hydrogen bromide in acetic acid (90 ml). After standing overnight at room temperature, the solution was refrigerated. The crystalline precipitate that deposited was collected by filtration under nitrogen and dried *in vacuo* over phosphorus pentoxide: yield, 2.28 g (93%); mp *ca.* 228° with predarkening and softening; λ_{max}, in mμ ($\epsilon \times 10^{-3}$), pH 1, 221 (24.8), 238 (26.2), 268 (sh) (8.91), 340 (12.0), pH 7 (unstable), 215, 237, 256, 280, 344, pH 13, 215 (20.7), 258 (sh) (8.91), 298 (sh) (6.36), 348 (12.4); σ, in cm^{-1}, 3405, 3240, 3150, 3010, 2950, 2915 (NH, CH), 1750, 1720 (C=O), 1660, 1640 (NH), 1610, 1510, 1480 (C=C, C=N), 1555, 1320 (NO_2), 1220 (C—O—C).

Anal. Calcd for $C_{11}H_{15}N_5O_5 \cdot HBr$: C, 34.93; H, 4.27; Br, 21.13; N, 18.52. Found: C, 35.03; H, 4.49; Br, 21.1; N, 18.33.

Ethyl 8-Amino-3,4-dihydro-2-methylpyrido[2,3-*b*]pyrazine-6-carbamate (XIV).—Aqueous 1 *N* sodium hydroxide (9.17 ml, 9.17 mmoles) was added dropwise under nitrogen to a stirred suspension of XIII hydrobromide (3.81 g, 10.1 mmoles) in ethanol (180 ml) and N,N-dimethylformamide (90 ml). The resulting solution was hydrogenated at room temperature and atmospheric pressure in the presence of Raney nickel (1.0 g, weighed wet with ethanol). After 16 hr the solution had absorbed 103% of the theoretical amount of hydrogen. The solution was filtered through Celite under nitrogen, evaporated to dryness *in vacuo* at 60°, and the residual oil was triturated with water (10 ml). The resultant yellow solid was collected by filtration, dissolved in hot methanol (30 ml), and treated with charcoal. The yellow crystals that deposited were collected by filtration, washed with methanol, and dried *in vacuo* over phosphorus pentoxide: yield, 1.17 g (51%); mp >260°; λ_{max}, in mμ ($\epsilon \times 10^{-3}$), pH 1, 232 (27.0), 318 (12.0), pH 7, 223 (29.2), 256 (sh) (15.3), 327 (7.91), pH 13, 223 (29.2), 256 (sh) (15.6), 327 (7.79); σ, in cm^{-1}, 3480, 3360, 3230 (NH), 2980, 2930, 2900, 2780 (CH), 1720 (C=O), 1620 (NH), 1620, 1590, 1540, 1520 (C=C, C=N), 1210 (C—O—C).

Anal, Calcd for $C_{11}H_{15}N_5O_2$: C, 53.00; H, 6.07; N, 28.10. Found: C, 53.01; H, 5.99; N, 27.74.

Ethyl 8-Amino-2-methylpyrido[2,3-*b*]pyrazine-6-carbamate (XVb).—Ethyl 8-amino-3,4-dihydro-2-methylpyrido[2,3-*b*]pyrazine-6-carbamate (XIV, 1.09 g, 4.37 mmoles) was dissolved in warm acetone (250 ml), and the solution was allowed to cool to room temperature. A 0.27% solution of potassium permanganate in acetone was added slowly with stirring over a period of 1 hr until the color of permanganate persisted (*ca.* 2.08 mmoles was consumed). The manganese dioxide was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The ultraviolet absorption spectrum and thin layer chromatogram of the yellow residue (0.910 g, 84%) were identical with those of an analytical sample obtained by recrystallization from ethanol: mp >260°; λ_{max}, in mμ ($\epsilon \times 10^{-3}$), pH 1, 228 (30.9), 250 (sh) (12.7), 323 (18.0), pH 7, 225 (30.0), 263 (23.7), 331 (10.3), pH 13, 226 (26.2), 263 (22.6), 334 (9.64); σ, in cm^{-1}, 3480, 3430, 3290, 3180, 3110, 2980, 2920 (NH, CH), 1730 (C=O), 1620 (sh) (NH), 1610, 1575, 1540, 1520, 1500 (C=C, C=N), 1200 (C—O—C).

Anal. Calcd for $C_{11}H_{13}N_5O_2$: C, 53.43; H, 5.30; N, 28.33. Found: C, 53.26; H, 5.39; N, 28.24.

6,8-Diamino-2-methylpyrido[2,3-*b*]pyrazine (XVI) Hyrochloride.—A suspension of XVb (700 mg, 2.83 mmoles) in a solution of potassium hydroxide (4.00 g, 71.3 mmoles) in ethanol (60 ml) was stirred at reflux under nitrogen for 7 hr. The resulting solution was cooled to room temperature, made slightly acidic with 6 *N* hydrochloric acid, and evaporated to dryness *in vacuo* at 40°. The residue was extracted with boiling ethanol (70 ml); the extract was evaporated to dryness *in vacuo*. The residue was recrystallized from hot 0.2 *N* hydrochloric acid (6 ml) with charcoal treatment to give the product as tan needles in two crops, which were dried at 78° *in vacuo* over phosphorus pentoxide: yield, 492 mg (82%); mp >260°; λ_{max}, in mμ ($\epsilon \times 10^{-3}$), pH 1, 221 (36.9), 334 (15.9), pH 7, 220 (33.7), 255 (9.32), 341 (12.1), pH 13, 220 (25.6), 259 (15.9), 354 (9.56); σ, in cm^{-1}, 3500, 3420, 3380, 3310, 3170 (NH), 1650 (NH), 1630 (sh), 1600 (sh), 1545, 1490 (C=C, C=N).

Anal. Calcd for $C_8H_9N_5 \cdot HCl$: C, 45.39; H, 4.76; N, 33.09. Found: C, 45.55; H, 5.02; N, 33.10.[8]

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and the members of the Analytical Chemistry Section of Southern Research Institute who performed the spectral and microanalytical determinations reported, and to Mr. W. E. Fitzgibbon and the Organic Preparations Section of Southern Research Institute who carried out the large-scale synthesis of some of the compounds.

[8] The Kjeldahl procedure was used for the nitrogen analysis due to low values obtained by the Dumas method.

Organic Sulfur Compounds. XV. Cationic Addition of O,O′-Diethylthiophosphoric Acid to Olefins

WOLFGANG H. MUELLER AND ALEXIS A. OSWALD

The Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

Received December 15, 1965

O,O′-Diethylthiophosphoric acid (phosphorothioic acid O,O′-diethyl ester) was added to isobutylene, isoprene, styrene, indene, cyclopentene, and norbornene by a cationic mechanism. The predominant formation of O,O′-diethyl-S-alkylthiophosphates was observed. In accordance with the Markovnikov rule, S-*t*-butyl-, S-α-phenylethyl-, S-1-indanyl-, and S-cyclopentylthiophosphates were formed with high selectivities. From isoprene the S-(3-methyl-2-butenyl)- and S-2-(2-methyl-3-butenyl)thiophosphates were obtained in a 4:1 ratio. With norbornene O- and S-alkylation was observed in an exceptionally high ratio of 2:3. It was shown that addition occurs only to strained cyclic olefins or to olefins which form on protonation relatively stable carbonium ions.

During the course of our investigation of the free-radical addition of O,O′-dialkylthiophosphoric acid (phosphorothioic acid O,O′-dialkyl esters) to unsaturates, we became concerned with the possibility of concurrent cationic additions in such systems. The cationic addition of O,O′-dialkyldithiophosphoric acids to olefins is a well-studied reaction, and the relevant literature indicates that it is rather generally applicable, *i.e.*, independent from the structure of the olefin.[1] Similar additions of O,O′-dialkylthiophosphoric acids, however, appear to be hardly investigated. Only a few ionic additions to nonhydrocarbon unsaturates, such as alkyl propiolates[2] and phenyl vinyl ethers or phenyl vinyl sulfides[3] have been described in the patent literature. While these additions were investigated as synthetic methods to obtain thiophosphate (phosphorothioate) esters of potential interest as insecticides,[4,5] no study of the scope or mechanism of such additions was made.

[1] W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

[2] L. A. Miller and G. H. Birum, U. S. Patent 3,059,014 (1962).

[3] G. Schrader, German Patent 1,070,171 (1959).

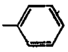
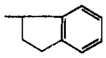
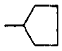
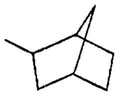
[4] G. Schrader, "Die Entwicklung neuer insektizider Phosphorsäure-Ester," Verlag Chemie, Weinheim, 1963.

[5] K. Sasse, "Methoden der Organischen Chemie," Houben-Weyl, Vol. XII/2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1964, pp 652–681.

TABLE I

NMR PARAMETERS OF DIETHYLTHIOPHOSPHORIC ACID ADDUCTS

$(C_2H_5O)_2P(O)SR$

R					C_2H_5		
	Group chemical shift[a]			J_{PSCH}, cps	Chemical shift[a]		J_{POCH}, cps
Group structure					CH_3	CH_2	
$-CH_2CH_3$	2.83[b] (Dq)	1.34 (t)		15	1.34[b] (t)	4.11 (Dq)	9
$-C(CH_3)_3$	1.50[c] (d)				1.33[b] (t)	4.08 (Dq)	9
$-CH_2CH{=}C(CH_3)_2$	1.72 (s)	3.41[d] (Dd)	5.30 (t)	13.5	1.33[b] (t)	4.08 (Dq)	9
$-C(CH_3)_2CH{=}CH_2$	1.58[c] (d)	5.08 (m)	5.9–6.5 (m)		1.32[b] (t)	4.06 (Dq)	9
$-CH(CH_3)-$ 	1.72[e] (d)	4.48 (Dq)	7.30 (m)	11	1.23[b] (t) 1.17[b] (t)	3.90 (m)	9
	2.0–3.2 (m)	7.1–7.6 (m)	4.79[f] (Dt)	10	1.33[b] (t)	4.12 (Dq)	9
	1.5–2.5 (m)	3.5–3.75 (m)		*g*	1.33[b] (t)	4.10 (Dq)	9
	1.0–2.0 (m)	2.2–2.5 (m)	2.9–3.4 (m)	*g*	1.33[b] (t)	4.08 (m)	*g*

[a] In parts per million. D, doublet of; T, triplet of; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] $J_{CH_2CH_3}$ = 7 cps. [c] J_{PSCCH_3} = 1.5 cps. [d] $J_{CH_2CH=}$ = 8 cps. [e] J_{CHCH_3} = 7 cps. [f] J_{CHCH_2} = 6 cps. [g] Unresolved.

In the present work the O,O'-dialkylthiophosphoric acid addition to various olefinic hydrocarbons was examined. As a readily available,[6] convenient model adding agent, O,O'-diethylthiophosphoric acid was chosen. As typical olefin substrates, 1-pentene, trichloroethylene, allene, 1,3-butadiene, isobutylene, isoprene, styrene, indene, cyclopentene, and norbornene were selected.

Results and Discussion

In contrast to the ready cationic addition of dialkyldithiophosphoric acids to olefins,[1] analogous additions of O,O'-diethylthiophosphoric acid occur at much slower rates and with only a few types of olefins.

Reaction mixtures of diethylthiophosphoric acid and olefins were kept without any solvent at ambient temperature for approximately 200 hr in the presence of 1 mole % of hydroquinone as a free-radical inhibitor. In the case of allene, butadiene, and isobutylene, the reaction was carried out in closed vessels under autogenous pressure. All the other olefins were allowed to react under a nitrogen atmosphere. The progress of the reaction was followed by semiquantitative nmr spectroscopy. After removal of the unconsumed starting materials, the products were analyzed by gas–liquid partition chromatography (glpc) and nmr spectroscopy. With the exception of cyclopentene, which yielded only 8% product, all the reactive olefins formed the corresponding adducts in 42–46% conversion. In contrast to the highly selective S-alkylation observed in all other cases, both O- and S-alkylation in a 2:3 ratio occurred with norbornene. In general, pure samples for analytical purposes were obtained as colorless liquids from fractional distillation *in vacuo*.

In a more detailed study of the reaction conditions with styrene, it was found that the relatively slow rate of addition can be considerably enhanced by catalytic amounts of perchloric acid or boron trifluoride etherate and/or elevated temperatures of 80–100°. Their nmr spectra revealed impurities which are presumably due to thermal decomposition of the adduct.

In general the nmr spectra of dialkyl thiophosphates (Table I) resemble those of the corresponding dialkyl dithiophosphates.[7] A special characteristic is the additional splitting of the protons on the α carbon due to spin–spin coupling to the phosphorus nucleus (I = 0.5) through the P–S–C or P–O–C bonds. Therefore, the O-methylene protons in O,O'-diethyl thiophosphates appear as a double quartet (J_{POCH} = 9 cps), and the methyl protons of the O-ethyl groups show the expected splitting into a triplet. From nmr analysis of the dialkylthiophosphoric acid–olefin adducts (the dialkyl thiophosphates), with the exception of the S-*t*-alkyl thiophosphates, the presence of the P–S–C bond was readily deduced. The α proton(s) appear at a considerably higher field than the corresponding proton(s) of a P–O–C bond. This difference in chemical shift (1.28 ppm) was demonstrated in the spectrum of O,O',S-triethyl thiophosphate (Table I). A strong infrared absorption at 1255 cm^{-1} due to the P=O stretching vibration[8] also aided in assigning a thiol ester structure to the adducts. In the case of styrene and cyclopentene the structure of the resulting thiol ester adducts was also confirmed by independent syntheses. The formation of a P-S-C bond rather than that of a P-O-C bond, observed in every case except that of norbornene, is in accord with the earlier reported examples of the cationic addition of diethylthiophosphoric acid to nonhydrocarbon substrates.[2,3] It also parallels the findings in free-radical additions of thiophosphoric acids and thiolacetic acid to olefins.[1,9] In displacement reactions using dialkyl thiophosphate salts and alkyl halides S-alkylation was also observed.[4,5]

1-Pentene, Trichloroethylene, Allene, and Butadiene.—Cationic additions to these hydrocarbons was attempted in order to compare these reactions with the corresponding free-radical additions studied earlier. However, no thiophosphoric acid addition occurred under the typical reaction conditions employed in this study.

---

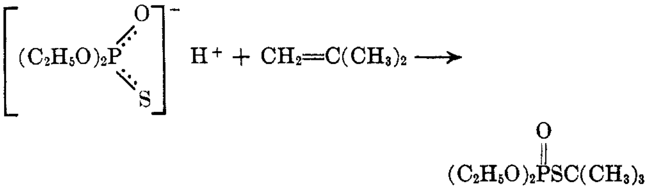
[6] M. I. Kabachnik and E. I. Golubeva, *Dokl. Akad. Nauk SSSR*, **127**, 575 (1959).

[7] A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 1262 (1963).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 312.

[9] F. W. Stacey and J. F. Harris, *Org. Reactions*, **13**, 152 (1963).

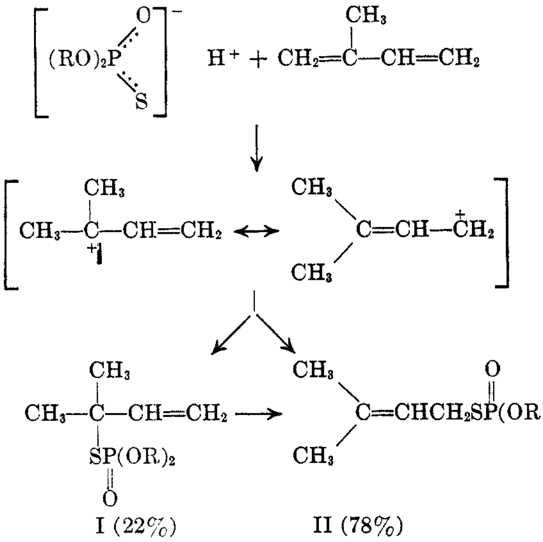
Isobutylene.—O,O′-Diethylthiophosphoric acid was added to isobutylene with an exclusively Markovnikov orientation to yield O,O′-diethyl *S*-*t*-butylthiophosphate 98% (glpc).



A pure sample obtained by distillation *in vacuo* shows an nmr spectrum which is in accord with the above adduct structure. In addition to the signals arising from the O,O′-diethylthiophosphoryl group, the spectrum shows a doublet at 1.50 ppm (J = 1.5 cps) which is due to the *t*-butyl group. It is suggested that the splitting of this signal into a doublet is due to long-range coupling of the phosphorus nucleus (I = 0.5) through the P–S–C–C bonds rather than to nonequivalence of the methyl groups. This is supported by a similar observation in the case of the 1,2 adduct of isoprene.

Isoprene.—O,O′-Diethyl *S*-2-(2-methyl-3-butenyl)-thiophosphate (I) and O,O′-diethyl *S*-(3-methyl-2-butenyl)thiophosphate (II) were obtained in an approximately 1:4 ratio from O,O′-diethylthiophosphoric acid and isoprene (Scheme I).

SCHEME I



The product distribution was established by semiquantitative nmr analysis of the mixture. As expected, glpc analysis showed only two peaks having comparable retention times; however, the isomer ratio could not be accurately confirmed in this manner, since the 1,2 adduct (I) partially decomposed on the column, as evidenced by the appearance of an isoprene peak.

While the thermodynamically more stable 1,4 adduct (II) is always the major product, analyses at various conversion levels revealed postisomerization of adduct I to II under the acidic reaction conditions (Table II). However, no further isomerization was observed during 45 days after the unreacted acid had been removed.

Fractional distillation *in vacuo* afforded the pure 1,4 adduct (II), and the 1,2 adduct (I) in admixture with 30% of II. Elemental analysis of this mixture confirmed their isomeric nature.

TABLE II

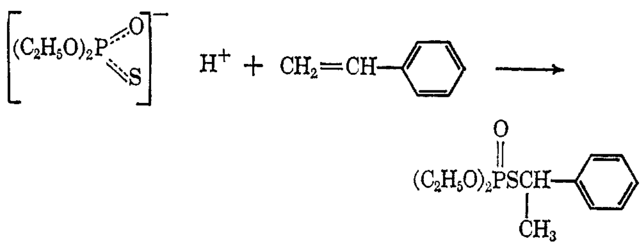
ISOMER DISTRIBUTION OF THIOPHOSPHORIC ACID–ISOPRENE ADDUCTS AT VARIOUS CONVERSION LEVELS

Reaction time, hr	Conversion, %	% isomers[a] 1,2 adduct I	1,4 adduct II
20	21	43	57
40	35	40	60
200	46	22	78

[a] By semiquantitative nmr analysis.

The structure assignment of the adducts is based on their nmr spectra. The 1,4 adduct (II) shows a double doublet at 3.41 ppm for the allylic methylene protons due to splitting by the phosphorus nucleus through the P–S–C bonds (J = 13.5 cps) and the vinyl proton on the adjacent carbon (J = 8 cps). A triplet appears at 5.30 ppm for the vinyl proton and a singlet at 1.72 ppm for the methyl protons. These parameters agree well with those of the corresponding 1,4 adduct of butadiene derived from free-radical addition. The 1,2 adduct (I) exhibits a doublet at 1.58 ppm split by the phosphorus nucleus through P–S–C–C (J = 1.5 cps), a partially resolved multiplet at 5.08 ppm for the terminal vinyl protons, and another multiplet at 5.9–6.5 ppm for the internal vinyl proton. The order of reactivity observed in thiophosphoric acid additions to 1-pentene, butadiene, isobutene, and isoprene parallels the reported relative solvolysis rates of the following halides: $(CH_3)_2CHX < CH_2{=}CHCHXCH_3 < (CH_3)_3CX < CH_2{=}CHC(CH_3)_2X$.[10] Assuming that these rates reflect in part the relative stability of the carbonium ions formed on solvolysis, this correspondence suggests that the relative stability of the intermediate carbonium ion formed on protonation is of critical importance in the addition of thiophosphoric acids to olefins. This fact receives further support from the facile addition of diethylthiophosphoric acid to styrene and indene.

Styrene.—O,O′-Diethyl *S*-(α-phenylethyl)thiophosphate was the sole product obtained from diethylthiophosphoric acid and styrene.



Glpc analysis indicated that the product was essentially pure. Attempted distillation *in vacuo* resulted in decomposition. The identity of the adduct with an authentic compound was confirmed by comparison of glpc retention times and nmr spectra. The authentic sample was prepared from 1-bromoethylbenzene and sodium O,O′-diethyl thiophosphate according to a general procedure.[11] Such displacements are known to give exclusively thiol esters.[4]

The methyl protons of the phenylethyl moiety appear as a doublet at 1.72 ppm split by the adjacent methine proton (J = 7 cps). The methine proton exhibits a double quartet caused by coupling with the adacent

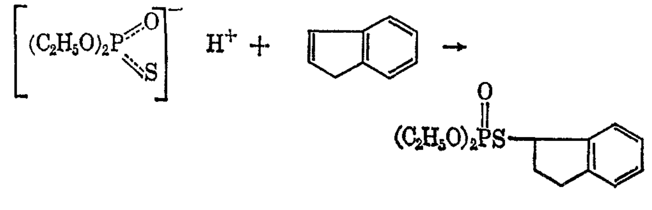
---

[10] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 78.

[11] G. Schrader, German Patent 830,509 (1950).

methyl protons ($J = 7$ cps) and the phosphorus nucleus ($J = 11$ cps). The nmr spectrum of this adduct shows anomalous features for the O,O′-diethylthiophosphoryl moiety. A double triplet of equal intensities at 1.17 and 1.23 ppm for the methyl protons together with an incompletely resolved multiplet at 3.90 ppm for the ethylene protons is due to nonequivalence of the ethyl groups.

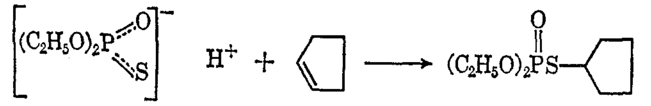
Indene.—O,O′-Diethylthiophosphoric acid and indene afforded O,O-diethyl S-(1-indanyl)thiophosphate.



The adduct decomposed on glpc analysis and was, therefore, purified by column chromatography on silica gel.

The nmr spectrum of the purified product showed the signals expected for the S-1-indanylthiophosphate. In addition to the usual parameters of the diethylthiophosphoryl moiety, a multiplet at 2.0–3.2 ppm appears for the methylene protons in the five-membered ring, another multiplet at 7.30 ppm for the phenyl protons, and a double triplet at 4.79 ppm for the methine proton. This double triplet is caused by splitting of the methine proton by the adjacent methylene protons ($J = 6$ cps) and by the phosphorus nucleus ($J = 10$ cps). In general, the difference in coupling constants of the α proton(s) and the phosphorus in P–O–C ($J = 9$–10 cps) and P–S–C ($J = 14$–15 cps) bonds appears to be diagnostic. However, the two benzylic thiophosphates, the indanyl- and the phenylethylthiophosphates, are exceptions. A comparison of the chemical shift of the methine proton in question with that of the corresponding O,O′-diethyl S-(α-indanyl)dithiophosphate[12] (double triplet at 4.75 ppm) confirmed the P–S–C bond of the monothiophosphate.

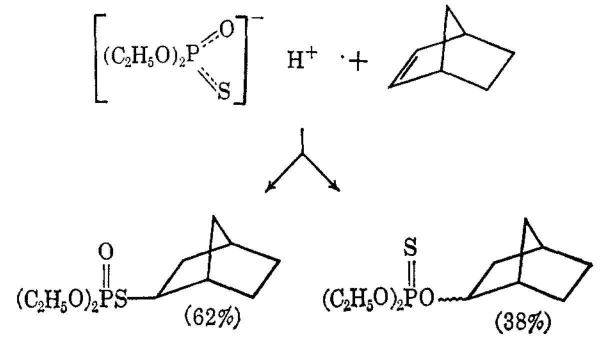
Cyclopentene.—Addition of O,O′-diethylthiophosphoric acid to cyclopentene produced the expected O,O′-diethyl S-cyclopentylthiophosphate. The conversion was, however, considerably lower (*ca.* 8%) than in all other cases. Glpc analysis of the product mixture indicated 90% of the expected adduct and two unidentified impurities of approximately 5% each. The possibility of significant O-alkylation was ruled out, since the glpc retention time of independently synthesized O,O′-diethyl O-cyclopentylthiophosphate was different from any of the three products obtained. This sample was synthesized by a displacement reaction[5] of O,O′-diethyl phosphorochloridothioate and cyclopentanol in the presence of triethylamine.



The distilled product showed identical glpc retention time and nmr parameters with those of the adduct derived from free-radical addition of diethylthiophosphoric acid to cyclopentene thus confirming its thiol ester structure.

In its nmr spectrum, the methine proton of the cyclopentyl moiety appears as an unresolved multiplet at 3.15–3.75 ppm. The residual methylene protons of the ring exhibit a multiplet at 1.5–2.5 ppm.

Norbornene.—O,O′-Diethyl S-(2-norbornyl)thiophosphate and O,O′-diethyl O-(2-norbornyl)thiophosphate were formed from O,O′-diethylthiophosphoric acid addition to norbornene.



Glpc analysis of the product indicated two well-resolved ($\Delta t = 4$ min) peaks of a 2:3 area ratio. Elemental analysis confirmed the isomeric nature of the two components. Pure samples of the individual isomers were obtained on fractional distillation. Both isomers were stable on glpc analysis when injected individually, thus confirming the validity of the glpc analysis of the original product mixture.

Free-radical addition of O,O′-diethylthiophosphoric acid to norbornene afforded a product identical with the major ionic adduct, thus confirming the latter's structure. Its stereochemistry is believed to be *exo*, since free-radical additions of mercaptans to norbornene have been reported to occur almost exclusively *exo*.[13]

The norbornyl moiety of the adduct showed few discernible features in its nmr spectrum. Two unresolved multiplets appear for the S-methine proton (2.9–3.4 ppm), and the two bridgehead protons (2.2–2.5 ppm), with an integral ratio of 1:2. In contrast to the thiol ester, the multiplet for the methine proton of O,O′-diethyl O-(2-norbornyl)thiophosphate is shifted downfield (*ca.* 4.1–4.5 ppm; partly overlapping with the signal for the methylene protons of the ethoxyl groups). All the other nmr parameters are very similar for each isomer. Furthermore, the absence of a P=O stretching band at 1255 cm^{-1} in the infrared spectrum of O,O′-diethyl O-(2-norbornyl)thiophosphate also confirms its P=S structure.

In conclusion, this investigation showed that cationic addition of dialkylthiophosphoric acids to olefins is not a general reaction. It appears to be limited to olefins forming a tertiary or benzylic carbonium ion on protonation or strained cyclic olefins. The addition occurs selectively with Markovnikov orientation and predominantly with the formation of a P–S–C bond.

Experimental Section

Materials.—All the liquid olefins were distilled prior to use and found to be pure on glpc analysis. Norbornene was freshly sublimed. The isobutylene used was a Matheson product of 99% minumum purity. The O,O′-diethylthiophosphoric acid em-

---

[12] Synthesized in an independent study of dialkyldithiophosphoric acids.

[13] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

ployed for the experiments was of 90% minimum purity. Its synthesis was carried out as described by Kabachnik.[6]

Method of Analyses.—The gas chromatographic analyses of the products were obtained using an F & M Model 500 linear programmed temperature gas chromatograph with a 3 ft × 0.25 in. o.d. column. The column packing consisted of 3% Dowfax 9N40 (an ethylene oxide–*p*-nonylphenol polyether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom P.

Operating conditions were as follows: detector, 250°; injector, 170°; flow rate, 60 cc/min; column heating rate, 5.6°/min; starting temperature, 50°; final temperature, 240°; sample size, 0.5 μl.

A Varian Model A-60 proton resonance spectrometer was used for the recording of nmr spectra. All chemical shifts were measured in parts per million against tetramethylsilane as internal reference standard. The spectra were taken on 50% solutions in carbon tetrachloride as solvent. The infrared spectra were obtained using a Beckman Model IR 10 infrared spectrophotometer. All boiling points reported are uncorrected.

General Procedure for the Addition of O,O′-Diethylthiophosphoric Acid to Olefins.—Equimolar amounts of O,O′-diethylthiophosphoric acid and an olefin were allowed to react in the presence of 1 mole % of hydroquinone as a free-radical inhibitor under nitrogen for approximately 200 hr at ambient temperature.

Before work-up the product mixture was sampled for semiquantitiative analysis by nmr spectroscopy. Then the mixture was diluted with ether and washed with a 5% aqueous solution of sodium hydrogen carbonate to remove the unconsumed acid. The ether phase was then dried over magnesium sulfate and subsequently concentrated on a rotary evaporator at 10 mm and ambient temperature. Part of the product was purified by fractional distillation *in vacuo*. This was frequently accompanied by a partial decomposition yielding considerable amounts of undistillable residue.

To Isobutylene.—To 8.5 g (0.05 mole) of O,O′-diethylthiophosphoric acid and 1 mole % of hydroquinone contained in an evacuated, Dry Ice cooled, Pyrex tube, equipped with a magnetic stirring bar, 3.3 g (0.059 mole) of isobutylene was condensed. The tube was then sealed and the mixture was allowed to react for 200 hr with stirring at ambient temperature. The reaction mixture was then worked up according to the general procedure. O,O′-Diethyl S-(*t*-butyl)thiophosphate was obtained as a colorless liquid, 4.8 g (44%), which was 98% pure by glpc analysis. Fractional distillation yielded a pure product (glpc), bp 64.5° (0.25 mm), $n^{20}\text{D}$ 1.4583.

Anal. Calcd for $C_8H_{19}O_3PS$: C, 42.47; H, 8.41; P, 13.71; S, 14.16. Found: C, 42.15; H, 8.48; P, 14.10; S, 14.30.

To Isoprene.—Work-up of a reaction mixture of 17 g (0.1 mole) O,O′-diethylthiophosphoric acid and 6.8 g (0.1 mole) of isoprene afforded 11 g (46%) of a colorless liquid. The nmr spectrum indicated a mixture of O,O′-diethyl S-2-(2-methyl-3-butenyl)thiophosphate (I) and O,O′-diethyl S-(3-methyl-2-butenyl)thiophosphate (II) in a 1:3 ratio. This ratio was also confirmed by glpc analysis; however, compound I showed some thermal instability under the conditions employed, as evidenced by the formation of isoprene. No other isomeric adducts were present. During distillation a mixture of 70% I and 30% II was obtained in one of the earlier fraction [bp 85–89° (0.15 mm)]. Elemental analysis of this mixture confirmed the isomeric nature of I and II.

Anal. Calcd for $C_9H_{19}O_3PS$: C, 45.37; H, 7.98; P, 13.01; S, 13.46. Found: C, 45.12; H, 8.09; P, 13.19; S, 13.55.

Adduct II was obtained pure (glpc) at bp 89–90° (0.15 mm) as a colorless liquid, $n^{20}\text{D}$ 1.4795.

Anal. Calcd for $C_9H_{19}O_3PS$: C, 45.37; H, 7.98; P, 13.01; S, 13.46. Found: C, 45.33; H, 7.95; P, 12.84; S, 13.38.

To Styrene.—A mixture of 6.8 g (0.04 mole) of O,O′-diethylthiophosphoric acid and 4.16 g (0.04 mole) of styrene was allowed to react and worked up in the general manner. Evaporation of the unreacted styrene at 50° (0.02 mm) afforded 4.4 g (40%) of *O,O′-diethyl S-(α-phenylethyl)thiophosphate as a colorless oil*, $n^{20}\text{D}$ 1.5227. The product was essentially pure on glpc analysis, free from isomeric impurities. Considerable decomposition was observed on attempted distillation at 107–113° (0.15 mm).

Anal. Calcd for $C_{12}H_{19}O_3PS$: C, 52.55; H, 6.93; P, 11.13; S, 11.61. Found: C, 52.65; H, 6.87; P, 10.98; S, 11.34.

To Indene.—From a reaction mixture of 8.5 g (0.05 mole) of O,O′-diethylthiophosphoric acid and 5.8 g (0.05 mole) of indene, 7.6 g of a yellow liquid was obtained on work-up. Nmr analysis indicated the presence of some unconverted indene, which could not be removed readily under high vacuum [70° (0.025 mm)]. This mixture was chromatographed on 10 g of silica gel (Grace, Davison Chemical, Grade 12; deactivated with 10% water). The indene was eluted with pentane, and the O,O′-diethyl S-(1-indanyl)thiophosphate with 10% ethanol in pentane. The adduct (2.89 g, 20%) was obtained as a tan liquid, $n^{20}\text{D}$ 1.5385, which decomposed considerably on glpc analysis. Nmr analysis, however, revealed no impurity.

Anal. Calcd for $C_{13}H_{19}O_3PS$: C, 54.54; H, 6.64; P, 10.84; S, 11.19. Found: C, 53.90; H, 6.79; P, 10.76; S, 11.07.

To Cyclopentene.—From 12.75 g (0.075 mole) of O,O′-diethylthiophosphoric acid and 5.16 g (0.075 mole) of cyclopentene, 1.5 g (8%) of crude O,O′-diethyl S-cyclopentylthiophosphate was obtained as a tan liquid. Glpc analysis indicated the presence of 90% adduct and two minor unidentified by-products. An analytical sample was obtained on fractional distillation: bp 79° (0.04 mm), $n^{20}\text{D}$ 1.4808.

Anal. Calcd for $C_9H_{19}O_3PS$: C, 45.38; H, 7.98; P, 13.02; S, 13.44. Found: C, 45.16; H, 7.98; P, 12.76; S, 13.34.

To Norbornene.—A mixture of 4.25 g (0.025 mole) of O,O′-diethylthiophosphoric acid and 2.35 g (0.025 mole) of norbornene yielded, after work-up and removal of the unconverted norbornene at 50° (10 mm), 3.1 g (42%) of a mixture of O,O′-diethyl S-(2-norbornyl)thiophosphate and O,O′-diethyl O-(2-norbornyl)-thiophosphate as a colorless liquid residue. The product exhibited two peaks of 62 and 38 area % on glpc analysis. Elemental analysis of this mixture confirmed the isomeric nature of the two products.

Anal. Calcd for $C_{11}H_{21}O_3PS$: C, 50.00; H, 7.95; P, 11.84; S, 12.12. Found: C, 50.11; H, 7.95; P, 11.20; S, 12.25.

Fractional distillation afforded the pure O,O′-diethyl O-(2-norbornyl)thiophosphate, bp 87–88.5° (0.05 mm), $n^{20}\text{D}$ 1.4860, and O,O′-diethyl S-(2-norbornyl)thiophosphate, bp 113–116° (0.08 mm), $n^{20}\text{D}$ 1.4941.

Both isomers were stable on glpc analysis when injected individually.

Acknowledgment.—The authors wish to thank Mr. W. C. Whitlock for excellent technical assistance and Dr. R. V. Moen for the interpretation of the nmr spectra.