identical to that prepared (60% yield) from authentic ethyl *n*-hexyl sulfide).

Anal. Calcd. for C₈H₁₈O₂S: C, 53.89; H, 10.18; S, 17.90. Found: C, 53.76; H, 10.30; S, 18.23.

Divinyl Sulfide.—A mixture containing β -hydroxyethyl vinyl sulfide¹⁰ (104 g., 1.0 mole) and an equal weight of potassium hydroxide was heated carefully to 165°. The product distilled slowly, and heating was discontinued when the reaction mixture began to foam considerably. The product was trapped in a Dry Ice-cooled receiver containing sodium sulfate. Distillation of the product gave 28.2 g. (33.6%, b.p. 82–86°) of divinyl sulfide.¹¹

Reaction of t-Dodecyl Vinyl Sulfide with n-Butyllithium. The reaction of butyllithium¹² (7.49 g., 0.117 mole) in heptane and t-dodecylvinyl sulfide¹⁰ (5.9 g., b.p. 86°/1.0 mm., n^{25} D 1.4795) in anhydrous ether was carried out by a procedure essentially identical to those described above. The dried ether extract was distilled and the following fractions were collected: 1) 2.8 g., b.p. 65–72°/8.5 mm., n^{26} D 1.4344–1.4352; 2) 0.3 g., b.p. 55–65°/1.3 mm., n^{25} D 1.4475; 3) 0.4 g., b.p. 50–61°/0.25 mm., n^{26} D 1.4771; 4) 1.6 g., undistilled residue.

Fraction 1 contained no sulfur, rapidly decolorized a solution of bromine and carbon tetrachloride, and the infrared spectrum showed absorption at 1640 cm.⁻¹ and 890 cm.⁻¹ consistent with a disubstituted terminal olefin structure.

Anal. Caled. for C_nH_{2n} : C, 85.60; H, 14.40. Found: C, 83.90; H, 14.12; S, 0.00.

It was concluded that this material was principally 2methyl-1-undecene (64.2% yield; reported,¹³ b.p. 204°, n^{25} p 1.4339).

Fraction 3 was recovered t-dodecyl vinyl sulfide (b.p. $86^{\circ}/1.0 \text{ mm.}$, n^{25} D 1.4795) as evidenced by physical constants and identity of infrared spectra. The infrared spectrum of fraction 2 showed it to be a mixture of 2-methyl-1-undecene and t-dodecyl vinyl sulfide.

The aqueous layer, obtained from the original reaction mixture subsequent to the addition of water and ether extraction, was acidified (HCl), and extracted with ether. The ether layer was dried (Na_2SO_4) and the ether was removed. A vile odor, but no residue, was observed.

Reaction of Phenyl β -Styryl Sulfide with *n*-Butyllithium.— A solution of phenyl β -styryl sulfide¹⁴ (21.0 g., 0.1 mole, b.p. 141°/0.5 mm., n^{25} D 1.6678) in anhydrous ether (100 ml.) was added dropwise to a solution of *n*-butyllithium (0.5 mole) in anhydrous ether (200 ml.), at 0° under an atmosphere of nitrogen. The reaction mixture was stirred for 4 hr. at 0°, water was added, and the resulting mixture was extracted with ether.

The dried ether extract was distilled and a number of fractions were combined into two principal products: (A) A sulfur-free olefin, 6.14 g., n^{26} p.1.5251, b.p. near 72°/1 mm., and (B) impure phenyl β -styrryl sulfide, > 9.31 g., b.p. near 114°/1 mm., n^{26} p.1.6000–1.6450. The recovered phenyl β -styryl sulfide amounted to about 54%. The olefin was identified, as described below, as 1-phenylhexene-1 (39% yield).

Ether was added to the water layer, obtained from the original reaction mixture, and the resulting mixture was made acidic by the addition of hydrochloric acid. Distillation of the dried, water-washed, ether extract gave phenyl mercaptan (4.3 g., 40% yield, b.p. 164° , n^{23} p 1.5837). Identification of 1-Phenylhexene-1.—The oil, described

Identification of 1-Phenylhexene-1.—The oil, described above, was redistilled (b.p. $74^{\circ}/2 \text{ mm.}$, $n^{23.5} \text{p}$ 1.5243).

Anal. Caled. for $C_{12}H_{16}:\ C,\ 89.94;\ H,\ 10.06.$ Found: C, 89.22; H, 10.12; S, 0.00.

Ozonolysis of this olefin gave benzaldehyde and *n*-valeraldehyde, identified by comparison of the corresponding 2,4dinitrophenylhydrazones with those prepared from authentic samples.

1-Phenylhexene-1, prepared from *n*-butyllithium and ω bromostyrene has n^{25} D 1.5377.¹⁵ A sample of 1-phenylhexene-1, prepared (24% over-all yield) from benzaldehyde and 1-bromopentane, through the intermediate Grignard reagent with subsequent dehydration of the derived alcohol with phosphoric acid, boiled at 97-100°/8 mm. and had n^{25} D 1.5528. The infrared and ultraviolet spectra of this sample of 1-phenylhexene-1 were identical to the corresponding spectra derived from the olefin described in the preceding section, and were consistent with the *trans* substituted ethylene structure.

(15) C. S. Marvel, F. D. Hager, and D. D. Coffman, J. Am. Chem. Soc., 49, 2327 (1927).

Reactions of Triisopropyl Phosphite with Diphenyldiazomethane

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Staudinger and his co-workers¹ prepared phosphazines from tertiary phosphines and substituted diazomethanes. The phosphazines reported were basic, moderately stable, highly reactive com-

$$R_3P + R'_2C = N_2 \longrightarrow R_3P = N - N = CR_2'$$

pounds; upon heating they decomposed to give nitrogen and other products. An ylide was identified among the decomposition products from fluorenone triphenylphosphazine.^{1b}

$$Ph_{3}P=N-N=C \xrightarrow{C_{6}H_{4}} Ph_{3}P=C \xrightarrow{C_{6}H_{4}} + N_{2}$$

Recently Bestmann and Buckschewski² treated triphenylphosphine with α -ketodiazomethanes. The resulting α -oxotriphenylphosphazines in 80% ethanol were hydrolyzed to the corresponding α oxoaldehyde al-hydrazones and converted by methyl iodide to diazoketones and methyltriphenylphosphonium iodide.

Diazomethane and other diazoalkanes also have been treated with phosphorus trihalides at low temperatures.³ Phosphazines, however, were not isolated and, if formed, were unstable; nitrogen was evolved and moisture-sensitive products were obtained. Furthermore, no phosphazine was isolated when benzene phosphorus tetrachloride

⁽¹¹⁾ W. E. Lawson and E. M. Reid, J. Am. Chem. Soc., 47, 2821 (1925).

⁽¹²⁾ Obtained from Lithium Corp. of America.

⁽¹³⁾ B. T. Brooks and J. Humphrey, J. Am. Chem. Soc., 40, 839 (1918).

⁽¹⁴⁾ H. R. Davis, Ph.D. thesis, University of Minnesota, p. 42 (1949).

⁽¹⁾⁽a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 2, 619 (1919).
(b) H. Staudinger and W. Braunholtz, *ibid.*, 4, 897 (1921).
(c) H. Staudinger and G. Lüscher, *ibid.*, 5, 75 (1922).

⁽²⁾ H. Bestmann, H. Buckschewski, and H. Leube, Ber., 92, 1845 (1959).

⁽³⁾ A. Ya. Yakubovich and V. A. Ginsburg, Zh. Obshch. Khim., 22, 1534 (1952).

reacted with diazomethane at -40° .⁴ Trialkyl phosphites also react with diazomethane⁵ to yield distillable liquid trialkylphosphorazines⁶ in less than 60% yield.

$$RO_3)P + CH_2N_2 \longrightarrow (RO)_3P = N - N = CH_2$$

These compounds, whose thermal stability is indicated by their distillation at low pressure, react vigorously with carbon disulfide to yield trialkyl phosphorothionates—a reaction analogous to that mentioned by Staudinger and Meyer^{1a} and examined in more detail by Braunholtz.⁷

We found that triisopropyl phosphite reacts with diphenyldiazomethane to give an essentially quantitative yield of benzophenone triisopropylphosphorazine, a white crystalline solid identified by elemental analysis and its molecular weight. The reaction was carried out by adding a petroleum ether solution of diphenyldiazomethane

$$[(CH_3)_2 - CHO]_3 - P + Ph_2CN_2 \longrightarrow \\ [(CH_3)_2 - CHO]_3 \stackrel{+}{P} - \bar{N} - N = CPh_2$$

to an excess of triisopropyl phosphite in petroleum ether at room temperature. The relatively stable phosphorazine can be handled under ordinary conditions. After approximately one week, however, the material turned pink, an odor of triisopropyl phosphate developed, and diphenylketazine was isolated and identified by comparison with the authentic compound. These observations suggest either hydrolysis to benzophenone hydrazone and disproportionation of the latter or disproportiona-

$$(\text{RO})_{\$}P - N - N = CPh_{2} \xrightarrow{H_{2}O} \\ (\text{RO})_{\$}PO + 1/2Ph_{2}C = N - N = CPh_{2} + 1/2H_{2}NNH_{2}$$

tion of the phosphorazine. A third possible source $2(RO)_P = N - N = CPH_0 \longrightarrow$

$$(RO)_{3}P = N - N = P(OR)_{3} + Ph_{2}C = N - N = CPh_{2}$$

of diphenylketazine, suggested by Staudinger and Meyer^{1a} to arise by reaction of the carbene intermediate with a diazalkane as a dissociation product, is unlikely under mild conditions prevailing in our case. The evidence for dissociation and carbene

(4) L. M. Yagupolskii and P. A. Yufa, Zh. Obshch. Khim., 28, 2853 (1958).

(5) M. I. Kabachnik and V. A. Gilyarov, Dokl. Akad. Nauk S.S. S.R., 106, 473 (1956).

(6) Kabachnik and Gilyarov named their compounds phosphatoazines. Our nomenclature is preferable to that proposed by the Russians because, aside from being more euphonious, it is consistent with that tentatively approved by the general nomenclature committee of the Organic Division and of the NRC Subcommittee on Organic Nomenclature (see Chem. & Eng. News, **30**, 4515 (1952), and "Handbook for Chemical Society Authors 1960," Spec. Publ. No. 14, The Chemical Society, London). Thus the adduct of diazoalkanes with phosphines are phosphazines (which Staudinger first used and seems to be generally accepted); with phosphinites (R2POR') phosphinazines; with phosphonites RP(OR')2, phophonazines; and with phosphites $(RO)_{3}P$, phosphorazines. The azines can be related in a simple and unambiguous way to the parent structures: phosphinic, phosphonic, and phosphoric acids. Alternatively, all these azines can be related to phosphazines—e.g., dialkylalkoxyphosphazines, alkyldialkoxyphosphazines, and trialkoxyphosphazines. When an assortment of substituents are present on the phosphorus atom, there is considerable merit in a nomenclature based on phosphine

(7) W. Braunholtz, J. Chem. Soc., 122, 300 (1922).

formation, however, is somewhat questionable. Thermolysis $(170-180^{\circ})$ of the triisopropylphosphorazine (I) failed to yield nitrogen as reported by Staudinger^{1a} for the analogous compounds from tertiary phosphines; instead, propylene and diisopropyl *N*-diphenylmethylenephosphorohydrazidate (III) were obtained quantitatively. The latter was identified by elemental analysis and molecular weight. The decomposition very likely proceeds through a transitory cyclic intermediate (II).



The belief that the product is a phosphorohydrazidate was further confirmed by hydrolyzing the compound with concentrated hydrochloric acid; benzophenone and hydrazine were isolated in 90%yield.

Diisopropyl N-diphenylmethylenephosphorhydrazidate was obtained (75% yield) directly from an excess phosphite and diphenyldiazomethane by decomposing the phosphorazine at $178 \pm 2^{\circ}$ without prior separation. Small amounts of triisopropyl phosphate and diphenylketazine were isolated also.

A low yield of nitrogen gas seems typical of phosphorus azine reactions. Even under favorable conditions Staudinger and Meyer^{1a} never found nitrogen evolution from thermal decomposition of phosphazines greater than 90% of that available and in most cases it was about 50%. When various reactants are present nitrogen is not evolved,⁷ but the nitrogenous products were not identified.

Experimental

Preparation of Benzophenone Triisopropylphosphorazine. —A purple solution of freshly prepared diphenyldiazomethane⁸ (13.0 g., 0.07 mole) in 25 ml. of petroleum ether was added in 15 min. to a stirred colorless solution of triisopropyl phosphite⁹ (31.2 g., 0.15 mole) in 10 ml. of anhydrous low boiling petroleum ether at 25°. The reaction temperature rose to 41° over a 25-min. period, but the purple color persisted. After 16 hr. at ambient temperatures the homogeneous reaction mixture became a clear light yellow. The solvent was distilled at 20 mm. (pot temperatures 25–30°) and the unchanged phosphite (14.6 g., n^{20} D 1.4101) recovered at 0.3 mm. (pot temperature < 50°). When the yellow oily still residue (27.2 g.) was cooled, it solidified to a crystalline

⁽⁸⁾ Diphenyldiazomethane was prepared according to Org. Syntheses, Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 351. The reaction product, a purple somewhat viscous oil, was used directly.

⁽⁹⁾ Triisopropyl phosphite (Virginia-Carolina Chem. Corp.) was redistilled and the fraction boiling at $62-63.5^{\circ}$ (12 mm), n^{∞} D 1.4113 was used in these experiments.

Anal. Calcd. for $C_{22}H_{31}N_2O_3P$: C, 65.65; H, 7.76; N, 6.96; P, 7.70. Found: C, 65.84; H, 7.67; N, 6.79; P, 7.56. Mol. wt. (determined cryoscopically in benzene): Calcd.: 402. Found: 387.

Reaction of Diphenyldiazomethane with Triisopropyl Phosphite.—Triisopropyl phosphite (52 g., 0.25 mole) was added rapidly at ambient temperature to diphenyldiazomethane (13.0 g., 0.07 mole). After 45 min., the purple reaction mixture turned a clear yellow, and the reaction temperature rose to 37°. At the end of 16 hr. at ambient temperatures no low-boiling condensate was found in a Dry-Ice trap connected to the system.

The reaction mixture was heated slowly; at 150-170° gas was evolved and a low-boiling liquid condensed in the cold trap. After refluxing the reaction mixture for 20 hr. at 178 \pm 3°, the cold trap contained 3.0 g. (0.072 mole) of propylene identified by boiling point and infrared spectrum. The main reaction mixture (60.6 g.) was distilled in vacuo to give: (a) 33.6 g. (0.16 mole) of triisopropyl phosphite, b.p. 67-67.5° (14.9 mm.), n^{20} D 1.4104; (b) 2.1 g. of a clear colorless liquid, b.p. 40-68° (2.4 mm.), n^{20} D 1.4082 (infrared indicated the presence of diisopropyl hydrogen phosphonate^{10a} and triisopropyl phosphate^{10b}; (c) 1.2 g. of triisopropyl phosphate, b.p. 68° (2.4 mm.), n^{20} D 1.4068; and (d) 23 g. of a turbid residual oil.

The residual oil solidified on cooling; it was triturated with cold hexane and filtered. The faintly yellow crystalline filter cake (17.4 g., m.p. 91.5–95°), after recrystallizing several times from hexane, melted at 96.5–98°.

Anal. Calcd. for $C_{19}H_{28}N_2O_3P$: C, 63.32; H, 6.99; N, 7.77; P, 8.60. Found: C, 63.14; H, 6.60; N, 7.92; P, 8.52. Mol. wt. by cryoscopy in benzene: Calcd. 360. Found 360.

The hexane filtrate was concentrated; the acidic yellow mushy solid (5.3 g.) was recrystallized from hot absolute alcohol to give 2.1 g. of diphenylketazine, m.p. 160–164°. Admixture with the authentic azine¹¹ gave no depression in melting point. The alcohol soluble material was not identified.

Thermal Decomposition of Benzophenone Triisopropylphosphorazine.—A sample (1.0 g., 0.0025 mole) of the azine was heated at 181° for 40 min. Propylene (52.8 ml. at STP, 0.0023 mole) was collected in a gas buret and identified by I.R. The light yellow residual oil (0.89 g.) solidified on cooling, m.p. 91.5–95°. The m.p. of mixture with authentic diisopropyl N-diphenylmethylenephosphorohydrazidate was not depressed.

Hydrolysis of Diisopropyl N-Diphenylmethylenephosphorohydrazidate.—The hydrazidate (5.0 g., 0.014 mole) was refluxed 24 hr. with 50 ml. of concentrated hydrochloric acid. Excess aqueous 20% sodium hydroxide was added and the immiscible oil extracted with ether. Distillation of the combined dried ether extracts left 2.3 g. (0.013 mole) of benzophenone, identified by m.p. and mixture m.p. The basic aqueous layer was acidified slightly and excess salicylaldehyde was added. The reaction mixture was shaken and the faint yellow solid present filtered, washed with low boiling petroleum ether, and air-dried to give 3.0 g. of

(10) (a) Reported b.p. 79° (14 mm). H. McCombie, B. C. Saunders, and G. J. Stacey, J. Chem. Soc., 380 (1945). (b) Reported b.p. 83.5° (5 mm.), n²⁰D 1.40573, A. I. Vogel and D. M. Cowan, *ibid.*, 16 (1943). material, m.p. 224.5-226°. A mixture m.p. with authentic salicylaldazine showed no depression.

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Aconite Alkaloids. The Structure of Hetisine

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Data presented below confirm certain features of structure I,^{1,2} but conflict with others, thus leading us to withdraw I as the tentative formulation for hetisine.



The presence of a methyl group on a fully substituted carbon atom is confirmed by NMR, the methyl group appearing as a sharp singlet at 9.02τ in hetisine, 9.02τ in dihydrohetisine,^{3,4} and 9.06τ in hetisine diacetate.² Similarly, the presence of the exocyclic methylene group is demonstrated by peaks which occur at 5.16 τ and 5.36 τ (vinyl hydrogen) in the spectrum of hetisine and do not occur in the spectrum of dihydrohetisine. However, the spectrum of dihydrohetisine does contain a new peak (apparently a doublet, partially obscured by the original methyl) at $\tau \approx 9.00$ attributable to a methyl group substituted on a carbon bearing a hydrogen.

The NMR spectrum of Jacobs' des-N-methylhetisine⁴ has singlets at 9.06 τ and 8.80 τ and no peaks in the range 5.0 τ to 5.4 τ , which is consistent with the presence of the original methyl plus a new methyl group of the type II, presumably arising from the exocyclic methylene of hetisine by *alkyl* migration.^{1,2} The N-methyl group appears as a singlet at 7.59 τ . Absorption at 4.37 τ (s) and 4.84 τ (d., $J \approx 5$ c.p.s.) suggests the presence of a new double bond of type III.

The spectrum of hetisine diacetate has peaks at 4.82τ , 4.98τ , 5.1τ , and 5.24τ corresponding in area to four protons. This indicates the presence, in addition to the exocyclic methylene group, of two protons on carbon atoms bearing acetoxyl groups, a feature *not* in accord with structure I.

(4) W. A. Jacobs and C. F. Huebner, *ibid.*, **170**, 189 (1947).

⁽¹¹⁾ Diphenylketazine was prepared from benzophenone and diphenylmethyl hydrazone, m.p. 164.5-165.5°, reported m.p. 164°. H. Szmant and C. McGinnis, J. Am. Chem. Soc., 72, 2890 (1950).

⁽¹⁾ A. J. Solo and S. W. Pelletier, J. Am. Chem. Soc., 81, 4439 (1959).

⁽²⁾ S. W. Pelletior, Tetrahedron, 14, 98 (1961).

⁽³⁾ W. A. Jacobs and L. C. Craig, J. Biol. Chem., 143, 605 (1942).