in a septum-sealed 2-dram vial, which also contained 29.7 mg of tetradecane (internal standard). Calibrated GLC analysis indicated a 91% yield of product; no starting material remained. After a total of 1 h, 200 mL of 3 M aqueous ammonium chloride (deoxygenated with nitrogen) was added to the reaction mixture, which was allowed to warm to ambient temperature. The final pH of the aqueous layer was 8. The mixture was filtered through Celite 545, and the filter deposit was washed with 200 mL of ether. The organic layer was separated and back-extracted with 250 mL of 0.2 M aqueous sodium thiosulfate, 200 mL of ammonium chloride solution, 250 mL of 0.4 M aqueous sodium thiosulfate, and finally 100 mL of ammonium chloride. The aqueous layers were sequentially extracted with 50 mL of ether, which was added to the original organic layer. Drying over anhydrous sodium sulfate (Baker, granular) and evaporation under reduced pressure (<30 °C, 30 torr) gave 9.31 g of a yellow oil, which was purified by flash chromatography on 180 g of Florisil (Fisher) slurry-packed in a  $3.5 \times 40$  cm column and eluted with 3.5 L of 5% ether/hexane followed by 0.5 L of 10% ether/hexane. All fractions collected were 50 mL (the column volume was 350 mL), and 5.61 g (98% pure by GLC) of product was recovered from fractions 11-76. An additional 0.53 g (98% pure) was obtained by stripping the column with 20% ether/hexane (~750 mL). The total yield of pure product was 6.14 g (80%).

Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O: C, 77.87; H, 11.76. Found: C, 77.60: H, 11.59.

3-Butylcyclohexanone (Method B). A suspension of butylcopper(I) was prepared by adding 36.8 mL (53.0 mmol) of 1.44 M (0.21 M residual base) butyllithium (Aldrich, hexane solution) to a suspension of 10.9 g (53.0 mmol) of CuBr-SMe<sub>2</sub> (Aldrich) in 60 mL of dry, oxygen-free ether in a septum-sealed 500-mL round-bottomed flask cooled to -50 °C. After the BuCu suspension had been stirred for 15 min at -50 °C, it was treated with a 0 °C suspension of lithium dicyclohexylphosphide, transferred by cannula from the septum-sealed 100-mL pear-shaped flask where it had been prepared by adding 36.8 mL (53.0 mmol) of 1.44 M butyllithium to 10.6 g (53.5 mmol) of dicyclohexylphosphine dissolved in 30 mL of ether and stirring the mixture for 1 h at 0 °C. After 15 min at -50 °C, the phosphidocuprate was cooled to -75 °C for 15 min, and then 4.83 g (50.3 mmol) of 2-cyclohexen-1-one (Aldrich, distilled and refrigerated) in 20 mL of ether in a septum-sealed 50-mL pear-shaped flask at -75 °C was transferred into it by cannula. After 1 h, a 2.0-mL sample (out of a total of 200 mL) contained 69.0 mg of product (90% yield) measured by calibrated GLC. No starting material was present; therefore, the reaction mixture was quenched with 3 M aqueous ammonium chloride and worked up as described under Method A (above) to give 9.3 g of pale yellow oil, which was distilled by using a short-path stillhead (Firestone design) to obtain three fractions: 1.44 g (40-50 °C/0.2 torr), 4.79 g (56-58 °C/0.2 torr), and 0.42 g (48 °C/0.1 torr). GLC analysis indicated that fractions 2 and 3 were 95% and 97% pure, respectively, but that fraction 1 was  $\sim 90\%$  pure. Therefore, it was chromatographed on the Florisil column from method A eluted with 1 L of hexane to remove impurities and then 3 L of 20% ether/hexane to obtain 1.22 g (98% pure by GLC) of product after evaporation under reduced pressure (<30 °C/30 torr). The total yield of 95-98% pure product was 6.43 g (83%): IR (neat) 2935, 2861, 1713, 1450, 1229 cm<sup>-1</sup>; <sup>13</sup>C NMR ( $CDCl_3/Me_4Si$ )  $\delta$  14.0, 22.8, 25.4, 28.9, 31.4, 36.3, 39.1, 41.6, 48.2, 211.7.

Anal. Calcd for  $C_{10}H_{18}O$ : C, 77.87; H, 11.76. Found: C, 77.73; H, 11.82.

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Registry No. MeCu(PCy<sub>2</sub>)Li, 88766-01-2; BuCu(PCy<sub>2</sub>)Li, 83944-05-2; BuCu(NCy<sub>2</sub>)Li, 83944-04-1; MeCu(NCy<sub>2</sub>)Li, 88766-02-3; Me<sub>2</sub>CuLi, 15681-48-8; MeCu(PPh<sub>2</sub>)Li, 88766-03-4; Me<sub>2</sub>Cu-(CN)Li<sub>2</sub>, 80473-70-7; LiBr, 7550-35-8; CuBr·SMe<sub>2</sub>, 54678-23-8; BuLi, 109-72-8; PCy<sub>2</sub>H, 829-84-5; BuCu, 34948-25-9; cyclohex-2-enone, 930-68-7; 1-iodooctane, 629-27-6; cyclohexene oxide, 286-20-4; diethyl cyclopropane-1,1-dicarboxylate, 1559-02-0; 3methylcyclohexanone, 591-24-2; 3-butylcyclohexanone, 39178-69-3; nonane, 111-84-2; trans-2-methylcyclohexanol, 7443-52-9; diethyl propylmalonate, 2163-48-6; diethyl hexylmalonate, 5398-10-7.

# Preparation of Dialkyl Carbonates via the Phase-Transfer-Catalyzed Alkylation of Alkali Metal Carbonate and Bicarbonate Salts

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Esters of carbonic acid are traditionally prepared by the reaction of phosgene with the appropriate alcohol/phenol in the presence of an acid acceptor. Alternatives to the use of phosgene include carbonylation of alcohols<sup>1</sup> and phenols<sup>2</sup> with carbon monoxide and transesterification of ethylene carbonate or certain activated carbonates with alcohols.3,4

Recent interest in the utilization of carbon dioxide as a synthetic building block has prompted investigations of the preparation of carbonic esters from CO<sub>2</sub> or its derivatives. For example, the preparation of dialkyl carbonates from CO<sub>2</sub> and alcohols<sup>5</sup> or alkoxides followed by alkylating agents<sup>6</sup> has been reported. Cyclic carbonates have been prepared by the reaction of  $CO_2$  with epoxides<sup>7</sup> or halohydrins<sup>8</sup> in the presence of various catalysts. Although preparation of carbonates from "inorganic" carbonates via alkylation at high temperatures or in dipolar aprotic solvents has been demonstrated,<sup>9</sup> a much more attractive approach is to conduct the alkylation using a phasetransfer catalyst. Thus, the alkylation of potassium carbonate with alkyl bromides can be effected in the presence of organostannyl catalysts.<sup>10</sup> Alkylpolycarbonates have likewise been prepared by alkylation of alkali metal carbonates with difunctional alkyl halides in the presence of crown ethers.<sup>11</sup> A recent report describing the preparation of aliphatic carbonates from potassium bicarbonate and alkyl halides in nonpolar solvents in the presence of phase-transfer catalysts<sup>12</sup> prompts us to disclose the results

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 Table I.
 Solubilities of Metal Carbonate Salts in Dipolar Aprotic Solvents<sup>a</sup>

	solvent	Li	Na	K	Cs	_		
	DMF	0.003	0.038	0.075	1.195			
	Me,SO	0.014	0.143	0.470	3.625			
	DMAC	0.004	0.021	0.046	0.490			
	sulfolane	0.021	0.031	0.160	3.950			
	NMP	0.014	0.208	0.237	7.224			

 $^a$  Solubilities in g/10 mL determined at ambient temperature by flame photometry.

of our work in this area.

# **Results and Discussion**

The solubility of most metal carbonate salts in nonpolar

solvents is negligible. This solubility is not appreciably better in dipolar-aprotic solvents (Table I). Not surprisingly, reactions of inorganic carbonate salts with alkyl halides in these solvents are sluggish even at elevated temperatures. For example,  $K_2CO_3$  does not react with methyl chloride in refluxing toluene (18 h). In DMAC at 150 °C only a 29.4% yield of dibenzyl carbonate is obtained from  $K_2CO_3$  and benzyl chloride. The use of cesium carbonate in dipolar aprotic solvents improves the situation considerably such that respectable yields of dibenzyl carbonate can be obtained via alkylation with benzyl chloride (Table II). Addition of ion complexing agents such as crown ethers or quaternary ammonium salts results in only slight improvement. The addition of KI has little effect on the reaction except to lower yields when qua-

Table II. Alkylation of Alkali Metal Carbonates<sup>a</sup>

example	e carbonate	halide	metal solvent <sup>b</sup>	alkyl time, h	PTC <sup>c</sup>	yield, %
1	K,CO,	MeI	toluene	18	18-C-6	10
2	K,CO,	MeI	toluene	18		0
3	K <sub>2</sub> CO <sub>3</sub>	MeCl	toluene	6	$A-464^{d}$	5
4	K,CO,	PhCH,Cl	toluene	12	$A-464^d$	15
5	K,CO,	PhCH <sub>2</sub> Cl	toluene	12	$18 \cdot C \cdot 6^d$	9
6	Cs, CO,	PhCH <sub>2</sub> Cl	toluene	12	18-C-6	33
7	K,CO,	PhCH,Cl	DMAC	12		29
8	K,CO,	PhCH,Cl	DMAC	12	$18 \cdot C \cdot 6^d$	70
9	Cs,CO,	PhCH,Cl	DMAC	12		70
10	Cs,CO,	PhCH <sub>2</sub> Cl	DMAC	12	$18 \cdot C \cdot 6^d$	63
11	K,CO,	PhCH,Cl	DMAC	5	Bu <sub>4</sub> NBr	3
12	K,CO,	PhCH <sub>2</sub> Cl	DMAC	5	Bu₄NBr <sup>e</sup>	5
13	K,CO,	PhCH,Cl	DMAC	5	A-464	5
14	K,CO,	PhCH_Cl	DMAC	5	$A-464^d$	5
15	K,CO,	PhCH,Cl	DMAC	5	$A-464^{e}$	32
16	K,CO,	PhCH <sub>2</sub> Cl	DMAC	5	Carb 4000	2
17	K,CO,	PhCH_Cl	DMAC	5	Carb 4000 <sup><i>d</i></sup>	5
18	K,CO,	PhCH,Cl	DMAC	5	Carb 4000 <sup>e</sup>	17
19	K,CO,	PhCH <sub>2</sub> Cl	NMP	20	$18 \cdot C \cdot 6^d$	53
20	K <sub>2</sub> CO <sub>3</sub>	$PhCH_{2}Cl$	NMP	20	18-C-6 <sup>e</sup>	40

<sup>a</sup> Reactions conducted at 100-110 °C. <sup>b</sup> DMAC = N,N-dimethylacetamide; NMP = N-methyl-2-pyrrolidone. <sup>c</sup> A-464 = Adogen-464; 18-C-6 = 18 crown-6; Carb 4000 = carbowax 4000; Bu<sub>4</sub>NBr = tetrabutylammonium bromide; PTC's added at 2 mol % level. <sup>d</sup> 10 mol % KI added. <sup>e</sup> 10 mol % KBr added.

Table III	Phase-Transfer-Catalyza	ed Alkylation	of Potassium	<b>Bicarbonate</b> <sup>a</sup>
1 apre 111.	Thase Transfer Oatary &	eu Aikylailoll	Of I Orassium	Dicarbonate

expt no.	alkyl halide	catalyst <sup>b</sup>	additive <sup>c</sup>	$solvent^d$	yield, %	
 1	PhCH <sub>2</sub> Cl	Hex₄NCl	KBr	DMAC	27	
2	PhCH,Cl	$Et_2(CH_2)_3$ , PPh_Br	KBr	NMP	33	
3	PhCH,Cl	$Et_{2}(CH_{2})_{3}, PPh_{3}Br$	KBr	Tol	0.2	
4	PhCH,Cl	Bu₄NBr		Tol	33	
5	PhCH,Cl	Bu NBr		NMP	61	
6	PhCH <sub>2</sub> Cl	Me		NMP	<b>24</b>	
7	PhCH <sub>2</sub> Cl	Hex <sub>4</sub> NBr	KBr	NMP	79	
8	PhCH <sub>2</sub> Cl	Bu₄PBr	KBr	ŃMP	80	
9	PhCH,Cl	A-464	KBr	DMAC	42	
10	PhCH,Cl	Aliquat	KBr	DMAC	52	
11	PhCH <sub>2</sub> Cl	Hex <sub>4</sub> NCl		DMAC	45	
12	PhCH <sub>2</sub> Br	HexANCI		DMAC	34	
13	CH <sub>3</sub> Cl	HexANC		DMAC	86	
14	CH <sub>3</sub> Cl	Bu₄NBr		DMAC	63	
15	CH <sub>3</sub> Cl	A-464		DMAC	49	
16	CH <sub>3</sub> Cl	Bu₄PBr		DMAC	53	
17	CH <sub>3</sub> Cl	$Ph_{3}P-C_{12}$		DMAC	56	
18	CH <sub>3</sub> Cl	Cyclohex <sub>3</sub> P-C <sub>12</sub>		DMAC	45	
19	CH <sub>3</sub> Cl	Hex <sub>4</sub> NCl		sulfolane	46	
20	CH <sub>3</sub> Cl	Hex <sub>4</sub> NCl		NMP	69	
21	1,2-dichloroethane	Hex₄NBr	KBr	DMAC	$15^{e}$	
22	<i>n</i> -octyl-Br	Bu₄PBr		NMP	47	
23	Allyl-Br	Bu₄PBr		NMP	50	
24	4-MeC, H, CH, Br	Hex.NBr		DMAC	88	

<sup>a</sup> In general, a twofold excess of KHCO<sub>3</sub> over alkyl halide was employed. Reactions were conducted at 150 °C or at reflux. <sup>b</sup> 5 mol % catalyst was employed. <sup>c</sup> 10 mol % additive was generally employed. <sup>d</sup> Abbreviations: DMAC, N,N-dimethylacetamide; NMP, N-methylpyrrolidione. All reactions were run at a 1 M concentration of alkyl halide. <sup>e</sup> Ethylene carbonate was the only product isolated.

ternary ammonium salts are used as catalyst.<sup>13</sup> In contrast, addition of KBr produces a beneficial effect in reactions catalyzed by quaternary ammonium salts. This effect is likely due to the in situ generation of alkyl bromides, which are displaced more rapidly than the chlorides.

A side reaction encountered in the preparation of dialkyl carbonates by this process is the formation of ethers. These products appear to be the result of decarboxylation of the intermediate monoalkylated carbonate salt to yield an alkoxide, which then displaces the alkyl halides (eq 1).



Attempted preparation of diaryl carbonates by reaction of carbonate salts with activated aryl halides under conditions described above produces only diaryl ethers. For example, treatment of o-fluoronitrobenzene with  $CsCO_3$ or K<sub>2</sub>CO<sub>3</sub> in the presence of 18-crown-6 afforded 2,2'-dinitrodiphenyl ether as the sole product in high yield. The exclusive formation of ethers in this case is undoubtedly due to the facility with which the intermediate aryloxy carbonate salts decarboxylate.<sup>14</sup>

The relatively poor yields obtained in the phase-transfer-catalyzed carbonate alkylation reactions is undoubtedly due, in part, to the inherent difficulty associated with transfer of a doubly charged ion into the organic phase. This rationale suggests that the singly charged bicarbonte ion should be transferred to the organic phase with greater facility and should thus undergo phase-transfer alkylation readily. The monoalkylated bicarbonate would be expected to undergo rapid proton transfer with additional base (carbonate or bicarbonate) to yield an alkoxy carbonate salt, which should readily suffer a second alkylation to produce a dialkyl carbonate. Indeed, the addition of catalytic amounts of bicarbonate to phase-transfer-catalyzed carbonate alkylations might induce a kind of "entrainment" catalysis (eq 2).



When solutions of various alkyl halides a variety of solvents were heated with excess potassium bicarbonate in the presence of phase-transfer catalysts, good yields of dialkyl carbonates were obtained (Table III).

Again, the combination of a dipolar aprotic solvent and a phase-transfer catalyst is necessary for obtaining good yields of dialkyl carbonates by this procedure. Sodium bicarbonate was dramatically inferior to potassium bicarbonate in these reactions. Of the catalysts investigated, tetra-n-hexylammonium bromide was generally the most N,N-Dimethylacetamide or N-methyleffective.

pyrrolidone were the preferred solvents. As in the case of the potassium carbonate alkylations, small amounts of dialkyl ethers were produced as by products in these alkylations; however, these products were rarely produced in yields exceeding 3-5%.

Attempts to prepare diaryl carbonates by reaction of potassium bicarbonate with o-nitrofluorobenzene in dipolar aprotic solvents in the presence of phase-transfer catalysts produced only diaryl ethers even when the reactions were conducted under several atmospheres of carbon dioxide. Evidently, the decarboxylation of alkali metal aryl carbonate salts is difficult to suppress. A similar result was noted on reaction of 2,2,2-trifluoroethyl bromide with potassium bicarbonated wherein only the ether was produced presumably due to the rapid loss of CO<sub>2</sub> from the intermediate alkyl carbonate salt.

Mixed dialkyl carbonates result when mixtures of alkyl halides are alkylated with potassium bicarbonate under these reaction conditions. For example, reaction of an equimolar mixture of benzyl chloride and 4-methylbenzyl bromide with excess potassium bicarbonate in DMAC in the presence of tetrabutylphosphonium bromide produced a nearly statistical (1:2.1:1) ratio of dibenzyl carbonate, 1, benzyl p-tolylmethyl carbonate, 2, and bis(p-tolylmethyl) carbonate, 3. Control experiments indicated that very



little scrambling of the carbonates occurs under the reaction conditions, indicating that the product mix is the result of very similar rates of alkylation of benzyl chloride and 4-methylbenzyl bromide in this reaction. Reaction of potassium benzyloxy carbonate with 4-methylbenzyl bromide under similar conditions produced a "mixed" carbonate rich product mix (1:2:3 = 4:80:16).

Benzyl methyl carbonate, 4, was produced in 95% yield by the alkylation of potassium methyl carbonate with benzyl chloride in toluene in the presence of 18-crown-6.



Attempted preparation of mixed arvl alkyl carbonates by reaction of potassium benzyl carbonate or potassium methyl carbonate with o-nitrofluorobenzene produced only the mixed aryl alkyl ethers 5 and 6. Control experiments indicated that methyl o-nitrophenyl carbonate is unstable to the reaction conditions.

In summary, the alkylation of potassium bicarbonate with alkyl halides (particularly primary or benzylic halides)

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in dipolar aprotic solvents in the presence of phase-transfer catalysts can be a useful method for the preparation of dialkyl carbonates. The reaction of alkali metal alkyl carbonate salts with alkyl halides in dipolar aprotic solvents produces mixed alkyl carbonates in good yields. The major limitation of this method is the failure of activated aryl halides or electronegatively substituted alkyl halides (i.e., 2,2,2-trifluoroethyl bromide) to produce carbonates due to the facility with which the intermediate alkoxy carbonate salts decompose. Finally, the reaction of potassium bicarbonate with activated aryl halides in dipolar aprotic solvents in the presence of phase-transfer catalysts can be a useful procedure for the preparation of diaryl ethers.

#### **Experimental Section**

General Methods. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. Proton NMR spectra were recorded on Varian EM-390 spectrometer with chemical shifts reported in parts per million relative to tetramethylsilane. Mass spectra were obtained on a Varian MAT 311 mass spectrometer operating in the EI mode. Gas chromatography was performed on a Varian 3700 gas chromatograph. A 6 ft ×  $^{1}/_{8}$  in. glass column packed with silicone OV-17 on Gas Chrom Q was employed for separations. Liquid chromatography was performed on a Waters liquid chromatograph. Separations were accomplished on a Du Pont micro-CN column using 10% THF in isooctane as the eluant.

All the compounds prepared in this study were known compounds that were either obtained from commercial sources or prepared according to standard literature procedures.

General Procedure for Alkylation of Carbonate and Bicarbonate Salts. In a typical procedure, a dry reaction flask was charged with 5.0 g (50 mmol) of freshly dried<sup>15</sup> potassium bicarbonate, 2.17 g (16.6 mmol) of benzyl chloride, 0.336 g (1.04 mmol) of tetra-n-butylammonium bromide, and 20 mL of dry DMAC. This mixture was immersed in an oil bath maintained at 115-125 °C. Progress of the reaction was monitored by gas chromatography until no further product formation was noted (usually 2-3 h). The cooled reaction mixture was filtered and subjected to an aqueous workup (when dipolar aprotic solvents were employed, the reaction mixtures were diluted with ether or toluene prior to the aqueous workup). The organic phase was dried  $(CaSO_4)$  and the solvent was removed to afford the crude dibenzyl carbonate, which was purified by vacuum distillation. This procedure was used essentially for all preparative reactions. Reactions run on an analytical scale were monitored by gas chromatography for formation of dialkyl carbonate using an internal standard.

Preparation of Dimethyl Carbonate via the Alkylation of KHCO<sub>3</sub>. A Fisher-Porter bottle was charged with 2.43 g, of a solution of methyl chloride in N-methylpyrrolidone (10 mmol), 3.12 g (31.2 mmol) of KHCO<sub>3</sub>, 0.1 g (0.30 mmol) of tetra-n-butylphosphonium bromide, 0.15 g (1.25 mmol) of KBr, and 10.0 mL of N-methylpyrrolidone. The vessel was sealed and immersed in a heated oil bath at 110 °C for 16 h. Contents of the vessel were stirred by means of a magnetic stirring bar during this period. Analysis of this mixture indicated that a 63% yield of dimethyl carbonate was produced. A similar experiment terminated after 5 h produced a 50.2% yield of dimethyl carbonate.

Preparation of Mixed Dialkyl Carbontes via Alkali Metal Carbonate Salt. Potassium benzyl carbonate was prepared by bubbling  $CO_2$  into a solution of potassium phenylmethoxide and benzyl alcohol in THF.<sup>15</sup> A solution of this salt, 0.57 g (5 mmol), in DMAC (15 mL), was treated with benzyl bromide, 0.86 g (5 mmol). The reaction mixture was stirred at 125 °C for 3 h. The usual workup afforded 1.0 g (72%) of dibenzyl carbonate.

Likewise, potassium methyl carbonate (prepared from potassium phenylmethoxide,  $CO_2$  and methanol in THF), 0.57 g (5 mmol), and benzyl chloride, 0.95 g (7.5 mmol), produced benzyl Reaction of Potassium Bicarbonate with "Activated" Aryl and Alkyl Halides. Reaction at Atmospheric Pressure. A dry 25-mL flask was charged with 3.00 g (30.0 mmol) of KHCO<sub>3</sub>, 1.41 g (10 mmol) of o-nitrofluorobenzene, 0.22 g (0.5 mmol) of tetrahexylammonium chloride, and 15 mL of dry DMAC. The flask was immersed in a 125 °C oil bath for 3 h. Analysis of the reaction mixture indicated that the only product produced was 2,2'-dinitrodiphenyl ether.

**Reaction under CO<sub>2</sub> Pressure.** A dry Fisher-Porter bottle was charged with 1.41 g (10 mmol) of o-nitrofluorobenzene, 3.00 g (30 mmol) of potassium bicarbonate, 0.1 g (0.25 mmol) of tetra-*N*-heptylammonium chloride, and 15 mL of dry DMAC. The vessel was sealed, evacuated, and then filled with CO<sub>2</sub> (150 psi). The evacuation refill process was repeated three times. The vessel was immersed in an oil bath maintained at 125 °C for 4 h. Analysis of this reaction mixture again indicated that only the diaryl ether (2,2'-dinitrodiphenyl ether) was produced.

**Mixed Carbonate Experiments.** A 25-mL flask was charged with 3.00 g (30 mmol) of potassium bicarbonate, 0.93 g (5 mmol) of 4-methylbenzyl bromide, 0.63 g (5 mmol) of benzyl chloride, 0.17 g (0.5 mmol) of tetrabutylphosphonium bromide and 15 mL of DMAC. The contents of the flask were stirred by means of a magnetic stirrer, and the flask was immersed in an oil bath maintained at 120 °C for 12 h. Aliquots of the reaction were removed periodically and analyzed by gas chromatography. The ratio of the three carbonates 1–3 did not change during the course of the reaction and remained approximately 1:2:1.

**Preparation of "Authentic" Mixed Carbonate.** A 25-mL flask equipped with a magnetic stirring bar was charged with 0.68 g (3.6 mmol) of potassium benzyl carbonate, 1.00 g (5.4 mmol) of 4-methylbenzyl bromide, 0.12 g (.18 mmol) of tetrabutyl-phosphonium bromide, and 10 mL of DMAC was heated at 120–125 °C for 3 h. The mixture was filtered and subjected to the usual aqueous workup conditions to afford the carbonate (approx. 85%), which was shown by gas chromatography to consist of a 4:80:16 mixture of 1:2:3.

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**Registry No.** 1, 3459-92-5; 2, 88730-69-2; 4, 13326-10-8; 5, 4560-41-2; 6, 91-23-6; Li<sub>2</sub>CO<sub>3</sub>, 554-13-2; Na<sub>2</sub>CO<sub>3</sub>, 497-19-8; K<sub>2</sub>CO<sub>3</sub>, 584-08-7; Cs<sub>2</sub>CO<sub>3</sub>, 534-17-8; CH<sub>3</sub>I, 74-88-4; CH<sub>3</sub>Cl, 74-87-3; PhCH<sub>2</sub>Cl, 100-44-7; 18-crown-6, 17455-13-9; tetrahexylammonium chloride, 5922-92-9; tetrabutylammonium bromide, 1643-19-2; tetramethylammonium bromide, 64-20-0; tetrahexylammonium bromide, 4328-13-6; tetrabutylphosphonium bromide, 3115-68-2; octyl bromide, 104-81-4; dimethyl carbonate, 616-38-6; potassium benzyl carbonate, 56135-94-5; potassium phenylmethoxide, 22379-62-0; potassium methyl carbonate, 14660-45-8; o-nitrofluorobenzene, 1493-27-2; 2,2'-dinitrodiphenyl ether, 2217-65-4; di-*n*-octyl carbonate, 1680-31-5; diallyl carbonate, 15022-08-9; bis(4-methylbenzyl) carbonate, 88730-70-5; potassium bicarbonate, 298-14-6.

# Nucleophilic Vinylic Substitution. The Reaction of 3,3-Dichloro-2-substituted-acrylonitriles with Sodium *p*-Toluenesulfinate

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Nucleophilic substitution of vinylic halogen in conjugated  $\pi$ -electron systems has been the subject of numerous investigations.<sup>1,2</sup> However, substitution studies in geminal dihalovinyl systems, e.g., 3,3-dichloroacrylonitriles or  $\beta$ , $\beta$ -

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