NMR ($CDCl_3$) δ 53.65, 96.84, 127.33, 128.05, 129.01, 134.29, 189.49. Anal. Calcd for $C_{16}H_{14}Cl_3NS_2$: C, 49.18; H, 3.62; Cl, 27.20; N, 3.58; S, 16.41. Found: C, 49.35; H, 3.64; Cl, 26.93; N, 3.52; S, 16.44.

Dichloro[(trichloromethyl)thio]methanesulfenyl Chloride (10). A solution of 1.1 g (15 mmol) of Cl_2 in 25 mL of CCl_4 was added to 3.5 g (15 mmol) of **2** in 25 mL of CCl_4 at 0 °C. The reaction mixture was allowed to warm to room temperature and after 5 h the solvent was removed in vacuo. The remaining yellow oil was distilled in vacuo, giving 2.7 g (60%) of a yellow oil (bp 134-137 °C (11 torr)), which could be identified as **10**: MS, *m/z* 298 (M^+), 263 ($M^+ - Cl$), 228 ($M^+ - Cl_2$), 193 ($M^+ - 3Cl$), 184 ($M^+ - Cl_2CS$), 149 (Cl_3CS^+), 117 (CCl_3^+), 79 ($CSCl^+$), 76 (CS_2^+); IR (NaCl, cm^{-1}) 830 (vs), 770 (vs), 745 (vs); ^{13}C NMR (C_6D_6) δ 95.63, 95.72. Anal. Calcd for $C_2Cl_6S_2$: C, 7.99; Cl, 70.70; S, 21.31. Found: C, 8.56; Cl, 70.83; S, 21.50.

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Registry No. 1, 594-42-3; **2**, 91631-89-9; **6**, 91631-90-2; **8**, 91631-91-3; **9**, 91631-92-4; **10**, 91631-93-5; $(PhCH_2)_2NH$, 103-49-1; Cl_2, 7782-50-5; CS, 2944-05-0; anthracene, 120-12-7.

Table I. Aldehydes by Reaction of Grignard and Organolithium Reagents with *N*-Formylmorpholine

RMgX or RLi	yield,[a] %	solvent	bp [°C/mmHg] found	bp [°C/mmHg] lit.[3]
$C_6H_5CH_2CH_2$-MgCl	70	ether	88/1	87/1
$C_6H_5CH{=}CH$-MgBr	81	ether	84/2	85/2
$C_6H_5CH_2MgCl$	84	ether	76-79/10	76-78/10
norbornyl-MgBr	74[b]	ether	51-53/7	52/7
c-C_5H_9MgBr	69	ether	74-75/100	73-76/100
1-naphthyl-MgBr	92	ether	142/6	142/6
C_6H_5MgBr	89	ether	51-52/2.2	63-64/10
C_6H_5Li	90	benzene	50/2.2	63-64/10
n-BuLi	78	*n*-hexane	100/760	102-103/760
$C_6H_5C{\equiv}CLi$	80	ether	65/0.1	65/0.1

[a] Yields of aldehydes refer to isolated (distilled) products; they gave IR, ^1H NMR, and ^{13}C NMR spectra which were identical with those of the authentic compounds. [b] Starting with pure *exo*-norbornyl bromide produces a mixture of *exo*- and *endo*-norbornene carboxaldehyde (3:1), which was characterized by NMR spectroscopy.

Synthetic Methods and Reactions. 119.[1] *N*-Formylmorpholine: A New and Effective Formylating Agent for the Preparation of Aldehydes and Dialkyl (1-Formylalkyl)phosphonates from Grignard or Organolithium Reagents

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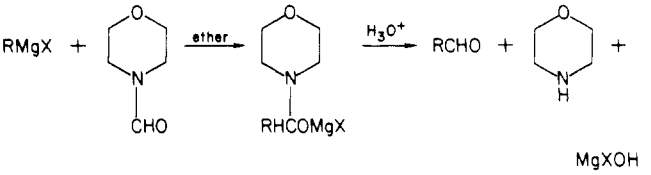
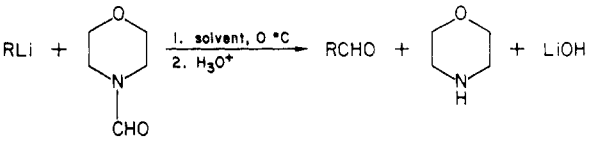
In recents years a number of reagents have been developed for formylation in organic synthesis. 2-(Formylmethylamino)pyridine has been used by Comins and Meyers[2] for the preparation of aldehydes from Grignard reagents. The presence of the additional ligand (pyridyl nitrogen) and the ready formation of a six-membered chelate ring was considered to prohibit release of aldehyde under the reaction conditions and thus protect the aldehydic product from the further reaction with the organometallic reagent. We subsequently reported[3] the use of *N*-formylpiperidine in related reactions and found that no additional ligand is in fact necessary for the reaction to be successful. More recently, Amaratunga and Frechet reported[4] a more extensive investigation of the formylation of Grignard reagents with alkylformylamines. The ready availability of dialkylformamides such as DMF makes them also increasingly useful in the preparation of aldehydes.[5] The reactions, however, have limitations and generally proceed satisfactorily with Grignard but not with organolithium reagents. Aboujaoude and Collignon reported[6] the preparation of dialkyl (1-formylalkyl)phosphonates, via treatment of dimethylformamide with the dialkyl (α-lithioalkyl)phosphonates. The isolated yields were from 52% to 88%.

Our continued interest in developing alternative and improved formylating systems prompted us to examine the readily available and inexpensive *N*-formylmorpholine as a formylating reagent. The reagent is commercially available or easily prepared by the reaction of morpholine with carbon monoxide. *N*-Formylmorpholine readily reacts with organometallic compounds. Reaction in ether at 0 °C with wide variety of organolithium or Grignard reagents results in formation, upon acidic workup, of the corresponding aldehydes (Table I) in good to excellent yield and high purity. The examples in Table I indicate the effectiveness of the method for aryl, alkyl, vinyl, and acetylenic Grignard or organolithium reagents alike.





The reaction of dialkyl (α-lithioalkyl)phosphonates with *N*-formylmorpholine in THF at −78 °C upon acidic workup also gives in excellent yield dialkyl (1-formylalkyl)phosphonates, affording a method of wide applicability for their one-step preparation from the parent phosphonates (Table II).[7]

The ease of the reactions and mild conditions, giving excellent preparative yields, make this formylating reagent

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(3) Olah, G. A.; Arvanaghi, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 878; *Organic Synthesis*, in press.
(4) Amaratunga W.; Frechet, J. M. J. *Tetrahedron Lett.* **1983**, *24*, 1143.
(5) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Synthesis*, in press, and references given therein.
(6) Aboujaoude, E. E.; Collignon, N. *Synthesis* **1983**, 634 and references cited therein.
(7) Ford-Moore, A. H.; Perry, B. J. "Organic Syntheses"; Wiely: New York, 1963; Collect. Vol. IV, p 325.

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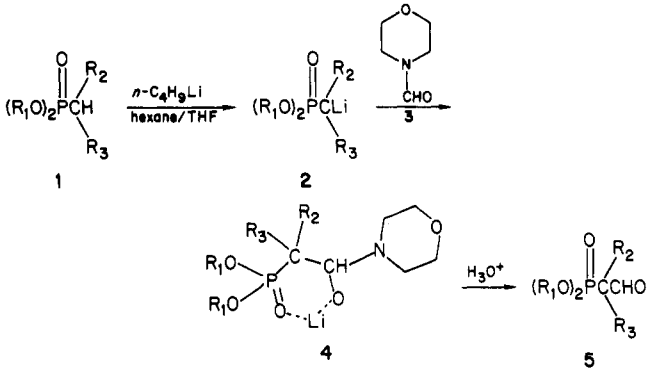
Table II. Preparation of Dialkyl (1-Formylalkyl)phosphonates 5

R_1	R_2	R_3	yield, present run	yield, reported[6]	bp [°C/mmHg], found	bp [°C/mmHg], lit.[6]
C_2H_5	H	H	85	53	72–76/0.25	76–79/0.3
i-C_3H_7	H	H	83	51	72–78/0.5	94–98/2
C_2H_5	CH_3	H	94	86	93–5/2	93–96/2
i-C_3H_7	CH_3	H	91	88	80–85/1	98–102/2
C_2H_5	CH_3	CH_3	83	79	98–100/4	88–91/2
C_2H_5	C_2H_5	H	80	78	98–102/2.8	96–99/2

[a] Yields of dialkyl (1-formylalkyl)phosphonates refer to isolated (distilled) products; they gave ^1H NMR and ^{31}P NMR spectra which were identical with those of the reported[6] compounds.

an attractive one complementing previously reported methods.



Experimental Section

A. General Procedure for the Formylation of Grignard Reagents with *N*-Formylmorpholine. To a stirred solution of freshly prepared Grignard reagent (10 mmol) in dry diethyl ether (20 mL), cooled to 0 °C, is slowly added during 2 min a solution of *N*-formylmorpholine (Aldrich) (10 mmol) in diethyl ether (10 mL). An exothermic reaction takes place. The reaction mixture is stirred for another 30 min at room temperature and then quenched with 3 N HCl until the solution becomes completely acidic (pH2). The product is extracted with diethyl ether, washed twice with water, and then with saturated sodium hydrogen carbonate and saturated sodium chloride solutions. The organic layers are combined and dried over anhydrous sodium sulfate. Removal of the solvent gives the corresponding aldehyde in almost pure form.[8] Further purification by either distillation or crystallization furnished pure products which were characterized by their bp, IR, NMR, and TLC.

B. General Procedure for the Formylation of Organolithium Compounds with *N*-Formylmorpholine. To a 0 °C solution of freshly prepared organolithium compound (10 mmol) in the appropriate solvent (see Table I) (10 mL) is added during 2 min a solution of *N*-formylmorpholine (10 mmol) in the same solvent (15 mL). The reaction is moderately exothermic. The solution is allowed to stir for an additional 30 min and then worked up following the procedure described above.[8]

C. General Procedure for the Formylation of Dialkyl Alkylphosphonates with *N*-Formylmorpholine. To a solution of 12 mmol (2.7 M) of *n*-butyllithium in tetrahydrofuran under N_2 at −78 °C is added during 2 min a solution of the dialkyl alkylphosphonate (10 mmol) in 10 mL of tetrahydrofuran. After stirring for 10 min, a solution of *N*-formylmorpholine (12 mmol) in 10 mL of THF is added. The mixture was allowed to warm to room temperature and then is quenched with 3 N HCl until the solution becomes acidic. The product is extracted with dichloromethane, dried over magnesium sulfate, and stripped of solvent to give the corresponding aldehydes in almost pure form. Further purification by distillation furnished pure products which were characterized by their bp, IR, ^{13}C NMR, ^1H NMR, and TLC.

(8) Spectroscopic evidence showed that the alcohol side product was detectable in some cases (≲5%) but could be easily removed in the purification of the crude product.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. 1 (R_1 = C_2H_5, R_2 = R_3 = H), 683-08-9; 1 (R_1 = i-C_3H_7, R_2 = R_3 = H), 1445-75-6; 1 (R_1 = C_2H_5, R_2 = CH_3, R_3 = H), 78-38-6; 1 (R_1 = i-C_3H_7, R_2 = CH_3, R_3 = H), 1067-69-2; 1 (R_1 = C_2H_5, R_2 = R_3 = CH_3), 1538-69-8; 1 (R_1 = R_2 = C_2H_5, R_3 = H), 18812-51-6; 2 (R_1 = C_2H_5, R_2 = R_3 = H), 41849-03-0; 2 (R_1 = i-C_3H_7, R_2 = R_3 = H), 91210-94-5; 2 (R_1 = C_2H_5, R_2 = CH_3, R_3 = H)., 91210-95-6; 2 (R_1 = i-C_3H_7, R_2 = CH_3, R_3 = H), 91210-96-7; 2 (R_1 = C_2H_5, R_2 = R_3 = CH_3), 91210-97-8; 2 (R_1 = R_2 = C_2H_5, R_3 = H), 91210-98-9; 3, 4394-85-8; 5 (R_1 = C_2H_5, R_2 = R_3 = H), 1606-75-3; 5 (R_1 = i-C_3H_7, R_2 = R_3 = H), 43186-09-0; 5 (R_1 = C_2H_5, R_2 = CH_3, R_3 = H), 34403-79-7; 5 (R_1 = i-C_3H_7, R_2 = CH_3, R_3 = H), 67398-17-8; 5 (R_1 = C_2H_5, R_2 = R_3 = CH_3), 35078-65-0; 5 (R_1 = R_2 = C_2H_5, R_3 = H), 32329-34-3; $C_6H_5CH_2CH_3MgCl$, 90878-19-6; $C_6H_5CH{=}CHMgBr$, 30094-01-0; $C_6H_5CH_2MgCl$, 6921-34-2; c-C_5H_9MgBr, 33240-34-5; C_6H_5MgBr, 100-58-3; C_6H_5Li, 591-51-5; $C_6H_5C{\equiv}CLi$, 4440-01-1; $C_6H_5CH_2CH_2CHO$, 104-53-0; $C_6H_5CH{=}CHCHO$, 104-55-2; $C_6H_5CH_2CHO$, 122-78-1; c-C_5H_9CHO, 872-53-7; C_6H_5CHO, 100-52-7; $C_6H_5C{\equiv}CCHO$, 2579-22-8; n-butyllithium, 109-72-8; norbornyl-MgBr, 51243-73-3; 1-naphthyl-MgBr, 703-55-9; norbornyl-CHO, 19396-83-9; 1-naphthyl-CHO, 66-77-3; n-butyl-CHO, 110-62-3; lithium, 7439-93-2.

Kinetic and Thermodynamic Control in the Metalation of Pyridine. A Direct Synthesis of 2- and 4-Substituted Pyridines

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We recently[1] succeeded in directly metalating pyridine with the complex of BuLi and t-BuOK[2] in a mixture of tetrahydrofuran (THF) and hexane.

The results of quenching the obtained solution with deuteriomethanol, dimethyl disulfide and trimethylchlorosilane indicated that the metalation had afforded a mixture of approximately equal amounts of 2- and 4-potassio derivatives of pyridine in addition to a minor quantity of the 3-potassio compound (~10 rel %). The ratio 2-: 3-: 4-potassiopyridine was completely different from the ratio of the rates with which the 2-, 3-, and 4-

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(2) Lochman, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 127. Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9.

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