ric reactions in isotropic chiral media.[2] Our results indicate that for the system studied, a chiral environment due only to molecular chirality is not sufficient for a significant asymmetric bias to occur. One predicts that a preponderance of (*S*)-(+)-2-phenylbutanoic acid would result by use of a cholesteric mesophase having chirality opposite to that used here and that a shorter helical pitch of the mesophase would result in increased optical purity. While the nature of the diastereomeric solute–solvent interaction is not known, we note a certain parallel to the induced circular dichroism phenomenon[6] in which achiral molecules become optically active when dissolved in a cholesteric mesophase. The induced circular dichroism presumably results in part from a particularly strong interaction between the solute and solvent molecules. Work on other asymmetric reactions in chiral liquid crystal solvents is in progress.

Experimental Section

NMR spectra were measured on a Varian A-60 instrument with internal Me_4Si as standard. The vapor phase chromatograph was a Hewlett-Packard Model 5750 with FID, modified for on-column injection. Optical rotations were measured on a Jasco photoelectric spectropolarimeter. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Temperatures are corrected.

Ethylphenylmalonic acid. Freshly distilled (152–155°, 1 Torr) diethyl ethylphenylmalonate (Eastman, 44.0 g, 0.166 mol) was dissolved in 100 ml of 95% ethanol and a solution of KOH (19.0 g, 0.34 mol) in 20 ml of water was added. The reaction mixture was stirred vigorously at 28° for 20 hr. The solvent was then removed by vacuum distillation and the remaining solid was dried in a vacuum desiccator. The solid was washed well with ether (150 ml). The remaining solid (33.5 g) was placed in 150 ml of ether and acidified with 6 *M* hydrochloric acid (ice bath) to the Congo Red point. Water (55 ml) was added and the mixture was stirred vigorously until all the solid had dissolved. The ether layer was separated, dried (anhydrous sodium sulfate), and filtered, and the ether was removed on a rotary evaporator. The remaining material was recrystallized from pentane followed by a second recrystallization from ether–ligroin (bp 30–60°) to afford ethylphenylmalonic acid (21.7 g, 63%): mp 158–161° dec; NMR (methyl ethyl ketone) δ 6.5–7.0 (aryl H's), 10.45 (singlet, carboxyl protons).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.15; H, 5.70.

Asymmetric Synthesis of 2-Phenylbutanoic Acid. Cholesteryl benzoate (50 g), prepared as described in ref 1 [crystal-cholesteric point 150.2°, cholesteric–isotropic point 178.0°, $[\alpha]^{27}D$ −20.8° (*c* 1.72, heptane)], was intimately mixed with 2.0 g of ethylphenylmalonic acid and the mixture was heated for 2 hr at 160° under a nitrogen atmosphere. The reaction flask was then attached to an 18-in. Teflon spinning band column and 1.6 g of 2-phenylbutanoic acid was collected at 95–97° (0.1 mm). The sample was examined for the presence of steroidal and other impurities by TLC on silica gel GF 254 [developing solvent ethyl acetate–heptane (1.6:1)] and by VPC on 1 m × 4 mm stainless steel columns packed with OV-1, 3% on 100/120 Gas Chrom Q and on 2 m × 4 mm copper columns packed with 10% Carbowax 20M on 100/120 Chromosorb W. No contaminants were observed under these conditions. Elemental analysis of 2-phenylbutanoic acid gave the following results.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.40; H, 7.68.

Measurement of the optical rotation yielded $[\alpha]^{27}D$ −14.2° (*c* 1.3, absolute ethanol) [lit.[5] $[\alpha]^{25}D$ 78.5° (absolute ethanol)].

Decarboxylation of ethylphenylmalonic acid in bornyl acetate [Aldrich Chemical Co., $[\alpha]^{27}D$ −38.0° (neat)] under the conditions described above led to 2-phenylbutanoic acid which exhibited no optical rotation.

Registry No.—Ethylphenylmalonic acid, 1636-25-5; diethylethylphenyl malonate, 76-67-5; 2-phenylbutanoic acid, 938-79-4; cholesteryl benzoate, 604-32-0.

References and Notes

(1) L. Verbit, *J. Chem. Educ.*, **49**, 46 (1972).
(2) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., Chapter 10.
(3) F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Am. Chem. Soc.*, **97**, 204 (1975).
(4) At this concentration the binary mixture is cholesteric between 149 and 166°.
(5) C. Aaron, D. Dull, J. L. Schmiegel, D. Jaeger, Y. Ohashi, and H. S. Mosher, *J. Org. Chem.*, **32**, 2979 (1967). The rotation of 2-phenylbutanoic acid is strongly solvent dependent: A. Horeau and A. Nouaille, *Tetrahedron Lett.*, 1939 (1971).
(6) F. D. Saeva in "Liquid Crystals and Ordered Fluids", J. F. Johnson and R. S. Porter, Ed., Plenum Press, New York, N.Y., 1974, p 581.

Electronic Structure of β-Vinyl Substituted Phosphonium Salts by Carbon-13 Nuclear Magnetic Resonance

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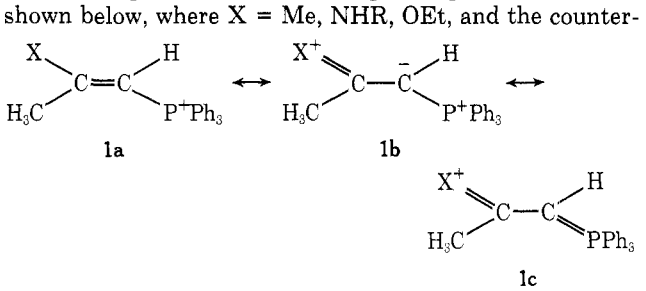
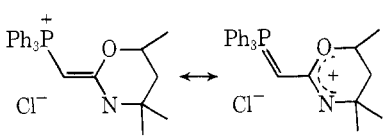
Received December 17, 1974

We have previously examined the ^{13}C NMR for a large variety of triphenylphosphonium salts and ylides.[1] The focus of the current work is directed toward β-vinyl substituted phosphonium salts having the general structure shown below, where X = Me, NHR, OEt, and the counter-



anion Br^- or Cl^-. One would expect that when X possesses unshared pairs of electrons, the resonance form **1b** should be a large contributor to the total electronic structure. In addition, there is also the possibility of the transfer of excess charge from the π system into empty d orbitals[2] on phosphorus. This latter interaction is illustrated by resonance form **1c**. It is expected that when X = CH_3 charge polarization via hyperconjugation[3] may contribute to **1b**. However, this effect should be of smaller magnitude than that previously described for X = –N̈– or –Ö–.

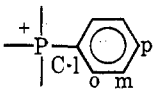
Support for the contribution of resonance forms **1b** and **1c** has been recently published by Trefonas.[4] In this study the X-ray structure of a related phosphonium salt, **2**, was examined. The shortened P–C, C–O, and C–N bond lengths and a long C=C bond compared to model compounds was claimed to be a result of the intervention of resonance structure **2b**.

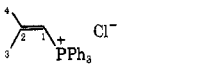
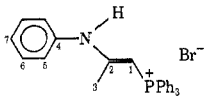
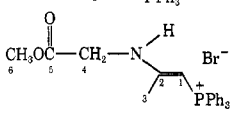
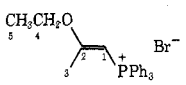
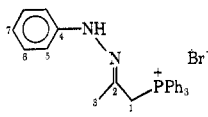
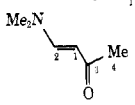


Results and Discussion

The ^{13}C chemical shifts and ^{31}P–^{13}C nuclear spin couplings of vinyltriphenylphosphonium salts and related compounds are reported in Tables I and II, respectively. The assignments of the carbons were made by the use of single frequency off-resonance decoupling and comparisons to model analogs. The assignments of the cis and trans methyl carbons in 2-methylpropenyltriphenylphosphonium chloride (**3**) were discussed previously.[1] The stereochemistry about the carbon–carbon double bond was

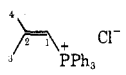
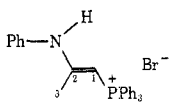
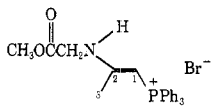
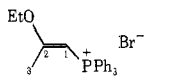
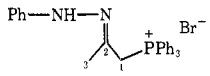
Table I
Carbon Chemical Shifts of Phosphonium Salts and Their Analogs[a]



Registry no.	Compd	No.	^{13}C chemical shift, ppm 1	2	3	4	5	6	7	C-1	O	M	P
42855-48-1		3	102.4	172.0	24.8	29.9				119.4	133.2	130.6	134.8
54774-75-3		4	60.8	163.2	21.4	138.4	124.1	129.5	125.8	122.6	133.0	130.1	134.0
54774-76-4		5	57.7	*	21.2	44.5	169.3	52.0		*	133.0	130.0	134.0
54774-77-5		6	76.5	178.9	20.6	66.1	14.0			120.9	133.0	130.0	134.2
5477-78-6		7	31.3	136.5	17.8	145.5	112.2	128.2	118.5	119.8	133.5	129.8	134.2
21477-76-9		8[b]	98.4	194.6	154.4	28.2							
109-92-2		9[c]	84.6	152.9									

[a] The chemical shifts are referenced to internal Me_4Si. The numbering system of the triphenylphosphonium group is as shown. An asterisk indicates that the resonance was obscured by another peak or too weak to be observed. All compounds were run in $CDCl_3$ except 5, in which the solvent was DMSO-d_6. [b] L. Kozerski and J. Dubrowksi, *Org. Magn. Reson.*, **5**, 459 (1973). [c] G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965).

Table II
^{31}P–^{13}C Coupling Constants for the Phosphonium Salts[a]

Compd	No.	^{31}P–^{13}C Coupling, Hz 1	2	3	4	C-1	O	M	P
	3	89.4	1.2	7.7	18.6	89.5	10.6	12.8	2.4
	4	120.2		4.3		90.3	10.4	12.9	
	5	120.2	*	4.9		*	10.4	12.2	
	6	96.4	3.0	12.2		92.2	11.0	13.4	3.0
	7	53.7	9.8	6.0		87.9	9.8	12.2	

[a] The numbering system is identical with that used in Table I. The digital resolution was ±0.6 Hz. No coupling from phosphorus was observed beyond the carbons numbered.

uniquely determined as the *E* form (as shown). This was done on the basis of the similarity of the three bonded cis ^{31}P–^{13}C nuclear spin coupling in **3** for carbon 3 compared to that found for the triphenylphosphonium salts **4–6**. The ^{13}C chemical shift for the cis methyl carbon in **3**, 24.8 ppm, is also much closer to that observed in compounds **4–6**, 21.4–20.6 ppm, than that observed for the trans methyl group in **3**, 29.9 ppm.

We wish to point out that carbon-1 in compounds **4–6** is found at unusually high fields for vinyl carbons. To our knowledge carbon-1 in **5** represents the most shielded vinyl carbon, 57.7 ppm, reported in the literature with the exception of conjugated carbanions.[5] This is consistent with the influence of resonance form **1b**. This suggestion is supported by a consideration of the ^{13}C NMR of the enamine **8**,[6] which is analogous to the β-amino vinyltriphenylphosphon-

ium salts, 4 and 5. Increased electron density on carbon-1 for analogs of 8 was found by CNDO/2 calculations, which is in complete agreement with the carbon chemical shifts.[7] The decreased shielding of carbon-1 in the conjugated enamine 8 compared to 4 or 5 is undoubtedly a consequence of delocalization of the charge into the acetyl group in 8. It should be noted that carbon-1 in the 2-ethoxyvinyltriphenylphosphonium bromide (6) is deshielded by 18.8–15.7 ppm compared to the carbon-1 resonances for 4 and 5. This is consistent with the notion that delocalization into a π system becomes increasingly inhibited when the atom possessing the unshared pair of electrons becomes more electronegative. That carbon-1 in 6 is shielded by 8.1 ppm from carbon-1 in ethoxyethane (9) is probably a result of the combined electronic changes induced into the π system by the substitution of the additional methyl group in 6 and steric differences between 6 and 9. It should be noted at this point that the accumulation of electron density on carbon-1 for 4 and 5 does not rule out the intervention of resonance structure 1c, since the diffuseness of the d orbitals[2] will still leave most of the electron density concentrated near carbon-1.

The hydrazone substituted methylenetriphenylphosphonium salt, 7, a tautomer of the enaminophosphonium salts, 4 and 5, exhibits no unusual behavior when comparing the ^{13}C chemical shifts and ^{13}C–^{31}P couplings to simple saturated phosphonium salts.[1] It is seen in Table II that the coupling of phosphorus to carbon-1 increases from 53.7 Hz in 7 to 89.4 Hz in 3. This increase is typical on going from an sp^3 to an sp^2 hybridized carbon as described previously.[1] The β-amino vinyl substituted phosphonium salts have a $^1J(^{31}P-^{13}C)$ which is 30.8 Hz larger for carbon-1 than their equivalently hybridized analog, 3. However, the electron density on carbon-1 is increased in 4 and 5 compared to 3 and if effective nuclear charge considerations[8] are valid in this situation, there should be a decrease in the magnitude of $^1J(^{31}P-^{13}C)$. A similar dramatic increase in $^1J_{P-C}$ was found on going from a phosphonium salt to a ylide.[1,9] It was rationalized[1] that this is a consequence of electron density being transfered from the carbon bearing the formal negative charge to phosphorus, presumably via d orbitals. Therefore, the inclusion of resonance structure 1c should cause $^1J(^{31}P-^{13}C)$ for carbon-1 to increase. This infers that electron density on C-1 is being transferred to a greater extent onto phosphorus in 4 and 5 than in 3. In keeping with this argument the slightly increased $^1J(^{31}P-^{13}C)$ coupling of carbon-1 of 6 compared to 3 (ΔHz = 7.0) is justified, since the contribution of 1b is diminished for 6 owing to the greater electronegativity of oxygen (the contribution of 1c must also diminish).

Further evidence for the contribution of resonance structure 1c is given by the slight, but definite, decrease in the shielding of the C-1 phenyl carbons in 4 and 6 compared to 3 (3.2 and 1.5 ppm, respectively). This effect was also noted in going from a phosphonium salt to an ylide, albeit the differences were greater (11.5–15.9 ppm)[1].

The extent of hyperconjugative interaction of the methyl group in 3 is difficult to ascertain. Comparison of $^1J(^{31}P-^{13}C)$ of carbon-1 in 3 vs. vinyltriphenylphosphonium bromide reveals an increase of only 9.1 Hz;[1] however, steric differences are also likely to make changes in the magnitude of the coupling. Thus, the additional contribution of resonance structure 1c for 3 by hyperconjugation must be small.

The electronic description of β-amino and alkoxyvinylphosphonium salts presented here is intriguing. These compounds, by virtue of the delocalization of electrons on nitrogen or oxygen onto d orbitals on phosphorus, seem to represent, electronically, a median between a "normal" phosphonium salt and a carbon–phosphorus ylide. An examination of the synthetic utility of these compounds is under active investigation.

Experimental Section

Spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C data were taken at an operating frequency of 22.63 MHz. The ^{13}C chemical shifts are reported as referenced to internal Me_4Si. All samples were run in approximately 0.05 *M* solutions of $CDCl_3$ or DMSO-d_6 (as indicated in footnote *a*, Table I) at 28° with broad band ^1H decoupling. The preparation of the phosphonium salts will be reported elsewhere.

Acknowledgment. Support from the University of Delaware is greatly appreciated.

References and Notes

(1) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2942, 2946 (1975).
(2) There also exists the possibility of a hybrid combination of empty 3d and 4p orbitals which could provide energetically more favorable overlap. This remains a matter for theoretical chemists to sort out. For recent reviews on the importance of d orbitals for chemical bonding, see C. A. Coulson, *Nature (London)*, **221**, 1106 (1969); K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1967); R. S. Mulliken and B. Liu, *J. Am. Chem. Soc.*, **93**, 6738 (1971).
(3) See, for example, L. Libit and R. Hoffmann, *J. AM/ Chem. Soc.*, **96**, 1370 (1974), and references cited therein.
(4) L. M. Trefonas and J. W. Brown, *J. Heterocycl. Chem.*, **9**, 985 (1972).
(5) R. B. Bates et al., *J. Am. Chem. Soc.*, **95**, 926 (1973).
(6) L. Kozerski and J. Dabrowski, *Org. Magn. Reson.*, **5**, 459 (1973).
(7) J. Dabrowski, K. Kamienska-Trela, and A. J. Sadlej, *J. Mol. Struct.*, **12**, 185 (1972); J. Dabrowski, K. Kamienska-Trela, and L. Kozerski, *Org. Magn. Reson.*, **6**, 43 (1973).
(8) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc*, **87**, 3994 (1965); and J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 324–325 and 377–378.
(9) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).

Photosensitized Oxygenation of *trans,trans*-1-Methylcyclodeca-1,6-diene. A Regiospecific Hydroperoxidation with Singlet Oxygen

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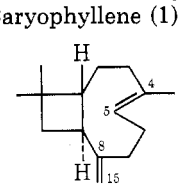
Received January 20, 1975

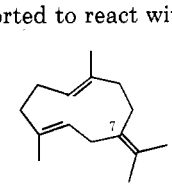
The reactive species of dye-sensitized photooxygenation is presumably singlet oxygen,[1] which is known to react with olefins and conjugated dienes in three ways, namely "ene" reaction, Diels–Alder reaction, and 1,2-dioxetane formation.[1,2] In principle, nonconjugated dienes can react with singlet oxygen to give either the transannular cycloaddition product when the geometry is favorable[3] or the "ene" products, a mixture of allylic hydroperoxides.[2]

The hydroperoxidation of olefins with singlet oxygen is an important synthetic method for the preparation of allylic hydroperoxides and allylic alcohols. Although this hydroperoxidation is generally believed to occur faster with tri- and tetrasubstituted olefins than with di- or monosubstituted ones, there are only a few literature reports in which a completely regiospecific hydroperoxidation of a double bond was actually observed within the molecule.[4]

(−)-Caryophyllene (1) was reported to react with singlet



1



2