Literature Cited

(1) Ladd, E. C. U.S. Patent 2 521 068, 1950; *Chem. Abstr.* **1951**, *45*, 653f.
(2) Ladd, E. C. U.S. Patent 2 573 580, 1951; *Chem. Abstr.* **1952**, *46*, 7588i.
(3) Goldwhite, H.; Gibson, M. S.; Harris, C. *Tetrahedron* **1965**, *21*, 2743.
(4) Truce, W. E.; Heuring, D. L.; Wolf, G. C. *J. Org. Chem.* **1974**, *39*, 238 and references cited therein.
(5) Kao Liu, L.; Chi, Y.; Jen, K. *J. Org. Chem.* **1980**, *45*, 406 and references cited therein.
(6) (a) Kharasch, M. S.; Zavist, A. F. *J. Am. Chem. Soc.* **1951**, *73*, 964. (b) Kharasch, M. S.; Mosher, R. A. *J. Org. Chem.* **1952**, *17*, 453.
(7) Tiers, G. V. D. U.S. Patent 2 846 472, 1958; *Chem. Abstr.* **1959**, *53*, 12175i.
(8) Binkley, W. W.; Degering, E. F. *J. Am. Chem. Soc.* **1938**, *60*, 2810.
(9) Truce, W. E.; Abraham, D.J.; Son, P. *J. Org. Chem.* **1967**, *32*, 990.
(10) Kharasch, M. S.; Zavist, A. F. *J. Org. Chem.* **1951**, *73*, 967.
(11) Johnson, W. K. U.S. Patent 3 311 650, 1967; *Chem. Abstr.* **1967**, *67*, 53680m.

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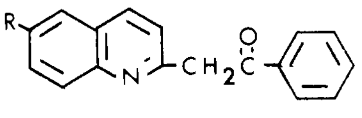
Syntheses of 1-Phenyl-2-(2-quinolyl)ethanones and Related Ethanones

Eldon H. Sund* and William D. Lowe

Department of Chemistry, Midwestern State University, Wichita Falls, Texas 76308

Seven 1-phenyl-2-[2-(6-substituted quinolyl)]ethanones were synthesized by the condensation of 2-methyl-6-substituted quinolines and methyl benzoate with sodium hydride as the condensing agent. Substituents in the 6 position were bromo, chloro, fluoro, methoxy, methyl, and trifluoromethyl as well as the parent compound. Picrate derivates were prepared from each ketone.

In connection with our interest in enolizable ketones (*1*) we recently had need of some 1-phenyl-2-(2-quinolyl)ethanones which carried substituents in the 6 position of the quinoline nucleus



the substituents being bromo, chloro, fluoro, methoxy, methyl, and trifluoromethyl. The parent compound has been prepared by Weiss et al. (*2*), Wolfe et al. (*3*), Yamazaki et al. (*4*), and Hay et al. (*5*). The method of Rauch et al. (*6*) was found to be a suitable procedure to produce the requisite ketones in adequate yield. All of the ketones were converted into picrate derivatives. NMR spectra of the ketones in $DCCl_3$ indicated that the ketones existed in an enamine and imine form in solution and the approximate enamine/imine ratios were determined.

Table I lists the 1-phenyl-2-(2-quinolyl)ethanones prepared as well as their melting points, yields, melting points of the picrates, and enamine/imine ratios.

Experimental Section

The 2-methylquinoline, 2,6-dimethylquinoline, and methyl benzoate were obtained commercially. The remaining quinolines, 6-bromo-2-methylquinoline (*7*), 6-chloro-1-methylquinoline (*8*), 6-fluoro-2-methylquinoline (*9*), 6-methoxy-2-methylquinoline (*10*), and 2-methyl-6-(trifluoromethyl)quinoline (*11*) have been reported in the literature by a procedure similar to that found in Vogel (*12*) upon which these syntheses were patterned. Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, CO 80033. Melting points were determined on a Thomas-Hoover melting point apparatus and were corrected. Yields represent single preparations and the yields increased as experience in the preparations was gained. The following example will illustrate the synthesis of 1-phenyl-2-(2-quinolyl)ethanones.

Table I. 1-Phenyl-2-(2-quinolyl)ethanones[a]

R	yield, %	mp, °C	enamine/ imine ratio	picrate mp, °C
H	41	115.5–117[b]	23	176.5–177.5[c]
CH_3	quant	121–123	16	184.5–185.5
OCH_3	71	146–147.5	5	191.5–193.5
CF_3	quant	151–152	19	137.5–138.5
F	94	132–133	6	161.5–162.5
Cl	39	147–148	9	183.5–184.5
Br	31	152–153	13	182.5–183.5

[a] Elemental analyses for C, H, N, F, Cl, and Br in agreement with theoretical values were obtained and submitted for review. [b] Reported mp 112–114 °C (*14*). [c] Reported mp 171.5–172.5 °C (*15*).

For 1-phenyl-2-[2-(6-methoxyquinolyl)]ethanone, 25 mL of anhydrous toluene and 6.48 mL (0.135 mol) of sodium hydride (50% oil dispersion) were placed in a stirred flask. There was added 4.67 g (0.027 mol) of 6-methoxyquinoline in 40 mL of anhydrous toluene, and the reaction heated to 70 °C. A solution of 3.24 g (0.027 mol) of methyl benzoate in 10 mL of anhydrous toluene was added dropwise while the temperature was maintained at approximately 70 °C. The reaction mixture was heated to reflux, refluxed overnight, and cooled in an ice bath. Acetic acid (5 mL) was added dropwise with caution, followed by 10 mL of a 50–50 acetic acid–water mixture, added in a similar manner. With caution initially, 50 mL of water was then added to the reaction mixture. At this point some of the 1-phenyl-2-[2-(6-methoxyquinolyl)]ethanone precipitated out of solution and was removed by filtration. The toluene layer was separated, dried, and rotary evaporated, resulting in the formation of an additional quantity of product. A total quantity of 5.30 g (71% yield) of 1-phenyl-2-[2-(6-methoxyquinolyl)]ethanone was obtained, which, after recrystallization from ethanol–water, had a melting point of 146–147.5 °C. A picrate was prepared by the method of Shriner et al. (*13*) mp 191.5–193.5 °C. The NMR spectrum in $DCCl_3$ showed signals at δ 6.1 (enamine) and 4.6 (imine). Me_4Si was used as an internal standard; the chemical shifts are reported in ppm relative to it in all cases. Several integrations of these two signals were performed, using the following formula: 2(area of enamine proton)/(area of the imine protons) gave an enamine/imine ratio of approximately 5. This agrees favorably with the work of Fukata et al. (*14*), who reported that the enamine form predominated in 1-phenyl-2-(2-quinolyl)ethanone. Elemental analyses for C, H, N, F, Cl, and Br in agreement with theoretical

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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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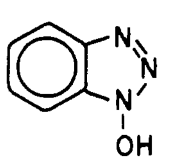
α,ω-Bis(benzotriazoloxy)alkane System

William A. Feld* and Dale G. Evans

Department of Chemistry, Wright State University, Dayton, Ohio 45435

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.

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.



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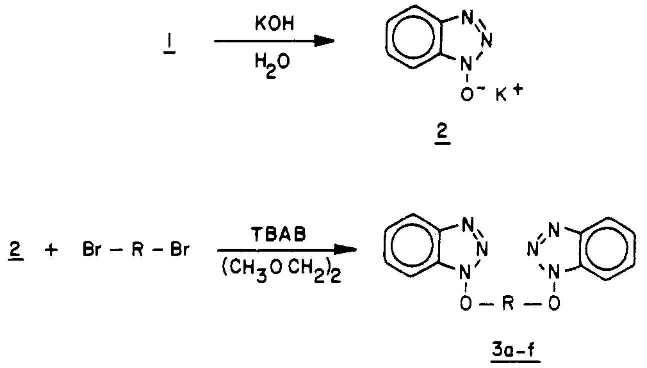
Initial reactions were carried out in a methylene chloride–water system but led to significant amounts of a methylene diether which will be the subject of a later report. Compounds **3a–f** were therefore prepared by the reaction of the potassium salt of 1-hydroxy-1,2,3-benzotriazole (**2**) with the 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