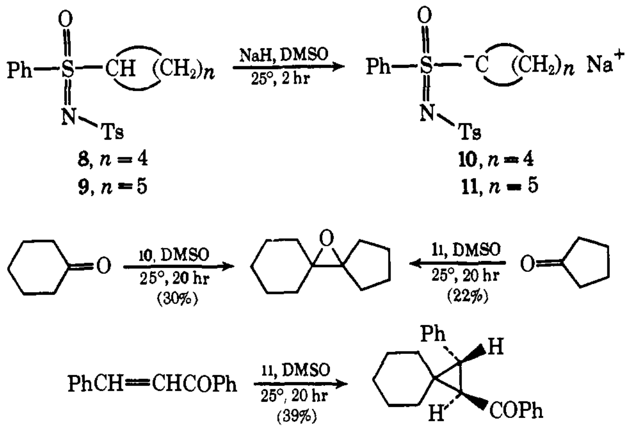
In a manner similar to that described for simpler reagents,[3] *S*-cyclopentyl- and *S*-cyclohexyl-*S*-phenyl-*N*-*p*-toluenesulfonyl sulfoximines (**8** and **9**) were prepared. Representative examples of the anions of these materials in the preparation of spiro compounds are illustrated below.



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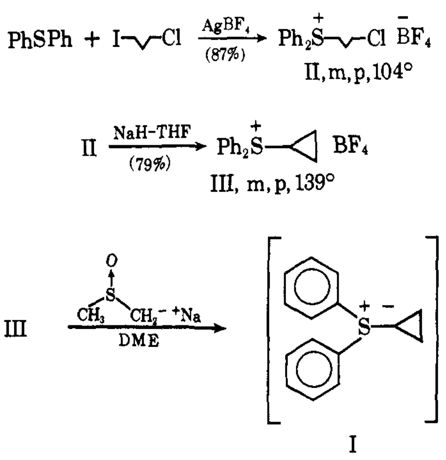
Diphenylsulfonium Cyclopropylide. A Useful Spiroalkylation Reagent

Sir:

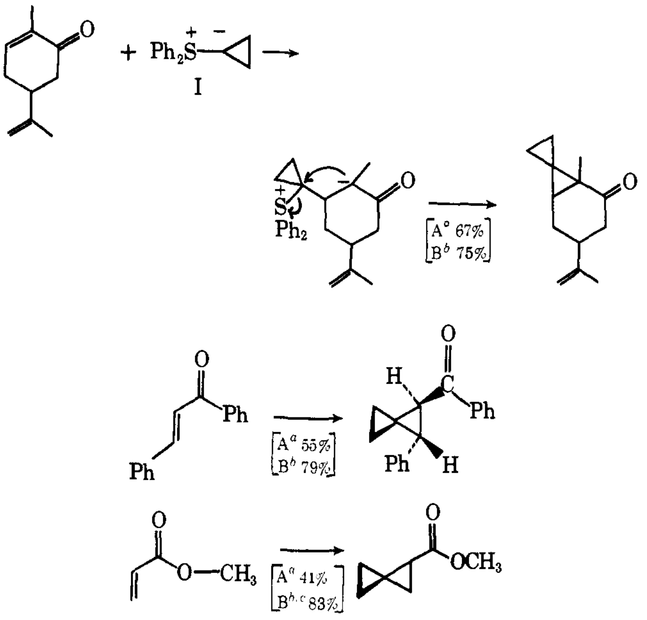
A novel spiroannelation technique invoking the intermediacy of diphenylsulfonium cyclopropylide (I) has been previously recorded.[1-3] We now wish to report a preferred route to diphenylsulfonium cyclopropylide and its utilization as a novel spiroalkylation reagent. This reagent makes spiropentanes and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

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 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).

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).

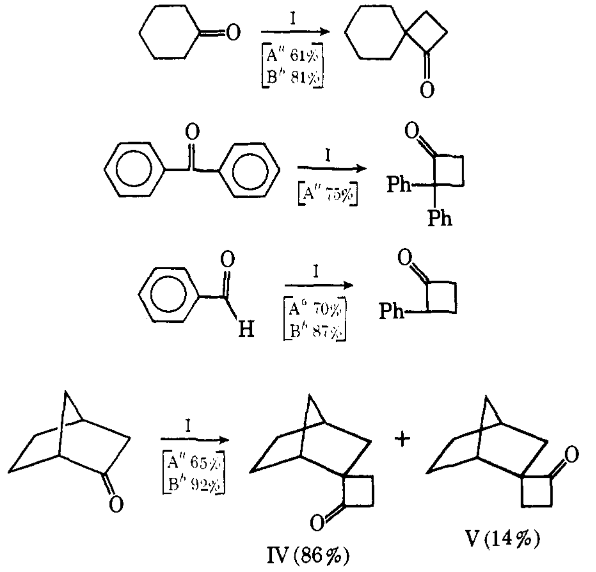
(2) For an alternative novel synthesis of cyclobutanones see J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

(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.

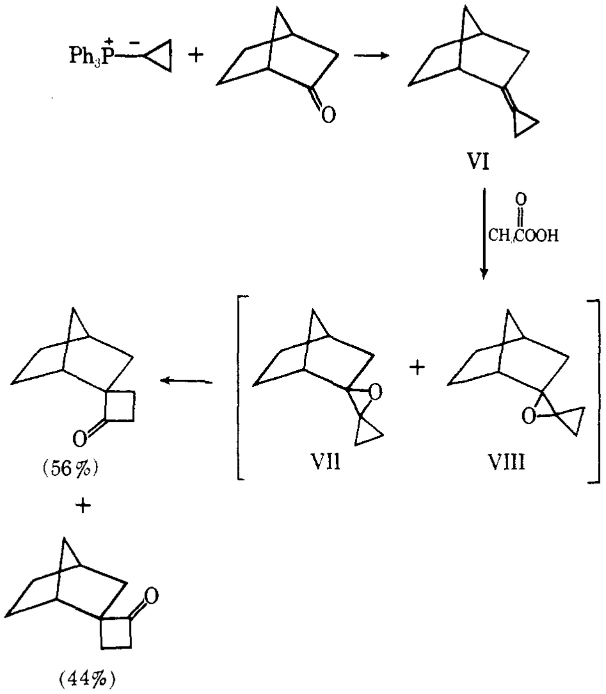
(5) E. F. Ullman and W. J. Fanshawe, *J. Amer. Chem. Soc.*, **83**, 2379 (1961).

Scheme III. Reactions with Carbonyl Functions[c]



[a] Reaction performed by method A. [b] Reaction performed by method B. [c] Yields were determined by vpc analyses.

Scheme IV. Phosphorus Ylide Based Synthesis



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(6) Camille and Henry Dreyfus, Teacher-Scholar Grant Recipient.

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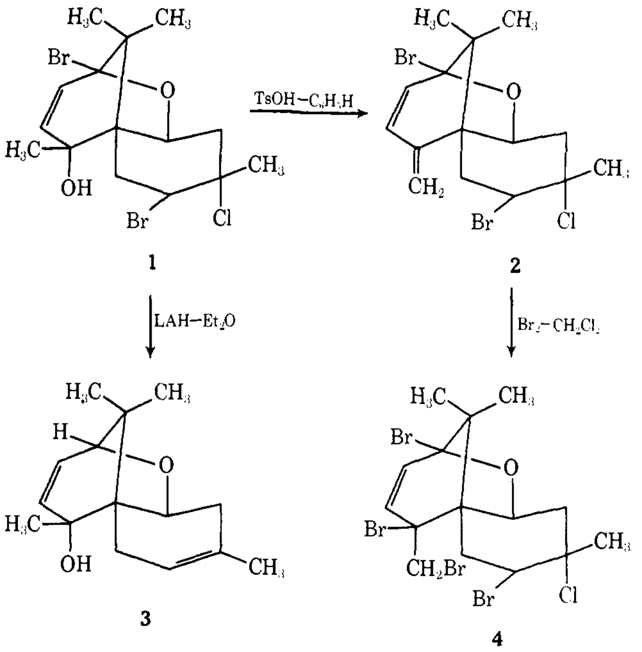
Marine Natural Products. I. Pacifenol, a Rare Sesquiterpene Containing Bromine and Chlorine from the Red Alga, *Laurencia pacifica*

Sir:

Recent reports[1a–i] on the structures of secondary metabolites[2] from marine organisms illustrate significant differences in structural types over those isolated from terrestrial organisms. We have now isolated a structural variant from *Laurenica pacifica*, a red alga indigenous to the Pacific Ocean. The major compound (0.4% of the dried plant), pacifenol (**1**), is a representative of a sesquiterpene class containing the spiro[5.5]undecane skeleton.[3] Pacifenol is, to our knowledge, the first natural compound isolated which contains Br and Cl.

Silica gel chromatography of the ether-soluble portion of an alcoholic extract of the fresh seaweed yielded **1**:[4] $C_{15}H_{21}O_2BrCl$; mp 149–150.5° (petroleum ether); *m/e* $M^+ - H_2O$ 408, 410, 412; high-resolution *m/e* 410 = 409.9469 (calcd for $C_{15}H_{19}OBr^{79}Br^{81}Cl^{35}$: 409.9472).



The orthorhombic needles of **1** obtained by recrystallization from petroleum ether were subjected to X-ray crystallographic analysis. The cell constants, a_0 = 19.176 (17), b_0 = 12.11 (15), c_0 = 7.012 (7) Å, were determined from a least-squares fit of 12 carefully centered reflections using Mo Kα, radiation (λ = 0.70926 Å). On the basis of systematic absences noted on precession and Weissenberg photographs, the space group was determined to be $P2_12_12_1$. The crystal density was 1.71 cm³, 1.74 g/cm³ being required for four molecules per unit cell.

The reflection data were collected under computer control using a Picker four-circle diffractometer with a 32.0-cm crystal to scintillation detector distance and a pulse height analyzer adjusted to accept 90% of a reflections intensity. Independent reflections (940)

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(1) (a) F. J. Schmitz and T. Pattabhiraman, *J. Amer. Chem. Soc.*, **92**, 6074 (1970); (b) R. L. Hale, J. Leclercq, B. Tursch, C. Djerassi, R. A. Gross, Jr., A. J. Weinheimer, K. Gupta, and P. J. Scheuer, *ibid.*, **92**, 2179 (1970); (c) N. C. Ling, R. L. Hale, and C. Djerassi, *ibid.*, **92**, 5281 (1970); (d) R. E. Moore and J. A. Pettus, Jr., *Tetrahedron Lett.*, 4787 (1968); (e) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970); (f) T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, **26**, 3271 (1970); (g) M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970); (h) E. Fatturuso, L. Minale, and G. Sodano, *Chem. Commun.*, 75 (1970); (i) W. Fulmor, G. E. Van Lear, G. O. Morton, and R. D. Mills, *Tetrahedron Lett.*, 4551 (1970).

(2) J. D. Bu'Lock, "The Biosynthesis of Natural Products, an Introduction to Secondary Metabolites," McGraw-Hill, London, 1965.

(3) S. Ito, K. Endo, T. Yoshida, M. Yatagai, and M. Kodama, *Chem. Commun.*, 186 (1967).

(4) Acceptable elemental analyses were obtained for all new compounds. These compounds were characterized by ir and nmr spectra, which are consistent with the structures assigned.