ported that more vigorous conditions are required for cycloaddition reactions employing triazines compared to the more electron-deficient tetrazines.[9] This was also observed in the preparation of **10** and **11** where the reaction required heating to 155 °C for 19 h. The addition occurs across carbons 3 and 6 of the triazine **9** to give an equal mixture of the regioisomers **10** and **11**. The structures were evident in the ^1H and ^{13}C NMR where the pyridine proton chemical shifts for the two isomers were observed; the isomer distribution was determined by ^1H NMR and high performance LC.

Experimental Section

Reagent-grade *p*-dioxane was purified by passage through an alumina column. HPLC analyses were carried out on a Waters Model 6000A instrument using a Whatman ODS 5 column. NMR spectra were obtained on a Varian Model FT-80 A or a Varian XL 300 spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethysilane. Chemical ionization mass spectra (CIMS) were recorded on a Varian CH-5 spectrometer. Microanalyses were performed on a Hewlett-Packard model 185 CHN analyzer.

5-Ethynyl-2′-deoxyuridines **5a** and **5b** were prepared by reported procedures[5] as were dimethyl 1,2,4,5-tetrazine-3-6-dicarboxylate[6] (**6**) and triethyl 1,2,4-triazine-3,5,6-tricarboxylate[8] (**9**).

5-(3,6-Dicarbomethoxypyridazin-4-yl)-2′-deoxyuridine (7a). 5-Ethynyl-2′-deoxyuridine (**5a**; 140 mg, 0.56 mmol) and 150 mg of dimethyl 1,2,4,5-tetrazinedicarboxylate (**6**; 0.76 mmol) were dissolved in 3 mL of dioxane. The reaction mixture was flushed with argon and sealed in a 10-mL Teflon-capped vial. The vial was heated at 60 °C for 19 h. Removal of the solvent in vacuo and chromatography (silica gel, 10% $C_2H_5OH/CHCl_3$ eluant) afforded 165 mg (71%) of pure product (**7a**): UV (MeOH) λ_{max} 295 nm; ^1H NMR (acetone-d_6) δ 8.65 (s, 1 H, H_5 pyridazine), 8.21 (s, 1 H, H_6), 6.25 (t, 1 H, $H_{1'}$), 3.88 and 4.00 (s, 3 H, CO_2Me) [plus sugar proton multiplets]; ^{13}C NMR (CD_3OD) 166.5 (CO_2Me), 163.2 (C_4), 154.9 (C_6 pyridazine), 153.6 (C_3 pyridazine), 151.6 (C_2), 143 (C_6), 135.4 (C_4 pyridazine), 130.2 (C_5 pyridazine), 110.7 (C_5), 89.4 ($C_{1'}$), 87.5 ($C_{4'}$), 71.6 ($C_{3'}$), 62.3 ($C_{5'}$), 53.8 (CO_2Me), 42.1 ($C_{2'}$) ppm; CIMS, *m/e* 423 (M + 1).

3′,5′-Di-*O*-acetyl 5-(3,6-Dicarbomethoxypyridazin-4-yl)-2′-deoxyuridine (7b). Compound **7b** was prepared by the same procedure as compound **7a** with the exception that it was purified on silica gel with 5% $C_2H_5OH/CHCl_3$: UV (H_2O) λ_{max} 295 nm (ϵ 10000), (0.1 M HCl) λ_{max} 293 nm (ϵ 10400), (0.1 M NaOH) λ_{max} 293 nm (ϵ 8200); ^1H NMR ($CDCl_3$) δ 8.2 (s, 1 H, H_5 pyridazine), 8.0 (s, 1 H, H_6), 4.2 and 4.1 (s, 3 H each, CO_2Me), 2.2 and 2.1 (s, 3 H each, OAc) [plus sugar multiplets]; ^{13}C NMR ($CDCl_3$) 170.3 (OAc), 165.1 and 163.7 (CO_2Me), 160.7 (C_4), 153.3 and 152 (C_3 and C_6, pyridazine), 149.4 (C_2), 139.2 (C_6), 132.4 (C_4, pyridazine), 128.4 (C_5, pyridazine), 110.3 (C_5), 86.2 ($C_{1'}$), 83 ($C_{4'}$), 74 ($C_{3'}$), 63.5 ($C_{5'}$), 53.6 (CO_2Me), 38 ($C_{2'}$), 20.8 (CH_3) ppm; CIMS, *m/e* 507 (M + 1). Anal. Calcd for $C_{21}H_{22}N_4O_{10}\cdot 1.5\ H_2O$ (M_r 517.44): C, 48.74; H, 4.87; N, 10.83. Found: C, 49.01; H, 5.00; N, 10.58.

3′,5′-Di-*O*-acetyl 3-*N*-Methyl-5-(3,6-dicarbomethoxypyridazin-4-yl)-2′-deoxyuridine (8). The pyridazine derivative **7b** (90 mg, 0.18 mmol) was dissolved in 3.0 mL of dioxane in a 10-mL teflon-capped vial. The vial was flushed with argon, and 120 μL (~1.5 mmol) of 1,1-dimethoxyethylene was added to the reaction via a syringe. The reaction was stirred and heated to 165 °C for 9 h. Purification by silica gel chromatography (5% $C_2H_5OH/CHCl_3$) afforded 55 mg (59%) of compound **8** as the major product: UV (CH_3OH) λ_{max} 296 nm; ^1H NMR ($CDCl_3$) δ [identical spectrum with that of **7b** with the addition of] 3.5 (s, 3 H, NCH_3); ^{13}C NMR ($CDCl_3$) 170.2 (OAc), 165.1 and 163.6 (CO_2Me), 160.3 (C_4), 153.4 and 151.9 (C_6 and C_3 pyridazine), 149.8 (C_2), 137 (C_6), 132.9 (C_4 pyridazine), 128.2 (C_5 pyridazine), 109.3 (C_5), 86.8 ($C_{1'}$), 82.9 ($C_{4'}$), 73.8 ($C_{3'}$), 63.3 ($C_{5'}$), 53.4 (CO_2Me), 38.1 ($C_{2'}$), 28.1 (NCH_3), 20.7 (Me) ppm; CIMS, *m/e* 521 (M + 1).

5-(2,5,6-Tricarbethoxypyridin-4-yl)-2′-deoxyuridine (10) and 5-(2,5,6-Tricarbethoxypyridin-3-yl)-2′-deoxyuridine (11). Compound **5a** (50 mg, 0.2 mmol) and 52 mg of triethyl 1,2,4-triazine-3,5,6-carboxylate (**9**; 0.2 mmol) were dissolved in 3 mL of dioxane in a 10-mL Teflon-capped vial. The reaction mixture was flushed with argon, sealed, and heated with stirring at 155 °C for 19 h. Purification by chromatography (silica gel, 10% $C_2H_5OH/CHCl_3$ as eluant) afforded 28 mg (32%) of an equal mixture of regioisomers **10** and **11** as determined by HPLC and ^{1}NMR: UV (H_2O) λ_{max} 275 nm (ϵ 10300); ^1H NMR (methanol-d_4) δ 8.16 and 8.25 (s, 1 H, C6), 8.31 and 8.34 (s, 1 H, H5 and H4 pyridine), 6.25 (t, 1 H, $H_{1'}$) [plus sugar proton multiplets and three carboethoxy groups]; ^{13}C NMR (CD_3OD) 167.2, 167.1, 166.9, 166.6, 165.6, 165.1 (CO_2Et), 163.4, 164 (C_4), 152.1, 151.8, 151.7, 151.3 (C_2 and C_6 4-pyridine, C_2 and C_6 3-pyridine), 151, 150 (C_2), 144.7 (C_4 4-pyridine), 142.3, 142.1 (C_6), 141.1 (C_4 3-pyridine), 132, 131.7 (C_3 4-pyridine and C_5 3-pyridine), 129.2 (C_5 4-pyridine), 129.2 (C_3 3-pyridine), 113.1, 112.3 (C_5), 89.3 ($C_{1'}$), 87.3 ($C_{4'}$), 72 ($C_{3'}$), 63.6 ($C_{5'}$), 62–63.7 (6-CO_2Et), 42 ($C_{2'}$), 14 (6-CO_2Et) ppm; CIMS, *m/e* 522 (M + 1). Anal. Calcd for $C_{23}H_{27}N_3O_{11}\cdot H_2O$ (M_r 539.49): C, 51.20; H, 5.41; N, 7.79. Found: C, 50.75; H, 5.38; N, 7.61.

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Registry No. **5a**, 61135-33-9; **5b**, 100021-00-9; **6**, 2166-14-5; **7a**, 100020-99-3; **7b**, 100021-01-0; **8**, 100021-02-1; **9**, 74476-38-3; **10**, 100021-03-2; **11**, 100021-04-3.

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Acylation of Organolithium Reagents by Esters in the Presence of Chlorotrimethylsilane

Manning P. Cooke, Jr.

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

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The preparation of carbonyl compounds through the acylation of organometallic reagents is often complicated by the formation of alcohols that result from the premature collapse of the initially formed adduct **1** (Scheme I).[1,2] Recently a number of clever methods for the acylation of Grignard reagents have appeared that center on the use of carboxyl derivatives designed to give intermediate adducts that are more resistant to premature release of the carbonyl compound.[3] Successful acylations of alkyllithium reagents, however, usually require additions to either carboxylate salts[4] or to amides that give stabilized intermediates.[3a,5] Esters of normal reactivity usually give tertiary alcohols.[2]

In light of the fact that alkyllithium reagents are known to react relatively slowly with some chlorosilanes,[6] we have

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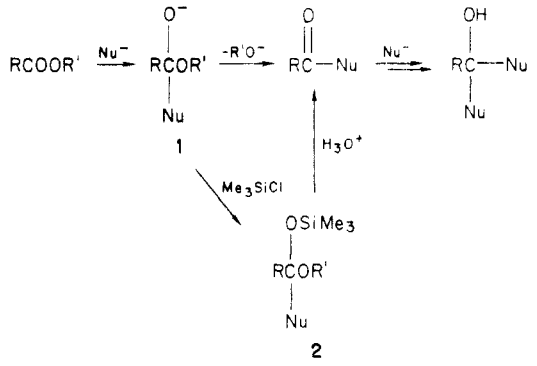
Table I. Acylation of Organolithium Reagents in the Presence of Me_3SiCl

$$R^1COX \xrightarrow[Me_3SiCl]{R^2Li} \xrightarrow{H_3O^+} R^1COR^2$$

entry	R^1	X	R^2Li	Me_3SiCl, equiv	T, (C)	solvent	yield,[a] % R^1COR^2	yield,[a] % $R^1(R^2)_2COH$
1	*n*-Bu	OEt	*n*-BuLi	0	−100	THF	28	20
2	*n*-Bu	OEt	*n*-BuLi	2	−100	THF	63	36
3	*n*-Bu	OEt	*n*-BuLi	5	−100	THF	82 (77)[f]	16
4	*n*-Bu	OEt	*n*-BuLi	>25[b]	−100	THF[b]	90	8
5	*n*-Bu	OEt	*n*-BuLi	5 Et_3SiCl	−100	THF	66	33
6	Et	OEt	*n*-BuLi	5	−100	THF	87	15
7	Et	OEt	*n*-BuLi	5	−78	THF	66	28
8	Et	OEt	*n*-BuLi	5	−115	THF–pentane (3:1)	80	13
9	*n*-Bu	O-*i*-Pr	*n*-BuLi	5	−100	THF	13	39
10	*n*-Bu	OMe	*n*-BuLi	5	−100	THF	73	19
11	*n*-Bu	OEt	*n*-BuLi	5	−100	pentane	17	44
12	*n*-Bu	OEt	*n*-BuLi	5	−100	DME	63	21
13	Et	OEt	*n*-BuLi	5	−100	Et_2O	26	49
14	*n*-Bu	OEt	*n*-BuLi	5	−100	THF+ 1.3 TMEDA	78	15
15	*n*-Bu	OEt	PhLi	5	−100	THF	4[c]	0
16	*n*-Bu	OEt	*n*-BuMgCl	5	−78→40	THF	<2	79
17	*n*-Bu	OEt	*s*-BuLi	5	−100	THF	24	53
18	*n*-Am	OEt	MeLi	5	−100	THF	82	8
19	Ph	OEt	MeLi	5	−100	THF	86	14
20	Ph	OEt	*n*-BuLi	5	−100	THF	82	21
21	EtO	OEt	*n*-BuLi	0	−100	THF	11	16,[d] 22[e]
22	EtO	OEt	*n*-BuLi	5	−100	THF	42	40,[d] 7[e]
23	H	OEt	*n*-BuLi	0	−100	THF	68	<1
24	H	OEt	*n*-BuLi	5	−100	THF	91	<1

[a] Determined by GC. [b] Reaction conducted in 1:1 Me_3SiCl–THF. [c] $PhSiMe_3$ was the major product with 82% ester recovery. [d] BuCOBu. [e] Bu_3COH. [f] Isolated yield.

Scheme I



explored the feasibility of trapping the crucial adduct (**1**) in the reaction of esters with alkyllithium reagents by conducting the reaction in the presence of Me_3SiCl.[7] Indeed, in many cases the course of the reaction is significantly altered and substantial yields of carbonyl compounds result after hydrolysis of the intermediate siloxy ketal **2**.[8] Results of these studies are shown in Table I.

As seen in entries 1–4, the yield of 5-nonanone increases steadily with increasing amounts of Me_3SiCl when ethyl valerate is treated with *n*-BuLi[9] in THF at −100 °C; diminishing improvement is seen with greater than 5 equiv of trapping agent, though it is interesting to note that even in the presence of massive amounts of Me_3SiCl only traces of butyltrimethylsilane are formed. Under identical conditions, Et_3SiCl is a somewhat less effective trapping agent (entry 5). Reaction temperature is also critical as seen in entries 6–8. Lower ketone to tertiary alcohol ratios result at temperatures greater than −100 °C, while any advantages of using lower temperatures are offset by the necessity of using a different solvent system (vide infra).

The efficiency of trapping **1** is also dependent on the nature of the ester's alkoxyl moiety (entries 3, 9, and 10). Best results are obtained with ethyl esters and notably poorer results with the isopropyl ester, likely owing to increased steric interference with the trapping process as well as a steric acceleration of the rate of collapse of **1**.

There is also a dramatic solvent effect (entries 3, 11, 12, and 13). Best results are obtained in THF and poor results with Et_2O or pentane. Surprisingly, the outcome in THF is not appreciably affected by additives such as TMEDA (entry 14), HMPA, or added salts ($MgBr_2$, LiBr), which might be expected to alter either the rate of collapse of **1** or its rate of reaction with Me_3SiCl.

Best results occur with *n*-alkyllithium reagents. Predominantly tertiary alcohol formation results from additions with *s*-BuLi (entry 17) while the use of phenyllithium (entry 15) results in ester recovery, owing to the apparently rapid consumption of PhLi by Me_3SiCl.[6b] Grignard reagents (entry 16) give mostly tertiary alcohol.

The best result is seen in the reaction of *n*-BuLi with ethyl formate (entry 24) where nearly exclusive aldehyde formation is observed. This suggests that the method may be especially useful in the formylation of alkyllithium reagents. While decreased steric interactions in **1** (R = H) undoubtedly facilitate the trapping process, it is clear from the control experiment (entry 23, no Me_3SiCl) that adduct

(7) For an example of in situ enolate trapping with Me_3SiCl, see: Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495. The in situ trapping of aryllithium derivatives has also been reported: Krizan, T. D.; Martin, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155.

(8) We have not attempted to isolate these intermediates, though they are observed in GLC chromatograms of crude reaction mixtures. Acetals of this type have been previously isolated: Reetz, M. T.; Heimbach, H.; Schwellnus, K. *Tetrahedron Lett.* **1984**, *25*, 511.

(9) In general, sufficient RLi was added to consume the ester (1.1–1.5 equiv).

(10) While there have been suggestions[11] that Me_3SiCl may act as a Lewis acid and interact with the oxygen atom of carbonyl groups, our failure to achieve greater than around 90% efficiency in the trapping of **1**—even at very high Me_3SiCl concentrations—suggests to us the absence of such an effect under our reaction conditions.

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1 (R = H) is considerably more long-lived ($t_{1/2}$ > 5 min at −100 °C) than its higher homologues.

Finally, the course of the reactions of acid anhydrides and chlorides with organolithium reagents is not noticeably altered by the presence of Me_3SiCl. The increased rate of collapse of the adduct analogous to 1 generated upon nucleophilic addition to these carbonyl systems apparently precludes their interception by Me_3SiCl. In the case of diethyl carbonate (entries 21 and 22) some adduct trapping is observed in both steps involving carbonyl addition, but trapping efficiency in the crucial first addition step to give a secure ortho ester is not high.

In summary, we have demonstrated that the intermediate formed in the reaction of esters with nucleophiles (1) in some cases may be intercepted with good efficiency through an intermolecular reaction by conducting the reaction in the presence of chlorotrimethylsilane. Other reactions where this might be advantageous are under investigation.

Experimental Section

Gas chromatographic analyses were performed with a Hewlett-Packard 5790A gas chromatograph and a 3390A integrator using a 12-m cross-linked methyl silicone capillary column. Quantitations were done with the aid of an added internal hydrocarbon standard and calibration factors obtained from mixtures of known composition. Products were identified by comparisons with authentic samples. *n*-BuLi in hexane, *s*-BuLi in cyclohexane, PhLi in cyclohexane–diethyl ether, MeLi in diethyl ether, and *n*-butylmagnesium chloride in diethyl ether were obtained from Aldrich Chemical Co. Organolithium solutions were titrated prior to use.[12] Chlorotrimethylsilane was distilled from CaH_2 prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Esters were freshly distilled and stored over 4A molecular sieves. Reactions conducted at −100 °C were cooled with a freezing MeOH bath (MeOH–liquid N_2), and those conducted at −78 °C were cooled with a dry ice–acetone bath. All reactions were conducted under an atmosphere of argon.

Acylation of *n*-BuLi with Ethyl Valerate. Typical Procedure. A solution containing 149 μL (1.0 mmol) of ethyl valerate in 6 mL of THF was cooled to −100 °C, and 630 μL (5.0 mmol) of Me_3SiCl was added. With vigorous stirring, 0.95 mL (1.25 mmol) of −78 °C 1.32 M *n*-BuLi was added dropwise over 3 min and the mixture was stirred 10 min at −100 °C. The mixture was stirred at −78 °C for 10 min and then brought to 0 °C where 300 μL of EtOH was added. At 20 °C, 1 mL of water was added and after stirring briefly 2 mL of 4 N HCl was added over 1 min. Vigorous stirring was continued for 2 min. Water (15 mL), NaCl (3 g), pentane (6 mL), and 100 μL of internal standard (tridecane in this case) were added, and the mixiture was vigorously stirred for 4 min. GC analysis of the pentane layer showed the presence of 116 mg (82%) of 5-nonanone and 32 mg (16%) of 5-butyl-5-nonanol. The remaining results shown in Table I were obtained in a similar manner with the variations noted in the table.

In a preparative scale run, 1.50 mL (0.01 mol) of ester and 6.3 mL of Me_3SiCl in 35 mL of THF was treated as above at −100 °C with 13.5 mmol of *n*-BuLi. After 10 min at −100 °C and 10 min at −78 °C, the mixiture was allowed to warm to 20 °C whereupon excess Me_3SiCl and most of the THF were removed under reduced pressure. The residue was stirred with 3 mL of EtOH for 1 min, treated with 3 mL of H_2O, and stirred for 3 min. The mixture was made acidic by the addition of a small amount of 4 N HCl followed by the addition of 10 mL of Et_2O. After stirring for 5 min, the mixture was diluted with water (25 mL) and extracted with pentane. Concentration and simple bulb-to-bulb distillation of the residue (150 °C, 30 mm) gave 5-nonanone (84%), which contained a small amount (6%) of 5-butyl-5-nonanol. When the crude reaction product was first chromatographed (SiO_2, CH_2Cl_2), distillation gave pure 5-nonanone in 77% yield.

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Reductive Dehalogenation of Electron-Poor Heterocycles:[1a] Nicotinic Acid Derivatives

George R. Newkome,* Charles N. Moorfield, and Bahman Sabbaghian[1b]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

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Recently, we reported the convenient synthesis of 2,6-diiodopyridine[2] by the chloro → iodo exchange of the corresponding commerically available dichloropyridine. This rarely used procedure[3-5] employed the prolonged treatment of chloro substituted electron-poor heterocycle with a high concentration of iodide ion, derived from concentrated HI and NaI. We herein report the specific reductive dehalogenation of 2-chloronicotinic acids under these reaction conditions.

Selective dechlorination was discovered during the attempted transformation of 2,6-dichloro- to 2,6-diiodonicotinic acid, from which 6-iodonicotinic acid was isolated, as the major product. An attempt to obtain 2-iodonicotinic acid under the classical Finkelstein conditions using 2-butanone, as a solvent,[6] was unsuccessful in that only unchanged starting 2-chloronicotinic acid was isolated. Although Hirshberg and Spoerri[7] reported the preparation of iodopyrazines via this method, when Graft and coworkers[8,9] and Hoffman and Behrmann[10] applied a similar procedure to chloro*iso*nicotinic acids, the major side reaction was, however, dechlorination; whereas, Sell and Dootson[11] obtained 2,6-diiodo*iso*nicotinic acid upon repetition of the reaction in an open vessel. Fischer[12] reported an analogous reduction when chloropurines were treated with hydriodic acid and a phosphonium iodide.

The selective reduction was herein proven by characterization of the products obtained by transforming 2-chloro-, 6-chloro-, and 2,6-dichloronicotinic acid to either unsubstituted or 6-iodonicotinic acids. In all of these transformations, the chemical shift of the position 4 ($\Delta\delta$ 0.4 upfield) and 5 ($\Delta\delta$ 0.4 downfield) protons is indicative of the desired halogen–halogen exchange. This general chemical shift trend for iodo substitution is realized in all of the series including the trifluoromethyl derivatives.

3,5-Dichloro-, 2-chloro-3-hydroxy-, and 2-chloro-5-hydroxypyridine did not undergo Cl → I exchange but afforded unchanged starting materials. Diazines, such as, 3,6-dichloropyridazine, 2,6-dichloropyrazine, and 2,4-dichloropyrimidine yielded only tars with no distinguishable NMR pattern. 2-Chloroquinoline solidified after 1 h under the reaction conditions and gave a grayish tarlike solid, which was insoluble in $CHCl_3$, ether, and water. In the reactions reported in Table I, no other characterizable products were isolated.

The results indicate that electron-deficient heterocycles with electron-withdrawing substituents can undergo a re-

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