α-Terpineol (5), Modified Sand Procedure. The original method[6] was exactly followed for the oxymercuration stage using 10 mmol of reagents (2.16 g of HgO and 1.54 g of 5). When the addition was complete, the subsequent reduction was performed by the standard procedure adding 10 ml of 3 *M* NaOH and 10 ml of 0.5 *M* $NaBH_4$ in 3 *M* NaOH to the reaction mixture and extracting with THF as stated above.

Analyses. Qualitative and quantitative analyses were made by glpc. After evaluation of several types of glpc columns, the best choice was a 3 m × 3.5 mm i.d. glass column packed with 5% QF-1 on Anakrom ABS, 90–100 mesh (10 min at 80–170°, 3°/min), which also worked well for the separation of 9 from 1. The dried THF extracts were gas chromatographed and the reaction products identified by comparison of their retention times with those of authentic samples. On the other hand, column chromatography on silica gel (Merck, 200 mesh ASTM) was found adequate for isolation of 1, 9, and 5, eluting with a benzene–ethyl acetate 40:60 mixture. Subsequent elution with methanol drew *cis*-7. In this case all these compounds were identified by ir spectroscopy after purity checks carried out by glpc and tlc on Merck silica gel G with various solvent systems.

Quantitative determinations were performed by glpc peak area evaluation using a Perkin-Elmer SIP-1 electronic integrator. Calculation of relative weight percentages required the determination of relative detector (FID) response factors from a THF standard solution of known amounts of 1, 9, 5, and *cis*-7. Each reaction was repeated to ascertain quantitative reproducibility, and percentages in the text represent average results. In every case reproducibility was within ±1.5%.

Acknowledgments. The support of the Cap.XI/b, Consiglio di Amministrazione dell'Università degli Studi di Firenze, is gratefully acknowledged. The authors would also like to thank Dr. G. Mazzi for assistance in the experimental work.

Registry No.—1, 138-86-3; 5, 10482-56-1; $Hg(OAc)_2$, 1600-27-7.

References and Notes

(1) M. Bambagiotti A., F. F. Vincieri, and G. Cosi, *Phytochemistry*, **11**, 1455 (1972).
(2) H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, **35**, 1844 (1970).
(3) All statements about reaction rates refer to grossly observed relative rates as described in the Experimental Section.
(4) Coxon, *et al.*,[5] stated that the oxymercuration of 5 in the presence of water followed by reduction under Brown's conditions gave terpine hydrate, with no mention of 9.
(5) J. M. Coxon, M. P. Hartshorn, J. W. Mitchell, and K. E. Richards, *Chem. Ind. (London)*, 652 (1968).
(6) J. Sand and F. Singer, *Ber.*, **35**, 3170 (1902).
(7) A. G. Brook and G. F. Wright, *J. Org. Chem.*, **22**, 1314 (1957).
(8) H. C. Brown, P. J. Geoghegan, Jr., J. T. Kurek, and G. J. Lynch, *Organometal. Chem. Syn.*, **1**, 7 (1970–1971).
(9) F. W. Semmler, *Ber.*, **36**, 1033 (1903).
(10) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965).
(11) A. Baeyer, *Ber.*, **26**, 2861 (1893).

Reaction of Terpenes with Diethyl Phosphonate under Free Radical Conditions

Robert L. Kenney and Gordon S. Fisher*[1a]

Naval Stores Laboratory,[1b] Olustee, Florida 32072

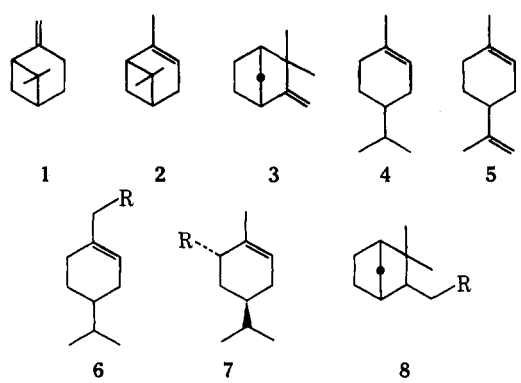
Received September 11, 1973

β-Pinene (1), α-pinene (2), camphene (3), carvomenthene (4), and limonene (5) were treated with commercial diethyl hydrogen phosphite to yield phosphonates. The phosphonate addition to the pinenes yielded *p*-menthenyl derivatives, to camphene yielded isocamphanyl derivatives, and to limonene yielded diphosphonates, with a bornyl derivative as a minor product. Structures based on ir and nmr data are discussed.

As part of this laboratory's efforts to produce flame-resistant naval stores derivatives, it was of interest to prepare some terpenyl phosphonic acids or phosphonates.

The preparation of alkyl phosphonates from olefins has been studied to some extent. Pudovik and Konovalona[2] used uv light or benzoyl peroxide to effect 1:1 anti-Markovnikov addition of dialkyl phosphonates to unsaturated hydrocarbons. They noted that telomers and polymers also were formed. Stiles, *et al.*,[3] obtained polymers when peroxides were used to initiate the addition of dialkyl phosphonates to olefins. Recently, Callot and Benezra,[4] using benzoyl peroxide, added dimethyl phosphonate to norbornadiene to yield a norbornene phosphonate, two diphosphonate derivatives, and a nortricyclene derivative.

In this study we treated commercial diethyl hydrogen phosphite (DEHP) with β-pinene (1), α-pinene (2), camphene (3), carvomenthene (4), and limonene (5) in the presence of di-*tert*-butyl peroxide (DTBP). From 1 a 94% yield of a single product (6) was obtained. The elemental analysis established that it was a 1:1 adduct. The presence of a P=O absorption[4] at 1245 cm^{-1} in its infrared spectrum showed that the terpenyl linkage was to the phosphorus, as expected, not to the oxygen. The appearance of a broad olefinic proton peak at 5.53 ppm in the nmr spectrum showed that the addition had been accompanied by ring opening, as in the case of other free radical additions to β-pinene.[5] The other features of the nmr spectrum were in accord with this assignment. It should be noted that the C_7-H_2 resonance at 2.16 ppm was deshielded by only about 0.2 ppm from the normal allylic methylene position[6] by the phosphonate group. As previously reported,[7] the ethoxy methylene was a quintet due to equal coupling to the methyl protons and to phosphorus.



R = $PO(OCH_2CH_3)_2$

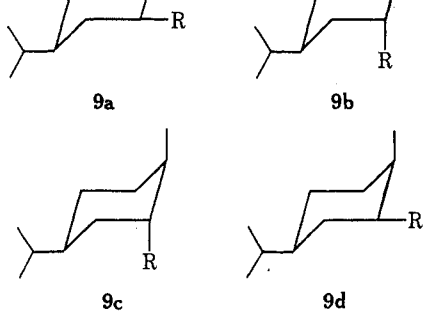
A single product (7) was also obtained from 2, but the yield was somewhat lower (56%). As with 6, elemental analyses and infrared spectrum indicated that it was a ring-opened 1:1 adduct. On steric grounds, the phosphonyl radical should attack 2 trans to C_6 leading to 7. This configuration was confirmed by the high molecular rotation of

the product,[8] which also strongly supports an equitorial isopropyl conformation. Again the effect of the phosphonate group on chemical shifts is of interest. The vicinal, allylic methyl group was deshielded by about 0.15 ppm, but the protons common to **6** and **7** had essentially the same shielding. The deshielding effect of the phosphonate group on the C_6-methine proton was difficult to evaluate, but appeared to be of the same order of magnitude as its effect on the C_7 methylene protons in **6**.

Compound **3** gave a 97% yield of a mixture of two isomers ($\alpha_{2:1}$ = 1.07) in a ratio of about 1:3 in order of emergence. The major isomer was isolated in about 90% purity by preparative gas chromatography (pgc). Davis, *et al.*,[9] added thiophenol to **3** under radical conditions and reported only the *endo*-isocamphanyl product, but they pointed out that with bulkier reagents both exo and endo products should be formed. In no case did they observe skeletal rearrangement of the norbornane ring. On this basis, the major product in the present case should be the *endo*-isocamphanyl phosphonate (**8**) and the minor one the exo epimer. The nmr spectrum supported the assignment of 10-camphanyl structures to both isomers. In particular, the difference in chemical shift between the geminal methyl groups of each isomer precluded a rearranged 10-bornyl structure. However, complexity of the low field region (five protons between 1.7 and 2.5 ppm) and the fact that both the cis and the trans methyls[10] of the major isomer were more shielded than the corresponding methyls of the minor isomer precluded any steric assignment based on the nmr spectrum.

In any case, much more endo transfer occurred with DEHP than with benzenethiol. The difference can be rationalized on the basis that the steric requirements of the diethylphosphonyl radical (or attached group) are greater than those of the phenylthioyl group, making the endo configuration less favorable, but that, because of the greater length of the P–H bond, steric requirements in the transfer step are less for the DEHP, permitting more endo transfer. Alternatively, it is reasonable that exo addition of the phosphonate radical at C_{10} will be favored leading to the less crowded endo C_3 radical, some of which will be trapped if diethyl phosphonate is a better transfer agent than the thiol.

The product obtained from **4** was an even more complex mixture. Analytical glc gave one major peak bracketed by two minor peaks and a fourth very minor peak with much shorter emergence time. Preparative glc readily separated the minor isomer with the longest retention time, but the other minor peak was difficult to separate. By analogy to results of other radical additions to 1,4-dialkylcyclohexenes,[11] the major product should be the neocarvomenthyl phosphonate (**9b**). The neighboring peaks should be the



9a **9b**

9c **9d**

$R = PO(OCH_2CH_3)_2$

carvomenthyl (**9a**) and neoisocarvomenthyl (**9d**) isomers. The infrared spectra of these three were very similar while that of the early peak was different. This supported assignments of diastereoisomeric structures to the three largest peaks and a different structure (*i.e.*, not **9c**) to the early peak.[12] The nmr spectrum of the last glc peak indicated that it was a single isomer with one $POCH_2$ quintet and one C_1-methyl doublet, slightly broadened by long range coupling with phosphorus. On the other hand, the nmr spectrum of the last two thirds of the major peak[13] exhibited two doublets for C_1 methyl and two quintets for methylene protons of the diethyl phosphonate group. Ratios of the corresponding peak heights for the two patterns fall in the range of 35:65 to 40:60, clearly indicating that this glc peak was a mixture of two isomers and that all four isomers of **9** were formed.

Heteronuclear decoupling of both samples confirmed the assumption that the abnormal multiplicity of the OCH_2CH_3 resonance was due to vicinal coupling with phosphorus[7] and sharpened the C_1-methyl bands enough to permit estimation of the methyl–methine coupling (J) for each isomer. Among the carvomenthols, J = 7 Hz for the 1-methyl of neoisocarvomenthol[14] and 6 Hz or less for the 1-methyl of the other three. Since in the present case J = ~6 Hz for the 1-methyl of both major isomers and 7 Hz for the isomer with the longest retention time, this isomer was assigned structure **9d**. The fact that neoisocarvomenthol also has a longer retention than its diastereomers[15] supports this assignment. A similar rationale based on optical rotation can be used to assign structure **9a** to the first minor peak. With C_4 fixed in the *R* configuration, carvomenthol is levorotatory. The other three isomers are dextrorotatory.[15,16] The agreement in molecular rotation [M_D] between **7** and *trans*-carvotanacetol[8] indicated that the hydroxyl group and phosphonate group make similar contributions to the molecular rotation, so only **9a** should be levorotatory. Although it was not practical to get enough of the first minor peak to determine its optical rotation, a reasonably accurate value could be calculated. A glc cut containing 35% of this isomer and 65% of the major peak (M_D = 45°) had M_D = 18°. This corresponds to M_D = −32° for the minor component, compared to M_D = −40° for carvomenthol.[15] Hence, this minor product was **9a** and the major peak was a mixture of **9b** and **9c**.

Rigorous interpretation of the nmr spectral differences in terms of structure was not feasible, but a tentative assignment of structure **9b** to the higher field isomer was made on the basis of the $POCH_2$ resonances. The resonances of the more abundant isomer and **9d** were nearly identical, but the less abundant isomer resonated at higher field. This can be rationalized by assuming that the resonance is determined by the conformation of the $POCH_2$. This group is certainly bulkier than OH; so **9c** should be predominantly the equatorial $POCH_2$ conformer[17] and would have the same resonance as **9d**. The different resonance would belong to the axial $POCH_2$ of **9b**. On this basis, in a typical product the ratio of **9a:9b:9c:9d** would be 8:32:49:11.

The most striking difference between these results and those obtained with 4-*tert*-butyl-1-methylcyclohexene and thiolacetic acid[11] was the formation of **9c** as the major product. None of the corresponding thiolacetate was formed. Radical attack trans to the isopropyl still accounted for 80% of the product, so the difference represented less selectivity in the hydrogen transfer step. This difference is most readily explained on the basis that the C_1 radical is pyramidal[18] and that hydrogen transfer occurs axially.[11] With the relatively small thiolacetate group and the very bulky *tert*-butyl group, the intermediate radical is effectively locked in the original 1-e,2-a,4-e conformation, which is retained after axial hydrogen transfer. Effectiveness of the transfer agent is not involved in the

Table I
Retention Times (Minutes) of Phosphonates on Various Columns[a]

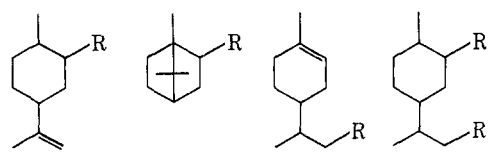
	Temp, °C	He, ml/min	9a	9b,c	9d	7	6
$^3/_{16}$ in. × 12 ft × 20% Carbowax 20M	230	63	15.0	16.0	19.1	16.1	29.2
$^3/_{16}$ in. × 12 ft × 5% Carbowax 20M	230	60	3.1	3.3	3.9	3.4	6.0
$^3/_{16}$ in. × 12 ft × 7.5% Versamid-900	230	67	5.0	5.5	6.3	4.9	9.0
$^1/_4$ in. × 15 ft × 10% Versamid-900	220	100	5.7	6.2	7.2	5.2	9.8
$^1/_4$ in. × 15 ft × 15% Carbowax 20M	225	100	18.9	20.4	21.5		
$^1/_4$ in. × 15 ft × 20% SE-33[b]	235	120	20.9	22.9	24.7		
$^1/_4$ in. × 20 ft × 10% SE-33	230	100	12.3	13.1	14.7		
$^1/_4$ in. × 20 ft × 20% OV-17	225	120	22.2	24.3	27.7		
$^1/_4$ in. × 20 ft × 10% SE-30	220	75	15.1	16.0	17.9		

[a] The $^3/_{16}$ in. columns were used on the Varian 1200 and the retention times were measured from the leading edge of the solvent peak (cyclohexane). The $^1/_4$ in. columns were used on the Wilkens Autoprep-700 and the measurements were from the air peak. All packings were on 70–80 mesh Chromsorb W. [b] Support coated with 1% alkaline Carbowax 20M.

specificity. In the present case, the phosphonate group is at least as bulky as the isopropyl group; so inversion to the 1-e,2-e,4-a conformation, leading to the stable conformer of **9c**, can occur. The product ratio will be influenced by the general effectiveness of the transfer agent, relative stabilities of the two radicals, and any differences in crowding during the transfer step. We can only say that the equilibrium favored the precursor of **9c** and that the phosphonate was not active enough to trap a high percentage of the initial radicals.

The ratios of the isomers arising from attack cis to the isopropyl group were also quite different in the two systems. Paradoxically, less inversion occurred in the carvomenthene–phosphonate system. As has been pointed out by others,[11] attack from the cis face of the molecule does not form an equatorial bond but rather a quasiaxial bond on a flexible skew-boat ring. Hydrogen transfer trans to the point of radical addition also involves a quasiaxial position, somewhat like the endo position in norbornanes and gives compounds like **9d**. The cis 2,4 substituents preclude any conformation of the skew-boat which would give **9a** structures by quasiaxial (or flagstaff) hydrogen transfer. On the other hand, inversion to the chair form followed by axial hydrogen transfer will give only 1-e,2-e,4-e conformations like **9a**. If, as suggested in discussing the addition to **4**, diethyl phosphonate is a better transfer agent than a thiol, more transfer to the flexible radical should occur. This would result in a greater proportion of **9d**, as was observed. Molecular models indicate that an isopropyl group does not restrict the flexibility of the skew-boat as much as a *tert*-butyl group does. This may also contribute to the higher yield of **9d** by increasing the life of the skew-boat radical.

Using the standard reaction conditions, compound **5** gave a mixture of 1:1 and 1:2 adducts. Due to the dimerization of **5**, efforts to get only the 1:1 adducts by using reverse addition to maintain a large excess of **5** were unsuccessful, but nearly quantitative yields of 1:2 adducts were obtained by adding more peroxide and increasing the reaction time. The nmr spectrum of the major 1:1 adduct



10a **10b** **11** **12**

R = $PO(CH_2CH_3)_2$

established its structure as **11**. Quantitative hydrogenation confirmed the presence of one double bond.

On the basis of its nmr spectrum and its failure to hydrogenate, the minor (shorter emergence time) 1:1 adduct was not **10a** but a saturated product. The nmr spectrum exhibited 6- and 3-proton singlets and a broad 1-proton doublet at 2.22 ppm (J = 17 Hz), presumably due to a PCH methine slightly coupled to other hydrogens. These spectral features require a structure such as **10b**. Since the exocyclic double bond reacted much more rapidly than the endo one, any **10a** formed would have been converted rapidly to **12**. So failure to build up any significant concentration of **10a** is not surprising. When a crude product that was mostly 1:1 adducts was hydrogenated, the early peak decreased and an equivalent amount of a peak corresponding to **9b,c** appeared. Hence, **10a** was present in the crude product and had the same emergence time as **10b**.

The nmr spectrum confirmed that the material with long retention time contained two phosphonate groups per mole of **5**. As in the case of **9**, all four isomers were obtained. No attempt was made to isolate and identify the individual isomers, but it is assumed that **12a** and **12d** have structures corresponding to **9a** and **9d**.

Formation of **10b** from **5** was unexpected, but it is reasonable. As in the case of **4** and **11**, the radical attack at C_2 of **5** trans to the isopropyl group should predominate. As previously discussed, formation of **9c** and **12c** demonstrated that some inversion of the initial radical at both C_2 and C_4 occurred faster than hydrogen transfer. Stepwise inversion leads to a flexible boat structure. One conformation of this boat places the partially filled p or sp_3 orbital at C_1 close to the π bond at C_8 and reasonably well aligned for overlap leading to s-bond formation. This would generate an unhindered radical, at C_9, that would pick up a hydrogen to give **10b**. On this basis, **10b** would have an exo methine hydrogen at C_2; *i.e.*, it should be the bornyl phosphonate. This assignment was confirmed by the molecular rotation (+52°). (+)-Limonene is structurally related to (+)-borneol (M_D = +58°) and to (−)-isoborneol.[19]

In order to determine whether the phosphonate derivatives would have significant flame retardance, pieces of filter paper were saturated with 10% solutions of each adduct, drained, and air-dried. The coated strips were mounted vertically and a lighted match was touched to the top edge. In general, the strips would ignite but would not sustain a flame.

Experimental Section

The terpenes and diethyl hydrogen phosphite (DEHP) used were freshly distilled from commercial samples.[20] Densities were determined in calibrated hairpin glass capillaries. Optical rotations were determined neat. Ir curves were run neat on a Perkin-Elmer, Model 21 infrared spectrophotometer. Nmr was determined in deuteriochloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard using Varian A-60A and Bruker 90-MHz instruments. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Table II
Nmr[a] Chemical Shift (Parts per Million), Multiplicity, and Coupling Constant (Hertz)

Isomer	$C_{9,10}$-CH_3	C_7-CH_3	$POCH_2$	$POCH_2CH_3$
9b,c (major)	0.89 (d, J = 6)	1.15 (d, J = 6)	1.32 (t, J = 7)	4.10 (qn, J = 7)
Decoupled[b]	0.90 (d, J = 6)	1.17 (d, J = 7)	1.34 (t, J = 7)	4.10 (q, J = 7)
9b,c (minor)		1.11 (d, J = 5)		4.08 (qn, J = 7)
Decoupled[b]		1.13 (d, J = 5)		4.09 (q, J = 7)
9d	0.91 (d, J = 6)	1.08 (d, J = 7)	1.33 (t, J = 7)	4.10 (qn, J = 7)
Decoupled[b]	0.92 (d, J = 6)	1.08 (d, J = 7)	1.34 (t, J = 7)	4.11 (q, J = 7)

[a] At 90 MHz, in $CDCl_3$ (J values in Hz). [b] p31 at 6342 Hz.

Table III
Composition, %[a]

Hr	10	11	12	Total
0.5	1.2	4.2	1.7	7.0
1.0	2.1	6.5	1.8	10.4
2.0	2.7	8.6	5.6	16.9
3.5	2.4	9.4	9.2	21.0
4.5	2.2	5.0	22.4	29.6
6.25	2.0	0.1	32.1	34.2

[a] Per cent of reaction mixture.

General Procedure. Adducts were prepared by heating 0.5 mol of DEHP to 140°, adding 0.005 mol of di-*tert*-butyl peroxide (DTBP), then adding 0.1 mol of terpene dropwise over a period of about 30 min and continuing heating for a total of 3.5 hr. Most of the unreacted materials were distilled off under vacuum. An ether solution of the residue was extracted with dilute base, washed with water, and dried and the ether pulled off under house vacuum. The products were isolated by vacuum distillation and by preparative gas chromatography on a Wilkens Autoprep, Model 700, using one or more of the columns listed in Table I. Analyses were run on a Varian Aerograph, Model 1200, gas chromatograph using one or more of the columns listed in Table I.

Diethyl 1-*p*-menthenyl 7-phosphonate (6) was prepared from **1** ($\alpha^{29}D$ −14.6°). Once initiated, this reaction was exothermic and heating had to be controlled to keep the reaction temperature below 150°. The yield was 32 g of crude **6** which glc analysis indicated was 80% (25.7 g) **6**, with an overall yield of 94%. An analytical sample was collected by pgc from a distillation cut (125–127° (0.1 mm)) of the crude product: d^{24} = 1.009, $n^{20}D$ 1.4649, $\alpha^{25}D$ −35.4°; ir 2910, 1430, 1385, 1360, 1245, 1160, 1095, 1045, 1025, 950, 845, 790 cm^{-1}; nmr δ 0.88 (d, 6, J = 6 Hz, $C_{9,10}$-CH_3), 1.25 (t, 6, J = 7 Hz, $C_{12,14}$-CH_3), 2.16 (d, 2, J = 22 Hz, C_7-CH_2), 4.02 (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2), and 5.53 ppm (bs, 1, C_2-vinyl).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92; P, 11.29. Found: C, 61.11; H, 10.03; P, 11.48.

Compound **6** was prepared in the absence of peroxide by heating 0.1 mol (13.8 g) of **1** and 0.5 mol (69.1 g) of DEHP at 140–150° for 3.5 hr. The yield was 10.2 g of crude product which glc analysis indicated was 83% (8.5 g) **6** with an overall yield of 31%. Another run in which 0.05 mol (6.8 g) of **1** and 0.25 mol (34.5 g) of DEHP were heated at 75–85° for 3.5 hr yielded 6.2 g of crude product which glc indicated was 76% (4.7 g) **6** or an overall yield of 34%.

Diethyl 1-*p*-menthenyl-6-phosphonate (7) was prepared from **2** ($\alpha^{29}D$ +21.4°). The yield was 21 g of crude **7** which glc analysis indicated contained 73% (15.3 g) **7** with an overall yield of 56%. An analytical sample was collected by pgc from a distillation cut (106° (0.1 mm)) of the crude product: d^{24} = 1.008; $n^{20}D$ 1.4662; $\alpha^{25}D$ +53.1°; ir 2930, 1440, 1385, 1360, 1240, 1160, 1095, 1045, 1020, 950, 788 cm^{-1}; nmr δ 0.89 (d, 6, J = 6 Hz, $C_{9,10}$-CH_3), 1.29 (t, 6, J = Hz, $C_{12,14}$-CH_3), 1.83 (bs, 3, C_7-CH_3), 2.48 (dd, 1, J = 6, 22 Hz, C_6-CH) 4.06 (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2), and 5.51 ppm (bs, 1, C_2-vinyl).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92; P, 11.29. Found: C, 61.13; H, 10.07; P, 11.16.

Compound **7** was prepared in the absence of the peroxide by heating 0.1 mol (18.6 g) of **2** and 0.5 mol (69.1 g) of DEHP at 140–150° for 3.75 hr. The yield was 9.2 g of crude **7** which glc analysis indicated was 72% of **7** with an overall yield of 24%.

Diethyl 10-*endo*- and -*exo*-isocamphanylphosphonates (8) were prepared from **3**. The yield was 25.5 g of crude product which glc analysis (12 ft × 3/16 in × 20% Carbowax 20M at 235° and He at 63 ml/min) indicated was 23% isomer 1, 73% isomer 2, and 4% unidentified. Isomers 1 and 2 were eluted at 14.4 and 15.4 min from the cyclohexane solvent peak. Isomer 1 was not isolated in high purity except for a few milligrams which were used for ir: isomer 1 ir 3400, 2900, 1460, 1385, 1360, 1240, 1155, 1080, 1050, 1020, 950, 856, 820, 800 cm^{-1}.

Diethyl 10-*endo*-isocamphanylphosphonate (8), isomer 2, was isolated by pgc (10 ft × 1/4 in. × 20% Carbowax 20M at 230° and He at 120 ml/min) in 90% purity: d^{24} = 1.0412; $n^{20}D$ 1.4704; ir, 3490, 2950, 1460, 1385, 1360, 1250, 1155, 1090, 1050, 1025, 955, 860, 792 cm^{-1}; nmr δ 0.81 (s, CH_3 cis to C_{10}) 0.98 (s, CH_3 trans to C_{10}), 1.32 (t, J = 7 Hz, $C_{12,14}$-CH_3), and 4.09 ppm (qn, J = 7 Hz, $C_{11,13}$-CH_2); for minor isomer 0.89 (s, CH_3 *cis* to C_{10}) and 1.05 ppm (s, CH_3 trans to C_{10}).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92; P, 11.29. Found: C, 61.09; H, 9.89; P, 11.45.

Isomers 1 and 2 were also prepared by heating 6.8 g (0.05 mol) of **4** and 34.5 g (0.25 mol) of DEHP at 140–150° for 3.5 hr. Work-up yielded 7.75 g of crude product which glc indicated was 23% isomer 1, 75% isomer 2, and 2% unidentified. This was a 55% crude yield.

Diethyl *p*-menthanyl-2-phosphonate (9) was prepared from **4** ($\alpha^{29}D$ +62.9°). The yield was 24.3 g of crude **9**. An analytical sample collected by pgc from a distillation cut (106–108° (0.2 mm)) of the crude product contained 7% **9a**, 77% **9b** and **c**, and 5% **9d**. It had d^{24} 1.0175, $n^{20}D$ 1.4578, $\alpha^{25}D$ +17.3°, nmr δ 0.88 (d, J = 5 Hz, $C_{9,10}$-CH_3), 1.12 (d, J = 6 Hz, C7-CH_3), 1.32 (t, J = 6 Hz, $C_{12,14}$-CH_3), and 4.10 (qn, J = 7 Hz, $C_{11,13}$-CH_2) ppm; ir 2910, 1450, 1385, 1360, 1240, 1200, 1160, 1095, 1055, 1030, 950, 782 cm^{-1}.

Anal. Calcd for $C_{14}H_{29}O_3P$: C, 60.84; H, 10.58; P, 11.41. Found: C, 61.01; H, 1070; P, 11.43.

Glc peaks **9a, b, c,** and **d** were isolated by repeated pgc collections from Carbowax 20M and then OV-17 columns. Isomer **9a** could not be isolated in better than 66% purity, with the major contaminant being **9b,c** (28%). Peak **9b,c** was isolated in 98% purity and **9d** in 94% purity: ir **9a** 3430, 2900, 1465, 1390, 1365, 1240, 1206, 1160, 1090, 1048, 1020, 945, 867, 788, 743, 698; **9b,c** 3430, 2910, 1465, 1390, 1365, 1235, 1200, 1155, 1090, 1050, 1025, 950, 782, 738; **9d** 3420, 2900, 1470, 1445, 1390, 1370, 1235, 1205, 1160, 1095, 1055, 1025, 950, 872, 784, 733, 697 cm^{-1}. See Table II for nmr data.

When heated at 140–150° for 3.5 hr, 6.9 g (0.05 mol) of **4** and 34.5 g (0.25 mol) of DEHP yielded only 0.96 g (7%) of crude **9**.

Reaction of DEHP with Limonene (5). A 34.5 g (0.25 mol) sample of DEHP was heated to 140° and 0.37 g (0.0025 mol) of DTBP added, then 6.8 g (0.05 mol) of **5** ($\alpha^{25}D$ +98.6°) was added dropwise over 0.5 hr, with heating and stirring continued for a total of 3.4 hr. Isolation of the product by diluting with water and extracting with ether yielded 13.1 g of crude product. Glc analysis (12 ft × 1/8 in. × 2% OV-17 at 250° and He at 32 ml/min) using methyl stearate as an internal standard, indicated that the product was 98% adduct (8.7% **10**, 32.2% **11**, 1.1% **12a**, 26.4% **12b**, 26.6% **12c**, and 2.9% **12d**). The response factor for **10** and **11** was 0.81× stearate and for **12a–d** was 0.39× stearate.

The isomers were concentrated by vacuum distillation through a spinning band column yielding a cut (98–102° (0.8 mm)) which contained 47% **10**, a trace of **11** and low-boiling materials, another cut (90–93° (0.5 mm)) containing 5% **10** and 91% **11**, and a cut (121–126° (0.1 mm)) containing 99% of the diadducts **12**. Isomers **10** and **11** were further purified by pgc (10 ft × 1/4 in. × 20 Carbowax 20M at 230° and He at 120 ml/min) to 95% purity.

In a similar run using 25.9 g (0.19 mol) of DEHP, 5.13 g (0.038 mol) of **5**, and 0.28 g (0.0019 mol) of DP and heating for 3.5 hr, then adding another 0.27 g of DTBP and continuing heating for 2.75 hr longer, the reaction was followed by sampling at intervals and analyzing by glc using the internal standard. The results are given in Table III.

Extractive isolation of the final product yielded 14.0 g of material (3.3% **10b**, 0.2% **11**, 2.0% **12a**, 40.5% **12b**, 44.2% **12c**, and 6.6%

12d). Allowing for sample withdrawal, the yield was 97.4% based on diphosphonate adduct.

Diethyl bornyl-2-phosphonate (10b): d^{24} = 1.0346, $n^{20}D$ 1.4692, $\alpha^{25}D$ 18.6°; ir 3450, 2910, 1455, 1385, 1365, 1285, 1235, 1155, 1090, 1055, 1025, 949, 787, 748 cm^{-1}; nmr δ 0.87 (s, 6, $C_{8,9}$-CH_3), 1.02 (s, 3, C_{10}-CH_3), 1.32 (t, 6, J = 7 Hz, $C_{12,14}$-CH_3), and 4.12 ppm (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29, H, 9.92; P, 11.29. Found: C, 61.09; H, 10.11; P, 11.44.

Diethyl 1-*p*-menthenyl-9-phosphonate (11): d^{24} = 1.0076, $n^{20}D$ 1.4680, $\alpha^{26}D$ +11.7°; ir 3415, 2880, 1430, 1380, 1235, 1155, 1090, 1050, 1025, 952, 875, 829, 792, 714 cm^{-1}; nmr δ 1.03 (d, 3, J = 6.5 Hz, C_{10}-CH_3), 1.32 (t, 6, J = 7 Hz, $C_{12,14}$-CH_3), 1.64 (s, 3, C_7-CH_3), 4.09 (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92; P, 11.29. Found: C, 61.43; H, 10.00; P, 11.17.

Diethyl *p*-methanyl-2,9-diphosphonate (12): glc 2.5% **12a**, 45.5% **12b**, 45.9% **12c**, 6% **12d**; d^{24} = 1.0894, $n^{25}D$ 1.4676, $\alpha^{25}D$ +4.9°; ir 3440, 2890, 1430, 1380, 1230, 1155, 1090, 1045, 1020, 942, 823, 784 cm^{-1}; nmr δ 1.04 (d, 6, J = 6 Hz, $C_{7,10}$-CH_3), 1.34 (t, 12, J = 7 Hz, $C_{12,14,16,18}$-CH_3), 4.11 ppm (qn, 8, J = 7 Hz, $C_{11,13,15,17}$-CH_2).

Anal. Calcd for $C_{18}H_{38}O_6P_2$: C, 52.41; H, 9.29; P, 15.02. Found: C, 52.23; H, 9.41; P, 14.96.

When heated at 140–150° for 3.5 hr, 13.6 g of **5** and 60.1 g of DEHP yielded 3.04 g (11.1%) of crude product which had a composition similar to the run with the peroxide.

Hydrogenation of the Limonene Adducts. A 0.3 g sample of **10** was reduced in 10 ml of acetic acid using 29.5 mg of PtO_2 as catalyst. The sample absorbed only 2.45 ml (STP 13% of theory) of H_2 in 42 min. Glc of the 0.29 g recovered indicated that it was mostly starting material.

A 0.16 g sample of **11** and 26.2 $MgPtO_2$ in 5 ml of acetic acid absorbed 12.84 ml (STP, 98% of theory) of H_2 in 44 min. Glc of the recovered material (0.15 g, $[\alpha]^{25}D$ 0° (15% EtOH)) showed a peak at α (**11**) 0.731. Ir bands at 1250–970 cm^{-1} indicated the presence of the phosphonate structure.

Acknowledgments. The authors wish to thank Mr. G. Boudreaux, Southern Regional Research Center, New Orleans, La., and Mr. R. C. Rosanski, Florida State University, Tallahassee, Fla., for determining the nmr spectra.

Registry No.—**1**, 18172-67-3; **2**, 7785-70-8; **3**, 79-92-5; **4**, 1195-31-9; **5**, 5989-27-5; **6**, 49830-14-0; **7**, 49830-15-1; *endo*-**8**, 49830-16-2; *exo*-**8**, 49830-17-3; **9a**, 49775-19-1; **9b**, 49775-20-4; **9c**, 49775-21-5; **9d**, 49775-22-6; **10b**, 49830-18-4; **11**, 49830-19-5; **12**, 49830-20-8.

References and Notes

(1) (a) Address correspondence to this author at the Southern Regional Center, New Orleans, La. 70179. (b) One of the Laboratories of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture.
(2) A. N. Pudovik and I. W. Konovalona, *Zh. Obsch. Khim.*, **29**, 3342 (1959); *Chem. Abstr.*, **54**, 15224*b* (1960).
(3) A. R. Stiles, W. E. Vaughan, and F. F. Rust, *J. Amer. Chem. Soc.*, **80**, 714 (1958).
(4) J. J. Callot and C. Benezra, *Can. J. Chem.*, **49**, 500 (1971).
(5) D. E. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *J. Amer. Chem. Soc.*, **72**, 2407 (1950).
(6) J. B. Strothers, *Tech. Org. Chem.*, **11**, 199 (1963).
(7) D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963).
(8) M_D = *ca.* +280° after allowance for the low optical purity of **2**. The corresponding alcohol, *trans*-carvotanacetol, has $M_D \sim 252°$ [E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **31**, 1937 (1966)].
(9) D. I. Davis, L. J. Parfitt, C. Kalden and J. A. Claisse, *J. Chem. Soc. C*, 1585 (1969).
(10) Data on 2,2-dimethylnorbornane are not available, but in 3-methylene derivatives the two methyls have the same chemical shift [A. T. Blomquist, R. J. Himics, and J. D. Meador, *J. Org. Chem.*, **33**, 2462 (1968)]. Hence, the observed differences are due to the cis–trans relationship to C_{10}. In the absence of data on analogous norbornanes, the high field signals were assigned to the cis methyls by analogy to methylcyclopentanes and 3,3-dimethylcyclopentenes. Methyls trans to a vicinal substituent experience very slight shielding [$\lesssim$0.05 ppm, M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3463 (1971)]. The methyls of 1,1-dimethylcyclopentane have δ 0.98 ppm. We have observed (unpublished results) shifts of 0.90 and 0.52 ppm for the geminal methyls of *cis*-1-(2-acetoxyethyl)-2,2,3-trimethylcyclopentane, indicating *ca.* 0.5 ppm shielding by the two cis substituents. An 0.18 ppm shielding of one of the methyls of 4-(2-acetoxyethyl)-2,3,3-trimethylcyclopentene relative to those of the 1-(2-acetoxyethyl) isomer confirmed the strong shielding effect of a cis vicinal CH_2X group on a cyclopentyl methyl, even when X is a deshielding group.
(11) N. A. LeBel, R. F. Czaja, and A. De Boer, *J. Org. Chem.*, **34**, 3112 (1969).
(12) No further work was done on this peak. It is assumed to be 1-*trans*-*p*-menthanyl phosphonate.
(13) Difficulty in separating this peak from the first minor isomer made it impractical to get a representative sample or to get enough of the first minor peak of nmr.
(14) Y.-R. Naves, *Helv. Chem. Acta*, **47**, 1617 (1964).
(15) S. H. Schroeter and E. E. Eliel, *J. Org. Chem.*, **30**, 1 (1965).
(16) This is in accord with J. H. Brewster's rules [*J. Amer. Chem. Soc.*, **81**, 5483 (1959)], which predict the same interrelationship for the isomeric phosphonates.
(17) Even with the OH group at least half has this conformation.[14,15]
(18) P. S. Skell and R. C. Woodward, *J. Amer. Chem. Soc.*, **77**, 4638 (1955).
(19) A. J. Birch, *Ann. Rep. Progr. Chem.*, **47**, 177 (1950).
(20) The carvomethene was kindly supplied by Newport Industries, the α-pinene by Arizona Chemical Co., the β-pinene by Crosby Chemicals, Inc., and the diethyl hydrogen phosphite by Mobil Chemical. Use of a company and/or product name by the department is for the convenience of the reader and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Some Properties and Reactions of 1-Methyl-3-phospholanone 1-Oxide[1]

Louis D. Quin* and Ronald C. Stocks

Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, North Carolina 27706

Received September 21, 1973

1-Methyl-3-phospholanone 1-oxide (**1**) is in tautomeric equilibrium with 1-methyl-3-hydroxy-2-phospholene 1-oxide, permitting uncatalyzed rapid exchange with D_2O at the 2 position. In appropriate media, the ^{13}C nmr spectra of both keto and enol forms can be observed, giving conclusive assignment of the enol structure. Reactions of **1** can occur at oxygen (with diazomethane or ethyl chloroformate), at C-2 (with *N*-bromosuccinimide or Michael addition to 2-butenone), at C-3 (enamine formation), or at phosphorus (ring opening with base). Some of the functionally substituted phosphine oxides so obtained were reduced to the phosphines with trichlorosilane. Of particular importance was the reduction of **1** itself which gave 1-methyl-3-phospholanone, the first known ketophospholane.

In 1968,[2] we reported the synthesis of the first keto derivative of the phospholane oxide system,[3] 1-methyl-3-phospholanone oxide (**1**). The compound was found to have considerable enolic character; depending on the medium, as much as 20–25% could be present as the enol **1b**. Conditions favoring the enol form were those where intermolecular hydrogen bonding was enhanced (high concentrations in aprotic solvents, or the solid state). The tautomeric forms were easily recognizable in admixture by substantial differences in their ir and nmr (^1H and ^{31}P) spectra.

In the present paper, we report further on the tautomeric character of this compound, particularly as it influences other properties. The compound has been demonstrated to