with water to complete precipitation. The yellow precipitate was filtered off and recrystallized from benzene. It proved to be the starting material (melting point and mixture melting point).

Phosphonic Acids and Esters. XIII. Nylen and Arbuzov Reactions with Propargyl Bromide[1]

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The treatment of propargyl bromide (**1**) with sodium diethylphosphonate in tetrahydrofuran has been reported to give a mixture of diethyl 1-propynylphosphonate (**2a**) and diethyl propargylphosphonate (**3a**)[3]; infrared studies showed **2a** to be the dominant isomer

$$\underset{\textbf{2}}{CH_3C{\equiv}CP(O)(OR)_2} \qquad \underset{\textbf{3}}{HC{\equiv}CCH_2P(O)(OR)_2}$$

$$\begin{aligned}\textbf{a},\ R &= C_2H_5\\ \textbf{b},\ R &= CH_3\end{aligned}$$

in the mixture. This Nylen reaction was repeated using sodium dimethylphosphonate in order to prepare the phosphonates **2b** and **3b** for proton magnetic resonance (p.m.r.) studies. In our hands, the only isomer isolated was dimethyl 1-propynylphosphonate (**2b**), identified by its p.m.r. spectrum ($C\mathit{H}_3$–C, doublet, τ = 7.96 p.p.m., $^4J_{PH}$ = 4.6 c.p.s.; $C\mathit{H}_3$–O, doublet, τ = 6.35 p.p.m., J_{PH} = 11 c.p.s.). The infrared characteristics of **2b** were consistent with those reported for **2a**.[3] In addition to the appropriate phosphorus–oxygen stretching frequencies, a strong band was observed at 2217 cm.$^{-1}$ (RC≡CR stretch). A weak band characteristic of terminal acetylenes (–C≡C– stretch), possibly owing to the presence of **3b**, was observed at 2092 cm.$^{-1}$, although p.m.r. analysis indicated the product to contain significantly less than 1% of **3b**. Identical results were obtained with sodium diethylphosphonate in a repetition of the reported[3] reaction. Only **2a** was isolated with less than 1% contamination by **3a** although a weak band was observed at 2071 cm.$^{-1}$, possibly indicative of the presence of **3a**. In neither reaction product was the ≡C–H stretching absorption (*ca.* 3300 cm.$^{-1}$) expected for **3a** or **3b** observed, although Guthrie and coworkers[3] reported a weak band at 3290 cm.$^{-1}$ for their product.[4]

As an alternative route to the propargylphosphonates, Arbuzov reactions between **1** and triethyl and trimethyl phosphites were carried out. Triethyl phosphite and **1** reacted exothermically at 90° and, again, **2a** was the only product isolated (15%).[6] Jensen and co-workers had previously reported a 5% yield of a material identified as **2a** from the same reaction.[7] However, the corresponding reaction of **1** with trimethyl phosphite under identical conditions led to completely unexpected results. A mixture of phosphonates was formed from which **3b** could be isolated in 5% yield. The structure of this product was established unambiguously by its p.m.r. spectrum (H–C≡, doublet of triplets, τ = 7.82 p.p.m., $^4J_{PH}$ = 6.7 c.p.s., $^4J_{HH}$ = 2.8 c.p.s.; –$C\mathit{H}_2$–, doublet of doublets, τ = 7.30 p.p.m., $^2J_{PH}$ = 21.9 c.p.s.; $C\mathit{H}_3$–O, doublet, τ = 6.27 p.p.m., J_{PH} = 11 c.p.s.). The infrared spectrum of **3b** showed a strong ≡C–H stretch at 3322 cm.$^{-1}$ and a weak terminal acetylenic (–C≡C–) stretch at 2123 cm.$^{-1}$. This material was contaminated with less than 5% of a mixture of **2b** and dimethyl allenylphosphonate as determined by p.m.r. spectroscopy. The infrared spectrum is consistent with this assignment showing weak bands at 2212 and 1976 cm.$^{-1}$ attributable to a disubstituted acetylene and an allene, respectively. The reasons for the pronounced differences in the products obtained from the two Arbuzov reactions are not apparent.

Long-range P^{31}–H^1 couplings, $^4J_{PH}$, were observed for both the propynyl (**2a** and **2b**, 4.6 c.p.s.) and propargyl (**3b**, 6.7 c.p.s.) phosphonates; analogous, but smaller, four-bond H^1–H^1 couplings (2–3 c.p.s.) are normally observed in acetylenic systems.[8] In **3b**, a normal H^1–H^1 coupling (2.8 c.p.s.), comparable in magnitude with that observed in **1** (2.6 c.p.s.), is seen. It should be noted that the magnitude of the long-range coupling constant ($^4J_{PH}$) is greater when the phosphorus atom is bonded to the tetrahedral carbon atom than when it is bonded to the sp hybridized atom. A similar trend has been observed in other H—C—C≡C—P and H—C≡C—C—P systems.[9,10] The magnitude of the geminal P^{31}–H^1 coupling constant (21.9 c.p.s., presumably negative) observed in **3b** is the same as that found for a large number of allyl- and benzylphosphonates[9]; the presence of the second π system in **3b** apparently does not cause a further decrease in the magnitude of the geminal coupling constant, contrary to the results observed for geminal H^1–H^1 coupling constants.[11] This behavior is consistent with that observed for geminal P^{31}–H^1 coupling constants in a number of other organophosphorus systems.[9]

Long-range (four-, five-, six-, and eight-bond) P^{31}–H^1 couplings have been observed previously in $P—(C{\equiv}C)_n—R$ (R = H or CH_3; n = 1–3) systems.[12] Those couplings most closely comparable with the ones observed in the present study were seen in $(C_6H_5)_2P(O)C{\equiv}CCH_3$ and the corresponding sulfide for which $^4J_{PH}$ = 3.8 and 4 c.p.s., respectively.[12]

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[1] Part XII: C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, in press.

[2] National Science Foundation Cooperative Graduate Fellow, 1961–1964.

[3] C. M. Welch, E. J. Gonzales, and J. D. Guthrie, *J. Org. Chem.*, **26**, 3270 (1961).

[4] These workers also cited the formation of a deep wine red color upon treatment of their product with an alkaline solution of sodium 3,5-dinitrobenzoate[5] as being diagnostic for the presence of **3**. No corresponding color reaction was observed with the products obtained in this study or with the model active hydrogen compound, ethyl propiolate.

[5] B. C. Saunders and B. P. Stark, *Tetrahedron*, **4**, 197 (1958).

[6] The p.m.r. spectra of all distillation fractions from this reaction and the two Nylen reactions were examined carefully, and in no case was any evidence indicative of the formation of **3a** or **3b** obtained. Spectra were determined at amplitudes such that a minimum of 1% of **3a** or **3b** could have been detected in the fractions.

[7] H. I. Jacobson, M. J. Griffin, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2608 (1957).

[8] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[9] M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965.

[10] Possible explanations for this behavior will be discussed in a more complete study of long-range phosphorus–proton coupling constants.

[11] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[12] C. Charrier, M-P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. rend.*, **258**, 1536 (1964).

Experimental Section[13]

Reactions of Sodium Dialkylphosphonates with Propargyl Bromide (1).—A solution of the sodium dialkylphosphonate, prepared from sodium hydride and the dialkylphosphonate by an established procedure,[14] was added dropwise to a solution of 1 (1 equiv.) in tetrahydrofuran in the manner reported by Guthrie and co-workers.[3] The dark reaction mixtures were worked up as reported and distilled to give a forefraction containing trialkyl phosphate and dialkyl alkylphosphonate and a higher boiling fraction containing the desired dialkyl 1-propynylphosphonate (**2a** or **2b**). A viscous dark undistillable oil remained in the distillation flask.

Dimethyl 1-propynylphosphonate (**2b**) was obtained as a clear colorless liquid distilling at 100–101° (2.0–2.1 mm.): infrared spectrum (CCl_4 solution): 2985 (w), 2950 (m), 2857 (m), 2217 (s), 2092 (w), 1629 (w), 1456 (m), 1285 (s) (sh), 1272 (s), 1186 (m), 1095 (s) (br), and 914 (w) cm.$^{-1}$.

Diethyl 1-propynylphosphonate (**2a**) was obtained as a clear colorless liquid distilling at 101–106° (0.9 mm.), lit.[3] b.p. 105.5–110.0° (1 mm.): infrared spectrum (film): 2980 (m), 2926 (m), 2894 (m), 2194 (s), 2071 (w), 1618 (w), 1478 (w), 1443 (m), 1390 (w), 1260 (vs), 1160 (m), 1090 (m) (sh), 1025 (s) (br), 956 (s), 790 (s), 755 (s), and 610 s cm.$^{-1}$; p.m.r. spectrum: CH_3–C–O, triplet, τ = 8.70 p.p.m.; $CH_3C{\equiv}C$–, doublet, τ = 7.98 p.p.m., $^{4}J_{PH}$ = 4.6 c.p.s.; and –CH_2–O, quintet, τ = 6.00 p.p.m.

Reactions of Trialkyl Phosphites with Propargyl Bromide (1).—The reactions were carried out by heating a mixture of 1 and the phosphite to 90° in exactly the same fashion used by Jensen and co-workers.[7] After the initial vigorous reaction had subsided, the solution was refluxed for a total of 2 hr. Distillation of the dark solutions gave a forefraction of trialkyl phosphite and a higher boiling fraction containing the desired phosphonate.

Dimethyl propargylphosphonate (**3b**) was obtained as a clear, colorless liquid distilling at 58° (0.2 mm.): infrared spectrum (CCl_4 solution): 3322 (s), 3003 (w), 2950 (m), 2899 (w), 2849 (w), 2212 (w), 2123 (w), 1976 (w), 1942 (w), 1449 (m), 1397 (w), 1271 (s), 1224 (w) (sh), 1183 (m), 1062 (s), 1037 (s), 962 (w), 914 (w), and 855 (m) cm.$^{-1}$.

Diethyl 1-propynylphosphonate (**2a**) was obtained as a clear, colorless liquid distilling at 112° (2 mm.). Jensen and co-workers[7] reported b.p. 98–103° (2 mm.) for the product from this reaction. The infrared and p.m.r. spectra of this material were identical with those of the sample of **2a** prepared by the Nylen reaction.

A less volatile fraction, b.p. 152–165° (0.2 mm.), was also obtained from the reaction of triethyl phosphite and 1, but could not be identified: infrared spectrum (film): 2994 (s), 2933 (m), 2899 (m), 2212 (w), 1961 (w), 1631 (w), 1600 (w), 1479 (w), 1443 (m), 1395 (m), 1370 (w), 1255 (s), 1164 (m), 1098 (w) (sh), 1065–1014 (vs), 962 (s), and 786 (s) (br) cm.$^{-1}$; p.m.r. spectrum: triplet, τ = 8.70 p.p.m. (39.0H)[15]; multiplets, τ = 8.25–7.42 p.p.m. (4.3H); broad singlet and multiplet, τ = 6.80 and 6.55 p.p.m. (4.5H); quintet, τ = 5.98 p.p.m. (26.0H); multiplet, τ = 5.37 p.p.m. (1.0H); multiplet, τ = 4.85 p.p.m. (2.7H).

A similar unidentified fraction of b.p. 150–152° (0.2 mm.) was also isolated by Jensen and co-workers[7] from this Arbuzov reaction. In view of the pronounced infrared absorptions characteristic of diethyl phosphonate functions and the ratio of P–OCH_2-CH_3 to other protons observed in the p.m.r. spectrum, it is probable that this material represents a mixture of products arising from the thermal reaction of either **2a** or **2b** with triethyl phosphite. The ease of formation of phosphonates by the thermal reaction of trialkyl phosphites with acetylenes has been noted previously.[3,7,16]

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[13] Infrared spectra were determined on a Beckman IR-8 spectrophotometer calibrated with a polystyrene film. P.m.r. spectra were obtained on a Varian Associates Model A-60 spectrometer at 37° (probe temperature) on 5–10% solutions in carbon tetrachloride. Chemical shifts are reported on the τ scale from internal tetramethylsilane (τ = 10.00 p.p.m.); these values are the average of at least two spectral determinations and are accurate to at least ±0.015 p.p.m. The coupling constants were obtained from 50-c.p.s. sweep width spectra and are the average of at least three runs; the values are accurate to ±0.15 c.p.s. or better.

[14] R. G. Harvey, T. C. Myers, H. I. Jacobson, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2612 (1957).

[15] Relative integrated intensity.

[16] C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935 (1965).

Chemistry of Ylids. XII. Effect of Phosphorus Substituents on the Stereochemistry of the Wittig Reaction[1a]

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Commencing with some of the earliest work on the Wittig reaction between phosphonium ylids and carbonyl compounds, the stereochemistry of the product olefins has been of interest.[2] Most such reactions lead to dominance of the *trans* isomer in the reaction mixture, sometimes to the complete exclusion of the *cis* isomer.[3] The flexibility of the Wittig reaction would be vastly improved were there available a means of forcing the *cis* olefins to dominate. This means relying on kinetic control of the reaction.

Bergelson and Shemyakin[4] claimed that addition of a variety of substances, lithium halides, amines, polar solvents, etc., to a Wittig reaction medium led to dramatic increases to near 9.0 in the *cis/trans* ratio of the olefins produced. However, House, *et al.*,[5] recently have shed doubt on some of this work and found, at the most, *cis/trans* ratios of 1.0 using a variety of phosphonium ylids and additives.

Ketcham, *et al.*,[6] found that the *cis/trans* ratio of 0.11 for the 4-nitro-4′-methoxystilbenes (**1**) formed from the reaction of *p*-nitrobenzylidenetriphenylphosphorane (**2a**) with *p*-anisaldehyde (**3a**) could be raised to 0.92 by interchanging the ylid and aldehyde substituents, using *p*-methoxybenzylidenetriphenylphosphorane (**2b**) and *p*-nitrobenzaldehyde (**3b**). However, this still is not a very satisfactory yield of *cis* isomer. They concluded that a more reactive ylid would afford the maximum yield of *cis* isomer (approaching 50%) owing to diminished reversibility of the betaine-forming step (*i.e.*, smaller k_2). House and Rasmusson[7] reached similar conclusions.

In contrast to this somewhat too general conclusion, Bestmann and Kratzer,[8] Speziale and Bissing,[9] and Bissing[10] all found that trialkylphosphonium ylids afforded almost exclusively *trans* isomers while the analogous but less nucleophilic triphenylphosphonium ylids afforded larger but still very small *cis/trans* ratios of olefins. For example, carbethoxymethylene-*triphenyl*phosphorane (**4**) and benzaldehyde gave a

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[1] (a) Paper XI: *Chem. Ind.* (London), in press. For paper X, see A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964). (b) To whom inquiries should be addressed: University of Saskatchewan, Regina Campus, Regina, Saskatchewan, Canada. (c) We acknowledge the partial support of this research by the U. S. Public Health Service, Grant No. GM-10488-01. (d) Taken from the senior thesis of V. L. K. submitted in partial fulfillment of the requirements for the degree of B.S. in Chemistry, June 1965.

[2] G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954).

[3] For a review of data to 1963, see S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[4] L. D. Bergelson and M. M. Shemyakin, *Pure Appl. Chem.*, **9**, 271 (1964); *Bull. Acad. Sci. USSR*, 1053 (1963); *Tetrahedron*, **19**, 149 (1963).

[5] H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

[6] R. Ketcham, D. Jambotkar, and L. Martinelli, *ibid.*, **27**, 4666 (1962).

[7] H. O. House and G. H. Rasmusson, *ibid.*, **26**, 4278 (1961).

[8] H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **95**, 1894 (1962).

[9] A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963).

[10] D. E. Bissing, *J. Org. Chem.*, **30**, 1296 (1965).