C_2H_3O).

Repandin B (2a): mp 127–128 °C; UV λ_{max} (MeOH) 210 nm (ϵ 2.3 × 10^4); CD $[\theta]_{207}$ −1.77 × 10^5, $[\theta]_{249}$ 1.01 × 10^4; IR_{max} ($CHCl_3$) 3450 (OH), 1760 (γ-lactone), 1725, 1710, 1700 (carbonyls), 1680, 1640 cm^{-1} (double bonds); significant low-resolution mass spectral peaks (20 eV, 125 °C), *m/e* (rel intensity) 506 (0.01, $C_{26}H_{34}O_{10}$), 488 (0.01, $C_{26}H_{32}O_9$), 475 (0.01, $C_{25}H_{31}O_9$), 409 (0.04), 404 (0.03, $C_{21}H_{24}O_8$), 391 (0.20, $C_{21}H_{27}O_7$), 390 (0.05, $C_{21}H_{26}O_7$), 323 (0.08), 307 (0.11), 306 (0.05, M − $C_5H_{10}O_2$ − $C_5H_6O_2$), 289 (0.06, $C_{16}H_{17}O_5$), 288 (0.07, $C_{16}H_{16}O_5$), 256 (0.19), 229 (0.41), 228 (0.13), 99 (0.76, $C_5H_7O_2$), 85 (0.53, C_5H_9O), 57 (100, C_4H_9).

Anal. Calcd for $C_{26}H_{34}O_{10}$: mol wt 506.2152. Found (MS): mol wt 506.2170. CI: M + 1, *m/e* 507.

Acetylation of 40 mg of **2a** gave 35 mg of the diacetate **2b** as a gum: IR_{max} (CCl_4) 1770, 1740, 1730, 1720, 1655 cm^{-1}; significant low-resolution mass spectral peaks (70 eV, 130 °C), *m/e* (rel intensity) 590 (not observed, $C_{30}H_{38}O_{12}$), 435 (0.07, $C_{22}H_{27}O_9$), 331 (0.02, $C_{18}H_{19}O_6$), 330 (0.02, $C_{18}H_{18}O_6$), 288 (0.21, $C_{16}H_{16}O_5$), 270 (0.12, $C_{16}H_{14}O_4$), 141 (0.84, $C_7H_9O_3$), 99 (0.26, $C_5H_7O_2$), 85 (0.28, C_5H_9O), 57 (0.56, C_4H_9), 43 (100, C_2H_3O).

Repandin C (3): gum; CD $[\theta]_{213}$ −1.34 × 10^5, $[\theta]_{249}$ 1.34 × 10^4; IR_{max} ($CHCl_3$) 3500 (OH), 1765 (γ-lactone), 1735, 1720 (carbonyls), 1660, 1640 cm^{-1}; significant low-resolution mass spectral peaks (70 eV, 150 °C), *m/e* (rel intensity) 492 (0.01, $C_{25}H_{32}O_{10}$), 461 (0.01, $C_{24}H_{29}O_9$), 404 (2.8, $C_{21}H_{24}O_8$), 377 (0.11, $C_{20}H_{25}O_7$), 376 (0.09, $C_{20}H_{24}O_7$), 289 (0.29), 288 (0.36, M − $C_5H_8O_3$ − $C_4H_8O_2$), 256 (0.26, $C_{15}H_{12}O_4$), 99 (0.06, $C_5H_7O_2$), 71 (100, C_4H_7O), 43 (0.70, C_3H_7).

Anal. Calcd for $C_{25}H_{32}O_{10}$: mol wt 492.1986. Found (MS): mol wt 492.1979.

Repandin D (4a): gum; CD $[\theta]_{212}$ −2.85 × 10^5, $[\theta]_{247}$ 2.53 × 10^4; IR_{max} ($CHCl_3$) 3480, 1760, 1730, 1720 cm^{-1}; significant low-resolution mass spectral peaks (70 eV, 150 °C), *m/e* (rel intensity) 506 (0.01, $C_{26}H_{34}O_{10}$), 475 (0.02, $C_{25}H_{31}O_9$), 405 (0.02, $C_{21}H_{25}O_8$), 404 (0.05, $C_{21}H_{24}O_8$), 391 (0.29), 390 (0.14, $C_{21}H_{26}O_7$), 289 (0.20), 288 (0.22, $C_{16}H_{16}O_5$), 256 (0.37, $C_{15}H_{12}O_4$), 85 (0.86, C_5H_9O), 57 (100, C_4H_9).

Anal. Calcd for $C_{26}H_{34}O_{10}$: mol wt 506.2152. Found (MS): mol wt 506.2148.

Acetylation of 55 mg of **4a** gave 50 mg of acetate **4b** as a gum: IR_{max} (CCl_4) 1770, 1745, 1735, 1720, 1650 cm^{-1}; significant low-resolution mass spectral peaks (70 eV, 120 °C), *m/e* (rel intensity) 548 (0.01, $C_{28}H_{36}O_{11}$), 517 (0.01, $C_{27}H_{33}O_{10}$), 488 (0.02, $C_{26}H_{32}O_9$), 447 (0.04, $C_{23}H_{27}O_9$), 433 (0.17, $C_{23}H_{29}O_8$), 404 (0.02, $C_{21}H_{24}O_8$), 390 (0.11, $C_{21}H_{26}O_7$), 372 (0.03, $C_{21}H_{24}O_6$), 288 (0.36, $C_{16}H_{16}O_5$), 270 (0.22, $C_{16}H_{14}O_4$), 257 (0.20, $C_{15}H_{13}O_4$), 256 (0.36, $C_{15}H_{14}O_4$), 85 (0.95, C_5H_9O), 71 (0.24, C_4H_7O), 57 (100, C_4H_9), 43 (0.48, C_2H_3O).

Oxidation of 4a. To a solution of 0.13 g of **4a** in 15 mL of acetone at 0 °C was added, dropwise with stirring, Jones reagent until the solution remained orange. After an additional 45 min, the reaction was quenched by addition of 30 mL of H_2O. The solution was extracted (3 × 40 mL) with ethyl ether; the ether phase was washed with an equal volume of 5% $NaHCO_3$ solution followed by repeated washes with H_2O. Preparative TLC of the ether residue yielded 20 mg of **6** as a gum: IR_{max} (CCl_4) 1775, 1735, 1715 cm^{-1}; significant low-resolution mass spectral peaks (70 eV, 140 °C), *m/e* (rel intensity) 504 (0.02, $C_{26}H_{34}O_{10}$), 473 (0.01, $C_{25}H_{31}O_9$), 403 (0.04, $C_{21}H_{25}O_8$), 389 (0.16, $C_{21}H_{27}O_7$), 388 (0.03, $C_{21}H_{26}O_7$), 286 (0.22, $C_{16}H_{16}O_5$), 271 (0.21, $C_{15}H_{13}O_5$), 85 (0.87, C_5H_9O), 71 (0.47, C_4H_7O), 57 (100, C_4H_9).

Acknowledgment. This work was supported by Grant No. 1-RO1-CA-19800, awarded by the National Cancer Institute, DHEW, and in part by the National Science Foundation (Grant No. DEB-76-20585). We thank Professor F. Bohlmann, Techinical University Berlin, for NMR and MS data and Professor Lowell Urbatch for collection and identification of the plants.

Registry No. 1a, 71155-66-3; **1b**, 71138-42-6; **2a**, 71170-76-8; **2b**, 71138-43-7; **3**, 71138-44-8; **4a**, 71138-45-9; **4b**, 71138-46-0; **5**, 71135-27-8; **6**, 71138-47-1.

Notes

A Method for Simple Titration of Organolithium Reagents in Ethers or Hydrocarbons Using Metalation of *N*-Benzylidenebenzylamine as Colored Reaction

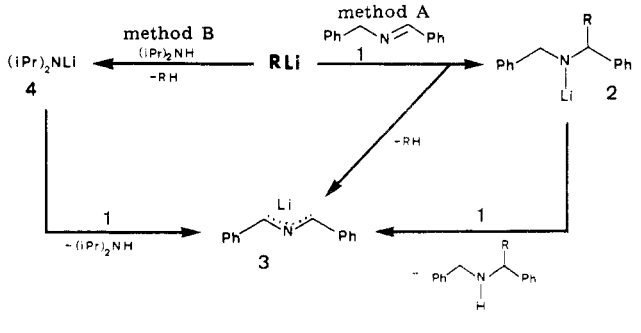
Lucette Duhamel* and Jean-Christophe Plaquevent

Laboratoire de Chimie Organique, Faculté des Sciences et des Techniques de Rouen, 76130 Mont Saint Aignan, France

Received February 8, 1979

Organolithium compounds are useful reagents in organic synthesis. Generally, it is necessary to know their accurate concentration before their use in metalation and addition reactions; the most widely used methods for their analysis are the double titration procedure of Gilman and Cartledge[1] and the complexometric method of Watson and Eastham, in alkanes or benzene at room temperature[2] or in ethers at −78 °C.[3] Recently, a method was described which used the organolithium in a colored reaction of carbon lithiation: the colored indicator was diphenylacetic acid, whose dianion is yellow while the monoanion is colorless.[4] The organolithium was run from a syringe in the tetrahydrofuran solution of indicator until the end point was reached.

Scheme I



We have observed in the metalation of Schiff base of amino esters that the reaction mixture containing enolate was red or orange, and became pale yellow after protonation of the anion by a carboxylic acid.[5] However, the end point of the protonation was impossible to observe in this case. Reaction mixtures of organolithium and *N*-

(1) H. Gilman and F. K. Cartledge, *J. Organomet. Chem.*, 2, 447 (1964).
(2) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, 9, 165 (1967).
(3) R. A. Ellison, R. Griffin, and F. N. Kotsonis, *J. Organomet. Chem.*, 36, 209 (1972).
(4) W. G. Kofron and L. M. Baclawski, *J. Org. Chem.*, 41, 1879 (1976).
(5) L. Duhamel and J. C. Plaquevent, *J. Am. Chem. Soc.*, 100, 7415 (1978).

0022-3263/79/1944-3404$01.00/0

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

organolithium[b]	titration conditions: solvent	method A	method B	Watson and Eastham[c] method	total alkali[d]
n-BuLi in hexane					
sample 1	Et_2O	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_2O	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_2O	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_2O	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.

(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).

(8) For example, titrations (method A) by an identical acid solution of an identical solution of *n*-BuLi/hexane in THF freshly distilled from $LiAlH_4$ and THF distilled some months prior to the experimentation yielded $N = 1.69$ and $N = 1.59$, respectively. The difference between these two values is attributed to impurities contained in "old" THF.

Photoassisted Cristol-Firth-Hunsdiecker Reaction

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

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

Received March 28, 1979

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

(1) National Service Award (NIH) Postdoctoral Fellow, IF32CA 05946-02.

(2) Wilson, C. V. *Org. React.* **1957**, *9*, 341.

(3) Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 280.

(4) Davis, J. A.; Hernyk, J.; Carroll, S.; Bunds, J.; Johnson, D. *J. Org. Chem.* **1965**, *30*, 415.

(5) Bunce, N. J. *J. Org. Chem.* **1972**, *37*, 664.

(6) Cason, J.; Walba, D. *J. Org. Chem.* **1972**, *37*, 669.

0022-3263/79/1944-3405$01.00/0