Organic Sulfur Compounds. XIX. Free-Radical Addition of Dialkylthiophosphoric Acids to Unsaturated Hydrocarbons

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O,O′-Diethyl- and O,O′-diisopropylthiophosphoric acids (phosphorothioic acid O,O′-dialkyl esters) were added by a free-radical mechanism to 1-pentene, 1,3-butadiene, and allene. Highly selective additions occurred to form the corresponding S-*n*-pentyl, -crotyl, and -allyl thiophosphates. Their formation is controlled by the factors observed in analogous additions of dialkyldithiophosphoric acids. Thiophosphoric acids, however, add at a much slower rate with lower conversions. Another distinguishing feature of these reactions is the absence of diadditions in the cases of butadiene and allene. Hydrogen bonding of the addend by the adduct ester is discussed as a possible factor causing these low conversions.

A variety of synthetic routes leading to phosphorothioic acid O,O,S-trialkyl esters *via* displacement reactions have been reported.[1] Many of these esters have been found to be of potential interest as pesticides[2] and, therefore, their chemistry has been much explored. The ionic addition of O,O′-dialkylthiophosphoric acids (phosphorothioic acid O,O′-dialkyl esters) to olefins[3] and nonhydrocarbon unsaturates[4] to form such esters has been described. No report of such additions by a free-radical mechanism is known.

In view of the successful free-radical-type addition of O,O′-dialkyldithiophosphoric acids (phosphorodithioic acid O,O′-dialkyl esters) to dienes in this laboratory,[5,6] we became interested in investigating similar additions of O,O′-dialkylthiophosphoric acids. In this study, first the reactivity of diethylthiophosphoric and -dithiophosphoric acids toward a simple monoolefin, *n*-pentene, was compared. Then the addition of dialkylthiophosphoric acids to 1,3-butadiene and to allene was investigated and compared to the corresponding diethyldithiophosphoric acid and thiol additions.[5–9] Diethyl- and diisopropylthiophosphoric acids were chosen as adding agents because they are more readily synthesized and purified than the dimethyl- or the higher dialkylthiophosphoric acids.[10]

Results

In contrast to O,O′-diethyldithiophosphoric acid[5,6] the dialkylthiophosphoric acids do not add to the olefins studied unless the addition is catalyzed by ultraviolet light or peroxides. This fact and the orientation of the addition indicate that the reaction proceeds by a free-radical chain mechanism.

Reaction mixtures of diethyl- or diisopropylthiophosphoric acids and olefins in closed quartz vessels were irradiated with ultraviolet light for 30–40 hr without any solvent at a temperature of 16 ± 3° to effect such additions. In the case of 1-pentene, the reaction mixture was kept under a nitrogen atmosphere, while, with butadiene and allene, the reactions were carried out under their own vapor pressure. The progress of the reaction was followed by semiquantitative nuclear magnetic resonance spectroscopy (nmr). After removal of the unreacted starting materials, the products were analyzed by a combination of gas–liquid partition chromatography (glpc) and nmr. With an equimolar reactant ratio, as well as with a molar excess of thiol acid, no diadduct formation was observed on nmr analysis of the product mixtures obtained from butadiene and allene. The corresponding monoadducts were formed in high selectivities, and pure samples of the major products were isolated on fractional distillation *in vacuo* (Table I).

In general, the nmr spectra of dialkylthiophosphates (Table II) resemble those of the corresponding dialkyldithiophosphates. A special characteristic is the additional splitting of the protons on the α carbon due to spin–spin coupling to the phosphorus nucleus ($I = {}^{1}/_{2}$) through the P–S–C or P–O–C bonds. Therefore, the O-methylene protons in O,O′-diethylthiophosphates appear as a double quartet, and the methine protons of O,O′-diisopropylthiophosphates exhibit a multiplet. The methyl protons of the O-ethyl and O-isopropyl groups show the expected splitting into a triplet and doublet, respectively.

From nmr analysis of the dialkylthiophosphoric acid–olefin adducts (the dialkylthiophates), 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 II). In addition, 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 (Table II). A strong infrared absorption at 1255 cm^{-1} due to the P=O stretching vibration[11a] also aided in assigning a thiol ester structure to the adducts.

1-Pentene.—Equimolar amounts of diethyl- or diisopropylthiophosphoric acids and 1-pentene afforded

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(1) G. Schrader, "Die Entwicklung neuer Insektizider Phosphorsäure-Ester," Verlag Chemie GMBH, Weinheim/Bergstr., Germany, 1963.

(2) K. Sasse, "Methoden der Organischen Chemie," Vol. XII/2, Houben-Weyl, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1964, p 652–681.

(3) W. H. Mueller and A. A. Oswald, *J. Org. Chem.*, **31**, 1894 (1966).

(4) L. A. Miller and G. H. Birum, U. S. Patent 3,059,014 (1962); G. Schrader, German Patent 1,070,171 (1959).

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

(6) A. A. Oswald, K. Griesbaum, D. N. Hall, and W. Naegele, 148th National Meeting of the American Chemical Society, Division of Petroleum Chemistry, Chicago, Ill., Sept 1964, Reprints, Vol. 9, 1964, No. 3, p 29.

(7) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

(8) K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963).

(9) A. A. Oswald, K. Griesbaum in "Organic Sulfur Compounds," Vol. 2, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1966, Chapter 9.

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

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons Inc., New York, N. Y., 1959: (a) p 312; (b) p 319; (c) p 351.

TABLE I

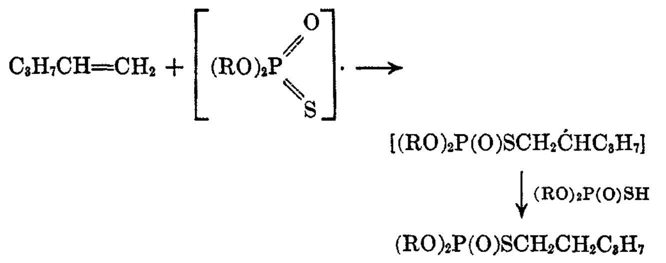
DIETHYL- AND DIISOPROPYLTHIOPHOSPHORIC ACID-OLEFIN MONOADDITIONS AND SOME PHYSICAL-ANALYTICAL DATA OF THE PRODUCTS

$(RO)_2P(O)SR'$

Olefin	Thiophosphoric acid	Moles of thio acid per mole of olefin	Conversion,[a] mole, %	Selectivity[b] for adduct, %	Adduct: Structure: R′	Adduct: Structure: R	Adduct: Formula	Adduct: Bp uncor (mm), °C	Adduct: $n^{20}D$	Calcd, %: C	Calcd, %: H	Calcd, %: P	Calcd, %: S	Found, %: C	Found, %: H	Found, %: P	Found, %: S
1-Pentene	$(C_2H_5O)_2P(O)SH$	1:1	41	100	$n\text{-}C_5H_{11}$	C_2H_5	$C_9H_{21}O_3PS$	88–89 (0.18)	1.4583	44.99	8.75	12.90	13.35	45.10	9.03	12.37	13.74
	$[(CH_3)_2CHO]_2P(O)SH$	1:1	43	100	$n\text{-}C_5H_{11}$	$i\text{-}C_3H_7$	$C_{11}H_{25}O_3PS$	85–86 (0.15)	1.4525	49.23	9.39	11.54	11.95	49.53	9.13	11.40	11.88
1,3-Butadiene	$(C_2H_5O)_2P(O)SH$	2:1	43	>91	$CH_2CH{=}CHCH_3$	C_2H_5	$C_8H_{17}O_3PS$	79.5–80 (0.18)	1.4759	42.86	7.59	13.84	14.28	43.19	7.66	13.80	14.43
	$[(CH_3)_2CHO]_2P(O)SH$	2:1	52	>88	$CH_2CH{=}CHCH_3$	$i\text{-}C_3H_7$	$C_{10}H_{21}O_3PS$	68–69 (0.07)	1.4670	47.62	8.33	12.30	12.70	47.28	8.25	11.93	12.83
Allene	$(C_2H_5O)_2P(O)SH$	2:1	62	84	$CH_2CH{=}CH_2$	C_2H_5	$C_7H_{15}O_3PS$	70–70.5 (0.25)	1.4724	40.00	7.14	14.76	15.23	40.27	7.12	14.80	15.18
	$[(CH_3)_2CHO]_2P(O)SH$	2:1	52	85	$CH_2CH{=}CH_2$	$i\text{-}C_3H_7$	$C_9H_{19}O_3PS$	62–63 (0.13)	1.4637	45.36	8.04	12.99	13.45	45.71	8.10	12.68	13.48

[a] Based on weight of product isolated; semiquantitative nmr analyses before work-up indicated 5–10% higher conversions. [b] Area per cent obtained from glpc analyses.

SCHEME I



O,O′-dialkyl S-pentyl thiophosphates as the sole products as indicated by glpc analysis (Scheme I).

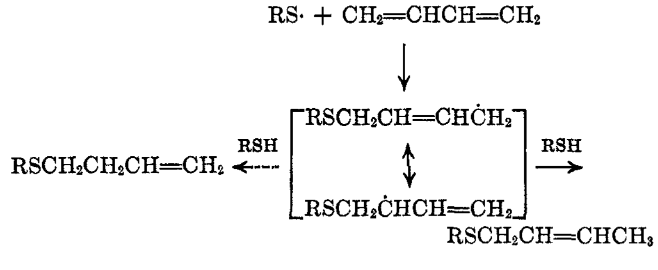
The assignment of a terminal position for the thiol ester group in the adduct is based on its nmr spectrum (Table II) which shows a double α-methylene triplet from splitting by the two β protons and the phosphorus nucleus.

Prolonged irradiation up to 70 hr or the addition of chemical initiators such as peroxides or azo compounds at temperatures up to 100° did not raise the conversions above 50%. However, with an increasing excess of thiophosphoric acid, the conversions improved so that half of the excess acid always reacted with the olefin (Table III).

In a competition experiment with O,O′-diethyldithiophosphoric acid and O,O′-diethylthiophosphoric acid, the relative reactivity of the latter acid toward *n*-pentene was found to be much lower. Equimolar amounts of the two acids and 1-pentene produced 97% of the dithiophosphoric acid adduct and 3% of the corresponding thiophosphate (glpc).

Butadiene.—The addition of O,O′-diethyl- or O,O′-diisopropylthiophosphoric acids to 1,3-butadiene occurred with at least 90% selectivity forming the 1,4 adduct, O,O′-dialkyl S-(2-butenyl) thiophosphates (Scheme II). Glpc analysis of the crude product revealed two impurities of approximately 5% each in addition to this adduct. These by-products had slightly longer glpc retention times than the major 1,4 adduct. One of these minor components is likely to be the O,O′-dialkyl S-(3-butenyl) thiophosphate derived from 1,2 addition to 1,3-butadiene.

SCHEME II



The disubstituted ethylene structure of the 1,4 adducts is clearly indicated by their nmr spectra (Table II). They show the two vinyl protons as a partially resolved multiplet of the MN portion of an A_2MNX_3 spin system.[12] The two methylene protons on the carbon α to the sulfur show a pair of doublets split by the vinyl proton on the adjacent carbon and by the phosphorus nucleus through the C–S–P bonds. The

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[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959: (a) p 242; (b) pp 400–421.

TABLE II

NMR PARAMETERS OF DIETHYL- AND DIISOPROPYLTHIOPHOSPHORIC ACID AND THEIR MONOADDUCTS

$(RO)_2P(O)SR'$

R′: Group structure 1 2 3 4	R′: Group chemical shift[a] 1	2	3	4	J_{PSCH} cps	R: Group structure	R: Chemical shift CH	CH_2	CH_3	J_{POCH}, cps
H	s 7.88					C_2H_5		Dq 4.15	t 1.36[b]	10
H	s 8.10					i-C_3H_7	m 4.72		d 1.33[g]	10
CH_2CH_3	Dq 2.83[b]	t 1.34			15	C_2H_5		Dq 4.11	t 1.34[b]	9
$CH_2(CH_2)_3CH_3$	Dt 2.80[c]	m 1.1–1.9	t 0.91		15	C_2H_5		Dq 4.11	t 1.33[b]	9.5
$CH_2(CH_2)_3CH_3$	Dt 2.78[c]	m 1.1–2.0	t 0.92		14.5	i-C_3H_7	m 4.67		d 1.32[g]	9
$CH_2CH{=}CHCH_3$	Dd 3.37[d]	m 5.60		d 1.70[e]	15	C_2H_5		Dq 4.08	t 1.33[b]	9.5
$CH_2CH{=}CHCH_3$	Dd 3.40[d]	m 5.60		d 1.69[e]	15	i-C_3H_7	m 4.66		d 1.32[g]	9.5
$CH_2CH{=}CH_2$	Dd 3.43[f]	m 5.86	m ~5.25		15	C_2H_5		Dq 4.11	t 1.33[b]	9.5
$CH_2CH{=}CH_2$	Dd 3.43[f]	m 5.83	m ~5.25		15	i-C_3H_7	m 4.67		d 1.32[g]	9.5

[a] In carbon tetrachloride with tetramethylsilane (TMS) as an internal standard. [b] $J_{CH_2CH_3} = 7$ cps. [c] $J_{CH_2CH_2} = 7$ cps. [d] $J_{CH_2CH=} = 5.5$ cps. [e] $J_{CH_3CH=} = 5$ cps. [f] $J_{CH_2CH=} = 6.5$ cps. [g] $J_{CH_3CH} = 6$ cps.

TABLE III

INCREASE OF ADDUCT FORMATION WITH EXCESS O,O′-DIETHYLTHIOPHOSPHORIC ACID

$C_3H_7CH{=}CH_2 + (C_2H_5O)_2P(O)SH \longrightarrow (C_2H_5O)_2P(O)SC_5H_{11}$

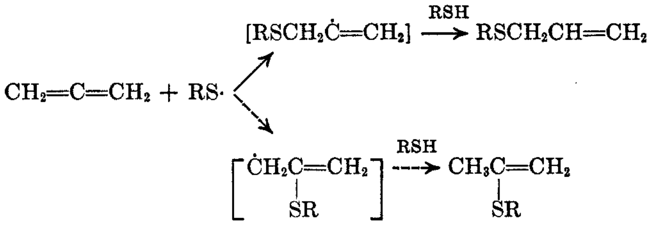
Excess thio acid, %	Yield of adduct, %: Found[a]	Calcd[b]
0	50	50
25	63	62.5
75	92	87.5
100	100	100

[a] Semiquantitative nmr analyses and/or titration of excess acid with 0.1 *N* NaOH. [b] Based on the assumption that 2 moles of acid are necessary for the formation of 1 mole of adduct (see Discussion).

methyl protons of the butenyl group appear as a doublet split by the vinyl proton on the adjacent carbon. Weak shoulders on each peak of this doublet are probably due to long-range coupling of the vinyl proton with the methyl group.

Allene.—The terminal adducts, O,O′-dialkyl S-allyl thiophosphates, were obtained in 85% selectivity from O,O′-diethyl- or O,O′-diisopropylthiophosphoric acid additions to allene (Scheme III).

SCHEME III



Glpc analysis of the product mixtures showed, in addition to the terminal adduct, 15% of the isomeric thiophosphate derived from a center attack of the phosphorylthiyl radical to allene. The retention time of this isomer is little shorter than that of the terminal adduct. A third component with a somewhat longer retention time than the terminal adduct constituted approximately 10% of the total product mixture. This by-product is presumably due to oligomer formation during the reaction.

The allyl structure of the terminal adducts was confirmed by their nmr spectra (Table II). A partially resolved multiplet indicates the terminal vinyl protons, and a multiplet at somewhat lower field is indicative for the interior vinyl proton. For the allylic methylene protons, a pair of doublets appears which is quite similar to that of the crotylic methylene protons in the 1,4 adducts of butadiene.

While the terminal adducts were isolated in a pure state by fractional distillation, the center adducts were only obtained as enriched mixtures together with the terminal adducts. Elemental analysis of such a mixture containing 33% (glpc) of the center adduct confirmed its isomeric nature. The structural assignment is based on the appearance of an nmr singlet somewhat broadened due to long-range splitting at 2.15 ppm for the methyl protons of the propenyl group and the distinct decrease of the integral value for the multiplet of the interior vinyl proton compared with that arising for the terminal vinyl hydrogens in the enriched mixture.

Discussion

The formation of a P–S–C bond rather than that of a P–O–C bond during the free-radical addition of dialkylthiophosphoric acids to olefins parallels the results of nucleophilic displacement reactions with their salts.[1,2] Analogously, free-radical additions of thiolacetic acid to olefins have been reported to form thiol esters exclusively.[7,13]

Free-radical addition of dialkyldithiophosphoric acids to monoolefins, *e.g.*, *n*-octene, was first reported by Bacon and LeSuer.[14] In the absence of a free-radical initiator, they observed a product with a Markovnikov orientation, and, in the presence of peroxides, they obtained one with an anti-Markovnikov orientation. However, in the present study no addition of diethylthiophosphoric acid to 1-pentene occurred in the absence of free-radical initiators.

The course of dialkylthiophosphoric acid addition to 1,3-butadiene and allene also indicates an exclusively free-radical mechanism. As expected, the factors determining the course of such monoadditions do not differ from those of analogous additions of dialkyldithiophosphoric acids or simple thiols. These were extensively discussed for both butadiene[5,15,16] and allene[6,8,17] in previous papers. A remarkable difference,

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

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

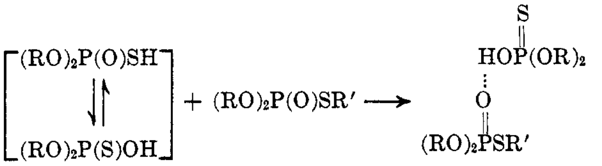
(15) A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961).

(16) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *ibid.*, **27**, 2439 (1962).

(17) T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

however, is the virtual absence of diadducts in the dialkylthiophosphoric acid additions.

The unusually low conversions of dialkylthiophosphoric acid–olefin additions can be overcome by using a molar excess of diethylthiophosphoric acid adding agent in the case of 1-pentene. The linear dependence of adduct formation on excess acid (Table III) suggests hydrogen-bonded complexing of the acid by the adduct formed. The experimental yields agree nicely with the calculated values based on the postulate that 1 mole of acid complexes with 1 mole of adduct and thus becomes unavailable for hydrogen abstraction (Table III). An increase in adduct formation with excess acid was also observed with butadiene and allene, although no correlation was attempted in these experiments. The consistently lower conversions observed in these latter cases are probably due to the less defined reaction conditions in the liquid–gas phase systems and to some oligomer formation.



$$\left[\begin{array}{c}(RO)_2P(O)SH\\ \downarrow\!\uparrow\\ (RO)_2P(S)OH\end{array}\right] + (RO)_2P(O)SR' \longrightarrow \begin{array}{c}\overset{\displaystyle S}{\overset{\|}{HOP}}(OR)_2\\ \vdots\\ O\\ \|\\ (RO)_2PSR'\end{array}$$

A 9° temperature rise observed on mixing of equimolar amounts of O,O′-diethyl S-pentyl thiophosphate and diethylthiophosphoric acid is consistent with the formation of a hydrogen-bonded complex. The relative extent of hydrogen bonding in mixtures of O,O′-diethylthiophosphoric acid and O,O′-diethyldithiophosphoric acid with the corresponding *n*-pentyl esters was obtained from infrared and nmr shifts of the acidic protons (Table IV). In general, an infrared shift of the POH or PSH stretching vibration to a lower frequency is indicative of hydrogen bonding.[11b,c] The observed downfield shifts of POH and PSH protons in the nmr spectra of these mixtures should also reflect the extent of hydrogen bonding since it is common knowledge that acidic protons participating in hydrogen bonding are shifted downfield.[12b]

From the shifts shown in Table IV, it becomes evident that hydrogen bonding of both thiophosphoric and dithiophosphoric acid to the P═O takes place. Very little or no hydrogen bonding occurs with the P═S grouping which is in agreement with the observed quantitative addition of O,O′-dialkyldithiophosphoric acids to unsaturates.[5,6]

TABLE IV

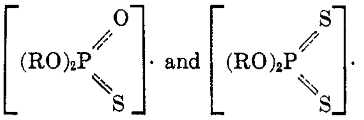
SH AND OH STRETCHING FREQUENCIES AND CHEMICAL SHIFTS OF ADDUCT–ACID MIXTURES IN REFERENCE TO THE ACID

Adduct + acid[a]	POH and/or PSH			
R = C_2H_5, R′ = *n*-C_5H_{11}	ν_{max}^{film}, cm^{-1}	$\Delta\nu$, cm^{-1}	δ, ppm[b]	$\Delta\delta$, ppm
$(RO)_2P(O)SH \rightleftharpoons (RO)_2P(S)OH$	2340	0	7.63	0
$(RO)_2P(O)SR' + (RO)_2P(S)OH$	2330	−10	8.83	−1.20
$(RO)_2P(S)SR' + (RO)_2P(S)OH$	2400	+60	7.25	+0.38
$(RO)_2P(S)SH$	2460	0	3.70	0
$(RO)_2P(O)SR' + (RO)_2P(S)SH$	2410	−50	4.69	−0.99
$(RO)_2P(S)SR' + (RO)_2P(S)SH$	2460	0	3.80	−0.10

[a] Equimolar mixtures. [b] Neat mixtures with TMS as an internal standard.

Unfortunately, the spectral data do not show to what extent the hydroxyl or the thiol form of O,O′-diethylthiophosphoric acid is involved in the observed complexing. It was shown, however, that diethyldithiophosphoric acid adds readily under ultraviolet initiation to 1-pentene in the presence of 1 equiv of O,O′-diethyl S-pentyl thiophosphate. If a formal comparison of thiophosphoric and dithiophosphoric acids is possible, this result suggests that the POH rather than the PSH form is involved in the complexing of the thiophosphoric acid.

Finally, the much slower rate of addition of O,O′-diethylthiophosphoric acid to 1-pentene, observed in a competition experiment with O,O′-diethyldithiophosphoric acid, may be due to an unfavorable equilibrium between the thiol and thiono form,[18] since only the thiol form can take part in the hydrogen-abstraction step. It may, however, also reflect the relative stability of the two thiyl radicals in question, *e.g.*



In conclusion, this study has demonstrated the feasibility of free-radical addition of dialkylthiophosphoric acids to unsaturates. Furthermore, it was shown that a molar excess of thiophosphoric acid is necessary to reach a quantitative addition to a 1-olefin.

Experimental Section

Method of Analyses.—The adduct mixtures were analyzed by gas chromatography 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 poly ether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom P. Operation 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.

Nmr spectra were recorded on a Varian Model A-60 proton resonance spectrometer. The infrared spectra were obtained on a Beckman Model IR-10 infrared spectrophotometer.

Starting Materials. Olefins.—1-Pentene of 99% minimum purity was obtained from the Phillips Petroleum Co. The 1,3-butadiene used was a Matheson product of +95% purity. Allene of 98.9% purity (glpc analysis) was also obtained from Matheson.

Dialkylthiophosphoric Acids.—The diethyl hydrogen phosphite, a Matheson product, and the diisopropyl hydrogen phosphite from Virginia Chemicals, employed in the syntheses of the thiophosphoric acids, were distilled prior to use.

O,O′-Diethylthiophosphoric Acid.—The corresponding sodium salt was prepared by the addition of sulfur to sodium diethyl hydrogen phosphite according to Foss.[19] It is a white, hygroscopic solid of mp 214–215° (lit.[20] 181°). The salt was dissolved in water and the free acid was generated on acidification with 3 equiv of concentrated HCl under ice cooling. The O,O′-diethylthiophosphoric acid was then extracted from the aqueous solution with ether and dried over anhydrous magnesium sulfate. Removal of the ether afforded the O,O′-diethylthiophosphoric acid as a tan liquid of approximately 90% purity on the basis of its nmr spectrum. This acid was used for the addition experiments. Fractional distillation afforded a pure sample of the acid: bp 79° (0.18 mm), n^{20}_D 1.4711 [lit.[10] 92–94 (0.5 mm), n^{20}_D 1.4719]. There was no apparent difference observed between the reactions of the distilled and undistilled acid. On titration of the distilled acid in ethanol with 0.1 *N* aqueous NaOH, using phenolphthalein as indicator, 1 equiv of base was consumed. Nmr parameters are given in Table II.

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(18) T. A. Mastryukova, *Khim. i Primenenie Fosfororgan. Soedin., Akad. Nauk SSSR, Kazansk. Filial, Tr. 2 Konf., 1959*, 57 (1962).

(19) O. Foss, *Acta Chem. Scand.*, **1**, 8 (1947).

(20) P. S. Pishchimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

Anal. Calcd for $C_4H_{11}O_3PS$: C, 28.23; H, 6.47; S, 18.82. Found: C, 28.33; H, 6.32; S, 19.25.

O,O′-Diisopropylthiophosphoric Acid.—The free acid was prepared directly by the addition of sulfur to diisopropyl hydrogen phosphite in dioxane according to the method of Kabachnik and Golubeva.[10] The yield (81%) of crude product was comparable to those reported (80–92%). However, nmr analysis of our product indicated 15–20% of impurities which could not be removed by distillation. Purification of the acid was accomplished through its sodium salt employing a method previously used in the case of dialkyldithiophosphoric acids.[14] The impurities removed by this procedure were of a "neutral" nature. Glpc analysis showed the starting hydrogen phosphite in addition to three unidentified components. The O,O′-diisopropylthiophosphoric acid obtained was essentially pure based on its nmr analysis and was used as such for the addition experiments. A sample was distilled for elemental analysis and other physical measurements: bp 79–81° (0.15 mm), $n^{20}D$ 1.4589 [lit.[10] 90° (1.5 mm), $n^{20}D$ 1,4600]. Nmr parameters are recorded in Table II.

Anal. Calcd for $C_6H_{15}O_3PS$: C, 36.35; H, 7.63; S, 16.17. Found: C, 36.29; H, 7.13; S, 15.91.

General Procedure for the Addition of O,O′-Dialkylthiophosphoric Acids to Olefins.—A magnetically stirred mixture of the thio acid and olefin in a sealed quartz tube was irradiated with a 100-w medium-pressure Hanau mercury immersion lamp for 30–40 hr in a water bath at 16 ± 3°. The liquid 1-pentene was allowed to react under a nitrogen atmosphere. The gaseous 1,3-butadiene and allene were condensed into Dry Ice cooled, evacuated tubes containing the thio acid and then allowed to react in the liquid phase under their own vapor pressures. After completion of the irradiation, the tubes were opened and the mixtures were sampled for semiquantitative analysis by nmr spectroscopy. Then the remaining material was diluted with ether and washed with 5% aqueous solution of sodium hydrogen carbonate to remove any unreacted acid. The ether phase was dried over anhydrous magnesium sulfate and then concentrated using a rotary evaporator at 10 mm and room temperature to remove the solvent. The residual crude product was then weighed and analyzed by a combination of glpc and nmr techniques. Part of the product was purified by fractional distillation at 0.1–0.25 mm for analyses. This was frequently accompanied by a partial decomposition yielding considerable amounts of undistillable residue.

Registry No.—$C_9H_{21}O_3PS$, 995-51-7; $C_{11}H_{25}O_3PS$, 10428-93-0; $C_8H_{17}O_3PS$, 10428-94-1; $C_{10}H_{21}O_3PS$, 10428-95-2; $C_7H_{15}O_3PS$, 10428-96-3; $C_9H_{19}O_3PS$, 10428-97-4; O,O′-diethylthiophosphoric acid, 2465-65-8; O,O′-diisopropylthiophosphoric acid, 10428-99-6; in Table II where $R' = CH_2CH_3$ and $R = C_2H_5$, 1186-09-0.

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Arylnorbornane Compounds. III. The 3-Phenyl-2-norbornanols and Derivatives. Preparation and Properties[1,2]

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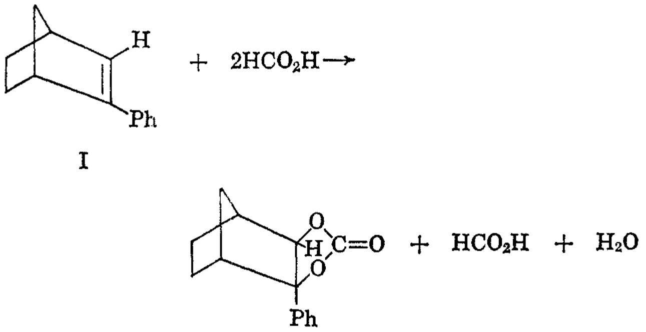
Preparations of the four isomeric 3-phenyl-2-norbornanols are described with particular emphasis on the routes to the more difficultly accessible *exo*-phenyl alcohols. Reduction of 3-*exo*-phenyl-2-norbornanone (VIII) appeared to be the best method for preparing these latter alcohols. Analyses of the infrared and nuclear magnetic resonance spectra are discussed in detail with emphasis on the observable effects of the 2 and 3 substituents.

Two possible mechanisms for the reaction of 2-phenylnorbornene (I) with performic acid to give the carbonate (II),[3] the result of a "*cis*" epoxide ring opening, involve (a) *endo*-phenyl participation at the 3 position followed by reaction of formic acid at C-3 from the *exo* side, a double-inversion process which leads to retention of C-3 configuration;[4] (b) stereoselective *exo* addition of formic acid to the tertiary carbonium ion at C-2, a mechanism similar to that offered by Brewster[5] for configurational retention in styrene-type epoxide openings.



I

II

In order to gain insight on the possibility of mechanism a and because we were interested in the geometrical requirements for aryl participation, we wished to find a norbornyl system whose solvolyses might involve a phenonium ion intermediate of the type postulated for acyclic systems. In addition, we desired to determine the relationship of dihedral angle between an aryl and another functional group on the spectral properties observed by infrared and nuclear magnetic resonance (nmr) spectroscopies. This present paper discusses the methods of preparation and characterization of the four 3-phenyl-2-norbornanols and their tosylate and *p*-nitrobenzoate derivatives.

Methods and Results

The two 3-phenyl-2-norbornanols with *endo*-phenyl substituents III and IV are readily available by hydroboration of I[6] and by hydride reduction of 3-*endo*-

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[2] For parts I and II, see (a) D. C. Kleinfelter and T. E. Dye, *J. Am. Chem. Soc.*, **88**, 3174 (1966); (b) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

[3] D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **83**, 2329 (1961).

[4] For example, see R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957).

[5] J. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956).

[6] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964).