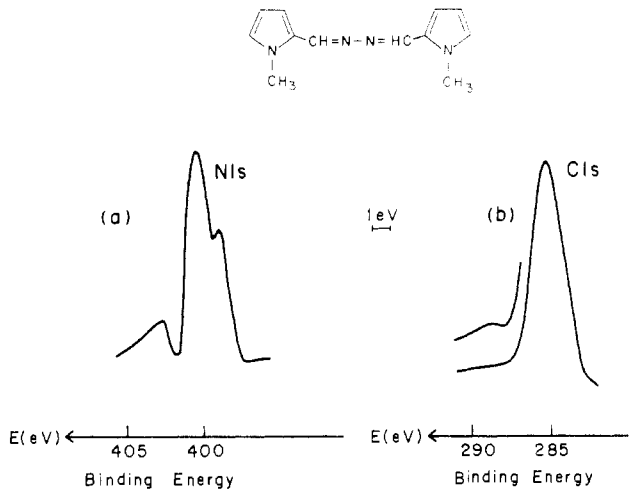

Figure 4. X-ray photoelectron spectrum of IIIf: (a) N(1s) energy region, (b) C(1s) energy region.

a pressure of less than 10^{-8} torr. Samples were mounted on aluminum mesh at room temperature.

(a) Reaction of Arylhydrazone-N-carboxylic Esters (I) and Hydrazine Hydrate. A mixture of the hydrazone ester (0.01 mol) and the hydrazine hydrate (0.01 mol) in 50 mL of ethanol was refluxed on a water bath for a period of 5 h. Evaporation of the solvent left a viscous oil, which proved to be the arylhydrazone (II). Crystallization of IIa from petroleum ether (60–80 °C) gave pale yellow crystals, mp 62 °C. The other hydrazones gave oily materials.

(b) Reaction of Arylhydrazones (IIa–g) and Hydrochloric Acid. A mixture of the arylhydrazone (0.01 mol) in ethanol (20 mL) and 6 N HCl (5 mL) was warmed on a water bath for 5 min. A heavy solid was precipitated, which was filtered off and crystallized from ethanol to give azines of thiophene-2-carboxaldehyde (IIIa), furan-2-carboxaldehyde (IIIb), pyrrole-2-carboxaldehyde (IIIc), 5-methylthiophene-2-carboxaldehyde (IIId), indole-3-carboxaldehyde (IIIe), *N*-methylpyrrole-2-carboxaldehyde (IIIf), and pyridine-4-carboxaldehyde (IIIg).

Azine IIIa was also prepared by refluxing an alcoholic solution of the arylhydrazone-*N*-carboxylic ester Ia and aqueous sodium hydroxide (10%) for 1 h. The alcohol was evaporated, and the product was crystallized from petroleum ether (60–80 °C) to give a product, which proved to be identical with IIa. This product was treated with hydrochloric acid, as mentioned above, to yield azine IIIa.

(c) Preparation of Authentic Samples. (1) Hydrazone IIa was prepared by refluxing equimolecular amounts of thiophene-2-carboxaldehyde and hydrazine hydrate in ethanol for a period of 5 h and then worked up as described previously. (2) Azines IIIa–g were prepared by refluxing the corresponding heterocyclic aldehyde (2 mol) and hydrazine hydrate (1 mol) in ethanol and then worked up. The products proved to be identical with those obtained from procedure b.

Elemental analyses were performed and submitted for review.

Registry No. Ia, 81291-64-7; Ib, 81291-65-8; Ic, 37526-50-4; Id, 83710-32-1; Ie, 15641-27-7; If, 83710-33-2; Ig, 83710-34-3; IIa, 31350-01-3; IIb, 31350-00-2; IIc, 83710-35-4; IId, 83719-44-2; IIe, 83710-36-5; IIf, 83710-37-6; IIg, 51832-68-9; IIIa, 24523-46-4; IIIb, 5428-37-5; IIIc, 75841-29-1; IIId, 83710-38-7; IIIe, 1233-49-4; IIIf, 59618-86-9; IIIg, 6957-22-8.

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One-Step Synthesis of Esters of Aliphatic β-Chloro Sulfonic Acids. Their Sequential Conversion to Other Sulfonic Acid Derivatives

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A one-step synthesis of methyl 2-chlorohexane-1- and 2-chlorooctane-1-sulfonate by the novel free-radical addition of methyl chlorosulfonate to 1-hexene and 1-octene, respectively, is reported. These products were converted by standard techniques into the corresponding sodium and benzylthiuronium β-chlorosulfonic acid salts and sulfonyl chlorides. Dehydrochlorination of these latter products with triethylamine afforded regiospecific formation of trans-α,β-unsaturated sulfonyl chlorides, which were transformed by conventional methods into sodium and benzylthiuronium unsaturated and saturated sulfonic acid salts. Eleven new compositions of matter are reported.

Introduction

The halogen–sulfur bond of the halosulfonyl group is readily amenable to homolytic cleavage. Studied extensively has been the free-radical addition of aliphatic and aromatic sulfonyl halides to a variety of carbon–carbon unsaturated systems to yield β-halo sulfones (*1–5*). Also, *N*-chlorosulfonylphthalimide (*6*) and sulfuryl chloride fluoride (*7*) have been added to olefins under free-radical conditions to give *N*-(β-chloroalkyl)sulfonylphthalimides and 2-chloroalkanesulfonyl fluorides, respectively. Further, the free-radical addition of sulfuryl chloride to olefins has been reported to give β-chloroalkyl sulfones (*6a*). These results suggest the possibility that alkyl or aryl halosulfonates also could undergo free-radical addition to unsaturated hydrocarbons to provide a novel one-step synthesis of esters of

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Table I. ^{1}H NMR and IR Data for Derivatives of Alkane-1- and Alkene-1-sulfonic Acids

compd	NMR (neat), δ	IR,[a] cm^{-1}
Ia	4.55–4.09 (m, 1 H, $CH_2CHClCH_2$), 3.89 (s, 3 H, OCH_3), 3.55 (d, J = 6 Hz, 2 H, $CH_2SO_2OCH_3$), 2.20–1.70 (m, 2 H, CH_2CH_2CHCl), 1.67–1.19 (m, 4 H, $CH_3(CH_2)_2$), 0.96 (t, J = 6 Hz, 3 H, CH_3CH_2)	1365 (ν_{as}, SO_2), 1175 (ν_{sym}, SO_2)
Ib	4.57–4.08 (m, 1 H, $CH_2CHClCH_2$), 3.89 (s, 3 H, OCH_3), 3.54 (d, J = 6 Hz, 2 H, $CH_2SO_2OCH_3$), 2.20–1.68 (m, 2 H, CH_2CH_2CHCl), 1.68–1.08 (m, 8 H, $CH_3(CH_2)_4$), 0.89 (t, J = 6 Hz, 3 H, CH_3CH_2)	1365 (ν_{as}, SO_2), 1175 (ν_{sym}, SO_2)
IIa		1230 and 1200[b] (ν_{as}, SO_2), 1072 (ν_{sym}, SO_2O)
IIb		1230 and 1200[b] (ν_{as}, SO_2O), 1072 (ν_{sym}, SO_2O)
IIIa	4.75–4.30 (m, 1 H, $CH_2CHClCH_2$), 4.16 (br d, 2 H, J = 6 Hz, CH_2SO_2Cl), 2.20–1.70 (m, 2 H, CH_2CH_2CHCl), 1.70–1.20 (m, 4 H, $CH_3(CH_2)_2$), 0.94 (t, J = 6 Hz, 3 H, CH_3)	1382 (ν_{as}, SO_2), 1170 (ν_{sym}, SO_2)
IIIb	4.78–4.30 (m, 1 H, $CH_2CHClCH_2$), 4.15 (br d, J = 6 Hz, 2 H, CH_2SO_2Cl), 2.22–1.73 (m, 2 H, CH_2CH_2CHCl), 1.73–1.14 (m, 8 H, $CH_3(CH_2)_4$), 0.93 (t, J = 6 Hz, 3 H, CH_3)	1382 (ν_{as}, SO_2), 1170 (ν_{sym}, SO_2)
IVa	7.13 (dt, J = 15.2, 6.2 Hz, 1 H, $CH_2CH{=}CHSO_2Cl$), 6.77 (dt, J = 15.2, 0.5 Hz, 1 H, $CH_2CH{=}CHSO_2Cl$), 2.56–2.13 (m, 2 H, $CH_2CH{=}CHSO_2Cl$), 1.65–1.08 (m, 4 H, $CH_3(CH_2)_2$), 0.92 (t, J = 6 Hz, 3 H, CH_3)	1620 (ν, C=C), 1375 (ν_{as}, SO_2), 1165 (ν_{sym}, SO_2), 970 (ω, CH=CH)
IVb	7.12 (dt, J = 15.0, 5.9 Hz, 1 H, $CH_2CH{=}CHSO_2Cl$), 6.72 (dt, J = 15.0, 0.6 Hz, 1 H, $CH_2CH{=}CHSO_2Cl$), 2.60–2.11 (m, 2 H, $CH_2CH{=}CHSO_2Cl$), 1.80–1.14 (m, 8 H, $CH_3(CH_2)_4$), 0.91 (t, J = 6 Hz, 3 H, CH_3)	1620 (ν, C=C), 1375 (ν_{as}, SO_2), 1165 (ν_{sym}, SO_2), 965 (ω, CH=CH)
Va		1185 (ν_{as}, SO_2O), 1065 (ν_{sym}, SO_2O), 965 (ω, CH=CH)
VIa		1217 and 1187[b] (ν_{as}, SO_2O), 1065 (ν_{sym}, SO_2O)

[a] Compounds Ia,b, IIIa,b, and IVa,b were run neat on NaCl; all others were run as KBr pellets. [b] Appear as a doublet.

β-halo sulfonic acids. In this paper we present two examples of such a reaction leading to methyl 2-chloroalkane-1-sulfonates and report their conversion through a series of reactions into other new aliphatic sulfonic acid derivatives.

Results and Discussion

Free-radical addition of methyl chlorosulfonate to 1-hexene and 1-octene afforded methyl 2-chlorohexane-1- and 2-chlorooctane-1-sulfonates (Ia,b), respectively. Structural assignments

$$CH_3OSO_2Cl + RCH{=}CH_2 \xrightarrow[C_6H_6,\ \Delta]{Bz_2O_2} RCH(Cl)CH_2SO_2OCH_3$$

Ia, R = n-C_4H_9

b, R = n-C_6H_{13}

of these 1:1 adducts were supported by elemental analysis, by IR and ^{1}H NMR spectral data (Table I), and by their conversion to known derivatives of hexane-1- and octane-1-sulfonic acids through the following series of reactions.

Treatment of Ia,b with sodium iodide in acetone gave the sodium salts of the corresponding β-chloro sulfonic acids (IIa,b). These products were converted into their benzylthiuronium sulfonate derivatives. Interaction of IIa,b with phosphorus pentachloride afforded β-chloro sulfonyl chlorides (IIIa,b). Dehydrochlorination of IIIa,b with triethylamine resulted in regiospecific formation of trans-α,β-unsaturated sulfonyl chlorides (IVa,b). Assignment of the trans configuration was made on the basis of their IR (ω_{vinyl} = 970–965 cm^{-1}) and ^{1}H NMR ($J \approx$ 15 Hz) spectra (Table I), which are typical of trans 1,2-disubstituted olefins. Hydrolysis of IVa,b with aqueous sodium bicarbonate yielded the corresponding trans unsaturated sulfonic acid salts (Va,b), which were characterized by formation of their benzylthiuronium sulfonate derivatives. Reduction of Va,b in an aqueous medium with hydrogen in the presence of 10% palladium on carbon gave the known hexane-1- and octane-1-sulfonic salts (VIa,b), from which their benzylthiuronium sulfonate derivatives were prepared. The reaction sequence for the conversion of Ia,b to VIa,b is summarized in Scheme I. The IR and ^{1}H NMR spectra of the new compounds formed in this series of reactions are presented in Table I.

Scheme I

$$\text{Ia,b} \xrightarrow[-CH_3I]{NaI/Me_2CO} RCH(Cl)CH_2SO_2ONa \xrightarrow{PCl_5}$$

IIa,b

$$RCH(Cl)CH_2SO_2Cl \xrightarrow[-HCl]{Et_3N/C_6H_6} \begin{matrix} R & & H \\ & C{=}C & \\ H & & SO_2Cl \end{matrix} \xrightarrow{NaHCO_3/H_2O}$$

IIIa,b IVa,b

$$RCH{=}CHSO_2ONa \xrightarrow{H_2/10\%\ Pd\text{-}C} RCH_2\text{-}CH_2SO_2Na$$

Va,b VIa,b

Experimental Section

Reagents. 1-Hexene and 1-octene, stored over commercial sulfate, were distilled shortly before use. Methyl chlorosulfonate was prepared from freshly distilled sulfuryl chloride and dry methanol essentially according to the method of Binkley and Degering (*8*) in 48% yield: bp 55–56 °C (39 mm); n^{25}_D 1.4112 (lit. (*8*) bp 48.1 °C (29 mm), n^{20}_D 1.414). Solvents and all other reagents, obtained from common commercial sources, were dried and/or purified whenever necessary by conventional methods.

Analysis. Infrared spectra were taken on a Perkin-Elmer 237B grating spectrophotometer. Proton magnetic resonance spectra were recorded on a Perkin-Elmer R-24 spectrometer using tetramethylsilane as an internal standard. Indices of refraction were taken on a Bausch and Lomb Abbe-3L refrac-

tometer. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Boiling points are uncorrected. Satisfactory elemental analyses for all new compounds were submitted for review.

Methyl 2-Chlorohexane-1-sulfonate (Ia). To a refluxing mixture of 39.17 g (0.20 mol) of methyl chlorosulfonate and 100 mL of dry benzene was added a solution of 25.3 g (0.30 mol) of 1-hexene, 4.85 g (0.02 mol) of benzoyl peroxide, and 100 mL of benzene over a period of 1.5 h. After the addition the mixture was refluxed for 16 h. The resulting dark amber solution was washed first with water (2 × 50 mL), then with 5% aqueous $NaHCO_3$ (5 × 30 mL), and finally with water (2 × 30 mL). The organic layer was dried over anhydrous calcium chloride, filtered, and concentrated in vacuo. The resulting liquid was distilled, the fraction boiling between 82 and 87 °C (0.35 mm) yielding 29.0 g (45%) of crude adduct. Further distillation gave an analytical sample: bp 105 °C (0.9 mm); n^{27}_D 1.4565. No attempt was made to resolve this or any of the other racemic modifications cited below into enantiomers.

Methyl 2-Chlorooctane-1-sulfonate (Ib). Following the procedure described above, 39.17 g (1.30 mol) of methyl chlorosulfonate, 33.67 g (0.30 mol) of 1-octene, and 4.85 g (0.02 mol) of benzoyl peroxide in a total of 200 mL of benzene were allowed to interact at refluxing temperatures for a total of 20 h. Distillation in vacuo afforded 35.7 g (49%) of crude adduct, bp 119–128 °C (0.8 mm). Further distillation gave an analytical sample: bp 113 °C (0.25 mm); n^{25}_D 1.4592.

Sodium 2-Chlorohexane-1-sulfonate (IIa). To a stirred mixture of 15.03 g (0.07 mol) of methyl 2-chlorohexane-1-sulfonate and 80 mL of dry acetone in a 250-mL, three-necked flask fitted with a paddle stirrer, a dropping funnel, and a calcium chloride drying tube was added 10.49 g (0.07 mol) of dry sodium iodide in 60 mL of dry acetone over a period of 1 h at room temperature. Rapid precipitation of a white solid occurred and the reaction was not exothermic. After the addition, the mixture was stirred at room temperature for 1 h and then filtered. The solid product was washed thoroughly with dry acetone and dried in vacuo at 80 °C to give 15.1 g (97%) of white powder.

The benzylthiuronium salt derivative was prepared and recrystallized from dilute methanol, mp 96–96.5 °C.

Sodium 2-Chlorooctane-1-sulfonate (IIb). Following the procedure described above, reaction of 30.9 g (0.127 mol) of methyl 2-chlorooctane-1-sulfonate with 19.1 g (0.127 mol) of sodium iodide gave 31.2 g (98%) of IIb.

The benzylthiuronium salt derivative was prepared and left in an impure state, mp 77–79.5 °C.

2-Chlorohexane-1-sulfonyl Chloride (IIIa). This compound was prepared from 14.5 g (0.067 mol) of sodium 2-chlorohexane-1-sulfonate and 14.6 g (0.070 mol) of phosphorus pentachloride according to the procedure of Truce and coworkers (*9*). The product was distilled in the presence of potassium carbonate in vacuo to give 13.3 g (91%) of crude sulfonyl chloride, bp 85–87 °C (1.0 mm). Further distillation gave an analytical sample: bp 76 °C (0.45 mm); n^{25}_D 1.4775.

2-Chlorooctane-1-sulfonyl Chloride (IIIb). Following the procedure described above, reaction of 30.1 g (0.12 mol) of sodium 2-chlorooctane-1-sulfonate with 27.0 g (0.13 mol) of phosphorus pentachloride gave 26.2 g (88%) of IIIb: bp 104–106 °C (0.8 mm); n^{25}_D 1.4740.

trans-1-Hexene-1-sulfonyl Chloride (IVa). Dehydrochlorination was carried out by treatment of 15.5 g (0.071 mol) of 2-chlorohexane-1-sulfonyl chloride in 100 mL of dry benzene with 7.2 g (0.071 mol) of triethylamine according to the procedure of Kharasch and Zavist (*10*). Precipitated triethylamine hydrochloride (mp 253–254 °C), obtained in quantitative yield, was separated by filtration. Benzene was removed from the filtrate and the residue was distilled in vacuo in the presence of potassium carbonate to give 10.9 g (84%) of trans unsaturated sulfonyl chloride: bp 76–77 °C (1.0 mm); n^{25}_D 1.4760.

trans-1-Octene-1-sulfonyl Chloride (IVb). Following the procedure described above, reaction of 21.7 g (0.088 mol) of 2-chlorooctane-1-sulfonyl chloride with 8.9 g (0.088 mol) of triethylamine gave 10.2 g (55%) of IVb: bp 99–99.5 °C (1.0 mm); n^{25}_D 1.4730.

Sodium trans-1-Hexene-1-sulfonate (Va). A mixture of 15.8 g (0.087 mol) of *trans*-1-hexene-1-sulfonyl chloride and 21.5 (0.26 mol) of sodium bicarbonate in 300 mL of water was heated at reflux for 1 h. Solvent was removed by distillation and the resulting solid was dried in vacuo at 80 °C. Extraction with dry ethanol gave 14.0 g (87%) of white solid.

The benzylthiuronium salt derivative was prepared and recrystallized from aqueous ethanol, mp 127–127.5 °C.

Sodium trans-1-Octene-1-sulfonate (Vb). Following the procedure described above, hydrolysis of 3.4 g (0.016 mol) of *trans*-1-octene-1-sulfonyl chloride gave 2.7 g (78%) of Vb.

The benzylthiuronium salt derivative was prepared and recrystallized from dilute ethanol, mp 117.5–118 °C.

Sodium Hexane-1-sulfonate (VIa). Into a 45-mL-capacity Parr bomb containing a magnetic stirring bar were placed 1.443 g (7.75 mmol) of sodium *trans*-1-hexene-1-sulfonate, 243 mg of 10% palladium on carbon, and 20 mL of water. After the system was purged well with hydrogen, the bomb was pressurized with hydrogen to 740 psig. Theoretical uptake of hydrogen was complete in 2 h. The reaction mixture was filtered and the filtrate was heated to dryness to give 1.434 g (98%) of white solid after drying in vacuo at 90 °C. Its IR spectrum was identical with that of an authentic sample of sodium hexane-1-sulfonate.

The benzylthiuronium salt derivative was prepared and recrystallized from dilute ethanol to give product melting at 110–110.5 °C, which was undepressed on admixture with authentic benzylthiuronium hexane-1-sulfonate prepared as described below. Its IR spectrum was identical with that of the authentic sample.

Sodium Octane-1-sulfonate (VIb). A small sample of sodium *trans*-1-octene-1-sulfonate (0.22 g) in water was hydrogenated in the presence of 10% palladium on carbon (0.138 g) catalyst at room temperature under an initial hydrogen pressure of 800 psig as described above. The reaction mixture was filtered and the filtrate concentrated to give a solution that was immediately combined with a concentrated solution of benzylthiuronium chloride (0.22 g). The resulting precipitate was recrystallized from dilute ethanol to give benzylthiuronium octane-1-sulfonate melting at 109–109.5 °C, which was undepressed on admixture with the authentic sample prepared as described below. Its IR spectrum was identical with that of the authentic sample.

Preparation of Benzylthiuronium Salt Derivatives of Hexane-1- and Octane-1-sulfonic Acids. These derivatives were prepared from commercial samples of the sodium salts of the corresponding sulfonic acids according to common practice: benzylthiuronium hexane-1-sulfonate, mp 110–110.5 °C from dilute ethanol; benzylthiuronium octane-1-sulfonate, mp 109–109.5 °C (lit. (*11*) 103–104 °C) from aqueous methanol.

Acknowledgment

We thank R. Chwastiak and N. Conzo for technical assistance.

Registry No. Ia, 83633-52-7; Ib, 83633-53-8; IIa, 83633-54-9; IIa·benzylthiuronium salt, 83633-63-0; IIb, 83633-55-0; IIb·benzylthiuronium salt, 83633-65-2; IIIa, 83633-56-1; IIIb, 83633-57-2; IVa, 83633-58-3; IVb, 83633-59-4; Va, 83633-60-7; Va·benzylthiuronium salt, 83633-67-4; Vb, 83633-61-8; Vb·benzylthiuronium salt, 83633-69-6; VIa, 2832-45-3; VIa·benzylthiuronium salt, 83633-70-9; VIb, 5324-84-5; VIb·benzylthiuronium salt, 16548-10-0; methyl chlorosulfonate, 812-01-1; 1-hexene, 592-41-6; 1-octene, 111-66-0.

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

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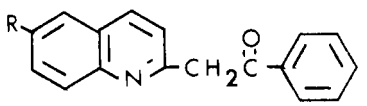
Seven 1-phenyl-2-[2-(6-substituted quinolyl)]ethanones were synthesized by the condensation of 2-methyl-6-substituted quinolines and methyl benzoate with sodium hydride as the condensing agent. Substituents in the 6 position were bromo, chloro, fluoro, methoxy, methyl, and trifluoromethyl as well as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