ence, and Culture (Grant-in-Aid for Scientific Research No. 56540285 and Grant-in-Aid for Special Project No. 57118002).

Registry No. 1, 70901-64-3; **2a**, 590-86-3; **2b**, 107-86-8; **2c**, 96-17-3; **2d**, 123-15-9; **2e**, 100-52-7; **2f**, 66-25-1; **2g**, 98-86-2; **2h**, 119-61-9; **2i**, 93-55-0; **2j**, 96-22-0; **2k**, 110-43-0; **3b**, 86361-23-1; **4a**, 14314-21-7; **4b**, 14434-41-4; **4c**, 70901-72-3; **4d**, 86361-19-5; **4e**, 86372-74-9; **4f**, 86372-75-0; **4g**, 86372-76-1; **4i**, 86372-77-2; **4j**, 86361-25-3; **4k**, 86372-78-3; TBAF, 429-41-4; 3-methyl-2-butenol, 556-82-1.

Nuclear Magnetic Resonance Phosphorus-31 Relaxation Times for Diastereomeric Phosphines and Phosphine Oxides

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In conjuction with our studies[2] of homogeneous asymmetric hydrogenations using chiral phosphine/rhodium I catalysts, we prepared and characterized four diastereomeric organophosphines, $(R)_P$- and $(S)_P$-menthylmethylphenylphosphines **1** and **2** and $(R)_P$- and $(S)_P$-neomenthylmethylphenylphosphines **3** and **4**, and the four corresponding oxides **5–8** (Figure 1). These same compounds have been made and studied by Valentine et al.[3] Proper interpretation of our asymmetric hydrogenation experiments ideally required the use of phosphine ligands which were diastereomerically pure. Since the synthetic route used to prepare the phosphines could lead to racemization,[2] an analytical method capable of distinguishing and quantifying the phosphorus diastereomers was required; Fourier transform (FT) ^{31}P NMR proved to be an appropriate convenient method.[4]

Although it is known that organophosphorus relaxation times can vary widely depending upon structure,[5] the magnitude of the difference does not seem to be widely appreciated; we were made aware of this phenomenon when we were attempting to quantify spectral data of samples containing known amounts of a phosphine and the corresponding oxide. A series of NMR spectra, in which the pulse width was varied, were taken of the same sample. The spectra did not accurately reflect the known relative amounts of phosphine and phosphine oxide present. We then determined that the two compounds had widely different ^{31}P relaxation times and that improper data collection conditions were responsible for saturating the signals so that the signal intensities did not accurately measure the relative amount of each nucleus present.

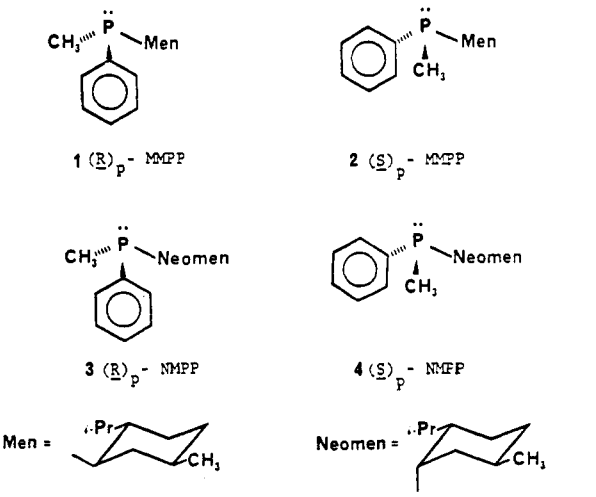
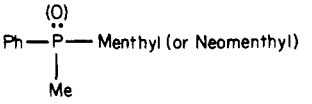


Figure 1. Structures for diastereomeric phosphines 1–4. The phosphine oxides (oxygen atom bonded to the electron pair) corresponding to 1–4 are respectively $(R)_P$-MMPP oxide (**5**), $(S)_P$-MMPP oxide (**6**), $(R)_P$-NMPP oxide (**7**), and $(S)_P$-NMPP oxide (**8**).

Table I. Structures,[a] Relaxation Times,[b] and Chemical Shifts[c] of Diastereomeric Menthyl- and Neomenthylphosphines and -Phosphine Oxides in C_6D_6



compd	substituent	config at phosphorus[a]	T_1 times,[b] s	chem shifts, δ [c]
1	menthyl	(*R*)-phosphine	15.4	34.7
2	menthyl	(*S*)-phosphine	14.6	31.9
3	neomenthyl	(*R*)-phosphine	16.0	38.9
4	neomenthyl	(*S*)-phosphine	17.0	36.4
5	menthyl	(*S*)-phosphine oxide	2.5	−37.6
6	menthyl	(*R*)-phosphine oxide	5.2[d] 7.1[e]	−35.9 −35.9
7	neomenthyl	(*S*)-phosphine oxide	9.9	−36.2
8	neomenthyl	(*R*)-phosphine oxide	11.0	−38.8

[a] Structures determined by X-ray crystallography.[2,3] Because of the *R,S* sequence rules, (*R*)-phosphine is configurationally related to (*S*)-phosphine oxide when oxygen takes the place of the electron pair. [b] See ref 2a for standard inversion-recovery data curves. [c] Chemical shifts are in parts per million from H_3PO_4: positive, upfield; negative, downfield. [d] Concentration in C_6D_6 15 mg/0.4 mL. [e] Concentration in C_6D_6 45 mg/0.4 mL.

Relatively few papers have appeared in the literature which report ^{31}P relaxation times (T_1) for organophosphorus compounds. Stanislawski and Van Wazer[6] and Pregosin and Kunz[4c] have addressed the problems involved with obtaining quantitatively accurate ^{31}P NMR spectra of organophosphorus compounds, and Ojima[7] is also aware of this potential problem. Yet, papers reporting the use of ^{31}P NMR as a chemical probe are appearing with increasing frequency in the organic literature without substantiating evidence for the quantitative accuracy of the measurements. *We hope that our results involving ^{31}P relaxation times will make others more cognizant of the conditions necessary for obtaining quantitative ^{31}P NMR data.*

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The standard inversion-recovery method was used to determine the spin-lattice relaxation times[8] (T_1) of each of the eight compounds (Table I).[9] The T_1 values were determined in benzene-d_6 under the conditions we were employing to analyze our samples. These numbers should not be considered to be absolute standard reference values because the solvent was not rigorously purged of oxygen; it is likely that benzene-d_6 does have an effect on the T_1 values as shown by an observed definite concentration effect. A T_1 measurement made on one sample containing 45 mg of **6** in 0.4 mL of benzene-d_6 showed a significantly longer T_1 (7.1 s) than one determined on 15 mg in the same amount of solvent (5.2 s). All subsequent analytical spectra were taken on samples containing 15 mg of compound in 0.4 mL of solvent so that the *relative* T_1 values in Table I are significant.

The observed T_1 differences[10] required that the NMR instrumental parameters be adjusted to accommodate the compound with the longest relaxation time present in the sample being analyzed. Typically, a pulse width, corresponding to a flip angle of ca. 30°, was employed,[11] with a delay time appropriate for the compound with the longest T_1 contained in a sample according to the guidelines given by Stanislawski and Van Wazer[6] for the collection of quantitative data for NMR spectra under these conditions. It was established by using standard samples that a component could be determined within 1% of its known composition and could be detected down to 0.5%.

Experimental Section

General Methods. The ^{31}P NMR spectra were taken on a Varian XL-100 spectrometer supported by a Nicolet TT100A Pulse and data system and were broad-band ^1H decoupled. The solvents used (C_6D_6 and $CDCl_3$) were purchased in 0.5-mL ampules sealed under N_2 (Aldrich) and handled in a glovebag for phosphine samples. Samples containing only phosphine oxides were prepared in air.

All samples were dissolved in 0.4 mL of C_6D_6. The phosphine oxide samples were freshly prepared with 15 mg of compound, except for one sample which contained 45 mg. The experiments on the phosphines were run on mixed sealed-tube samples containing approximately 40 mg of each phosphine.

Relaxation Time (T_1) Studies. The experiments were run automatically by a standard inversion-recovery sequence in the NTCFT software program supplied by Nicolet for its computers. After the 90° and 180° pulses were determined, values for the variable τ were supplied to the computer. The inversion-recovery sequence was run, and resulting spectra were examined. If necessary, the τ values were adjusted, and the experiment was repeated. The T_1 value was calculated on the basis that no signal appears when $\tau = \ln 2T_1$.

Registry No. 1, 65440-73-5; 2, 65440-74-6; 3, 74298-25-2; 4, 74298-24-1; 5, 65440-75-7; 6, 65440-76-8; 7, 74298-26-3; 8, 74298-27-4.

(8) The spin-lattice relaxation time is generally recognized as the most important relaxation process. For more complete discussions of relaxation phenomena and methods for their determination, see: (a) Shaw, D. "Fourier Transform NMR Spectrscopy"; Elsevier: Amsterdam, 1976. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience: New York, 1980.

(9) See ref 2a for the complete standard inversion-recovery diagrams.

(10) Aside from the analytical implications, the differences in T_1 values are interesting from a stereochemical viewpoint. Within the group of phosphines and the phosphine oxides, the neomenthyl isomers show longer T_1's than do the menthyl derivatives. The difference is much greater in the neomenthyl series (Table I). On the basis of X-ray crystal structures for the four compounds,[2a] the neomenthyl oxides are more sterically hindered than the menthyl oxides. More extensive T_1 and NOE experiments with degassed samples would be required to determine the source of the differences. However, based on the quantitatively prepared but not degassed reference samples, the relative NOE effects were the same within the analytical accuracy of the measurements.

(11) See: Schaeublin, S.; Hoehener, A.; Ernst, R. R. *J. Magn. Reson.* **1974**, *13*, 196.

Primary Alcohol Oxidation with *N*-Iodosuccinimide

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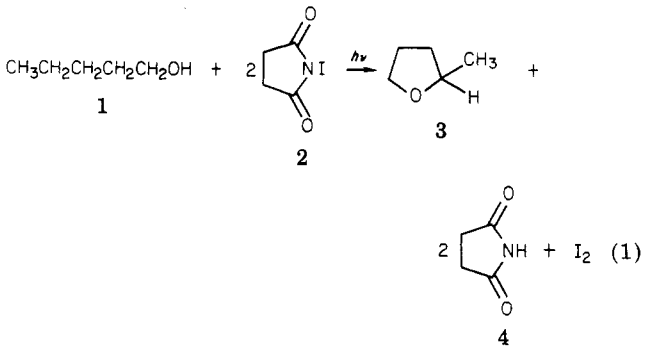
Some time ago, we studied the reaction of secondary[1] and tertiary[2] alcohols with *N*-iodosuccinimide (NIS). At this time, we report the oxidation of some primary alcohols with NIS. We subjected a series of eight primary alcohols to NIS oxidation with irradiation. The identity of the products obtained supports the belief[3] that alkyl hypoiodites are formed when alcohols and NIS react, followed by homolytic decomposition of the intermediate hypoiodites.

Three of the alcohols, 1-pentanol, 1-butanol, and 3-methyl-1-butanol, give, almost exclusively, tetrahydrofuran products (Table I). The yields of tetrahydrofurans obtained by treatment of these primary alcohols with NIS are much better than when the same alcohols are oxidized with lead tetraacetate[4] or cerium(IV)[5]. Tetrahydrofuran formation is one of the pathways of decomposition available for alkyl hypoiodites, the other two being carbon-carbon bond cleavage to produce alkyl iodides and alkoxy radical disproportionation to form aldehydes. The above three primary alcohols give very small percentages of the other two product possibilities.

The formation of a tetrahydrofuran product can be illustrated by a discussion of the oxidation of 1-pentanol (**1**) with NIS (**2**). When the alcohol **1** is dissolved in benzene and mixed with **2**, high yields of 2-methyltetrahydrofuran (**3**; 92-94%) could be obtained at ambient temperatures after 3 h with irradiation. Less than 2% of 1-iodobutane and pentanal were found. The stoichiometry shown in eq 1 is supported by good yields of iodine and succinimide



(**4**). If the same two chemicals in chlorobenzene are allowed to combine in the dark at ambient temperatures, less than 1% of product is found in 6 h. A fourth primary alcohol, 2-methyl-1-propanol, gives 2-iodopropane

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