Second-order rate constants were determined under pseudo-first-order conditions, Br_2 concentration $\simeq 5 \times 10^{-4}$ M, excess of unsaturated substrate varied from 160 to 20 (for phenylpropiolic acid due to low solubility in water only tenfold excess of substrate was used).

The second-order rate constant of *trans*-cinnamic acid in water was determined at comparable concentrations of both substrates, both being about 5×10^{-4} m and containing 1% of CH_3OH to ensure solubility. For runs carried out on a Cary 16 spectrophotometer, a 10-cm cell was used to obtain the absorption change of ca. 0.2 absorbance unit.

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Registry No.—Styrene, 100-42-5; phenylacetylene, 536-74-3; *trans*-cinnamic acid, 140-10-3; sodium cinnamate, 18509-03-0; phenylpropiolic acid, 637-44-5; sodium phenylpropiolate, 7063-23-2; *p*-nitrocinnamic acid, 619-89-6; *p*-nitrophenylpropiolic acid, 2216-24-2.

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Unusual Shielding Effects in the Proton Nuclear Magnetic Resonance Spectrum of 1-Methyl-3-phospholene 1-Oxide

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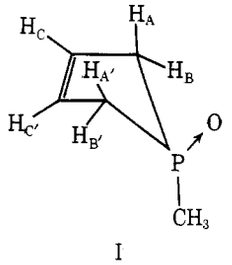
In the course of a study of the chemical and physical properties of phospholene derivatives[1-4] we were puzzled by the ^1H NMR spectrum of one of the compounds of this class, 1-methyl-3-phospholene 1-oxide[3] (I). In agreement with a



I

previous report[5] we found that a solution of I in $CDCl_3$ showed a simple 60-MHz ^1H NMR pattern consisting of three doublets (due to coupling with ^{31}P), for CH_3 at δ 1.60 ($^2J_{HCP}$ = 13 Hz), CH_2 at δ 2.43 ($^2J_{HCP}$ = 11 Hz), and CH at δ 5.87 ppm ($^3J_{HCCP}$ = 28 Hz), suggesting a high degree of symmetry for the molecule. From such spectra it was concluded earlier[5] that protons H_A and H_B in I fail to show the nonequivalence expected of protons in cis and in trans position to the P→O bond, relative to the plane of the ring. Although the ^1H NMR spectrum of the phospholene derived from I, obtained by reduction of the tertiary phosphine oxide I to the corresponding tertiary phosphine, did show nonequivalent protons[5] H_A and H_B and thus suggests an AA'BB'X pattern (X = ^{31}P), no explanation was advanced for the inconsistency in the ^1H NMR spectrum of I.

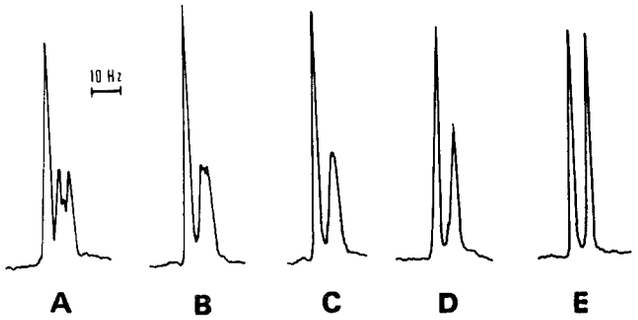


Figure 1. ^1H NMR spectrum (Varian T-60) of the CH_2 protons in 1-methyl-3-phospholene 1-oxide at various dilutions; A, neat; B, 0.2 parts; C, 0.3 parts; D, 0.5 parts; E, 1 part of $CDCl_3$ (v/v).

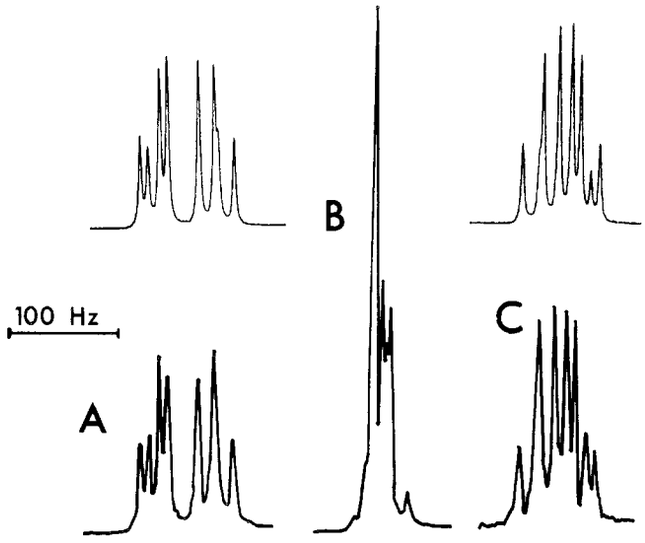


Figure 2. Experimental (bottom) and computer-simulated (top) 270-MHz ^1H NMR spectra of the CH_2 protons in 1-methyl-3-phospholene 1-oxide; A, neat (at 50 °C); B, 50% solution in $CDCl_3$ at room temperature; C, 9% solution in $CDCl_3$ at room temperature.

Nonequivalence of the methylene protons was also observed for the sulfide[1] derived from I and for the 1-chloro- and 1-hydroxy-3-phospholene 1-sulfides.[4] In view of these observations and of the known rigidity of the stereochemistry around the phosphorus atom, the ^1H NMR pattern obtained for I was difficult to rationalize. We, therefore, undertook a more detailed study of concentration and temperature effects on the ^1H NMR spectra of the methylene protons of I.

Results and Discussion

Proton spectra of I recorded at room temperature and at 60 MHz in the neat state and at various degrees of dilution in $CDCl_3$ are shown in Figure 1. Surprisingly, with increasing dilution, the initially complex methylene proton spectrum simplifies to the doublet reported earlier.[5] This effect is also shown upon dilution with benzene as solvent.

Two possible explanations suggest themselves for this observation: (a) a dynamical effect, which renders the A and B protons equivalent within the NMR time scale, or (b) an accidental simplification of an AA'BB'X spectrum. In order to shed more light on this problem proton spectra were obtained at 270 MHz as shown in Figure 2 for the following concen-

Table I. NMR Parameters[a] (in Hertz at 270 MHz) of the CH_2 Protons in 1-Methyl-3-phospholene 1-Oxide

	Neat	9% solution ($CDCl_3$)
$\delta_A - \delta_B$	−53.2	+35.5[b]
$\lvert^2J_{AB}\rvert$	17.4	17.64
$^2J_{AP}$	±14.32	±16.04[c]
$^2J_{BP}$	∓7.95	∓9.18[c]

[a] The olefinic protons H_C give rise to a clean doublet due to coupling with ^{31}P and show no evidence of coupling with the methylene protons H_A and H_B. [b] Absolute shifts: H_A, 2.59; H_B, 2.47 ppm. [c] H_A in I is cis to P→O in accordance with J and δ assignments made for 1,2,5-trimethyl-3-phospholene 1-oxide.[7]

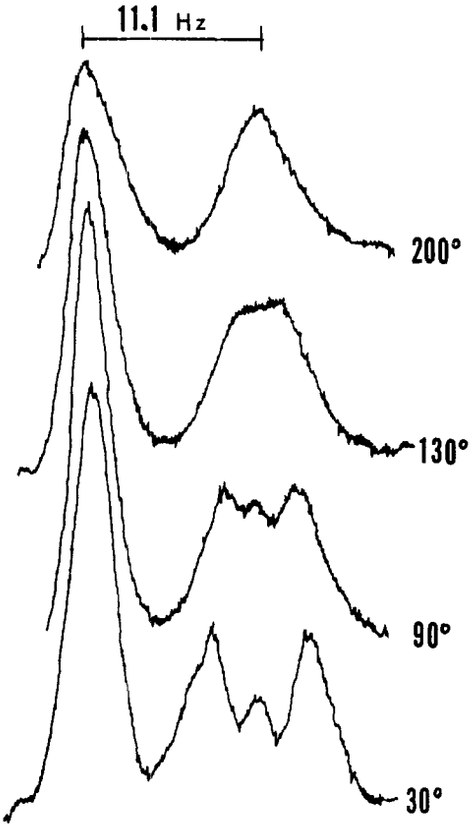


Figure 3. ^1H NMR spectrum (Varian A-50/60) of the CH_2 protons in a neat sample of 1-methyl-3-phospholene 1-oxide at various temperatures.

trations: neat sample I, 50 and 9% *solutions of* I in $CDCl_3$. The spectrum of the neat sample had to be recorded at 50 °C because of the difficulty of preventing the sample from crystallizing at room temperature. The others were recorded at room temperature. In view of the temperature effect discussed below, the spectrum of the neat sample is, therefore, not directly comparable with the corresponding 60-MHz spectrum. The spectra of the neat compound and of the 9% solution, however, are satisfactorily interpreted in terms of the AB part of ABX spectra,[6] with the parameters summarized in Table I. Computer-simulated spectra of I for the two cases of Table I are also shown in Figure 2. While the coupling constants are only slightly affected (to within 12%) by dilution, the chemical shifts reflect an inversion in the relative shielding experienced by A and B.

The spectrum of the 50% solution in Figure 2 cannot be understood as an AB part of an ABX pattern; however, computer simulations revealed that it could qualitatively be explained as the AA'BB' part of an AA'BB'X pattern. Exact parameters were not obtained because of the insufficiency of actual experimental values provided by the spectrum in Figure 2.

These observations show clearly that the methylene protons A and B of I are nonequivalent, basically giving rise to an AA'BB' spectrum, which degenerates, under proper conditions of the environment (dilution, temperature), into apparent ABX or even A_2X spectra.

The temperature dependence of a neat sample at 60 MHz is shown in Figure 3. With increasing temperature the spectrum becomes simpler and more symmetrical, in a way similar to the effect observed upon dilution at 60 MHz. The underlying reason for this is, as in the dilution study, not a dynamical but a shielding effect.

We believe that the reason for these observations, based solely on the present NMR study, is a matter of speculation. It is, however, plausible to suggest that various degrees of molecular association or short-range molecular ordering are the basis of these interesting shielding effects.

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Registry No.—I, 930-38-1.

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A Novel Synthesis of Trifluoromethylthioacetic Acid

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The synthesis of trifluoromethylthioacetic acid,[1,2] an important intermediate in the preparation of the semisynthetic cephalosporin antibiotic cefazaflur (SKF 59962),[3] is made difficult by the limited methods available for the elaboration of the trifluoromethylthio moiety.[4] We wish to report a facile route to this compound from ethyl mercaptoacetate which provides a potentially useful method for the conversion of thiols to trifluoromethyl sulfides.

Chlorination of a methyl group adjacent to sulfur followed by halogen exchange with an inorganic fluoride at elevated temperature is one of the most widely used methods for the synthesis of a trifluoromethylthio group.[5] Thus, our initial approach to the synthesis of trifluoromethylthioacetic acid was to prepare the corresponding trichloride and convert it by existing methods to the trifluoride. However, in methylthioacetic acid the methylene adjacent to the sulfur is sufficiently activated by the carboxyl group to preclude selective chlorination of the methyl.

As an alternate approach we tried fluorination of the readily available disulfide **1**, followed by sulfur extrusion to give an ester of trifluoromethylthioacetic acid. Although the fluoride exchange could not be carried out by the usual method, i.e., antimony trifluoride–antimony pentachloride, we discovered that it occurred rapidly under mild conditions using phase transfer catalysis. Treatment of a hexane solution of **1**, pre-