perature. Partly as a further check of the purity of our solvents and partly to form a link between this work and theirs, we determined k_1 for triphenylene using our emission apparatus to follow both the decay of the triplet emission and the decay in the delayed fluorescence.[12,13] The values obtained for k_1, 1.6×10^3 and 1.4×10^3 sec^{-1}, respectively, agree well with the published value of 1.6×10^3 sec^{-1}.[11] Thus at present we would agree with the assessment of Bell and Linschitz that it is unlikely that the short lifetime of triplet benzophenone in benzene is accounted for by impurity quenching, but rather specific interaction between solvent benzene and the triplet has to be sought. In the case of isooctane solvent the short lifetime is undoubtedly accounted for by hydrogen abstraction from the solvent. Using $1/\tau = k_a[\text{solv}]$, the rate constant for hydrogen abstraction from isooctane by triplet benzophenone (k_a) = $6.6 \times 10^4\ M^{-1}$ sec^{-1} which agrees well with other estimates.[3,14]

The above techniques allow the rate constants of interaction (k_{ir}) of a wide range of substrates (S) with triplet ketones to be determined through eq 2 and 3 with k_{ir} and S replacing k_q and Q. We have obtained data for azoalkanes, ethers, alcohols, and amines, and we shall report later on these studies.

Acknowledgments. We are grateful to the National Science Foundation (Grants GP-8463, GP-9247) for support of this work. We also thank J. Guttenplan and S. G. Cohen for many helpful discussions.

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"Active" Sulfuration of Norbornenes

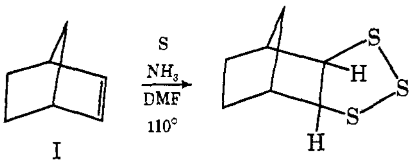
Sir:

There are many reports in the literature which describe the reaction of olefins with elemental sulfur. Temperatures of 140–180° are routinely employed and complex mixtures of polysulfides result.[1] Amines are known to enhance the reaction.[2]

We now wish to report a new reaction which results in selective and stereospecific sulfuration of certain olefins in 80–90% yields. The reaction proceeds between 90 and 110° when elemental sulfur is "activated" by ammonia in the presence of a suitable amide promotor.

Amorphous sulfur (7.5 g-atoms) slurried in 3.5 kg of dimethylformamide was treated by bubbling ammonia (0.50 mole) at 35°. Bicyclo[2.2.1]hept-2-ene (I) (4.45 moles) was added and the mixture was stirred for 2 hr at 110°. After quenching with ice water and extracting with ether, vacuum distillation afforded 2.155 moles of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (II), isolated as a pale yellow oil (86% yield based on sulfur).

The nmr spectrum (CS_2) of II shows a complex pattern between δ 0.80 and 2.30 (6 H) with a narrow multiplet at 2.42 (2 H, norbornyl bridgehead).

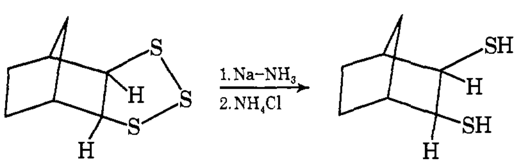


I

II

A doublet ($J \sim 2$ Hz) at 3.60 (2 H, sulfur geminal) indicates coupling between the bridge *anti* proton and the sulfur geminal protons in the *endo-cis* position.[3] Compound II also shows a mass spectral parent peak at *m/e* 190 and a uv absorption at $\lambda_{\max}^{C_6H_{12}}$ 284 mμ (log ε 3.576). The elemental analysis requires $C_7H_{10}S_3$.

Further confirmation was obtained by sodium–ammonia reduction of II to bicyclo[2.2.1]hepta-*exo-cis*-2,3-dithiol (III) in 69% yield. The nmr spectrum (CS_2)

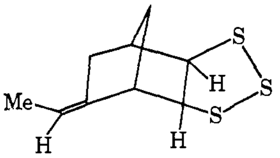


II

III

of III possesses a complex pattern between δ 0.80 and 2.30 (10 H) containing two clear doublets ($J \sim 2$ Hz) centered at δ 1.81 (2 H, thiol); a pair of three-line patterns ($J \sim 2.2$ Hz) also appears at δ 3.15 (2 H, sulfur geminal). Simplification of the spectrum occurs when D_2O–pyridine is employed as solvent. The complex pattern between δ 0.80 and 2.30 (8 H) remains essentially unchanged except for the absence of the thiol doublets, and the protons geminal to sulfur become a doublet ($J \sim 2$ Hz) at 3.19 (2 H). The mass spectral parent peak at *m/e* 160 and elemental analysis conforming with $C_7H_{12}S_2$ further agree with the structure of III.

3,4,5-Trithianes have also been prepared in good yields from other norbornyl olefins and diolefins. For



V

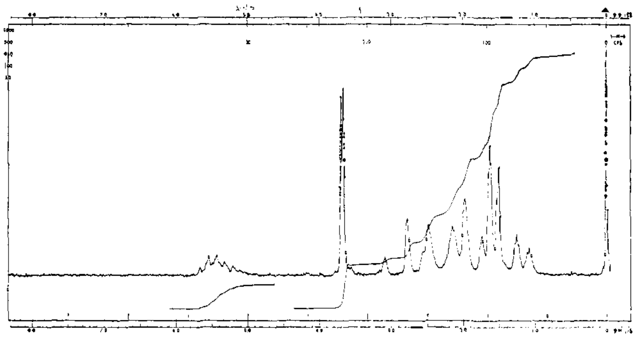


Figure 1. Nmr spectrum (60 MHz) of 8-ethylidene-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane in 50% (v/v) CS_2.

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(1) E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947); L. Bateman, C. G. Moore, and M. Porter, *ibid.*, 2866 (1958).

(2) R. E. Davis and H. F. Nakshbendi, *J. Am. Chem. Soc.*, 84, 2085 (1962); C. G. Moore and R. W. Saville, *J. Chem. Soc.*, 2082 (1954); 2089 (1954).

(3) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 4293 (1965).

example, 5-ethylidenebicyclo[2.2.1]hept-2-ene (IV) undergoes sulfuration on the ring double bond only to give a 71% yield of 8-ethylidene-*exo*-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]decane (V) (Figure 1).

The solvent may consist of as much as 99% dimethyl sulfoxide or some other inert component. Catalytic amounts of both an amide such as N-methylpyrrolidinone or formamide and an amine such as aniline or ammonia to "activate" the sulfur are essential for the reaction to take place. In all cases studied sulfur adds *exclusively to the norbornenyl ring double bond and in a stereospecific manner.* Such a reaction with hydrocarbons and elemental sulfur is to our knowledge without precedent.[4]

A full paper describing the reaction's scope, byproducts, and solvent variation effects is in preparation.

Acknowledgments. The authors wish to thank Dr. W. T. Pace for nmr spectra, Mr. Ralph Harless for mass spectra, Mr. Saul Gottlieb for elemental analyses, and Mr. C. O. Allen for infrared spectra.

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(4) For comprehensive discussion of sulfuration see W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and references cited therein.

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Book Reviews

Properties of Ordinary Water Substance in All Its Phases: Water-Vapor, Water, and All the Ices. Compiled by N. Ernest Dorsey, Physicist, National Bureau of Standards. Hafner Publishing Co., Inc., 31 East 10th St., New York, N. Y. Facsimile of the 1940 Edition. xxiv + 673 pp. 15.5 × 23.5 cm. $22.50.

In a period when interest in water is so active and the need to understand it better is so widely felt, this reissue of Dorsey's classic monograph is very timely. Several new books devoted to water and aqueous solutions have appeared in recent years and more are in prospect, but no present-day author or group of authors will have either the time or the inclination to go over again all of the material that "Dorsey" covers. While some parts of that material well deserve the oblivion into which they have sunk, there are other "old" facts and speculations which the modern worker cannot, in the long run, afford to ignore, and this is the place where they are all assembled.

It is, of course, true that many of the experimental data about water which are currently of great interest (*e.g.*, dielectric and nmr relaxation times; effects of temperature and pressure on acoustic properties; Raman and absorption spectra measured on recording instruments and/or with laser excitation; elastic and inelastic scattering of cold neutrons) could not have been obtained at the time this book appeared, and that some others have since been remeasured with higher accuracy than was attainable before 1938 (*e.g.*, effect of temperature and pressure on viscosity and on static dielectric constant). It is also true, however, that many of the thermodynamic properties of water had been measured with high accuracy (V–T behavior at 1 atm; C_p) and the classical puzzles presented by the behavior of water were well known (density maximum and effect of pressure on it; effect of pressure on viscosity of cold water), and that a number of brilliant workers had offered suggestions on how these puzzles might be solved. Not all of the speculations will now stand scrutiny, but not all can be rejected out of hand either, and it is thus very useful to have them, and the observations which gave rise to them, once more made readily available.

To give an idea of the comprehensiveness of Dorsey's work, the book contains nearly 2200 footnotes, mostly literature citations, but sometimes explanatory; and the analytical index at the end of the volume lists some 2000 page references. Some of these are devoted to quantities that the physical chemist or the biochemist has less interest in than does the hydraulic engineer, *e.g.*, the Joule–Thomson coefficient of the liquid (p 270) and the way in which direct measurements of it at various pressures and temperatures deviate from the values computed from the specific heat and the coefficient of thermal expansion. Inclusion of such material is, of course, consistent with the author's intention, expressed in the preface: "It is hoped that no important article bearing on the subject and appearing before 1938 has been overlooked."

The degree to which this hope was fulfilled is remarkable, and no less so is the author's success in writing for the nonspecialist when data in so many recondite subjects had to be made accessible (*e.g.*, Verdet constant; Cerenkov effect) and reports of improbable observations had to be mentioned without necessarily being endorsed (*e.g.*, that ice can sometimes be superheated; Derjaguin's 1933 report that thin films of water possess a rigidity that increases as the film becomes thinner; that the growth of certain organisms in water freshly formed from steam differs from that in water freshly formed from ice). In the latter connection, the critical balance with which Dorsey wrote seems to this reviewer to be admirable.

The rather clumsy title "ordinary water substance" was chosen so to include all three states of matter, and their equilibria, but to exclude solutions (except for some properties of solutions of atmospheric gases) and, in particular, the question of isotopic composition. Enough was known about isotope effects in 1938 to make it clear (a) that these could be important, and (b) that a great deal more information would be required before a thorough survey could be made, and "ordinary water substance" is thus to be construed as referring to water, in whatever state, of natural isotopic composition.

In 1940, when this volume was first published, F. G. Keyes reviewed it for the *Journal of the American Chemical Society*, concluding: "It is not easy to express adequately in words the value of Doctor Dorsey's work, but he may rest assured that scientific men everywhere and in all fields will never cease to be grateful for his having presented them with a stupendously valuable and enduring piece of work." Although we would now hestitate to write "never," it is nonetheless true that this is one of the rare scientific books which are worth reprinting after three decades. We can therefore still be grateful to Dorsey, and grateful also the American Chemical Society and to the Hafner Publishing Company for once more putting his book into our hands.

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