to be largely complete, since otherwise a "maximum" k_H/k_D value could not be realized without making undesirable corrections for the presence of the more reactive protio substrate. This condition was achieved to a satisfactory extent by storing the nearly fully deuterated substrate in toluene over 99.5% D_2O and injecting only the D_2O-saturated solution. Moreover, since the H-D exchange occurs very rapidly, each "rate" injection into the helium gas stream was immediately preceded by an injection of D_2O to diminish the possible influence of adventitious water vapor in the flowing gas. Such precautionary measures resulted in an apparently high order of reproducibility and accuracy.

An Arrhenius plot of the data for both protio and deutero substrates (see Table I) over the full temperature range of measurement is presented in the accompanying graphs (see Figure 1). The dotted line drawn through the deutero points traces the theoretical curve of the "maximum" values[3] of k_H/k_D for one stretching vibration of the hydroxyl bond in the respective substrates, *i.e.*, assuming the zero-point energy difference, O-H *vs.* O-D, alone determines the k_H/k_D value. The experimental points and the theoretical line for a fully symmetrical transition state[1,2] are nearly coincident in all instances. The slopes and intercepts (see Table I) of the experimental and theoretical lines are no more than 5% and most often less than 3% apart. In fact, the degree of departure of the deuterated cases from the "theoretical" line in all the plots is no greater than could be expected in view of the problems experienced in achieving total deuteration of the hydroxyl function.

Table I. Experimental and Theoretical Values of the Maximum Deuterium Isotope Effect[e]

Substrate	—Theoretical[a]— −Slope[c]	Intercept[c]	—Obsd[b]— −Slope[c]	Intercept[d]
4-Penten-2-ol	20.9	26.3	21.4 ± 0.4	27.2 ± 0.5
3-Butenoic acid	19.9	25.3	19.9 ± 0.4	25.4 ± 0.6
3-Butyn-1-ol	21.4	26.9	21.3 ± 0.3	26.7 ± 0.4

[a] Presuming zero-point energy difference (O-H *vs.* O-D) alone determines the rate difference anticipated. [b] Calculated by a regression analysis of all the experimental points displayed in Figure 1. [c] Slope = $-\Delta Ea/R$, for the Arrhenius plots in Figure 1. [d] Intercept = ln A, for the Arrhenius plots. [e] The $\Delta Ea = 40 \pm 0.6$ kcal/mol and $\Delta S = -10 \pm 1$ eu for the nondeuterated substrates.

These results, therefore, appear to answer most doubts and qualifications of the validity of the kinetic deuterium isotope criterion. They confirm the absence of any serious effects arising from change in hybridization and valence geometry of the carbon to which H is transferred. Moreover, the ionic character of the O-H bond and the hybridization of other atoms involved in the cyclic transition state, factors which could also be implicated in tunneling[6] and other causes of the anticipated deviations[4-8] from the Westheimer[1]-Bigeleisen[2] correlation, do not appear to be of primary consequence in determining the k_H/k_D magnitude in concerted H transfer mechanisms.[15] In continuation of these studies, we are presently examining the effects of changing the heteroatom (from oxygen to nitrogen to sulfur) and of a variety of substituents on the transition-state skeleton.

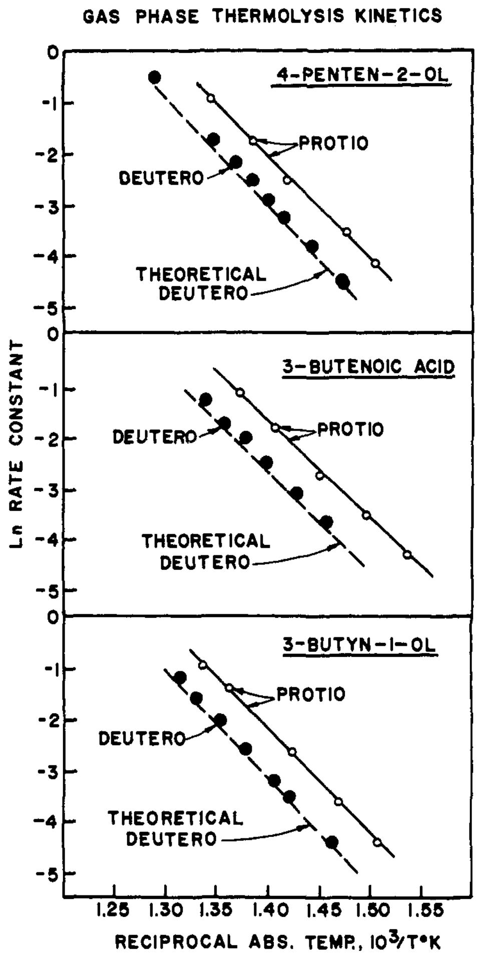

Figure 1.

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[15] A referee has contended that the results reported above "... might show that the transition states have different symmetries and that k_H/k_D is insensitive to transition state symmetry." However, in the opinion of the authors, the referee's conclusion is unwarranted in view of the fact that current theory[1,2] of the origin of k_H/k_D was developed from a very clear definition of the symmetrical transition state[5a] and predicts what sensitivity the relationship should show. We propose that there is no evident disparity in the nature of predictions which can be made, respectively, on the basis of a concerted and a symmetrical transition state.

Nucleophilic Alkylidene Transfer Reagents. Synthesis of Spiro Compounds[1]

Sir:

The synthetic value of ylides derived from salts of sulfoximines[2] and anions derived from *N*-*p*-toluenesulfonyl sulfoximines,[3] as nucleophilic alkylidene transfer reagents, has previously been recorded. We now

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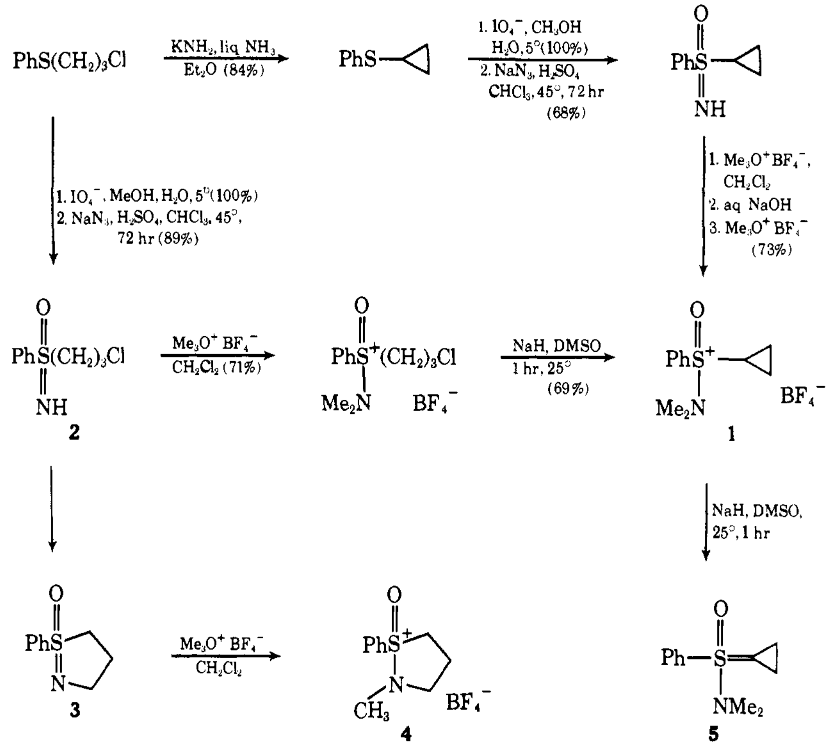
(1) Part XXX in the series Chemistry of Sulfoxides and Related Compounds.

(2) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, **90**, 3890 (1968); C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968); C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

(3) C. R. Johnson and G. F. Katekar, *ibid.*, **92**, 5753 (1970).

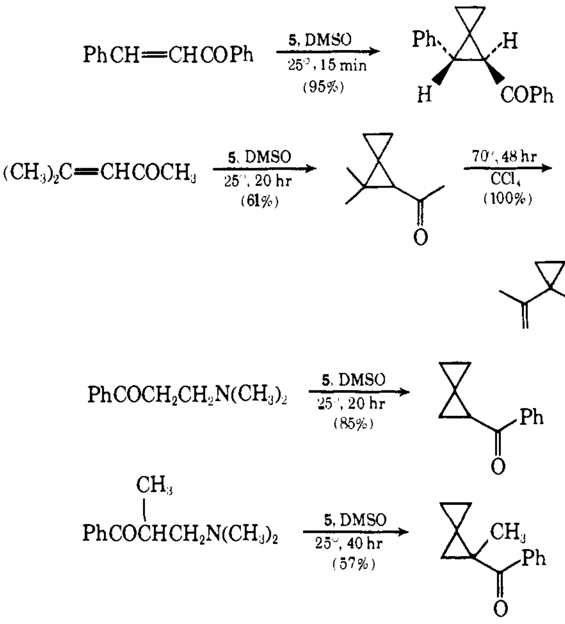
Scheme I



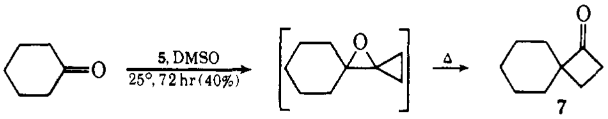
describe the utilization of such reagents for the syntheses of spiro compounds. In particular, the remarkably facile synthesis of typically difficultly accessible spiropentane derivatives has prompted communication of our results.

Scheme I outlines alternate routes for the preparation of *N*,*N*-dimethylaminocyclopropylphenyloxosulfonium fluoroborate (**1**), mp 121–122°, beginning with phenyl 3-chloropropyl sulfide.[4a] For large-scale preparation the route involving cyclopropyl phenyl sulfide[4b] is preferable. The slow spontaneous cyclization of **2** to **3** (as the hydrochloride) provided an interesting sidelight to the second route. Apparently, compound **3** is the first example of a sulfoximine with the sulfur and nitrogen contained within a ring. Methylation of **3** afforded salt **4**.

The cyclopropylide **5** was generated by reaction of salt **1** with sodium hydride in dimethyl sulfoxide. At room temperature the half-life of the cyclopropylide **5**, estimated by nmr observations in DMSO-d_6 of the production of *N*,*N*-dimethylbenzenesulfinamide, is approximately 4 days. Reaction of ylide **5** with α,β-unsaturated carbonyl compounds (or Mannich bases[5]) gave substituted spiropentanes.[6] The 1-acetyl-2,2-dimethylspiropentane from the mesityl oxide reaction underwent a quantitative rearrangement at 70° to 1-acetonyl-1-isopropenylcyclopropane. A similar thermolysis of 1-acetyl-2,2-dimethylcyclopropane has been reported.[7]



Reaction of ylide **5** with cyclohexanone produced the unstable dispiro epoxide **6**, which rearranged during isolation by preparative glc to **7**.[8] The reaction of cyclohexanone with diphenylsulfonium cyclopropylide has recently been reported by Trost, LaRochelle, and Bogdanowicz.[9] From the reaction compound **7** was obtained in unspecified yield.



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(4) (a) H. E. Zimmerman and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **82**, 2505 (1960); (b) W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *J. Org. Chem.*, 33, 43 (1968).

(5) For other examples of the direct reaction of sulfonium ylides with Mannich bases see H.-G. Lehmann, H. Miller, and R. Wiechert, *Chem. Ber.*, **98**, 1470 (1965).

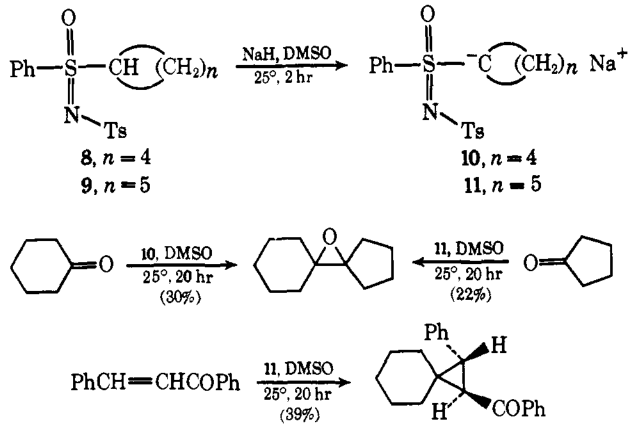
(6) Isolated yields are indicated. All new compounds gave satisfactory analyses.

(7) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).

(8) J. R. Wiseman and H.-F. Chan, *ibid.*, **92**, 4749 (1970). We thank Professor Wiseman for spectral data on this compound.

(9) B. M. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Lett.*, 3449 (1970).

In a manner similar to that described for simpler reagents,[3] S-cyclopentyl- and S-cyclohexyl-S-phenyl-N-p-toluenesulfonyl sulfoximines (**8** and **9**) were prepared. Representative examples of the anions of these materials in the preparation of spiro compounds are illustrated below.



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Diphenylsulfonium Cyclopropylide. A Useful Spiroalkylation Reagent

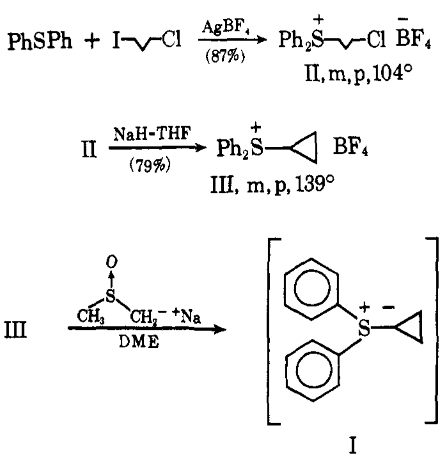
Sir:

A novel spiroannelation technique invoking the intermediacy of diphenylsulfonium cyclopropylide (I) has been previously recorded.[1-3] We now wish to report a preferred route to diphenylsulfonium cyclopropylide and its utilization as a novel spiroalkylation reagent. This reagent makes spiropentanes and cyclobutanones easily available in a simple one-step process.

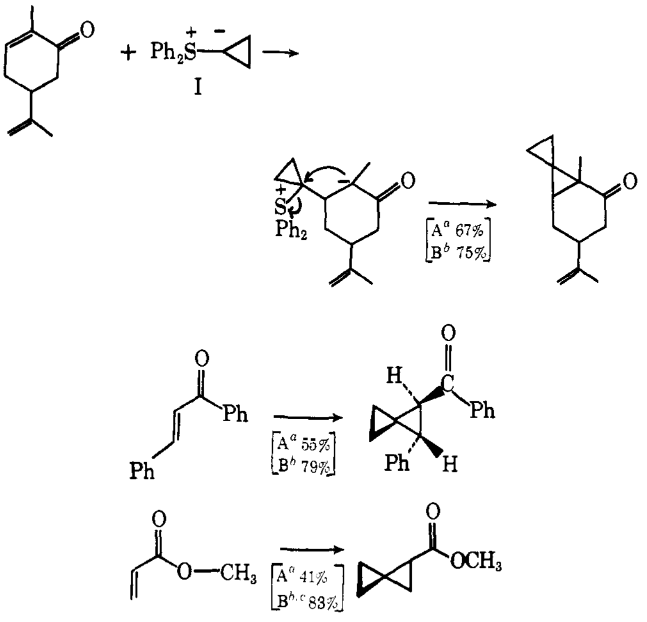
The reaction of diphenyl sulfide, silver fluoroborate, and a 5 M excess of 1-chloro-3-iodopropane in nitromethane at 25° resulted after 16 hr in the isolation of 3-chloropropyldiphenylsulfonium fluoroborate (II) in 87% yield (see Scheme I).[4]

The cyclopropylide I was generated from III by treatment with sodium methylsulfinyl carbanion in dimethoxyethane at −45° (method A). Alternatively, the ylide was generated reversibly by utilization of potassium hydroxide in dimethyl sulfoxide at 25° (method B). The reaction of ylide I thus produced with α,β-unsaturated carbonyl compounds results in selective cyclopropylidene transfer to the α,β carbon–carbon double bond to form spiropentanes rather than addition to the carbonyl group. Isolated carbon–carbon double bonds are not susceptible to cyclopropylidene transfer as shown with carvone. This selectivity is in contrast to spiropentane formation from alkylidenecyclopropanes *via* the Simmons–Smith reagent[5] where isolated double bonds will interfere (see Scheme II).

Scheme I. Generation of Diphenylsulfonium Cyclopropylide



Scheme II. Reaction with Michael Acceptors[d]



[a] Reaction performed by method A. [b] Reaction performed by method B. [c] Only 1 equiv of potassium hydroxide utilized. [d] Yields were determined by vpc analyses.

The reaction of I generated *via* III with ketones and aldehydes produces substituted cyclobutanones in good yields. As the examples in Scheme III show, diaryl and dialkyl ketones as well as aldehydes undergo reaction quite readily. Of particular interest is the fact that norcamphor produces IV and V upon reaction with I in the ratio of approximately 6:1. Confirmation of IV and V arose through independent synthesis as outlined in Scheme IV. Exo nucleophilic attack on norcamphor is usually preferred. Therefore, ylide I should produce predominately dispiroepoxide VIII whereas epoxidation of olefin VI would produce predominately VII. The difference in product distribution from the two independent routes reflects a preference in rearrangement of these epoxides involving inversion at the migration terminus.

Thus, the use of sulfonium cycloalkylides provides a simple solution to difficult synthetic transformations.

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(1) B. M. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Lett.*, 3449 (1970).

(2) For an alternative novel synthesis of cyclobutanones see J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

(3) For an approach using sulfoximine ylides see the accompanying communication by C. R. Johnson, G. F. Katekar, R. M. Huxol, and E. R. Janiga, *ibid.*, 93, 3771 (1971).

(4) All new compounds gave satisfactory spectra and analyses.

(5) E. F. Ullman and W. J. Fanshawe, *J. Amer. Chem. Soc.*, **83**, 2379 (1961).