Reactions of Phosphorus Compounds. VII. A General Chain-Extension Reaction

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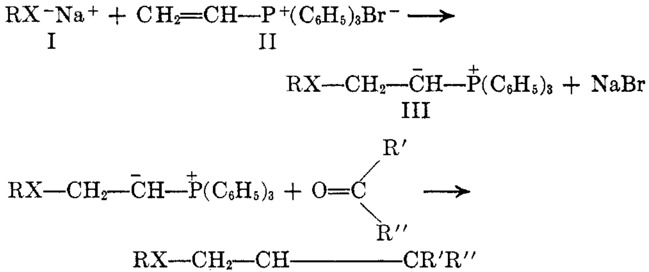
A general chain-lengthening process has been developed, using vinyltriphenylphosphonium bromide as a substrate in the reaction. A series of olefins has been synthesized and the nmr spectra of the geometrical isomers are discussed.

In previous publications,[1-3] we have shown the usefulness of vinyltriphenylphosphonium bromide (II) as a reagent for the synthesis of a variety of carbocyclic and heterocyclic ring systems. In the present work, we wish to demonstrate that salt II is also useful as a general chain-lengthening reagent, as shown in Scheme I.

SCHEME I



$$\underset{\text{I}}{\mathrm{RX^-Na^+}} + \underset{\text{II}}{\mathrm{CH_2{=}CH{-}P^+(C_6H_5)_3Br^-}} \longrightarrow \underset{\text{III}}{\mathrm{RX{-}CH_2{-}\bar{C}H{-}\overset{+}{P}(C_6H_5)_3}} + \mathrm{NaBr}$$

$$\mathrm{RX{-}CH_2{-}\bar{C}H{-}\overset{+}{P}(C_6H_5)_3} + \mathrm{O{=}C(R')(R'')} \longrightarrow \mathrm{RX{-}CH_2{-}\underset{\overset{|}{P_+(C_6H_5)_3}}{CH}{-}\underset{\overset{|}{O_-}}{CR'R''}} \longrightarrow \mathrm{RXCH_2{-}CH{=}CR'R''} + \mathrm{(C_6H_5)_3PO}$$

X = O, NH, N, S, C
R = aliphatic, aromatic, heterocyclic, *p*-tosyl
R′, R″ = aliphatic, aromatic, or hydrogen

The anion I was formed by reaction of the species RXH with sodium hydride or with sodium ethoxide. It is apparent that the nucleophilic addition of anion I to the vinyl salt II occurs prior to the Wittig reaction, since the bright red (or orange) ylide III is formed before the addition of the carbonyl compound to the reaction medium. The intermediate ylides III have not been isolated.

One further example of this reaction has been disclosed by Seyferth,[4] who employed phenyllithium, salt II, and acetone to give a 33% yield of 2-methyl-4-phenyl-2-butene; using methyllithium, salt II, and cyclohexanone, he obtained a 13% yield of propylidenecyclohexane.

A variety of species has been added to vinylphosphonium salts, by the present[5] and other groups,[6] in phosphonioethylation-type[6] reactions to give substituted ethyl phosphonium salts IV. One would

$$\mathrm{RXH} + \underset{\text{II}}{\mathrm{CH_2{=}CH{-}\overset{+}{P}(R')_3\bar{B}r}} \longrightarrow \underset{\text{IV}}{\mathrm{RXCH_2CH_2\overset{+}{P}(R')_3\bar{B}r}}$$

predict that each of the species RXH which were found to give phosphonioethylation reactions, as listed in our previous paper[5] and that of Keough and Grayson,[6] could be used with success in a chain-extension reaction of the type reported herein.

An indication of the scope of this reaction may be found by examining Table I, where the yields (not necessarily optimum) are shown to range from 14 to 68%.

The relative ratios of geometric isomers of some of the products are also shown in Table I. The effects of the reaction conditions on these relative ratios have not been studied; however, it is shown that in the reaction with ethanol and benzaldehyde the yield of *cis* isomer obtained is increased in the presence of dimethylformamide. This result is in agreement with the reported increase for the *cis* isomer in dimethylformamide solvent using nonstabilized ylides.[7]

The *cis/trans* ratio was not determined in three cases. In the reaction with diethylamine and propionaldehyde, the product showed only one major peak on the vapor phase chromatograph, and the infrared and nmr analyses did not indicate whether the product was *cis*, *trans*, or a mixture of the isomers. In the reaction of *p*-toluenesulfonamide with benzaldehyde, the *trans* isomer was isolated by column chromatography; the *cis* isomer was shown to be present but was not isolated. In the reaction of pyrrole and benzaldehyde, an analytically pure sample of the *trans*-N-cinnamylpyrrole was isolated, but the *cis* isomer was not isolated.

Small yields of triphenylphosphine have appeared in the reactions involving the *p*-toluenesulfonamides. The origin of this triphenylphosphine is unknown. Several cases of β elimination of triphenylphosphine from inner phosphonium salts are known[8]; a β elimination may be postulated in this case as shown below,

$$\underset{\text{III}}{\mathrm{RX{-}CH_2\bar{C}H{-}\overset{+}{P}(C_6H_5)_3}} \rightleftarrows \underset{\text{V}}{\mathrm{RX{-}\bar{C}HCH_2{-}\overset{+}{P}(C_6H_5)_3}} \longrightarrow \underset{\text{VI}}{\mathrm{RXCH{=}CH_2}} + \mathrm{(C_6H_5)_3P}$$

where the inner salt, V, is made more favorable by electron-withdrawing substituents RX; however, none of the olefin VI was found in the present work.

The geometrical isomers were characterized by their physical constants, their nmr spectra, and their absorption or lack of absorption in the infrared region of 925–1000 cm^{-1}, a region which is known to be characteristic for *trans* olefins.[9]

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[1] E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).

[2] E. E. Schweizer and K. K. Light, *ibid.*, **86**, 2963 (1964).

[3] E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **30**, 2082 (1965).

[4] D. Seyferth, J. Fogel, and J. Heeren, *J. Am. Chem. Soc.*, **86**, 307 (1964).

[5] E. E. Schweizer and R. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

[6] P. T. Keough and M. Grayson, *ibid.*, **29**, 631 (1964).

[7] L. D. Bergelson and M. Shemyakin, *Tetrahedron*, **19**, 149 (1963).

[8] A discussion of β elimination and references are given in C. E. Griffin and G. Witschard, *J. Org. Chem.*, **29**, 1001 (1964).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 45–48.

TABLE I

YIELDS OF CHAIN-EXTENDED PRODUCTS

RXH[a]	Carbonyl reagent	Solvent[b]	Time, days	Temp, °C	% yield of $RXCH_2$-$CH=CR'R''$	*cis*/*trans*
Diethylamine	Propionaldehyde	Diethylamine–DMF	0.75	*c*	17	*d*
Piperidine	Benzaldehyde	Piperidine–DMF	0.75	*e*	66	21/79
Piperidine	Cyclohexanone	Piperidine–DMF	1	*e*	60	None
Pyrrole	Benzaldehyde	Pyrrole	1	*e*	51	*d*
Pyrrole	Cyclohexanone	Pyrrole	*f*	*f*	59	None
Ethanol	Benzaldehyde	Ethanol	4	*e*	54	10/90
Ethanol	Benzaldehyde	DMF–ethanol	4	98	57	50/50
p-Toluenesulfonamide	Benzaldehyde	Xylene–DMF	2	*c*	43	*d*
N-Propyl-*p*-toluenesulfonamide	Benzaldehyde	Ether–DMF	0.75	*c*	65	100/0
p-Toluenesulfonanilide	Benzaldehyde	Ether–DMF	2	*c*	30	100/0
Thiophenol	Benzaldehyde	Thiophenol	4	90	68	0/100
Diethyl ethylmalonate	Cyclohexanone	DMF	8	90–100	14	None

[a] Sodium hydride or sodium ethoxide was employed to prepare the anion, RX^-, followed by addition of solvent, salt I, and carbonyl reagent (in order given). [b] Solvent ratios given in Experimental Section. [c] Reflux temperature. [d] Not determined. [e] Room temperature. [f] Room temperature for 2 days; then 70° for 3 days.

The nmr spectra for these compounds show patterns which are characteristic for the *cis*- and the *trans*-cinnamyl isomers. These patterns may be seen by examination of the spectra of *cis*- and *trans*-N-cinnamylpiperidine (Figures 1 and 2). The vinyl protons exhibit an ABX_2 system for both the *cis* and the *trans* isomers.

In the *cis* isomer, the α-proton (carbon α to the phenyl) appears as a pair of triplets ($J_{\alpha,\beta} = 12$ cps, $J_{\alpha,CH_2} = 1$ cps) centered at 6.50 ppm downfield from tetramethylsilane. The β-proton appears as an overlapping pair of triplets ($J_{\alpha,\beta} = 12$ cps, $J_{\beta,CH_2} = 6$ cps) centered at 5.80 ppm.

In the *trans* isomer the α-proton appears as a doublet ($J_{\alpha,\beta} = 16$ cps) centered at 6.48 ppm. The β-proton appears as a pair of triplets ($J_{\alpha,\beta} = 16$ cps, $J_{\beta,CH_2} = 5$ cps), which overlaps with the α-proton doublet, centered at 6.14 ppm.

It has been shown that the coupling constants for the *trans* isomers are greater than those for *cis* isomers[10,11]; thus, the values of $J = 12$ and 16 cps for *cis*- and *trans*-N-cinnamylpiperidine, respectively, give further validity to the stereochemical assignments made.

Experimental Section

The vinyltriphenylphosphonium bromide was prepared according to the reported[5] procedure.

Infrared spectra were obtained on a Perkin-Elmer Infracord 137 and nmr spectra were obtained on a Varian A-60 analytical nmr spectrometer, using tetramethylsilane as standard. The vapor phase chromatographic data were obtained using a column of 20% SE-30 on Gas-Pack W, 60–80 mesh on a Matronic instrument. All melting points were uncorrected and obtained on a Fischer-Johns melting point apparatus. Analyses were by Micro-Analysis, Inc., Wilmington, Del.

General Procedure for Liquids.—Sodium hydride (0.09 mole) was stirred with 100 ml of the protonic species (piperidine, diethylamine, etc.) under a nitrogen atmosphere at reflux temperature. After 14–18 hr the mixture was cooled to room temperature, and 0.09 mole of vinyltriphenylphosphonium bromide and 50 ml of dimethylformamide were added to the mixture and allowed to react for 3–5 min. Then a solution of 0.09 mole of the carbonyl compound dissolved in 50 ml of dimethylformamide was introduced dropwise through a pressure-equalizing funnel. The mixture was stirred at room temperature for an additional 18 hr, after which time water and ether were added, and several ether extractions of the water layer were followed by washing the ether with water and drying over anhydrous magnesium sulfate. The water solution was then extracted with chloroform and the dried chloroform extracts were evaporated. The resulting oil was taken up in ether–petroleum ether (bp 30–60°), and triphenylphosphine oxide (identified by infrared spectrum and mixture melting point with authentic sample) was recrystallized from this mixture. The dried ether extracts were concentrated and the residue was distilled *in vacuo* to give the olefin product. Ether was added to the distillation pot and additional triphenylphosphine oxide was obtained by recrystallization.

1-Diethylamino-2-pentene.—The general procedure as given was followed, using diethylamine as the protonic species and propionaldehyde as the carbonyl compound. The product, 1-diethylamino-2-pentene, bp 70–75° (20 mm), $n^{24}D$ 1.4336, was obtained in 17% yield, and a 33% yield of triphenylphosphine oxide was found. The product was purified by collecting from a gas chromatograph column (made up with SE-30, 20% weight on Gas-Pack W, 60–80 mesh) and then was short-path distilled before analysis.

Anal. Calcd for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92. Found: C, 76.84; H, 13.34; N, 9.47.

The nmr spectrum, neat, showed a triplet centered at 0.75 ppm, wt 9.1 (three methyl groups); an unresolved quartet ranging from 1.55 to 2.0 ppm, wt 2.0 ($CH_3CH_2CH=$); a quartet centered at 2.2 ppm, wt 4.1 ($CH_3CH_2NCH_2$-CH_3); a doublet centered at 2.8 ppm, wt 2.0 ($NCH_2CH=$); and a multiplet ranging from 5.08 to 5.30 ppm, wt 2.0 (vinyl protons).

The infrared spectrum showed a weak C=C stretch at 1650 cm^{-1}, only weak bands in the 960–990-cm^{-1} *trans* absorption region, and was otherwise in accordance with the structure assigned.

N-Cinnamylpiperidine.—The general procedure described above was followed, using piperidine as the protonic species and benzaldehyde as the carbonyl compound. The crude product, a mixture of *cis*- and *trans*-N-cinnamylpiperidine, bp 98–114° (0.3 mm), $n^{24}D$ 1.5540 [lit.[12] bp 130–132° (2 mm), $n^{18}D$ 1.5572], was obtained in 66% yield, and a 65% yield of triphenylphosphine oxide was obtained. The ratio of the *cis* (first eluted) to the *trans* isomer was 71/29, as indicated by the area of the vpc

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[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, pp 84–87.

[11] (a) D. Seyferth and L. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963); (b) P. Laszlo and P. Schleyer, *Bull. Soc. Chim. France*, 87 (1964).

[12] S. Foldeik, *et al.*, *Acta Univ. Szeged. Acta Phys. Chem.*, **6**, No. 1–4, 105 (1960); *Chem. Abstr.*, **55**, 13433*b* (1959).

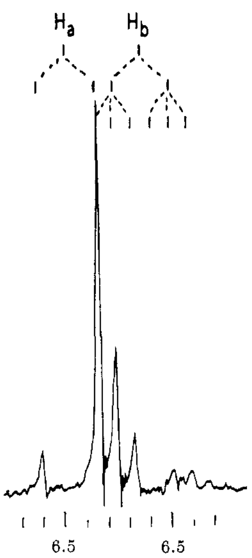

Figure 1.—Nmr spectrum of the vinyl hydrogens of *trans*-N-cinnamylpiperidine. Chemical shifts are shown in parts per million downfield from tetramethylsilane.

curves. The crude product was redistilled on a 45-cm spinning-band column to give analytical samples of the geometrical isomers.

cis-N-Cinnamylpiperidine had bp 71–79° (0.2 mm), n^{18}_{D} 1.5548. (*Anal.* Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.69. Found: C, 83.39; H, 9.72; N, 7.04). The nmr spectrum, neat, showed a multiplet centered at 1.45 ppm, wt 5.9 (3,4,5-protons of piperidyl ring); a multiplet centered at 2.3 ppm, wt 4.0 (2,6-protons of piperidyl ring); split doublets (J = 6 and 1 cps) centered at 3.15 ppm, wt 2.0 ($\mathrm{NC}H_2\mathrm{C}$); a pair of overlapping triplets (J = 12 and 6 cps) centered at 5.80 ppm, wt 1.3 ($\mathrm{CH_2C}H{=}\mathrm{C}$); a pair of triplets centered at 6.50 ppm (J = 12 and 1 cps), wt 1.0 ($\mathrm{CH\ C}H\mathrm{C_6H_5}$); and a multiplet ranging from 7.1 to 7.3 ppm, wt 5.3 (aryl protons). The infrared spectrum showed a weak-to-medium C=C stretching band at 1675 $\mathrm{cm^{-1}}$ and a strong band at 770 $\mathrm{cm^{-1}}$ which did not appear on the spectrum of the *trans* compound.

The hydrochloride of the *cis*-N-cinnamylpiperidine was prepared in ether and recrystallized in acetone, mp 163–164°.

Anal. Calcd for $C_{14}H_{20}ClN$: C, 70.80; H, 8.40. Found: C, 70.56; H, 8.58.

trans-N-Cinnamylpiperidine had bp 82–90° (0.2 mm), n^{18}_{D} 1.5594 [lit.[13] bp 84–90° (0.2 mm)]. The sample reported here was shown to contain 95% of the *trans* isomer and 5% of the *cis* isomer by vpc analysis. (*Anal.* Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.23; H, 9.49; N, 7.20.) The nmr spectrum, neat, showed a multiplet centered at 1.40 ppm, wt 5.9 (3,4,5-protons of piperidyl ring); a multiplet centered at 2.30 ppm, wt 3.9 (2,6-protons of piperidyl ring); a doublet, J = 5 cps, centered at 2.96 ppm, wt 2.0 ($\mathrm{NC}H_2\mathrm{C}$); a complex multiplet ranging from 5.9 to 6.6 ppm, wt 2.1 (vinyl protons—see discussion for detailed analysis); and a complex multiplet ranging from 7.0 to 7.4 ppm., wt 5.7 (aryl protons). The infrared spectrum showed a weak-to-medium C=C stretch at 1630 $\mathrm{cm^{-1}}$ and strong *trans* absorption at 965 $\mathrm{cm^{-1}}$.

The hydrochloride of the *trans*-N-cinnamylpiperidine was prepared in ether and recrystallized from acetone: mp 209–211° (lit.[13] mp 210–211°).

1-(2-Cyclohexylideneethyl)piperidine.—The general procedure described above was followed, using piperidine as the protonic species and cyclohexanone as the carbonyl compound. The product, 1-(2-cyclohexylideneethyl)piperidine, bp 89–91° (12 mm), n^{24}_{D} 1.5013, was obtained in 60% yield, and triphenylphosphine oxide was obtained in 61% yield.

Anal. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.25. Found: C, 80.62; H, 11.89; N, 7.27.

The nmr spectrum, neat, showed a multiplet centered at 1.5 ppm, wt 12.0 (3,4,5-protons on piperidine ring + 3,4,5-protons on cyclohexylidene ring); a multiplet ranging from 1.9 to 2.4 ppm, wt 8.2 (2.6-protons on piperidine ring + 2,6-protons on cyclohexylidene ring); a doublet centered at 2.82 ppm, wt 1.9 ($\mathrm{NC}H_2\mathrm{C}$); and a triplet centered at 5.13 ppm, wt 0.9 ($\mathrm{CH_2C}H{=}\mathrm{C}$). The infrared spectrum showed a weak C=C stretching band at 1680 $\mathrm{cm^{-1}}$ and was otherwise in accordance with the structure assigned.

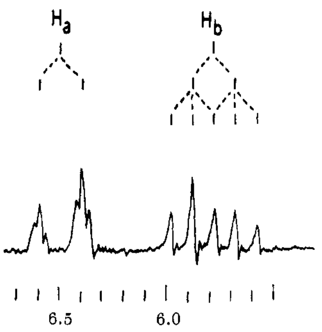

Figure 2.—Nmr spectrum of the vinyl hydrogens of *cis*-N-cinnamylpiperidine. Chemical shifts are shown in parts per million downfield from tetramethylsilane.

N-Cinnamylpyrrole.—Sodium hydride (0.1 mole) was stirred with 150 ml of pyrrole under a nitrogen atmosphere at 50–60°. After 16 hr the mixture was cooled to room temperature and 0.1 mole of vinyl salt II was added and allowed to react for 10 min. Then 0.1 mole of benzaldehyde was added and the mixture was stirred at room temperature for 24 hr and then at reflux for 1 hr. After cooling to room temperature, ether extraction was carried out as described in the general procedure. The dried ether extracts were concentrated and the residue was distilled *in vacuo* to give a 51% yield of a mixture of *cis*- and *trans*-N-cinnamylpyrrole, bp 114–130° (0.5 mm), n^{22}_{D} 1.5848. Distillation of this sample on a 45-cm spinning-band column gave a pure sample of the *trans*-N-cinnamylpyrrole, bp 127–129° (1.4 mm), n^{25}_{D} 1.5929. This sample solidified after sitting overnight. Recrystallization from methanol gave analytically pure white crystals, mp 35–36°.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.65. Found: C, 85.13; H, 7.06; N, 7.53.

The nmr spectrum of the *trans*-N-cinnamylpyrrole, neat, showed a doublet centered at 4.07 ppm, wt 1.9 ($\mathrm{NC}H_2\mathrm{C}$); a multiplet ranging from 5.6 to 6.1 ppm, wt 2.0 (vinyl protons); a triply split peak centered at 6.2 ppm, wt 2.0 (${=}\mathrm{C}H\mathrm{NC}H{=}$); a triply split peak centered at 6.45 ppm, wt 2.0 (${=}\mathrm{C}H\mathrm{C}H{=}$); and a singlet at 7.02 ppm, wt 5.0 (phenyl protons). The infrared spectrum showed a weak C=C stretching band at 1600 $\mathrm{cm^{-1}}$ and a strong *trans*-vinyl absorption at 970 $\mathrm{cm^{-1}}$.

A pure sample of the *cis* isomer was not isolated; however, its presence was shown in an nmr spectrum of a mixture of the *cis* and *trans* isomers. The methylene group adjacent to the nitrogen appears as a doublet centered at 4.07 ppm for the *trans* isomer; in the *cis* isomer this doublet is centered at 4.30 ppm. The characteristic absorptions for the *cis*-vinyl protons (explained in the discussion section) further identified this *cis* isomer.

1-(2-Cyclohexylideneethyl)pyrrole.—Sodium hydride (0.084 mole) was stirred with 150 ml of pyrrole under a nitrogen atmosphere at room temperature. After 14 hr 0.05 mole of vinyltriphenylphosphonium bromide and 0.05 mole of cyclohexanone were added. The mixture was stirred at room temperature for 2 days and then at 70° for an additional 3 days. Vacuum distillation of the reaction mixture gave a 59% yield of 1-(2-cyclohexylideneethyl)pyrrole, bp 76° (0.2 mm), n^{24}_{D} 1.5276.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.18; H, 9.86; N, 7.97.

The nmr spectrum in CCl_4 showed a multiplet ranging from 1.4 to 2.45 ppm, wt 10.0 (cyclohexyl protons); a doublet centered at 4.4 ppm, wt 2.1 ($\mathrm{NC}H_2\mathrm{C}$); a triplet at 5.35 ppm, wt 1.1, ($\mathrm{CH_2C}H{=}\mathrm{C}$); a triply split peak centered at 6.0 ppm, wt 1.9 (${=}\mathrm{CHNC}H{=}$); and a triply split peak centered at 6.0 ppm, wt 1.9 (${=}\mathrm{C}H\mathrm{C}H{=}$). The infrared spectrum showed a medium C=C stretch at 1670 $\mathrm{cm^{-1}}$ and a strong band at 720 $\mathrm{cm^{-1}}$ due to the pyrrole hydrogens.

1-(2-Cyclohexylethyl)pyrrole.—A mixture of 0.018 g. of 10% palladium-on-charcoal catalyst and 15 ml of dry ethanol was placed in a microhydrogenator at 1 atm of hydrogen and stirred until equilibrium was reached. 1-((2-Cyclohexylideneethyl)pyrrole (0.287 g) was added and the mixture was stirred for 18 hr.

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(13) C. Kaiser, *et al.*, *J. Org. Chem.*, **27**, 768 (1962).

A quantitative uptake of 1 mole of hydrogen/mole of olefin was observed. Distillation *in vacuo* gave 0.223 g (75%) of 1-(2-cyclohexylethyl)pyrrole, bp 65° (0.2 mm), n^{24}_{D} 1.5013.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.49; H, 11.08; N, 8.19.

The nmr spectra in CCl_4 showed a multiplet ranging from 0.7 to 1.9 ppm, wt 13.0 ($NCH_2CH_2C_6H_{11}$); a triplet at 3.85 ppm, wt 1.8 (N—CH_2—); a triply split peak centered at 6.0 ppm, wt 1.8 (=CHNCH=); and a triply split peak centered at 6.5 ppm, wt 1.8 (=CHCH=).

Cinnamyl Ethyl Ether.—Sodium (0.15 mole) was added to 300 ml of dry ethanol in a 500-ml three-necked flask under a nitrogen atmosphere. After the sodium had reacted completely, 0.15 mole of benzaldehyde and 0.15 mole of vinyltriphenylphosphonium bromide were added. After stirring for 4 days at room temperature, the reaction mixture was held at reflux temperature for 1 day. After cooling, water and ether were added and ether extraction was carried out. Distillation of the dried (anhydrous $MgSO_4$) ether extracts gave a 54% yield of a 10:1 ratio of *trans*- to *cis*-cinnamyl ethyl ether, bp 86–90° (3.5 mm). The pure *trans* isomer was isolated by distillation on a 45-cm spinning-band column, bp 88° (2.0 mm), n^{23}_{D} 1.5341 [lit.[14] values for cinnamyl ethyl ether, isomer distribution not specified: bp 135° (27 mm), n^{25}_{D} 1.536].

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.24; H, 8.53.

The nmr spectrum, neat, showed a triplet at 1.13 ppm, wt 3.2 (OCH_2CH_3); a quartet at 3.33 ppm, wt 3.1 (OCH_2CH_3); a doublet at 3.95 ppm, wt 2.1 (=CCH_2O); a multiplet centered at 6.25 ppm, wt 2.1 (vinyl protons); and a multiplet centered at 7.15 ppm, wt 5.1 (aryl protons). The infrared spectrum showed a weak C=C stretch at 1610 cm^{-1}, a strong aliphatic ether stretch at 1120 cm^{-1}, and a strong *trans* hydrogen band at 965 cm^{-1}.

The procedure above was modified slightly to carry out the reaction in the presence of dimethylformamide. Using 0.08 g-atom of sodium, 0.08 mole of vinyltriphenylphosphonium bromide, 150 ml of ethanol, and 250 ml of dimethylformamide, the reaction mixture was heated with stirring at 90° for 4 days. The work-up of this reaction mixture gave a 57% yield of a 1:1 ratio of *cis*- to *trans*-cinnamyl ethyl ether, bp 86–87° (3.5 mm). The *cis* isomer was collected from the vapor phase chromatograph and identified by nmr spectroscopy; an analytical sample was not prepared.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found (for the 1:1 mixture of *cis–trans* isomers): C, 81.41; H, 8.76.

The nmr spectrum of *cis*-cinnamyl ethyl ether, neat, showed a triplet at 1.08 ppm, wt 3.0 (OCH_2CH_3); a multiplet at 3.51 ppm, wt 3.9 ($CH_2OCH_2CH_3$); a multiplet at 4.45 ppm, wt 0.9 (CH_2-CH=C); a pair of triplets centered at 5.82 ppm, wt 0.9 (C=CHC_6H_5); and a multiplet at 7.09 ppm, wt 5.0 (aromatic protons).

Ethyl 3-Phenylpropyl Ether.—The 1:1 mixture of *cis*- and *trans*-cinnamyl ethyl ethers (0.0018 mole) from the previous experiment, 0.025 g of 10% palladium on charcoal, and 15 ml of dry ethanol were placed in a microhydrogenation apparatus at 1 atm of hydrogen. After equilibrium was reached, the mixture was stirred for 45 min. A quantitative uptake of 1 mole of hydrogen/mole of olefin was observed. Distillation gave 0.20 g (69% yield) of ethyl 3-phenylpropyl ether, bp 88° (0.5 mm), n^{24}_{D} 1.4879 [lit.[15] bp 90–95° (10 mm), n^{23}_{D} 1.4938].

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.48; H, 9.74.

The nmr spectrum in CCl_4 showed a triplet at 1.2 ppm, wt 3.0 (OCH_2CH_3); a quartet at 1.9 ppm, wt 2.1 ($CH_2CH_2C_6H_5$); a triplet at 2.68 ppm, wt 2.1 ($CH_2C_6H_5$); a quartet at 3.44 ppm, wt 4.0 (CH_2OCH_2); and a singlet at 7.16 ppm, wt 5.3 (aryl protons).

N-Cinnamyl-*p*-toluenesulfonamide.—*p*-Toluenesulfonamide (0.04 mole) was treated with 0.04 mole of sodium hydride in 150 ml of xylene, and the mixture was refluxed under a nitrogen atmosphere for 20 hr. After cooling to 60°, 0.04 mole of vinyltriphenylphosphonium bromide and 75 ml of dimethylformamide were added. Benzaldehyde (0.04 mole) was introduced in a solution of 25 ml of dimethylformamide and the mixture was allowed to reflux for 48 hr. Ether extraction was carried out as described in the general procedure. The ether extracts were evaporated to give 16.4 g of oil, 4.9 g of which were put on a 1-in. chromatographic column made up with 75 g of Florisil. Elution with 50% benzene in petroleum ether gave 0.11 g of triphenylphosphine (identified by mixture melting point and comparison of infrared spectrum with authentic sample). Further elution with benzene gave 1.45 g (43% yield) of the known[3] N-cinnamyl-*p*-toluenesulfonamide. The crude product, a viscous liquid, was rechromatographed to prepare an analytical sample, and to separate the *cis* and *trans* isomers. Separation was not complete, but the *trans* isomer was separated as a solid and recrystallized from methanol to give white crystals melting at 108–109° (lit.[16] mp 110°). The analytical sample was a mixture of the *cis* and *trans* isomers.

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.88. Found: C, 66.77; H, 6.05; N, 4.76.

The nmr spectrum for *trans*-N-cinnamyl-*p*-toluenesulfonamide in CCl_4 showed a singlet at 2.30 ppm, wt 3.0 ($ArCH_3$); a triplet centered at 3.70 ppm, wt 1.9 (NCH_2C); a triplet centered at 5.25 ppm, wt 1.0 (NH); a complex multiplet ranging from 5.75 to 6.55 ppm, wt 2.1 (*trans*-vinyl protons); and a multiplet ranging from 7.1 to 7.9 ppm, wt 9.4 (aryl protons). The infrared spectrum of the *trans*-N-cinnamyl-*p*-toluenesulfonamide showed a weak C=C stretch at 1610 cm^{-1} and a medium-strong *trans*-vinyl band at 970 cm^{-1}.

***cis*-N-Cinnamyl-N-propyl-*p*-toluenesulfonamide.**—N-Propyl-*p*-toluenesulfonamide[17] (0.0225 mole) was treated with 0.0225 mole of sodium hydride in 150 ml of anhydrous ether, and the mixture was stirred under a nitrogen atmosphere at reflux temperature for 2 hr. To this mixture was added 0.0225 mole of vinyltriphenylphosphonium bromide, 0.0225 mole of benzaldehyde, and 100 ml of dimethylformamide. Ether extraction was carried out as described in the general procedure. Evaporation of the dry ether extract gave 10.0 g of oil, 4.4 g of which were placed on a 1-in. chromatographic column made up with 75 g of Florisil, 60–200 mesh. Elution with 50% benzene in petroleum ether gave 0.1 g of triphenylphosphine (identified by comparison of infrared spectrum and mixture melting point with authentic sample). Benzene elution yielded 2.1 g of the *cis*-N-cinnamyl-N-propyl-*p*-toluenesulfonamide, a viscous, colorless liquid, bp 170–180° (0.3 mm), n^{24}_{D} 1.5740.

Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.38; H, 6.87; N, 4.32.

The nmr spectrum in CCl_4 showed a triplet centered at 0.72 ppm, wt 2.5 (C—CH_3); a sextet centered at 1.32 ppm, wt 2.0 (CCH_2C); a singlet at 2.33 ppm, wt 2.9 ($ArCH_3$); a triplet centered at 2.95 ppm, wt 2.0 (NCH_2CH=); a multiplet centered at 5.48 ppm, wt 1.0 (CCH=CHC_6H_5); a doublet centered at 6.48 ppm, wt 1.0 (CH=CHC_6H_5); and a multiplet ranging from 7.0 to 7.7 ppm, wt 9.4 (aryl protons). The infrared spectrum showed a medium-strong C=C stretching band at 1602 cm^{-1}, the asymmetric and symmetric SO_2 stretching bands at 1170 and 1340 cm^{-1}, respectively, and no strong bands in the 950–990-cm^{-1} *trans* absorption region.

The total yield of *cis*-N-cinnamyl-N-propyl-*p*-toluenesulfonamide was 65%. Further elution of the chromatographic column with 20% methanol in chloroform gave 1.7 g of oil from which 0.7 g of triphenylphosphine oxide was isolated and identified as above. The total yield of triphenylphosphine oxide was 52%.

***cis*-N-Cinnamyl-*p*-toluenesulfonanilide.**—*p*-Toluenesulfonanilide (0.0225 mole) was treated with 0.0225 mole of sodium hydride in 200 ml of anhydrous ether, and the mixture was refluxed under a nitrogen atmosphere for 18 hr. To this mixture were added 0.0225 mole of vinyltriphenylphosphonium bromide, 0.0225 mole of benzaldehyde, and 150 ml of dimethylformamide. This mixture was refluxed for 48 hr. Ether extraction was carried out as described in the general procedure. The ether extracts were evaporated to an oil; short-path distillation gave 1.1 g of benzaldehyde, bp 35–50° (0.5 mm). Ether was added to the pot and 2.6 g of white crystals was filtered off. Column chromatography proved these crystals to be 59.7% triphenylphosphine oxide and 40.3% *p*-toluenesulfonanilide (shown by their infrared spectra and mixture melting points with authentic samples). The remaining oil (4.7 g) was placed on a 1-in. chromatographic column made up with 75 g of Florisil. Elution with 10% benzene in petroleum ether gave 0.44 g of triphenyl-

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[14] M. Darmon, *Bull. Soc. Chim. France*, **8**, 414 (1941).

[15] L. Summers and M. Larson, *J. Am. Chem. Soc.*, **74**, 4498 (1952).

[16] P. A. Briscoe, *et al.*, *J. Chem. Soc.*, 1755 (1956).

[17] Prepared following the general procedure given by A. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1963, p 653.

phosphine (infrared spectrum and mixture melting point with an authentic sample). Further elution with benzene gave 1.3 g of *cis*-N-cinnamyl-*p*-toluenesulfonanilide. Based on a 53% conversion (0.0119 moles reacted) of the benzaldehyde, the total yields are 14% triphenylphosphine, 47% triphenylphosphine oxide, and 30% *cis*-N-cinnamyl-*p*-toluenesulfonanilide. Recrystallization of the *cis*-N-cinnamyl-*p*-toluenesulfonanilide from methanol gave analytically pure, white crystals, mp 83.5–84.0°.

Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.71; H, 5.82; N, 3.85. Found: C, 72.76; H, 5.82; N, 4.01.

The nmr spectrum in deuteriochloroform showed a singlet at 2.31 ppm, wt 3.0 ($ArCH_3$); a split doublet centered at 4.46 ppm, wt 2.1 (CCH_2N); a multiplet centered at 5.63 ppm, wt 0.84 ($ArCH{=}CH$); a doublet at 6.47 ppm, wt 0.84 ($ArCH{=}CH$); and a multiplet ranging from 6.9 to 7.6 ppm, wt 14.4 (aryl protons). The infrared spectrum showed a weak–medium C=C stretching band at 1600 cm^{-1} and only very weak bands in the 960–990-cm^{-1} *trans* absorption region.

Phenyl *trans*-Cinnamyl Sulfide.—Sodium hydride (0.05 mole) was allowed to react with 150 ml of thiophenol. After 14 hr 0.05 mole of vinyl triphenylphosphonium bromide and 0.05 mole of benzaldehyde were added and the temperature was held at 90° for 4 days. Ether and water were added and ether extraction was carried out. The ether layer was washed well with 2 *N* NaOH and with water and dried over magnesium sulfate. Evaporation of the ether solution gave a solid to which was added dry ethanol. From this solution was recrystallized 7.7 g (68%) of the phenyl cinnamyl sulfide, mp 77–77.5° (lit.[18] mp 78°). Vapor phase chromatograph indicated only one peak, shown by infrared and nmr analysis to be the *trans* isomer.

The nmr spectrum in CCl_4 showed a doublet at 3.6 ppm, wt 1.9 (SCH_2); a multiplet from 6.1 to 6.6 ppm, wt 1.9 (vinyl protons); and a singlet at 7.33 ppm, wt 10.0 (aryl protons). The infrared spectrum showed a medium-strong C=C stretch at 1580 cm^{-1} and a strong *trans* hydrogen band at 965 cm^{-1}.

Diethyl Ethyl(2-cyclohexylideneethyl)malonate.—Sodium hydride (0.06 mole) was allowed to react with 0.06 mole of diethyl ethylmalonate in 100 ml of anhydrous ether. At the completion of the reaction, the ether was distilled off and 350 ml of dimethylformamide was added, followed by addition of 0.06 mole of cyclohexanone and 0.061 mole of vinyltriphenylphosphonium bromide. The reaction mixture was held at 90–100° for 8 days. Ether and water were added and ether extraction was carried out. The dry ether extracts were distilled to give a 14% yield of diethyl ethyl(2-cyclohexylideneethyl)malonate, bp 134–135° (0.9 mm), $n^{25}\text{D}$ 1.4714 [lit.[19] bp 152–153° (3 mm)].

The nmr spectrum in CCl_4 showed a complex multiplet centered at 4.1 ppm, wt 4.8 (assigned to the four protons from the methylene groups adjacent to the oxygen in the ester linkage, and to the one proton on the double bond); and a complex multiplet ranging from 0.61 to 2.42 ppm, wt 23.2 (assigned to all other hydrogens in the molecule). The infrared spectrum showed a medium C=C stretch at 1600 cm^{-1}, a strong C=O stretch at 1740 cm^{-1}, and was otherwise in accordance with the structure assigned.

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The Constitution of Crude O,O-Dimethyl- and O,O-Diethyldithiophosphoric Acids Prepared from Phosphorus Pentasulfide

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The chief constituents of the neutral fraction of crude O,O-dimethyl- and O,O-diethyldithiophosphoric acids were characterized; all but one of these were shown to be convertible to the corresponding phosphorochloridothioate on chlorination.

The neutral fraction of crude O,O-diethyldithiophosphoric acid, obtained from phosphorus pentasulfide and ethanol, was investigated by Bacon and LeSuer[1] and by McIvor, *et al.*[2] The former authors obtained triethyl phosphorothionate and O,O,O,O-tetraethyl trithiopyrophosphate, together with elemental sulfur, by fractional distillation. The latter authors reported O,O,S-triethyl phosphorodithioate and S,S-bis(diethylphosphorothionyl)-O-ethyl phosphorothionate by a similar treatment, and state that O,O,S-trimethyl phosphorodithioate was obtained from the reaction of methanol with phosphorus pentasulfide.

With the availability of the nmr analytical method, it became of interest to reinvestigate the neutral fraction of crude methyl and ethyl phosphorodithioates, with a view particularly to determining which constituents are convertible to phosphorochloridothioates on chlorination. Table I shows the nmr peaks found in the neutral fractions of crude methyl and ethyl phosphorodithioic acids, together with the approximate percentage range found in different samples and the structure assignments made.

The structure assignments were made on the following basis.

Methyl Series.—Vacuum distillation of the neutral fraction derived by conventional methods[1,2] from crude O,O-dimethylphosphorodithioic acid gave a distillate showing identical nmr peaks at −88.0- and −60.2-ppm shift, together with a minor peak at −73.0 ppm. Refractionation gave an analytical sample [bp 84° (56 mm), $n^{23}\text{D}$ 1.4772] with nmr peaks as above, less that at −73.0 ppm. The two peaks were 655 cps apart, each split into seven parts (14.1 cps). On H^1 decoupling, they fused to a single peak at −74.1-ppm shift. Physical constants (other than nmr) are in good agreement with reported values[3] for O,O-dimethyl hydrogen phosphonothioate.

The peak at −73.4 ppm was assigned to trimethyl phosphorothionate on the basis of the nmr spectrum, which had identical shift and splitting with that shown by an authentic specimen.

The peak at −89.0 ppm was assigned to the disulfide structure $[(CH_3O)_2PS]_2S_2$ on the basis of its chemical shift, which was the same as that shown by an authentic specimen prepared from O,O-dimethyl phosphorodi-

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