of methyl acetyloleanolate showed no depression, and the infrared spectra were identical.

Anal. Calcd. for $C_{33}H_{46}O_6$: C, 73.57; H, 8.61. Found: C, 73.79; H, 8.63.

Methylmicromerol Bromoacetate.—Methylmicromerol (0.048 g.) in benzene (2.8 ml.) was treated with bromoacetyl bromide (0.1 ml.) and diethylaniline (0.2 ml.) at room temperature for 20 hr. Water and ether were added, and the ethereal solution was washed with water, dilute hydrochloric acid, and water. Evaporation of the ether left a reddish-brown oil which was chromatographed on Davidson silica gel to give a colorless oil which crystallized from pentane. Repeated crystallizations from pentane gave crystals suitable for X-ray studies, m.p. 146–150°.

Anal. Calcd. for $C_{33}H_{51}O_4Br$: C, 66.98; H, 8.68; Br, 13.50. Found: C, 67.10; H, 8.63; Br, 13.30.

X-Ray data were collected photometrically from Weissenberg photographs taken on a Nonius camera which was set to integrate in two directions.[18] Levels $h = 0$ to $h = 5$ were taken on a crystal rotating about the a axis. The final parameters relative to the conventional origin[19] are given in Table I. The final over-all temperature factor was B = 3.29 Å.[2]

Acknowledgment.—This work was supported in part by the National Institutes of Health, grant CY-4082.

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Organic Sulfur Compounds. IX.[1] Addition of Diethyldithiophosphoric Acid to Dienes

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O,O′-Diethyldithiophosphoric acid (phosphorodithioic acid O,O′-diethyl ester) was added by a radical mechanism to a variety of diolefins to study the factors determining the formation of the various isomeric monoadducts. Selective monoadditions of diethyldithiophosphoric acid to the unsubstituted olefinic bond in the bicycloheptene part of polycyclic diolefins (*endo*-dicyclopentadiene, Aldrin, 2,5-norbornadiene) could be readily carried out, probably in a *cis–exo* manner. On radical addition of diethyldithiophosphoric acid to 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, and 2,5-dimethyl-2,4-hexadiene, the thiophosphoryl-thiyl radical preferentially attacked the first carbon atom of the basic 1,3-butadiene skeleton in the first propagation step so as to give the more stable intermediate allylic radical. The latter in turn abstracted a hydrogen from the dithiophosphoric acid at the less highly substituted allylic carbon atom to yield the corresponding 1,4- and 1,2-monoadducts. Addition to piperylene, which proceeds *via* a radical intermediate having two secondary allylic carbon atoms, resulted in almost equal quantities of 1,2- and 1,4-adducts.

I. Introduction

The addition of crude O,O′-dialkyldithiophosphoric acids (phosphorodithioic acid O,O′-dialkyl esters) to olefins is a much explored reaction[4] since many of the adducts are important oil additives[4–7] and insecticides.[7–11] Additions of crude dialkyldithiophosphoric acids, which are synthesized from alcohols and phosphorus pentasulfide,[12,13] to unsymmetrical olefins yield the normal addition products according to Markownikoff's rule.[4] This is probably the result of the presence of P_4S_3 in the crude acid. P_4S_3 could reduce the peroxide type catalysts of radical addition.[13]

Bacon and LeSuer[13] added purified O,O′-diethyldithiophosphoric acid (phosphorodithioic acid O,O′-diethyl ester, O,O′-diethylphosphorodithioate) to the monoölefins in an anti-Markownikoff manner. Radical type additions of dialkyldithiophosphoric acids to diolefins, however, remained unexamined. We became interested in the latter reaction in connection with our studies of thiol–diolefin addition reactions.[14–16] At first the reactivity, towards the addition of diethyldithiophosphoric acid, of different types of double bonds in various diolefins containing isolated double bonds was determined and compared to the corresponding thiol additions.[14] Then a study of dialkyldithiophosphoric acid-conjugated diene additions was undertaken to determine whether the "1,2-" or "1,4-mechanism" of these reactions is affected by the same factors as it was in the case of thiol–diene systems.[15,16]

Diethyldithiophosphoric acid was chosen as a reagent because it is readily available and easy to purify.[13] Some polycyclic diolefins—*endo*-dicyclopentadiene, Aldrin, and 2,5-norbornadiene—were selected for the study as diolefins containing isolated double bonds. Simple diolefins—1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, piperylene, and 2,5-dimethyl-2,4-hexadiene—were used as conjugated diolefins.

II. Results

It was found that purified diethyldithiophosphoric acid and other dialkyldithiophosphoric acids readily add at room temperature to most of the diolefins examined (Table I). The addition can be catalyzed by

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

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TABLE I

ADDITION OF DIETHYLDITHIOPHOSPHORIC ACID TO DIOLEFINS[a]

Name of diolefin used	Diethyldithiophosphoric acid reacted, %[b] Without added catalyst	In the presence of cumene hydroperoxide[c]	With ultraviolet irradiation[d]
Dicyclopentadiene	64	67	76
Aldrin	28	42	63
Norbornadiene	99	..[e]	..
2,3-Dimethyl-1,3-butadiene	91	93	..
Isoprene	75	90	..
2,5-Dimethyl-2,4-hexadiene	47	61	57

[a] *n*-Heptane solutions (50 ml. each) containing diethyldithiophosphoric acid and a diolefin, both in 0.5 mole/l. concentration, were stirred for 3 hr. at room temperature in the presence of air. [b] Determined on the basis of the potentiometric titration of the acid left. [c] About 0.02 mole/l. of cumene hydroperoxide was added to the reaction mixture. [d] Round-bottom reaction flask of quartz was irradiated from 20-cm. distance during the reaction. [e] Very exothermic reaction occurred on the addition of the hydroperoxide.

peroxides or ultraviolet light. The distribution of the isomeric products of the catalyzed reactions are the same as those of the noncatalyzed reactions. These facts indicate that the reaction proceeds by a chain mechanism.

Most of the adducts were purified either by crystallization from ethanol or by distillation *in vacuo* (Table II). Simple vacuum fractionation did not result in a complete separation of the isomeric monoadducts. They could be separated, however, on a capillary gas chromatography (g.c.) column coated with a *n*-tridecyl polyethylene glycol ether. Identification of g.c. peaks was possible by semiquantitative determination of the isomers in the product mixtures by nuclear magnetic resonance spectroscopy (n.m.r., Table III). The n.m.r. spectra of diethyldithiophosphoric acid adducts generally resemble those of the corresponding thiol adducts.[14-16] There is one special characteristic of the dithiophosphoric acid adducts: the proton(s) on the α-carbon of the S-alkyl group of the O,O′-dialkyl-S-alkyl dithiophosphate products show an additional splitting of 15 c.p.s. due to electron coupling to the phosphorus nucleus ($I = {}^1/_2$) through the thiolester bond. The O-ethyl groups of the phosphate ester products show a triplet for the methyl protons and a double quartet for the methylene protons. The methylene protons are split into the usual 7-c.p.s. triplet by the methyl protons; this triplet is then split by spin coupling to the phosphorus through the oxygen (10 c.p.s.).

The infrared spectra of the products were also studied (Table IV) but gave little help in structure determination because of the very strong absorption bands of the P—O—ethyl stretching vibration[17a] at about 9.8 μ and of an unassigned vibration at 10.4 μ obscured the out of plane hydrogen deformation vibrations of trans-disubstituted ethylenes[17b] and vinyl compounds.[17c] Another very strong band, probably due to the P═S stretching vibration,[17d] could interfere with possible out of plane hydrogen deformation vibrations of *cis*-disubstituted ethylenes.[17e]

TABLE II

DIETHYLDITHIOPHOSPHORIC ACID–DIENE ADDUCTS

Adduct no.	Starting diene	Adduct formula	Conversion at room temperature %	After hr.	With ultraviolet	Yield,[a] %	Adduct isomers by cap. g.c. (n.m.r.) 1,2-	1,4-	4,1-	B.p.,[b] °C. (mm.) [M.p.]	Calculated C	H	P	S	Found C	H	P	S
II	*endo*-Dicyclopentadiene	$C_{14}H_{21}O_2PS_2$	90	3	No	85	(One major component)			. . .	53.14	6.69	9.79	20.27	52.95	6.79	9.52	20.20
IV	Aldrin	$C_{16}H_{19}Cl_6O_2PS_2$	87	15	No	50				[89.5–90.5]	34.86	3.47	5.62	11.64	34.89	3.49	5.65	11.57
VIII	2,5-Norbornadiene[c]	$C_{15}H_{30}P_2S_4O_4$[c]	90	3	No	51				[96.5–97.5]	38.78	6.51	13.33	27.61	38.74	6.53	13.40	27.56
IX	1,3-Butadiene	$C_8H_{17}O_2PS_2$	95	8	Yes[d]	45	6	94	..	75–76 (1)	39.99	7.13	12.88	26.69	40.08	7.37	12.52	27.32
	2,3-Dimethyl-1,3-butadiene	$C_{10}H_{21}O_2PS_2$	100	24	Yes[d]	77	4	96	..	127–128 (2)	44.76	7.88	11.54	23.90	44.62	7.74	11.37	24.44
X	Isoprene	$C_9H_{19}O_2PS_2$	100	24	Yes[d]	78	..	(90)	..	100–103 (0.5)	42.50	7.52	12.17	25.22	42.34	7.45	11.90	25.40
XI–XIII	Piperylene	$C_9H_{19}O_2PS_2$	98	10	Yes[d]	86	(50)	(40)	(10)	110–113 (1)	42.50	7.52	12.17	25.22	42.60	7.67	12.26	25.43
XIV	2,5-Dimethyl-2,4-hexadiene	$C_{12}H_{25}O_2PS_2$	80	72	Yes[d]	86	(85)	(15)		128–130 (1)	48.63	8.50	10.44	21.64	48.25	8.44	10.17	21.55

[a] Based on conversion. [b] Uncorrected. [c] Diadduct. [d] Vycor reaction flask.

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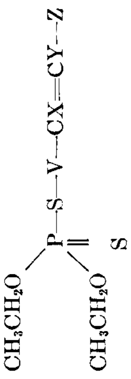
(17) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1959: (a) p. 317; (b) p. 45; (c) p. 49; (d) p. 322; (e) p. 48; (f) pp. 42–43; (g) pp. 35–42.

TABLE III

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF DIETHYLDITHIOPHOSPHORIC ACID–DIENE ADDUCTS



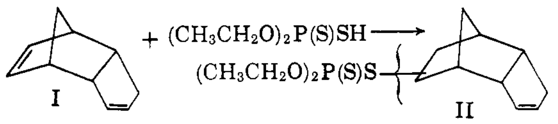
$$(CH_3CH_2O)_2P(=S)\text{—}S\text{—}V\text{—}CX\text{=}CY\text{—}Z$$

Adduct no.	Starting diene	Adduct type	V	X	Y	Z	Isomer by g.c. (n.m.r.) %	CH₃—	—CH₂—O—P(S)—	—S—V—	—CX=	=CY—	—Z
				In general formula of adduct				Chemical shifts of structural units, p.p.m., downfield from tetramethylsilane, internal reference s, singlet, d, doublet, q, quartet, m, multiplet (D double)					
VI	1,3-Butadiene	1,4	CH_2	H	H	CH_3	94	t 1.30^a	Dq 4.12^{a,b}	Dd 3.43^{c,a}	m 4.9–6.1	m 4.9–6.1	d 1.67^e
	2,3-Dimethyl-1,3-butadiene	1,4	CH_2	CH_3	CH_3	CH_3	96	t 1.30^a	Dq 4.13^{a,b}	d 3.51^d	s 1.65^f	s 1.70^f	s 1.70^f
VII	Isoprene	1,4	CH_2	CH_3	H	CH_3	82	t 1.30^a	Dq 4.12^{a,b}	d 3.47^d	s 1.71	q 5.55^a	d 1.61^a
		4,1	CH_2	H	CH_3	CH_3	18						
VIII	Piperylene	1,4	CH_2	H	H	CH_2–CH_3	(40)	t 1.32^a	Dq 4.13^{a,b}	Dd 3.46^{c,d}	m 5.2–5.8		m 1.75–2.2, t 0.97^a
IX		1,2	CH_2–CH_2	H	H	CH_3	(50)	t 1.32^a	Dq 4.13^{a,b}	Dt 2.87,$^{c-e}$ m 2.2–2.5	m 5.2–5.8		d 1.66^e
X		4,1^h	$CH(CH_3)$	H	H	CH_3	(10)			d 1.43			d 0.96^e
XI	2,5-Dimethyl-2,4-hexadiene	1,4^h	$C(CH_3)_2$	H	H	$C(CH_3)_2$	(15)						
		1,2	$C(CH_3)_2$–CH_2	H	CH_3	CH_3	(85)	t 1.32^a	Dq 4.15^{a,b}	s 1.44, d2.42^a	t 5.25^a	s 1.63^i	s 1.74^f

^{a} $J = 7$ c.p.s. ^{b} $J_{P-O-CH_2} = 10$ c.p.s. ^{c} $J = 6$ c.p.s. ^{d} $J_{P-S-CH_2} = 15$ c.p.s. ^{e} $J_{CH-CH_3} = 5$ c.p.s. ^{f} The specific assignment is arbitrary. ^{g} Triplets are enhanced toward high field. ^{h} Definite observation of n.m.r. signal is impossible because of the low concentration of the isomer. ^{i} Due to the protons of the methyl group.

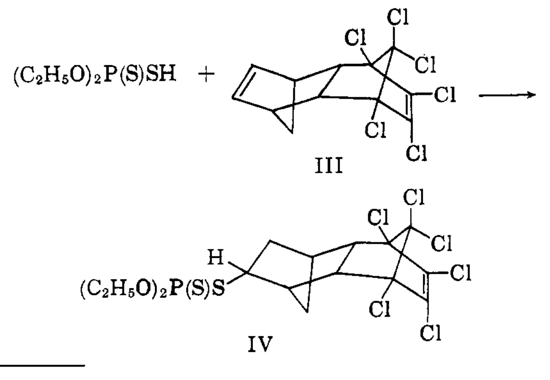
Diolefins with Isolated Double Bonds. Dicyclopentadiene. An equimolar amount of diethyldithiophosphoric acid spontaneously adds to *endo*-dicyclopentadiene[18] (I) at room temperature to yield a light yellow liquid adduct. When a mixture of two moles of diethyldithiophosphoric acid and one mole of dicyclopentadiene reacted in the absence of a catalyst, one mole of the dithiophosphoric acid was recovered unchanged. This showed that normally only one double bond of the dicyclopentadiene takes part in the addition reaction to form S-5 or/and 6-(3a,4,5,6,7,7a-hexahydro-4,7-methano)indenyl O,O′-dialkyldithiophosphate (or phosphorodithioate), II.

Capillary g.c. indicated two major components. Comparison of the n.m.r. and infrared spectra (Tables III, IV) with those of dicyclopentadiene and of the 4-chlorobenzenethiol–dicyclopentadiene monoadduct indicated that in both cases addition of the thiol group to the bicycloheptene double bond had occurred. The triplet signal at 5.9 p.p.m. downfield from the tetramethylsilane internal reference, originating from vinylic hydrogens of the bicycloheptene part of the dicyclopentadiene molecule, was absent. The singlet signal of the vinylic hydrogens of the cyclopentenyl moiety at about 5.5 p.p.m., on the other hand, was retained in the adduct. The *endo* structure of the dicyclopentadiene ring system was probably preserved.



Aldrin.—An equimolar amount of diethyldithiophosphoric acid readily reacts with Aldrin (III), a widely used insecticide,[19] in a spontaneous, somewhat exothermic reaction to yield a crystalline adduct. The reaction can be catalyzed by a peroxide or ultraviolet light. A second molecule of diethyldithiophosphoric acid could not be added to the Aldrin molecule without catalysis.

N.m.r. spectra showed that the vinylic protons which gave signals at a low field (6.35 p.p.m.) in Aldrin were absent in both the diethyldithiophosphoric acid and the 4-chlorobenzenethiol adduct. Therefore, it was assumed that diethyldithiophosphoric acid, like thiols,[14,20] adds to Aldrin in a *cis–exo*-manner to yield *exo*-2-diethylthiophosphorylmercapto-*endo*-5,6,7,-



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(18) A. Etart and P. Lambert, *Compt. rend.*, **112**, 945 (1891).

(19) C. W. Kearns, C. J. Weinman, and G. C. Decker, *J. Econ. Entomol.*, **42**, 127 (1949); R. E. Lidov, U. S. Patent 2,635,979.

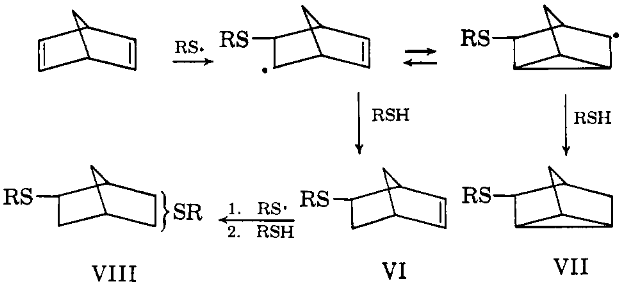
(20) S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 6039 (1957).

8,9,9 - hexachloro - *exo* - *endo* - 1,2,3,4,4a,5,8,8a - octahydro-1,4,5,8-dimethanonaphthalene, IV.

Norbornadiene.—The synthesis of a monoadduct of diethyldithiophosphoric acid and norbornadiene (V) has been described in a U. S. patent.[7] Monoaddition of 4-toluenethiol to norbornadiene by Cristol, Brindell, and Reeder[21] resulted in the formation of *exo*-5-norbornen-2-yl 4-tolyl sulfide and 3-nortricyclyl 4-tolyl sulfide in a 2:3 ratio.

We found that the synthesis of the diethyldithiophosphoric acid–norbornadiene monoadduct yields two major components in about 2:1 ratio.

On the addition of a second mole of diethyldithiophosphoric acid, the larger component gave a crystalline diadduct. This indicated that the main product of the monoaddition was probably O,O′-diethyl-S-*exo*-5-norbornen-2-yl dithiophosphate (phosphorodithioate) (VI) and the minor product was O,O′-diethyl-S-3-nortricyclyl dithiophosphate (VII).



The sharp melting point of the diadduct obtained indicated a uniform compound (VIII). Elemental analyses (Table II), n.m.r., and infrared spectra (Table IV) of the compound supported the formation of a diadduct with a concurrent disappearance of unsaturation. The exact position of the addition of the second diethyldithiophosphorylthiyl radical could not be determined.

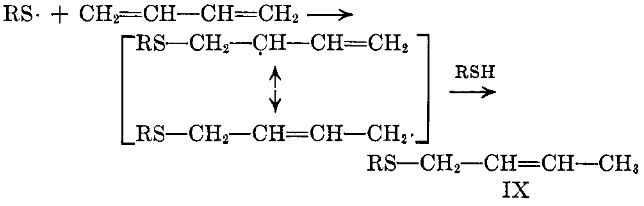
A similar crystalline diadduct of benzenethiol to norbornadiene was also obtained.

Diolefins with Conjugated Double Bonds.—On radical addition of various thiols to conjugated diolefins it was found that the adduct is derived from the intermediate allylic radical at the less highly substituted carbon atom.[15,16] It was of interest to determine whether the same rule holds for additions of dialkyldithiophosphoric acids.

Butadiene.—Addition of an equimolar amount of diethyldithiophosphoric acid to 1,3-butadiene could be catalyzed by ultraviolet irradiation. Capillary g.c. showed that the adduct was 95% one isomer.

The disubstituted ethylene structure of the adduct is clearly indicated by its n.m.r. spectrum (Table III). Two *trans*-vinyl protons show up as an incompletely resolved multiplet representing the MN portion of a A_2MNX_3 spin system.[22] The signal of the methylene protons on the carbon α to the sulfur is split into a double doublet with 6 c.p.s. coupling to the vinyl proton on the adjacent carbon, and 15 c.p.s. coupling to phosphorus through the sulfur. The methyl protons of the 2-butenyl group can be clearly recognized as a doublet at about 1.7 p.p.m.

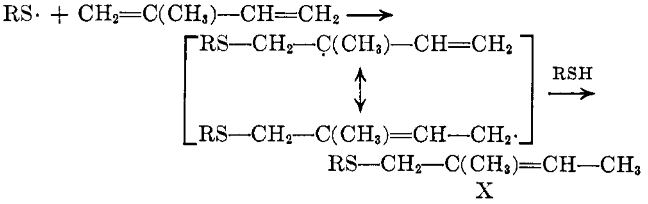
On the basis of g.c. and n.m.r. analyses, it is assumed that the addition of diethyldithiophosphoric acid to butadiene took place in an essentially 1,4-*trans* manner to yield O,O′-diethyl-S-2-buten-1-yl dithiophosphate (phosphorodithioate) (IX).



$$RS\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \left[\begin{array}{c} RS{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \\ \updownarrow \\ RS{-}CH_2{-}CH{=}CH{-}CH_2\cdot \end{array}\right] \xrightarrow{RSH} \underset{\text{IX}}{RS{-}CH_2{-}CH{=}CH{-}CH_3}$$

Dimethylbutadiene.—Capillary gas chromatography of the 1:1 adduct of diethyldithiophosphoric acid and 2,3-dimethyl-1,3-butadiene showed that the main isomer was formed in more than 96% yield. This was shown by n.m.r. to be the 1,4-adduct, O,O-diethyl-S-(2,3-dimethyl)buten-1-yl dithiophosphate (Table III). No vinylic protons resulting from 1,2-addition could be observed in the spectra. The virtual absence of 1,2-addition is also indicated by the doublet methylene signal which is split only by the phosphorus. The protons of the three methyl groups of the adduct show two signals, one of them of double intensity. The less intensive signal is probably due to the methyl group on the carbon α to the methylene, since that methyl group is situated differently from the other two methyl groups. The absence of a =C—H stretching band and the weak C=C stretching band[17f] (Table IV) in the infrared spectrum indicate that the 1,2-isomer is not present.

Isoprene.—Capillary gas chromatography (Table III) of the undistilled adduct of diethyldithiophosphoric acid and isoprene (2-methyl-1,3-butadiene) showed essentially two components present in about 1:4 ratio. N.m.r. analyses (Table II) indicated that the main component was the 1,4-adduct (X). The formation of this compound could be rationalized by the following mechanism.



$$RS\cdot + CH_2{=}C(CH_3){-}CH{=}CH_2 \longrightarrow \left[\begin{array}{c} RS{-}CH_2{-}\dot{C}(CH_3){-}CH{=}CH_2 \\ \updownarrow \\ RS{-}CH_2{-}C(CH_3){=}CH{-}CH_2\cdot \end{array}\right] \xrightarrow{RSH} \underset{\text{X}}{RS{-}CH_2{-}C(CH_3){=}CH{-}CH_3}$$

Methylene protons of the 1,4-adduct are represented by a doublet with a 15 c.p.s. coupling constant to phosphorus through sulfur. One methyl group signal appears as a singlet while the other is split into a doublet by the single vinyl proton. The presence of a possible "reverse," 4,1-adduct, in contrast to the reverse-adducts of thiol-isoprene additions,[16] could not be ascertained by n.m.r.

No terminal vinyl unsaturation corresponding to a 1,2- or 4,3-adduct could be observed in the n.m.r. spectrum. The infrared spectrum supports the proposed structures by excluding the presence of the 1,2- or 4,3-adducts. The absence of a distinct =C—H stretching band[17c] and the weak C=C stretching band[17f] indicate that these structural units (vinyl or unsaturated methylene group) are absent in the product.

N.m.r. indicated changes on the distillation *in vacuo* of the adduct which could not be interpreted.

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[21] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

[22] 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, p. 242.

TABLE IV

INFRARED ABSORPTION SPECTRA OF DIETHYLDITHIOPHOSPHORIC ACID–DIENE ADDUCTS

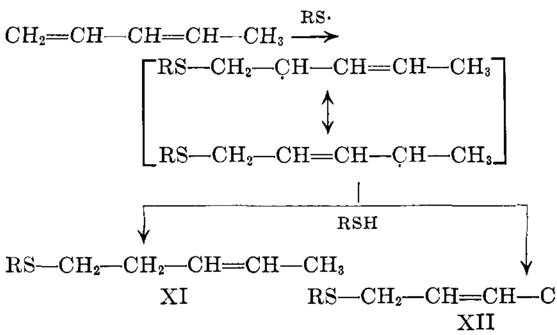
Diethyldithiophosphoric acid adduct			Stretching region		Characteristic Fingerprint region (including P–O–Et				
Adduct no.	Starting diene	Isomer type	=C—H	C=C					
I	Dicyclopentadiene	Monoadduct	3.30 s	6.20 w	8.04 i		*8.60 s*		9.10 s
II	Aldrin	*exo*-2-		6.23 s	8.00 m	8.48 s	*8.58 m*	8.71 w	9.00 s
V	Norbornadiene	Diadduct			8.10 m	8.43 m	*8.58 s*	8.75 i	9.10 s
VI	1,3-Butadiene	1,4-	3.32 i	6.00 m	8.16 s		*8.63 s*		9.10 s
	2,3-Dimethyl-1,3-butadiene	1,4-		6.00 m	8.12 m	8.38 m	*8.60 s*		9.10 s
VII	Isoprene	1,4-	3.29 i	6.02 m	8.10 m	8.29 m	*8.62 s*		9.13 s
VIII–IX	*trans*-Piperylene	1,2- and 1,4-	3.31 i	6.01 w	8.18 m		*8.60 s*		9.10 s
XI	2,5-Dimethyl-2,4-hexadiene	1,2-	3.26 i	6.00 m	8.25 m	8.38 m	*8.60 s*	8.92 s	9.10 s
	(Diethyldithiophosphoric acid reference)		4.05 s[a]				*8.60 s*		9.10 s

[a] Due to SH stretching.

Piperylene.—As a starting material for the addition, an equimolar amount of pure *trans*-piperylene (*trans*-1,3-pentadiene) was used. After the addition of 95% of the calculated amount of diethyldithiophosphoric acid, the unchanged piperylene was isomerized. Separation of the monoadducts by capillary g.c. showed two major peaks which are not completely separated and a small peak of much shorter retention time. Possible configurational isomers of the addition products were apparently not separated.

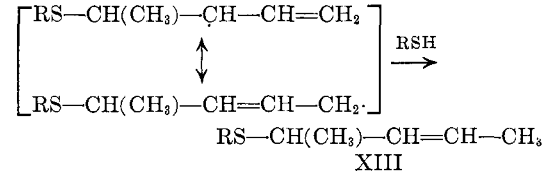
N.m.r. (Table III) indicated that the two major components of the product mixtures were the 1,2- and 1,4-adducts (XI and XII). The 1,4-isomer showed a double doublet similar to that of the 1,4-butadiene adduct for the methylene protons. The methyl protons of this isomer were split into a triplet by the adjacent methylene protons. The 1,2-isomer could be easily recognized from the doublet signal of the single methyl group of the pentenyl moiety. One of the two methyl doublets of the 4,1-adduct is almost obscured by the methyl triplets of the ethyloxy groups while the other virtually coincides with the methyl doublet of the 1,2-isomer. No significant amount of 4,3-adduct was formed since signals of terminal vinylic protons were absent from the infrared (Table IV) and n.m.r. spectra of the product.

The addition of diethyldithiophosphoric acid to piperylene apparently proceeds in the same manner as the addition of thiols. The diethylthiophosphorylmercapto radical preferentially adds to the first carbon atom of piperylene to yield the more stable allylic radical intermediate, having both of its reactive positions at a secondary carbon. Subsequent hydrogen abstraction from the dithiophosphoric acid then occurs at these carbons to yield the isomeric O,O′-diethyl-S-pentenyl dithiophosphates (phosphorodithioates), XI and XII.



$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_3} \xrightarrow{\mathrm{RS\cdot}} \left[\begin{array}{c} \mathrm{RS{-}CH_2{-}\dot{C}H{-}CH{=}CH{-}CH_3} \\ \updownarrow \\ \mathrm{RS{-}CH_2{-}CH{=}CH{-}\dot{C}H{-}CH_3} \end{array}\right] \xrightarrow{\mathrm{RSH}} \underset{\mathrm{XI}}{\mathrm{RS{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3}} + \underset{\mathrm{XII}}{\mathrm{RS{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3}}$$

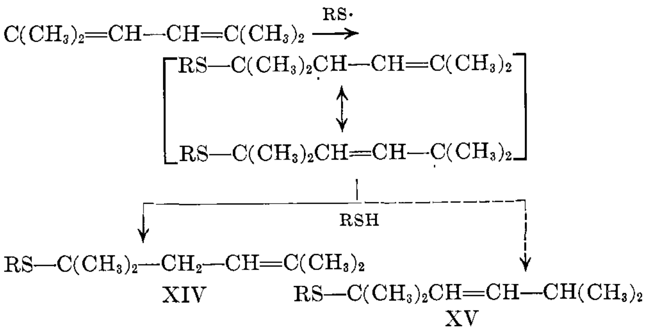
The small amount of 4,1-adduct (XIII) probably results from addition to carbon four of piperylene, followed by hydrogen abstraction at the primary carbon.



$$\mathrm{CH_3{-}CH{=}CH{-}CH{=}CH_2} \xrightarrow{\mathrm{RS\cdot}} \left[\begin{array}{c} \mathrm{RS{-}CH(CH_3){-}\dot{C}H{-}CH{=}CH_2} \\ \updownarrow \\ \mathrm{RS{-}CH(CH_3){-}CH{=}CH{-}CH_2\cdot} \end{array}\right] \xrightarrow{\mathrm{RSH}} \underset{\mathrm{XIII}}{\mathrm{RS{-}CH(CH_3){-}CH{=}CH{-}CH_3}}$$

Dimethylhexadiene.—The addition of diethyldithiophosphoric acid to 2,5-dimethyl-2,4-hexadiene, like that of thiols, required ultraviolet light initiation and a longer reaction time. Gas chromatography of the product showed again a single major component.

Examination of the monoadduct by n.m.r. (Table III), in contrast to the other diene adducts examined, indicated that the main isomer was the 1,2-adduct (XIV). The spectrum showed a characteristic doublet at 2.42 p.p.m. for the methylene protons which are expected to be absent in the 1,4-adduct (XV). The vinyl proton resonance pattern also showed a characteristic triplet at 5.25 p.p.m. as a result of spin splitting by the adjacent methylene group. The isomeric dimethylhexenyl structures could be distinguished on the basis of the relative chemical shifts and splittings of their terminal methyl group signals. The two methyl groups on the unsaturated carbon atom of the 1,2-adduct produced separate singlet peaks as a result of their *cis* and *trans* locations with respect to the single vinyl proton. The signal of the corresponding methyl groups of the 1,4-adduct appears at a higher field and is split into a doublet by the single methine proton. The other signals of the 1,4-adduct cannot be observed in the spectrum because of the low concentration of this isomer. On the basis of the n.m.r. analysis it is con-



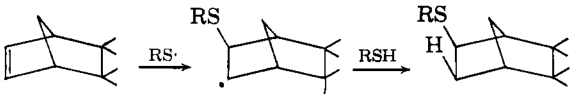
$$\mathrm{C(CH_3)_2{=}CH{-}CH{=}C(CH_3)_2} \xrightarrow{\mathrm{RS\cdot}} \left[\begin{array}{c} \mathrm{RS{-}C(CH_3)_2\dot{C}H{-}CH{=}C(CH_3)_2} \\ \updownarrow \\ \mathrm{RS{-}C(CH_3)_2CH{=}CH{-}\dot{C}(CH_3)_2} \end{array}\right] \xrightarrow{\mathrm{RSH}} \underset{\mathrm{XIV}}{\mathrm{RS{-}C(CH_3)_2{-}CH_2{-}CH{=}C(CH_3)_2}} + \underset{\mathrm{XV}}{\mathrm{RS{-}C(CH_3)_2CH{=}CH{-}CH(CH_3)_2}}$$

absorption peaks, microns, vs, very strong, m, medium, w, weak, i, inflection												
above eight microns stretching vibrations)				=C—H deformation region (including P=S stretching)								
		9.60 vs	*9.80 vs*	10.45 vs		11.15 m	11.87 i	12.15 vs		13.55 s	14.95 vs	*15.15 vs*
9.15 m	9.27 m	9.56 vs	*9.80 vs*	10.40 vs	10.96 s	11.21 m	11.55 w	12.03 s	12.28 s	14.48 m	14.70 m	*15.15 vs*
		9.56 vs	*9.80 vs*	10.40 vs		11.06 m	11.58 w	12.10 s	12.30 s		14.88 vs	*15.10 vs*
		9.60 vs	*9.85 vs*	10.45 vs				12.10 s			14.90 vs	*15.15 vs*
		9.60 vs	*9.80 vs*	10.45 vs		11.25 i		12.10 vs			14.95 vs	*15.23 vs*
		9.60 vs	*9.80 vs*	10.45 vs		11.15 i	11.50 w	12.20 vs			14.95 vs	*15.23 vs*
		9.60 vs	*9.80 vs*	10.45 vs				12.10 vs	12.30 vs		14.85 vs	*15.20 vs*
		9.60 vs	*9.80 vs*	10.45 vs			11.70 m	12.15 vs	12.30 vs		14.95 vs	*15.20 vs*
		9.60 vs	*9.80 vs*	10.50 vs			11.85 vs			13.00 vs	14.95 vs	*15.15 vs*

cluded that the main addition product is the 1,2-isomer, O,O′-diethyl-S-2-(2,5-dimethyl-4-hexen)yl dithiophosphate, XIV. Its formation can be explained by the mechanism on p. 1266, bottom of col. 2.

III. Discussion

Diethyldithiophosphoric acid and some other dialkyldithiophosphoric acids (*e.g.*, O,O′-dialkylphosphorodithioates) can be readily and selectively added by a radical mechanism to nonconjugated diolefins having a reactive unsubstituted bicyclo[2.2.1]heptene group. The n.m.r. spectra of these monoadducts were very similar to those of the corresponding thiol monoadducts. Since the stereochemistry of the thiol adducts is known,[13,20,21,23] it is suggested that the additions of diethyldithiophosphoric acid, like thiol additions, occurred in a *cis–exo* manner without any inversion.



As expected two moles of diethyldithiophosphoric acid readily add to a mole of 2,5-norbornadiene, a diene which has both olefinic bonds in a bicycloheptene ring.

The course of radical additions of diethyldithiophosphoric acid to conjugated diolefins is apparently affected by the stability and the substitution of the intermediate allylic radical formed on radical addition to the diene. The thiophosphorylthiyl radical preferentially adds to the first carbon atom of unsymmetrically substituted butadienes so as to yield the more stable allylic radical. The latter than abstracts a hydrogen from the thiol predominantly at the less highly substituted of the two allylic positions.

The above course of the addition is similar to that of thiols examined earlier.[14,15] The hydrogen abstraction step of both reactions requires a significant activation energy.[24] Therefore, according to Hammond's correlation[25] the stability of the final product should make an important contribution to that of the transition state. Indeed the thermodynamically more stable olefinic product is formed in such reactions, *i.e.*, the allylic radical is considerably reorganized in the transition state and the product is derived from its less contributing resonance form.

Experimental

Materials.—The diethyldithiophosphoric acid used was purified before use according to the method of Bacon and LeSuer.[13] Dimethyl- and diisopropyldithiophosphoric acids were purified by distillation *in vacuo*. Dicyclopentadiene of Enjay Chemical Co., bicyclo[2.2.1]2,5-heptadiene and 2,5-dimethyl-2,4-hexadiene of Matheson, 2,3-dimethyl-1,3-butadiene of Houdry Corp., and isoprene of Eastman were redistilled before use. Aldrin, a 95% pure experimental sample of Shell Chemical Corp., was recrystallized from *n*-heptane and then from methanol. The purified compound had a melting point of 101–102°. A commercial mixture of *cis*- and *trans*-piperylenes of Enjay was custom purified by Columbia Organic Chemicals Co. to yield 98% *trans*-piperylene, containing 2% cyclopentene but free from *cis*-piperylene. Benzenethiol was obtained from Matheson Co., Inc. and was distilled *in vacuo* under nitrogen before use. The cumene hydroperoxide catalyst used was from Hercules Powder Co. and had a hydroperoxide content of 81% according to the thiol method.[26] The *n*-heptane and ethanol solvents were 99%+ grade.

Methods of Analyses.—The n.m.r. spectra were recorded with a Varian Model A-60 proton resonance spectrometer. The liquid products were run as such, the solid compounds in carbon tetrachloride solution. Tetramethylsilane was used as an internal reference. The infrared spectra were obtained using a Baird, Model B, recording spectrophotometer. Purity of isoprene, 2,3-dimethyl-1,3-butadiene, piperylene and norbornadiene was checked by g.c. at room temperature using a Perkin-Elmer, Model D, vapor fractometer with a 2-m. "E" column (2,4-dimethylsulfolane). The other dienes and the monoadducts were separated at 150° by capillary g.c., on a Barber-Coleman IDS, Model 20, chromatograph using a 50-ft. column coated with a *n*-tridecyl polyethylene glycol ether obtained from 30 moles of ethylene oxide per mole of *n*-tridecyl alcohol. The progress of the addition reactions was determined by potentiometric titration of the diethyldithiophosphoric acid in the mixtures with silver nitrate using a silver–glass electrode pair. To detect any post-isomerization of the liquid adducts, they were analyzed before washing with aqueous sodium carbonate solution and before distillation *in vacuo*.

Addition of Diethyldithiophosphoric Acid to *endo*-Dicyclopentadiene.—Elemental analyses of the adducts are given in Table II. Characteristic infrared absorption peaks are recorded in Table IV.

For the removal of the unchanged diethyldithiophosphoric acid, the solution of the reaction mixture in 20 ml. of benzene was washed with 50 ml. of 5% aqueous sodium carbonate solution and then with 30 ml. of water. The organic phase was dried over anhydrous sodium sulfate and the benzene, unchanged dicyclopentadiene, and any other volatile component were removed by distillation. The remaining product (27 g., 85%) is

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[23] N. Kharasch, ed., "Organic Sulfur Compounds I," Chap. 13 by G. Brindell and S. J. Cristol, "Additions of Thiols and Related Substances to Bridged Bicyclic Olefins," Pergamon Press, New York, N. Y., 1961, pp. 121–133.

[24] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 314.

[25] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[26] A. A. Oswald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, **26**, 3969 (1961).

a light yellow, mobile liquid of $n^{20}\text{D}$ 1.5452, with a characteristic phosphate ester smell. Capillary g.c. analysis indicated that it contains two major components in two to three ratio.

Saponification Value. Calcd. for the monoadduct, $C_{14}H_{21}O_2PS_2$: 316. Found: 314.

In another experiment, 9.3 g. (0.05 mole) of diethyldithiophosphoric acid was added to 3.3 g. (0.025 mole) of dicyclopentadiene in the same manner. Three hours after the addition 48% of the dithiophosphoric acid had reacted. This percentage remained essentially unchanged during 3 days standing of the reaction mixture at room temperature. Work-up of the reaction mixture in a manner described above yielded the monoadduct.

Dimethyl- and diisopropyldithiophosphoric acid reacted with dicyclopentadiene in a similar manner to yield liquid monoadducts.

Addition of Diethyldithiophosphoric Acid to Aldrin.—To a solution of 18.2 g. (0.05 mole) of Aldrin (m.p. 101–102°) in 50 ml. of *n*-heptane, 9.3 g. (0.05 mole) of diethyldithiophosphoric acid was added. The reaction mixture was allowed to stand for 16 hr. A subsequent titration of a sample with potassium hydroxide in the presence of neutral red indicator showed that only 12.5% of the diethyldithiophosphroic acid remained unchanged. The diethyldithiophosphoric acid monoadduct of Aldrin crystallized from the solution on cooling. The crude crystals were recrystallized from ethanol to yield 13.8 g. (50%) of *exo*-2-diethylthiophosphorylmercapto - *endo* - 5,6,7,8,9,9 - hexachloro-*exo–endo*-1,2,3,4,4a,5,8 - dimethanonaphthalene, II, as colorless crystals of m.p. 89.5–90.5°.

A similar procedure starting with 7.9 g. (0.05 mole) of dimethyl dithiophosphoric acid and 18.2 g. (0.05 mole) of Aldrin yielded 14.3 g. (55%) of *exo*-2-dimethylthiophosphorylmercapto-*endo*-5,6,7,8,9,9-hexachloro-*exo–endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,-5,8-dimethanonaphthalene, m.p. 112–113.5°.

Anal. Calcd. for $C_{14}H_{15}Cl_6O_2PS_2$: C, 32.08; H, 2.88; Cl, 40.59; O, 6.11; P, 6.10; S, 12.24. Found: C, 32.18; H, 2.89; Cl, 40.80; O, 6.10; P, 5.94; S, 12.60.

Addition of Diethyldithiophosphoric Acid to Norbornadiene.—To 9.2 g. (0.1 mole) of norbornadiene, 37.4 g. (0.02 mole) of diethyldithiophosphoric acid was added in the manner described in the previous example. The spontaneous exothermic reaction was 90% completed in 3 hr. On further standing, partial crystallization of the mixture occurred. The crystals were filtered off and recrystallized from ethanol to yield 23.7 g. (51%) of the colorless diadduct, m.p. 97.5–99°.

In another experiment equimolar amounts of norbornadiene and diethyldithiophosphoric acid were reacted in the same manner. Titration of the reaction mixture indicated that practically all the diethyldithiophosphoric acid reacted within an hour. A slightly yellow liquid adduct of $n^{20}\text{D}$ 1.5236 was obtained which according to g.c. consisted 70% of one and 30% of another isomer. G.c. analysis of the liquid part of the diaddition reaction showed the presence of the smaller component only.

Addition of Benzenethiol to Norbornadiene.—To 22 g. (0.2 mole) of benzenethiol, 9.2 g. (0.1 mole) of norbornadiene was added in the manner described in the previous example. However, the sequence of addition was reversed to repress the formation of 3-nortricyclyl 4-tolyl sulfide by the excess of thiol present. After the completion of the addition, the mixture was heated to 70° and kept at that temperature for 1 hr. A subsequent thiol determination indicated that only 28% of the original thiol was still present unreacted in the reaction mixture.

On scratching and cooling, crystals were formed in the reaction mixture. To complete the crystallization, the mixture was kept and recrystallized from *n*-heptane. In this manner, 10.8 g. (24%) of bisphenylmercaptonorbornadiene, m.p. 122–123° was obtained as colorless, large rhombic crystals.

Anal. Calcd. for $C_{19}H_{20}S_2$: C, 73.03; H, 6.45; S, 20.52 Found: C, 72.92; H, 6.53; S, 20.36.

In another experiment, 9.2 g. (0.1 mole) of norbornadiene was added to 11 g. (0.1 mole) of benzenethiol with cooling at room temperature. Then the mixture was allowed to stand for 5 days. By that time, all the thiol had reacted. Analysis of the crude product by capillary g.c. showed four peaks of 1.5%, 34.4%, 6.9% and 57.2% intensity. G.c. analysis of the liquid part from the diaddition experiment showed the absence of the 34.4% peak.

Addition of Diethyldithiophosphoric Acid to Conjugated Dienes.—A mixture of 0.25 mole of a thiol and 0.25 mole of a diene reacted in a closed 100-ml. round-bottom flask with magnetic stirring at room temperature. In the case of 2,5-dimethyl-2,4-hexadiene ultraviolet irradiation of the reaction mixture was necessary to increase the reaction rate. Water cooling of the irradiated reaction mixtures was necessary to avoid any rise of the temperature. Relative rates of the additions were determined on the basis of the decrease of the diethyldithiophosphoric acid content. Some of the comparative rate data are shown in Tables I and II.

After an arbitrary length of time the reaction was discontinued and the mixture was worked up. The unchanged diethyldithiophosphoric acid was removed by washing with 5% aqueous sodium carbonate solution. If separation was difficult, the organic phase was diluted with ether or benzene. After the drying, the separated organic phase was fractionally distilled. The adducts were usually obtained at about 1 mm. as mobile, colorless or slightly yellow liquid distillates having a characteristic phosphate ester odor. Separation of the isomeric monoadducts by superfractionation was not attempted. Some of the physical and analytical data of the isomeric adduct mixtures are given in Table II. The various isomers were identified and semiquantitatively determined by n.m.r. (Table III). Quantitative determination of the isomers was accomplished by capillary g.c. (Table II).

Acknowledgment.—The authors wish to thank T. G. Jermansen and A. M. Palmer for valuable technical help.

Reactivity of Thiophosphates. I. Hydrolysis of Phosphorothioic Acid[1–3]

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The hydrolysis of phosphorothioic acid (H_3PO_3S) in aqueous solution at constant ionic strength has rate maxima at pH ~3.0 and at pH ~8.0 and the rate minima at pH ~7.0 and at pH ~ −0.30. The reactivity of the dianion at pH 8 is unusual since the dianions of most simple organic phosphate esters are inert. In acid solutions stronger than 2 *M* a rate increase is observed which is interpreted as a salt effect on the rate of hydrolysis of the neutral acid.

Phosphorothioic acid, H_3PO_3S, is reported to decompose readily to hydrogen sulfide and phosphoric acid although its anhydrous trisodium salt is stable.[5] This investigation was undertaken in order to compare quantitatively the rate of hydrolysis of phosphorothioic

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(1) We are grateful to the National Institutes of Health for support of this work (grant A-1023).

(2) For experimental details, see O. B. Ramsay, Ph.D. thesis, University of Pennsylvania, 1960.

(3) Reported at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(4) Department of Chemistry, Syracuse University, Syracuse 10, N. Y.

(5) A. Wurtz, *Compt. rend.*, **24**, 288 (1847); R. Klement, *Z. anorg. allgem. Chem.*, **253**, 237 (1947); J. V. Karabinos, R. A. Paulson, and W. H. Smith, *J. Res. Natl. Bur. Std.*, **48**, 322 (1952); S. K. Yasuda and J. L. Lambert, *J. Am. Chem. Soc.*, **76**, 5356 (1954); F. Binkley, *J. Biol. Chem.*, **181**, 317 (1949).