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 dried¹⁵ 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 KHCO₃. 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 KHCO₃, 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.¹⁵ 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 KHCO₃, 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 CO₂ 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 CO₂ (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; Li₂CO₃, 554-13-2; Na₂CO₃, 497-19-8; K₂CO₃, 584-08-7; Cs₂CO₃, 534-17-8; CH₃I, 74-88-4; CH₃Cl, 74-87-3; PhCH₂Cl, 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 π -electron systems has been the subject of numerous investigations.^{1,2} However, substitution studies in geminal dihalovinyl systems, e.g., 3,3-dichloroacrylonitriles or β , β -

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(2) Rappoport, Z. Adv. Phys. Org. Chem. 1969, 7, 1-114.

dichlorovinyl ketones are less numerous^{3,4} and present unique problems concerning the mechanism and geometry of the reaction intermediates.^{1,2,5} Typically, monosubstitution products are not isolated as the second halogen is more rapidly displaced than the first. Vinylic substitution reactions are further complicated whenever aryl sulfinate ions are employed as the reactive nucleophile. For example, sodium benzenesulfinate reacts with either 2,3- or 3,3-dichloroacrylonitrile to yield (phenylsulfonyl)acetonitrile.⁶ Under similar reaction conditions, benzenesulfinate salts react with 4,4-dichloro-3-buten-2-one to yield bis(phenylsulfonyl)methane.⁷ We have recently found that arylsulfinate salts react with either tetrachlorocyclopropene or 1,2-dichloro-3,3-difluorocyclopropene to yield (E)-1,2-bis(arylsulfonyl)ethene.⁸ In each of these examples, the reactions proceeded rapidly, and in most cases reaction intermediates could not be isolated.

Substitution rates of the β chlorine atoms in 3,3-dichloroacrylonitriles are strongly influenced by the nature of the α substituent.³ α alkyl groups, for example, retard the reaction rate and thus are logical candidates to attempt isolation of the monosubstitution products and determine the stereochemistry of the reaction mechanism.

Results and Discussion

In this study we report on the reaction of sodium ptoluenesulfinate with four α -substituted-3,3-dichloroacrylonitriles and the isolation and structure determination of the initially formed 2-substituted-3-chloro-3-(p-tolylsulfonyl)acrylonitriles.

The reaction of 3,3-dichloro-2-alkylacrylonitriles^{3,9,10} with sodium p-toluenesulfinate dihydrate (2) was carried out in a chilled solution of dimethylformamide (Scheme I). Slow addition of a slurry of 2 in DMF to a DMF solution of the chloroacrylonitrile 1 or 4 and stirring the reaction mixture at room temperature for a few hours or overnight and then pouring the mixture into water resulted in isolation of monosubstitution products 3 and 5. Thus, in contrast with 3,3-dichloroacrylonitrile,6 introduction of an alkyl or aryl group in the α position of 3,3-dichloroacrylonitrile resulted in lower reactivity of these compounds toward nucleophilic substitution by the ptoluenesulfinate anion. The reaction of acrylonitriles 1b and 4 with sodium *p*-toluenesulfinate was carried out with a 1:2 molar ratio although only the monosubstitution products were isolated. A 1:1 molar ratio of reactants was employed with 1a to simplify the purification of product **3a** from the unwanted disubstitution product.

¹H NMR spectra of monosubstituted p-(tolylsulfonyl)acrylonitrile products revealed that the general substitution pattern for dichloroacrylonitriles 1a, 1b, and 4 produced the Z isomers.¹¹ Thus the main pathway was the substitution of the chlorine atom trans to the nitrile group.

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This supports the generally accepted addition–elimination mechanism in which a rotation of the intermediate carbanion occurs preferentially in the direction to allow eclipsing of the smaller groups on the α and β carbon.¹² It is particularly dramatic proof in this case since this places the largest groups (tolylsulfonyl and *tert*-butyl) cis in the product.

The methyl group of (Z)-3a was considerably deshielded by the cis ary lsulfonyl group and appeared at δ 2.48, very close to the resonance of the methyl group on the benzene ring at δ 2.52. A weaker signal from the methyl group of (E)-3a appeared at δ 2.23. The isomer ratio (Z)-3a: (E)-3a was estimated from peak areas to be 10:1. Thus the content of (E)-3a in the reaction mixture did not exceed 10%. The acrylonitrile 4 also gave a mixture of two geometrical isomers (Z)-5 and (E)-5 in the ratio of 5:2. The ¹H NMR spectrum of this mixture showed again that the resonance of *tert*-butyl group of (Z)-5 was shifted downfield to δ 1.60 while the *tert*-butyl group of (*E*)-5 appeared at δ 1.37. The presence of a bulky *tert*-butyl group on the α -carbon atom in acrylonitrile 4 seems responsible for higher percentage of the (E)-5 isomer in the mixture of isomers. We were not able to establish unequivocally the structure of 3chloro-2-phenyl-3-(p-tolylsulfonyl)acrylonitrile (3b), but the general pattern of the nucleophilic substitution of investigated acrylonitriles and the results of TLC analysis indicate that in this case a sharp-melting solid (mp 122 °C) was essentially pure (Z)-3b. The compounds 3a and 5 were also analyzed by TLC and the presence of E and Z isomers in these products was further confirmed. Using silica gel

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⁽¹¹⁾ It is well established that the presence of strongly electronegative groups cis to the vinylic proton or an alkyl group causes downfield shift of resonances of vinyl, methyl, or methylene protons in their ¹H NMR spectra when compared with trans isomers. This phenomenon allows differentiation between E and Z isomers and elucidation of their ratio, see: Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 225.

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$$^{\alpha} \mathbf{X} = \mathbf{H}_{3} \mathbf{C} \mathbf{C}_{6} \mathbf{H}_{4} \mathbf{S} \mathbf{O}_{2}.$$

coated plates and chloroform-n-heptane (1:1) as a developing phase, we were able to obtain clear separation of Eand Z isomers of 3a and 5. The R_f values of (Z)-3a, (Z)-5, and also (Z)-3b were in very close range and had higher value than R_f of (E)-3a and (E)-5. Furthermore, in contrast with 3a and 5, TLC analysis of 3b showed the presence of only one component. Infrared spectra of (tolylsulfonyl)acrylonitriles showed extremely weak absorption of the cyano group at 2210 cm⁻¹ for 3b and 5 and of moderate intensity at 2218 cm⁻¹ for 3a.

The reaction of trichloroacrylonitrile (6) with sodium p-toluenesulfinate in a 1:1 or 1:3 molar ratio gave p-(tolylsulfonyl)acetonitrile (7) as the only product (Scheme II). In this case, the extensive substitution of all chlorine atoms renders the double bond of the intermediate product susceptible for addition of water, which results in the formation of 7 as the stable end product.

Experimental Section

Melting points are uncorrected. Sodium p-toluenesulfinate dihydrate (Aldrich Chemical Co.) was used as received. Elemental analyses were performed by Huffman Laboratories. Wheatridge, CO. The mass spectra were obtained on a DuPont 21-491 instrument, and the IR spectra were obtained on a Perkin-Elmer 1320 IR instrument. The ¹H NMR spectra were obtained on a Perkin-Elmer R-12A (60 MHz) spectrometer as solutions in deuteriochloroform with Me₄Si as an internal standard. The TLC separations were carried out on Eastman 13181 silica gel plates with fluorescent indicator and a mixture of chloroform-n-heptane (1:1) as a developing phase.

(Z)-3-Chloro-2-methyl-3-(p-tolylsulfonyl)acrylonitrile (3a). The acrylonitrile 1a^{9,10} (1.0 g, 7 mmol) was dissolved in 4 mL of DMF in a flask equipped with a magnetic stirrer, an addition funnel, and a thermometer. The solution was cooled to 10 °C, and a slurry of sodium *p*-toluenesulfinate dihydrate (1.6 g, 7 mmol) in 20 mL of DMF was added while stirring for 15 min. The mixture was stirred for an additional 3 h at room temperature and then poured into 200 mL of cold water. The colorless precipitate was filtered off, washed with water, dried in a dessicator, and sublimed under reduced pressure. Recrystallization from petroleum ether (bp 65-75 °C) afforded 1.2 g (64%) of 3a as colorless plates: mp 93-95 °C; IR(KBr) 2920, 2218, 1596, 1450, 1342, 1158, 1088, 928, 837, 813, 703 cm⁻¹; ¹H NMR δ (Z)-3a 7.87 (d, 2 H, J = 8 Hz, Ar H), 7.43 (d, 2 H, J = 8 Hz, Ar H), 2.52 (s,3 H, Ar CH₃), 2.48 (s, 3 H, CH₃), the resonance of the vinylic methyl group of (E)-3a appeared at δ 2.23; MS (70 eV), m/e 257, 255 (M⁺), 240, 155, 139, 124, 92, 91 (base).

Anal. Calcd for C₁₁H₁₀ClNO₂S (255.7): C, 51.66; H, 3.94; Cl, 13.86; N, 5.68; S, 12.54. Found: C, 51.16; H, 3.99; Cl, 14.07; N, 5.46: S. 12.13.

(Z)-3-Chloro-2-phenyl-3-(p-tolylsulfonyl)acrylonitrile (3b). A solution of 1b^{3,13} (0.6 g, 3 mmol) in 8 mL of DMF was cooled to 10-15 °C and while stirring a slurry of sodium p-

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toluenesulfinate 2, 1.3 g, 6 mmol) in 15 mL of DMF was slowly added. The mixture was stirred at room temperature for 2 days and then poured into 300 mL of water. The precipitated product was collected, washed with water, sublimed in vacuo, and recrystallized from petroleum ether (bp 65-75 °C) to give 0.65 g (67%) of 3b as colorless fluffy clusters: mp 122 °C; IR (KBr) 2910, 2210, 1592, 1448, 1350, 1163, 1090, 900, 811, 763, 702 cm⁻¹, ${}^{1}H$ NMR δ 7.43 (m, 9 H, Ar H), 2.47 (s, 3 H, Ar CH₃); MS (70 eV), m/e 319, 317 (M⁺), 253, 218, 155, 149, 141, 140, 139 (base), 127, 126, 124, 100, 92, 91, 89.

Anal. Calcd for C₁₆H₁₂ClNO₂S (317.8): C, 60.47; H, 3.81; Cl, 11.16; N, 4.41; S, 10.09. Found: C, 60.71; H, 3.98; Cl, 11.17; N, 4.36; S, 10.26.

2-(tert-Butyl)-3-chloro-2-(p-tolylsulfonyl)acrylonitrile (5). A slurry of 2 (1.2 g, 6 mmol) in 15 mL of DMF was slowly added to the stirred and cooled (10 °C) solution of the acrylonitrile $4^{9,10}$ (0.5 g, 3 mmol) in 5 mL of DMF. The suspension was then stirred at room temperature overnight and poured into 200 mL of water. After standing overnight, the precipitated solid was filtered off, washed with water, and sublimed in vacuo. Recrystallization from petroleum ether (bp 35-50 °C) furnished 0.46 g (55%) of a E and Z mixture of 5 as colorless crystals: mp 68–70 °C; IR (KBr) 2973, 2922, 2210, 1590, 1336, 1162, 1081, 888, 810 cm⁻¹; ¹H NMR δ (Z)-5, 7.87 (d, 2 H, J = 8 Hz, Ar H), 7.42 (d, 2 H, J = 8 Hz, Ar H), 2.48 (s, 3 H, Ar CH₃), 1.60 (s, 9 H, C(CH₃)₃), (E)-5, 1.37 (s, C(CH₃)₃) (the (Z)-5:(E)-5 ratio was 5:2); MS (70 eV), m/e 298,297(M⁺), 282, 218, 191, 157, 155, 144, 142, 139, 107, 92, 91 (base), 79.

Anal. Calcd for C₁₄H₁₆ClNO₂S (297.8): C, 56.46; H, 5.41; Cl, 11.90; N, 4.70; S, 10.77. Found: C, 56.31; H, 5.56; Cl, 11.79; N, 4.74; S, 10.66.

Reaction of 2,3,3-Trichloroacrylonitrile (6) with Sodium p-Toluenesulfinate. A slurry of 2 (4.1 g, 19 mmol) in 20 mL of DMF was added during 20 min to the stirred and cooled (10 °C) solution of trichloroacrylonitrile 6^{3,14} (1.0 g, 6 mmol) in 4 mL of DMF. Stirring was continued for additional 3 h at room temperature, and the mixture was poured into 200 mL of water. After the usual isolation procedure the precipitate was sublimed in vacuo and recrystallized from benzene to give 0.8 g (64%) of p-(tolylsulfonyl)acetonitrile (7) as colorless crystals: mp 149-150 °C [lit.6 mp 149.5-150.5 °C]; IR (KBr) 2980, 2925, 2257, 1595, 1380, 1318, 1152, 1082, 813, 736 cm⁻¹; ¹H NMR δ 7.94 (d, 2 H, J = 8 Hz, Ar H), 7.44 (d, 2 H, J = 8 Hz, Ar H), 4.05 (s, 2 H, CH₂), 2.50 (s, 3 H, CH₃); MS (70 eV), m/e 195 (M⁺), 155, 139, 124, 123, 92, 91 (base), 77.

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Registry No. 1a, 31413-58-8; 1b, 31413-60-2; (Z)-3a, 88703-71-3; (E)-3a, 88703-72-4; 3b, 88703-73-5; 4, 42867-44-7; (Z)-5, 88703-74-6; (E)-5, 88703-75-7; 6, 16212-28-5; 7, 5697-44-9; sodium toluenesulfinate, 824-79-3.

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Structure and Dynamics of Tröger's Base and Simple Derivatives in Acidic Media

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Tröger's base $(1)^{1-4}$ was the first amine, dissymmetric solely due to pyramidal geometry about nitrogen, to be

⁽¹⁾ IUPAC name: 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1.5]diazocine

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