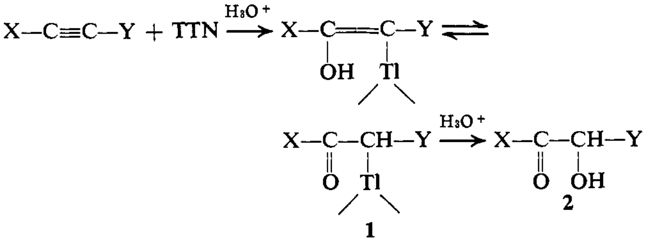
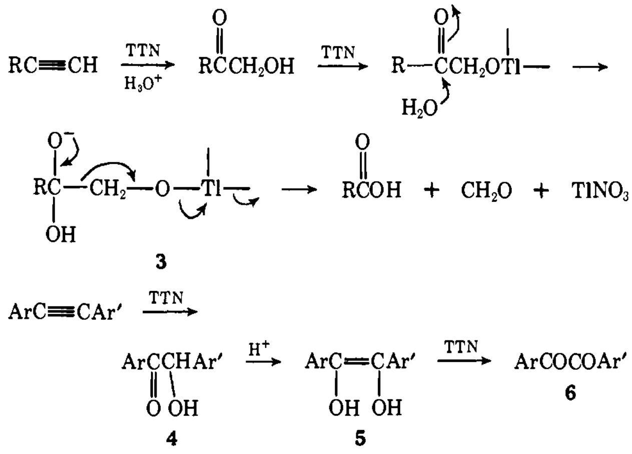
of acetylenes with 1 equiv of TTN in aqueous solution proceeds, as shown in Scheme I, to give initially the corresponding α-hydroxy ketone (2). The solvolytic instability of organothallium(III) derivatives of the type 1 is well documented[8] and hence the conversion 1 → 2 is unexceptional. This reaction sequence thus accounts for the formation of acyloins from dialkylacetylenes, and independent studies have established that acyloins are only slowly oxidized to the corresponding α-diketones with TTN. With both monoalkylacetylenes and diarylacetylenes, however, a second oxidation step occurs relatively rapidly, and hence 2 equiv of oxidant were required for completion of reaction. The mechanisms of these further oxidations are shown in Scheme II. Thallium(III) salts are known to undergo rapid ligand exchange with primary alcohols;[9] the intermediate 3 thus formed in the case of monoalkylacetylenes can then fragment to the observed carboxylic acid as shown. With diarylacetylenes the initial oxidation product is the corresponding benzoin 4; subsequent oxidation of 4 to the benzil 6 *via* the enediol tautomer 5 has been shown to occur smoothly and in high yield under identical reaction conditions.[10,11]

Scheme I[a]



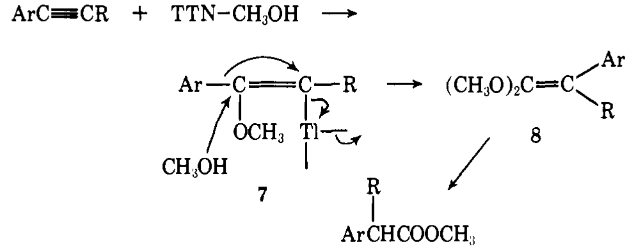
[a] X = Y = H, alkyl, aryl.

Scheme II



In none of the reactions summarized in eq 1–3 (*i.e.*, under aqueous conditions) was any product isolated which was derived from oxidative rearrangement of the initial oxythallation intermediate. This result is entirely in accordance with the reactions shown in Scheme I. Thus, 1,2-alkyl or -aryl migration in 1 would necessitate preliminary heterolysis of the C–Tl bond and formation of a carbonium ion α to an already electron-deficient carbon. Consequently, the preferred pathway in aqueous solution is SN2 type solvolysis of the thallium substituent. Smooth oxidative rearrangement of alkylarylacetylenes to methyl α-alkylarylacetates was observed, however, in methanol solution (see eq 4 and Table II); the probable course of this conversion is represented in Scheme III, where the assumed initial methoxythallation product 7 is now (in contrast to 1) ideally disposed for aryl migration. Attempts to isolate intermediates of the type 7 or 8 have so far proved unsuccessful, but the reaction sequence shown explains in a qualitative sense the relative ease of rearrangement with differently substituted aromatic groups. Thus, for the conversions $4\text{-}XC_6H_4C{\equiv}CH \rightarrow 4\text{-}XC_6H_4CH_2CO\text{-}OCH_3$ the yields of esters for X = NO_2, H, and CH_3O were 0, 17, and 61%, respectively, consistent with the relative migratory aptitudes of the aromatic groups.

Scheme III



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Received August 28, 1971

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(8) W. Kitching, *Rev. Pure Appl. Chem.*, **19**, 1 (1969).

(9) R. Criegee, L. Kraft, and B. Rank, *Justus Liebigs Ann. Chem.*, **507**, 159 (1933).

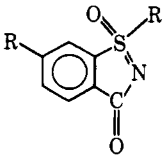
(10) A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron Lett.*, 5281 (1970).

(11) A. McKillop, M. E. Ford, B. P. Swann, and E. C. Taylor, to be published.

New Ring Systems of Carbon, Nitrogen, and Chiral Sulfur[1]

Sir:

In connection with our interest in compounds chiral at sulfur, we have prepared six new heterocyclic systems in which the sulfur, nitrogen, and carbon of the sulfoximide function are part of the ring system (1–6), one of them (3) in an optically active state. The first two heterocyclic systems (7[2] and 8[3]) based on this function were announced when all new systems but 3 were in hand. Inspired by the report of 7, we prepared 9 and confirmed the stability of the ring system.



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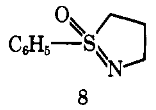

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Our syntheses[4] are outlined in Charts I, II, and III.

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(1) This investigation was supported by the U. S. Public Health Service, Research Grant No. GM 12540-07 from the Department of Health, Education, and Welfare.

(2) P. Stoss and G. Satzinger, *Angew. Chem., Int. Ed. Engl.*, **10**, 79 (1971).

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(4) All new compounds gave carbon and hydrogen analyses within

Chart I

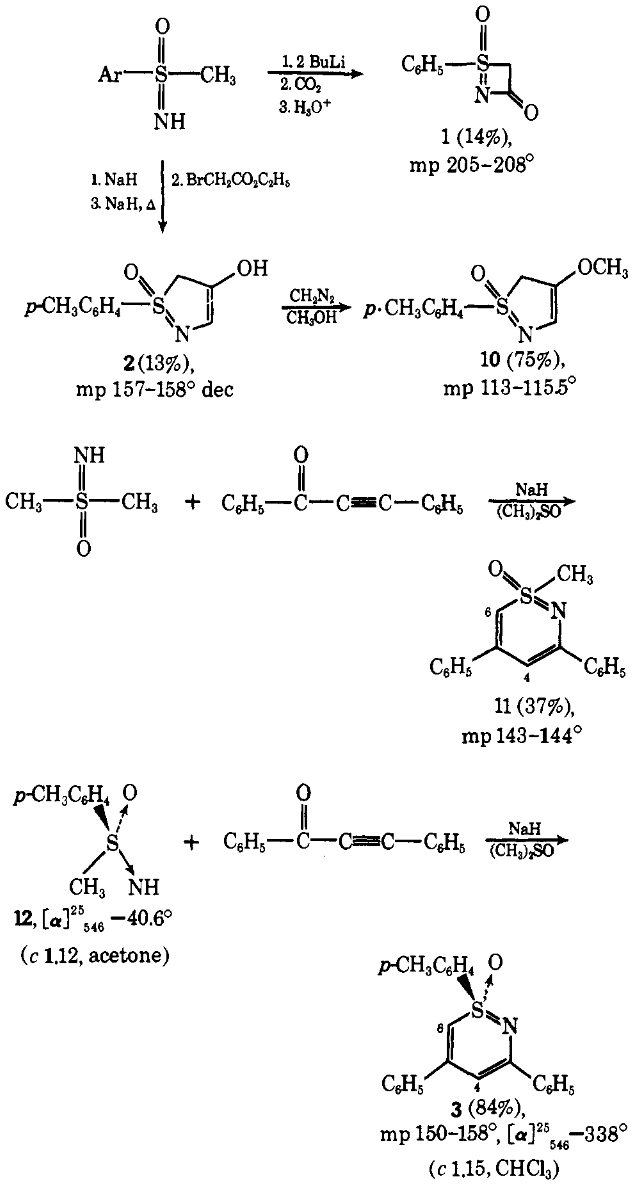
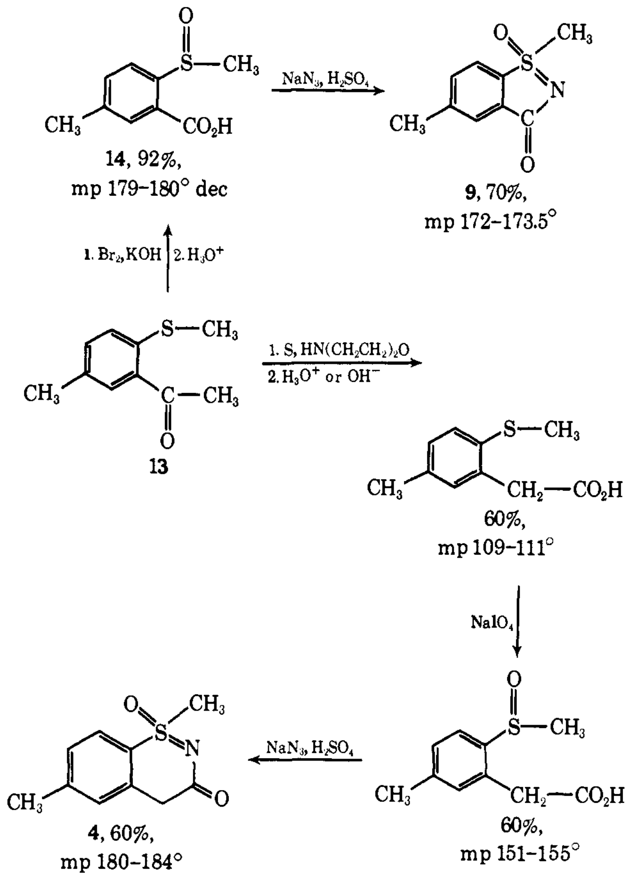


Chart II



Those of Chart I involve condensations in which the anions derived from the S—CH$_3$ 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 decomposes 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 synthesis[6] 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 phase[7] 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-

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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.

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

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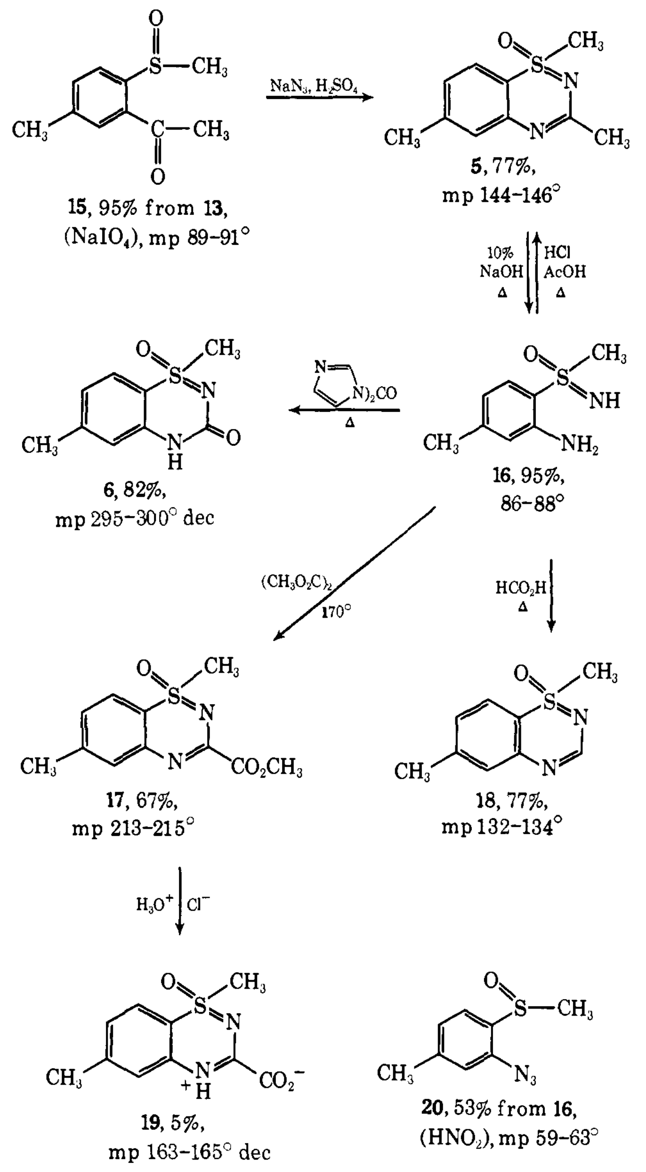
Chart III



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 sulfoximide **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: quinazoline[8] (CCl_4), proton 2, 9.29; compound **3** ($CDCl_3$), proton 4, 5.90, proton 6, 6.70; compound **11** ($CDCl_3$), proton 4, 6.10, proton 6, 6.60; compound **18** ($CDCl_3$), proton 3, 8.15.

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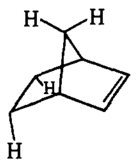
(8) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 707 (1965).

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, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$, 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]



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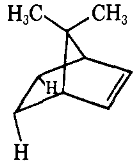

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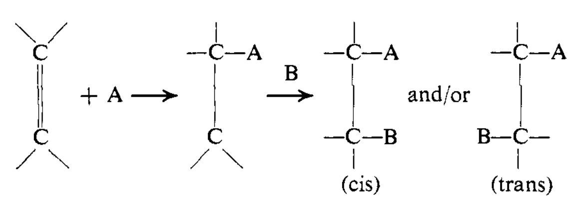
Generally speaking, there are two categories of addition reactions, cyclic and noncyclic, according to the structure of the transition state or intermediate. In cyclic addition a cyclic transition state or intermediate is involved, and the stereochemistry of the product may either be cis or trans dependent 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 benzenesulfenyl 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,



(3)

cis hydrochlorination has been observed with both **1**[5] 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

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

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

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