values were obtained and submitted for review.

**Registry No.** 2-Methylquinoline, 91-63-4; 2,6-dimethylquinoline, 877-43-0; 6-methoxy-2-methylquinoline, 1078-28-0; 2-methyl-6-(trifluoromethyl)quinoline, 66023-21-0; 6-fluoro-2-methylquinoline, 1128-61-6; 6-chloro-2-methylquinoline, 92-46-6; 6-bromo-2-methylquinoline, 877-42-9; 1-phenyl-2-(2-quinolyl)ethanone, 1531-38-0; 1-phenyl-2-(2-quinolyl)ethanone picrate, 83719-88-4; 1-phenyl-2-(6-methyl-2-quinolyl)ethanone, 83719-89-5; 1-phenyl-2-(6-methyl-2-quinolyl)ethanone picrate, 83719-90-8; 1-phenyl-2-(6-methoxy-2-quinolyl)ethanone, 83719-91-9; 1-phenyl-2-(6-methoxy-2-quinolyl)ethanone picrate, 83719-92-0; 1-phenyl-2-[6-(trifluoromethyl)-2-quinolyl]ethanone, 83719-93-1; 1-phenyl-2-[6-(trifluoromethyl)-2-quinolyl]ethanone picrate, 83719-94-2; 1-phenyl-2-(6-fluoro-2-quinolyl)ethanone, 83719-95-3; 1-phenyl-2-(6-fluoro-2-quinolyl)ethanone picrate, 83719-96-4; 1-phenyl-2-(6-chloro-2-quinolyl)ethanone, 83719-97-5; 1-phenyl-2-(6-chloro-2-quinolyl)ethanone picrate, 83719-98-6; 1-phenyl-(6-bromo-2-quinolyl)ethanone, 83719-99-7; 1-phenyl-(6-bromo-2-quinolyl)ethanone picrate, 83720-00-7; methyl benzoate, 93-58-3.

## Literature Cited

(1) Wursthorn, K. R.; Sund, E. H. *J. Heterocycl. Chem.* **1974**, *11*, 123.
(2) Weiss, M. J.; Hauser, C. R. *J. Am. Chem. Soc.* **1949**, *71*, 2023.
(3) Wolfe, J. F.; Portlock, D. E.; Feuerback, D. J. *J. Org. Chem.* **1974**, *39*, 2006.
(4) Yamazaki, M.; Noda, K.; Hamana, M. *Chem. Pharm. Bull.* **1970**, *18*, 908.
(5) Hay, J. V.; Hudlicky, T.; Wolfe, J. F. *J. Am. Chem. Soc.* **1975**, *97*, 374.
(6) Rauch, E. B.; Dickinson, P.; Welch, J. A. U.S. Patent 3 375 258.
(7) Moudgill, K. L. *J. Am. Chem. Soc.* **1921**, *43*, 2257.
(8) Bartow, E.; McCollum, E. V. *J. Am. Chem. Soc.* **1904**, *26*, 700.
(9) Mirek, J. *Zesz. Nauk. Uniw. Jagiellon., Ser. Nauk. Chem.* **1962**, *7*, 173; *Chem. Abstr.* **1965**, *62*, 5252.
(10) Cocker, W.; Turner, D. G. *J. Chem. Soc.* **1941**, 143.
(11) Krainer, Z. Ya.; Gudz, P. F.; Yagupol'skii, L. M., *Khim. Geterotsikl. Soedin.* **1978**, 76; *Chem. Abstr.* **1978**, *88*, 137879.
(12) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. "Vogel's Textbook of Practical Organic Chemistry", 4th ed.; Longman: London, 1978; p 913.
(13) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. "The Systematic Identification of Organic Compounds", 6th ed.; Wiley: New York, 1980; p 236.
(14) Fukata, G.; O'Brien, C.; O'Ferrall, R. A. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 792.
(15) Bergstrom, F. W.; Moffat, A. *J. Am. Chem. Soc.* **1937**, *59*, 1494.

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# α,ω-Bis(benzotriazoloxy)alkane System

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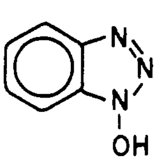
**A series of α,ω-bis(benzotriazoloxy)alkanes have been synthesized by employing a phase transfer catalyst (PTC) and have been characterized by physical, spectral, and analytical properties.**



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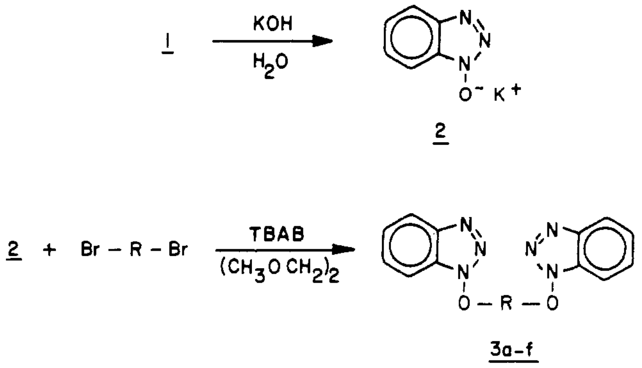
Derivatives of the 1-hydroxy-1,2,3-benzotriazole (**1**) molecule have been shown to possess varying degrees of biological activity and are of photochemical interest (*1–3*). Recently, we reported the use of a phase transfer catalyst (PTC) in the alkylation of **1** with several alkyl halides (*4*). The procedure was characterized by mild reaction conditions, ease of product isolation, and high yields. Our interest in polymer chemistry prompted the PTC synthesis of a series of α,ω-bis(benzotriazoloxy)alkanes (**3a–f**) as potential polymer model compounds or precursors.



Initial reactions were carried out in a methylene chloride–water system but led to significant amounts of a methylene diether which will be the subject of a later report. Compounds **3a–f** were therefore prepared by the reaction of the potassium salt of 1-hydroxy-1,2,3-benzotriazole (**2**) with the appropriate alkyl halide (Table I) in the presence of tetrabutylammonium bromide (TBAB) employing 1,2-dimethoxyethane (DME) as a nonreactive solvent. Salt **2** was prepared by the reaction of equimolar quantities of **1** and potassium hydroxide. The TBAB acts, in this case, as a transfer agent between solid **2** and the alkyl halide solution. All new compounds gave satisfactory elemental analyses.

Each of the compounds exhibited infrared absorptions at about 1240, 1270, and 1390 cm$^{-1}$ indicative of a five-membered ring fused to a benzene nucleus (*5*), a pair of bands in the 1030- and 1100-cm$^{-1}$ region which have been reported for the 1,2,3-triazole nucleus (*6*), and a band at about 950 cm$^{-1}$ which has been assigned to the N–O stretch in alkyl nitrites (*7*).

The nuclear magnetic resonance spectra of **3a–f** all contain appropriate absorptions. In particular, protons adjacent to the N–O functionality are shifted downfield about 1–1.5 ppm relative

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Table I. Physical, Analytical, and Spectral Properties

| compd no. | R | yield, % | mp, °C | IR (KBr), $cm^{-1}$ | NMR ($CDCl_3$), δ |
|---|---|---|---|---|---|
| 3a | $CH_2$ | 19 | 182-184 | 1450 (s), 1370 (s), 1290 (s), 1250 (s), 1090 (s), 970 (s), 800 (s), 770 (s) | 5.68 (s, 2 H), 7.70 (m, 8 H) |
| 3b | $(CH_2)_2$ | 75 | 102-103 | 1450 (s), 1350 (s), 1250 (s), 1170 (m), 1110 (s), 1030 (s), 880 (s), 760 (s) | 5.02 (s, 4 H), 7.65 (m, 8 H) |
| 3c | $(CH_2)_3$ | 10 | 141-142 | 1470 (m), 1450 (m), 1370 (m), 1350 (m), 1270 (s), 1250 (s), 1100 (s), 1045 (s), 950 (s), 800 (m), 760 (s) | 2.38 (t, 2 H, *J* = 5 Hz), 4.95 (t, 4 H, *J* = 5 Hz), 7.60 (m, 8 H) |
| 3d | $(CH_2)_4$ | 82 | 89-91 | 1475 (m), 1445 (m), 1365 (m), 1275 (m), 1250 (s), 1100 (s), 1035 (m), 950 (s), 795 (m), 765 (s) | 2.20 (m, 4 H, broad, 4.67 (m, 4 H, broad), 7.50 7.50 (m, 8 H) |
| 3e | $(CH_2)_5$ | 73 | 65-66 | 1470 (m), 1450 (s), 1370 (s), 1280 (s), 1250 (s), 1110 (s), 970 (s), 880 (s), 770 (s) | 1.93 (m, 6 H, broad), 4.60 (m, 4 H, broad), 7.50 (m, 8 H) |
| 3f | $(CH_2)_6$ | 91 | 68-71 | 1450 (s), 1350 (s), 1270 (m), 1240 (s), 1100 (s), 1050 (s), 960 (s), 860 (s), 750 (s) | 1.73 (m, 8 H, broad), 4.57 (m, 4 H, broad), 7.60 (m, 8 H) |

to the corresponding dibromide as has been observed for other 1-alkoxy-1,2,3-benzotriazoles. A smaller shift is observed for **3a** due probably to the proximity of the halogens in dibromomethane as compared to the other dibromides.

In view of the excellent yields, except for **3a** and **3c** (for which multiple runs failed to alter the results), we are encouraged in our efforts to incorporate the benzotriazole nucleus as a backbone segment in a polymer system and in our investigation of the applicability of PTC to the synthesis of derivatives of 1-hydroxy-1,2,3-benzotriazole (**1**).

## Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 735B spectrometer. The NMR spectra were obtained on a Varian EM-360 spectrometer. The reaction of equimolar quantities of potassium hydroxide and 1-hydroxy-1,2,3-benzotriazole (**1**) in an aqueous solution followed by vacuum drying provided the potassium salt of 1-hydroxy-1,2,3-benzotriazole (**2**) which was used without further purification.

***General Phase Transfer Catalyzed Alkylation Procedure.*** A mixture of **2** (0.02 mol), the appropriate dibromide (0.01 mol), tetrabutylammonium bromide (0.002 mol), and 50 mL of 1,2-dimethoxyethane was stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent removed under vacuum. The products were recrystallized from methanol. Properties of all new compounds are summarized in Table I.

**Registry No.** **2**, 62244-77-3; **3a**, 83615-76-3; **3b**, 83615-77-4; **3c**, 83615-78-5; **3d**, 83615-79-6; **3e**, 83615-80-9; **3f**, 83615-81-0; TBAB, 1643-19-2.

## Literature Cited

(1) Serve', M. P.; Seybold, P. G.; Feld, W. A.; Chao, M. A. *J. Heterocycl. Chem.* **1976**, *13*, 509-12.
(2) McGee, A. W.; Serve', M. P.; Seybold, P. G. *J. Heterocycl. Chem.* **1978**, *15*, 1043-6.
(3) Feld, W. A.; Seybold, P. G.; Serve', M. P. *J. Heterocycl. Chem.* **1980**, *17*, 1115-6.
(4) Paessun, R. J.; Serve', M. P.; Feld, W. A. *J. Macromol. Sci., Chem.* **1981**, *A15*, 891-6.
(5) Sheppard, N.; Simpson, D. M. *Q. Rev., Chem. Soc.* **1953**, *7*, 19-55.
(6) Hartzel, L. W.; Benson, F. R. *J. Am. Chem. Soc.* **1954**, *76*, 667-70.
(7) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 2nd ed.; Wiley: New York, 1964; p 303.

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# Synthesis and Spectroscopic Data of Chlorinated 4-Hydroxybenzaldehydes

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**All chlorinated 4-hydroxybenzaldehydes including three hitherto unknown compounds have been synthesized from chlorinated phenols by applying the Reimer–Tiemann method. $^1H$ NMR, $^{13}C$ NMR, and mass-spectral data on all compounds are reported.**

In connection with our interest in chlorinated phenolic compounds occurring in pulp bleach liquors we recently had need of some chlorinated aromatic aldehydes. We now wish to report on the synthesis and spectroscopic properties of chlorinated 4-hydroxybenzaldehydes (see Figure 1). Some of them

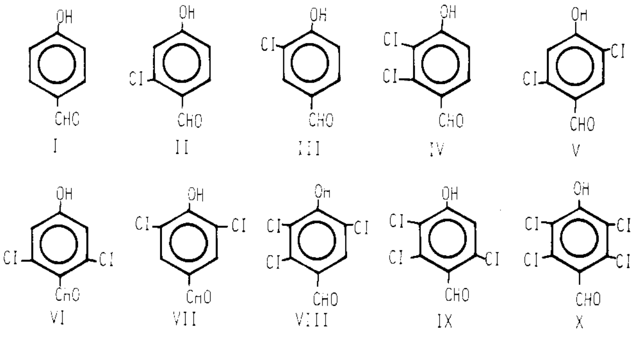

**Figure 1.** Structures and notation of compounds studied.

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