Preparation of Diphenylmethylenetriphenylphosphorane (1).—The ylide 1 was prepared according to the procedure of Staudinger.[1] The physical properties were identical with reported data.

Preparation of Carbethoxymethylenetriphenylphosphorane (6a).—The ylide **6a** was prepared according to the procedure of Denney and Ross.[6] The physical properties were identical with reported data.

Reaction of Diphenylmethylenetriphenylphosphorane (1) with Diphenylcarbodiimide.—A mixture of 0.025 mol of the ylide 1 and 0.025 mol of diphenylcarbodiimide was stirred at 160–180° for 4 hr under nitrogen stream. The reaction mixture was extracted (petroleum ether), and 4.7 g (53%) of the insoluble solid was separated and recrystallized (ethyl ether) to give N-phenyliminotriphenylphosphorane (2), mp 135–136°.

Anal. Calcd for $C_{24}H_{20}NP$: C, 81.57; H, 5.70; N, 3.96; P, 8.76. Found: C, 81.82; H, 5.64; N, 4.07; P, 8.63.

The extract (petroleum ether) was evaporated to give the yellow solid, ir 2000 cm^{-1}, but recrystallization did not give a pure sample. The column chromatography (Al_2O_3, benzene) of the solid gave 6.8 g (94%) of diphenylacetanilide (4) and 0.2 g of diphenylurea. The acetanilide 4 was identified by ir comparison with an authentic sample and by the mixture melting point test (mmp 185–186°).

Reaction of Carbethoxymethylenetriphenylphosphorane (6a) with Diphenylcarbodiimide.—A mixture of 0.05 mol of the ylide **6a** and 0.025 mol of diphenylcarbodiimide was stirred at 140–150° for 4 hr under nitrogen stream. The reaction mixture was chromatographed (Al_2O_3, benzene) to give 8.2 g (93%) of N-phenyliminotriphenylphosphorane (7) and 13.5 g (100%) of the ylide **8a**. The ir spectrum of the iminophosphorane 7 was identical with that of the sample 2 described above. The ylide **8a** was recrystallized (MeOH) to give white crystals: mp 164.5–165.5°; ir (Nujol mull) 1720 (C=O), 1640 (C=O, conjugated to P=C), 1575 cm^{-1} (C=N); nmr (benzene) δ 0.58 (t, 3, J = 7.1 Hz, CH_3), 1.02 (t, 3, J = 7.1 Hz, CH_3), 3.85 (q, 2, CH_2Me), 4.11 (s, 2, $CH_2C{=}N$), 4.12 (q, 2, CH_2Me).

Anal. Calcd for $C_{33}H_{32}O_4NP$: C, 73.72; H, 6.00; N, 2.61; P, 5.76. Found: C, 73.33; H, 5.97; N, 2.69; P, 5.91.

Reaction of Phenylmethylenetriphenylphosphorane (6b) with Diphenylcarbodiimide.—Sodium *t*-butoxide (0.05 mol) and triphenylbenzylphosphonium chloride (0.04 mol) were dissolved in 100 ml of benzene under nitrogen stream. Diphenylcarbodiimide (0.02 mol in 50 ml of benzene) was added dropwise to the solution with stirring over a period of 4 hr at room temperature. Stirring was continued for 3 hr. After separation of 2.1 g (91%) of sodium chloride, the filtrate was concentrated and chromatographed (Al_2O_3, benzene–methanol) to give 0.7 g (10%) of N-phenyliminotriphenylphosphorane, 6.2 g (56%) of triphenylphosphine oxide, 1.4 g (33%) of diphenylurea, and 1.4 g (13%) of the ylide **8b**. Ir spectra of these compounds except the ylide **8b** were identical with those of authentic samples. The ylide **8b** was recrystallized (benzene–hexane) to give yellow crystals: mp 209–210° (lit.[7] 209–210°); mass spectrum (70 eV) m/e 546 (M^+ calcd 546).

Anal. Calcd for $C_{39}H_{32}NP$: C, 85.84; H, 5.91; N, 2.57; P, 5.68. Found: C, 86.11; H, 61.5; N, 2.41; P, 5.51.

Reaction of Methylenetriphenylphosphorane (11) with Diphenylcarbodiimide.—Sodium hydride (0.02 mol) and methylenetriphenylphosphonium bromide (0.02 mol) were dissolved in 140 ml of dimethyl sulfoxide.[8] Diphenylcarbodiimide (0.02 mol) was added dropwise to the solution with stirring; color of the solution changed from yellowish green to deep red. The reaction mixture was allowed to stand for 2 days. The reaction mixture was poured into 200 ml of ice water and extracted with ethyl ether. The ethereal extract was washed (water), dried ($CaSO_4$), concentrated, and chromatographed (Al_2O_3, benzene–methanol) to give 3.3 g (81%) of N,N′-diphenylacetamidine (mp 134–135°) and 5.4 g (97%) of triphenylphosphine oxide. These compounds were identified by ir spectra and mixture melting point test with authentic samples.[9]

Registry No.—2, 2325-27-1; **8a**, 24375-91-5; **8b**, 14630-48-9; diphenylcarbodiimide, 622-16-2.

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[6] D. B. Denney and S. T. Ross, *J. Org. Chem.*, **27**, 998 (1962).

[7] R. Huisgen and J. Wulff, *Tetrahedron Lett.*, 917 (1967).

[8] J. Asunskis and H. Schechter, *J. Org. Chem.*, **33**, 1164 (1968).

[9] M. Sen and J. N. Ray, *J. Chem. Soc.*, 646 (1926).

Solvolysis of 9-Bromo-1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane[1]

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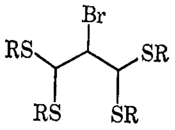
The high solvolytic reactivity of β-halo sulfides has been extensively investigated, particularly that of β-chloroethyl sulfides, the "mustard gases."[2] The effect of sulfur as a neighbouring group[3] is readily demonstrated, for example, by comparing the rates of solvolysis (aqueous dioxane, 100°) of β-chloroethyl ethyl sulfide with that of β-chloroethyl ethyl ether ($k_{\text{sulfide}}/k_{\text{ether}}$ = 15,000).[4] Halogen atoms in a β relationship to more than one sulfur atom may undergo displacement with still greater facility, and, in accord with this possibility, compounds **1a** and **1b** are described as fuming liquids which lose HBr spontaneously at room temperature.[5]



1a, R = CH_3
b, R = CH_2CH_3

We wish to describe the preparation of a β-halo sulfide which incorporates the functional group arrangement 1 and the results of qualitative solvolysis experiments with this substance (3). In the course of an investigation of the chemistry of tetrathiaadamantanes,[6] the reaction of tetramethyltetrathiaadamantane 2 with bromine was examined. With a fourfold excess of bromine, the monobromo derivative 3 was obtained in 33% yield. More highly brominated products may have been formed but could not be isolated.

The structure of the bromide 3 is based mainly on its nmr spectrum. The spectrum contains a six-proton singlet at 1.70 ppm and two three-proton singlets at 1.58 and 1.73 ppm establishing the presence of one pair of equivalent methyl groups and one pair of nonequivalent methyl groups. (For comparison, the CH_3 signals in 2 appear at 1.65 ppm.) The methylene protons appear as a singlet at 2.21 ppm and the proton on the brominated carbon atom appears as a singlet at 4.79 ppm. The substance can be recrystallized from alcohols without serious decomposition. This moderate stability is rather surprising since the *trans*-coplanar stereoelectronic requirement for sulfur-assisted ionization is already satisfied in this rigid system.[7]

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[1] Research supported by the National Science Foundation (GP-10950).

[2] Reviewed by E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., Inc., New York, N. Y., 1960, Vol. II, Chapter 5.

[3] For reviews, see K. D. Gunderman, *Angew. Chem. Int. Ed. Engl.*, **2**, 674 (1963); B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 108.

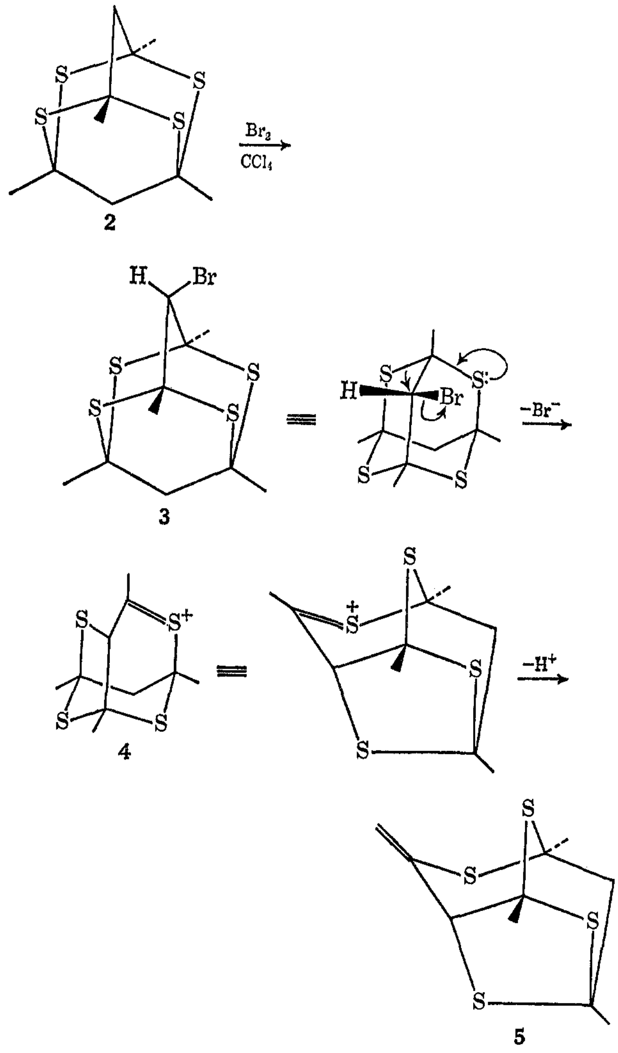
[4] H. Böhme and K. Sell, *Chem. Ber.*, **81**, 123 (1948).

[5] E. Rothstein and R. Whiteley, *J. Chem. Soc.*, 4012 (1953).

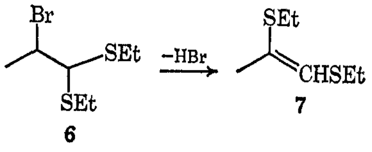
[6] D. L. Coffen, P. E. Garrett, and D. R. Williams, *Chem. Comm.*, 652 (1968); K. C. Bank and D. L. Coffen, *ibid.*, 8 (1969).

[7] *Cf.* S. J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc.*, **79**, 3441 (1957).

When a solution of bromide **3** in glacial acetic acid buffered with sodium acetate is heated under reflux for 2 hr, the bromide is completely transformed into a new substance whose ir spectrum establishes at once that it is not an acetate but an olefin (ν_{max} 1600 cm^{-1}). Structure **5** is assigned to this olefin on the basis of its nmr spectrum. The spectrum contains three three-proton singlets at 1.70, 1.82, and 1.98 ppm indicating three nonequivalent methyl groups. The endocyclic methylene protons appear as an AB quartet at 2.58 ppm (J_{AB} = 14 cps) whence they are no longer equivalent. A one-proton singlet at 4.63 ppm is assigned to the methine proton and two one-proton singlets at 5.12 and 5.31 ppm are assigned to the exocyclic methylene protons. Neither geminal nor allylic coupling is evident for these last three protons.



The rearrangement to tricyclic structure **5** is rationalized in terms of sulfur assisted ionization of the carbon–bromine bond, a 1,2-sulfur shift leading to the cationic intermediate **4**, and subsequent loss of a proton from the adjacent methyl group giving the olefin **5**. Rothstein proposed a similar pathway for the rearrangement of bromide **6** resulting in olefin **7**.[5] It has been suggested, however, that such rearrangements are "best explained by assuming cyclic sulfonium intermediates."[8] Since the 2-adamantyl cation does not undergo a similar rearrangement,[9] the sulfur atoms and not the ring system clearly provide the incentive for compound **3** to rearrange.



Methanolysis of bromide **3** (22 hr at reflux) gave olefin **5** and an unstable by-product assumed to arise from the trapping of cation **4** by methanol. The formation of this by-product was evident from tlc but it changed to olefin **5** during attempts at isolation and purification. Similarly, hydrolysis in aqueous dioxane gave, in addition to olefin **5**, an unstable by-product presumed to be an alcohol formed in the reaction of cation **4** with water.

Experimental Section[10]

9-Bromo-1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane (3).—Bromine (11.0 g, 68 mmol)[11] was added dropwide during 1 hr to a boiling solution of 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane[12] (4.0 g, 15 mmol) in carbon tetrachloride (250 ml). After a total of 3 hr at reflux, the solution was filtered, washed with aqueous sodium bicarbonate, dried, and evaporated. The residue was triturated with a small amount of ether and chilled, and the crystalline product was filtered out and washed with cold ether. The filtrate contains more bromide (tlc) but, on standing, hydrogen bromide was evolved and a tarry precipitate formed. The crude bromide (1.75 g, 33.6%) was recrystallized from chloroform–isopropyl alcohol giving colorless crystals (70% recovery) with mp 182–4° dec; ir (Nujol) 1400, 1175, 1095, 1065, 1030, 945, 775, and 677 cm^{-1}; nmr (CDCl$_3$) 1.58 (3 H, s), 1.70 (6 H, s), 1.73 (3 H, s), 2.21 (2 H, s), and 4.79 ppm (1 H, s); mass spectrum *m/e* 344 and 342 (M$^+$ peaks), 263 (ion **4**), 139, 131 (100%), and 59.[13]

Anal. Calcd for $C_{10}H_{15}BrS_4$: C, 34.98; H, 4.40; Br, 23.27; S, 37.35. Found: C, 35.18; H, 4.52; Br, 23.09; S, 37.17.

Acetolysis of Bromide 3.—A solution of bromide **3** (50 mg) and sodium acetate (50 mg) in acetic acid (10 ml) was heated under reflux for 2.5 hr. The acetic acid was evaporated from the cooled solution and the residue was partitioned between methylene chloride and aqueous sodium carbonate. The dried methylene chloride layer left 38 mg (100%) of colorless oil after evaporation which, by tlc, contained only one substance. Crystallization from methanol gave colorless crystals with mp 59–61°; ir (Nujol) 1600, 1170, 1140, 1095, 934, 884, and 740 cm^{-1}; nmr (CDCl$_3$) 1.70 (3 H, s), 1.82 (3 H, s), 1.98 (3 H, s), 2.58 (2 H, AB, J = 14 cps), 4.63 (1 H, s), 5.12 (1 H, s), and 5.31 (1 H, s); mass spectrum *m/e* 262 (M$^+$), 131, and 59 (100%).

Anal. Calcd for $C_{10}H_{14}S_4$: C, 45.76; H, 5.38; S, 48.86. Found: C, 45.83; H, 5.52; S, 48.89.

Registry No.—3, 24378-10-7; **5,** 24378-11-8.

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[8] W. E. Parham, J. Heberling, and H. Wynberg, *J. Amer. Chem. Soc.*, **77**, 1169 (1955).

[9] P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 182 (1961).

[10] Melting points are uncorrected. Ir, nmr, and mass spectra were recorded on Perkin-Elmer 137, Varian A-60A, and Atlas CH-7 instruments respectively. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

[11] With less bromine the product contains starting material.

[12] K. Olsson and S-O Almquist, *Ark. Kemi*, **27**, 571 (1967).

[13] The electron-impact fragmentation reactions of tetrathiaadamantanes are discussed by K. Olsson, *ibid.*, **26**, 435 (1967), and K. Olsson and S-O Almquist, ref 12.