($CDCl_3$) δ 163.73 ($C_4$), 151.65 ($C_2$), 139.08 ($C_6$), 113.46 ($C_5$), 62.10 ($C_{4'}$), 36.64 ($N_1$ Me), 27.81 ($N_3$ Me), 31.93, 26.89, 24.67 ($C_{1'}$–$C_{3'}$); mass spectrum, *m/z* (relative intensity) 212 (23, $M^{+\cdot}$). Anal. Calcd for $C_{10}H_{16}N_2O_3$: C, 56.6; H, 7.60; N, 13.20. Found: C, 56.4; H, 7.43; N, 12.97.

**(*S*)-5-[4-Hydroxy-5-(methoxymethoxy)pentyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (14).** A mixture of **4** (92 mg, 0.33 mmol), palladium (10%) on activated carbon (20 mg), and methanol (50 mL) was shaken under hydrogen (35 psi) for 2 h. Filtration (Celite) and evaporation of volatiles in vacuo gave an oil. Chromatography (preparative TLC, ethyl acetate) afforded 64 mg (70%) of **14** as an oil: $^1H$ NMR ($CDCl_3$) δ 6.96 (s, $H_6$), 4.64 (s, $OCH_2O$), 3.90–3.40 (m, 3 H), 3.36 (s, OMe, NMe), 3.33 (s, NMe), 2.45–2.18 (m, 2 H), 1.75–1.30 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) δ 163.68 ($C_4$), 151.74 ($C_2$), 139.03 ($C_6$), 113.43 ($C_5$), 96.99 ($OCH_2O$), 73.05 ($C_{5'}$), 70.23 ($C_{4'}$), 55.60 (OMe), 36.75 ($N_1$ Me), 27.92 ($N_3$ Me), 32.52, 27.15, 24.45 ($C_1$–$C_{3'}$); mass spectrum, *m/z* (relative intesnity) 286 (10, $M^{+\cdot}$), 255 (31, $M^{+\cdot} - CH_3O$); calcd for $C_{13}H_{22}N_2O_5$, 286.1529, found, 286.1548.

**5-(Tetrahydro-2′-furanyl)-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (15).** A mixture of **1** (75 mg, 0.36 mmol), palladium (10%) on activated carbon (20 mg), and tetrahydrofuran (20 mL) was shaken under hydrogen (37 psi) for 1.5 h. Filtraton (Celite) and evaportion in vacuo gave an oil. Purification using preparative TLC (ether) afforded 56 mg (75%) of **15**: mp 94–95 °C; $^1H$ NMR ($CDCl_3$) δ 7.20 (d, *J* = 1.1 Hz, $H_6$), 4.88–4.65 (m, $H_{1'}$), 4.15–3.68 (m, $H_{4'}$, $H_{4''}$), 3.37, 3.31 (s's, NMe's), 2.60–1.50 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) δ 162.38 ($C_4$), 151.68 ($C_2$), 138.14 ($C_6$), 115.17 ($C_5$), 74.59 ($C_{1'}$), 68.33 ($C_{4'}$), 36.89 ($N_1$ Me), 27.63 ($N_3$ Me), 32.25, 25.59 ($C_{2'}$, $C_{3'}$). Anal. Calcd for $C_{10}H_{14}N_2O_3$: C, 57.1; H, 6.71; N, 13.32. Found: C, 57.1; H, 6.43; N, 13.07.

**(2′*S*)-*trans*-5-[Tetrahydro-5′-[(methoxymethoxy)methyl]-2′-furanyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (16).** A mixture of **4** (70 mg, 0.25 mmol), palladium (10%) on activated carbon (20 mg), and tetrahydrofuran (125 mL) was shaken under hydrogen (35 psi) for 1 h. Filtration (Celite) and evaporation of volatiles in vacuo gave an oil. Chromatography (preparative TLC, ethyl acetate) affoded 60 mg (85%) of **16**: $^1H$ NMR ($CDCl_3$) δ 7.30 (d, $H_6$), 5.00–4.75 (m, $H_{1'}$), 4.68 (s, $OCH_2O$), 4.45–4.20 (m, $H_{4'}$), 3.67–3.50 (m, $H_{5'}$, $H_{5''}$), 3.40, 3.38, 3.30 (s's, NMe's, OMe), 2.65–1.52 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) δ 162.32 ($C_4$), 151.62 ($C_2$), 138.27 ($C_6$), 114.52 ($C_5$), 96.56 ($OCH_2O$), 78.11 ($C_{4'}$), 74.59 ($C_{1'}$), 70.17 ($C_{5'}$), 55.17 (OMe), 36.83 ($N_1$ Me), 32.63, 28.27 ($C_{2'}$, $C_{3'}$), 27.59 ($N_3$ Me); mass spectrum, *m/z* (relative intensity) 284 (2, $M^{+\cdot}$), 253 (2, $M^{+\cdot} - CH_3O$); calcd for $C_{13}H_{20}N_2O_5$, 284.1372, found, 284.1370.

**Acknowledgment.** Financial support of this work from the National Institute of General Medical Science (Grant GM 30310), from S. Söderlundhs Minnesfond, and from Thuns fond is greatly appreciated. We thank William R. Anderson, Jr., for help with the mass spectrometry.

**Registry No.** **1**, 84143-13-5; **2**, 87116-53-8; **3**, 87172-23-4; **4**, 85442-29-1; **5**, 85442-23-5; **6**, 85442-24-6; **7**, 84132-74-1; **8**, 87116-54-9; **9**, 84132-75-2; **10**, 87116-55-0; **11**, 85442-25-7; **12**, 10017-66-0; **13**, 87116-56-1; **14**, 87116-57-2; **15**, 87136-16-1; **16**, 87116-58-3.

## Iodine Chloride as an Intermediate for α Iodination of Aliphatic Acids with Iodine–Thionyl Chloride[1]

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Thus far two methods are known for the one-step α iodination of aliphatic acids using molecular iodine: (a) Chlorosulfonic acid-promoted iodination in 1,2-dichloroethane via a hypothetic intermediate of monoacyl sulfate,[3] $RR'CHCO_2SO_2H$ and (b) Harpp's iodination with thionyl chloride as a solvent.[4]

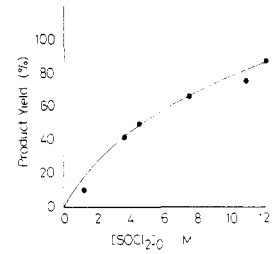


**Figure 1.** Effect of initial concentration of $SOCl_2$ on the product yield for α iodination of propionyl chloride with iodine in 1,2-dichloroethane at 80 °C for 6 h; $[CH_3CH_2COCl]_0$ = 1.52 M; $[I_2]_0$ = 0.75 M.

Acyl chlorides, which should be formed by the reaction of carboxyic acids with $SOCl_2$ in the Harpp's method, do not react with molecular iodine in solvents other than $SOCl_2$ such as 1,2-dichloroethane and acetonitrile. This suggests that $SOCl_2$ is not only a solvent but that it also plays an unknown role in the iodination. The present paper intends to clarify the mechanism of this $SOCl_2$ promoted α iodination of aliphatic acids.[4]

### Results and Discussion

**Effect of $SOCl_2$ on α Iodination of Acyl Chloride with Molecular Iodine.** Propionyl chloride was allowed to react with half an equivalent amount of iodine in a mixture of 1,2-dichloroethane (EDC) and $SOCl_2$ at 80 °C for 6 h. The yields of α-iodopropionyl chloride were plotted against the initial concentration of $SOCl_2$ and are shown in Figure 1. The figure shows that the yield increases with increasing $[SOCl_2]_0$ (i.e., initial concentration of $SOCl_2$) and that $SOCl_2$ is not a solvent, but participates in the iodination.

**Formation of Iodine Chloride in Solution of $SOCl_2$–$I_2$. Spectrophotometric Evidence.** A dilute (below $8.7 \times 10^{-4}$ M) solution of iodine in $SOCl_2$ has an absorption maximum at 500 nm (ε 910), but the maximum shifts at room temperature to shorter wavelength, down to 450 nm after 12 h, which is close to $\lambda_{max}$ 430 nm (ε 120) of ICl in $SOCl_2$. Whereas, no change of spectrum was observed with ICl dissolved in $SOCl_2$. These observations suggest that $I_2$ is gradually transformed to ICl in $SOCl_2$ solution and stabilized at room temperature. Addition of water to this pale yellow $SOCl_2$ solution of ICl generated purple molecular iodine. This is explicable by reactions 1a,b.

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl \quad (1a)^5$$

$$2ICl + 2H_2O + SO_2 \rightarrow I_2 + 2HCl + H_2SO_4 \quad (1b)^6$$

No color change was observed on heating a $10^{-2}$ M $I_2$ solution of $SOCl_2$ at 80 °C, and the purple color of iodine appeared on heating a $10^{-2}$ M ICl solution of $SOCl_2$ in EDC

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Table I. α Iodination of Propionyl Chloride in $SOCl_2$-$ClCH_2CH_2Cl$

| reagent[a] | $SOCl_2$, vol % | $[SOCl_2]$, M | product yield,[b] % |
|---|---|---|---|
| ICl | 0 | 0 | 66 |
| ICl | 15 | 1.8 | 71 |
| ICl | 50 | 6.0 | 76 |
| ICl | 100 | 12.1 | 83 |
| $I_2$ | 100 | 12.1 | 89 |

[a] At 80 °C for 6 h; $[CH_3CH_2COCl]_0 = 1.52$ M; $[I_2]_0 = 0.75$ M. [b] Determined by means of NMR.

at 80 °C. These facts imply the following sequence of reactions. Equation 2a was assumed from the reaction of $SOCl_2$ with KI, forming $SOI_2$.

$$I_2 + SOCl_2 \rightarrow ICl + SOClI \quad (2a)^7$$

$$3ICl \rightarrow ICl_3 + I_2 \quad (2b)^8$$

$$ICl_3 \rightarrow ICl + Cl_2 \quad (2c)^9$$

**Chemical Trapping of ICl by Addition to Double Bond.** Methyl *trans*-cinnamate was used to trap ICl formed by eq 2a. The reaction of methyl *trans*-cinnamate with 0.5 equiv of $I_2$ in a $SOCl_2$ solution gave methyl β-chloro-α-iodo-β-phenylpropionate on heating at 80 °C for 3 h (eq 3).

$$PhCH{=}CHCO_2CH_3 + ICl \rightarrow PhCHClCHICO_2CH_3 \quad (3)$$

The product was identified by NMR and mass spectra by comparison with the authentic specimen. The same product was obtained by the reaction of methyl cinnamate with ICl in EDC or $SOCl_2$ alone.

**α Iodination of Acyl Chloride with Iodine Chloride.** The reaction of propionyl chloride with ICl in EDC gave α-iodopropionyl chloride as shown in Table I. This shows that ICl can give α-iodo product even in nonpolar solvents such as EDC. The mechanism for the reaction may involve an electrophilic addition of $I^{\delta+}$–$Cl^{\delta-}$ to the double bond of ketene ($RHC{=}C{=}O$)[9] or less probably to the enol of acyl chloride ($RCH{=}CClOH$).[10] The observed moderate increase of yield by incresing the fraction of $SOCl_2$ in the solvent EDC is ascribed to the ability of $SOCl_2$ to reproduce ICl from $I_2$ formed by the decomposition of ICl.

**Effect of $SOCl_2$ on the Rate of α Iodination of Acyl Chloride with ICl.** For the examination of the effect of $SOCl_2$ on the α iodination of propionyl chloride with ICl, the rate of consumption of ICl was measured at different concentrations of $SOCl_2$. The conversion curves were analogous, indicating that $SOCl_2$ had a small effect. The rates at various concentrations of $SOCl_2$ and reactants fit eq 4, and the values of $k$ are listed in Table II. The $k$

$$v = k[CH_3CH_2COCl][ICl] \quad (4)$$

values hold almost constant with a considerable change of concentration of reactants and solvent composition. But after 1.5 h, which corresponds to ca. 70% conversion of ICl, the $k$ value tends to decrease, probably because of the decomposition of ICl at 80 °C. This trend is more remarkable at higher concentrations of ICl.

Table II. Second-Order Rate Constants for the α Iodination of Propionyl Chloride with $SOCl_2$-$I_2$ and ICl in EDC at 80 °C

| $[CH_3CH_2COCl]_0$, M | $[ICl]_0$, M | $SOCl_2$, vol % | $[SOCl_2]_0$, M | $10^3k$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 1.50 | 1.50 | 100 | 12.1 | 1.64 |
| 1.50 | 1.50 | 50 | 6.0 | 1.21 |
| 1.50 | 1.50 | 15 | 1.8 | 1.65 |
| 1.50 | 1.50 | 0 | 0 | 1.65 |
| 0.719 | 0.195 | 0 | 0 | 2.03 |
| 0.350 | 0.201 | 0 | 0 | 2.00 |
| 0.189 | 0.102 | 0 | 0 | 2.13 |

This kinetic means that the change of acyl chloride to ketene or enol is not accelerated by $SOCl_2$ and that the rate of α iodination is determined by an electrophilic addition of ICl to the double bond of the ketene or enol derived from acyl chloride.

## Experimental Section

GLC analysis was done on a Yanagimoto G-180 gas chromatograph by using a colomn packed with PEG 20M. NMR spectra were measured on a Hitachi R-24B NMR spectrometer with tetramethylsilane as an internal standard. A Hitachi 124 UV spectrophotometer was used for UV analysis and a JEOL JMS D-300 mass spectrometer for GLC/MS analysis.

**Materials.** Propionyl chloride, thionyl chloride, iodine, and iodine chloride were of commercial guaranteed grade. 1,2-Dichloroethane was rectified after being dried over $CaCl_2$. Methyl *trans*-cinnamate was prepared by the reaction of *trans*-cinnamic acid with $SOCl_2$ followed by methanolysis of the chloride obtained; bp 102–103 °C (4 mm). Methyl β-chloro-α-iodo-β-phenylpropionate was prepared by the reaction of methyl *trans*-cinnamate with ICl in acidic (aqueous HCl) solution and recrystallized from ligroin: mp 98–100 °C (lit.[12] mp 97–98 °C); NMR ($CCl_4$) δ 3.9 (s, 3 H, $CO_2CH_3$), 4.7 (d, 1 H, CHCl), 5.3 (d, 1 H, CHI), 7.4 (s, 5 H, Ph); mass, (EI, 20 eV), $m/e$ 324 ($M^+$), 289, 254, 197, 162.

**α Iodination of Propionyl Chloride with Iodine in a Mixture of 1,2-Dichloroethane and Thionyl Chloride.** Molecular iodine (4.4 g, 17 mmol) was dissolved in a mixture of EDC and $SOCl_2$ (20 mL), heated to 80 °C, and added with propionyl chloride (3 mL, 35 mmol). An aliquot (0.5 mL) of the reaction mixture was pipetted out after 6 h and added with EDC (20 mL). Then $SOCl_2$ along with EDC was distilled off in vacuo to leave the residual liquid (ca. 2 mL). The residue was added with naphthalene (0.1 M methanol solution, 1 mL) as an internal standard, diluted to 10 mL by methanol, and analyzed by means of GLC.

**Iodochlorination of Methyl *trans*-Cinnamate. (a) Reaction with $I_2$–$SOCl_2$.** Iodine (2.2 g, 8.7 mmol) and methyl *trans*-cinnamate (2.8 g, 17.3 mmol) were dissolved in $SOCl_2$ (20 mL) and heated at 80 °C for 3 h. After analysis by NMR (see below), $SOCl_2$ was removed from the reaction product under vacuum, the residue being recrystallized from ligroin to give methyl β-chloro-α-iodo-β-phenylpropionate: 0.5 g (10%); mp 97–98 °C. Its NMR and mass spectra were identical with those of the authentic specimen. The yield based on NMR reached 60–70%.

**(b) Reaction with a Mixture of ICl–$SOCl_2$.** Iodine chloride (2.50 g, 15 mmol) and methyl *trans*-cinnamate (2.50 g, 15 mmol) were dissolved in $SOCl_2$ (20 mL) and heated at 80 °C for 3 h. The NMR of the product was identical with that of part a. The solvent was removed from the product solution. The residue was recrystallized from ligroin to give β-chloro-α-iodo-β-phenylpropionate: 1.8 g (40%); mp 98–100 °C (lit.[10] mp 97–98 °C). A better yield was obtained in a reaction in pure EDC.

**α Iodination of Propionyl Chloride with ICl in a Mixture of 1,2-Dichloroethane and Thionyl Chloride.** Iodine chloride (5.6 g, 35 mmol) was dissolved in a mixture of EDC–$SOCl_2$ (20 mL) of an appropriate ratio, heated to 80 °C, and then added to

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propionyl chloride (3 mL, 35 mmol). An aliquot (1 mL) was pipetted out at an interval of 15 min, added to $CCl_4$ (1 mL) and $CHCl_3$ (0.1 mL), and analyzed by means of NMR. The yields were calculated by the NMR area ratio of the proton of $CHCl_3$ and the $\alpha$-proton of the product.

The second-order rate constants were calculated by using the conversion curves and the rate equation shown in eq 5, where subscripts 0 and $t$ mean initial and any times, respectively.

$$v = k([CH_3CH_2CO_2H]_0 - [CH_3CHICO_2H]_t)([I_2]_0 - [I_2]_t) \quad (5)$$

**Kinetics of the Reaction of Propionyl Chloride with ICl.** A typical kinetic procedure for $\alpha$ iodination of propionyl chloride with ICl was as follows. An EDC solution of ca. 0.2 M ICl was heated under a reflux condenser in a thermostated flask, and propionyl chloride (1 or 2 mL) was added by pipet. An aliquot (1 mL) was taken out at appropriate intervals of time, poured into aqueous KI–$H_2SO_4$, and titrated with 0.01 N $Na_2S_2O_3$ to follow the consumption of ICl. The volume change on addition of propionyl chloride (sp gr 1.0646) was taken into account for the calculation of reactant concentrations.

**Acknowledgment.** We are grateful to Whei-Ing Woo for her helpful assistance in the kinetic experiments and preparation of manuscripts and also to Tsong Ueng for his pertinent advice in conducting experiments. Financial support from National Science Council, ROC, and the Japanese Ministry of Education is gratefully acknowledged.

**Registry No.** $CH_3CH_2CO_2H$, 79-09-4; $CH_3CH_2COCL$, 79-03-8; *trans*-PhCH=$CHCO_2CH_3$, 1754-62-7; $SOCl_2$, 7719-09-7; $I_2$, 7553-56-2; ICl, 7790-99-0; $PhCHClCHICO_2CH_3$, 87207-03-2.

## Metal–Ammonia Reduction of 1-Acetylnaphthalenes

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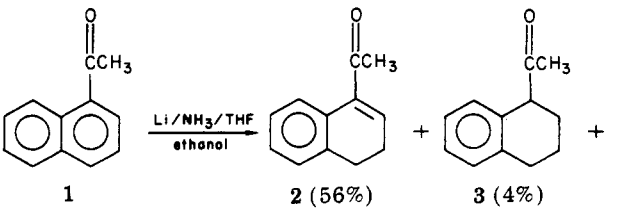
*Received March 15, 1983*

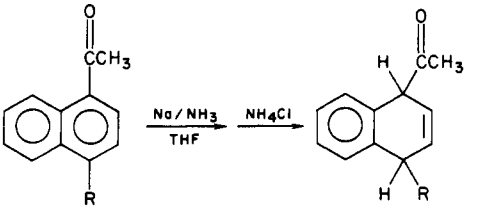
Although the reduction of aromatic rings by metal–ammonia solutions is a general method for the preparation of the corresponding dihydroaromatic structures, application to aryl ketones is often accompanied by partial or complete reduction of the carbonyl.[1] For example, acetophenone is reduced to ethylbenzene under normal reduction conditions even though the use of cation-exchange techniques facilitates reductive alkylation, providing 1-alkyl-1,4-dihydroacetophenones in fair to good yields.[1]

Some polynuclear ketones may be reduced without loss of the carbonyl group, and 1-acetylnaphthalene has recently received a considerable amount of attention.[2-6] In one report,[2] a detailed product analysis was given, and the 3,4-dihydro derivative **2** was indicated as the major product (56%, eq 1). The same conjugated product was also indicated in a very recent report, and although other products were not mentioned, the yield of **2** was 75%. In any event, 1-acetyl-3,4-dihydronaphthalene appears to be generally accepted[2-6] as the usual reduction product of 1-acetylnaphthalene without mention of any detection of the expected[7] 1,4-dihydro product. This prompts us to report our results which indicate that rapid quenching techniques can, in fact, produce this latter 1,4-dihydro isomer exclusively.



(1)

We have found that the sodium–ammonia reductions of 1 and its 4-methyl (**4**) and 4-ethyl (**5**) derivatives provide the corresponding 1,4-dihydro products[8] in essentially quantitative yields[9] (eq 2). These products are quite



(2)

1, R = H
4, R = $CH_3$
5, R = $CH_2CH_3$

stable, and we have not noted any unusually facile conversion to the conjugated isomers such as **2**. These compounds can be purified by vacuum distillation or steam distillation, although the latter process does produce a little rearomatization. However, no trace of the conjugated isomers was detected by either process.

The marked contrast to previous results warrants some attempt at explanation, and a careful comparison of reaction conditions must be made. Although we obtained good results under all of the conditions which we employed, we did observe an improvement proceeding as follows from a to c: (a) rapid quenching with aqueous $NH_4Cl$, (b) inverse quenching into aqueous $NH_4Cl$,[10] and (c) addition of 1.5 equiv of $H_2O$ *before* the addition of the sodium.[11] The latter method ensures efficient conversion to the monoanion **6** (eq 3) which is resistant to side reactions sometimes observed with radical anions (e.g., dimerization). An inverse quench also quickly eliminates the presence of strong base which could cause subsequent isomerization.[11]

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(8) Both cis and trans products are formed with **4** and **5**. The stereochemistry of reduction (as well as the conformational analysis of products) of a variety of naphthalene and anthracene ketones and esters is the subject of current research.
(9) NMR analysis of the crude reaction mixture shows no other products. However, some material is lost in isolation (see Experimental Section).
(10) We have previously reported on the importance of the quenching process and the general usefulness of an inverse quench: Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283.
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