without further purification: NMR (CCl_4 with Me_4Si) δ 5.82 (1 H, br s), 6.84–7.44 (4 H, AA'BB' m); IR (neat) 3050, 2990, 2150, 1565, 1450, 1435, 1315, 1200, 1180, 875, 740 cm^{-1}. Anal. Calcd for $C_7H_5N_3S_2$: C, 43.06; H, 2.58; N, 21.52. Found: C, 43.30; H, 2.42; N, 21.30.

Similarly **9** and sodium azide gave a 73% yield of 1,3-dithiol-2-yl azide (**10**) as a pale yellow liquid, which was unstable at room temperature: NMR (CCl_4 with Me_4Si) δ 5.95 (1 H, br s), 6.22 (2 H, s); IR (neat) 2180, 1520, 1305, 1295, 1175, 860, 785, 680 cm^{-1}.

Reaction of 1,3-Dithiol-2-yl, 1,3-Benzodithiol-2-yl, and Tropyl Azides (10, 2, and 12) with Trityl Tetrafluoroborate (6). To a stirred, ice-cooled solution of 1.70 g (8.7 mmol) of **2** in 20 mL of anhydrous acetonitrile was added dropwise, over a period of 40 min, a solution of 2.97 g (9 mmol) of **6** in 20 mL of anhydrous acetonitrile. The mixture was stirred for 0.5 h at 0–3 °C and diluted with 250 mL of anhydrous ether. The resulting precipitate was collected and washed with ether to give 1.82 g of **1** as near-white crystals, mp 149–150 °C dec (lit.[2] mp 150–150.5 °C dec). The filtrate was washed with water, dried over Na_2SO_4, and evaporated. The residue was chromatographed on a silica gel column (eluent hexane) to give 2.23 g (90%) of trityl azide, mp 65–66 °C (lit.[10] mp 64–65 °C).

In a manner similar to that described above, 1.06 g (7.3 mmol) of **10** and 2.64 g (8 mmol) of **6** were allowed to react to give 1.39 g (81%) of **9** and 1.66 g (70%) of trityl azide.

Similarly, 1.18 g (78%) of **11** and 1.53 g (63%) of trityl azide were obtained from 1.13 g (8.5 mmol) of **12** and 2.90 g (8.8 mmol) of **6**.

Registry No. 1, 57842-27-0; **2**, 73198-37-5; **6**, 341-02-6; **9**, 53059-75-9; **10**, 73198-38-6; **11**, 27081-10-3; **12**, 698-84-0; trityl azide, 14309-25-2.

(10) W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

Halogenated Ketenes. 33. Cycloaddition of Ketenes and Trimethylsilyl Enol Ethers

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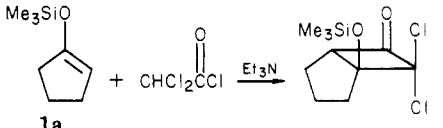
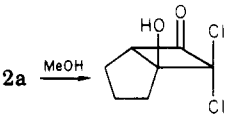
We recently reported the cycloaddition of dichloroketene with a number of trimethylsilyl enol ethers to produce trimethylsiloxy- and hydroxy-functionalized cyclobutanones.[1] In view of the general synthetic utility of the trimethylsilyl enol ethers as masked enol equivalents[2] and the ease of preparation from readily available aldehydes and ketones,[3] we now report on the cycloaddition of several mono- and disubstituted ketenes with trimethylsilyl enol ethers. The ketenes are generated in the presence of the trimethylsilyl enol, thus resulting in 3-(trimethylsiloxy)-cyclobutanones in good yield. Previous reports of cycloadditions of silyl enol ethers with ketenes are mainly limited to dichloroketene generated by the zinc dechlorination of trichloroacetyl chloride.[1,4a,b]

The generation of dichloroketene by the dehydrochlorination of dichloroacetyl chloride in the presence of the trimethylsilyl enol ether derived from cyclopentanone (**1a**) resulted in the [2 + 2] cycloaddition product.[5] Vacuum



1a **2a**

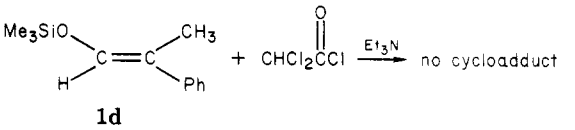
distillation provided the siloxycyclobutanone **2a** in 77% yield. Spectral data for **2a** were in accord with those of an authentic sample prepared by the zinc dehalogenation method.[4a] Several other mono- and disubstituted ketenes were found to react smoothly with trimethylsilyl enol ether **1a** to provide the [2 + 2] cycloadducts (see Table I). Reaction of the trimethylsilyl substituent with methanol afforded the bridgehead hydroxycyclobutanones without rearrangement.



3a

The silyl enol ethers derived from isobutyraldehyde (**1b**) and 3-cyclohexenecarboxaldehyde (**1c**) were also found to yield cycloadducts with the halogenated ketenes as seen in Table II. The yields of the cycloadducts of dichloroketene and the three silyl enol ethers were about the same regardless of the method of generation of the ketene, i.e., zinc dehalogenation of trichloroacetyl chloride[6] or dehydrohalogenation of dichloroacetyl chloride. Dichloroketene also gave the highest yield with the silyl enol ethers **1b** and **1c**, while the yield decreased with methylchloroketene and phenylchloroketene. Although a small amount of cycloadduct could be observed, as evidenced by a band in the infrared at 1800 cm^{-1}, it was not possible to isolate the cycloadduct of phenylchloroketene with either **1b** or **1c**. The major product in these reactions was a red viscous polymeric material.

The attempted cycloaddition of dichloroketene, generated by the dehydrohalogenation of dichloroacetyl chloride, with the trimethylsilyl enol ether of 2-phenylpropanal (**1d**) was unsuccessful. However, this cycloaddition proceeds



1d

readily when dichloroketene is generated by the zinc dehalogenation of trichloroacetyl chloride and is consistent with an earlier report.[1,4a] Apparently, the zinc or zinc chloride has a catalytic role in the reaction.

The reactions of unsymmetrical ketenes were found to be quite sensitive to steric influences. The cycloaddition of methylchloroketene with trimethylsilyl enol ether **1a** yielded two products as evidenced by the NMR spectrum of the crude reaction mixture. These distilled products were found to be in a ratio of 2.5:1. The major isomer was assigned the structure **4a**$_1$ with the 7-methyl substituent in the endo position, and the minor isomer, **4a**$_2$, has the 7-methyl in the exo position. These assignments were based on the chemical shifts of the 7-methyl and the H_5 protons in the NMR spectrum as seen in Table III. This assignment is consistent with literature precedents for the closely related cycloaddition products of cyclopentadiene and alkylhaloketenes, where the downfield proton H_5 has

(1) Brady, W. T.; Lloyd, R. M. *J. Org. Chem.* **1979**, *44*, 2560.
(2) Rasmussen, J. K. *Synthesis* **1977**, 91.
(3) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.
(4) (a) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 3173. (b) Hassner, A.; Pinnick, H. W.; Ansell, J. M. *J. Org. Chem.* **1978**, *43*, 1774.
(5) This result conflicts with ref 4a, which states that the cyclobutanone **2a** was not observed by the dehydrohalogenation method.
(6) Bak, D. A.; Brady, W. T. *J. Org. Chem.* **1979**, *44*, 107.

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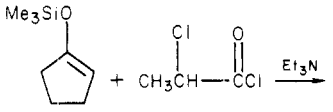
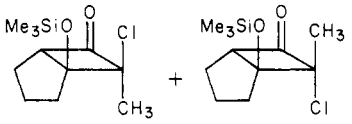


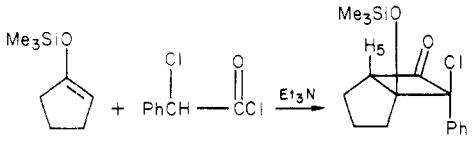
1a



$4a_1$ $4a_2$

been identified as the *endo*-methyl isomer.[7] Reaction of the trimethylsilyl substituent with moist methanol gave the alcohols $5a_1$ and $5a_2$ in a ratio of 2.5:1 without isomerization.

The cycloadduct of phenylchloroketene and silyl enol ether **1a** afforded only the *endo*-phenyl isomer (**6a**) as expected. This assignment is based on the H_5 chemical



1a 6a

shift as seen in Table III. This assignment is also in accord with results obtained with the cyclopentadiene adduct with this ketene.[8]

In all of the cycloadditions with trimethylsilyl enol ether **1a**, a preference for the larger substituent of an unsymmetrical ketene to appear in the endo position is observed. When there is a large difference in size between the two ketene substituents, the isomer with the larger substituent in the exo position is not observed. In the cycloaddition of chloroketene and phenoxyketene, only the *endo*-chloro (**7a**) and *endo*-phenoxy (**8a**) cycloadduct isomers were observed. The stereochemistry of the cycloaddition of phenoxymethylketene, however, appears somewhat anomalous. The phenoxy group occupies the exo position while the methyl group is found in the endo position as evidenced by NMR spectroscopy. Examination of molecular models suggests that the methyl group has a larger steric requirement than the oxygen atom and that the phenyl group is significantly removed from the reaction site. A similar result was observed with cyclopentadiene and phenoxymethylketene.[9]

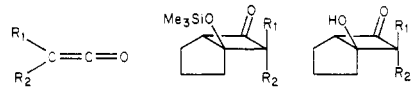
In conclusion, the reaction of ketenes and trimethylsilyl enol ethers proceeds readily to yield [2 + 2] cycloadducts when the ketene is generated in situ by dehydrohalogenation of an appropriately substituted acid chloride. Mono- and disubstituted ketenes have been found to react in both a regio- and stereospecific manner with trimethylsilyl enol ethers to give functionalized cyclobutanones.

Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer R-24B nuclear magnetic resonance spectrometer with carbon tetrachloride or deuteriochloroform as the solvent with tetramethylsilane or chloroform as the internal standard. Infrared spectra were obtained with a Beckman IR 33, and mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer.

Hexane and triethylamine were distilled from sodium–potassium alloy prior to use. The trimethylsilyl enol ethers used in this study were prepared by the procedure of House[3] and were redistilled prior to use.

Table I. Cycloadducts of Ketenes and 1-(Trimethylsiloxy)cyclopentene



R_1	R_2	cyclo-adduct	% yield	hydrolysis product	% yield
Cl	Cl	**2a**	77	**3a**	87
Cl	CH_3	**4a**	79	**5a**	91
Cl	Ph	**6a**	80	**7a**	94
PhO	CH_3	**8a**	79	**9a**	94
H	PhO	**10a**	68	**11a**	89
H	CH_3O	**12a**	67	**13a**	84
H	Cl	**14a**	53	**15a**	71

Typical Procedure for Ketene Cycloadditions with Trimethylsilyl Enol Ethers. A solution of 0.03 mol of freshly distilled acid chloride in 250 mL of dry hexane was added over 4 h to a stirred solution of 0.06 mol of trimethylsilyl enol ether and 0.032 mol of triethylamine in 250 mL of dry hexane under a nitrogen atmosphere. The reaction was stirred for 4 h after the addition was complete. The triethylammonium salt was removed by filtration, and the reaction solution was concentrated. The residue was vacuum distilled to give the product where possible or isolated by column chromatography on silica gel.[10]

7,7-Dichloro-1-(trimethylsiloxy)bicyclo[3.2.0]hept-6-one (2a).[4a] From 9.36 g (0.06 mol) of silyl enol ether **2a**, 3.6 g (0.035 mol) of triethylamine, and 4.4 g (0.03 mol) of dichloroacetyl chloride was isolated 6.12 g (77%) of **2a** with spectral data identical with that of the known compound.

7,7-Dichloro-1-hydroxybicyclo[3.2.0]hept-6-one (3a).[4a] Reaction of 2.0 g (0.075 mol) of siloxycyclobutanone **2a** with moist methanol afforded 1.28 g (87%) of **3a** as a crystalline solid, mp 57–59 °C. Spectral data were identical with that of the known compound.

7-Chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-6-one (4a).[4b] From 9.36 g (0.06 mol) of silyl enol ether **1a**, 3.66 g (0.029 mol) of 2-chloropropanoyl chloride, and 3.23 g (0.032 mol) of triethylamine was obtained 5.75 g (79%) of **4a** as a pale yellow oil after distillation at 79–85 °C (0.06 mm). Two isomers were indicated in the NMR spectrum with a ratio of 2:1 (endo methyl/exo methyl); IR 1790, 1450, 1328, 1255, 1120, 905, 845 cm^{-1}; NMR endo isomer δ 3.63 (m, 1 H), 1.48 (s, 3 H); exo isomer δ 3.35 (m, 1 H), 1.62 (s, 3 H); both isomers δ 2.3–1.6 (m, 6 H), 0.25 (s, 9 H); mass spectrum, *m/e* (%) 248 (M + 2, 0.9), 246 (1.6), 233 (0.9), 231 (1.7), 205 (2.7), 203 (6.3), 183 (61.3), 156 (50.5), 141 (6.3), 127 (4.5), 94 (20.7), 93 (20.7), 73 (100).

7-Chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-6-one (5a). Hydrolysis of 2.1 g (0.085 mol) of (trimethylsiloxy)cyclobutanone **4a** with methanol containing several drops of dilute hydrochloric acid gave 1.34 g (91%) of **5a** as a clear colorless oil after distillation at 53–55 °C (0.1 mm); IR 3600–3200, 1785, 1450, 1325, 1215, 1106, 845 cm^{-1}. Two isomers were indicated in the NMR spectrum in a ratio of 2:1 (endo methyl/exo methyl); NMR endo isomer δ 3.58 (m, 1 H), 1.43 (s, 3 H); exo isomer δ 3.31 (m, 1 H), 1.59 (s, 3 H); both isomers δ 3.37 (br s, 1 H), 2.2–1.6 (m, 6 H); mass spectrum, *m/e* (%) 176 (M + 2, 1.0), 174 (2.1), 138 (16.5), 131 (6.8), 129 (15.5), 111 (100), 90 (57.3), 84 (91.3), 83 (54.4), 55 (42.7).

7-Chloro-7-phenyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-6-one (6a). Addition of 5.67 g (0.03 mol) of phenylchloroacetyl chloride to 9.4 g (0.06 mol) of silyl enol ether **1a** and 3.33 g (0.033 mol) of triethylamine afforded 9.8 g of crude reaction material. Attempted distillation of a portion of this material led to extensive decomposition of the product. When 3.4 g of this material was chromatographed on silica gel with hexane as the eluant,[10] 2.61 g (80%) of **6a** was isolated as a clear colorless oil: IR 1788, 1455, 1328, 1257, 1105, 845 cm^{-1}; NMR δ 7.24 (m, 5 H), 3.7 (m, 1 H), 2.3–1.6 (m, 6 H), 0.31 (s, 1 H); mass spectrum, *m/e* (%) 310 (M + 2, 1.3), 308 (3.7), 2.67 (4.0), 2.65 (3.4), 245 (6.3), 56 (100), 155

(7) Brady, W. T.; Roe, R. *J. Am. Chem. Soc.* **1970**, *92*, 4618.
(8) Brady, W. T.; Parry, F. H.; Roe, R.; Hoff, E. F. *Tetrahedron Lett.* **1970**, 819.
(9) Brady, W. T.; Parry, F. H.; Stockton, J. D. *J. Org. Chem.* **1971**, *36*, 1486.
(10) Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 248.

Table II. Cycloadducts of Chloroketenes and Silyl Enol Ethers

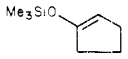
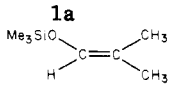
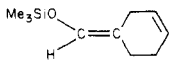
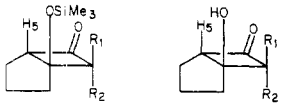
silyl enol ether	product, % yield			
	$Cl_2C{=}C{=}O$	$CH_3CCl{=}C{=}O$	$PhCCl{=}C{=}O$	$Cl_2C{=}C{=}O$ (dehalogenation)
 1a	2a, 77	4a, 79	6a, 80	794a
 1b	2b, 82	4b, 61	trace	891, 924a
 1c	2c, 70	4c, 49	trace	791

Table III. Proton NMR Chemical Shift Data for H_5 (δ)



R_1	R_2	(trimethylsiloxy)cyclobutanone	hydroxycyclobutanone
Cl	Cl	3.60	3.60
Cl	CH_3	3.62	3.58
CH_3	Cl	3.35	3.31
Cl	Ph	3.69	3.59
PhO	CH_3	3.72	3.61
H	PhO	3.33	3.36
H	CH_3O	3.28	3.26
H	Cl	3.27	3.32

(31.3), 141 (11.3), 128 (10.6), 105 (10.0), 85 (22.5), 73 (66.3).

***endo*-7-Chloro-1-hydroxy-7-phenylbicyclo[3.2.0]hept-6-one (7a).** Hydrolysis of 1.30 g (0.0043 mol) of **6a** with methanol afforded 0.95 g (94%) of **7a** as a pale yellow oil: IR 3600–3300, 1790, 1458, 1329, 1220, 1110, 848, 745 cm^{-1}; NMR δ 7.3 (m, 5 H), 4.75 (br s, 1 H), 3.69 (m, 1 H), 2.2–1.6 (m, 6 H); mass spectrum, *m/e* (%) 238 (3.2), 236 (9.9), 201 (17.9), 200 (2114), 199 (14.3), 171 (21.0), 152 (79.3), 111 (100), 105 (32.1), 84 (28.6), 58 (42.3).

***endo*-7-Methyl-7-phenoxy-1-(trimethylsiloxy)bicyclo[3.2.0]heptan-6-one (8a).** From 4.6 g (0.025 mol) of 2-(phenoxy)propanoyl chloride, 3.03 g (0.03 mol) of triethylamine, and 7.8 g (0.05 mol) of silyl enol ether **1a** was isolated 6.01 g (79%) of a white crystalline solid: mp 45–47 °C; IR 1782, 1605, 1260, 1225, 845, 760 cm^{-1}; NMR δ 7.1 (m, 5 H), 3.72 (m, 1 H), 2.2–1.6 (m, 6 H), 1.42 (s, 3 H), 0.33 (s, 9 H); mass spectrum, *m/e* (%) 304 (M^+, 34.8), 261 (5.0), 248 (10.1), 187 (37.1), 183 (48.8), 156 (48.3), 121 (25.8), 105 (16.3), 77 (15.7), 73 (100).

Anal. Calcd for $C_{17}H_{24}O_3Si_1$: C, 67.08; H, 7.93. Found: C, 67.34; H, 7.88.

1-Hydroxy-*endo*-7-methyl-7-phenoxybicyclo[3.2.0]heptan-6-one (9a). Hydrolysis of 1.8 g (0.006 mol) of **8a** gave 1.31 g (94%) of **9a** as a clear colorless oil: IR 3600–3300, 1783, 1602, 1498, 1230, 765 cm^{-1}; NMR δ 7.07 (m, 5 H), 5.3 (s, 1 H), 3.61 (m, 1 H), 2.2–1.6 (m, 6 H), 1.38 (s, 3 H); mass spectrum, *m/e* (%) 232 (M^+, 35.7), 187 (7.1), 176 (7.8), 121 (78.6), 111 (51.0), 105 (14.3), 95 (100), 77 (35.7).

***endo*-7-Phenoxy-1-(trimethylsiloxy)bicyclo[3.2.0]heptan-6-one (10a).** From 5.1 g (0.03 mol) of (phenoxy)acetyl chloride, 9.4 g (0.06 mol) of silyl enol ether **1a**, and 3.23 g (0.032 mol) of triethylamine was isolated 9.1 g of crude product. Column chromatography of 2.46 g of the product mixture on silica gel gave 1.84 g (68%) of **10a** as a pale yellow oil. Attempted distillation of a portion of the crude material led to decomposition: IR 1785, 1601, 1490, 1255, 845 cm^{-1}; NMR δ 7.1 (m, 5 H), 5.25 (d, 1 H), 3.33 (m, 1 H), 2.2–1.6 (m, 6 H), 0.31 (s, 1 H); mass spectrum, *m/e* (%) 290 (10.7), 169 (18.6), 156 (50.7), 155 (40.0), 141 (16.4), 77 (11.5), 73 (100).

1-Hydroxy-*endo*-7-phenoxybicyclo[3.2.0]heptan-6-one (11a). From 0.81 g (0.0028 mol) of **10a** was recovered 0.54 g (89%) of **11a** after hydrolysis with methanol: IR 3600–3300, 1788, 1600, 1225, 1120, 880 cm^{-1}; NMR δ 7.2 (m, 5 H), 5.45 (d, 1 H), 4.71 (s, 1 H), 3.36 (m, 1 H), 2.3–1.6 (m, 6 H); mass spectrum, *m/e* (%), 218 (M^+, 42.0), 200 (5.8), 166 (7.3), 111 (100), 107 (79.5), 94 (43.5), 86 (23.2), 77 (42.0).

***endo*-7-Methoxy-1-(trimethylsiloxy)bicyclo[3.2.0]heptan-6-one (12a).** From 2.7 g (0.025 mol) of methoxyacetyl chloride, 7.02 g (0.045 mol) of silyl enol ether **1a**, and 3.03 g (0.03 mol) of triethylamine was isolated 5.36 g of crude product. Column chromatography of 1.34 g (25%) of the crude product gave 0.97 g (68%) of **12a**: IR 1785, 1460, 1340, 1255, 1150, 860 cm^{-1}; NMR δ 4.46 (d, 1 H), 3.52 (s, 3 H), 3.28 (m, 1 H), 2.2–1.6 (m, 6 H), 0.31 (s, 9 H); mass spectrum, *m/e* (%) 228 (M^+, 2.5), 200 (1.9), 169 (25.4), 156 (18.6), 155 (8.5), 111 (47.5), 73 (100).

1-Hydroxy-*endo*-7-methoxybicyclo[3.2.0]heptan-6-one (13a). Hydrolysis of 0.68 g (0.003 mol) of **12a** with methanol gave 0.40 g (87%) of **13a** as a clear colorless oil which slowly darkened: IR 3600–3200, 1785, 1465, 1230, 1125 cm^{-1}; NMR δ 5.5 (s, 1 H), 4.56 (d, 1 H), 3.53 (s, 3 H), 3.26 (m, 1 H), 2.2–1.5 (m, 6 H); mass spectrum, *m/e* (%) 156 (M^+, 12.5), 111 (64.3), 100 (35.7), 72 (53.6), 55 (57.1), 45 (100).

***endo*-7-Chloro-1-(trimethylsiloxy)bicyclo[3.2.0]heptan-6-one (14a).** From 2.83 g (0.025 mol) of dichloroacetyl chloride, 3.03 g (0.03 mol) of triethylamine, and 7.8 g (0.05 mol) of silyl enol ether **1a** was isolated 4.83 g of crude reaction product. Distillation at 52–58 °C (0.05 mm) gave 3.08 g (53%) of **14a** as a pale yellow oil: IR 1795, 1455, 1260, 1120, 860 cm^{-1}; NMR δ 4.84 (d, 1 H), 3.27 (m, 1 H), 2.2–1.5 (m, 6 H), 0.21 (s, 9 H); mass spectrum, *m/e* (%), 234 (M + 2, 2.5), 232 (7.6), 219 (1.7), 2.7 (5.9), 204 (2.1), 169 (100), 156 (10.2), 111 (3.4), 107 (7.3), 73 (23.7).

***endo*-7-Chloro-1-hydroxybicyclo[3.2.0]heptan-6-one (15a).** Hydrolysis of 2.3 g (0.009 mol) of **14a** afforded 1.18 g (71%) of **15a** as a colorless oil after distillation at 58–63 °C (0.06 mm); IR 3600–3300, 1785, 1455, 1220, 1110, 810 cm^{-1}; NMR δ 5.41 (s, 1 H), 5.01 (d, 1 H), 3.32 (m, 1 H), 2.2–1.5 (m, 6 H); mass spectrum, *m/e* (%) 162 (M + 2, 10.8), 160 (31.1), 125 (9.7), 111 (100), 97 (48.6), 83 (2.7), 55 (45.9).

2,2-Dichloro-4,4-dimethyl-3-(trimethylsiloxy)cyclobutanone (2b).[1] From 6.62 g (0.045 mol) of dichloroacetyl chloride, 5.56 g (0.055 mol) of triethylamine, and 5.76 g (0.04 mol) of silyl enol ether **1b** was isolated 8.3 g (82%) of **2b** which gave spectra identical with those of an authentic sample.

2,2-Dichloro-3-hydroxy-4,4-dimethylcyclobutanone (3b).[1] Hydrolysis of **2b** afforded **3b** as previously described. Spectra were identical with those of an authentic sample.

2-Chloro-2,4,4-trimethyl-3-(trimethylsiloxy)cyclobutanone (4b). From 5.76 g (0.04 mol) of silyl enol ether **1b**, 7.35 g (0.04 mol) of 2-chloropropanoyl chloride, and 5.6 g (0.055 mol) of triethylamine in refluxing hexane was isolated 8.1 g of a mixture of **4b** and the vinyl ester in a 4:1 ratio after distillation at 35–44 °C (0.05 mm). Chromatography on silica gel of 2.025 g (25%) of the mixture gave 1.43 g (61%) of **4b** as a pale yellow oil: IR 1802, 1250, 1135, 895 cm^{-1}; NMR δ 4.12 (s, 1 H), 1.48 (s, 3 H), 1.24 (s, 3 H), 1.05 (s, 3 H), 0.15 (s, 9 H); mass spectrum, *m/e* (%) 199 (M − 35, 5.1), 166 (18.3), 164 (52.2), 144 (33.0), 126 (18.30), 73 (100).

2-Chloro-3-hydroxy-2,4,4-trimethylcyclobutanone (5b). Hydrolysis of 1.18 g (0.005 mol) of **4b** with methanol gave 1.01 g (87%) of **5b** as a crystalline solid: mp 74–75 °C; IR 3600–3300, 1795, 1460, 1140, 1090, 790 cm^{-1}; NMR δ 4.37 (s, 1 H), 3.13 (br s, 1 H), 1.65 (s, 3 H), 1.39 (s, 3 H), 1.22 (s, 3 H); mass spectrum,

m/e (%) 127 (M - 35, 2.7), 99 (5.4), 92 (8.9), 70 (100), 57 (51.8), 41 (75.0).

Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.7; H, 6.82. Found: C, 51.7; H, 6.75.

3-Cyclohexenespiro-3′,3′-dichloro-4′-(trimethylsiloxy)-cyclobutan-2′-one (2c).[1] From 9.1 g (0.05 mol) of silyl enol ether **1c**, 5.88 g (0.04 mol) of dichloroacetyl chloride, and 5.56 g (0.055 mol) of triethylamine was isolated 8.2 g (70%) of **2b** as a pale yellow oil with spectra identical with those of an authentic sample.

3-Cyclohexenespiro-3′,3′-dichloro-4′-hydroxycyclobutan-2′-one (3c).[1] Hydrolysis of **2c** with methanol afforded **3c** as previously described. Spectra were identical with those of an authentic sample.

3-Cyclohexenespiro-3′-chloro-3′-methyl-4′-(trimethylsiloxy)cyclobutan-2-one (4c). From 7.28 g (0.04 mol) of silyl enol ether **1c**, 6.62 g (0.045 mol) of 2-chloropropanoyl chloride, and 6.06 g (0.06 mol) of triethylamine in refluxing hexane was isolated 5.35 g (49%) of **4c** as a pale yellow oil after distillation at 92–98 °C (0.04 mm); IR 1790, 1610, 1445, 1252, 1170, 845 cm^{-1}; NMR δ 5.74 (m, 2 H), 4.28 (m, 1 H), 2.3–1.9 (m, 6 H), 1.6–1.4 (m, 3 H), 0.26 (s, 9 H); mass spectrum, *m/e* (%) 274 (M + 2, 0.2), 272 (0.5), 237 (8.3), 182 (16.7), 166 (15.3), 164 (44.4), 128 (16.7), 110 (53.0), 92 (92.0), 73 (100).

3-Cyclohexenespiro-3′-chloro-4′-hydroxy-3′-methylcyclobutan-2-one (5c). Hydrolysis of 1.25 g (0.0046 mol) of **4c** gave 0.72 g (78%) of **5c** as a pale yellow oil after distillation at 88–94 °C (0.07 mm): IR 3550–3200, 1785, 1625, 1438, 1250, 1170, 1090 cm^{-1}; NMR δ 5.5 (m, 2 H), 4.15 (s, 1 H), 3.2 (s, 1 H), 2.3–1.7 (m, 6 H), 1.6–1.4 (m, 3 H); mass spectrum, *m/e* (%) 202 (M + 2, 0.5), 200 (1.4), 110 (95.0), 92 (77.9), 81 (54.9), 79 (100), 77 (51.9), 63 (93.5).

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Registry No. 1a, 19980-43-9; **1b**, 6651-34-9; **1c**, 51075-25-3; **2a**, 73210-23-8; **2b**, 66324-00-3; **2c**, 70320-74-0; **3a**, 66324-06-9; **3b**, 66324-05-8; **3c**, 70320-75-1; *endo*-**4a**, 73199-34-5; *exo*-**4a**, 73245-86-0; **4b**, 73199-35-6; **4c**, 73199-36-7; *endo*-**5a**, 73199-37-8; *exo*-**5a**, 73245-87-1; **5b**, 73199-38-9; **5c**, 73199-39-0; *endo*-**6a**, 73199-40-3; *endo*-**7a**, 73199-41-4; *endo*-**8a**, 73199-42-5; *endo*-**9a**, 73199-43-6; *endo*-**10a**, 73199-44-7; *endo*-**11a**, 73199-45-8; *endo*-**12a**, 73199-46-9; *endo*-**13a**, 73199-47-0; *endo*-**14a**, 73199-48-1; *endo*-**15a**, 73199-49-2; phenylchloroacetyl chloride, 2912-62-1; 2-phenoxypropanoyl chloride, 122-35-0; methoxyacetyl chloride, 38870-89-2; phenoxyacetyl chloride, 701-99-5; 2-chloropropanoyl chloride, 7623-09-8; dichloroacetyl chloride, 79-36-7; 2-methylpropenyl 2-chloropropanoate, 73199-50-5.

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Ion Pairing of Arenediazonium Salts in Solvents of Low Polarity

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Due to the ionic nature of arenediazonium salts, their reactions are usually conducted in aqueous media or in highly polar organic solvents, such as methanol or dimethyl sulfoxide. In such solvents, significant interactions between an arenediazonium cation and its counterion are usually absent. For example, Penton and Zollinger[1] have observed that the azo coupling rates of *p*-toluenediazonium tetrafluoroborate and bisulfate with *N,N*-dimethylaniline are exactly the same in either acetonitrile or nitromethane.

Solubility of arenediazonium salts in less polar organic solvents such as chlorocarbons and benzene may be achieved by attaching lipophilic groups to the aromatic ring of the arenediazonium cation,[2-4] by anion interchange,[5] or by complexation with crown ethers.[6] For the determination of the importance of ion pairing for arenediazonium salts in organic solvents of low polarity, a kinetic and spectroscopic investigation was undertaken. The results of this study are now reported.

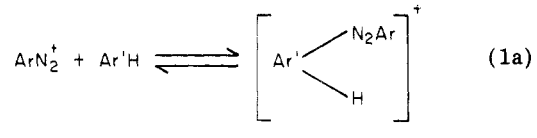
Table I. Observed Pseudo-First-Order Rate Constants for the Coupling of *p-tert*-Butylbenzenediazonium Hexafluorophosphate (2) with *N,N*-Dimethylaniline (3) in 1,2-Dichloroethane at 25.0 °C

10^4[2], M	10^4[3], M	$10^4 k_{obsd}$, s^{-1}
0.149	2.56	4.22
0.149	4.25	9.18
0.149	5.94	16.0

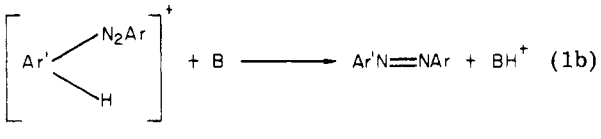
Results and Discussion

The arenediazonium salts employed in this investigation are *p-tert*-butylbenzenediazonium tetrafluoroborate[4] and hexafluorophosphate, **1** and **2**, respectively. Observation of anion effects with counterions as similar as tetrafluoroborate and hexafluorophosphate would indicate that even more important effects should be expected for dissimilar anions. Both arenediazonium salts have reasonable solubility in chlorocarbon solvents, but the solubility of **1** is greater than that of **2** in such media.

Azo Coupling Reactions. We have previously reported[7] a detailed kinetic study of the reaction of **1** with excess *N,N*-dimethylaniline (**3**) in 1,2-dichloroethane at 25 °C. The reaction was found to be first order in arenediazonium salt and second order in **3**, with a third-order rate constant of 7.05×10^2 s^{-1} M^{-2}. The observed rate expression is consistent with an S_E2 mechanism (eq 1) in which proton abstraction from the σ complex by a second molecule of **3** is rate limiting.



(1a)



(1b)

When the reaction of the hexafluorophosphate salt **2** with **3** was conducted under the same conditions, the observed pseudo-first-order rate constants listed in Table I were obtained. Yields of the anticipated coupling product 4-*tert*-butyl-4′-(dimethylamino)azobenzene were quantitative. For the coupling reaction of **2** and **3**, a simple second-order behavior in **3** is not observed. Instead the kinetic data are consistent with the rate expression[8] in eq 2. Apparently, the hexafluorophosphate anion is sufficiently basic to compete with **3** in removing the proton

$$\text{rate} = k_2[2][3] + k_3[2][3]^2 \quad (2)$$

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(8) If the rate = $k_2[2][3] + k_3[2][3]^2$ under the pseudo-first-order conditions employed, $k_{obsd}/[3] = k_{appar} = k_2 + k_3[3]$. A plot of k_{appar} vs. [3] was perfectly linear with an intercept of k_2 and a slope of k_3.

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