CHAPTER II

RADICAL ADDITION OF PHOSPHONATES TO OLEFINS: CHARACTERISATION AND SOME REACTIONS OF THE ADDUCTS

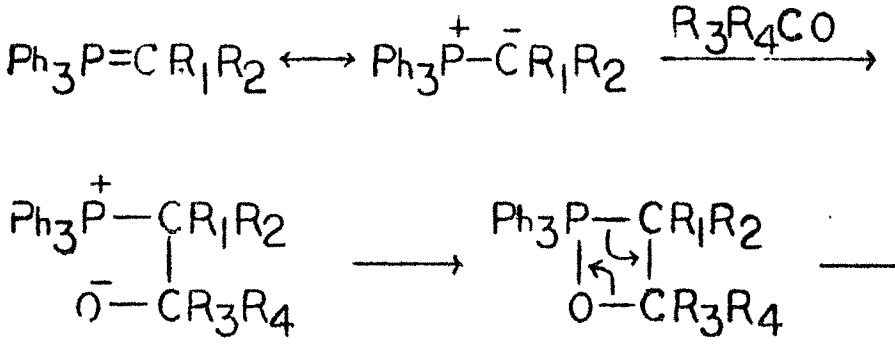
ABSTRACT

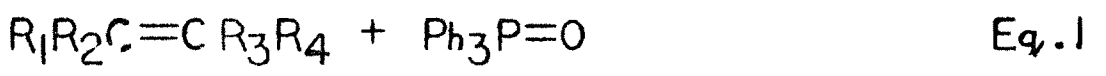
The role of dialkyl alkylohosphonates and thiophosphonates in olefin synthesis has been briefly discussed. Additions of diethyl phosphonate, $HP(O)(OEt)_2$ and thiophosphonate, $HP(S)(OEt)_2$ to selected olefins under free radical conditions have been investigated. Spectral data useful for the characterisation of the adducts are described. Some reactions, particularly aimed at C-P bond cleavage have been investigated and are recorded in this Chapter.

RADICAL ADDITION OF PHOSPHONATES TO OLEFINS. CHARACTERISATION AND SOME REACTIONS OF THE ADDUCTS

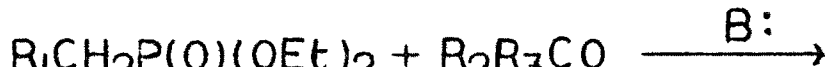
I N T R O D U C T I O N

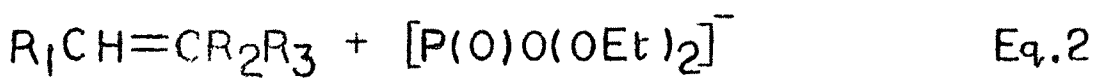
Wittig reaction, first reported[1] in 1953, has become an important synthetic method for making olefins[2] from carbonyl compounds and alkylidene triphenylphosphoranes (Eq.1). However, phosphoranes carrying electronegative groups (e.g. R_1 or R_2 = CN, CO_2Me etc.) are too stabilised and hence unreactive in olefin synthesis. The situation was sought to be rectified by modifications introduced by Horner and co-workers[3] and Wadsworth and Emmons.[4] They described an olefin synthesis in which dialkyl alkylphosphonate is employed in the place of alkylidene triphenylphosphorane (Eq. 2). This phosphonate olefin synthesis is superior to classical Wittig reaction in that the phosphoryl stabilised carbanions are much more reactive nucleophiles than the corresponding alkylidene phosphoranes and separation of the required olefin from the water-soluble phosphonate ion is much easier than from phosphine oxide. However, the scope of this reaction is still restricted by the fact that only those phosphonates in which the carbanion can be stabilised by another electron-withdrawing group (like CO, CN etc.) in addition to P=O can be successfully employed. This drawback was overcome by two



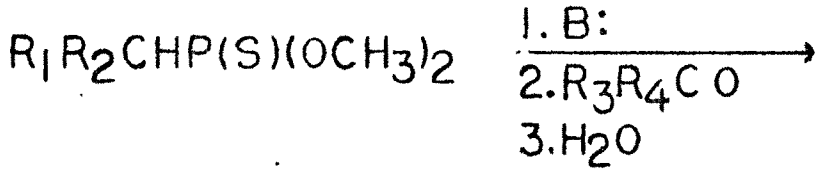


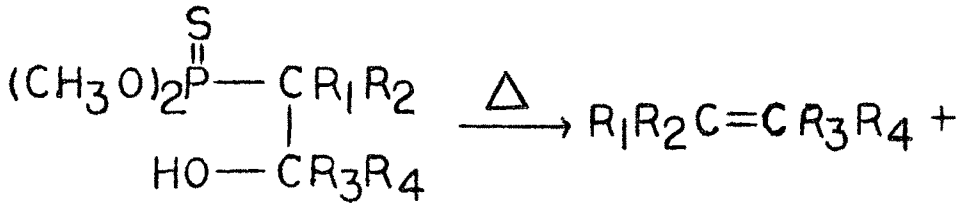
Eq.1





Eq.2





Eq.3

CHART I

variations introduced by Corey in the phosphonate olefin synthesis:

(a) Dialkyl alkylphosphonates like $R_1CH_2P(O)(OMe)_2$ form carbanions with n-BuLi and add to carbonyl compounds, but the resulting β-hydroxyphosphonates, $R_2R_3C(OH)CH(R_1)$-$P(O)(OMe)_2$, however, failed to decompose to olefins. This was circumvented by base-catalysed addition of alkylthiophosphonates to carbonyl compounds, when the resulting β-hydroxythiophosphonates readily decomposed to give olefins[5] (Eq. 3).

(b) Phosphonamides can be conveniently used for olefin synthesis[6] (Eq. 4).

Methods of preparation of the phosphonates: Dialkyl alkylphosphonates have generally been prepared by Michaelis or Arbuzov reaction.[7,8] The former involves treatment of alkali metal derivatives of dialkyl phosphites with alkyl halides (Eq. 5), whereas the Arbuzov reaction involves reaction of trialkyl phosphites with alkyl halides (Eq. 6).

The following methods are generally used to prepare dialkyl alkylthiophosphonates.

(a) Reaction of alkyl phosphonothioic dichloride, $RP(S)Cl_2$ with sodium alkoxide or with an appropriate alcohol and base.[9,10]

$$R_1R_2CHP(O)(NRR)_2 \xrightarrow[2.\ R_3R_4CO\ \ 3.\ H_2O]{1.\ B:}$$

$$(RRN)_2P(O)\underset{\displaystyle HO-CR_3R_4}{\overset{\displaystyle |}{C}}R_1R_2 \xrightarrow{\Delta}$$

$$R_1R_2C{=}CR_3R_4 + (RRN)_2P(O)OH \qquad \text{Eq.4}$$

$$(RO)_2P(O)H \xrightarrow{Na} (RO)_2\bar{P}(O) \xrightarrow{R_1X}$$

$$(RO)_2P(O)R_1 \qquad \text{Eq.5}$$

$$(RO)_3\ddot{P} + R_1X \longrightarrow [(RO)_3\overset{+}{P}R_1]\,X^-$$

$$\longrightarrow R_1P(O)(OR)_2 + RX \qquad \text{Eq.6}$$

$$R_1R_2C{=}CH_2 + \cdot P(X)(OR)_2 \longrightarrow$$

$$R_1R_2\dot{C}-CH_2P(X)(OR)_2 \xrightarrow{HP(X)(OR)_2}$$

$$R_1R_2CHCH_2P(X)(OR)_2 + \cdot P(X)(OR)_2$$

$$(X=O,S) \qquad \text{Eq.7}$$

CHART 2

(b) Treatment of O,O'-dialkyl sodium phosphothioite, $(RO)_2P^-SNa^+$ with an alkyl halide.[11]

(c) Addition of sulphur to the corresponding dialkyl alkylphosphonates.[9,10]

Alkyl phosphonic diamides are conveniently prepared (a) by reaction of lithio derivative of $(R_2N)_2P(O)H$ with appropriate alkyl halides[12] or (b) by reaction of alkylphosphonyl dichlorides $R_1P(O)Cl_2$ with the appropriate dialkylamine.[13]

Radical addition of diethyl phosphonate (DEP) and diethyl thiophosphonate (DETP) to olefins: Diethyl phosphonate, $HP(O)(OEt)_2$ and diethyl thiophosphonate, $HP(S)(OEt)_2$ add to olefins under free radical conditions in anti-Markonikow fashion.[14] The chain-carrying process is shown in Eq. 7.

It appears that this reaction is not recognised as a potential method of making intermediate thiophosphonates for olefin synthesis. Lewis and co-workers[15] studied the isotope-effect in the H-atom transfer in the addition of dimethyl thiophosphonate to olefins. Kumamoto and co-workers[16] studied the photochemical addition of DETP to certain unsaturated sugars. A few patents were field on similar additions to 2-(perfluoroalkyl)-alkenes and vinyl and vinylidene fluorides.[17]

In the field of terpenes there is but one report by Kenny and Fisher,[18] who studied the addition of DEP to a few monoterpenes, but such adducts have little use for olefin synthesis.

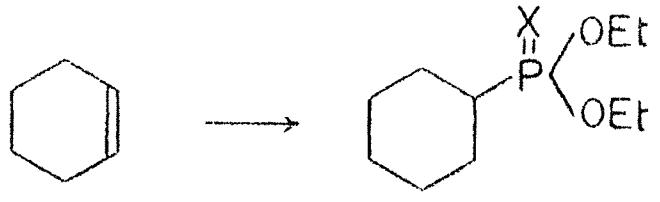
PRESENT WORK

It was envisaged that adducts from radical addition of DETP, N,N,N',N'-tetraethylphosphonic diamide, $HP(O)(NEt_2)_2$ and thiophosphonic diamide, $HP(S)(NEt_2)_2$ could be useful intermediates in olefin synthesis. Further, the carbanions derived from dialkyl alkylphosphonates (which can be easily prepared by radical addition of DEP to olefins) should be prone to easy alkylation or addition to carbonyl compounds.[15] It was thought that such adducts would be potentially useful in C-C bond formation provided the C-P bond can be cleaved. Chemical behaviour of all these adducts, specially with respect to C-P bond cleavage was planned to be studied.

The radical additions can be carried out with UV-irradiation or using one of the three common chemical initiators, namely, azobis (isobutyronitrile), benzoyl peroxide or di-t-butyl peroxide.[19]

Additions of diethyl phosphonate: Initially, cyclohexene (1) was used as the model compound to standardise the reaction conditions. Addition of DEP to cyclohexene (1) initiated by di-t-butyl peroxide at 140° gave diethyl cyclohexylphosphonate (2) in 75% yield (Eq. 8) (IR: P=O 1250 cm^{-1}; P-O-C 1035 cm^{-1}. PMR: OCH_2CH_3's, 6H, t, 1.3 ppm, J = 7Hz; OCH_2CH_3's, 2H, quartets at 3.97, 4.06 ppm, J = 7 Hz). Similar reaction with β-pinene (6) gave diethyl 1-p-menthenyl-7-phosphonate[18] (7; 70%; Eq. 10). Also, addition of DEP to p-3-menthene (11) and longifolene (22) gave diethyl p-3-menthanylphosphonate (12; 75%; IR: P=O 1250 cm^{-1}; P-O-C 1035 cm^{-1}. PMR: OCH_2CH_3's, 6H, t, 1.3 ppm, J = 7Hz; OCH_2CH_3's, 4H, m, 3.84-4.26 ppm) (Eq. 12) and diethyl 14-longifolanylphosphonate (23; 75%; IR: P=O 1250 cm^{-1}; P-O-C 1030 cm^{-1}. PMR: OCH_2CH_3's, 6H, t, 1.32 ppm, J = 7Hz; OCH_2CH_3's, 2H, quartets at 4.06, 4.14 ppm, J = 7 Hz) (Eq. 16) respectively.

Additions of diethyl thiophosphonate: Addition of DETP to cyclohexene (1) initiated by di-t-butyl peroxide at 140° gave poor yield (40%) of diethyl cyclohexylthiophosphonate (3), due to thermal decomposition with deposition of sulfur. However, with benzoyl peroxide as initiator at 85-90°, the reaction went smoothly and 75% yield of 3 could be realised (Eq. 8) (IR: P-O-C 1030 cm^{-1}; P=S 780 cm^{-1}. PMR: OCH_2CH_3's, 6H, t, 1.29 ppm, J = 7 Hz; OCH_2CH_3's, 4H, bm, 3.88-4.38 ppm). Hence, subsequent additions of DETP were carried out under these conditions.

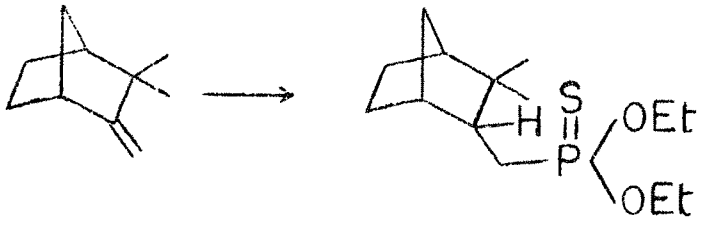


Eq.8

1

2: X=O

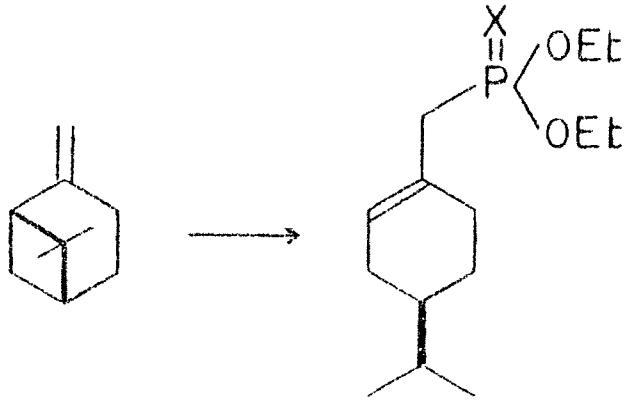
3: X=S



Eq.9

4

5



Eq.10

6

7: X=O

8: X=S

CHART 3

Addition of DETP to camphene (4) gave a single isomer in 72% yield. Davis and co-workers[20] investigated the radical addition of benzenethiol to norbornene and camphene and concluded that, in these systems, endo-chain transfer is not favoured due to the eclipsing by bridge-head hydrogen. Consequently, the present adduct is formulated as diethyl 10-endo-isocamphanylthiophosphonate (5) (Eq. 9) (IR: P-O-C 1035 cm^{-1}; P=S 790 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.29 ppm, J = 7 Hz; P-C<u>H</u>, 1H, bs, 2.34 ppm, W_h=9Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.85-4.4 ppm).

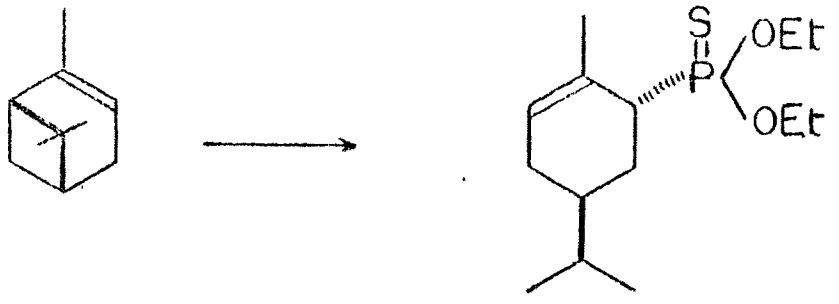
Addition of DETP to β-pinene (6) gave a single product in 71% yield. The appearance of a broad olefinic proton peak at 5.54 ppm in the PMR spectrum indicated that the addition was accompanied by opening of the cyclobutane ring, as is the case with other free radical additions to β-pinene.[21] The adduct is formulated as diethyl 1-p-menthenyl-7-thiophosphonate (8; Eq. 10) (IR: P-O-C 1040 cm^{-1}; P=S 790 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.28 ppm, J = 7Hz; P-$\underline{CH_2}$, 2H, d, 2.62 ppm, J= 20 Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.82-4.34 ppm).

Reaction of α-pinene (9) with DETP gave a single product in slightly less yield (60%). Once again, a broad olefinic peak at 5.52 ppm in the PMR spectrum indicates the rupture of the cyclobutane ring. On steric grounds, the thiophosphonate radical should attack α-pinene at C-2 <u>trans</u> to C-6.

Consequently, the adduct is assigned the structure 10 (Eq. 11) (IR: P-O-C 1035 cm^{-1}; P=S 795 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J = 7Hz; C=C-$\underline{CH_3}$, 3H, s, 1.81 ppm; $OCH_2\underline{CH_3}$'s, 4H, bm, 3.80-4.32 ppm).

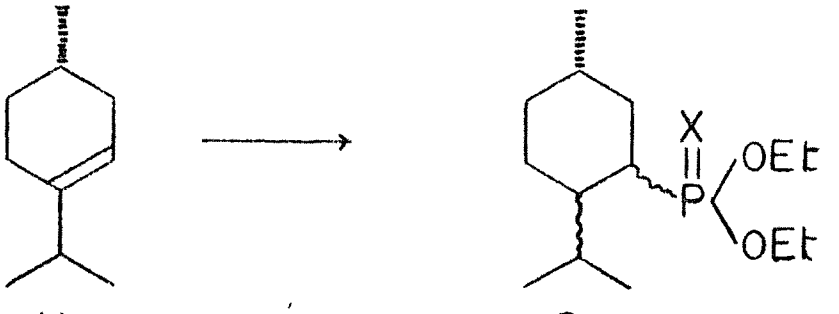
Reaction of DETP with p-3-menthene (11) gave a mixture of four isomeric adducts (TLC; R_f 0.59, 0.605, 0.62 and 0.64) in 75% yield (Eq. 12). The major isomer (R_f 0.64) was isolated in pure state by chromatography on SiO_2-gel. In the radical additions to substituted cyclohexenes, the products are predominantly, cis,[22] because the chain-transfer occurs from the side opposite to that of the phosphonate group, i.e., the addition takes place in a trans sense. Presently, assuming that the attack of thiophosphonate radical on the double bond predominantly takes place trans to C_1-methyl, the adduct was assigned the structure 13a (Chart 4) (IR: P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J = 7Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.88-4.40 ppm).

Addition of DETP to 3-carene (14) gave a mixture of isomers, from which the predominant (~90%) one was isolated in pure state by chromatography on SiO_2-gel in 69% yield. Since the thiophosphonate radical should attack the double bond trans to the cyclopropane ring, the adduct is formulated as 15 (Eq. 13) (IR: P-O-C 1035 cm^{-1}; P=S 785 cm^{-1}. PMR:



Eq.11

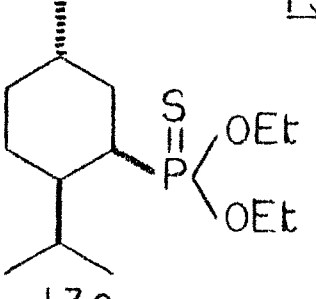
9 10



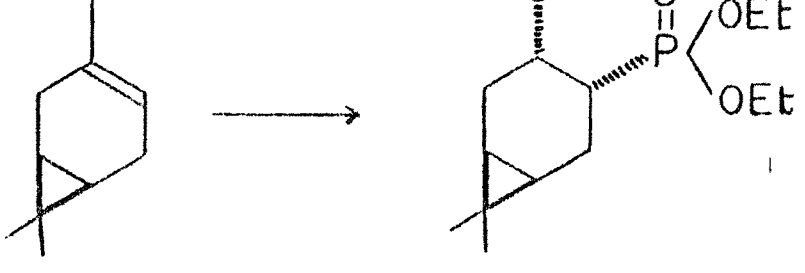
Eq.12

11

12 : X = O
13 : X = S



13a



Eq.13

14 15

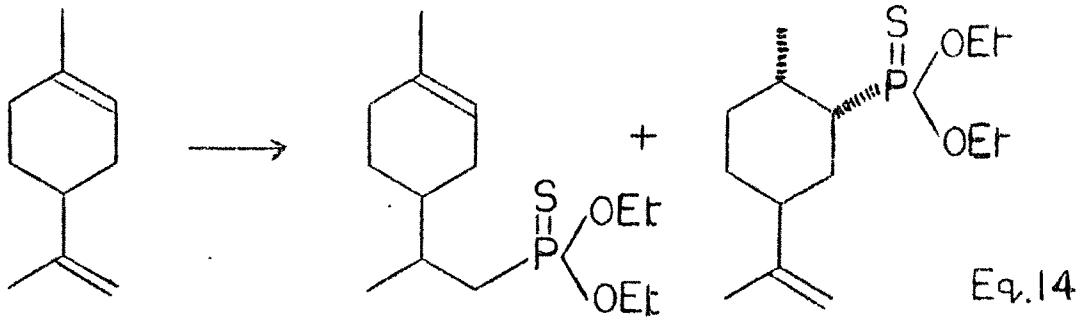
CHART 4

$OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J = 7Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.85-4.38 ppm).

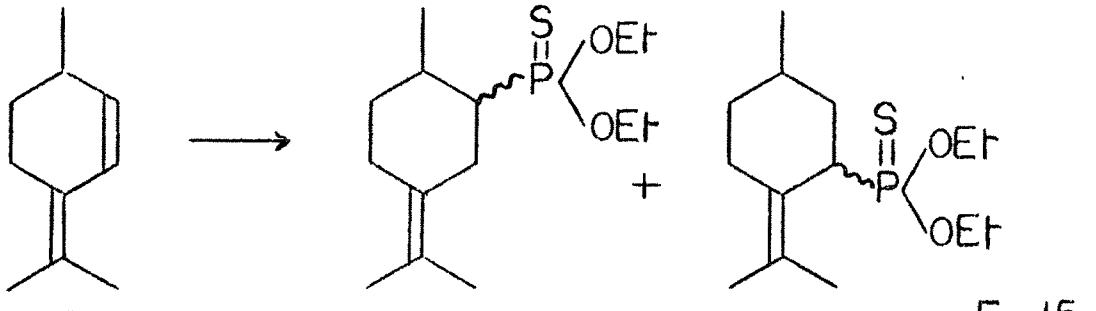
Reaction of DETP with limonene (16) was carried out by reverse addition, namely, by adding the latter to a mixture of DETP and Bz_2O_2 at 85-90°. The product was a mixture of diethyl 1-p-menthenyl-9-thiophosphonate (17) (PMR: C=C$\underline{H}$, bs, 5.34 ppm, W_h=9Hz) and diethyl 8-p-menthenyl-2-thiophosphonate (18) (PMR: C=C$\underline{H_2}$, bs, 4.76 ppm) in the ratio 67:33 (Eq. 14). Even ten fold increase in the concentration of limonene did not appreciably alter this ratio. The major product 17 was isolated in 40% yield by chromatography over $AgNO_3$-SiO_2 gel (IR: P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J=7Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.82-4.30 ppm).

Addition of DETP to isoterpinolene (19) gave a mixture of adducts (20) and (21) (IR: P-O-C 1035 cm^{-1}; P=S 785 cm^{-1}. PMR: $OC\underline{H_2}CH_3$'s, bm, 3.80-4.35 ppm) (Eq. 15). No 1,4-addition product was formed, as evident from the absence of olefinic proton in the PMR spectrum of the product.

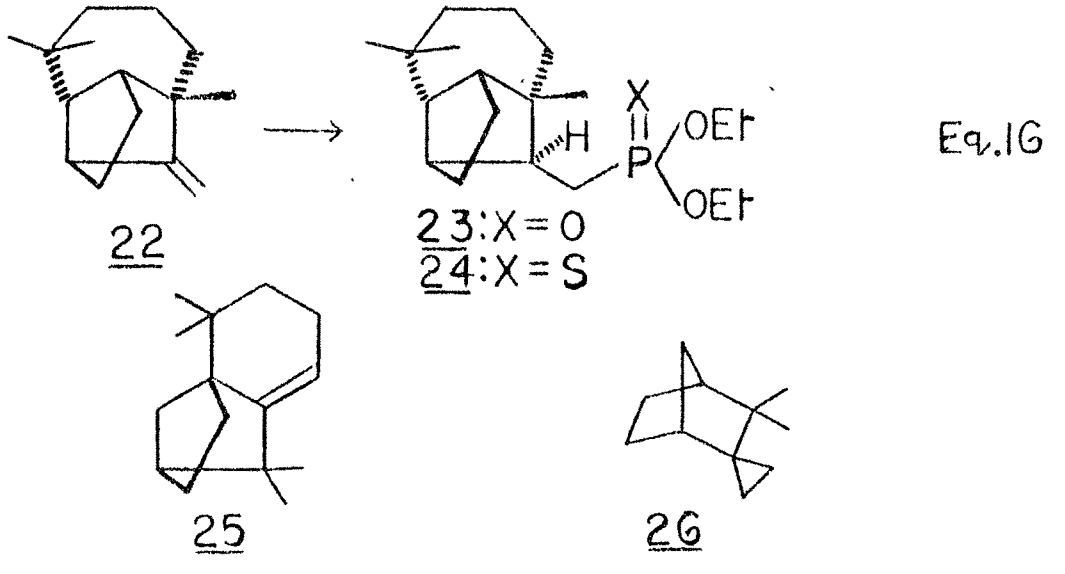
Addition of DETP to longifolene (22) gave the expected adduct (24) in 76% yield (Eq. 16) (IR: P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}. PMR: $OCH_2\underline{CH_3}$'s, 6H, t, 1.31 ppm, J = 7Hz; $OC\underline{H_2}CH_3$'s, 4H, bm, 3.86-4.48 ppm). Radical additions to longifolene are known to take place via 1,5-transannular hydrogen shift.[23]



16 17(67%) 18(33%) Eq.14



19 20 21 Eq.15



22 23: X = O
24: X = S Eq.16

25 26

CHART 5

There was no appreciable reaction between isolongifolene (25) and DETP (or diethyl phosphonate) due to the hindered nature of the double bond. Also, there was no reaction between DETP and 3,3-dimethylspiro [bicyclo(2.2.1)-heptane-2,1'-cyclopropane](26) (Chart 5).

Attempted addition of phosphonic diamides: Additions of N,N,N',N'-tetraethyl phosphonic diamide, $HP(O)(NEt_2)_2$ and thiophosphonic diamide, $HP(S)(NEt_2)_2$ were attempted using cyclohexene as the substrate. The initiation was done by using azobis (isobutyronitrile) at 50° or by UV-irradiation at room temperature (~30°). In either case, no adduct formation was noticed. The diamides are unstable at or above 60°.

Spectral characteristics of the adducts:

UV: Russian workers[24] have used UV to study the conjugative effects in phosphorous compounds. Little data is available about the UV absorptions of thiophosphonates. Presently, diethyl 14-longifolanylphosphonate (23) absorbs at 220 and 235 nm. All the thiophosphonates absorb in the region 211-235 nm with ϵ_{max} varying between 1127-3294 (Table 1). These absorptions are presumably due to η-π^* transitions of P=X linkage.

IR: Alkyl phosphonates are reported to absorb in the IR region at 1240-50 cm^{-1} (P=O)[18] and 1025-40 cm^{-1}(P-O-C).[25]

TABLE I : Spectral data of the adducts

Entry	Adduct	UV λ_{max} nm (ϵ_{max})	IR ν_{max} cm^{-1}	Mass m/e (%)
1	2	-	1250,1065, 1035,965	-
2	3	211(1127)	1060,1030, 950,780	236(36),155(15), 154(55),121(100),93(25), 83(7), 81(7), 65(13).
3	5	235(1334) 222(1189)	1390,1370, 1060,1035, 960,790	290(63, 247(11), 168(7), 154(38), 137(25, 121(100), 97(21),93(25),61(16).
4	7	-	1385,1360, 1245,1045 1025,950	-
5	8	217(2546)	1395,1370, 1060,1040, 960,790	290(87),247(31, 168(17,155(15), 154(19),136(89),121(92), 93(100),81(48),65(21).
6	10	219(3033)	1390,1370, 1060,1035, 960,795	290(44),247(3),245(3), 155(22),154(7),137(26), 136(100),121(41),93(80), 92(35),81(24),65(17).
7	12	-	1390,1370, 1250,1055, 1035,950	-
8	13a	216(1965)	1395,1370, 1060,1030, 960,790	292(38),249(8),155(49), 154(53),138(18), 121(100),97(19),95(22), 93(18),81(17),65(18).

...contd.

TABLE I ..contd.

Entry	Adduct	UV	IR	Mass
9	15	218(2376)	1390,1060, 1035,960,785	292(17),290(23), 247(7),155(31,154(43), 136(44),121(100), 93(50),81(18),65(24).
10	17	-	1640,1060, 1030,955,790	-
11	23	216(1480) 223(1480)	1390,1380, 1250,1055, 1030,960	342(100),327(12), 314(15),299(11), 286(10),217(10),259(14), 231(13),204(29),152(64), 138(27),109(18),81(24).
12	24	235(3294) 220(3204)	1390,1375, 1060,1030, 955,790	358(71),205(39),204(39), 154(39),121(100),93(26), 81(19),65(10).

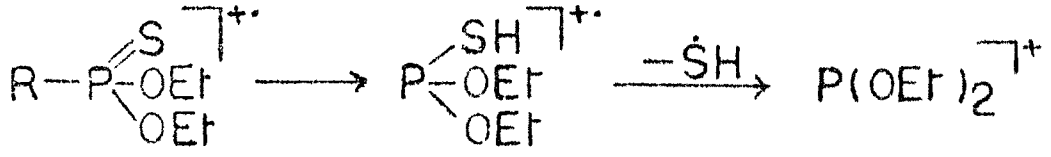
Alkylthiophosphonates are known to absorb at 770-835 cm^{-1} (P=S)[26]. Presently, all the compounds show these characteristic absorptions (Table 1). In addition, from the IR data of phosphonates and thiophosphonates presented in Table 1, it appears that absorptions at 1045-60 and 950-65 cm^{-1} also characterise these adducts.

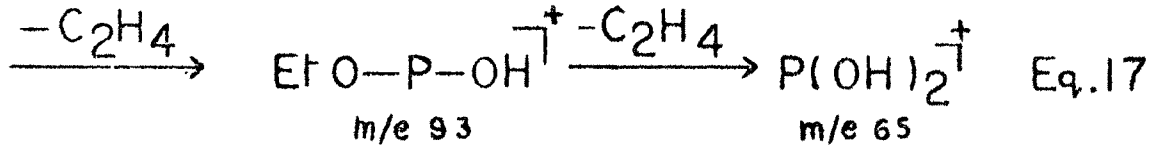
Mass: The mass spectral fragmentation of diethyl 14-longifolanylphosphonate (23) follows the known[27] pattern. In the case of thiophosphonates, all the compounds show prominent peaks at m/e 154, 121, 93 and 65 (Table 1). Thus, an important mode of fragmentation characteristic of these compounds appears to be as shown in Eq. 17.

Some reactions of the adducts

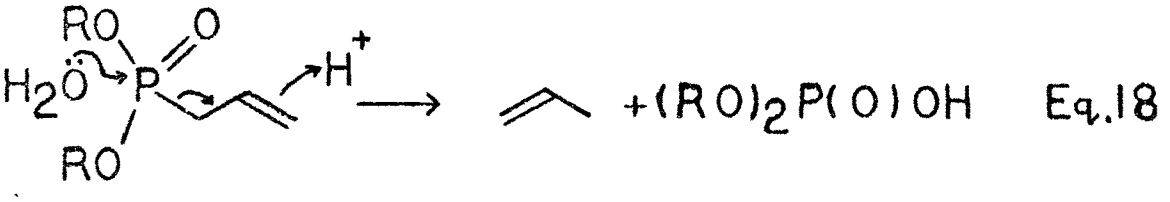
As mentioned earlier, adducts from radical addition of diethyl thiophosphonate could be useful in olefin synthesis. Also, since the carbanions derived from dialkyl alkylphosphonates are known[5] to react with electrophilic reagents, these adducts could be potentially useful for C-C bond formation, provided C-P bond can be easily cleaved. So, it was planned to investigate some reactions of both classes of adducts with particular emphasis on C-P bond cleavage.

Phosphonates: Known methods of C-P bond cleavage of phosphonates are (a) Horner-Emmons reaction with carbonyl compounds,

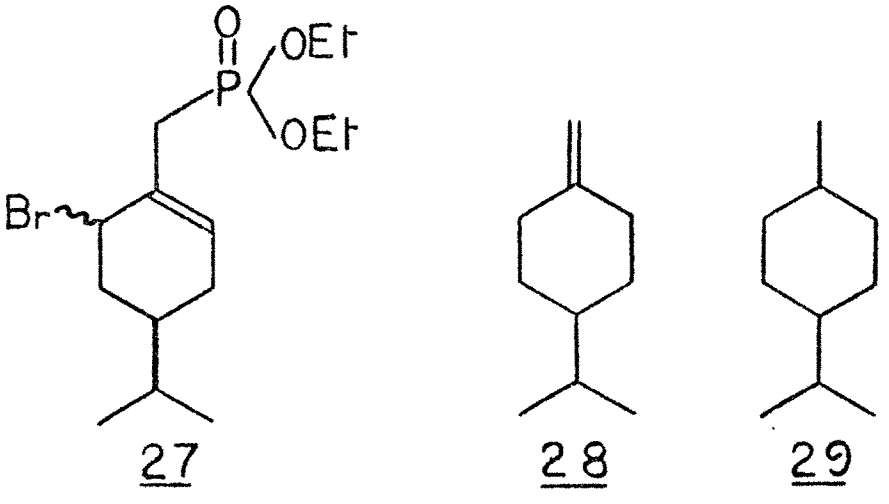




Eq.17



Eq.18



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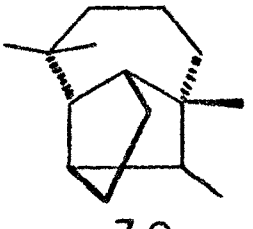

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CHART 6

(b) base-catalysed reaction with oxygen to give ketones,[28] (c) reductive cleavage of C-P bond in β-ketophosphonates with Zn or Al-Hg[28] and (d) reductive cleavage of C-P bond in allylic phosphonates with LAH.[29]

We attempted oxidative cleavage of C-P bond with diethyl cyclohexylphosphonate (2) as substrate using a variety of mild and strong oxidising agents (like Py/CrO_3, Jones' reagent etc.), but it did not cleave. Next, C-P bond cleavage was attempted in the allylic phosphonate 7 using Br_2 in CCl_4. But the product was diethyl 6-bromo-1-p-menthenyl-7-phosphonate (27) (IR: P=O 1250 cm^{-1}; P-O-C 1025 cm^{-1}. PMR: P-CH_2, 2H, dd, 2.75 ppm, J_1=20Hz, J_2=4Hz; CHBr, 1H, bs, 3.95 ppm). Formation of this bromide can be exolained as resulting from"Steric Diversion".[30]

Hutchinson[31] reports that allylic phosphonates undergo hydrolysis in aqueous acids to give an olefin (Eq. 18). However, in our hands, the allylic phosphonate 7 did not undergo such hydrolysis.

Finally, reduction of the allylic phosphonate 7 with LAH in ether gave p-1(7)-menthene (28) (PMR: C=CH_2, 1H, singlets at 4.52, 4.82ppm). Also, similar reductive cleavage of saturated phosphonates 2, 12 and 23 gave cyclohexane, p-menthane (29) and longifolane (30) (Chart 6) respectively.

This reduction coupled with prior alkylation[29] of the phosphonate can be of use in C-C bond formation.

Thiophosphonates: The reactions of thiophosphonates were investigated using the adduct 3. Like phosphonates, 3 resisted C-P bond cleavage with oxidising agents. Also, there was no reaction with LAH. This may be due to the low polarity of P=S bond compared to P=O.

In conclusion, the phosphonate adducts could be useful in C-C bond formation, whereas the thiophosphonates are useful for olefin synthesis.

EXPERIMENTAL

For general remarks, see Chapter I, Section I.

Diethyl phosphonate:

Diethyl phosphonate was prepared according to the known[32] method; b.p. 85-90°/20 mm (lit.[32] b.p. 87°/20 mm).
IR (liq. film): P-H 2420 cm^{-1}; P=O 1260 cm^{-1}; P-O-C 1050 cm^{-1}.
PMR (CCl_4): $OCH_2\underline{CH_3}$'s, 6H, t, 1.38 ppm, J = 7Hz; $O\underline{CH_2}CH_3$'s, 4H, m, 3.9-4.3 ppm; P-$\underline{H}$, 1H, d, 2.36, 10.55 ppm, J = 682 Hz.

Diethyl thiophosphonate:

Diethyl thiophosphonate was prepared following the known[33] procedure; b.p. 85-8°/16 mm (lit.[33] b.p. 75-6°/14 mm).
UV (EtOH): λ_{max} 218 nm, ϵ_{max} 1623.
IR (liq. film): P-H 2400 cm^{-1}; P-O-C 1030 cm^{-1}; P=S 770 cm^{-1}.
PMR (CCl_4): $OCH_2\underline{CH_3}$'s, 6H, t, 1.35 ppm, J = 7 Hz; $O\underline{CH_2}CH_3$'s, 4H, m, 3.96-4.33 ppm; P-$\underline{H}$, 1H, d, 4.05, 11.30 ppm, J = 653 Hz.

N,N,N',N'-Tetraethylphosphonic diamide:

Water (1.8 g, 0.1 mole) in THF (10 ml) was added dropwise to a refluxing solution of hexaethylphosphorous triamide,

$P(NEt_2)_3$ [34] (24.7 g, 0.1 mole) in THF (30 ml). Refluxing was continued for 15 min. Solvent was removed under reduced pressure and the residue distilled to give the desired compound (12.5 g, 65%); b.p. 80°/0.2 mm (lit.[35] b.p. 59-60°/0.03 mm).

UV (EtOH): λ_{max} 211 nm, ϵ_{max} 208.

IR (liq. film): P-H 2320 cm^{-1}; P=O 1200 cm^{-1}.

PMR ($CDCl_3$): $CH_2\underline{CH_3}$'s, 12H, t, 1.12 ppm, J = 7Hz; $\underline{CH_2}CH_3$'s, 8H, m, 2.88-3.25 ppm; P-$\underline{H}$, 1H, d, 3.6, 9.92 ppm, J = 570Hz.

N,N,N',N'-Tetraethylthiophosphonic diamide:

H_2S (dried over P_2O_5) was passed slowly into a solution of hexaethylphosphorous triamide (24.7 g, 0.1 mole) in dry benzene (150 ml) with stirring at room temperature (~30°), till a yellow polymer starts appearing on the walls of the flask (35-40 min). Flow of H_2S was stopped at this stage. Removal of solvent at reduced pressure followed by distillation gave $HP(S)(NEt_2)_2$ as a pale yellow liquid (10.4 g, 50%); b.p. 85-90°/0.2 mm.

IR(liq. film): P-H 2310 cm^{-1}; P=S 790 cm^{-1}.

PMR (CCl_4): $CH_2\underline{CH_3}$'s, 12H, t, 1.14 ppm, J = 7Hz; $\underline{CH_2}CH_3$'s, 8H, m, 2.84-3.20 ppm; P-$\underline{H}$, 1H, d, 3.5, 9.7 ppm, J = 558 Hz.

General procedure for the addition of diethyl phosphonate:

Diethyl phosphonate (0.5 mole) was heated to 140° and di-t-butyl peroxide (0.005 mole) was added dropwise with stirring. Then the olefin (0.1 mole) was added dropwise over a period of about 30 min. and the heating continued for a total period of 3.5 h. The unreacted materials were recovered by distillation under vacuum (15-20 mm). The residue was taken up in ether (50 ml), washed with water (15 ml), 5% $NaHCO_3$ aq (10 ml x 2), water (10 ml) and brine (10 ml) and dried (Na_2SO_4). Removal of solvent followed by vacuum distillation (0.1-0.5 mm) gave the adducts.

Diethyl cyclohexylphosphonate (2): Colorless liquid, b.p. 110°/1.5 mm (lit.[36] 87°/0.8 mm).

PMR ($CDCl_3$): $OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J = 7 Hz; $OC\underline{H_2}CH_3$'s, 2H, quartets at 3.97, 4.06 ppm, J = 7Hz.

Diethyl 1-p-menthenyl-7-phosphonate (7): Colorless liquid, b.p. 132-6°/0.2 mm (lit.[18] 125-7°/0.1 mm).

PMR (CCl_4): $CH\underline{Me_2}$, 6H, d, 0.88 ppm, J = 6Hz; $OCH_2\underline{CH_3}$'s, 6H, t, 1.3 ppm, J = 7Hz; P-$C\underline{H_2}$, 2H, d, 2.42 ppm, J = 22Hz; $OC\underline{H_2}CH_3$'s, 4H, m, 3.9-4.24 ppm; C=$C\underline{H}$, 1H, bs, 5.58 ppm, W_h = 12 Hz.

Diethyl p-3-menthanylphosphonate (12): Colorless liquid, b.p. 125-30°(bath)/0.4 mm.

PMR (CCl_4): CH-Me's, 3H, doublets at 0.87, 0.91, 0.96 ppm, J = 6 Hz; OCH_2CH_3's, 6H, t, 1.3 ppm, J = 7 Hz; OCH_2CH_3's, 4H, m, 3.84-4.26 ppm.

Diethyl 14-longifolanylphosphonate (23): Colorless liquid, b.p. 135-40°/0.1 mm; n_D^{25} 1.4882.

IR (liq. film) (Fig. 1): P=O 1250 cm^{-1}; P-O-C 1030 cm^{-1}.

PMR ($CDCl_3$) (Fig. 2): C-CH_3, 3H, s, 0.76 ppm; CMe_2, 6H, s, 1.06 ppm; OCH_2CH_3's, 6H, t, 1.32 ppm, J = 7 Hz; OCH_2CH_3's, 2H, quartets at 4.06, 4.14 ppm, J = 7 Hz.

Analysis: Found : C, 66.24; H, 9.768; P, 8.798.

$C_{19}H_{35}O_3P$ requires: C, 66.67; H, 10.23; P, 9.064%.

General procedure for the addition of diethyl thiophosphonate:

A mixture of diethyl thiophosphonate (0.5 mole) and benzoyl peroxide (0.005 mole) was heated with stirring at 85-90°. The olefin (0.1 mole) was added dropwise over a period of 30 min and the heating continued for 20-24 h. The unreacted starting materials were recovered by vacuum distillation. Usual work up gave the adducts. Recovered olefin was taken into account while reporting the yields.

Diethyl cyclohexylthiophosphonate (3): Colorless liquid, b.p. 120-5°/1.5 mm; n_D^{25} 1.4876.

IR (liq. film) (Fig. 3): P-O-C 1030 cm^{-1}; P=S 780 cm^{-1}.

PMR ($CDCl_3$) (Fig. 4): $OCH_2\underline{CH_3}$'s, 6H, t, 1.29ppm, J = 7Hz; $OCH_2\underline{CH_3}$'s, 4H, m, 3.88-4.38ppm.

Analysis: Found : C, 50.62; H, 8.99; P, 12.87.
$C_{10}H_{21}O_2PS$ requires: C, 50.85; H, 8.898; P, 13.14%.

Diethyl 10-endo-isocamphanylthiophosphonate (5): Pale yellow liquid, b.p. 135-40°(bath)/0.1 mm; n_D^{25} 1.4991.

IR (liq. film) (Fig. 5): P-O-C 1035 cm^{-1}; P=S 790 cm^{-1}.

PMR ($CDCl_3$) (Fig. 6): C-Me's, 3H, singlets at 0.8, 0.98 ppm; $OCH_2\underline{CH_3}$'s, 6H, t, 1.29 ppm, J = 7Hz; P-CH, 1H, bs, 2.34 ppm, W_h=9Hz; $OCH_2\underline{CH_3}$'s, 4H, bm, 3.85-4.4 ppm.

Analysis: Found : C, 57.67; H, 9.0; P, 10.70.
$C_{14}H_{27}O_2PS$ requires: C, 57.93; H, 9.31; P, 10.69%.

Diethyl 1-p-menthenyl-7-thiophosphonate (8): Colorless liquid, b.p. 125-30°/0.5 mm. n_D^{25} 1.4935. $[\alpha]_D$-52.2°($CHCl_3$).

IR (liq. film) (Fig. 7): P-O-C 1040 cm^{-1}; P=S 790 cm^{-1}.

PMR (CCl_4) (Fig. 8): $CH\underline{Me}_2$, 6H, d, 0.9 ppm, J = 7Hz; $OCH_2\underline{CH_3}$'s, 6H, t, 1.28 ppm, J = 7 Hz; P-$\underline{CH_2}$, 2H, d, 2.62 ppm, J = 20 Hz; $OCH_2\underline{CH_3}$'s, 4H, bm, 3.82-4.34 ppm; C$\underline{H}$=C, 1H, bs, 5.54 pom, W_h = 12 Hz.

Analysis: Found : C, 57.56; H, 9.002; P,10.34.

$C_{14}H_{27}O_2PS$ requires: C, 57.93; H, 9.31; P,10.69%.

Diethyl 1-p-menthenyl-6-thiophosphonate (10): Colorless liquid, b.p. 115-20°/0.4 mm; n_D^{25} 1.4965; $[\alpha]_D$ + 12° ($CHCl_3$).

IR (liq. film) (Fig. 9): P-O-C 1035 cm^{-1}; P=S 795 cm^{-1}.

PMR ($CDCl_3$) (Fig. 10): CHMe's, 3H, doublets at 0.9, 0.92 ppm, J = 7 Hz; OCH_2CH_3's, 6H, t, 1.3 ppm, J = 7 Hz; C=C-CH_3, 3H, s, 1.81 ppm; OCH_2CH_3's, 4H, bm, 3.8-4.32 ppm; C = CH, 1H, bs, 5.52 ppm, W_h = 10 Hz.

Analysis: Found : C, 57.67; H, 8.962; P, 10.26.

$C_{14}H_{27}O_2PS$ requires : C, 57.93; H, 9.31; P,10.69%.

Diethyl 3-p-menthanylthiophosphonate (13a): Colorless liquid, b.p. 130-5°(bath)/0.1 mm; n_D^{25} 1.4932; $[\alpha]_D$ + 16° ($CHCl_3$).

IR (liq. film) (Fig. 11): P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}.

PMR ($CDCl_3$) (Fig. 12): $CHCH_3$, 3H, d, 0.84 ppm, J = 7 Hz; $CH(CH_3)_2$, 6H, d, 1.0 ppm, J = 7 Hz; OCH_2CH_3's, 6H, t, 1.3 ppm, J = 7 Hz; OCH_2CH_3's, 4H, bm, 3.88-4.40 ppm.

Analysis: Found : C, 57.17; H, 9.60; P, 10.36.

$C_{14}H_{29}O_2PS$ requires : C, 57.53; H, 9.932; P, 10.62%.

Diethyl 4-caranylthiophosphonate (15): Pale yellow liquid, b.p. 125-30°/0.3 mm; n_D^{25} 1.4945; $[\alpha]_D$ -73.7° ($CHCl_3$).

IR (liq. film) (Fig. 13): P-O-C 1035 cm^{-1}; P=S 785 cm^{-1}.

PMR ($CDCl_3$) (Fig. 14): $CHC\underline{H}_3$, 3H, d, 0.85 ppm, J = 6 Hz; $C\underline{Me}_2$, 3H, singlets at 0.95, 1.01 ppm; $OCH_2C\underline{H}_3$'s, 6H, t, 1.3 ppm, J = 7 Hz; $OC\underline{H}_2CH_3$'s, 4H, bm, 3.85-4.38 ppm.

Analysis: Found : C, 57.48; H, 8.955; P, 10.81.
$C_{14}H_{27}O_2PS$ requires: C, 57.93; H, 9.31; P, 10.69%.

Diethyl 1-p-menthenyl-9-thiophosphonate (17): Pale yellow liquid, b.p. 140-5°(bath)/0.1 mm; n_D^{25} 1.5067.

IR (liq. film) (Fig. 15): P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}.

PMR (CCl_4) (Fig. 16): $CHC\underline{H}_3$, 3H, d, 1.02 ppm, J = 7 Hz; $OCH_2C\underline{H}_3$'s, 6H, t, 1.3 ppm, J = 7 Hz; C=C-$C\underline{H}_3$, 3H, s, 1.62 ppm; $OC\underline{H}_2CH_3$'s, 4H, bm, 3.82-4.30 ppm; C=C$\underline{H}$, 1H, bs, 5.34 opm, W_h = 9 Hz.

Analysis: Found : C, 58.01; H, 9.52; P, 10.35.
$C_{14}H_{27}O_2PS$ requires: C, 57.93; H, 9.31; P, 10.69%.

Diethyl 14-longifolanylthiophosphonate (24): Pale yellow liquid, b.p. 150-5°(bath)/0.1 mm; n_D^{25} 1.5188.

IR (liq. film) (Fig. 17): P-O-C 1030 cm^{-1}; P=S 790 cm^{-1}.

PMR ($CDCl_3$) (Fig. 18): C-$C\underline{H}_3$, 3H, s, 0.77 ppm; $C\underline{Me}_2$, 6H, s, 1.01 ppm; $OCH_2C\underline{H}_3$'s, 6H, t, 1.31 ppm, J = 7 Hz; $OC\underline{H}_2CH_3$'s, 4H, bm, 3.86-4.48 opm.

Analysis: Found : C, 63.90; H, 9.42; P, 8.279.

$C_{19}H_{35}O_2PS$ requires: C, 63.69; H, 9.777; P, 8.66%.

Diethyl 6-bromo-1-p-menthenyl-7-phosphonate (27): A solution of Br_2 (59 mg, 0.37 mmol) in CCl_4 (2 ml) was added dropwise to a chilled (5°) solution of the adduct 7 (0.1 g, 0.37 mmol) in CCl_4 (2 ml). The bromine was instantaneously decolorised. Removal of solvent followed by distillation gave 27 as a pale yellow thick viscous liquid (0.103 g, 80%), b.p. 160-5°(bath)/ 0.1 mm.

IR (liq. film): P=O 1250 cm^{-1}, P-O-C 1025 cm^{-1}.

PMR ($CDCl_3$): CHMe's, 6H, d, 0.93 ppm, J = 7 Hz; OCH_2CH_3's, 6H, t, 1.37 ppm, J = 7 Hz; P-CH_2, 2H, dd, 2.75 ppm, J_1 = 20 Hz, J_2 = 4 Hz; CHBr, 1H, bs, 3.95 ppm; OCH_2CH_3's, 2H, quartets at 4.17, 4.24 ppm, J = 7 Hz; C=CH, 1H, bs, 5.28 ppm, W_h = 8 Hz.

LAH reduction of phosphonates: The following procedure is representative.

The mixture of diethyl 3-p-menthanylphosphonate (12, 0.102 g, 0.37 mmol) in dry ether (10 ml) and LAH (25 mg) was stirred at room temperature (≈30°) for 4 h. The reaction mixture was decomposed with saturated NH_4Cl aq (10 ml) and filtered through celite. The organic layer was separated and the aqueous layer was extracted with ether (10 ml). The combined ether extracts were washed with brine (10 ml) and dried (Na_2SO_4). Removal of solvent followed by distillation gave p-menthane (29) (45 mg, 85%), b.p. 95-100°(bath)/40 mm.

PMR (CCl_4): C-Me's, 9H, doublets at 0.88, 0.93 ppm, J = 7 Hz.

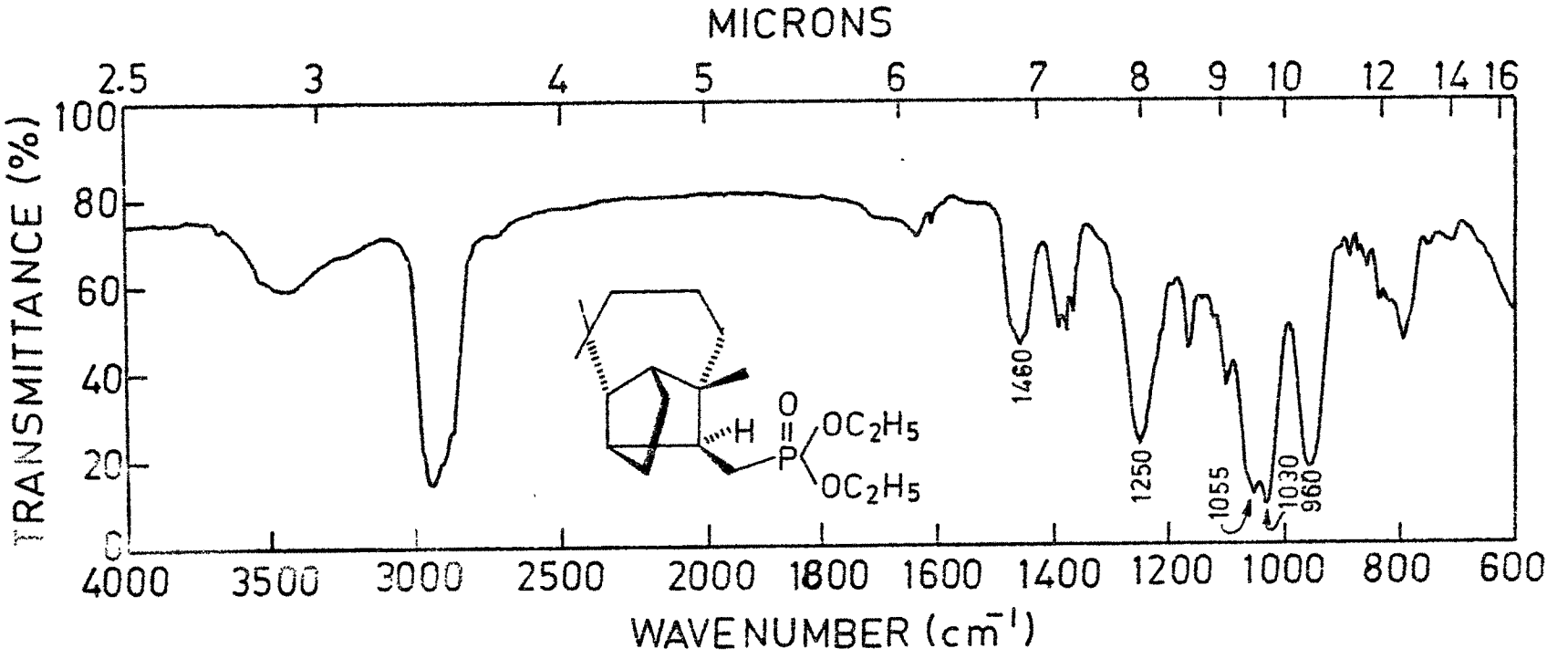

FIG. 1 - IR SPECTRUM OF DIETHYL 14-LONGIFOLANYLPHOSPHONATE (23)

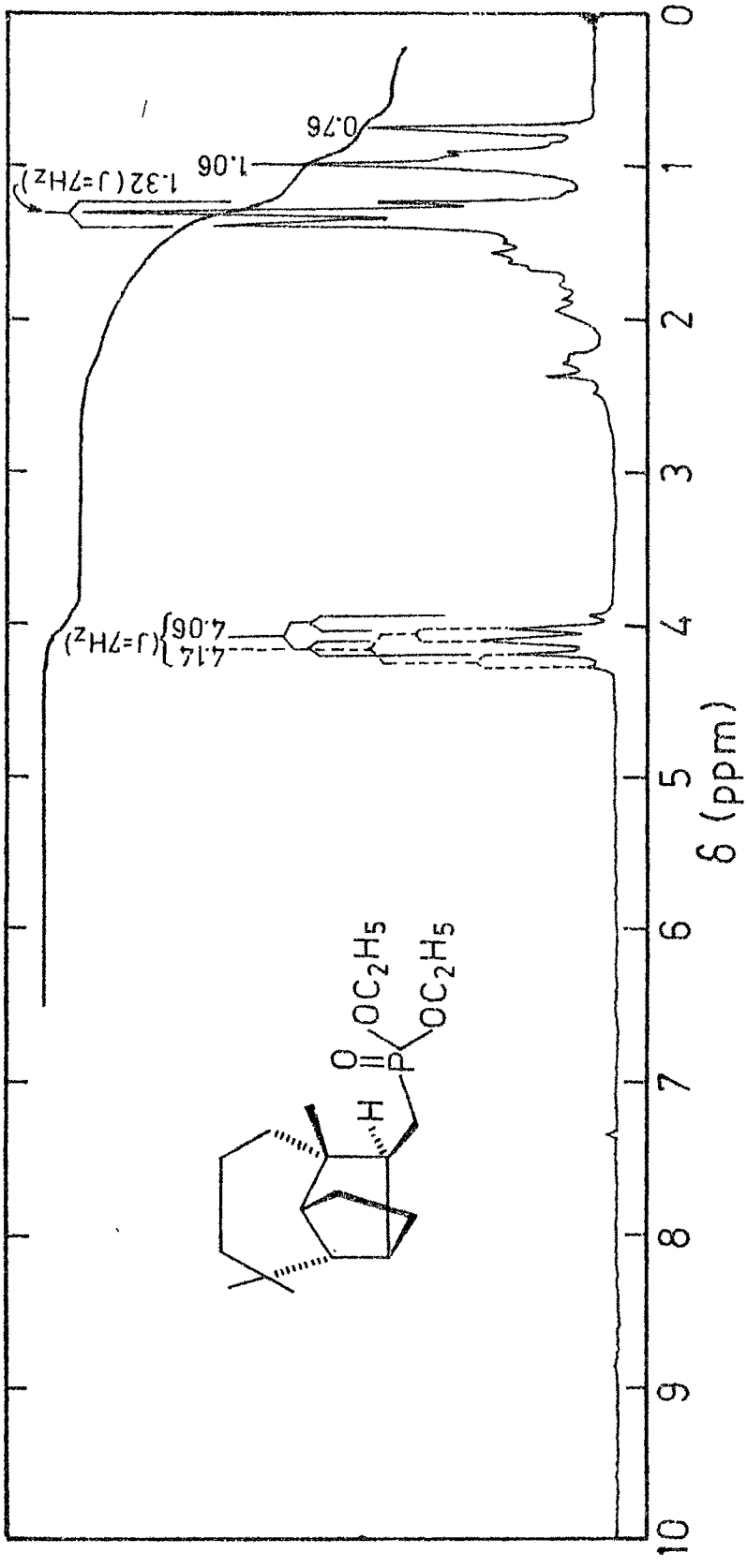

FIG. 2 -PMR SPECTRUM OF DIETHYL 14-LONGIFOLANYLPHOSPHONATE (23)

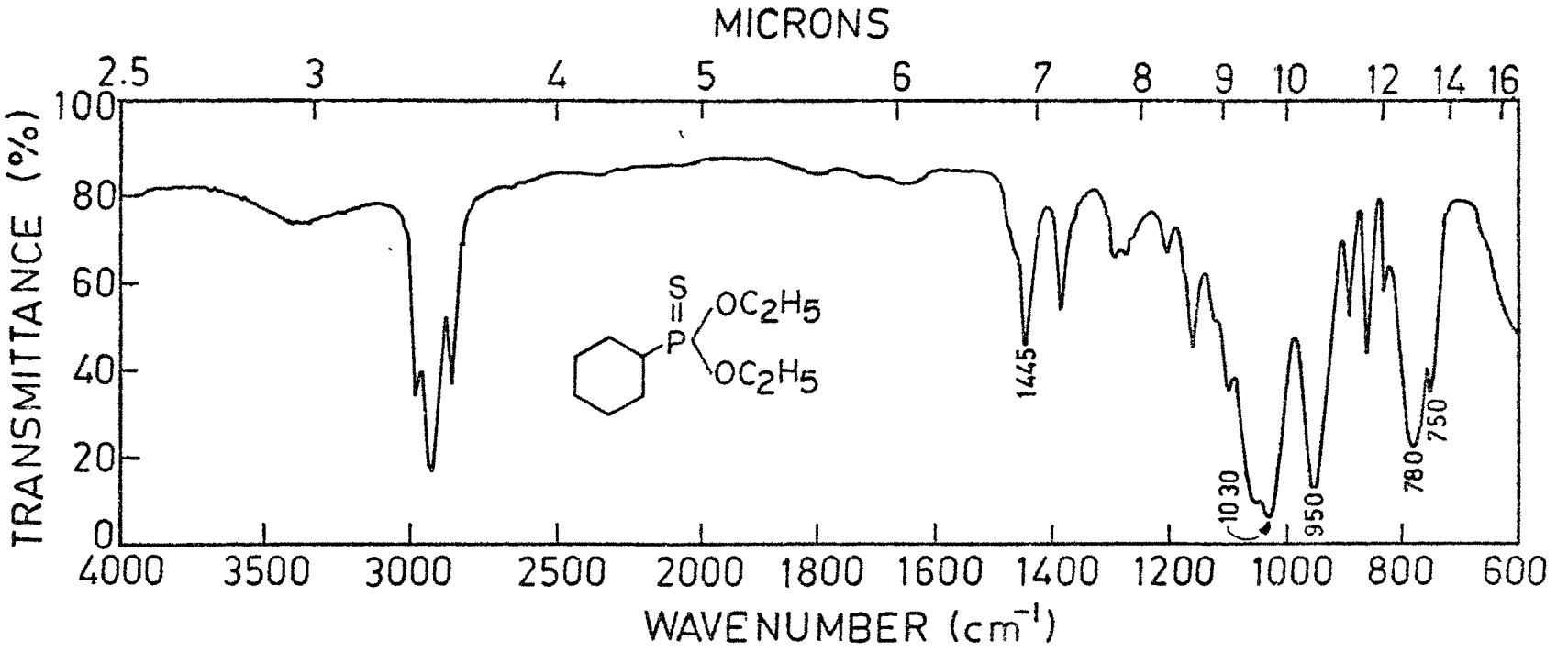

FIG. 3 - IR SPECTRUM OF DIETHYL CYCLOHEXYLTHIOPHOSPHONATE (3)

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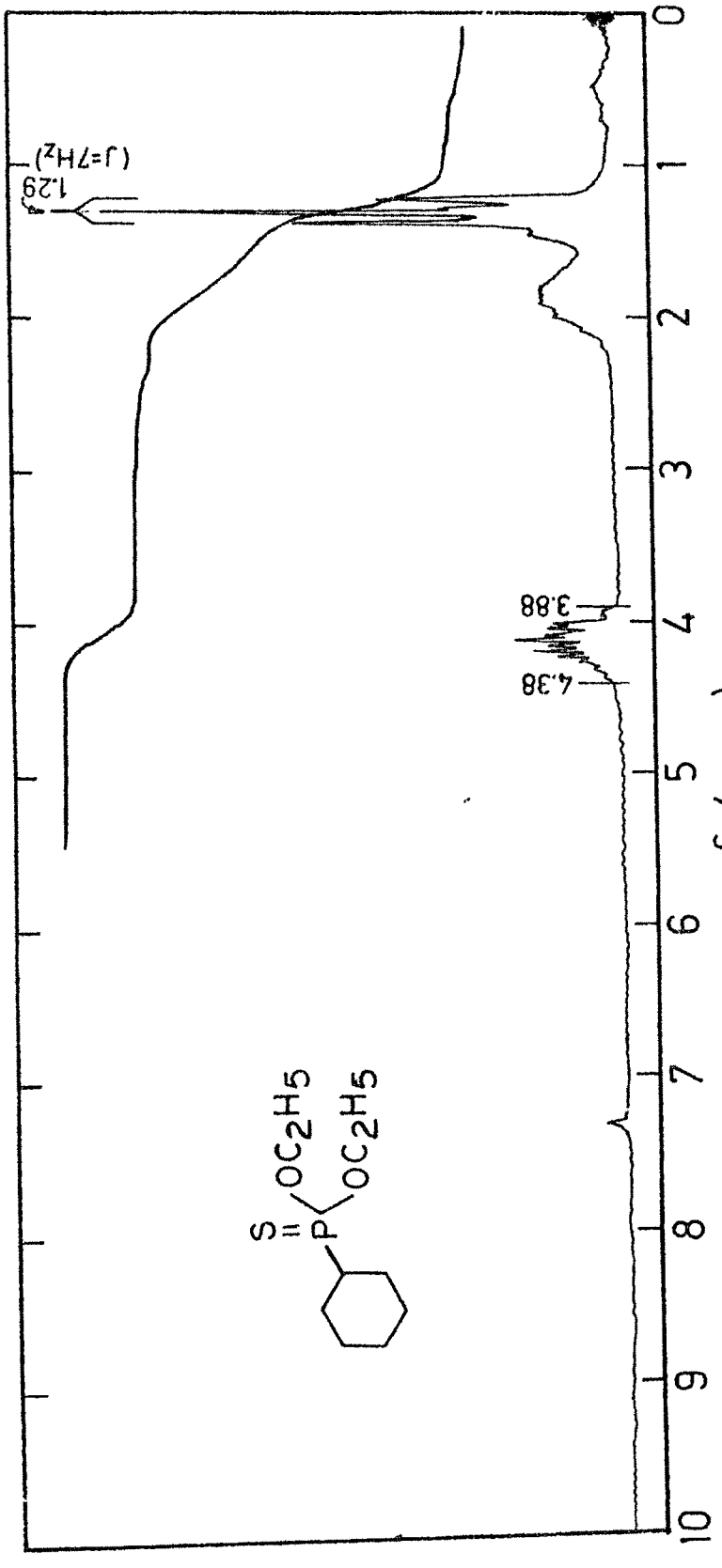

FIG. 4 - PMR SPECTRUM OF DIETHYL CYCLOHEXYLTHIOPHOSPHONATE (3)

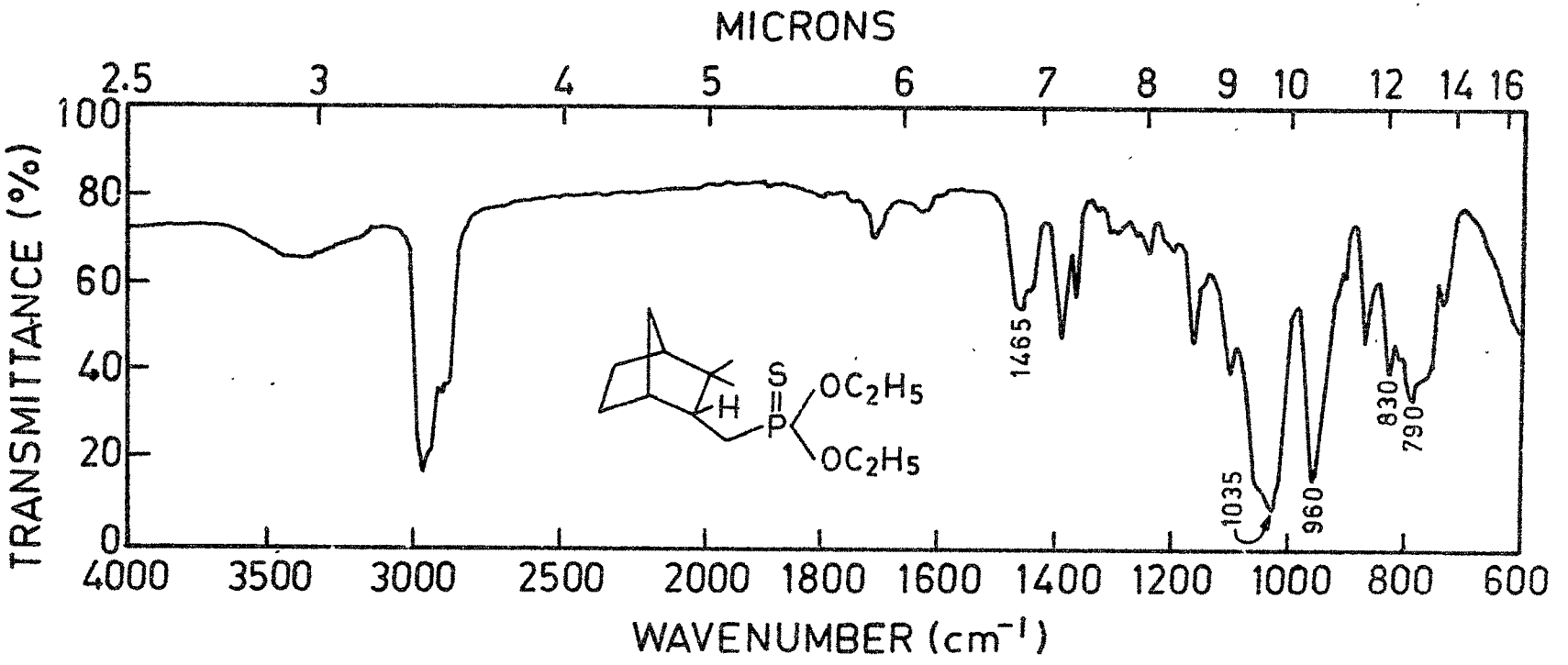

FIG. 5 - IR SPECTRUM OF DIETHYL 10-ENDO-ISOCAMPHANYLTHIOPHOSPHONATE (5)

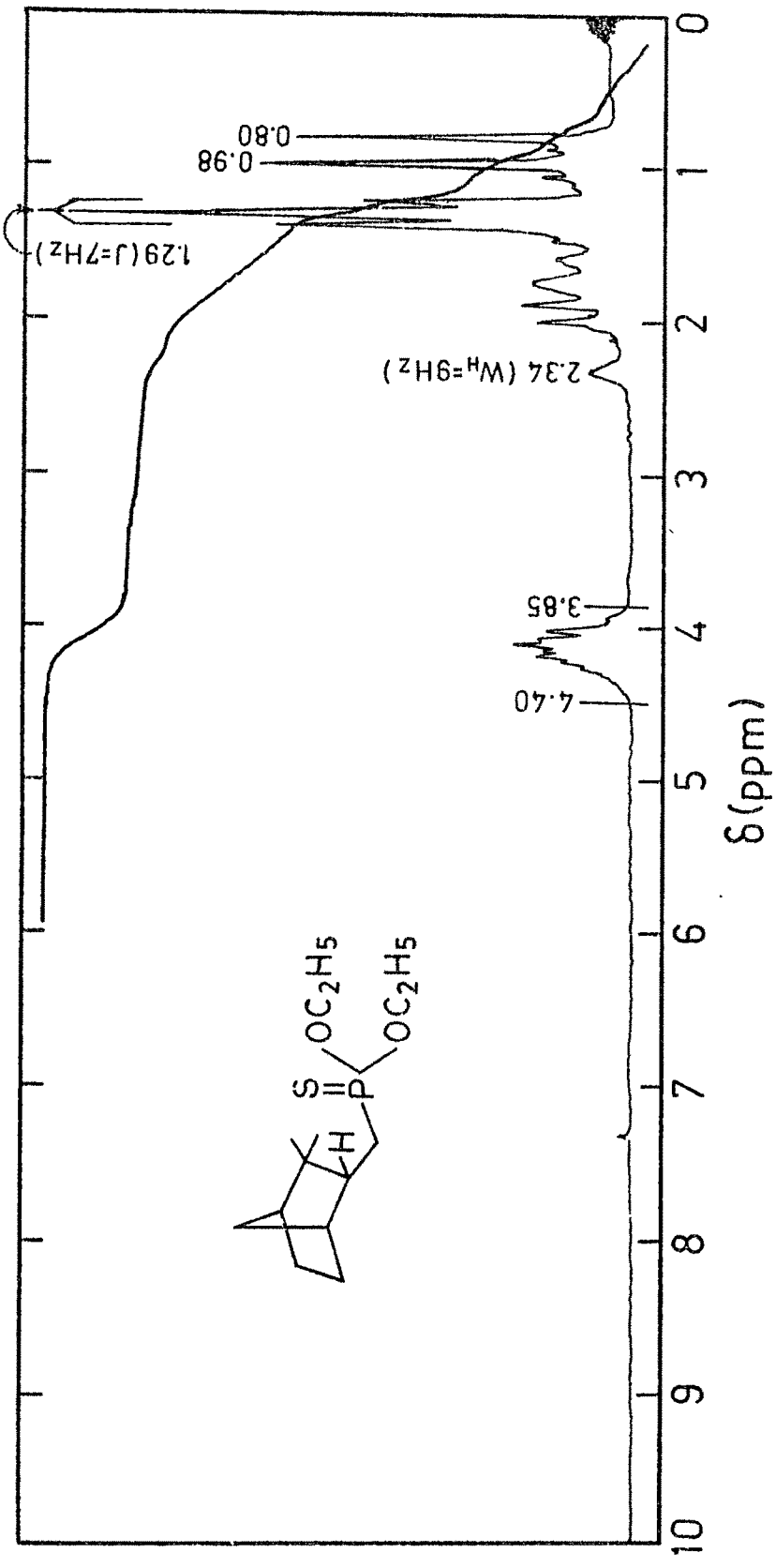

FIG. 6 -PMR SPECTRUM OF DIETHYL 10-ENDO-ISOCAMPHANYLTHIOPHOSPHONATE (5)

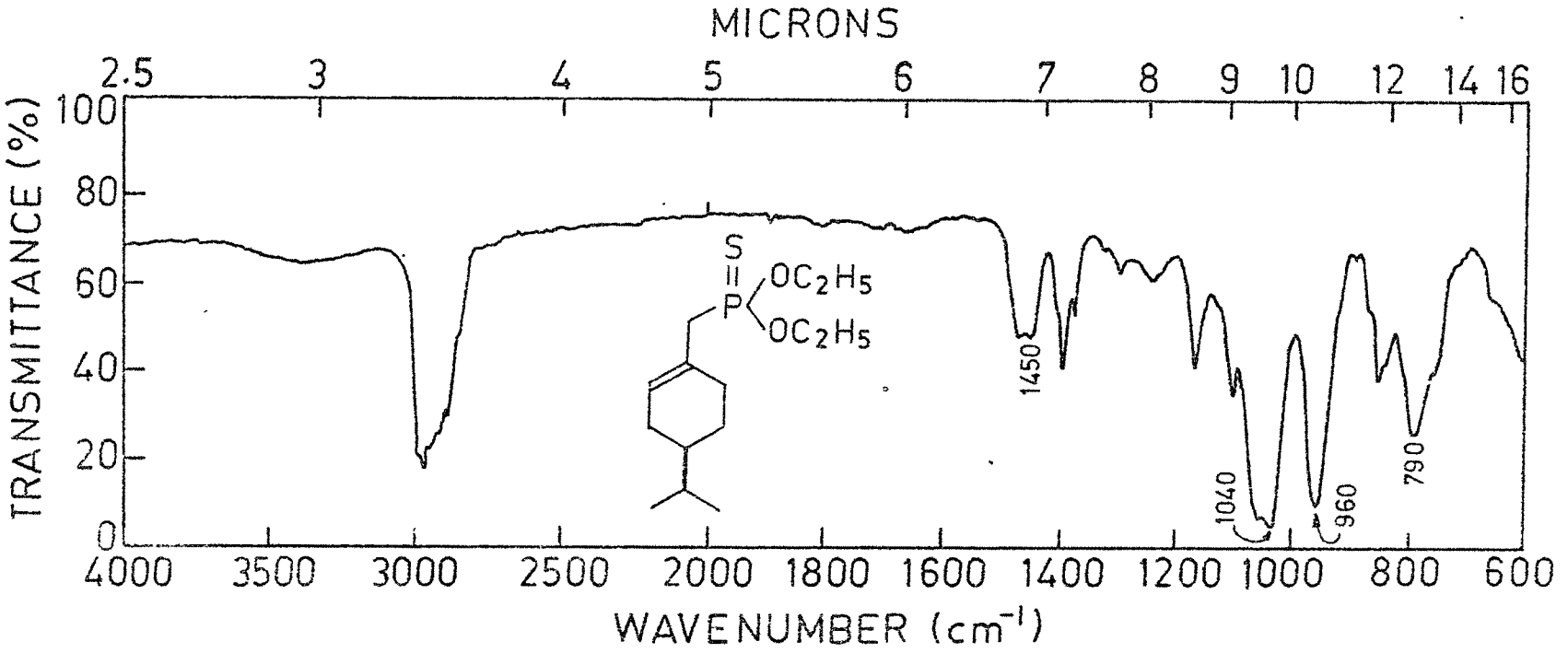

FIG. 7 -IR SPECTRUM OF DIETHY 1-p-MENTHENYL-7-THIOPHOSPHONATE (8)

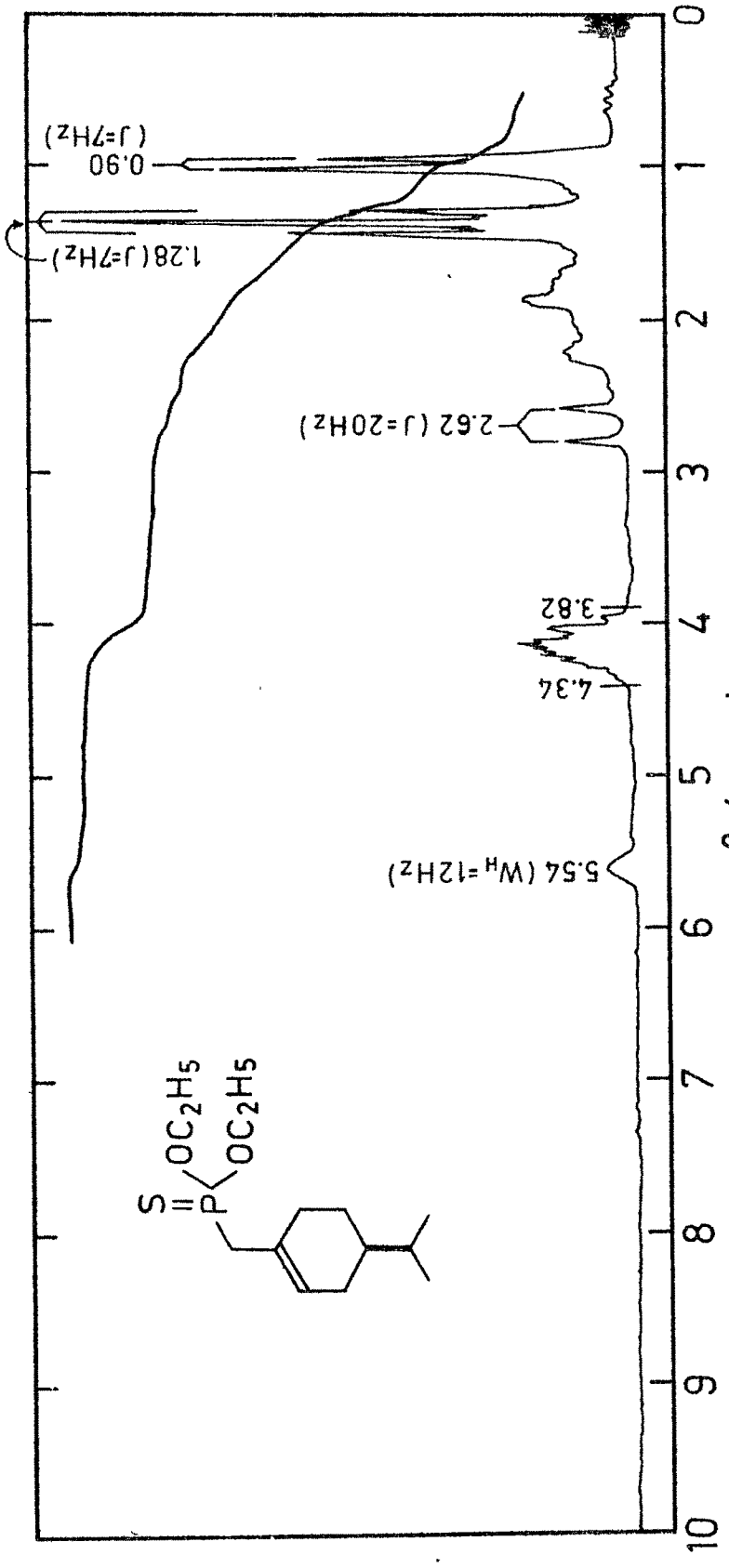

FIG. 8 - PMR SPECTRUM OF DIETHYL 1-p-MENTHENYL-7-THIOPHOSPHONATE (8)

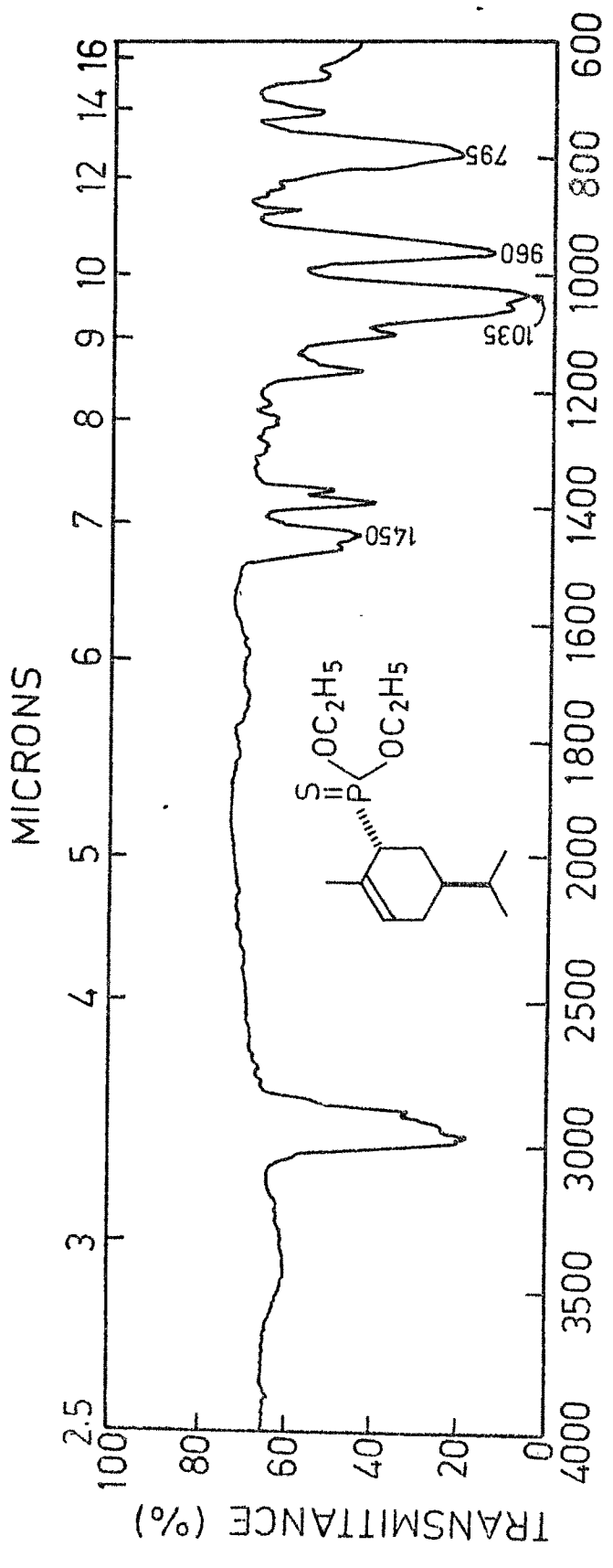

FIG. 9 -IR SPECTRUM OF DIETHY 1-p-MENTHENYL-6-THIOPHOSPHONATE (10)

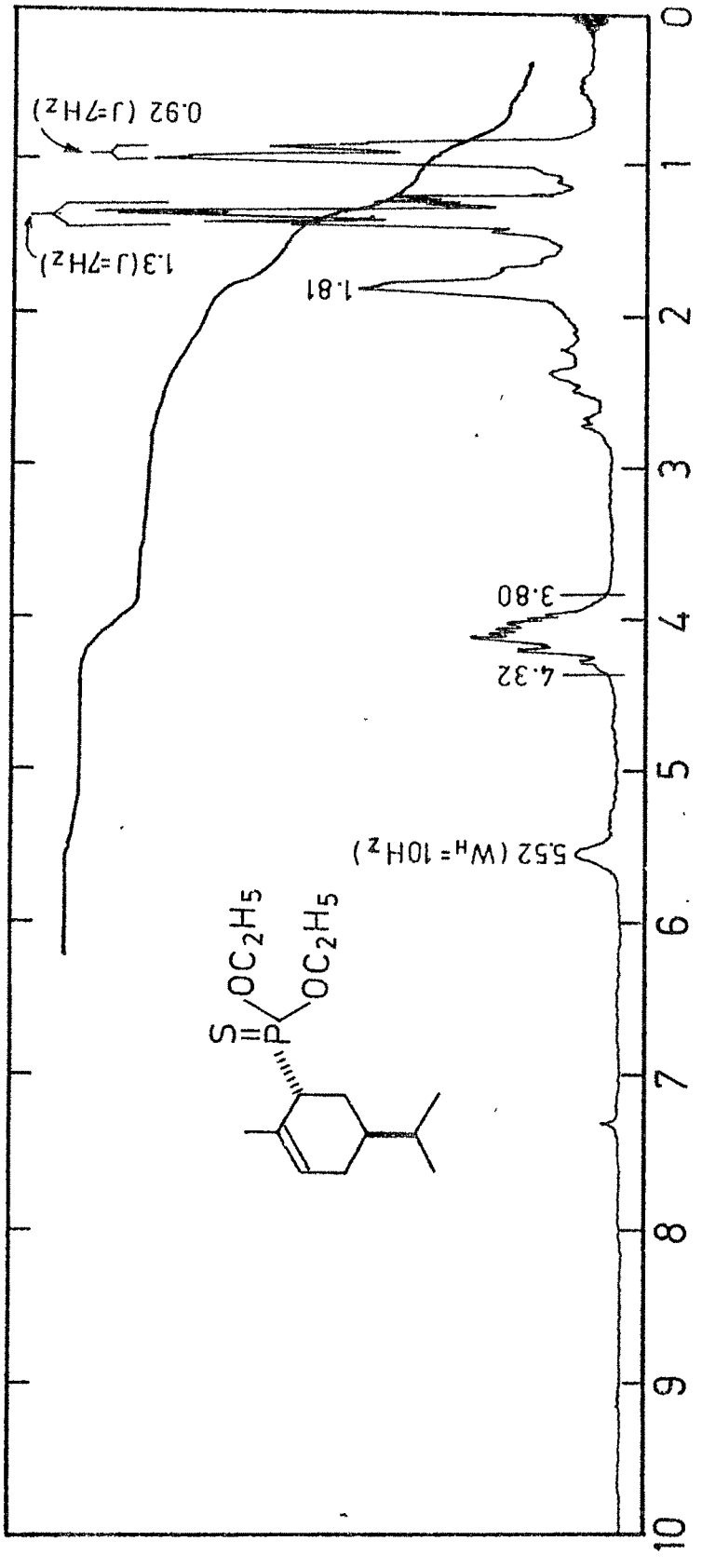

FIG. 10 -PMR SPECTRUM OF DIETHY 1-p-MENTHENYL-6-THIOPHOSPHONATE (10)

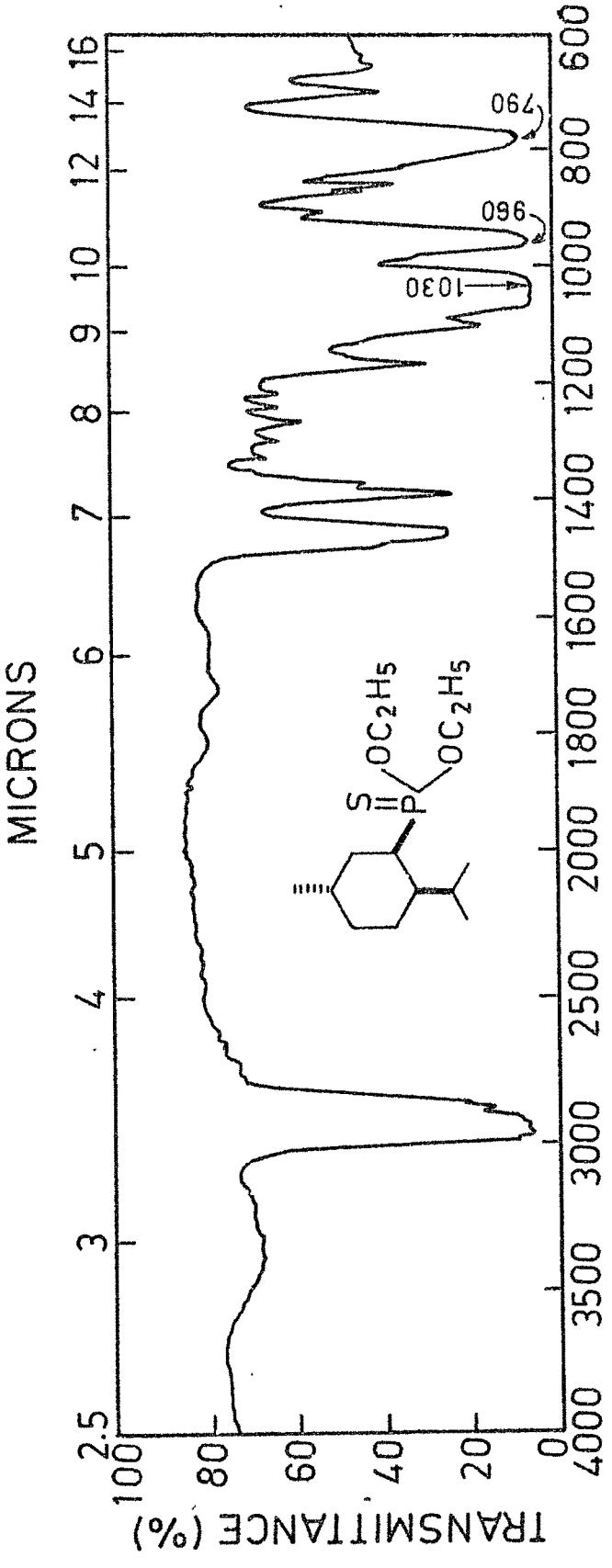

FIG. 11 - IR SPECTRUM OF DIETHYL p-MENTHANYL-3-THIOPHOSPHONATE (13a)

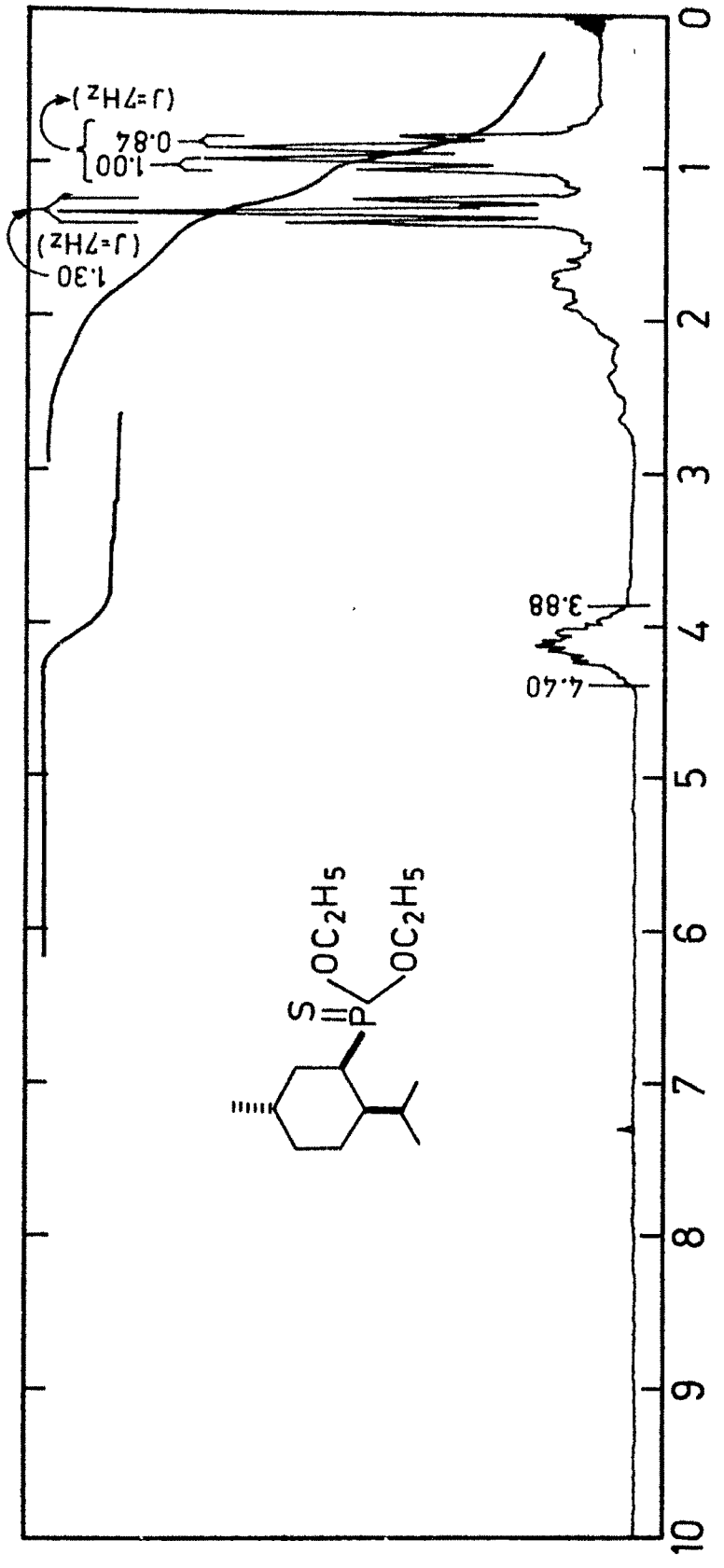

FIG. 12 - PMR SPECTRUM OF DIETHYL p-MENTHANYL-3-THIOPHOSPHONATE (13a)

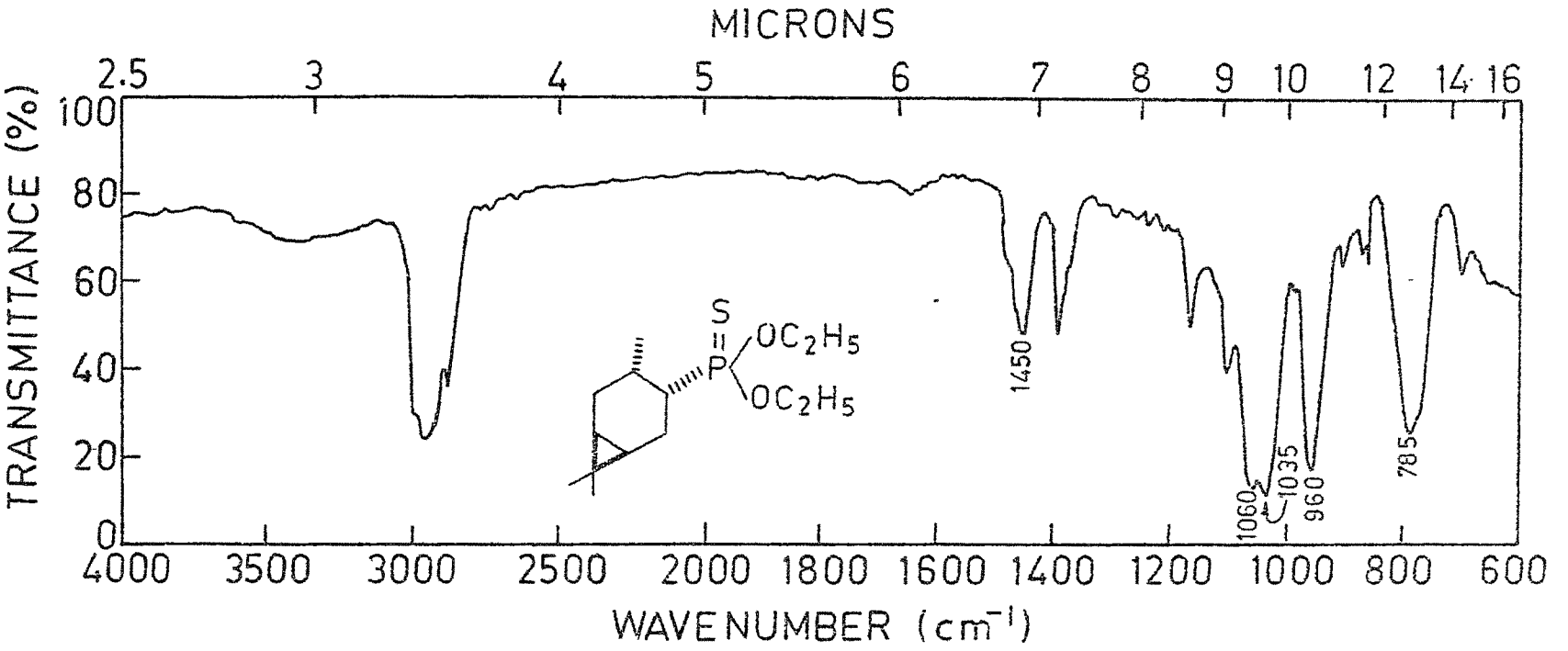

FIG. 13 -IR SPECTRUM OF DIETHYL 4-CARANYLTHIOPHOSPHONATE (15)

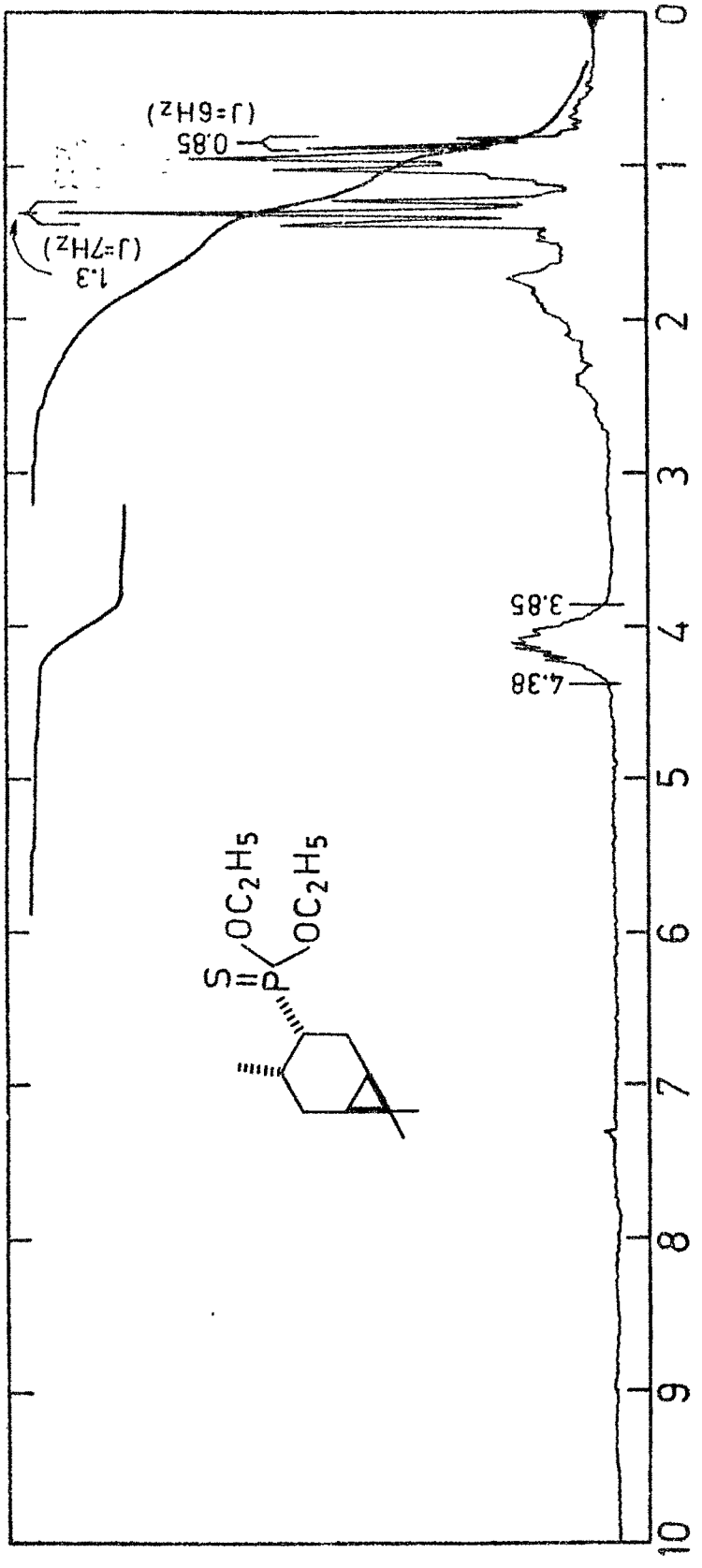

FIG. 14 - PMR SPECTRUM OF DIETHYL 4-CARANYLTHIOPHOSPHONATE (15)

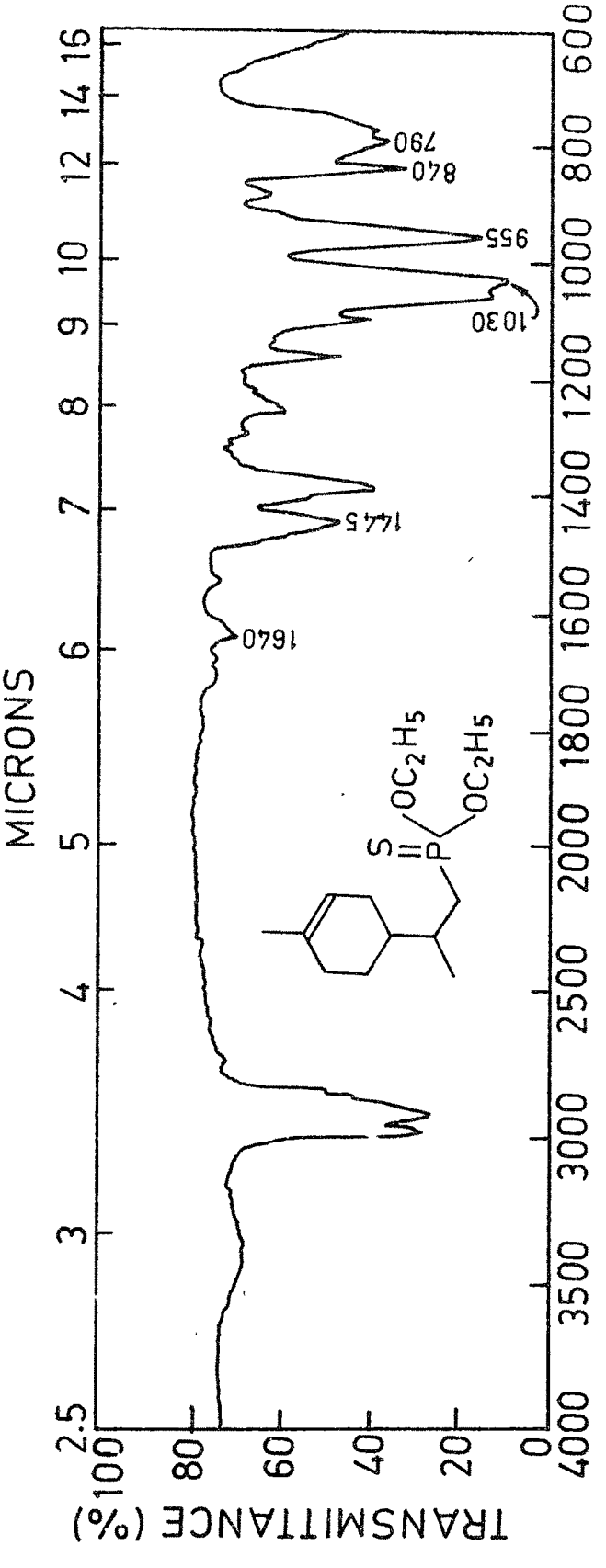

FIG. 15-IR SPECTRUM OF DIETHYL 1-p-MENTHENYL-9-THIOPHOSPHONATE (17)

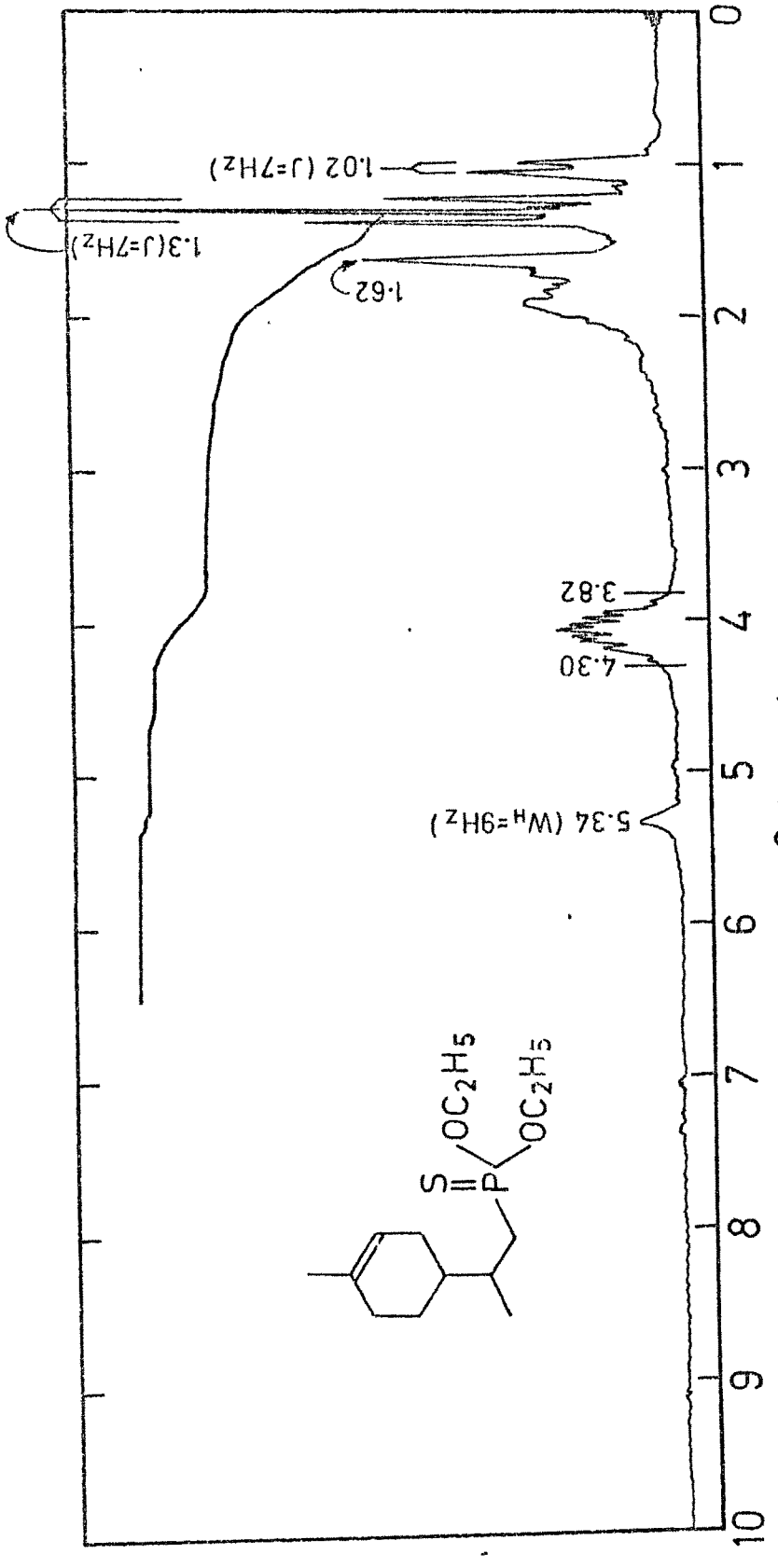

FIG. 16 -PMR SPECTRUM OF DIETHYL 1-p-MENTHENYL-9-THIOPHOSPHONATE (17)

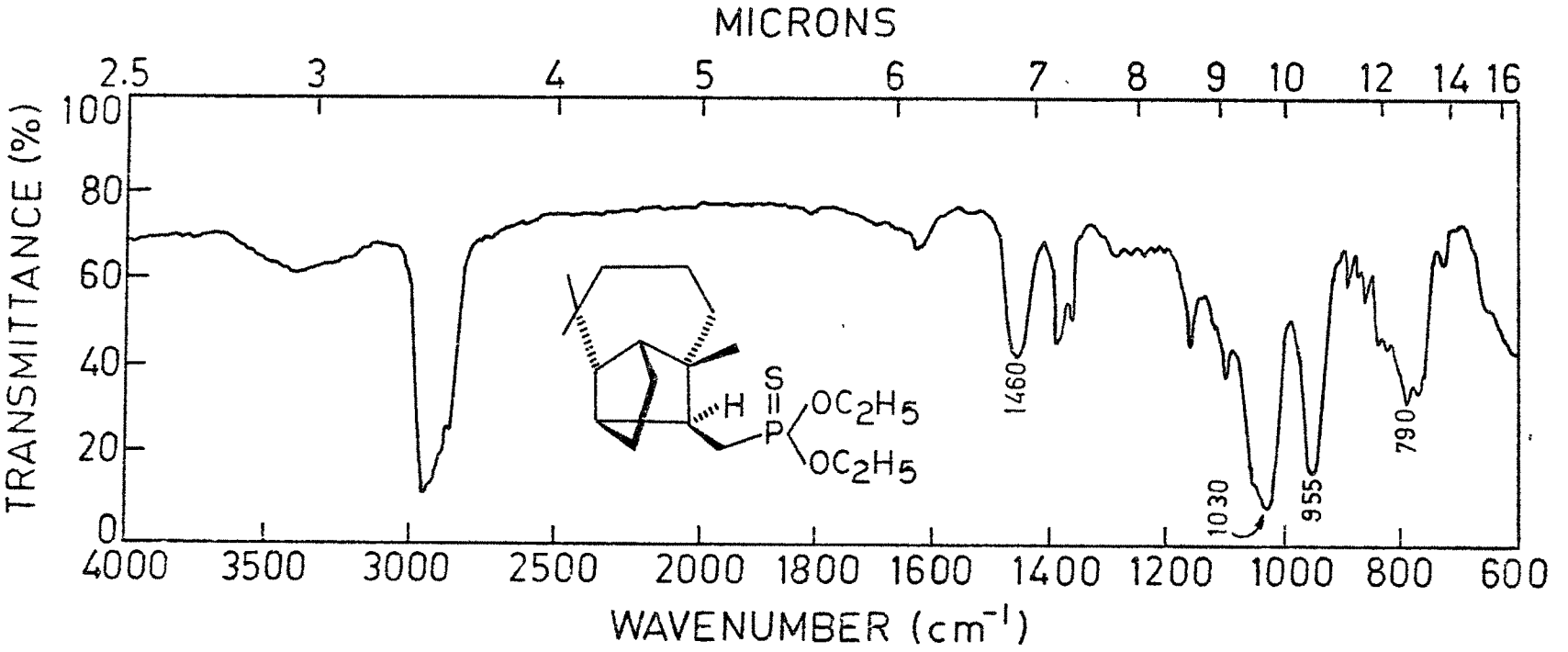

FIG. 17 -IR SPECTRUM OF DIETHYL 14-LONGIFOLANYLTHIOPHOSPHONATE (24)

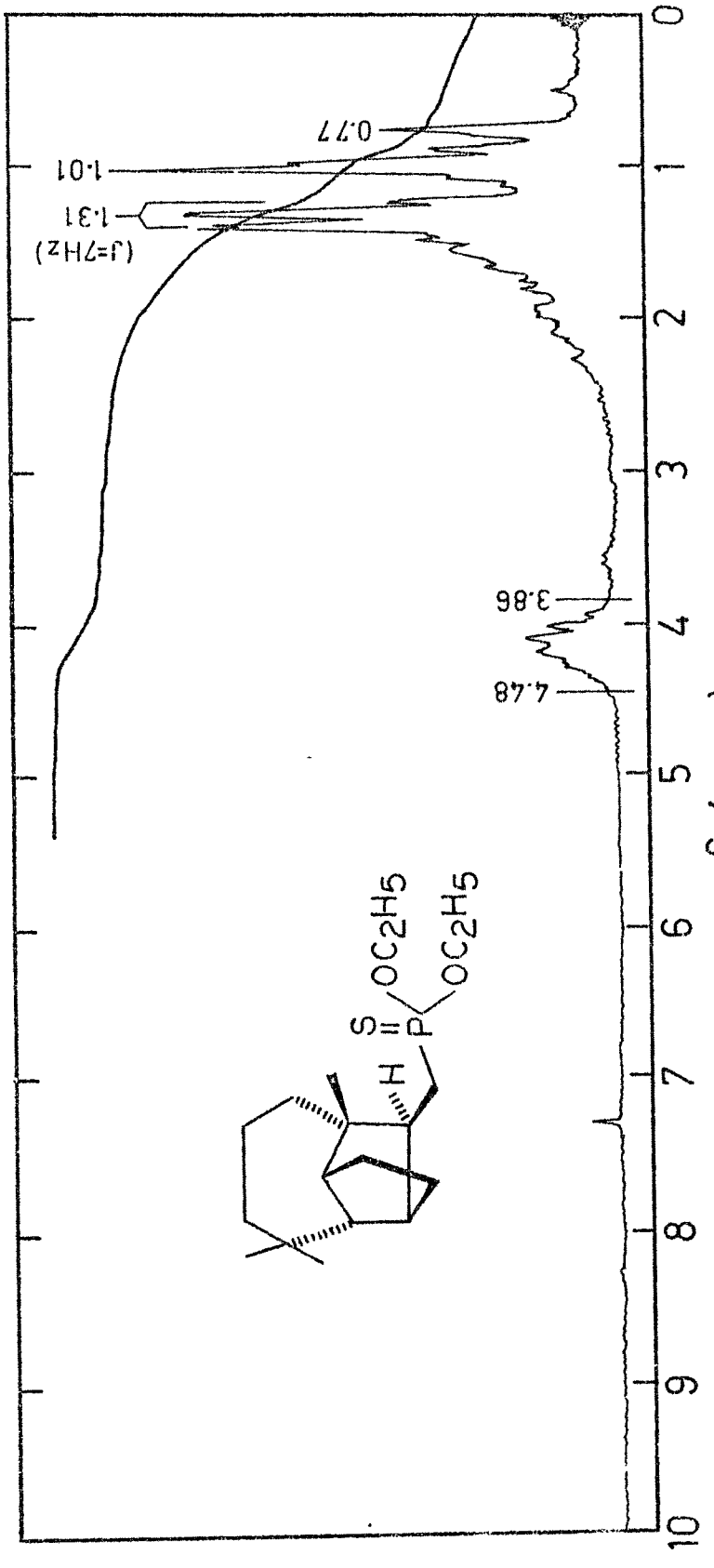

FIG. 18 - PMR SPECTRUM OF DIETHYL 14-LONGIFOLANYLTHIOPHOSPHONATE (24)

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