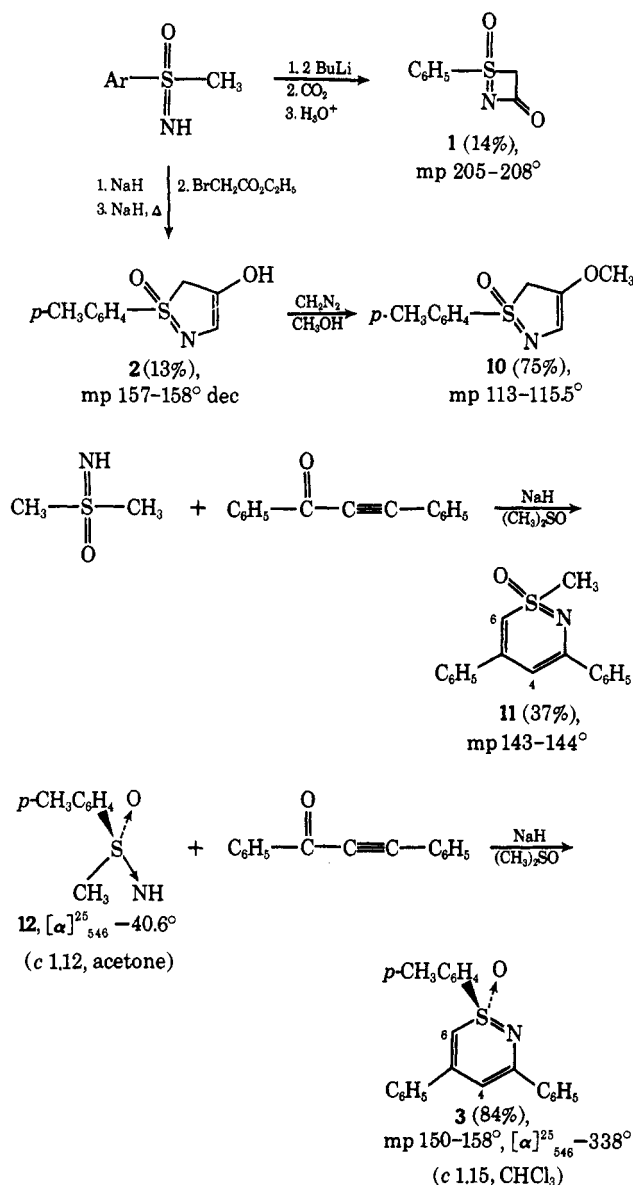


Chart I

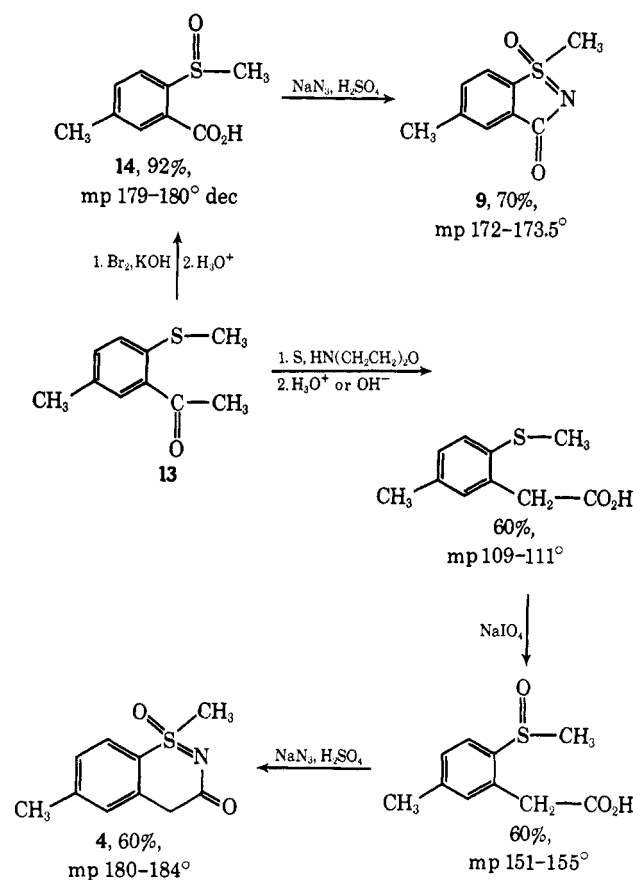


Those of Chart I involve condensations in which the anions derived from the S—CH₃ and S=NH groups of the sulfoximide serve as nucleophiles. Compound 1 contains an unusual small ring that includes both sulfur and nitrogen, and is formally a β -lactam. The carbonyl absorbs at 1690 cm⁻¹ in chloroform in the infrared at somewhat lower energy than the 1745 cm⁻¹ of a normal β -lactam.⁵ This difference indicates that the carbonyl of 1 has more single bond character than a usual β -lactam, possibly because of an expanded N—C—C bond angle due to the length of the S—C bond, or because of the dipolar character of the S=N—C=O linkage (S⁺—N=C—O⁻ contributions), or both. Compound 2 is insoluble in nonpolar solvents, and decom-

0.3% of theory. Their ir and nmr spectra were consistent with the assigned structure. Aryl methyl sulfoximide starting materials are known: (a) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952); (b) R. Fusco and F. Tenconi, *Chim. Ind. (Milan)*, 47, 61 (1965); (c) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, 92, 7369 (1970). Key starting material, 3-methyl-2-methylthioacetophenone (13), is also known; (d) K. Auwers and F. Arndt, *Chem. Ber.*, 42, 537 (1909).

(5) K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden-Day, San Francisco, Calif., and Nankodo Co., Ltd., Tokyo, 1962, p 47.

Chart II



poses on melting to give a gas (possibly ketene). Enol 2 is acidic enough to react with diazomethane in methanol without catalyst to give vinyl ether 10, whose uv spectrum is very similar to that of 2. Tentative assignment of the position of the double bond of 2 and 10 depends on nmr chemical-shift comparisons with model compounds of known structure.

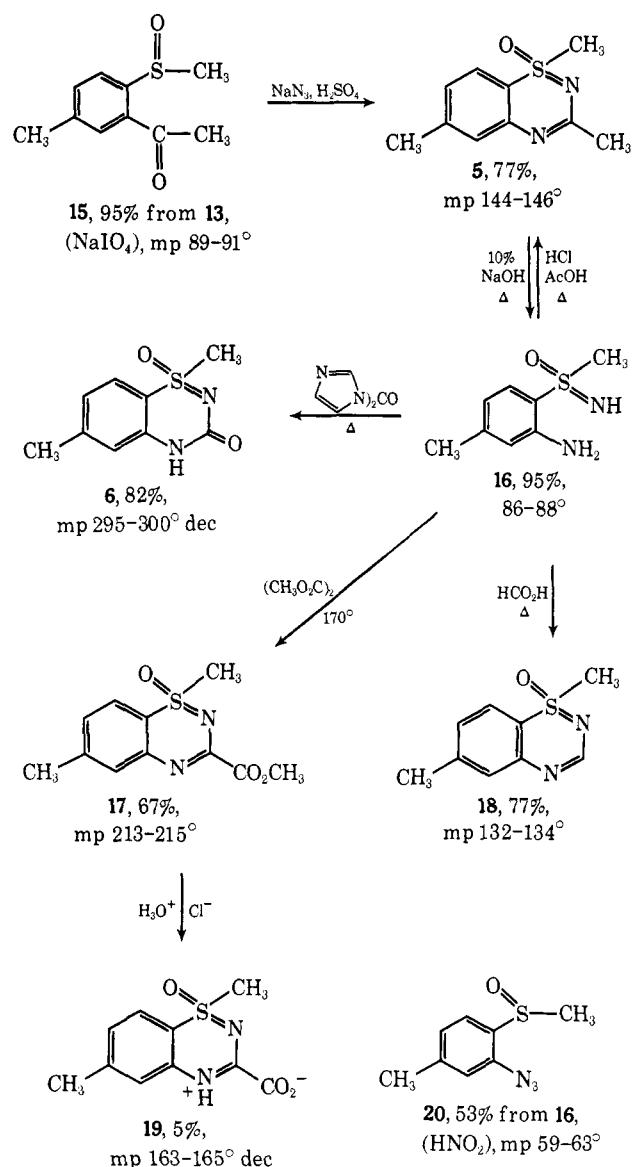
Syntheses of 3 and 11 were modeled after the synthesis⁶ of the carbon analog of 11 (thiabenzene oxides). We substituted the sodium salts of the sulfoximides for the dimethyloxosulfonium methylide of Hortmann and Harris. As expected, 3 gave a much higher optical rotation than the more symmetrical 12 (O and NH are of similar polarizability). Optically pure 12 was employed,^{4c} so optically pure 3 should have been produced since no bonds to sulfur were made or broken. The broad melting point of 3 persisted on repeated recrystallization from many solvents, and we demonstrated with a polarizing microscope that the substance does not pass through a nematic phase⁷ when it melts. Molecular models of 3 indicate a puckered disc shape from whose convex face the oxygen protrudes. At 150° the substance starts to undergo phase change from one solid to a second, and becomes completely liquid at 158°.

Common to the syntheses of Charts II and III, the S=NH group serves as a nucleophile to close a heterocyclic ring to ortho substituents on the S—Ar of the sulfoximide. Lactam 4 is base hydrolyzed to the open-chain salt, which upon acidification regen-

(6) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, 93, 2471 (1971).

(7) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

Chart III



erated 4. The stretching frequency of the C=O of 4 in chloroform absorbs at 1655 cm⁻¹, and thus has less double bond character than the four-membered lactam, 1. The double oxidation of keto sulfide 13 to sulfoxide acid 14 is without analogy, to our knowledge.

Chart III contains a triple reaction in the combined imidation-Schmidt rearrangement-ring closure to produce 5 from 15. The open-chain hydrolysis product of 5, amino sulfoximine 16, served as a starting material for the preparation of the new heterocyclic system 6, as well as a number of interesting derivatives of 5, e.g., 19. Treatment of 16 with nitrous acid produced sulfoxide azide 20, probably passing through still another new heterocyclic system in the process, one that contains an N=N=N=S linkage. Attempts to isolate this system failed.

Although heterocycles 3, 11, and 18 formally contain six π electrons, the nmr chemical shifts of their ring protons are unlike those of aromatic models, e.g., quinazoline as a model for 18.⁸ The chemical shifts (δ) are as follows: quinazoline⁸ (CCl₄), proton 2, 9.29; compound 3 (CDCl₃), proton 4, 5.90, proton 6, 6.70;

(8) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 707 (1965).

compound 11 (CDCl₃), proton 4, 6.10, proton 6, 6.60; compound 18 (CDCl₃), proton 3, 8.15.

Todd R. Williams, Donald J. Cram*

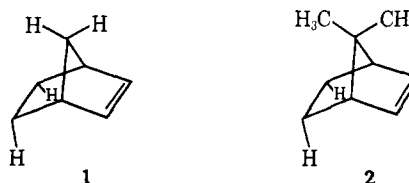
Contribution No. 2900, Department of Chemistry
University of California at Los Angeles
Los Angeles, California 90024

Received September 29, 1971

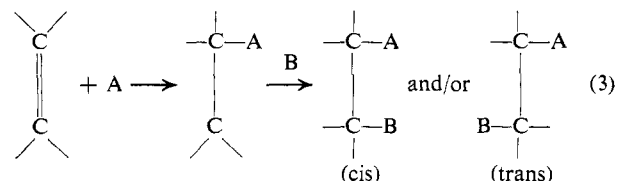
Relative Rate of Exo Addition to Norbornene and 7,7-Dimethylnorbornene. A New Criterion for Distinguishing between Cyclic and Noncyclic Addition Processes

Sir:

The ratio, $k_{\text{exo-norbornyl}}/k_{7,7\text{-dimethyl-exo-norbornyl}}$, of rates of exo addition to norbornene (1) and 7,7-dimethylnorbornene (2) is relatively high for additions involving cyclic transition states or intermediates (cyclic addition), and is relatively low for additions not involving cyclic transition states or intermediates (noncyclic addition). Consequently, this phenomenon provides a valuable criterion for exploring the mechanisms of addition reactions.^{1,2}



Generally speaking, there are two categories of addition reactions, cyclic and noncyclic, according to the structure of the transition state or intermediate. In cyclic addition a cyclic transition state or intermediate is involved, and the stereochemistry of the product may either be cis or trans dependent upon whether the reaction proceeds *via* one stage or two (eq 1 and 2). For example, hydroboration gives cis adduct,³ whereas the addition of benzenesulfonyl chloride is trans.⁴ On the other hand, the transition state or intermediate for noncyclic addition is "open," and the stereochemistry is governed by the steric features of the specific system and the nature of the addend (eq 3). For instance,



cis hydrochlorination has been observed with both 1⁵ and cyclohexene,⁶ whereas oxymercuration is cis with 1 and trans with cyclohexene.⁷

It is generally accepted that the preference for exo addition in the reactions of norbornenes results from

(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(2) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).

(3) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(4) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).

(5) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

(6) R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).

(7) For review see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).