7

Anal. Calcd for $C_{12}H_{17}N_5 \cdot H_2O$: N, 28.09; H₂O, 7.33. Found: N, 28.16; H₂O, 7.9.

2-Benzyl-5-benzylmethylaminotetrazole.-Benzylation of sodium 5-benzylmethylaminotetrazolate in an analogous manner gave a 55% yield of mixed 1- and 2-benzyl-5-benzylmethylaminotetrazole (1:5 based on ¹H nmr analysis), mp 56-57°. The 2 isomer, mp 58-59°, was recovered when the crude product was recrystallized from n-hexane.

Anal. Caled for C₁₆H₁₇N₅: C, 68.79; H, 6.14; N, 25.07. Found: C, 68.49; H, 6.09; N, 25.40. No ylide was found.

5-(3-Chlorobenzyldimethylammonium)tetrazolate.--This ylide, prepared in 33% yield, decomposed at 227-228° after recrystallization from 95% ethanol.

Anal. Calcd for C10H12N5Cl: N, 29.47; Cl, 14.91. Found: N, 29.33; Cl, 15.01.

The ratio of 1- and 2-(3-chlorobenzyl)-5-dimethylaminotetrazoles, also recovered (56% yield) in this alkylation, was 1:10.

Registry No.-2-Benzyl-5-benzylmethylaminotetrazole, 24302-07-6.

The Chemistry of Cumulated Double-Bond Compound. VIII. The Reaction of Phosphonium Ylide with Carbodiimide

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Reactions of phosphonium ylides with ketenes or isocyanates have been reported in a few papers. Luscher had reported that the reaction of diphenylmethylenetriphenylphosphorane with diphenylketene yielded tetraphenylallene and triphenylphosphine oxide.¹ On the other hand, Staudinger and Meyer reported that the reaction of the same ylide with phenyl isocyanate yielded ketenimine.² Trippet and Walker observed that the products varied with the structure of ylides.³

In this paper, we studied the reactions of phosphonium ylides with carbodiimides.

The reaction of diphenylmethylenetriphenylphosphorane (1) with diphenylcarbodiimide yielded Nphenyliminotriphenylphosphorane (2) and triphenylketenimine (3) in good yield. The ketenimine 3 exhibited the principal infrared peak at 2000 cm^{-1} (C= C=N) and was hydrolyzed easily to diphenylacetanilide (4). The reaction process seemed to involve

 $\begin{array}{c} Ph_{3}P = CPh_{2} + PhN = C = NPh \longrightarrow \\ 1 & Ph\overline{N} - C = NPh \\ 5 & 5 \end{array}$ $Ph_3P=NPh + Ph_2C=C=NPh$ 2 3 ↓ H₂O Ph₂CHCONHPh 4

(1) G. Luscher, Diss. Eidg. Techn. Hochschule, Zurich (1922); A. W. John-"Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 132. son,

(2) H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 635 (1919).

(3) S. Trippet and D. M. Walker, J. Chem. Soc., 3874 (1959).

the intermediate 5 according to Wittig-type reaction. Bestmann and Seng⁴ reported a similar reaction between phenylmethylenetriphenylphosphorane and benzalaniline to afford stilbene and N-phenyliminotriphenylphosphorane.

In the reaction of the ylides 6, containing a hydrogen atom on the ylide carbon, diphenylcarbodiimide reacted with two molecules of the ylide 6, and Nphenyliminotriphenylphosphorane (7) and the ylides 8 were obtained.

 $Ph_{3}P = CHR + PhN = C = NPh \longrightarrow$ 6a, R = COOEt $\mathbf{b}, \mathbf{R} = \mathbf{P}\mathbf{h}$ RCH=C=NPh + Ph₃P=NPh 9 $\downarrow^{\rm Ph_{\$}P=CHR}$ $Ph_3 \tilde{P}$ —CHR Ph₃P==CR RCH-C=NPh -C=NPh

In the nmr spectrum of the ylide 8a, the chemical shifts of the two ethyl protons were separated at δ 0.58 (t, CH₃)-3.85 (q, CH₂) and δ 1.02 (t, CH₃)-4.12 (q, CH_2) ; the methylene group adjacent to the imino group was seen as a singlet at δ 4.11. The infrared spectrum of the ylide 8a in a Nujol mull indicated the peak at 1570 cm⁻¹ (imino group). Similar absorption was observed at 1530 cm^{-1} for the ylide **8b**. In these reactions, the ketenimines 9, formed in the initial step, react immediately with additional ylide 6 to give 8 via the betaine 10 by a prototropic shift.

Methylenetriphenylphosphorane (11) reacted with an equimolar quantity of diphenylcarbodiimide in dimethyl sulfoxide; N,N'-diphenylacetamidine (12) and triphenylphosphine oxide were obtained by treatment with water. The ylide 13 was not isolated; only the acetamidine 12, presumably formed by hydrolysis of the ylide 13, was obtained as a major product.

$$\begin{array}{c} Ph_{3}P = CH_{2} + PhN = C = NPh \longrightarrow \begin{array}{c} Ph_{3}\dot{P} - CH_{2} \\ Ph\overline{N} - C = NPh \end{array} \longrightarrow \begin{array}{c} Ph_{3}\dot{P} - CH_{2} \\ Ph\overline{N} - C = NPh \end{array} \longrightarrow \begin{array}{c} Ph_{3}P = CH \\ Ph_{3}P = CH \\ PhNH - C = NPh \end{array} \xrightarrow{H_{2}O} \begin{array}{c} NPh \\ H_{2}O \\ CH_{3} - C - NHPh \end{array} + Ph_{3}P = O \end{array}$$

No reaction was observed between dicylohexylcarbodiimide and the ylides 2 and 6. This may be due to the lower reactivity of the carbodiimide.

Experimental Section

Preparation of the Carbodiimides.--A mixture of 15.7 g of phenyl isocyanate and 1.73 g of triphenylphosphine was refluxed for 10 hr and distilled to give 8.9 g (70%) of diphenylcarbodi-imide, bp 122-127° (1 mm). The physical constants and the infrared spectrum were identical with the reported data.⁵

Dicyclohexylcarbodiimide was purchased and distilled, bp 135-138° (1 mm).

⁽⁴⁾ H. J. Bestmann and F. Seng, Angew. Chem., 75, 475 (1963); Tetrahedron, 21, 1373 (1965)

⁽⁵⁾ F. Kurzer and K. Douraghizadeh, Chem. Rev., 67, 107 (1962).

Notes

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 (Al₂O₃, benzene) of the solid gave $6.8 ext{ g}$ (94%) of diphenylacetanilide (4) and 0.2 $ext{ g}$ 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 Nphenyliminotriphenylphosphorane (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-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 C39H32NP: 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 (CaSO₄), concentrated, and chromatographed (Al₂O₃, 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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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_{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 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_8 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 transcoplanar stereoelectronic requirement for sulfur-assisted ionization is already satisfied in this rigid system.⁷

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