to methadone metabolites, together with a new compound **6**.

Oxidation of methadone with neutral potassium permanganate proved to be very rapid under mild conditions. Thus, when **1** was stirred with the excess oxidant at 25 °C, the reaction was complete in minutes and afforded in a high yield a mixture of two neutral, crystalline compounds, **5** and **6**, in a 4:1 ratio.[13] The ratio of these products was independent of the temperature and concentration of the reactants. The major compound was characterized as 1,5-dimethyl-3,3-diphenyl-2-pyrrolidone (**5**) by comparison with an authentic sample.[14] According to Pohland's observations, it underwent nearly quantitative reaction with ethyllithium to yield the metabolite **3**.[4] The transformation of **3** with hydroiodic acid to the second metabolite **4** has already been reported by other workers.[3,4] The above procedure thus represents a convenient method for preparation of methadone metabolites from the drug.

The minor product analyzed for $C_{19}H_{19}NO_2$, showed two carbonyl absorption bands at 1660 and 1735 cm^{-1} in its IR spectrum, and exhibited a 60-MHz proton NMR spectrum very similar to that of **5** except in the aromatic region, where it displayed a ten-proton multiplet. The UV spectrum of **6** showed a long wavelength n–π^* transition at 340 nm due to an α-dicarbonyl system.[15,16] Its mass spectrum showed a weak molecular ion at *m/e* 293 (6%) followed by a base peak at *m/e* 265 ($M^+ - CO$). The peak at *m/e* 265 and subsequent fragments were identical with those for **5**, thereby indicating their close structural relationship. Based on the above data, the minor product is considered to be 4,4-diphenyl-3-keto-2-piperidone (**6**), and the structure is in accord with its ^{13}C and 300-MHz proton NMR spectra (see Experimental Section).

Experimental Section[17]

Oxidation of Methadone 1 with Neutral Potassium Permanganate. Formation of Pyrrolidone 5 and α-Keto Lactam 6. To a stirred solution of methadone hydrochloride (9.0 g) in water (125 mL) at 25 °C was added dropwise 10% aqueous sodium hydroxide solution until the reaction mixture was distinctly basic (pH 10–12). The solution was extracted with ether, and the extract was dried and evaporated to afford free methadone as a thick, colorless oil (ca. 8 g). The oil was dissolved in acetone (700 mL), and to this was added a solution of potassium permanganate in acetone/water (2 L, 1:1). The reaction mixture was vigorously stirred for 20 min at room temperature and then cooled in an ice bath. The excess oxidant was removed by bubbling sulfur dioxide through the cold solution until it was nearly colorless. The solution was filtered through a bed of Celite, and the filtrate was concentrated on a rotary evaporator. After an oily material had separated, the aqueous solution was extracted with ether. The organic extract was washed with 5% aqueous sodium carbonate and water. Removal of the solvent from the dried extract gave a mixture of **5** and **6** as a thick, pale yellow oil (6.4 g). Preparative silica gel TLC (chloroform/methanol, 9:1) afforded 1,5-dimethyl-3,3-diphenyl-2-pyrrolidone (**5**) as a white, crystalline compound (3.7 g, 55%) which, when recrystallized from ethanol, had mp 120–121 °C (lit.[12] mp 121–122 °C) and showed the following spectral data: ν_{max} (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (d, J = 6 Hz, 3 H), 2.05–2.4 (m, 2 H), 2.9 (s, 3 H), 3.3–3.8 (m, 1 H), and 7.3 (broad singlet, 10 H); mass spectrum (70 eV), *m/e* 265 (M^+, 100), 250 (13), 208 (32), 193 (58), 179 (25), 165 (29), 130 (32), 115 (40), 91 (29), and 56 (40).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.51; H, 7.17; N, 5.28. Found: C, 81.84; H, 7.04; N, 5.17.

The second compound, **6** (1.1 g, 15%), was crystallized from ethanol, mp 212–213 °C, and it showed the following spectral data: ν_{max} (KBr) 1660 and 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (d, J = 6 Hz, 3 H), 2.5–2.9 (m) and 2.85 (s) (total 5 H), 3.0–3.6 (m, 1 H), and 6.8–7.5 (m, 10 H); λ_{max} (EtOH) 258 nm (ϵ 3700) and 340 (75); ^{13}C NMR ($CDCl_3$) δ 21.0, 31.0, 39.3, 50.0 ($N-CH_3$), 58.5 ($>CPh_2$), 126–129 (aromatic), 136.7 and 140 (aromatic quaternary carbons), 158.5 ($CONH_2$), and 191.5 (C=O);[18] mass spectrum (70 eV), *m/e* 293 (M^+, 6), 265 (100), 250 (11), 208 (36), 193 (70), 179 (30), 165 (26), 130 (45), 115 (44), 91 (30), and 56 (20).

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.81; H, 6.48; N, 4.77. Found: C, 77.29; H, 6.44; N, 4.78.

The 300-MHz NMR spectrum ($CDCl_3$) exhibited signals at δ 1.35 (d, J = 6 Hz, 3 H), 2.66 (d of d, J = 15.0 and 10.5 Hz, 1 H, H_a), 2.85 (s, 3 H), 2.99 (d of d, J = 15.0 and 4.5 Hz, 1 H, H_b), 3.43 (m, 1 H, H_c), and 6.97–7.50 (m, 10 H).

Preparation of Metabolite 3. The methadone metabolite **3** and its perchlorate salt were prepared according to Pohland et al.[4] and found to be identical in all respects with the previously synthesized material.[4]

Acknowledgments. The authors would like to thank Dr. E. F. Ullman for helpful discussions and Mr. J. Shoolerey of Varian Associates, Palo Alto, for recording the ^{13}C and 300-MHz NMR spectra.

Registry No.—1 HCl, 1095-90-5; **3**, 30223-73-5; **3** $HClO_4$, 66729-78-0; **5**, 30223-75-7; **6**, 68715-73-1.

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(17) Melting points are determined in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Solutions in organic solvents were dried over anhydrous sodium sulfate. UV spectra were recorded on a Cary 15 spectrophotometer, while IR spectra were recorded on a Perkin-Elmer instrument. Unless specified otherwise, the NMR spectra were recorded on a Varian T-60 instrument and the values are given in parts per million downfield from tetramethylsilane as an internal standard.
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N-Alkylation of β-Ketocarboxylic Acid Amides

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A recent synthesis of indeno[1,2,3-*de*]quinolin-2-ones involves the acid-catalyzed cyclization of 2,2-dichloro-*N*-substituted β-ketoamides of type **1**; compounds **1** are derived by sulfuryl chloride chlorination of the corresponding amide **2**.[1] We present here an alternative route to **1** which obviates the need for **2** and its prerequisite *N*-alkylarylamine[1-3] and utilizes as substrate the usually more accessible β-ketoamide **3**. Indeed, compound **2** itself can be obtained, if desired, using this method.

To our knowledge direct N-alkylation of **3** as a preparative route to **2** has not been described. When treated with sodium

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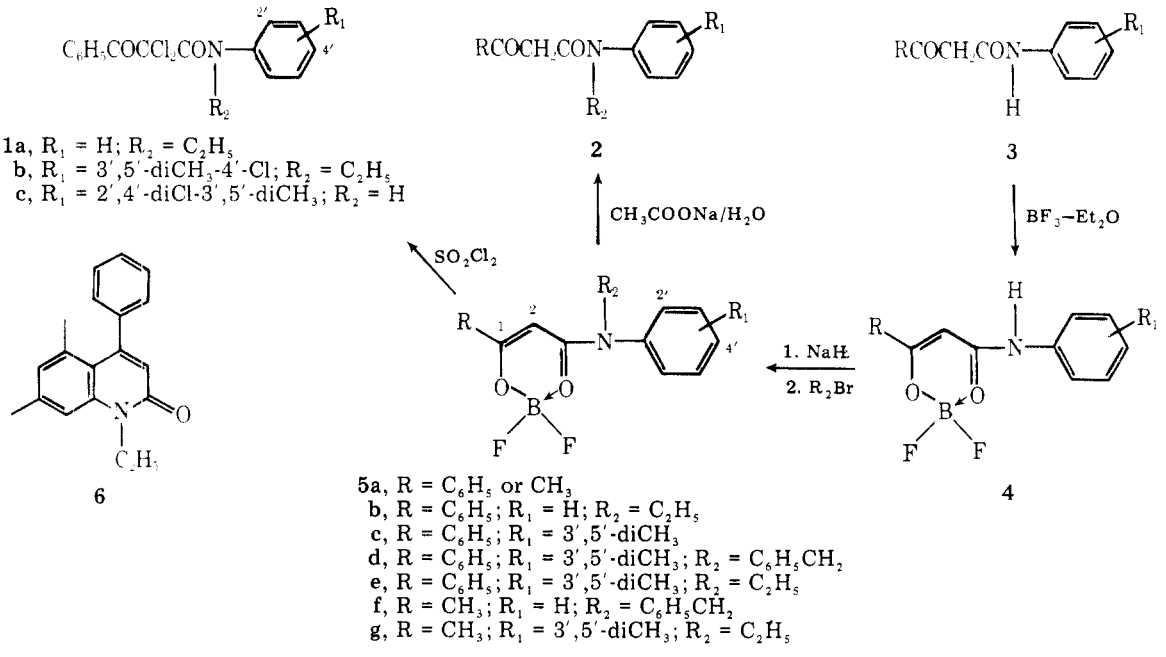
Scheme I



hydride and an alkyl halide, in dimethylformamide or in absolute ethanol, **3** is normally C-alkylated, and the product is often accompanied by some O-substituted derivative.[4] On the other hand, related substrates, such as α-benzoylacetamide, are N-acylated with sodium hydride and methyl benzoate in refluxing monoglyme,[5] and N-acetylated by acetic anhydride and boron trifluoride diacetic acid.[6] The latter procedure involves an intermediate boron difluoride complex,[6] and we have extended its scope to the preparation of N-alkylated β-ketoamides **1** and **2**. In essence, the analogous difluorooxyborane **4**[7] is deprotonated and the anion[8] reacted with an alkyl halide. The *N*-alkyldifluorooxyborane product **5** is hydrolyzed to **2**, or, alternatively, is treated with sulfuryl chloride to afford **1**.

The method (Scheme I) is outlined for the preparation of **2d** and **1b**, respectively. Amide **3c** in benzene was converted to **4c** (95%) with boron trifluoride etherate. Treatment of **4c** in dimethylformamide with sodium hydride followed by alkylation with benzyl bromide at room temperature gave **5d** (75%); no significant amount of C- or O-alkylated material appeared to be formed. Compounds **5e–g** were similarly obtained in satisfactory yields.[9] The IR characteristics and mass spectral fragmentations[8] of the respective difluorooxyboranes **4** and **5** confirmed their structures. In the instances where solvent solubility permitted, ^{1}H NMR spectra of **5** were recorded ($CDCl_3$); the singlet olefinic proton (H-2) absorbed near δ 4.8 in the 1-methyl derivatives **5f** and **5g**, and near δ 5.4 in the 1-phenyl compounds **5d** and **5e**.

Heating **5d** with sodium acetate[10] in aqueous dimethylformamide resulted (71%) in *N*-benzyl-3′,5′-dimethylbenzoylacetanilide (**2d**) (~50% overall yield, based on **3c**). It is noteworthy and convenient that difluorooxyborane **5** can be utilized as substrate in the Knorr quinolinone synthesis. Thus, **5e** and polyphosphoric acid gave **6** in 88% yield.

The effect of excess sulfuryl chloride on **5e** in acetonitrile solution was studied. Chlorination was fortunately accompanied by concomitant removal of the BF_2 moiety, presumably from the action of liberated hydrogen chloride; on subsequently adding water, the product proved to be the desired 2,2,4′-trichloroanilide **1b**, contaminated with minor dichloro material. With no acetonitrile in the reaction and retention of hydrogen chloride, the major product likewise was **1b**. An excellent conversion of **5b** to the 2,2-dichloro derivative **1a** was also achieved, and the sequence **3** → **4** → **5** → **1** constitutes a new approach to the preparation of **1**.

The reaction of **5e** with sulfuryl chloride (in the absence of acetonitrile) took an unexpected and different course on allowing hydrogen chloride to escape into the atmosphere; addition of water afforded a mixture which now contained a substantial proportion (>47%) of a new substance, "A", and only minor **1b**. The production and nature of "A" are being further investigated, as are also the alkylation and acylation of the anions derived from **4** and related metal chelates of **3**.

Experimental Section[11,12]

Difluoro([1-phenyl-2-(3′,5′-dimethylphenylcarbamoyl)-vinyl]oxy)borane (4c). This compound was prepared (method B)[7] from anilide **3c** (16.0 g, 60 mmol), suspended in dry benzene (160 mL), and excess boron trifluoride etherate (Merck, Darmstadt; 40 mL); the sparingly soluble **4c** commenced to separate from solution within minutes. After 1 h at room temperature, the mixture was chilled and the solid **4c** was collected by filtration, washed with benzene and ether, and dried (17.9 g, ~95% yield; mp 240 245 °C) at 50 °C; pale yellow crystals (from aqueous dimethylformamide);[13] mp 251–253 °C; IR 3325 (s, NH), 1620 (s, coordinated amide C=O) cm^{-1}; mass spectrum, *m/e* 315 (M^+), 296 (M − F), 195 ($C_6H_5C(OBF_2)$=CHC=O), 169 [$(CH_3)_2C_6H_3NHBF_2$], 121 [$(CH_3)_2C_6H_3NH_2$], 105 (C_6H_5CO).

Anal. Calcd for $C_{17}H_{16}BF_2NO_2$: C, 64.79; H, 5.12; N, 4.45. Found: C, 65.09; H, 5.10; N, 4.29.

Compound **4c** dissolved in dimethylformamide and was sparingly soluble in ethanol, tetrahydrofuran, chloroform, ether, and benzene.

***N*-Benzyldifluoro([1-phenyl-2-(3′,5′-dimethylphenylcarbamoyl)vinyl]oxy)borane (5d).** A solution of **4c**[14] (3.15 g, 10 mmol) in dry dimethylformamide (25 mL) was added dropwise over 20 min to a stirred mixture of sodium hydride (0.60 g of a 70% dispersion in mineral oil, ~17 mmol) in dry dimethylformamide (5 mL) under N_2 at room temperature. After another 10 min, benzyl bromide (3 mL, 24 mmol) was added and stirring was continued for 2 h; the yellow color of the mixture was discharged within a few minutes, indicating a rapid alkylation. The mixture was poured into ice water (~50 mL) and extracted with chloroform (2 × 30 mL). The organic phase was washed with water, dried (Na_2SO_4), and concentrated to a few milliliters under reduced pressure. The residue was triturated with ethanol to give **5d** as a white solid which was chilled, collected by filtration, washed with ethanol, and dried (3.05 g, 75%; mp 178–180 °C): colorless tiny crystals (from aqueous ethanol); mp 181–182 °C; IR 1600 cm^{-1} (s, coordinated amide C=O); ^{1}H NMR [$CDCl_3$ (CD_3COCD_3)] δ 2.28 (2.28) (s, 6 H, $ArCH_3$), 5.01 (5.12) (s, 2 H, $CH_2C_6H_5$), 5.44 (5.62) (s, 1 H, CH), 6.62 (6.90) (s, 2 H, ArH), 7.06 (7.12) (s, 1 H, ArH), 7.2–7.8

(7.2–7.8) (m, 10 H, ArH); mass spectrum, *m/e* 405 (M^+), 386 (M − F), 295 (M − $C_6H_5CH_2F$), 259 [$(CH_3)_2C_6H_3N(BF_2)CH_2C_6H_5$], 211 [$(CH_3)_2C_6H_3NHCH_2C_6H_5$], 210, 195 ($C_6H_5C(OBF_2)$=CHC=O), 146 ($C_6H_5COCH$=C=O), 105 ($C_6H_5CO$), 91 ($C_6H_5CH_2$).

Anal. Calcd for $C_{24}H_{22}BF_2NO_2$: C, 71.13; H, 5.47; N, 3.46. Found: C, 71.65; H, 5.50; N, 3.42.

The reaction was also conducted in ethanol solvent; substrate **4c** (3.15 g, 10 mmol) was added portionwise over 20 min to a stirred alcoholic solution of sodium ethoxide [constituted from absolute ethanol (30 mL) and sodium hydride (0.51 g of a 70% dispersion, 15 mmol)] under N_2 at 20 °C. The procedure above was continued, and **5d** was isolated in 70% yield.

***N*-Benzyl-3′,5′-dimethylbenzoylacetanilide (2d).** A mixture of **5d** (1.0 g), sodium acetate trihydrate (2 g), water (3 mL), and dimethylformamide (7 mL) was kept at ~90 °C for 0.75 h with intermittent stirring and then was poured into ice water. The product was extracted into ether, and the ethereal phase (~50 mL) was washed with water, dried (Na_2SO_4), and evaporated. The residual oil (0.8 g) was triturated with a few milliliters of aqueous methanol containing several drops of 2 M HCl and chilled when it solidified. Filtration afforded 0.62 g (71%) of **2d** (mp 89–91 °C): colorless crystals (from aqueous methanol); mp 92–93 °C; mass spectrum, *m/e* 357 (M^+), 211 [$(CH_3)_2C_6H_3NHCH_2C_6H_5$], 210, 147 ($C_6H_5COCH_2CO$), 105, 91.

Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.48; N, 3.92. Found: C, 80.68; H, 6.56; N, 3.86.

***N*-Ethyldifluoro([1-phenyl-2-(3′,5′-dimethylphenylcarbamoyl)vinyl]oxy)borane (5e).** Anilide **4c**[14] (3.15 g, 10 mmol) was alkylated with ethyl bromide (6 mL, ~70 mmol) in dimethylformamide as for **5d.** Reaction for 8 h gave **5e** (2.25 g, 66%; mp 188–190 °C): colorless tiny crystals (from aqueous ethanol); mp 189–190 °C; IR 1610 cm^{-1} (s, coordinated amide C=O); ^1H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 2.38 (s, 6 H, $ArCH_3$), 3.92 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 5.42 (s, 1 H, CH), 6.84 (s, 2 H, ArH), 7.12 (s, 1 H, ArH), 7.2–7.75 (m, 5 H, ArH); mass spectrum, *m/e* 343 (M^+), 324 (M − F), 197 [$(CH_3)_2C_6H_3N(BF_2)C_2H_5$], 195 ($C_6H_5C(OBF_2)$=CHC=O), 149 [$(CH_3)_2C_6H_3NHC_2H_5$], 105 ($C_6H_5CO$).

Anal. Calcd for $C_{19}H_{20}BF_2NO_2$: C, 66.50; H, 5.88; N, 4.08. Found: C, 66.75; H, 5.78; N, 4.06.

Product **5e** was identical (IR, mixture melting point) with that derived from anilide **2e** (mp 63–64 °C) and boron trifluoride etherate (method A).[7]

In a variation of the procedure, dry tetrahydrofuran (50 mL) was added in one portion to a stirred mixture of **4c** (3.15 g, 10 mmol) and sodium hydride (0.60 g of a 70% dispersion, 17 mmol) under N_2, and stirring was continued for 30 min; the sparingly soluble **4c** dissolved with evolution of H_2, and reaction was accompanied by a fair exothermic effect. After addition of ethyl bromide (5 mL, excess) and alkylation for 8 h, **5e** was isolated in 60–65% yield.[15]

5,7-Dimethyl-*N*-ethyl-4-phenylquinolin-2-one (6). A mixture of **5e** (1.0 g) and polyphosphoric acid (10 g) was heated at 145–150 °C for 1 h with intermittent stirring and then was cooled somewhat and diluted with ice water. The product was extracted into ether (~50 mL), and the ethereal phase was washed with water, dried (Na_2SO_4), and evaporated to yield **6** as a solid [0.70 g, 88%; mp 112–114 °C; one spot on TLC (benzene)]: colorless needles (from aqueous methanol); mp 115 °C; mass spectrum, *m/e* 277 (M^+), 276 (M − 1), 262 (M − 15), 249 (M − 28), 234 (249 −15).

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.55; H, 7.07; N, 5.15.

Action of Sulfuryl Chloride on 5e. Formation of 2,2,4′-Trichloro-3′,5′-dimethyl-*N*-ethylbenzoylacetanilide (1b). To a suspension of **5e** (0.30 g) in acetonitrile (1 mL) contained in a 25-mL conical flask was added an excess of sulfuryl chloride (1.5 mL). The flask was immediately stoppered and left to stand at room temperature for 2.5–3 h; reaction rapidly occurred with liberation of gas and dissolution of the **5e**, and the (glass) stopper was momentarily loosened now and then to alleviate the pressure in the flask. Ice water was added, and the mixture was stirred intermittently until the precipitated material had solidified. This was filtered, washed with water, and dried (0.31 g, 88%; mp 98–118 °C); IR, MS, and TLC (benzene) established the product to be **1b**[1] mixed with minor dichloroamide and negligible tetrachloroamide.[16] Chlorination for a shorter period (1–1.5 h) led to mixtures containing a decreased proportion of **1b.** Treatment of **4c** (0.30 g) in acetonitrile (1 mL) with sulfuryl chloride (1.5 mL) for 3 h, as for **1b,** afforded 2,2,2′,4′-tetrachloroanilide **1c,** associated with minor trichloro material [MS and TLC (benzene)], in almost quantitative yield. Chlorination of **5b** (0.30 g) for 2 h as for **1b** gave amide **1a** [IR, MS, TLC (benzene)] in >90% (crude) yield.

Acknowledgment. The author is grateful to the South African Council for Scientific and Industrial Research, Pretoria, for financial support and would like to thank Mr. N. Blom and Mr. A. Zafirellis for assistance with some of the experimental work and spectral determinations.

Registry No.—**1a,** 19359-43-4; **1b,** 52827-58-4; **1c,** 40624-92-8; **2d,** 68646-50-4; **2e,** 52827-50-6; **3c,** 40624-75-7; **4c** charged, 68682-89-3; **4c** uncharged, 68646-51-5; **5b** charged, 15387-97-0; **5b** uncharged, 68646-52-6; **5d** charged, 68682-90-6; **5d** uncharged, 68646-53-7; **5e** charged, 68682-91-7; **5e** uncharged, 68646-54-8; **5f** charged, 68682-92-8; **5f** uncharged, 68646-55-9; **5g** charged, 68682-93-9; **5g** uncharged, 68646-56-0; **6,** 68646-57-1; benzyl bromide, 100-39-0; ethyl bromide, 74-96-4.

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(9) Compounds **5f** (mp 113–114 °C) and **5g** (mp 136–137 °C) had IR, ^1H NMR, and mass spectroscopic and analytical data in agreement with the assigned structures.
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(11) Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra (KBr disk) were recorded on a Perkin-Elmer Model 521 spectrophotometer (s = strong). ^1H NMR spectra were obtained at 60 MHz using a Hitachi Perkin-Elmer R-20 instrument, with Me_4Si as an internal reference. Mass spectra (70 eV) were measured on a Varian CH-5 spectrometer. Reagent grade dimethylformamide was dried over 4Å molecular sieves. Tetrahydrofuran was distilled as needed from benzophenone sodium ketyl under N_2. Sodium hydride was used as a 70% dispersion in mineral oil. Thin-layer chromatography was performed on silica gel F_{254} precoated plates (E. Merck, Darmstadt) of 0.25-mm thickness; spots were visualized with a UV lamp, and/or in an iodine chamber.
(12) No serious attempts were made to optimize yields in the alkylations.
(13) The presence in **4** (and **5**) of acid impurity generally led to acid-catalyzed partial conversiion to **3** (and **2**) during crystallization.
(14) Crude substrate (**4c,** mp 240–245 °C) was utilized in several alkylations (to **5d** and **5e**) with equal success.
(15) The N-alkylation reaction was noticeably slower in absolute ethanol than in either dimethylformamide or tetrahydrofuran.
(16) A similar chlorination (without acetonitrile) in a flask loosely stoppered with cotton wool gave as major product "A" (mp 197–199 °C; sparingly soluble in warm ethanol; $C_{19}H_{16}Cl_5NO$ by elemental and mass specral analysis). The effect, if any, of atmospheric oxygen on the reaction remains to be clarified.

Reaction of Thionyl Chloride with 3,4-Dihydro-2(1*H*)-quinolinone

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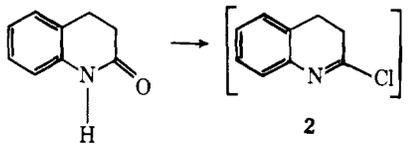
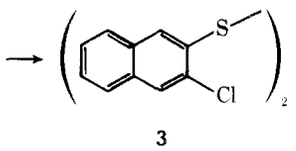
The attempted conversion of 3,4-dihydro-2(1*H*)-quinolinone, **1,** to the corresponding imidoyl chloride, **2,** using thionyl chloride in DMF gave instead of the expected imidoyl chloride a number of unusual and unexpected products. The nature



1 **2**



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