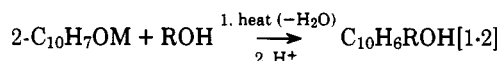


Table I. Yields and Physical Properties of 1-Alkyl-2-naphthols



M	Alkyl group (R)	Conditions		Yield, %	Bp, °C (mmHg)	Mp, °C	Registry no.
		Temp, °C	Time, h				
K	CH ₃ (CH ₂) ₂	270	5	44	116–121 (1.5)		17324-09-3
K	CH ₃ (CH ₂) ₃	270	5	77	120–124 (0.15)	80.8 ^a	50882-63-8
K	(CH ₃) ₂ CHCH ₂	280	5	54	154–156 (3)		52096-47-6
K	CH ₃ (CH ₂) ₄	280	5	79	142–144 (0.6)	81.6	13255-83-9
Na	CH ₃ (CH ₂) ₄	280	5	75			
K	(CH ₃) ₂ CH(CH ₂) ₂	280	5	85	135–138 (0.1)		61769-84-4
K	CH ₃ (CH ₂) ₅	260	12	76	135–136 (0.25)		57744-65-7
K	CH ₃ (CH ₂) ₅	280	5	84			
K	CH ₃ (CH ₂) ₆	280	5	90	159–160 (0.7)		61769-85-5
K	CH ₃ (CH ₂) ₇	280	5	74	143–144 (0.1)		61351-11-9
K	CH ₃ (CH ₂) ₁₁	280	6	55	205–210 (2)		57744-66-8
K	C ₆ H ₅ CH ₂	280	5	50	163–167 (0.2)	109 ^b	36441-31-3

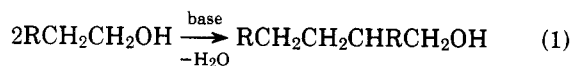
^a Lit. 79–81 °C (ref 4). ^b Lit. 111–112 °C (ref 4).

A product with a boiling point of 154–156 °C (3 mmHg) obtained from the reaction of potassium 2-naphthyl oxide and isobutyl alcohol was analyzed by gas chromatography–mass spectrometry (GC–MS). The product contained two components and the mass spectra were similar; one is 1-isobutyl-2-naphthol and the other is probably a nuclear isomer. There is steric hindrance between the hydrogen atom at the 8 position and a bulky isobutyl group when substitution occurs at the 1 position of 2-naphthol. The isomer is presumably formed for this reason.

The structures of these products were determined by means of mass spectrum, NMR, and IR. As an example, the confirmation of 1-butyl-2-naphthol will be described here.

The molecular formula (C₁₄H₁₆O) was obtained by high-resolution mass spectrometry. The NMR spectra suggest strongly that a normal butyl chain is attached to the 1 position of the naphthalene nucleus; that is, the butyl group did not isomerize. The IR absorptions at 806 and 742 cm⁻¹ also support the presence of 1,2 disubstitution. The structures of other products were confirmed by similar methods. In addition, the NMR spectra (in acetone, 60 MHz) due to the aromatic protons of 1-butyl-, 1-isobutyl-, 1-pentyl-, and 1-hexyl-2-naphthol were compared with each other. These spectra were identical in detail.

In addition to 1-alkyl-2-naphthol, polyalkyl-2-naphthols and 2-substituted alcohols were formed in the present reaction; the former are produced by further alkylation of 1-alkyl-2-naphthol and the latter by the Guerbet reaction (eq 1).⁸



The formation of dialkyl-2-naphthols was confirmed by the GC–MS method, but the positions of the two substituents are not yet determined. These results are not listed in Table I.

Experimental Section

The NMR spectra were obtained on a JEOL JNM-C-60 HL (60 MHz) or PS-100 (100 MHz) spectrometer, with Me₄Si used as the internal standard. The mass spectra were obtained on a Hitachi mass spectrometer (RMU-6L) and on a Shimadzu mass spectrometer (LKB-9000), using an electron-accelerating voltage of 70 eV. The IR spectra were measured with a Japan Spectroscopic spectrometer (IRA-2). Gas chromatography was performed with a Yanagimoto apparatus (G-1800).

Alkylation. Because of the similarity of the procedures, only one example will be described in detail.

In a 300-mL autoclave, with an electromagnetic stirrer, were placed

9.61 g (0.0528 mol) of potassium 2-naphthyl oxide and 48.0 g (0.648 mol) of butyl alcohol. After the air had been replaced by nitrogen, the autoclave was heated at 270 °C for 5 h. The pressure reached 32 kg/cm². The autoclave was cooled, and the reaction mixture was washed with 3% aqueous sodium hydroxide, in which most 1-alkyl-2-naphthols are practically insoluble, then dilute hydrochloric acid, and dried over anhydrous magnesium sulfate. Vacuum distillation of the mixture, with 15-cm Widmer column, gave 1-butyl-2-naphthol in a 77% yield. The boiling point and melting point are given in Table I.

Anal. Calcd for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 83.79; H, 8.07. NMR (CCl₄, 100 MHz) δ 8.0–6.9 (m, 6 H), 4.82 (s, 1 H), 3.00 (t, 2 H), 1.8–1.2 (m, 4 H), 0.96 (triplet but with some distortion, 3 H).

A singlet peak appearing at δ 7.16 of 2-naphthol in acetone (60 MHz) (a proton at the 1 position) was completely absent from the spectrum of 1-butyl-2-naphthol.

Registry No.—Potassium 2-naphthyloxy, 36294-21-0; sodium 2-naphthyloxy, 875-83-2; propanol, 71-23-8; butyl alcohol, 71-36-3; isobutyl alcohol, 78-83-1; pentanol, 71-41-0; isopentyl alcohol, 123-51-3; hexanol, 111-27-3; heptanol, 111-70-6; octanol, 111-87-5; dodecanol, 112-53-8; benzyl alcohol, 100-51-6.

References and Notes

- (1) T. Kito and K. Ota, *Chem. Lett.*, 1019 (1975).
- (2) M. L. Khorana, S. Y. Pandit, and A. D. Pishawikar, *J. Pharm. Sci.*, **56**, 993 (1967); L. F. Gol'tsova, G. D. Kharlampovich, and L. K. Il'ina, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1302 (1969), etc.
- (3) N. P. Buu-Hoi, D. Lavit, and J. Collard, *J. Org. Chem.*, **23**, 542 (1958); R. D. Desai and W. S. Waravdekar, *Chem. Abstr.*, **40**, 6456⁴ (1946); C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).
- (4) E. Wenkert, R. D. Youssefeyeh, and R. G. Lewis, *J. Am. Chem. Soc.*, **82**, 4675 (1960); V. A. Zagorevskii, *Chem. Abstr.*, **52**, 14572d (1958).
- (5) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 626 (1949); J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 682 (1942).
- (6) J. Szmuszkovicz and H. Born, *J. Am. Chem. Soc.*, **75**, 3350 (1953); K. Takeda and H. Osaka, *J. Pharm. Soc. Jpn.*, **75**, 210 (1955).
- (7) F. Poppelsdorf and S. J. Holt, *J. Chem. Soc.*, 1124 (1954).
- (8) M. Guerbet, *C. R. Acad. Sci.*, **165**, 559 (1917), and earlier papers.

The Importance of Alkene and Alkyne Structure on Their Relative Rates of Bromination

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The effect of solvent upon the relative rates of bromination of alkenes and alkynes has been explained in two different

Table I. Effect of Solvent and Structure of Alkene and Alkyne on Rates of Bromination

Solvent	Styrene, $k_2, M^{-1} s^{-1}$	Phenyl- acetylene, $k_2, M^{-1} s^{-1}$	k_o/k_a	<i>trans</i> -Cinnamic acid, $k_2, M^{-1} s^{-1}$	Phenylpropionic acid, $k_2, M^{-1} s^{-1}$	k_o/k_a	4-Nitro- cinnamic acid, $k_2, M^{-1} s^{-1}$	4-Nitro- phenyl- propionic acid, $k_2, M^{-1} s^{-1}$
H ₂ O	1.1×10^7 ^a	3.1×10^4 ^{b,g}	360	$(1.27 \pm 0.01) \times 10^4$ ^b	$(6.70 \pm 0.06) \times 10^3$	1.90		
H ₂ O-CH ₃ OH 1:1	2.3×10^6 ^a	1.5×10^3 ^g	1590	73 ± 1	233 ± 2	0.31		
H ₂ O-CH ₃ OH 1:3				2.49 ± 0.01	17.3 ± 0.2	0.14		
CH ₃ OH	1.16×10^3 ^a	8.8×10^{-1} ^{c,g} 9.0×10^{-1} ^{d,g}	1318	$(2.40 \pm 0.03) \times 10^{-2}$	$(7.25 \pm 0.07) \times 10^{-3}$	3.32	1.7×10^{-2}	2.9×10^{-3}
CH ₃ OH 0.075 N HCl in CH ₃ OH				3.43 ± 0.05 ^e 0.108 ± 0.001	3.16 ± 0.03 ^e 0.0436 ± 0.0004	1.08 ^e 2.47		
HOAc	11.2 ^f	4.33×10^{-3} ^f	2580					

^a Reference 5. ^b 1% CH₃OH added to ensure solubility. ^c Direct measurement in absence of KBr. ^d Taken as the intercept of the plot $k_o(1 + K[Br^-])$ vs. $[Br^-]$. ^e Sodium salt. ^f Reference 4. ^g Unpublished data of G. Modena, F. Rivetti, and U. Tonellato, Centro Meccanismi di Reazioni Organiche del C.N.R. Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy.

ways. One involves specific nucleophilic solvation of the positively charged carbon portion of the rate-determining transition state.¹⁻⁴ The other involves specific electrophilic solvation of the bromide ion in the rate-determining transition state.⁵ In both of these explanations, the structure of the substrate has been largely ignored. We would like to present data which establish the importance of alkene and alkyne structure on their relative rates of bromination.

The rates of bromination, which are presented in Table I, were obtained by direct kinetic measurements. In the absence of KBr, the rate constants were obtained by following the disappearance of the bromine absorbance at 405–450 nm. For phenylacetylene, a second method was used. The rates were measured in the presence of KBr by following the disappearance of the Br₃⁻ complex at various wavelengths. The rate constant for the addition of free bromine was taken as the intercept of the plot of $k_o(1 + K[Br^-])$ vs. $[Br^-]$.⁶ The rate constants obtained by these two methods are in good agreement. From the kinetic data, the ratios $k_{olefin}/k_{acetylene}$ (k_o/k_a) were calculated and are included in Table I.

The ratio k_o/k_a for the bromination of styrene and phenylacetylene in water given in Table I differs considerably from that reported previously.⁴ Since the data in Table I were obtained by direct kinetic measurement, they are more reliable than those obtained previously by an indirect competition technique.

The data in Table I clearly indicate that a change in solvent has a large effect upon the rates of bromination of all four compounds studied. However, changing the solvent does not significantly alter the ratio k_o/k_a . This can best be illustrated by plotting $\log k_2^a$ vs. $\log k_2^b$ in the solvents studied. From the rates of bromination of styrene and phenylacetylene obtained in four solvents the following correlation is obtained.

$$\log k_2^a = 1.09 \log k_2^b - 3.45 \quad r = 0.996 \quad s \text{ (slope)} = 0.069$$

For the rates of bromination of cinnamic and phenylpropionic acids in five solvents the following correlation is obtained:

$$\log k_2^a = 1.06 \log k_2^b - 0.013 \quad r = 0.972 \quad s \text{ (slope)} = 0.15$$

Clearly solvent changes have a similar effect upon the rates of bromination of alkenes and alkynes. However, the rate ratio k_o/k_a is strikingly different for the two series. For the pair styrene-phenylacetylene, the ratio is approximately 10^3 while for the acids the ratio is around 1.0.

Nucleophilic additions of Br₃⁻ to unsaturated carboxylic acids are known to occur. To rule out this mechanism, the

rates of bromination of 4-nitrocinnamic and 4-nitrophenylpropionic acids in methanol were determined. The rates are slower for bromination of the 4-nitro-substituted than the unsubstituted acids as shown in Table I. This result is consistent with an electrophilic addition of bromine and clearly establishes that the change in the k_o/k_a ratio is not due to a change in mechanism.

For the acids, there is a somewhat larger variation in the k_o/k_a ratio with changing solvent than for the styrene-phenylacetylene pair. This may be due to the fact that the rate constant for bromination of a carboxylic acid is actually a sum of two terms: one for the acid and one for the anion. The effect of changing solvent on the rate of bromination of these two species is similar but not identical. For example, the ratio k_o/k_a for bromination in 0.075 N HCl in methanol is 2.47. Under these conditions, the predominant species present are the undissociated acids. Bromination of the anions in methanol gives a ratio k_o/k_a of 1.08. While the two values are not substantially different, the difference is probably enough to cause the observed variation in the ratio k_o/k_a .

The data presented here clearly establish that the electrophilic bromination of alkenes is not always faster than for alkynes. Their relative rates depend greatly upon the structure of the substrate. While there is no doubt that electrophilic solvation of the departing bromide ion is important, solvation of the organic portion in the rate-determining transition state is also important. It is not yet clear if this effect is specific nucleophilic solvation or a general medium effect on the ground or transition states.

Experimental Section

Materials. *trans*-Cinnamic, phenylpropionic, *p*-nitrocinnamic, and *p*-nitrophenylpropionic acids were commercially available and were purified by crystallization.

Sodium cinnamate and phenylpropionate were prepared by neutralizing the acid with a stoichiometric amount of 1 N solution of NaOH in aqueous methanol, and evaporating to dryness followed by crystallization from aqueous methanol.

Methyl alcohol was refluxed with Br₂ and then distilled twice from bromine and K₂CO₃.⁷ Distilled water was prepared by the method of Harbison.⁸ The solution of HCl in MeOH was prepared by passing dry HCl gas through methanol. The HCl concentration was determined by standard titration with 0.1 N aqueous NaOH.

Kinetics. The rates of addition to the olefins and acetylenes were measured using a Durrum-Gibson stopped flow spectrophotometric system or Cary 16 spectrophotometer as previously reported.^{9,10} The consumption of bromine was measured by the decrease in the absorption at 490 nm. The reported rate coefficients are the mean values of two to seven independent determinations.

Second-order rate constants were determined under pseudo-first-order conditions, Br_2 concentration $\approx 5 \times 10^{-4}$ M, excess of unsaturated substrate varied from 160 to 20 (for phenylpropionic 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; phenylpropionic acid, 637-44-5; sodium phenylpropionate, 7063-23-2; *p*-nitrocinnamic acid, 619-89-6; *p*-nitrophenylpropionic acid, 2216-24-2.

References and Notes

- (1) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).
- (2) R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968).
- (3) G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).
- (4) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973).
- (5) J. R. Ruisse and J. E. Dubois, *J. Org. Chem.*, **97**, 1977 (1975).
- (6) J. E. Dubois and X. Q. Huynh, *Bull. Soc. Chim. Fr.*, 1468 (1968).
- (7) J. E. Dubois and H. Herzog, *Bull. Soc. Chim. Fr.*, 57 (1968).
- (8) K. B. Harbison, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.
- (9) K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, **38**, 2460 (1973).
- (10) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

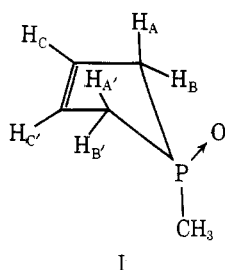
Unusual Shielding Effects in the Proton Nuclear Magnetic Resonance Spectrum of 1-Methyl-3-phospholene 1-Oxide

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In the course of a study of the chemical and physical properties of phospholene derivatives¹⁻⁴ we were puzzled by the ^1H NMR spectrum of one of the compounds of this class, 1-methyl-3-phospholene 1-oxide³ (I). In agreement with a



previous report⁵ 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 ($^2J_{\text{HCP}} = 13$ Hz), CH_2 at δ 2.43 ($^2J_{\text{HCP}} = 11$ Hz), and CH at δ 5.87 ppm ($^3J_{\text{HCCP}} = 28$ Hz), suggesting a high degree of symmetry for the molecule. From such spectra it was concluded earlier⁵ that protons H_A and H_B in I fail to show the nonequivalence expected of protons in *cis* and *trans* position to the $\text{P} \rightarrow \text{O}$ bond, relative to the plane of the ring. Although the ^1H NMR

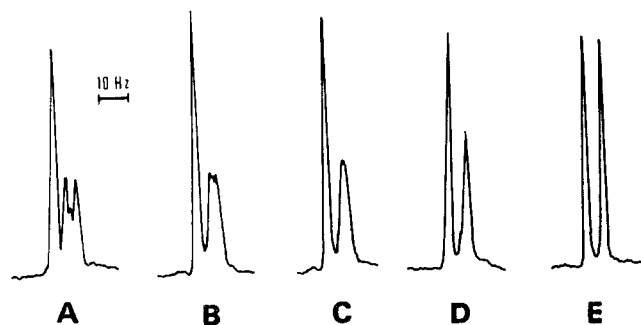


Figure 1. ^1H NMR spectrum (Varian T-60) of the CH_2 protons in 1-methyl-3-phospholene 1-oxide at various dilutions; A, neat; B, 0.2 parts; C, 0.3 parts; D, 0.5 parts; E, 1 part of CDCl_3 (v/v).

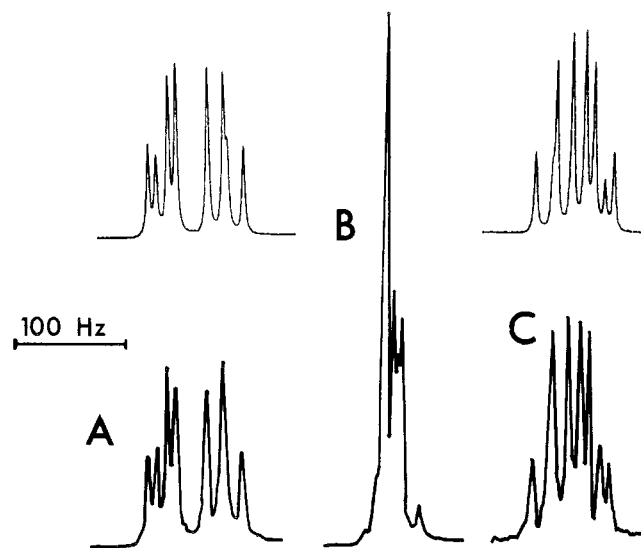


Figure 2. Experimental (bottom) and computer-simulated (top) 270-MHz ^1H NMR spectra of the CH_2 protons in 1-methyl-3-phospholene 1-oxide; A, neat (at 50°C); B, 50% solution in CDCl_3 at room temperature; C, 9% solution in CDCl_3 at room temperature.

spectrum of the phospholene derived from I, obtained by reduction of the tertiary phosphine oxide I to the corresponding tertiary phosphine, did show nonequivalent protons⁵ H_A and H_B and thus suggests an $\text{AA}'\text{BB}'\text{X}$ pattern ($\text{X} = ^{31}\text{P}$), no explanation was advanced for the inconsistency in the ^1H NMR spectrum of I.

Nonequivalence of the methylene protons was also observed for the sulfide¹ 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 $\text{AA}'\text{BB}'\text{X}$ 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-