

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-phenylimino-triphenylphosphorane (2), mp 135–136°.

Anal. Calcd for C₂₄H₂₀NP: 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 (Al₂O₃, 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 (Al₂O₃, benzene) to give 8.2 g (93%) of N-phenylimino-triphenylphosphorane (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, CH₃), 1.02 (t, 3, J = 7.1 Hz, CH₃), 3.85 (q, 2, CH₂Me), 4.11 (s, 2, CH₂C=N), 4.12 (q, 2, CH₂Me).

Anal. Calcd for C₃₃H₃₂O₄NP: 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 (Al₂O₃, benzene-methanol) to give 0.7 g (10%) of N-phenylimino-triphenylphosphorane, 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 C₃₀H₃₂NP: C, 85.84; H, 5.91; N, 2.57; P, 5.68. Found: C, 86.11; H, 6.15; 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 poured into 200 ml of ice water and extracted with ethyl ether. The ethereal extract was washed (water), dried (CaSO₄), concentrated, and chromatographed (Al₂O₃, benzene-methanol) to give 3.3 g (81%) of N,N'-diphenylacetamide (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.

(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).

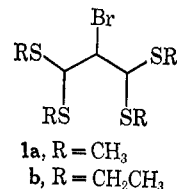
Solvolysis of 9-Bromo-1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane¹

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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 group³ 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



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, 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 non-equivalent methyl groups. (For comparison, the CH₃ 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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(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. Gundersman, *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. Böhrne 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).