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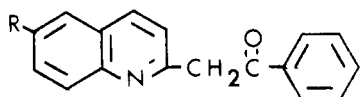
Syntheses of 1-Phenyl-2-(2-quinolyl)ethanones and Related Ethanones

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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 derivatives 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: $2(\text{area of enamine proton})/(\text{area of the imine protons})$ 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

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.

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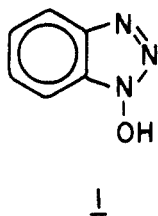
α,ω -Bis(benzotriazoloxo)alkane System

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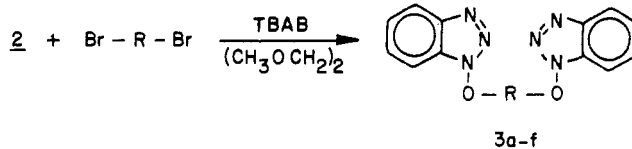
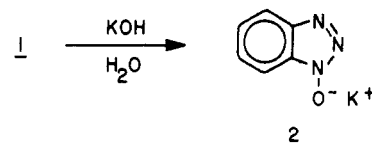
A series of α,ω -bis(benzotriazoloxo)alkanes have been synthesized by employing a phase transfer catalyst (PTC) and have been characterized by physical, spectral, and analytical properties.

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(benzotriazoloxo)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