Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found for **8a**: C, 76.48; H, 8.47; N, 6.73. Found for **8b**: C, 76.73; H, 8.81; N, 6.82.

Anal. Calcd for $C_{12}H_{14}ClNO$: C, 64.43; H, 6.31; N, 6.26. Found for **8c**: C, 64.35; H, 6.16; N, 6.17.

6-*o*-Tolyl-6-(1-piperidyl)hexanenitrile (9a).—A mixture of 400 mg (0.000915 mol) of 1-(1-*o*-tolyl-5-cyanopentyl)pyridinium *p*-toluenesulfonate (**7a**)[14] and 80 mg of 10% palladium on carbon in 20 ml of absolute ethanol was shaken for 24 hr under 30 psi of hydrogen in a Parr hydrogenator. The catalyst was removed by filtration through Celite and the solvent removed under reduced pressure on a rotary evaporator, giving 340 mg of oily material, ir 2240 cm^{-1} (C≡N). The nmr showed the absence of the pyridine ring, the replacement of the triplet of the methine benzylic hydrogen of the pyridinium salt **7a** (Figure 1) at τ 3.59 by a multiplet at τ 5.50, the increase of the integration of signals above τ 7.0 by ten hydrogens compared to **7a**, and the presence of the tosylate group. The oil was dissolved in 20 ml of chloroform, the solution washed with 10% NaOH, followed by water, and dried (Na_2SO_4). Removal of the solvent gave 220 mg of a yellow oil, ir 2240 cm^{-1} (C≡N). The major differences of the nmr compared to that of the tosylate salt was the absence of signals due to the tosylate group and an upfield shift of the signal of the methine benzylic hydrogen from τ 5.50 to 6.50. The free base was converted into the HCl salt by bubbling HCl in a hexane solution of the base, and the salt recrystallized from 2-propanol, mp 188–191°.

Anal. Calcd for $C_{18}H_{27}N_2Cl$: C, 70.45; H, 8.87; N, 9.15. Found: C, 70.37; H, 8.72; N, 9.09.

Deuterated Oximes 1a-d_3 and 1a-d_4.—The deuterated oximes were prepared from the corresponding deuterated ketones by the method described for nondeuterated 1a.

2-*o*-Tolylcyclohexanone-2,6,6-d_3 was prepared by base-catalyzed deuterium exchange on 1.5 g of 2-*o*-tolylcyclohexanone in a mixture of 6.2 ml of anhydrous purified dioxane and 3.0 ml of D_2O with trace amount of sodium methoxide as source of base. The mixture was stirred at 90° for 2 hr, cooled, poured into 10 ml of water, extracted with ether, and dried (Na_2SO_4); the ether was removed. The process was carried out three times. After the third exchange the nmr integration indicated that the exchange was essentially complete: yield 1.3 g; mp 54.0–55.0° [lit.[11] (nondeuterated) mp 55.5–56.5°].

2-*o*-Tolylcyclohexanone-3,3,6,6-d_4 was prepared by the method previously reported.[15]

Registry No.—**1a**, 19640-09-6; **1a**-d_3, 19640-10-9; **1b**, 19640-11-0; **1c**, 19640-12-1; **6a**, 19643-00-6; **7a**, 19643-01-7; **8a**, 19643-02-8; **8b**, 19643-03-9; **8c**, 19643-04-0; **9a** (HCl salt), 19643-05-1; tosyl chloride, 98-59-9.

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[14] Pyridinium tosylate salt **7a** was obtained by chloroform extraction of the aqueous layer resulting from the lactam formation by hydrolysis of the reaction mixture with 15% *p*-toluenesulfonic acid, as explained in the text.

[15] A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2145 (1963).

Sulfur-Bridged Carbocycles. II. Extrusion of the Sulfur Bridge[1]

E. J. COREY AND ERIC BLOCK

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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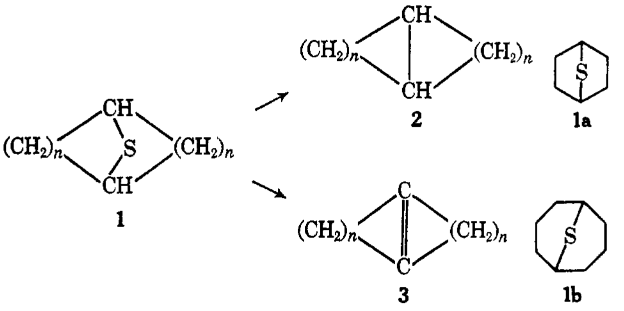
The extrusion of the sulfur bridge from 7-thiabicyclo[2.2.1]heptane (**1a**) and 9-thiabicyclo[3.3.1]nonane (**1b**) and their derivatives, a synthetically useful procedure for the controlled formation of transannular single and double bonds, is described. A novel synthesis of $\Delta^{1,5}$-bicyclo[3.3.0]octene (**8**) has been achieved through the Ramberg–Bäcklund rearrangement of 1-bromo-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (**7**). Thermal extrusion of sulfur dioxide from 7-thiabicyclo[2.2.1]heptane 7,7-dioxide (**4**) and 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (**5**) affords 1,5-hexadiene and bicyclo[3.3.0]octane (**14**), respectively, as major products. Photochemical extrusion of sulfur from **1a** and **1b** in trivalent organophosphorus solvents affords, as the major products, cyclohexene and an equimolar mixture of **14** and cyclooctene, respectively. Related studies on the photochemical extrusion of sulfur from bivalent sulfur compounds in organophosphorus solvents are also described.

We have previously described several convenient synthetic routes to two members of the class of symmetrical sulfur-bridged carbocycles represented by **1**.[1] A variety of other bicyclic and polycyclic sulfur-bridged carbocycles has recently become readily available.[2] It is apparent that, if the bridging sulfur, in any of its valence states, could be extruded from such sulfur-bridged rings with the concomitant formation of a bond between the carbon atoms previously joined to sulfur, affording bicyclic structures **2** or **3**, an interesting synthetic method would be at hand for the controlled formation of transannular single or double bonds.[3] Extension of this procedure to the synthesis of bridgehead- and/or ring-substituted bicyclic or polycyclic structures from the appropriately substituted sulfur-bridged precursors should be possible. The general utility of the proposed synthetic procedure requires the elaboration of suitable methods for the conversion of the C–S–C linkage to a C–C single or double bond.



Advantage has been taken in these studies of several unique and characteristic properties of organically bound sulfur, including its ability to exhibit multiple valence states (thereby making available a variety of sulfur bridges), its ability to stabilize adjacent bridgehead carbanions (making bridgehead substitution possible), and the relative photochemical and thermal lability of the C–S bond.

Formation of Transannular Double Bonds. The Ramberg–Bäcklund Reaction.—In 1940, Ramberg and

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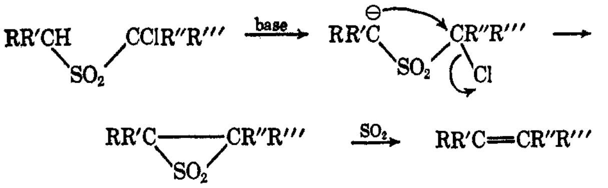
[1] (a) For paper I of this series, see E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); (b) also see E. Block, Ph.D. Thesis, Harvard University, 1967 [*Dissertation Abstr.*, **28**, 1849-B (1967)].

[2] (a) For a general survey, see ref 1b; (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1669 (1966); (c) F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966); (d) F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966); (e) P. Y. Blanc, P. Diehl, H. Fritz, and P. Schlapfer, *Experimentia*, **23**, 896 (1967); (f) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620, 2627 (1968).

[3] For a thorough review of the subject of extrusion, see B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1967.

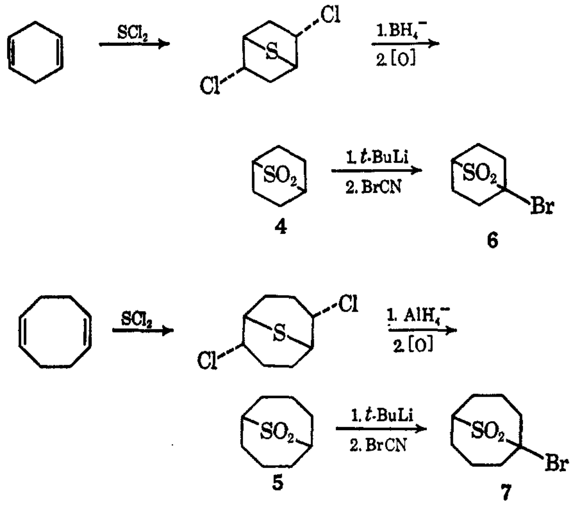
Bäcklund reported that α-halo sulfones, on treatment with aqueous alkali, are transformed into olefins.[4a] Since then the Ramberg–Bäcklund reaction has been studied in considerable detail and is believed to proceed by the sequence illustrated in eq 1.[4b] The reaction is general for molecules containing the structural elements of a sulfonyl group, an α halogen, and at least



(1)

one α-hydrogen atom, and with few exceptions allows the clean replacement of a sulfonyl group by a double bond. The Ramberg–Bäcklund reaction fails in those cases in which the carbanion is geometrically incapable of displacing the α-halogen atom.[4b]

It was of considerable interest to determine if the Ramberg–Bäcklund reaction could be applied to bridgehead halo sulfones such as 6 or 7. The required bridgehead-substituted sulfones, 1-bromo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide (6) and 1-bromo-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (7), were conveniently prepared from the corresponding unsubstituted sulfones 4 and 5 by treatment with *t*-butyllithium at low temperatures followed by addition of a source of Br^+, such as cyanogen bromide (eq 2). The



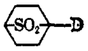
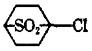
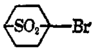
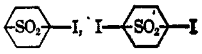
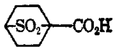
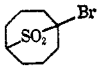
(2a)

(2b)

preparation of the requisite sulfones 4 and 5 has been described in an earlier publication.[1a,5] A variety of other bridgehead-substituted sulfones were prepared (see Table I) by taking advantage of the ability of the sulfone function to stabilize bridgehead anions.[7]

Table I

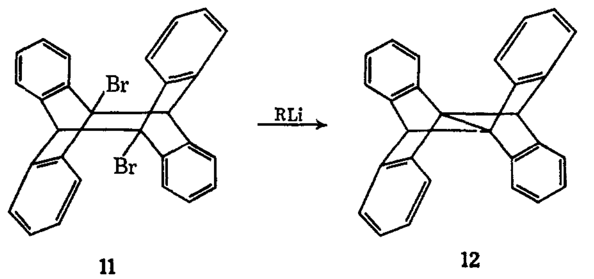
Bridgehead-Substituted Sulfones Prepared from Bridgehead Carbanions

Compound	Reagent	Yield, %
	D_2O	82
	Cl_3CSO_2Cl	72
(6) 	Br_2, BrCN	63, 76
	I_2	60, 2
	CO_2	67
 (7)	BrCN	76

Treatment of bromo sulfone 7 with sodium *t*-pentoxide in tetraglyme at 70° gave the desired transannular Ramberg–Bäcklund rearrangement product, $\Delta^{1,5}$-bicyclo[3.3.0]octene (8), in 81% yield. Thus, through a series of several convenient steps, 1,5-cyclooctadiene can be transformed into $\Delta^{1,5}$-bicyclo[3.3.0]octene (8) in *ca.* 60% over-all yield. The only previous synthesis of the unsubstituted olefin 8 is a low yield multistep sequence starting with cyclobutanone.[8] Using variously substituted sulfones,[9] a variety of substituted $\Delta^{1,5}$-bicyclo[3.3.0]octenes of known stereochemistry should be preparable.

Treatment of bromo sulfone 6 with base under a variety of experimental conditions led to the disappearance of starting material 6, but no volatile hydrocarbons, such as the intriguing olefin $\Delta^{1,4}$-bicyclo[2.2.0]hexene (9) or its valence tautomer 1,2-dimethylenecyclobutene (10), could be detected. The unsubstituted sulfone 4 is stable under the basic Ramberg–Bäcklund rearrangement conditions. The products of the reaction of bromo sulfone (6) with base were water soluble; attempts to characterize the products were not successful.

The novel transannular Ramberg–Bäcklund rearrangement deserves further comment. The conversion of 1-bromo-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (7) into $\Delta^{1,5}$-bicyclo[3.3.0]octene (8) is postulated to involve backside displacements of a bridgehead halogen (see Scheme I). Another possible example of this unusual type of SN2 reaction was reported by Applequist for the anthracene photodimer system 11 → 12.[10] It is probable that inversion of carbanion



11

12

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[4] (a) L. Ramberg and B. Bäcklund, *Arkiv Kemi Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940); B. Bäcklund, Thesis, Uppsala, 1945. (b) For recent reviews of the Ramberg–Bäcklund reaction, see F. G. Bordwell in "Organosulfur Chemistry," M. J. Janssen, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968; L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968).

[5] It has recently come to our attention that the use of the Brown and Bell[6] procedure for the large-scale borohydride reduction of 2,5-bis-*endo*-dichloro-7-thiabicyclo[2.2.1]heptane has resulted in a serious explosion. (L. A. Paquette, personally communicated. We thank *Professor Paquette* for his communication.) We therefore recommend that the alternate procedure described[1a] for the preparation of 7-thiabicyclo[2.2.1]heptane from 7-oxabicyclo[2.2.1]heptane be used.

[6] H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

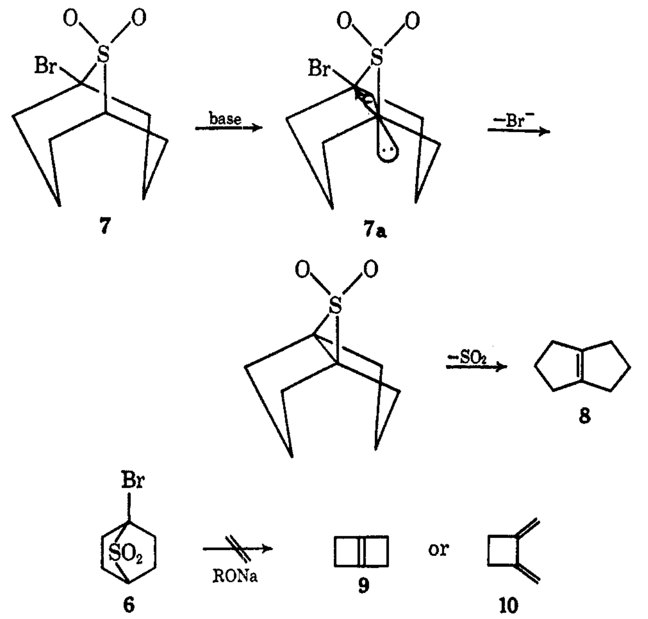
[7] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962.

[8] E. Vogel, *Chem. Ber.*, **85**, 25 (1952).

[9] The preparation of substituted derivatives of 9-thiabicyclo[3.3.1]nonane and the corresponding sulfone are described in ref 1a, 1b, 2b, and 2d.

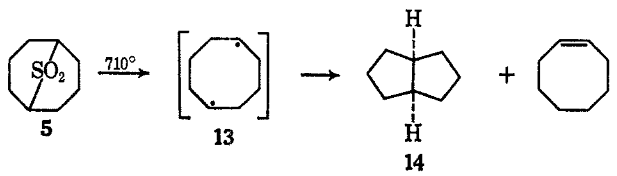
[10] D. E. Applequist, R. L. Little, E. C. Friedrich, and R. E. Wall, *J. Amer. Chem. Soc.*, **81**, 452 (1959); D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

SCHEME I

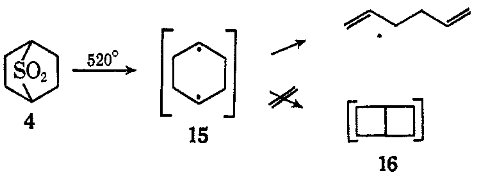


7a is synchronous with transannular bond formation and departure of the bromide ion, as postulated by Applequist for the reaction **11** → **12**.[10] Because of the proximity of the bridgehead carbon atoms in **7** (the C$_1$–C$_5$ distance in bicyclo[3.3.1]nonane itself is 2.50 Å[11]), the presence of even a fraction of a negative charge in the rear lobe of the bridgehead carbanion orbital might well lead to considerable transannular repulsive forces which would be relieved by departure of the bromide ion.

Formation of Transannular Single Bonds. Extrusion of Sulfur Dioxide from Bicyclic Sulfones.—Desulfonylation reactions have been the subject of several recent reviews.[3,12] The thermal extrusion of sulfur dioxide occurs readily in those systems in which strain is relieved or aromatization occurs. Sulfur dioxide can be extruded from less reactive sulfones by pyrolysis at temperatures of 600–700°.[12,13] Sublimation of 9-thiabicyclo[3.3.1]nonane 9,9,dioxide (**5**) at 0.1 mm through a quartz tube heated electrically to 710° led to the isolation of *cis*-bicyclo[3.3.0]octane (**14**, 40–50% yield) in addition to minor amounts of cyclooctene (*ca.* 10%). In accord with the proposed mechanism for the pyrolytic extrusion of sulfur dioxide from sulfones,[12] a probable intermediate in this reaction would be diradical **13**.



Sublimation of 7-thiabicyclo[2.2.1]heptane 7,7-dioxide (**4**) at 0.04 mm through a quartz tube at 520° led to the isolation of 1,5-hexadiene in *ca.* 60% yield. Analytical vapor phase chromatography (vpc) failed to reveal significant amounts of bicyclo[2.2.0]hexane (**16**). This hydrocarbon, however, is known to isomerize to 1,5-hexadiene at temperatures above 200°[14] and if formed probably would not survive the pyrolysis conditions. A diradical of the type **15** may be an intermediate in the pyrolysis of sulfone **4**. It is also conceivable that 1,5-hexadiene is formed from sulfone **4** by a concerted mechanism, although this possibility is not very likely in view of the high temperature (520°) necessary to effect the transformation.[15]



Application of this sulfur dioxide extrusion reaction to bicyclic sulfones bearing radical-stabilizing functions at the bridgehead (such as alkyl, aryl, vinyl, or fluorine groups) might permit the synthesis of various bridgehead-substituted hydrocarbons not conveniently synthesized by other methods.

Photochemical Extrusion of Sulfur from Sulfides.—The ultraviolet (uv) spectra of simple dialkyl sulfides reveal two absorption maxima: one at 210–220 mμ with an extinction coefficient of *ca.* 1000 and a second near 230 mμ with an extinction coefficient of less than 200. The stronger, shorter wavelength band is attributed to an $n_s \rightarrow \sigma^*$ transition (*i.e.*, the promotion of a nonbonding electron from an s or sp hybrid orbital on sulfur to an antibonding C–S σ orbital) while the weaker longer wavelength band is ascribed to an $n_p \rightarrow \sigma^*$ transition (the promotion of a nonbonding electron from a p orbital on sulfur to an antibonding C–S σ orbital). Since the energy of a 3p electron is higher than that of a 3s electron, and since the σ* orbital has a larger p than s character, $n_p \rightarrow \sigma^*$ transitions require less energy (and therefore appear at longer wavelengths), but are less probable and hence give rise to weaker absorption than $n_s \rightarrow \sigma^*$ transitions.[18]

The introduction of strain into cyclic sulfides by decreasing the C–S–C angle results in a bathochromic shift of the long wavelength $n_p \rightarrow \sigma^*$ band.[19] Table II presents several examples of the effect of C–S–C angle strain on the position of the longer wavelength uv maximum in saturated alkyl sulfides.[20] The bathochromic shift is thought to be a consequence of rehybridization of the C–S bonds.[18] Ethylene sulfide may be an anomalous case because of the possibility of

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[11] Calculated from the X-ray structural results of W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

[12] J. L. Kice in "The Chemistry of Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 115.

[13] E. C. Leonard, *J. Org. Chem.*, **30**, 3258 (1965).

[14] S. Cremer and R. Srinivasan, *Tetrahedron Lett.*, No. 21, 24 (1960).

[15] A concerted loss of sulfur dioxide would be a thermally allowed 2 + 2 + 2 process in the terminology of Woodward and Hoffmann[16] if sulfur dioxide is treated as a simple two π-electron system.[17]

[16] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

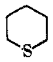
[17] See W. L. Mock, *ibid.*, **88**, 2857 (1966), and S. D. McGregor and D. M. LeMal, *ibid.*, **88**, 2858 (1966), for an application of the Woodward-Hoffmann rules to the pyrolysis of sulfones.

[18] S. F. Mason in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 1. These band assignments may represent an over simplification and in view of recent studies [*e.g.*, P. Salvadori, *Chem. Comm.*, 1203 (1968)] may require modification.

[19] R. E. Davis, *J. Org. Chem.*, **23**, 1380 (1958).

[20] The position of the absorption maximum in alkyl sulfoxides (*ca.* 230 mμ) shows no variation with C–S–C angle strain. Thus, the uv spectrum of 7-thiabicyclo[2.2.1]heptane 7-monoxide was found to be essentially identical with that of dibutyl sulfoxide.

TABLE II
ULTRAVIOLET ABSORPTION SPECTRA OF SATURATED SULFIDES

Compound	Solvent[a]	λ_{max}, mμ[b] (ϵ)	References
$C_2H_5SCH_3$	E	229 (139)	19
	E	229 (183)	19
 [c]	E	235 (sh) (167)	This work
 [d]	E	239 (sh) (87)	This work[e]
	E	239 (54)	19
	I	242 (43)	*f*
	E	247 (43)	This work
	E	257 (40)	19
	E	270 (32)	19
	E	278 (14)	*h*

[a] Solvents: E, ethanol; I, isooctane. [b] Longer wavelength band given; sh, shoulder. [c] Registry number: 281-15-2. [d] Registry number: 6522-54-9. [e] We are grateful to the Hooker Chemical Corp., Niagara Falls, N. Y., for providing us with a sample of 9-thiabicyclo[4.2.1]nonane. [f] American Petroleum Institute Research Project No. 44, Ultraviolet Spectrum No. 843. [g] Registry number: 279-59-4. [h] We are grateful to Professor J. K. Stille of the University of Iowa for the ultraviolet spectrum of 6-thiabicyclo[3.1.1]heptane.

excited states involving the electrons of the C–C as well as the C–S bonds.[19]

Irradiation of simple dialkyl sulfides yields products derived from alkyl and thiyl radicals.[21] The introduction of strain into alkyl sulfides enhances their photochemical reactivity. Thus, both thiacyclobutane and 6-thiabicyclo[3.1.1]heptane undergo ready light-initiated radical polymerization.[22] The complex array of products often obtained from the photolysis of sulfides[23] is a consequence of reactions involving both thiyl and carbon free radicals. By applying the discovery[24] that thiyl radicals can be converted into alkyl radicals by trivalent phosphorus compounds (see eq 3), considerable simplification can be achieved.

$$\mathrm{RSH} \xrightarrow[\text{initiator}]{h\nu \text{ or}} \mathrm{RS}\cdot \xrightarrow{\mathrm{R'_3P}} \mathrm{RS{-}\dot{P}R'_3} \longrightarrow \mathrm{R}\cdot + \mathrm{R'_3P{=}S} \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{RSH} \longrightarrow \mathrm{RH} + \mathrm{RS}\cdot$$

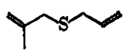
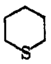
Thus, if the photolysis of a sulfide is carried out in a trivalent organophosphorus solvent (such as a phosphite or phosphine), the only reactive intermediates to be considered should be carbon free radicals (provided that the thiyl radical is desulfurized before it has a chance to react).

$$\mathrm{RSR'} \xrightarrow[\mathrm{R''_3P}]{h\nu} \mathrm{R}\cdot + \mathrm{R'}\cdot + \mathrm{R''_3P{=}S} \tag{4}$$

In fact, irradiation of a solution of 9-thiabicyclo[3.3.1]nonane (**1b**) in isooctyl phosphite gave in 47% total yield a hydrocarbon mixture which consisted of *cis*-bicyclo[3.3.0]octane (**14**, 46%), the product expected from simple intramolecular coupling of the 1,5-cyclooctyl diradical (**13**), in addition to cyclooctene (46%) and cyclooctane (8%).

Table III summarizes the results of irradiating a variety of organic sulfur compounds in trivalent organophosphorus solvents. Certain of these results will be considered in greater detail.

TABLE III
PHOTOLYSIS OF ORGANIC SULFUR COMPOUNDS IN ORGANOPHOSPHORUS SOLVENTS

Reactant	Solvent[a]	Yield, %	Products (relative amounts, %)
	$(R'O)_3P$	47	*cis*-Bicyclo[3.3.0]-octane (46), cyclooctene (46), cyclooctane (8)
	$(R'O)_3P$	49	Cyclohexene (85), cyclohexane (8), 1,5-hexadiene (6)
	R_3P	49	Cyclohexene (83), cyclohexane (7), 1,5-hexadiene (7)
	$(R_2N)_3P$	*ca.* 4[b]	Cyclohexene (71), cyclohexane (8), 1,5-hexadiene (20)
$(C_6H_5CH_2)_2S$	$(R''O)_3P$	59	Dibenzyl
	$(R'O)_3P$	38	1,5-Hexadiene
	R_3P	68	1,5-Hexadiene (23), 2-methyl-1,5-hexadiene (52), 2,5-dimethyl-1,5-hexadiene (25)
	R'_3P	Traces	1-Pentene (?)
	$(R'O)_3P$		Complex mixture

[a] R = C_4H_9; R′ = C_8H_{17}; R″ = CH_3. [b] Photolysis was not carried to completion.

Irradiation of a solution of 7-thiabicyclo[2.2.1]heptane (**1a**) in trivalent phosphorus solvents gave a mixture of cyclohexene, cyclohexane, and 1,5-hexadiene in relative amounts which varied with the solvent. Thus, for the solvent sequence $(C_7H_{13}O_3)P$, $(C_4H_9)_3P$, and $[(C_4H_9)_2N]_3P$, the relative amount of cyclohexene decreases, the relative amount of 1,5-hexadiene increases, and the relative amount of cyclohexane remains unchanged. Since this solvent sequence represents the order of increasing nucleophilicity at phosphorus,[25] and therefore the order of increasing affinity of the phosphorus solvent for the electrophilic thiyl radical,[26–28] it would appear that the cyclohexene is derived, at least in part, from a thiyl diradical at the

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(21) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 488–492.

(22) S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958).

(23) For example, a complex mixture of products is obtained from the photolysis of dibenzyl sulfide: W. H. Laarhoven and Th. J. H. M. Cuppen, *Tetrahedron Lett.*, 5003 (1966); W. Curruthers, *Nature*, **209**, 908 (1966); W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. Chim. Pays-Bas*, **86**, 821 (1967).

(24) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1243 (1959).

(25) See E. H. Amonoo-Neizer, *et al.*, *J. Chem. Soc.*, 4296 (1965).

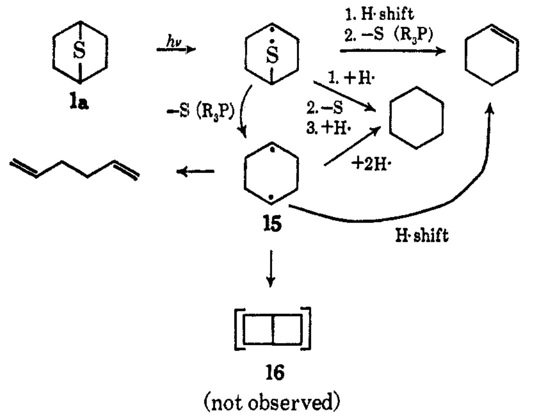
(26) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 318–322.

(27) For an example of the enhanced effectiveness of tris(diethylamino)-phosphine as a desulfurizing agent compared with other phosphines and phosphites, see D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968).

(28) For an example of an especially thiophilic organophosphorus heterocycle, see E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968).

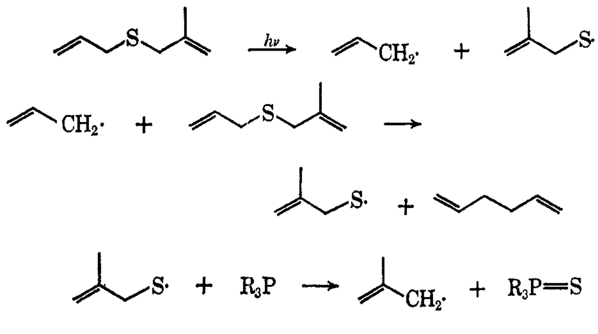
expense of 1,5-hexadiene. Significant quantities of bicyclo[2.2.0]hexane (**16**) could not be detected. A plausible scheme for the formation of the various products is given in Scheme II. A similar scheme could be written for the photochemical reactions of 9-thiabicyclo[3.3.1]nonane (**1b**) (omitting the fragmentation reaction characteristic of the 1,4-cyclohexyl diradical).

SCHEME II



Unsuccessful attempts were made to prepare bicyclo[2.2.0]hexane (**16**) from 7-thiabicyclo[2.2.1]heptane (**1a**) by irradiation of the blood-red tetracyanoethylene charge-transfer complex of **1a**, by irradiation of **1a** in the presence of the Lewis acid phosphorus trifluoride, or by warming **1a** with the powerful phosphorus nucleophile 2-phenyl-3-methyl-1,3,2-oxazaphospholidine.[29]

A second interesting result recorded in Table III is the completely statistical product distribution obtained from the photolysis of allyl methallyl sulfide. The ratio of the amounts of 1,5-hexadiene, 2-methyl-1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene obtained in the photolysis is 23:52:25. Consistent with the observed product ratio would be a mechanism involving completely random combination of allylic radicals, a chain mechanism involving attack of an allylic radical at a terminal methylene carbon on unreacted starting material affording a diene and a thiyl radical (eq 5), or some combination of these two mechanisms.



(5)

Experimental Section[30]

1-Bromo-7-thiabicyclo[2.2.1]heptane 7,7-Dioxide (6).—A solution of 4.00 g (27.4 mmol) of 7-thiabicyclo[2.2.1]heptane 7,7-dioxide (**4**) in 200 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was cooled in a nitrogen atmosphere to −78° and treated all at once with 20 ml of 1.97 *M* *t*-butyllithium (39.4 mmol). After stirring at −70° for 30 min, the yellow solution was added in 20-ml portions during 30 min to a vigorously stirred solution of 7 g of cyanogen bromide (66 mmol) in 150 ml of anhydrous ether at −112° in a nitrogen atmosphere. The reaction mixture was stored overnight at −50°, warmed to 0°, and washed several times with 10% aqueous potassium hydroxide and saturated aqueous sodium hydrogen sulfite. The organic phase was dried over anhydrous magnesium sulfate, concentrated to a minimal volume, and treated with excess *n*-pentane to precipitate 5.35 g of crude **6**. Recrystallization of the crude solid from methanol gave 4.87 g (76%) of colorless crystals: mp 149–151°; ir $\lambda_{max}^{CHCl_3}$ 7.58, 7.71, 8.70, 8.82 (all intense sulfone bands) in addition to "fingerprint" bands at 9.30 (w), 10.01 (s), 11.06 (br, w), 11.70 (w), 12.06 μ (s); nmr (CF_3COOH) peaks appeared at δ 2.40 (multiplet, eight protons) and 3.25 (singlet, one proton—bridgehead position).

Anal. Calcd for $C_6H_9SO_2Br$: C, 31.99; H, 4.03; Br, 35.51; S, 14.25. Found: C, 31.79; H, 3.98; Br, 35.37; S, 13.82.

1-Bromo-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (7).—To a suspension of 5.00 g (28.7 mmol) of 9-thiabicyclo[3.3.1]nonane 9,9-dioxide (**5**) in 350 ml of anhydrous tetrahydrofuran at −78° in a nitrogen atmosphere was added all at once with vigorous stirring 20 ml of 1.97 *M* *t*-butyllithium (39.4 mmol) precooled to Dry Ice temperature. The resulting homogeneous yellow solution was stirred at −78° for 30 min and then added to a vigorously stirred solution of 7.5 g (71 mmol) of cyanogen bromide in 250 ml of anhydrous ether in a nitrogen atmosphere at −112°. The colorless suspension was stored at −50° overnight and then, after warming to −10°, washed several times with saturated aqueous sodium bicarbonate and 10% aqueous potassium hydroxide. The organic phase was dried over anhydrous magnesium sulfate and then concentrated *in vacuo*. Treatment of the residue with excess *n*-pentane followed by recrystallization of the crude solid from boiling methanol afforded 4.11 g (56%) of **7** as colorless needles: mp 182–183° (after several recrystallizations); ir $\lambda_{max}^{CHCl_3}$ 6.75 (m, characteristic band of 3.3.1 system), 6.95 (m), 7.66, 8.91, and 8.99 μ (all intense sulfone bands); nmr (CF_3COOH) peaks appeared at δ 2.5–3.2 (complex methylene multiplet, twelve protons) and 3.59 (bridgehead proton multiplet, one proton).

Anal. Calcd for $C_8H_{13}SO_2Br$: C, 37.95; H, 5.17; Br, 31.57; S, 12.67. Found: C, 38.42; H, 4.73; Br, 31.72; S, 12.77.

1-Chloro-7-thiabicyclo[2.2.1]heptane 7,7-Dioxide.—A solution of 200 mg (1.37 mmol) of bicyclic sulfone **4** in 5 ml of anhydrous tetrahydrofuran was cooled to −78° in a nitrogen atmosphere and treated with *t*-butyllithium (2.3 mmol) in pentane. The yellow solution was stirred for 1 hr at −78° and then added during the course of several minutes to a vigorously stirred solution of 600 mg (3 mmol, 100% excess) of trichloromethyl sulfonyl chloride (recrystallized from hexane prior to use) in 7 ml of anhydrous tetrahydrofuran at −78° in a nitrogen atmosphere. The reaction mixture was slowly warmed to 0° during the course of 2 hr and then stirred for 30 min at 0° with 4 ml of pyridine and 0.5 ml of water to destroy the unreacted sulfonyl chloride. The solution was then diluted with aqueous hydrochloric acid and extracted with several portions of methylene chloride. The organic phase was shaken consecutively with aqueous hydrochloric acid, 2 *N* aqueous copper sulfate, and brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was recrystallized from methylene chloride–*n*-hexane to give 179 mg (72%) of the chloro sulfone as colorless, odorless crystals, mp 146–150°, homogeneous by thin layer chromatography (tlc). The ir spectrum had $\lambda_{max}^{CHCl_3}$ at 7.62, 7.72, 8.70, 8.85 (all intense sulfone bands) and 9.25 (m), 9.91 (s), 10.55 (w), 10.82 (m), 11.61 (m), 12.06 μ (s) ("fingerprint"

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[29] E. J. Corey and C. C. Cumbo, unpublished findings.

[30] Elemental analyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark, and by C. Daessle, Montreal, Canada. Exact molecular weights and mass spectra were determined on an Associated Electrical Industries Ltd., Model MS-9 double-focusing mass spectrometer. All melting points were obtained on a Büchi melting point apparatus and are corrected. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60 nmr spectrometer (60 Mc) with tetramethylsilane as internal standard. Spin decoupling at 60 Mc was accomplished using a Varian Associates Model V-6058 spin decoupler in conjunction with the Varian A-60 nmr spectrometer. Infrared (ir) spectra were obtained on a Perkin-Elmer Model 137 sodium chloride spectrophotometer and a Perkin-Elmer Model 237 grating ir spectrometer using polystyrene as a calibration standard. Uv data were obtained using a Perkin-Elmer Model 202 spectrophotometer and Cary Models 11M and 14 spectrophotometers with ethanol as solvent unless otherwise indicated. Vpc was performed on F & M Models 300, 609, and 810 chromatographs.

region bands); the nmr spectrum (CF_3COOH) had peaks at δ 2.0 (multiplet, eight protons) and 3.0 (singlet, one proton) using an external tetramethylsilane standard. The molecular weight determined mass spectrometrically was 180.0010 (calcd for $C_6H_9SO_2Cl$: 180.0013).

1-Iodo-7-thiabicyclo[2.2.1]heptane 7,7-Dioxide.—A solution of 1.10 g of bicyclic sulfone **4** (7.55 mmol) in 50 ml of anhydrous tetrahydrofuran was cooled in a nitrogen atmosphere to −78° and then treated with 10 ml of 1.97 *M* *t*-butyllithium (20 mmol). The clear yellow solution was stirred at −60 to −70° for 45 min and then treated with a saturated solution of iodine in ether until the iodine color remained. The reaction mixture was allowed to warm to −20° and then shaken with saturated aqueous sodium bisulfite solution until the organic layer was colorless. The organic phase was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The solid residue was washed with excess pentane and dried giving 1.55 g of crude product showing two spots on tlc. The spot with the greater R_f value was considerably fainter than the more slowly moving spot; neither spot corresponded to starting material.

Recrystallization of 1.30 g of crude product from boiling carbon tetrachloride gave 0.82 g of colorless crystals homogeneous on tlc analysis (the product corresponding to the more slowly moving spot) and 0.28 g of residue. Preparative tlc of the residue (silica gel, chloroform containing 5% ethyl acetate) gave an additional 0.19 g of the major product (total yield 1.02 g, 60%) and 0.06 g of a second product.

The major product had mp 174–175° and ir $\lambda_{max}^{CHCl_3}$ at 7.65, 7.78, 8.71, and 8.88 (intense sulfone bands) as well as at 9.34 (w), 10.10 (s), 11.75 (w), and 12.09 μ (s). The ir spectrum of this chromatographed product was essentially identical with that of the crude product. The nmr spectrum ($CDCl_3$) showed peaks at δ 1.6–2.7 (complex multiplet, eight protons) and 2.85 (singlet, one proton). The molecular weight determined mass spectrometrically was 271.9358 (calcd for $C_6H_9SO_2I$: 271.9370). The major product was assigned the structure of 1-iodo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide.

The minor chromatography product had mp 213–215°. The colorless solid had ir $\lambda_{max}^{CHCl_3}$ at 7.55 and 8.75 (intense sulfone bands) as well as at 9.22 (m), 9.95 (m), 10.30 (s), 11.50 (w), and 11.80 μ (w). The nmr spectrum ($CDCl_3$) showed an AB quartet centered at δ 2.53 ($J_1 = 9.5, J_2 = 5.5$ cps). The molecular weight determined mass spectrometrically was 397.8338 (calcd for $C_6H_8SO_2I_2$: 397.8338). The minor product, assigned the structure of 1,4-diiodo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, was formed in about 2% yield.

7-Thiabicyclo[2.2.1]heptane-1-carboxylic Acid 7,7-Dioxide.—A Solution of 200 mg (1.37 mmol) of bicyclic sulfone **4** in 10 ml of anhydrous tetrahydrofuran was cooled to −78° in a nitrogen atmosphere and treated with *t*-butyllithium (2.3 mmol) in pentane. The yellow solution was stirred for 70 min at −78° and then treated during the course of 6 hr at −78° with gaseous "bone dry" grade carbon dioxide (used from the cylinder without preliminary drying). The reaction mixture was warmed to room temperature, treated with a few milliliters of 10% aqueous potassium hydroxide, extracted several times with ether, filtered, and brought to pH 1 with hydrochloric acid. The aqueous phase was extracted several times with ether and ethyl acetate and the organic extract was dried and concentrated *in vacuo*. The slightly yellow residue was recrystallized from boiling ethyl acetate–carbon tetrachloride giving 171 mg (67% yield) of the title compound as a colorless solid decomposing above 200°: ir λ_{max}^{KBr} at 2.5–4 (broad carboxylic acid bands), 5.86 (carbonyl), 7.64, 7.70, 7.78, 8.74, 8.92 μ (all intense sulfone bands); nmr (CF_3COOH) δ 1.9 (sextet, seven protons) and 2.9 (singlet, single bridgehead proton) using an external tetramethylsilane standard.

Anal. Calcd for $C_7H_{10}SO_4$: C, 44.18; H, 5.30; S, 16.86. Found: C, 44.04; H, 5.18; S, 16.76.

1-Deuterio-7-thiabicyclo[2.2.1]heptane 7,7-Dioxide.—A solution of 435 mg (2.98 mmol) of 7-thiabicyclo[2.2.1]heptane 7,7-dioxide **4** in 20 ml of anhydrous tetrahydrofuran was cooled under nitrogen to −80° and treated dropwise with 2 ml of 2.5 *M* *t*-butyllithium (5 mmol) in pentane. After the yellow solution had stirred for 5 min at −80°, a solution of 1 ml of deuterium oxide in 5 ml of anhydrous tetrahydrofuran was added causing immediate decolorization. The reaction mixture was warmed to room temperature and neutralized with methanolic hydrochloric acid, and the organic layer was decanted from lithium chloride and concentrated *in vacuo*. The residue was taken up in methylene chloride, dried over anhydrous magnesium sulfate, concentrated, and then recrystallized from methylene chloride–carbon tetrachloride–*n*-hexane to give 360 mg (82% yield) of colorless, fluffy needles: mp 248° (with sublimation); ir $\lambda_{max}^{CHCl_3}$ 7.72 and 8.80 (intense sulfone bands) as well as 9.35 (w), 10.20 (w), 11.38 (w), 11.85 (m), and 12.62 μ (w); nmr ($CHCl_3$) δ 2.02 (multiplet, integrated area 8.8) and 2.88 (singlet, broad, integrated area 1).

Deuteration of 9-Thiabicyclo[3.3.1]nonane 9,9-Dioxide (5).—A solution of 400 mg (2.3 mmol) of bicyclic sulfone **5** in 4 ml of anhydrous tetrahydrofuran was added to a solution of 515 mg of potassium *t*-butoxide (4.6 mmol) in 4 ml of *t*-butyl alcohol-OD (93% deuterium by nmr analysis) in a nitrogen atmosphere at 24°. After stirring for 18 hr at 24–29°, 55% of the bridgehead protons had been replaced by deuterium (by nmr analysis); after an additional 2 hr at 50°, 80% of the bridgehead protons had been exchanged. The bridgehead deuterated sulfone could be isolated in 90% yield from the basic solution.

$\Delta^{1,5}$-Bicyclo[3.3.0]octene (8).—In a 25-ml three-necked flask equipped with a stirring bar, a rubber septum, and a wide-bore three-way stopcock leading to a liquid nitrogen trap was placed 1.0 g of 55% sodium hydride in mineral oil (23 mmol). The sodium hydride was washed three times with pentane, and 10 ml of tetraglyme (freshly distilled from lithium aluminum hydride) and 1.08 ml of *t*-amyl alcohol (10 mmol, distilled from calcium hydride) were added. The suspension was warmed to 70° with stirring and, when hydrogen evolution ceased, evacuated to 0.02 mm for 30 min. The reaction mixture was cooled to 30° and 1.00 g (4 mmol) of bromo sulfone **7** was added all at once. The reaction mixture was placed under nitrogen and, with vigorous stirring, warmed to 70° for 1 hr to convert the *t*-amyl alcohol formed from the acidic proton of bromo sulfone **7** into alkoxide. After cooling to 30°, the system was connected by means of the three-way stopcock to the liquid nitrogen trap and the system was evacuated to 0.1 mm. The temperature of the reaction mixture was gradually raised to 70° and kept at this temperature for 1 hr. At the end of 1 hr, 0.34 g (81%) of the colorless bicyclic olefin **8** was collected in the liquid nitrogen trap. The liquid, having a heavy, sweet odor, had $n^{25}D$ 1.4803 (lit.[31] $n^{25}D$ 1.4802) and was homogeneous on several different vpc columns, having practically the same retention time as cyclooctene. The mass spectrum indicated the molecular formula C_8H_{12}. The ir spectrum (neat) was very simple, showing no bands characteristic of unsaturation as expected for a symmetrical tetrasubstituted double bond.[32] The nmr spectrum showed a sharp singlet at δ 2.15 in benzene and at 2.18 in deuteriochloroform (lit.[33] δ 2.12 in carbon tetrachloride).

Attempted Preparation of $\Delta^{1,4}$-Bicyclo[2.2.0]hexene (9).—A solution of 450 mg of recrystallized bromo sulfone **6** (2 mmol) in 8 ml of anhydrous tetraglyme was added dropwise to a freshly prepared solution of 5 mmol of sodium *t*-amyloxide in tetraglyme at 70° under high vacuum using the apparatus described for the preparation of bicyclic olefin **8**. *t*-Amyl alcohol (164 mg, 93% yield based on bromo sulfone **6**), characterized by ir spectroscopy and demonstrated to be homogeneous by vpc (on a column giving excellent separation of *t*-amyl alcohol and C_6 hydrocarbons and olefins), was isolated in the liquid nitrogen trap.

Bromo sulfone **6** could be recovered in good yield after being exposed for 10.5 hr to refluxing 6 *N* aqueous sodium hydroxide.

Treatment of 0.9 g of bromo sulfone **6** with a solution of 1 g of potassium *t*-butoxide in 7 ml of *t*-butyl alcohol at reflux for 12 hr gave an orange solution from which 0.1 g of 7-thiabicyclo[2.2.1]heptane 7,7-dioxide (**4**) could be isolated by concentration *in vacuo* followed by extraction of the residue with ether and concentration of the extract. From the acidified residue there could be isolated 0.3 g of a water-soluble red-brown viscous oil having complex ir and nmr spectra. This product was not further investigated.

Pyrolysis of 9-Thiabicyclo[3.3.1]nonane 9,9-Dioxide (5).—The pyrolysis apparatus used consisted of a 40-cm-long quartz tube (7-mm inside diameter) sealed at one end and wrapped in the middle 20-cm section with nichrome wire which in turn was wrapped with asbestos tape as insulation. The open end of the tube contained a standard taper joint. A thermocouple was held

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(31) A. C. Cope, *et al.*, *J. Amer. Chem. Soc.*, **82**, 4306 (1960).

(32) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, New York, N. Y., 1963, p 58.

(33) H. Krieger, *Suomen Kemistilehti*, B**38**, 260 (1965).

against the quartz tube by the nichrome wire. The standard taper joint of the pyrolysis tube could be connected to a trap. Recrystallized bicyclic sulfone **5** (0.50 g, 2.9 mmol) was placed in the bottom of the pyrolysis tube and the entire system was evacuated to 0.1 mm. The pyrolysis zone was warmed electrically to 710°, the trap was cooled in liquid nitrogen, and the sulfone **5** was sublimed into the pyrolysis zone during the course of 1.5 hr by immersing the sealed 10-cm portion of the quartz tube in an oil bath warmed to 135–140°. A yellow oil (0.18 g) was collected in the low temperature trap (volatile gases such as sulfur dioxide and hydrogen sulfide were removed by warming the distillate on a steam bath). The product showed a single major peak on vpc analysis (using a 10-ft 25% TCEP on Chromosorb P column) having the same retention time as authentic *cis*-bicyclo[3.3.0]octane (**14**). The yield of **14**, as estimated from vpc analysis of the crude product, was 40–50%. Minor amounts (*ca.* 5%) of a product having the same vpc retention time as cyclooctene were also obtained. The major product was further characterized by the ir spectrum of product purified by vpc; the ir spectrum of the vpc sample was identical with that of authentic *cis*-bicyclo[3.3.0]octane (**14**). When the pyrolysis was carried out at 590° (temperature of pyrolysis zone) some hydrocarbon **14** was formed in very low yield. At this temperature most of the sulfone **5** simply sublimed through the pyrolysis zone and could be recovered unchanged.

Pyrolysis of 7-Thiabicyclo[2.2.1]heptane 7,7-Dioxide (4).—Using the pyrolysis apparatus described above, 0.500 g of sulfone **4** was sublimed at 0.04 mm into the pyrolysis zone, heated electrically to 520°, during 75 min by warming the sealed end of the quartz tube to 110°. A yellow oil (0.188 g) was isolated in the low temperature trap. Vpc analysis indicated the presence of one major product, characterized as 1,5-hexadiene by ir spectroscopy, formed in 56% yield, in addition to a minor unidentified product, possessing a much greater retention time than 1,5-hexadiene. No significant amounts of bicyclo[2.2.0]hexane (**16**) could be detected by vpc analysis on a silver nitrate column. Lower pyrolysis temperatures led only to sublimation of sulfone **4** through the pyrolysis zone without undergoing any reaction.

Photochemical Studies. General Procedure.—A solution of the sulfide in an organophosphorus solvent was placed in a 10-ml quartz tube. The reaction mixture was repeatedly evacuated and flushed with argon to remove oxygen. Irradiation using vycor filtered light from a 450-W Hanovia medium pressure mercury lamp (Model 450L) was carried out for the indicated time period while the reaction mixture was maintained at 5–10° by a circulating water bath. The progress of the reaction was followed by ir or nmr spectroscopy. After completion of the reaction, the volatile products were isolated from the high boiling solvent by flash distillation. The distillate was collected at liquid nitrogen temperatures and analyzed by vpc combined with spectroscopic methods.

A key to the analytical methods used to identify the various reaction products follows: (a) comparison of ir spectrum of crude distillate with that of an authentic spectrum; (b) comparison of the nmr spectrum of the crude distillate with that of an authentic spectrum; (c) comparison of the vpc retention time with that of an authentic compound; (d) comparison of the ir spectrum of the vpc fraction with that of an authentic spectrum; (e) comparison of the nmr spectrum of the vpc fraction with that of an authentic spectrum; (f) comparison of the mass spectrum of the vpc fraction with that of an authentic spectrum.

Photolysis of 7-Thiabicyclo[2.2.1]heptane (1a). A. In Isooctyl Phosphite.—Irradiation of 400 mg (3.5 mmol) of sublimed **1a** in 6 ml of redistilled isooctyl phosphite for 18 hr gave a yellow solution (no precipitate) from which 140 mg (49% yield) of a colorless volatile fraction was isolated. Analysis of the volatile product on an 8-ft vpc column (30% saturated silver nitrate in triethylene glycol on Chromosorb P) at 0° showed the following products: 8% cyclohexane (a, c, d), 85% cyclohexene (a, c, d), 6% 1,5-hexadiene (a, c, f) (in order of increasing retention times), and several minor products (<1% of each) some of which were derived from the solvent (according to mass spectral analysis).

B. In Tributylphosphine.—Irradiation of 400 mg of **1a** in 6 ml of freshly distilled tributylphosphine for 17 hr gave a yellow solution (no precipitate) from which 140 mg (49% yield—corrected for aliquots taken) of a colorless volatile fraction was isolated. Analysis of the volatile product on the silver nitrate vpc column at 0° indicated the following composition: 7% cyclohexane (c), 83% cyclohexene (a, b, c), 7% 1,5-hexadiene (a, b, c), and several minor products (<1% each).

C. In Tris(dibutylamino)phosphine.—Irradiation of 400 mg of **1a** in 6 ml of distilled tris(disbutylamino)phosphine for 60 hr gave a yellow solution (no precipitate) which still contained considerable starting material (about 85% according to nmr analysis).[34] Analysis of the volatile fraction (69 mg, mainly **3**) indicated the following highly volatile components: 8% cyclohexane (c), 71% cyclohexene (b, c), 20% 1,5-hexadiene (c, d), and 2% unidentified product.

D. In the Presence of an Equivalent of Tetracyanoethylene.—Irradiation of the blood-red charge-transfer complex ($\lambda_{\max}^{CH_3CN}$ 410–460 mμ) from equimolar amounts of **1a** and TCNE (doubly sublimed) gave no indication of reaction involving **1a**.

E. In the Presence of Phosphorus Trifluoride.—Irradiation of **1a** in trioctyl phosphine in the presence of phosphorus trifluoride gave a brown precipitate but no evidence of reaction involving **1a**.

In none of the above photolyses could the presence of bicyclo[2.2.0]hexane (**16**) be unequivocally established; if it were formed it constituted less than 1% of the hydrocarbon products.

Photolysis of 9-Thiabicyclo[3.3.1]nonane (1b). A. In Isooctyl Phosphite.—Irradiation of 800 mg (5.63 mmol) of sublimed **1b** in 6 ml of distilled isooctyl phosphite for 20 hr gave a yellow solution (no precipitate) from which 293 mg (47% yield) of a colorless volatile fraction was isolated. Vpc analysis on the silver nitrate column at 24° gave the following results: 46% *cis*-bicyclo[3.3.0]octane (**14**) (d, e, f), 8% cyclooctane (c, d, f), 46% cyclooctene (b, c, d) (in order of increasing retention times), and trace amounts (<1%) of products presumably derived from the solvent.

B. In Tris(dibutylamino)phosphine.—Irradiation of **1b** in tris(dibutylamino)phosphine for 6 days did not lead to appreciable quantities of products derived from **1b**.

Photolysis of Diallyl Sulfide.—Irradiation of 400 mg of diallyl sulfide (3.5 mmol) in 6 ml of trioctylphosphine for 72 hr gave 173 mg of a colorless volatile fraction which analyzed for 60% 1,5-hexadiene (a, b, c) (38% yield) and 37% *n*-octane (a, b, c) derived from the solvent.

Photolysis of Allyl Methallyl Sulfide.—Irradiation of 504 mg (3.93 mmol) of redistilled allyl methallyl sulfide (this was prepared from the reaction of methallyl chloride and sodium allyl mercaptide at 0°; mass measurement indicated a molecular weight of 128; and the nmr spectrum was in full accord with indicated structure) in 6 ml of redistilled tributylphosphine for 18.5 hr gave a colorless solution (no precipitate) from which 253 mg of colorless distillate (60% yield) was isolated. Analysis of the distillate on an 8-ft TCEP vpc column at 60° gave the following composition: 23% 1,5-hexadiene (b, c), 52% 2-methyl-1,5-hexadiene (b, c), and 25% 2,5-dimethyl-1,5-hexadiene (b, c) (in order of increasing retention times; product composition corrected by calibration of the column with a mixture of known composition).

Photolysis of Benzyl Sulfide.—A solution of 748 mg of benzyl sulfide (3.34 mmol) in 6 ml of distilled trimethyl phosphite was irradiated for 72 hr (the reaction was over after 17 hr). Removal of the solvent at 25° (0.01 mm), followed by treatment of the residue with methanol, gave 377 mg (59% yield) of a yellow solid, mp 41–50°, which after recrystallization twice from *n*-pentane (the solid was colorless after recrystallization) had mp 50.2–52.6°, undepressed on admixture with authentic dibenzyl. It had an ir spectrum identical with that of authentic dibenzyl. The residue from the precipitation of the crude dibenzyl consisted principally of trimethyl thiophosphate.

Photolysis of Thiacyclohexane.—Irradiation of 394 mg (3.86 mmol) of thiacyclohexane in 6 ml of trioctylphosphine for 72 hr and analysis of the product by the usual procedure indicated mainly unreacted starting material and products arising from solvent decomposition. In addition, trace amounts of other products, possibly 1-pentene and *n*-pentane, were found on vpc analysis.

Registry No.—**6**, 19669-15-9; **7**, 19669-16-0; 1-chloro-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, 19643-36-8; 1-iodo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide,

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[34] Compounds containing P–N bonds are not completely transparent below 250 mμ and thus filter out a portion of the effective radiation, slowing the photolysis considerably.

19643-37-9; 1,4-diiodo-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, 19643-38-0; 7-thiabicyclo[2.2.1]heptane-1-carboxylic acid 7,7-dioxide, 19643-39-1; 1-deuterio-7-thiabicyclo[2.2.1]heptane 7,7-dioxide, 19643-40-4.

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The Chemistry of Ylides. XIX. β-Carbonyl Sulfonium Ylides[1]

A. William Johnson[2] and Ronald T. Amel

Division of Natural Sciences, University of Saskatchewan, Regina, Canada, and the Chemistry Department, University of North Dakota, Grand Forks, North Dakota

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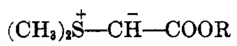
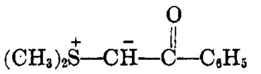
The preparation, isolation, and physical and chemical properties of dimethylphenacylidenesulfurane (II) and dimethyl(carbomethoxymethylene)sulfurane (Ia) are described. Both ylides exhibit decreased nucleophilicity and basicity as a result of the delocalization of the carbanion electrons through the carbonyl groups, the decrease being larger for II. Spectroscopic methods and chemical reactions (alkylation, acylation, and reaction with carbonyl compounds and nitrosobenzene) served to illustrate the differences. The mechanism of the thermal decomposition of sulfonium ylides to cyclopropanes appears to involve a carbenic moiety.

This paper reports the details of our work on a group of stabilized, isolable sulfonium ylides, the β-carbonyl ylides Ia and II, part of the results having been reported in a preliminary communication.[3] At the time this work was undertaken no carboalkoxy sulfonium ylides or β-keto sulfonium ylides were known. In fact, very few isolable sulfonium ylides had been prepared or studied, most of the chemistry of sulfonium ylides having been elaborated utilizing complex solutions of the ylides.[4] We feel it is important actually to isolate and characterize ylides to describe accurately their properties and behavior.



$(CH_3)_2\overset{+}{S}-\overset{-}{C}H-COOR$

Ia, R = CH_3
b, R = C_2H_5



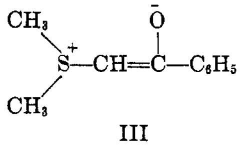
$(CH_3)_2\overset{+}{S}-\overset{-}{C}H-\overset{O}{\overset{\|}{C}}-C_6H_5$

II

Since our preliminary report on the chemistry of the phenacylide II, several groups[5,6] have reported the results of their similar studies. Nozaki, *et al.*,[7] have studied the related S-methyl-S-phenylphenacylide. Several groups[5,8–11] have reported on the chemistry of Ib while Casanova and Rutolo[12] recently reported on the properties of Ia.

Dimethylphenacylidenesulfurane (II).—The crystalline ylide II was prepared from dimethylphenacylsulfonium bromide in ethanol solution by proton abstraction with triethylamine. The anhydrous ylide, mp 67–68°, was converted into a hydrate of mp 57–58° upon standing exposed to the atmosphere or upon standing in a solvent to which a few drops of water had been added. Payne,[13] Trost,[6] and Ratts[5a] all have reported similar behavior for II. The water was detectable in the nuclear magnetic resonance (nmr) spectrum (δ 3.38) and the infrared (ir) spectrum (3260 cm^{-1}).

The ylide II could be converted into the starting sulfonium salt (ylide conjugate acid) upon treatment with hydrogen bromide. The sulfonium salt showed a pK_a of 7.68 in 95% ethanol solution.[14] Nmr studies showed the methyl groups of the ylide (δ 2.92) to be more highly shielded than those of the conjugate acid (3.05). In addition, the methine proton of II (δ 4.31), as expected, appeared at higher field than the methylene protons of the ylide conjugate acid (5.74). The carbonyl group of the ylide conjugate acid absorbed at 1665 cm^{-1} in the ir while that of the ylide II absorbed at 1508 cm^{-1}, indicating considerable enolate character for the ylide (*i.e.*, considerable contribution of structure III). The stability of the phenacylide undoubtedly is largely due to the delocalization provided the carbanion by the adjacent carbonyl group. X-Ray crystallographic studies of the analogous phosphonium phenacylides have provided significant evidence to this effect.[15] The broadened methine peak at δ 4.31 indicates the contribution of the two geometric isomers of III.[6a,16]



III

The shielding effects of various carbon and sulfur substituents for a series of sulfonium ylides are presented in Table I. Interestingly, the nmr spectra of the closely related phenacylides $(CH_3)(C_6H_5)S{=}CHCOC_6H_5$ and $(C_6H_5)_2S{=}CHCOC_6H_5$ revealed that the presence of one or two phenyl groups on sulfur had the effect of deshielding both the methine protons (δ 4.55 and 4.75, respectively) and the remaining methyl

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[1] For part XVIII in this series, see A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968).

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