Table I. Titration of Organolithium Reagents Using *N*-Benzylidenebenzylamine (1) as Indicator[a]

organolithium[b]	titration conditions			Watson and Eastham[c] method	total alkali[d]
	solvent	method A	method B		
n-BuLi in hexane					
sample 1	Et$_2$O	1.60[e]	1.62[e]	1.60	1.76
	THF		1.61[e]		
sample 2	THF	1.68[e,f]	1.68[e,f]	1.69	
sec-BuLi in cyclohexane					
sample 1	Et$_2$O	1.48[e]	1.50[e]	1.49	1.64
	THF		1.50[e]		
sample 2	THF	1.13[e,f]	1.15[e,f]	1.14	
t-BuLi in pentane					
sample 1	Et$_2$O	1.25[e]	1.26[e]	1.25	1.48
	THF		1.24[e]		
sample 2	THF	1.45[e,f]	1.46[e,f]	1.46	
PhLi in benzene-diethyl ether					
	Et$_2$O	1.00[e]	1.01[e]	1.00	1.96
	THF	1.01[e]	0.99[e]		
	benzene	1.02[e]	1.00[e]		
	hexane	1.02[e]	1.00[e]		

[a] Each value is an average of two or more titrations. [b] The organolithium solutions were purchased from Aldrich. The concentrations indicated by Aldrich were 1.6 M for *n*-BuLi, 1.4 M for *sec*-BuLi, 1.6 M for *t*-BuLi, 1.67 M for PhLi. [c] 1,10-Phenanthroline as indicator, benzene or hexane as solvent, *sec*-butyl alcohol/xylene as acid solution, according to ref 2. [d] Obtained by titration by a standard acid using phenolphthalein as indicator, after hydrolysis of a 5-mL aliquot of the organolithium solution by 10 mL of distilled water. [e] *sec*-Butyl alcohol/xylene as acid solution. [f] Benzoic acid/THF as acid solution.

benzylidenebenzylamine (1) are known to produce a red purple color,[6] and this coloration remains intense as long as carbanion is present in the solution. We used this property for the analysis of organolithium reagents by two methods (see Scheme I).

In method A, the organolithium reacts with a solution of an excess of the Schiff base 1 by addition and metalation. The colored anion 3 is obtained by metalation of the Schiff base by means of RLi or the lithium amide 2 formed by addition. In method B, the organolithium is converted to lithium diisopropylamide (4), which produces anion 3 from a few drops of Schiff base 1. The lithium compound RLi is quantitatively transformed into 2 and 3 (method A) or 4 and 3 (method B). Titration is made by addition of an acid solution which reacts both with the lithium amide 2 or 4, and with the colored anion 3. At the end point, the added acid is equal to the initial quantity of RLi. Results are summarized in Table I.

These methods have the advantage of using organolithium compounds in the common conditions of use of these reagents in various solvents such as diethyl ether, tetrahydrofuran, benzene, and hexane. These are single titrations, simple and rapid to realize in the laboratory, and present a sharp and easy to observe end point. The Schiff base 1, easily prepared from benzylamine and benzaldehyde,[6,7] is a liquid at room temperature and can be stored as a solid at -30 °C. Finally, these methods can be used to control the quality of the solvents.[8]

Experimental Section

Solvents were dried on molecular sieves, then distilled from LiAlH$_4$ prior to use.

Method A. A 5-mL aliquot of the solution to be analyzed was added at room temperature under nitrogen to a solution of 2 g of imine 1 (in excess) in 10 mL of solvent (see Table I). A strong crimson color appeared immediately with the addition of organolithium; the solution was then titrated by a 1 M solution of *sec*-butyl alcohol in xylene or a 1 M solution of benzoic acid in tetrahydrofuran.

Method B. A 5-mL aliquot of the solution to be analyzed was added at room temperature under nitrogen to a solution of 2 mL of diisopropylamine (in excess) in 10 mL of solvent (see Table I). Imine 1 (2–3 drops) was added to this mixture, and the crimson color appeared immediately. The solution was then titrated as in method A.

In the two methods, the end point was reached when the color of the solution became a persistent yellow.

Registry No. 1, 780-25-6; *n*-BuLi, 109-72-8; *sec*-BuLi, 598-30-1; *t*-BuLi, 594-19-4; PhLi, 591-51-5.

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(6) (a) T. Kauffmann, K. Habersaat, and E. Köppelmann, *Chem. Ber.*, 110, 638 (1977). (b) L. I. Sivova, N. A. Sivov, R. A. Gracheva, and V. M. Potapov, *Zh. Org. Khim.*, 14, 791 (1978).

(7) For a review see for example: R. W. Layer, *Chem. Rev.*, 63, 489 (1963).

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Photoassisted Cristol-Firth-Hunsdiecker Reaction

A. I. Meyers* and Michael P. Fleming[1]

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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A well-known route to aryl and alkyl bromides is the Hunsdiecker reaction[2] or its more recent modification by Cristol and Firth.[3] The latter workers found that mercuric salts of carboxylic acids could replace the more tediously prepared and sensitive silver salts in the key bromodecarboxylation step upon treatment with bromine. Recent studies on the scope and mechanism[4-6] of the Cristol–Firth modification indicate that the carboxylic

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Table I. Conversion of RCO_2H to RBr ($HgO-Br_2$-light)[a]

	RBr	
RCO_2H	% yield (with light)[b]	% yield (without light)
p-$ClC_6H_4CO_2H$	80	~0[e]
p-$NO_2C_6H_4CO_2H$	95	42, 0,[e] 70[f]
3,5-$(NO_2)_2C_6H_3CO_2H$	97	0[e]
3-NO_2-4-Cl-5-$MeOC_6H_2CO_2H$	96[c]	~40
m-$BrC_6H_4CO_2H$	83	
p-$BrC_6H_4CO_2H$	86	
o-$ClC_6H_4CO_2H$	81	
m-$ClC_6H_4CO_2H$	75	
o-$MeOC_6H_4CO_2H$	*d*	
o-phthalic acid	42	85[f]
1-naphthoic acid	*d*	
n-$C_{13}H_{27}CO_2H$	99	91[f]
n-$C_{15}H_{31}CO_2H$	90	90[f]
n-$C_{17}H_{35}CO_2H$	85	95[f]

[a] Reactions run in carbon tetrachloride at reflux, molar ratios of $RCO_2H-HgO-Br_2$ are 1.00:1.50:1.50, respectively. [b] All yields are for pure (distilled or crystallized) products and were identified by comparison with published IR and NMR data (Aldrich or Sadtler). [c] J. M. Kane and A. I. Meyers, *Tetrahedron Lett.*, 771 (1977). [d] Gave only polybrominated products. [e] See ref 5. [f] Based on carbon dioxide produced. Actual isolated yields were much lower in those instances where isolation was attempted (see ref 4).

acids form a diacyloxy mercury salt **1**, which then leads to the acyl hypobromite **2** followed by thermal decomposition to the alkyl bromide. During the course of other

$$2RCO_2H \xrightarrow{HgO} \underset{\mathbf{1}}{(RCO_2)_2Hg} \xrightarrow{2Br_2} \underset{\mathbf{2}}{2RCO_2Br} \rightarrow 2RBr$$

studies, we had occasion to investigate the CFH reaction with aromatic acids. The observed trend[4-6] is that aromatic acids form rather insoluble mercuric salts and give lower yields than aliphatic acids. We now describe a further modification of the CFH reaction which simply involves irradiating the reaction mixture with a 100-W bulb. In this fashion excellent and reproducible yields of aryl and alkyl bromides were obtained (Table I). For those aromatic acids containing electron-rich substituents (e.g., anisic acid) the reaction gave only polybrominated products.

Experimental Section

General Procedure for Light-Assisted Bromodecarboxylation. Into a dry, nitrogen-purged, three-neck, 100-mL flask containing a spin bar and fitted with a reflex condenser were placed the carboxylic acid (10.0 mmol), carbon tetrachloride (reagent grade, 50 mL), and red mercuric oxide (B & A, 15.0 mmol). The flask and an adjacent 100-W bulb were enclosed in aluminum foil. The mixture was heated to reflux in an oil bath while being irradiated, and bromine (Baker, "purified", 15.0 mmol) was cautiously added via syringe. The mixture was heated at reflux and irradiated for 3 h, and cooled to room temperature. Saturated aqueous $NaHCO_3$ (30 mL) was added and the mixture was vigorously stirred for 15 min. The two-phase mixture was vacuum filtered through a Celite pad and the pad was washed several times with chloroform. The organic phase of the filtrate was washed with saturated $NaHCO_3$ (30 mL) and brine (30 mL) and dried ($MgSO_4$). Removal of solvent and distillation gave the bromide.

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Registry No. *p*-$ClC_6H_4CO_2H$, 74-11-3; *p*-$NO_2C_6H_4CO_2H$, 62-23-7; 3,5-$(NO_2)_2C_6H_3CO_2H$, 99-34-3; 3-NO_2-4-Cl-5-$MeOC_6H_2CO_2H$, 71001-78-0; *m*-$BrC_6H_4CO_2H$, 585-76-2; *p*-$BrC_6H_4CO_2H$, 586-76-5; *o*-$ClC_6H_4CO_2H$, 118-91-2; *m*-$ClC_6H_4CO_2H$, 535-80-8; *o*-$MeOC_6H_4CO_2H$, 579-75-9; *o*-phthalic acid, 88-99-3; 1-naphthoic acid, 86-55-5; *n*-$C_{13}H_{27}CO_2H$, 544-63-8; *n*-$C_{15}H_{31}CO_2H$, 57-10-3; *n*-$C_{17}H_{35}CO_2H$, 57-11-4; *p*-ClC_6H_4Br, 106-39-8; *p*-$NO_2C_6H_4Br$, 586-78-7; 3,5-$(NO_2)_2C_6H_3Br$, 18242-39-2; 3-NO_2-4-Cl-5-$MeOC_6H_2Br$, 63603-16-7; *m*-BrC_6H_4Br, 108-36-1; *p*-BrC_6H_4Br, 106-37-6; *o*-ClC_6H_4Br, 694-80-4; *m*-ClC_6H_4Br, 108-37-2; *o*-BrC_6H_4Br, 583-53-9; *n*-$C_{13}H_{27}Br$, 765-09-3; *n*-$C_{15}H_{31}Br$, 629-72-1; *n*-$C_{17}H_{35}Br$, 3508-00-7.

Maximum Optical Rotation of 2-Fluorooctane? Survey of Fluorinating Reagents

Jacques Leroy,[1a] Eric Hebert,[1b] and Claude Wakselman[1a]*

C.N.R.S., 94320 Thiais, France

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Optically active 2-alkyl halides are of particular interest as they can serve as models in the study of numerous reactions of organic chemistry. 2-Chloro-, 2-bromo-, or 2-iodooctane is commonly used[2] and their optical purities are determined without ambiguity.[3] By contrast, however, the maximum optical rotation of 2-fluorooctane remains unknown, as no chemical correlation has been established, owing to the poor leaving-group character of fluorine. Thus, only an estimate of optical purity has been made for 2-fluorooctane (**1**) based on a correlation between molecular rotation and bond refraction.[4]

Recent results obtained with methyltri-*n*-butylfluorophosphorane[5] (**2**) leading to 2-fluorooctane of higher optical rotation than that of San Filippo and Romano[4] (stated as about 100% optical purity) have prompted us to check other fluorinating reagents.[6] Phenyltetrafluorophosphorane[7] (**3**), *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine[8] (**4**) (FAR), and (diethylamino)sulfur trifluoride[9] (**5**) (DAST) were used according to slightly modified procedures.

$$C_6H_{13}CH(OTs)CH_3 + \underset{\mathbf{2}}{(n\text{-}C_4H_9)_3PFCH_3} \rightarrow \underset{\mathbf{1}}{C_6H_{13}CHFCH_3} + \text{octenes} + (n\text{-}C_4H_9)_3P(OTs)CH_3 \quad (1)$$

$$C_6H_{13}CH[OSi(CH_3)_3]CH_3 + \underset{\mathbf{3}}{C_6H_5PF_4} \rightarrow \mathbf{1} + C_5H_{11}CHFCH_2CH_3 + \text{octenes} + FSi(CH_3)_3 + C_6H_5POF_2 \quad (2)$$

$$C_6H_{13}CHOHCH_3 + \underset{\mathbf{4}}{(C_2H_5)_2NCF_2CHFCl} \rightarrow \mathbf{1} + \text{octenes} + (C_2H_5)_2NCOCHFCl + HF \quad (3)$$

$$C_6H_{13}CHOHCH_3 + \underset{\mathbf{5}}{(C_2H_5)_2NSF_3} \rightarrow \mathbf{1} + \text{octenes} + (C_2H_5)_2NSOF + HF \quad (4)$$

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