Registry No. 1, 57-88-5; 1 nitrite, 6709-70-2; 2, 521-18-6; 2 nitrite, 86727-47-1; 3, 67776-06-1; EtONO, 109-95-5; *n*-PrONO, 543-67-9; *n*-BuONO, 544-16-1; *n*-PentONO, 463-04-7; *i*-BuONO, 542-56-3; *i*-PentONO, 110-46-3; *neo*-PentONO, 77212-96-5; *i*-PrONO, 541-42-4; *sec*-BuONO, 924-43-6; *t*-BuONO, 540-80-7; EtOH, 64-17-5; *n*-PrOH, 71-23-8; *n*-BuOH, 71-36-3; *i*-BuOH, 78-83-1; *neo*-PentOH, 75-84-3; benzyl alcohol, 100-51-6; *p*-nitrobenzyl alcohol, 619-73-8; 2-ethoxyethyl alcohol, 110-80-5; *i*-PrOH, 67-63-0; 2-adamantyl alcohol, 700-57-2; 1-phenyl-2-propyl alcohol, 698-87-3; *t*-BuOH, 75-65-0; *N*-acetyl-D,L-penicillamine, 59-53-0; *tert*-butyl thionitrite, 15459-95-7; benzyl thionitrite, 4862-09-3; *tert*-butyl mercaptan, 75-66-1; benzyl mercaptan, 100-53-8.

Synthesis, Regiochemistry, and Reactions of Dichlorocyclobutenones[1]

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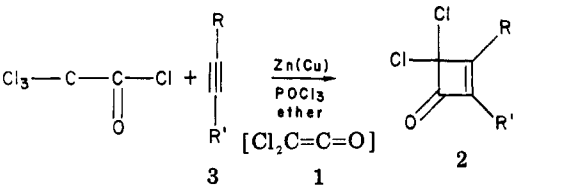
Dichlorocyclobutenones previously obtained only with difficulty were prepared by the cycloaddition of dichloroketene with alkynes in the presence of phosphorus oxychloride in fair to good yields. The regiochemistry of addition can be rationalized on the basis of electronic factors except in the case of (trimethylsilyl)acetylenes which exhibit unusual regioselectivity. Thermolysis of the cyclobutenones in the presence of alcohol led to electrocyclic ring cleavage, giving vinylketene intermediates which were trapped by the alcohol; on the other hand, reaction with alkoxide took place at room temperature and led either to ring opening or allylic substitution.

Our interest in cyclobutanone chemistry[2] led us to a study of cyclobutenones since the latter provide a route to vinylketenes by thermal electrocyclic ring opening.[3] While the cycloaddition of dichloroketene to alkenes has received considerable attention,[2,4] relatively few studies have appeared regarding analogous reactions with alkynes.[5-7] Historically, investigators have been unable to effect the cycloaddition of dichloroketene to unactivated alkynes with good efficacy, and only strained or electron-rich alkynes were found to give good yields of adducts.[5,6a] For example, dehydrohalogenation of dichloroacetyl chloride in the presence of 2-butyne produced 4,4-dichloro-2,3-dimethyl-2-cyclobuten-1-one in only 12% yield.[6b] These results prompted us to investigate whether dichloroketene is intrinsically unreactive toward unactivated alkynes or whether suitable reaction conditions or methodology had remained undiscovered. Recently we reported an improved synthesis of a variety of dichlorocyclobutenones[7] using a method previously developed in our laboratory for related cycloadditions.[8] In this paper we describe the detailed results regarding the synthesis of these compounds as well as the regiochemistry of addition and some reactions of the resulting adducts.

Results and Discussion

(A) Synthesis of Cyclobutenones 2 and Structure Assignment. Reaction of 2-butyne with dichloroketene 1, generated in situ by zinc dehalogenation of trichloroacetyl chloride in the presence of phosphorus oxychloride,[7,8] produces 4,4-dichloro-2,3-dimethyl-2-cyclobuten-1-one (**2a**) in 85% yield. A variety of additional alkynes were shown to react by this procedure (Table I).

Table I. Formation of Cyclobutenones 2 from Reaction of Dichloroketene with Alkynes 3

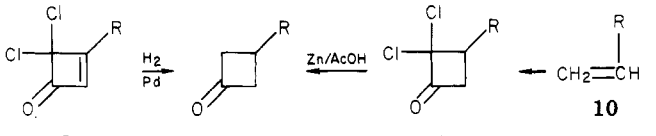


3 1 2

2	R	R'	% yield[a]
a	Me	Me	85
b	Et	Et	57
c	Ph	Ph	45
d	$CH_3(CH_2)_3$	H	77
e	$CH_3(CH_2)_4$	H	70
f	Ph	H	75
g	Me_3Si	H	60
h	Me_3Si	Me	30[b]
i	Me	Me_3Si	30[b]
j	isopropenyl	H	45

[a] Isolated. [b] Yield determined by NMR of mixture (ratio of 2h to 2i was 7:5).

Scheme I[a]



2 4 5 10

[a] f, R = Ph; g, R = $SiMe_3$.

The advantage of added $POCl_3$ lies in a cleaner reaction and the higher yield of adducts **2**. The reaction of 3-hexyne with **1** in the presence of $POCl_3$ gave **2b** in 57% yield, while without $POCl_3$ a tarry reaction product was obtained which was difficult to purify.

The reaction works well with mono- as well as disubstituted alkynes and is regioselective[9] (see **2d-g**). Addition

(1) Cycloaddition. 30. For the previous paper in this series see: Hassner, A.; Chau, W.; D'Costa, R. *Isr. J. Chem.* **1982**, *22*, 76.
(2) (a) Fletcher, V. R.; Hassner, A. *Tetrahedron Lett.* **1970**, 1071. (b) Hassner, A.; Cory, R. M.; Sartoris, N. *J. Am. Chem. Soc.* **1976**, *98*, 7698. (c) Hassner, A.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3173.
(3) (a) Jenny, E. F.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 2005. (b) Huisgen, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, *55*, 57.
(4) Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mallet, P. *Tetrahedron* **1971**, *27*, 615. Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.
(5) (a) Krebs, A.; Kimling, H. *Justus Liebigs Ann. Chem.* **1974**, 2974. (b) Kirksey, J. W.; Hill, R. K.; Carlson, R. M.; Isidor, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 2267.
(6) (a) Wong, H. N. C.; Sonderheimer, F. *Tetrahedron Lett.* **1976**, 2715. (b) Knoche, H.; *Justus Liebigs Ann. Chem.* **1969**, *722*, 232.
(7) For a preliminary account of this work see: Hassner, A.; Dillon, J., Jr. *Synthesis*, **1979**, 689.
(8) Hassner, A.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 2897.
(9) The term *regioselective*, proposed by A. Hassner (*J. Org. Chem.* **1968**, *33*, 2684) refers to *selectivity* in bond formation (or breaking) at one of two different locations *involving the same functional group*, whereas the term *chemoselective* (see: Trost, B. M. *Science (Washington, D.C.)* **1983**, *219*, 245) is used when *differentiation between two functional groups occurs*. Although **2j** was isolated only in 45% yield, no other product was detected.

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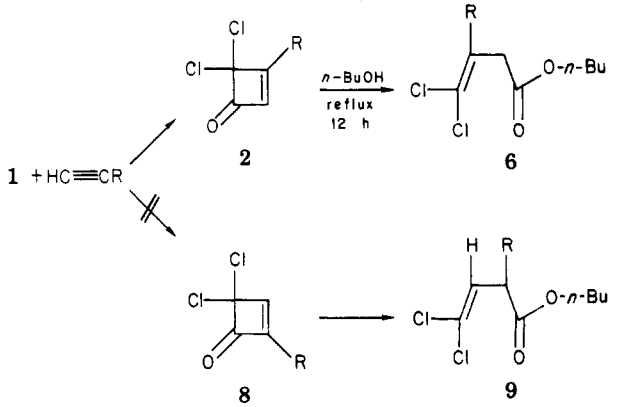
Scheme II[a]



[a] e, R = C_5H_{11}; g, R = $SiMe_3$.

of **1** to ene–yne **3j** leads chemoselectively[9] to cyclobutenone **2j**. Reaction of acetylene itself as well as of electron-deficient alkynes such as dimethyl acetylenedicarboxylate was unsuccessful under the above conditions.

That the regiochemistry of cycloaddition of monosubstituted alkynes parallels that of alkenes was established by hydrogenation of **2f** to 3-phenylcyclobutanone **4f** (Scheme I), identical with the zinc dehalogenation product of the styrene adduct (**5f**).[8] This reduction of **2f** to **4f** also illustrates the utility of dichloroketene–alkyne cycloadditions in the preparation of substituted cyclobutanones since certain olefins are not as reactive as their alkyne counterparts (for example, *cis*-stilbene vs. diphenylacetylene).

For the alkyl-substituted cyclobutenone **2e** the regiochemistry was determined by electrocyclic ring cleavage (see discussion below) in the presence of *n*-butyl alcohol (*n*-BuOH) at 117 °C. This resulted in the production of a single isomer. The lack of olefinic CH absorption in the ^1H NMR spectrum and the presence of a singlet at δ 3.3 (2 H) rules out structure **9e** derived from a possible regioisomer **8e**. The isomeric α,β-unsaturated ester **7** is likewise ruled out by these data. The regiochemical results are consistent with a transition state in which an electron releasing R substituent stabilizes a partial positive charge.

Silyl groups are believed to stabilize α carbanions and β carbocations.[10] Hence, the cycloaddition of **1** to (trimethylsilyl)acetylene (**3g**) may a priori be expected to produce regioisomer **8g** (Scheme II). However, the cycloadduct proved to be **2g**[11] since when heated in *n*-BuOH it was converted into **6g** in 80% yield, and reduction led to **4g**. The structure of **6g** was apparent from a singlet at δ 3.3 (2 H) and the lack of olefinic hydrogen absorption as required by **9g**.

1-(Trimethylsilyl)-1-propyne (**3h**) reacts with **1** to give a mixture of regioisomers, **2h** and **2i**, identified by the presence of two multiplets centered at δ 2.35 and 2.2 in the ratio of 7:5.[11]

Since we have shown that hydroboration of **3h** proceeds by attack of electrophilic boron α to silicon,[12] the trimethylsilyl group in **3g** and **3h** appears to have an unusual directive effect when dichloroketene is the electrophile. In fact, even trimethylvinylsilane (**10g**) reacts with dichloroketene to produce primarly **5g** (Scheme I).[11,14] By

Scheme III

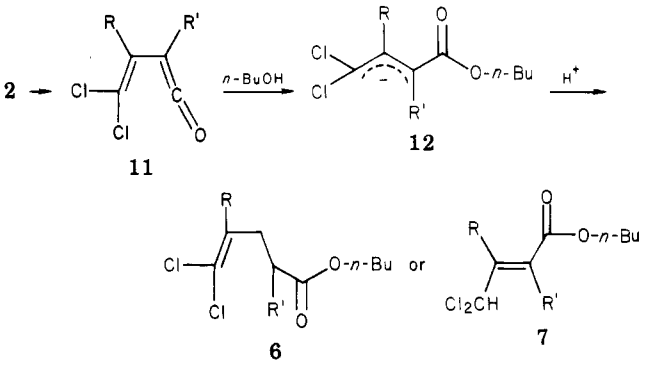


Table II. Thermolysis of Cyclobutenones 2 in *n*-Butyl Alcohol to Produce Esters 6 or 7

cyclobutenone	product(s) 6 or 7	R	R'	% yield
2a	7a	Me	Me	84
2b	7b	Et	Et	80
2c	7c, *E* and *Z*	Ph	Ph	80[a]
2e	6e	C_5H_{11}	H	90
2f	6f	Ph	H	97
2g	6g	Me_3Si	H	88

[a] Refers to yield of crude mixture which was separated by chromatography.

comparison, **10g** is attacked with equal facility at the α- and β-carbon by borane but predominatly at the β-carbon by more bulky boranes such as 9-BBN.[13]

The structure of **5g** was indicated by Eu(fod)$_3$-induced shifts[15] in which the four sets of doublets integrating for two protons at δ 3.4 shifted to a much lower field (e.g., Δ = 64 Hz) than the one proton doublet of doublets at δ 2.35 (e.g., Δ = 34 Hz). Zinc reduction gave the known **4g**.[16]

The effect of the trimethylsilyl group in these ketene cycloadditions may be attributed to one or a combination of three factors: (1) the steric requirement of the relatively large trimethylsilyl group, (2) an increase in the HOMO coefficient at the β-carbon,[11] and (3) a free radical rather than ionic character of the transition state in these quasi-concerted cycloadditions.[17]

The mass spectra of the cyclobutenones **2** deserve some comment. All exhibit a weak parent peak. Aryl- and methyl-substituted cyclobutenones such as **2a,c,f** undergo fragmentation (loss of CO and Cl) to give the corresponding cyclopropenyl cation species as evidenced by strong peaks (80–100%) at *m/e* 101, 225, and 149, respectively.

(B) Reactions of Cyclobutenones. Thermolysis of cyclobutenones proceeds by electrocyclic ring cleavage to vinylketenes.[3] Such intermediates can be trapped by alcohols to produce unsaturated esters or by olefins to form vinylcyclobutanones.[3b] In our case, the electrocyclic ring cleavage of cyclobutenones **2** in refluxing *n*-BuOH led to β,γ- or α,β-unsaturated esters **6** or **7** (Scheme III) in good to excellent yields (Table II). The 2,3-dialkylated cyclo-

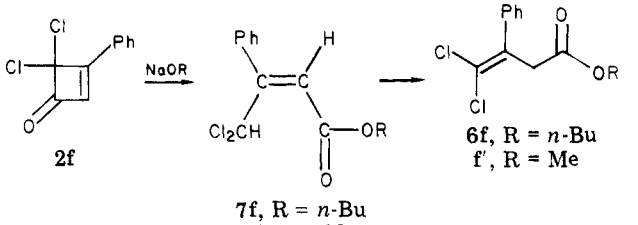
(10) For a review see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.
(11) After this work was completed (see Ph.D. Thesis of J.D., SUNY, Binghamton, 1982), Danheiser and Sard (Danheiser, R.; Sard, H. *Tetrahedron Lett.* **1983**, *24*, 23) disclosed similar independent results on dichloroketene cycloadditions to silylacetylenes and trimethylvinylsilane. Our use of $POCl_3$ offers some advatages in the formation of **5g**.
(12) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, 1.
(13) Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1978**, *156*, 12.
(14) It is possible that a small amount of isomeric 4,4-dichloro-2-(trimethylsilyl)cyclobutanone is produced in this reaction, but we were unable to ascertain this by 60-MHz NMR. Danheiser[11] reports that ~18% of the above isomer is produced by his procedure. It is possible that this regioisomer did not survive our reaction conditions or the vacuum distillation used in purification.
(15) Cory, R.; Hassner, A. *Tetrahedron Lett.* **1972**, 1245.
(16) Brady, W. T.; Cheng, T. C. *J. Organomet. Chem.* **1977**, *137*, 287.
(17) At this point we need more data to be able to choose between these three explanations.

butenones (i.e., **2a–c**) produced α,β-unsaturated esters **7** while 3-monosubstituted cyclobutenones (i.e., **2e–g**) afforded β,γ-unsaturated esters **6**. To explain the formation of α,β- vs. β,γ-unsaturated esters in such reactions, Roberts and co-workers[18] have predicted that alcohols add 1,4 to the vinylketene if a cisoid conformation (e.g., **11**) is preferred; otherwise, 1,2-addition takes place to produce β,γ-unsaturated esters. Such an explanation could not apply to our results; for instance, the vinylketene derived from **2a** and leading to **7a** would certainly not be expected to maintain the crowded cisoid conformation **11** (R = R' = CH_3). We prefer to describe the results as involving nucleophilic attack by the alcohol on the thermally formed vinylketene. The allylic carbanion **12** thus produced is then protonated either at the α- or the γ-carbon to ultimately furnish the thermodynamically more stable unsaturated ester.

In the case of α,β-disubstituted esters the tetrasubstituted ester-conjugated double bond appears to be favored over the equally substituted but nonconjugated double bond in a β,γ-unsaturated ester; hence, the products are **7a–c** rather than **6**. On the other hand, the tetrasubstituted double bond in **6e–g** is favored over the alternate trisubstituted double bond in the isomeric **7** (R' = H). Indeed, we showed that **7a–c** as well as **6e–g** are stable to heating with alkoxide, while α,β-unsaturated ester **7f** (prepared from **2f** and stable to refluxing *n*-BuOH) isomerizes in the presence of *n*-BuONa slowly at 20 °C and faster on heating to the nonconjugated ester **6f** (as followed by NMR).

The *E* stereochemistry in **7a** (as well as in **7b**) was surmized from the large coupling (quartets, J = 2 Hz) between the methyl protons, consistent with trans rather than cis olefinic substituents.[19] Coupling for the $CHCl_2$ proton in **7a** or **7b** is nonobservable at 60 MHz. Product **7c** was isolated as a mixture of *E* and *Z* isomers, probably due to crowding of the phenyl substituents.

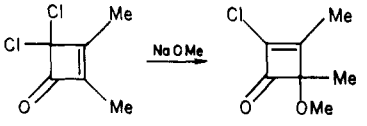
A constrasting behavior was observed when 3-mono- or 2,3-disubstituted cyclobutenones were exposed to sodium alkoxide. While **2f** underwent ring opening with methoxide or *n*-butoxide at −20 °C to produce ester **7f'** or **7f**, respectively (eq 1), as the kinetic product, the dimethyl



2f **6f**, R = *n*-Bu; **f'**, R = Me

7f, R = *n*-Bu; **f'**, R = Me

(1)



2a **13** (2)

analogue **2a** gave an allylic substitution product, **13** (eq 2). Since an S_N2' process, with alkoxide attacking at C-2, should be more favorable for less hindered **2f** than for **2a**, we suggest that the formation of **13** is the result of an S_N1' ionization of **2a** reminiscent of of allyl cation formation observed in chlorocyclobutanones.[20]

Reduction of the chlorine substituents of cyclobutenones proved to be a difficult task. Zinc or tributyltin hydride, which reduced dichlorocyclobutanones well, were largely ineffective or led to tars. Chromium(II) chloride reduced **2f** to 3-phenyl-2-cyclobutenone (**14**) in 80% yield but was not effective with **2a**. It is possible that the reluctance of **2** to undergo one- or two-electron reduction is due to unfavorable formation of cyclobutadienyl oxide anion or radicals.

Conclusion

It is clear that dichloroketene addition to alkynes provides a useful entry into substituted dichlorocyclobutenones **2**, as well as into substituted cyclobutanones. The dichlorocyclobutenone can be readily converted by thermolysis above 110 °C in alcohol to an α,β- or a β,γ-unsaturated ester, whichever is the thermodynamically more stable product. Reaction of **2** with alkoxide proceeds readily at room temperature or below and leads either to ring opening or to a substituted cyclobutenone. Reduction of the chlorines in **2f** can be achieved with $CrCl_2$.

Experimental Section

Spectral recording and reaction conditions were as previously indicated.[8] Ether and THF were purified by distillation from Na–K alloy/benzophenone ketyl under argon. *n*-Butanol and methanol were distilled from magnesium alkoxide and stored under argon. All reactions were performed under nitrogen or argon, unless otherwise noted.

General Procedure for Cycloaddition of Dichloroketene to Alkynes. To a flame-dried 100-mL flask placed under argon by a series of evacuate–fill cycles and equipped with a reflux condenser (or dry ice condenser for more volatile alkynes), constant pressure addition funnel, and argon inlet is added activated zinc[8] (0.018 mol), the alkyne (0.006 mol), and 50 mL of anhydrous ether. To this vigorously stirred mixture is added a solution containing phosphorus oxychloride (0.012 mol), distilled from K_2CO_3, trichloroacetyl chloride (0.012 mol), and 10 mL of anhydrous ether over a period of 1 h. The mixture is refluxed for 4–14 h, and the unreacted zinc is filtered on a pad of Celite. The ether solution is washed successively with water, 5% sodium bicarbonate solution, and saturated sodium chloride solution and dried over potassium carbonate. Removal of the ether in vacuo gives product which is purified at reduced pressure by bulb-to-bulb distillation or by chromatography over Woelm silica gel.

4,4-Dichloro-2,3-dimethyl-2-cyclobuten-1-one (2a): bp 65 °C (bath, 1 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.2 (q, 3 H, J = 1.5 Hz), 1.8 (q, 3 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 181.1, 176.0, 148.4, 92.6, 9.4, 7.9; IR (neat) 1800, 1645 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 166 (M + 2, 22), 164 (M$^+$, 31), 149 (100), 101 (80), 83 (40), 69 (57), 57 (80), 55 (80), 43 (90), 41 (80). Anal. Calcd for $C_6H_6Cl_2O$: C, 43.67; H, 3.67. Found: C, 43.51; H, 3.71.

4,4-Dichloro-2,3-diethyl-2-cyclobuten-1-one (2b): bp 60 °C (bath, 0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.7 (q, 2 H), 2.15 (q, 2 H), 1.35 (t, 3 H), 1.03 (t, 3 H); IR (neat) 1800, 1605 cm^{-1}. Anal. Calcd for $C_8H_{10}Cl_2O$: C, 49.76; H, 5.22. Found: C, 49.58; H, 5.30.

4,4-Dichloro-2,3-diphenyl-2-cyclobuten-1-one (2c): mp 121 °C (lit.[21] mp 121 °C); ^{1}H NMR ($CDCl_3$) δ 8.1, 7.8, 7.63 (3 br m); IR (CCl_4) 1780, 1595 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 290 (M + 2, 24), 288 (M$^+$, 35), 253 (11), 227 (32), 225 (100), 189 (37), 94 (20).

4,4-Dichloro-3-*n*-butyl-2-cyclobuten-1-one (2d). Compound **2d** was purified by chromatography over silica gel (5% diethyl

(18) (a) Roberts, J. D.; Streitweiser, A.; Regan, C. *J. Am. Chem. Soc.* **1952**, *74*, 4579. (b) Silversmith, E. F.; Kitacharv, Y.; Caserio, M. C.; Roberts, J. D. *Ibid.* **1958**, *80*, 5840.

(19) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: London, 1969; p 326.

(20) Hassner, A.; Dillon, J., Jr.; Krepski, L. R.; Onan, K. *Tetrahedron Lett.* **1983**, *24*, 1135. (b) Since a cationic center next to a carbonyl group is energetically unfavorable, it is possible that hemiketal formation precedes allyl cation formation, the latter being more favorable due to additional "substitution" in the cyclobutane ring.

(21) Dehmlow, E. V. *Chem. Ber.* **1967**, *100*, 3829.

(22) Harding, K.; Trotter, J.; May, L. *J. Org. Chem.* **1977**, *42*, 2715.

ether in petroleum ether) to give a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.23 (t, 1 H, J = 2 Hz), 2.72 (t, 2 H, J = 6Hz), 2.0–0.7 (m, 7 H); IR (neat) 1800, 1590 cm^{-1}. Anal. Calcd for $C_8H_{10}Cl_2O$: C, 49.70; H, 5.18. Found: C, 49.76; H, 5.22.

4,4-Dichloro-3-*n*-pentyl-2-cyclobuten-1-one (2e): bp 100 °C (bath, 0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.12 (m, 1 H, J = 2 Hz), 2.7 (t, 2 H, J = 6 Hz), 2–0.7 (m, 9 H); IR (neat) 1800, 1585 cm^{-1}. Anal. Calcd for $C_9H_{13}Cl_2O$: C, 52.19; H, 5.85. Found: C, 52.10; H, 5.79.

4,4-Dichloro-3-phenyl-2-cyclobuten-1-one (2f): mp 82 °C, ^{1}H NMR ($CDCl_3$) δ 7.7 (m, 2 H), 7.45 (m, 3 H), 6.45 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 178.9, 175.9, 134.0, 130.6, 129.9, 129.5, 126.0, 89.8; IR (CCl_4) 1788, 1568 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 214 (M + 2, 35), 212 (M$^+$, 54), 151 (32), 149 (100), 114 (22), 105 (26), 74 (19). Anal. Calcd for $C_{10}H_6Cl_2O$: C, 56.37; H, 2.84. Found: C, 56.37; H, 2.89.

4,4-Dichloro-3-(trimethylsilyl)-2-cyclobuten-1-one (2g): bp 40 °C (bath, 0.1 mmHg); mp 25 °C; ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 1 H), 0.4 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 191.8, 180.5, 149.2, 95.6, −1.4 (dioxane as secondary reference); IR (neat) 1810 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 210 (M + 2, 4), 208 (M$^+$, 6), 195 (16), 193 (24), 167 (13), 165 (22), 145 (21), 139 (30), 137 (43), 115 (32), 113 (45), 102 (31), 100 (90), 95 (31), 93 (60), 73 (100), 65 (25), 63 (22), 45 (21), 43 (52). Anal. Calcd for $C_7H_{10}Cl_2OSi$: C, 40.19; H, 4.83. Found: C, 40.26; H, 4.89.

4,4-Dichloro-2-methyl-3-(trimethylsilyl)-2-cyclobuten-1-one (2h) and 4,4-Dichloro-3-methyl-2-(trimethylsilyl)-2-cyclobuten-1-one (2i). The compounds were obtained as a mixture in a ratio of 7:5 and were separated from unreacted starting material by preparative VPC (100 °C): ^{1}H NMR ($CDCl_3$) δ 2.35 (m, 3 H, J = 1.5 Hz), 2.2 (m, 3 H, J = 1.5 Hz), 0.4 (s, 9 H), 0.2 (s, 9 H); IR (neat) 1790 cm^{-1}.

4,4-Dichloro-3-isopropenyl-2-cyclobuten-1-one (2j): bp 25 °C (bath, 0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.3 (s, 2 H), 5.93 (s, 1 H), 2.1 (s, 3 H); IR (neat) 1800, 1625 cm^{-1}. Anal. Calcd for $C_7H_6Cl_2O$: C, 47.49; H, 3.42. Found: C, 47.54; H, 3.46.

2,2-Dichloro-3-phenylcyclobutanone (5f). By use of the procedure of Hassner and Krepski,[8] **5f** was obtained as white needles, mp 66–67 °C.

2,2-Dichloro-3-(trimethylsilyl)cyclobutanone (5g). The use of vinyltrimethylsilane instead of styrene (above) and overnight reflux led to **5g** in 90% yield as a clear oil by bulb-to-bulb distillation: bp 50 °C (bath, 0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.5 (dd, 1 H, J = 12.5, 17.5 Hz), 3.2 (dd, 1 H, J = 10.17, 5 Hz), 2.4 (dd, 1 H, J = 10.17, 5 Hz), 0.2 (s, 9 H); IR (neat) 1810 cm^{-1}.

Reduction of 5g with activated zinc in acetic acid gave 3-(trimethylsilyl)cyclobutanone (**4g**). Removal of ether in vacuo gave a clear oil (bulb-to-bulb distillation): 90% yield; ^{1}H NMR ($CDCl_3$) δ 3.2–2.5 (m, 4 H), 1.8–1.1 (m, 1 H), 0.0 (s, 9 H); IR (neat) 1790 cm^{-1}.[16]

Catalytic hydrogenation of 2g (10% Pd/C, EtOAc) gave **4g** in 60% yield, identical with the compound produced by zinc reduction of **5g**.

Zinc dust reduction of 5f in glacial acetic acid (60 °C for 1 h) gave **4f** as a colorless cinnamon-smelling liquid (bulb-to-bulb distilled) in quantitative yield and identical with the compound reported previously[23] and with that obtained by catalytic hydrogenation of **2f**: ^{1}H NMR ($CDCl_3$) δ 6.95 (s, 5 H), 3.7–2.7 (m, 5 H); IR (neat) 1780 cm^{-1}.

2-Chloro-4-methoxy-3,4-dimethyl-2-cyclobuten-1-one (13). To 1.0 g (6.1 mmol) of **2a** in 15 mL of anhydrous MeOH at −20 °C was added a solution containing 0.35 g (6.4 mmol) of NaOMe in 10 mL of MeOH over 10 min. After 15 min, 5% HCl was added, and the workup followed by bulb-to-bulb distillation at reduced pressure gave 880 mg (90%) of **13** purified by flash chromatography (ether–petroleum ether, 1:10): bp 25 °C (bath, 0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.2 (s, 3 H), 2.17 (s, 3 H), 1.4 (s, 3 H); IR (neat) 1780, 1625 cm^{-1}. Anal. Calcd for C_7H_9ClO: C, 52.34, H, 5.66. Found: C, 52.39; H, 5.67.

Methyl 4,4-dichloro-3-phenyl-2-butenoate (7f′) performed as for **2a** except that 2 mL of THF was added to solubilize **2f**. **7f′** was purified by chromatography over silica gel (ether–petroleum ether, 1:4): 88% yield. ^{1}H NMR ($CDCl_3$) δ 8.2 (s, 1 H), 7.7–7.2 (m, 5 H), 5.95 (s, 1 H), 3.8 (s, 3 H); IR (neat) 1720, 1630 cm^{-1}. Anal. Calcd for $C_{11}H_{10}Cl_2O_2$: C, 53.86; H, 4.12. Found: C, 53.81; H, 4.10.

Butyl 4,4-dichloro-3-phenyl-3-butenoate (7f) was prepared as above by using sodium *n*-butoxide. The product contains **7f** and **6f** in a ratio of 3:1 and was separated by chromatography over silica gel: ^{1}H NMR δ 8.1 (s, 1 H), 7.2 (m, 5 H), 5.8 (s, 1 H), 4.1 (5, 1 H, J = 6 Hz), 1.8–0.5 (m, 7 H); IR (neat) 1740 cm^{-1}. Heating **7f** for 12 h in 0.2 equiv of *n*-butoxide (or at 20 °C for several days) gave a mixture of **7f** and **6f** in a ratio of 1:2.

General Procedure for Ring Opening of 4,4-Dichlorocyclobutenones 2 with *n*-Butyl Alcohol. A 25-mL two-necked flask equipped with a reflux condenser and a gas inlet was charged with 500 mg of cyclobutenone and 8 mL anhydrous *n*-butyl alcohol. The mixture was refluxed 12 h, and the alcohol was removed in vacuo. The resulting esters are purified by distillation (bulb to bulb) at reduced pressure or by chromatography over silica gel.

Butyl 4,4-dichloro-3-*n*-pentyl-3-butenoate (6e): bp 120 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.1 (t, 2 H, J = 6 Hz), 3.2 (s, 2 H), 2.4 (m, 2 H), 1.9–0.7 (m, 16 H); IR ($CDCl_3$) 1740 1605 cm^{-1}. Anal. Calcd for $C_{13}H_{22}Cl_2O_2$: C, 55.52; H, 7.87. Found: C, 55.66; H, 7.91.

Butyl 4,4-dichloro-3-phenyl-3-butenoate (6f) was chromatographed over silica gel (30% ethyl acetate in petroleum ether): ^{1}H NMR δ 7.22 (s, 5 H), 4.0 (t, 2 H, J = 6 Hz), 3.58 (s, 2 H), 1.8–0.7 (m, 7 H); IR (CCl_4) 1740, 1630 cm^{-1}. Anal. Calcd for $C_{14}H_{16}Cl_2O_2$: C, 58.55; H, 5.63. Found: C, 58.47; H, 5.69.

Butyl 4,4-dichloro-3-(trimethylsilyl)-3-butenoate (6g): bp 100 °C (0.5 mmHg); ^{1}H NMR δ 4.1 (t, 2 H, J = 6 Hz), 3.3 (s, 2 H), 1.8–0.5 (m, 7 H), 0.25 (s, 9 H); IR (CCl_4) 1740 cm^{-1}. Anal. Calcd for $C_{11}H_{20}Cl_2O_2Si$: C, 46.64; H, 7.13. Found: C, 46.73; H, 7.17.

Butyl 4,4-dichloro-2,3-dimethyl-2-butenoate (7a) was chromatographed over silica gel (10% ethyl acetate in petroleum ether): ^{1}H NMR ($CDCl_3$) δ 5.2 (s, 1 H), 4.1 (t, 2 H, J = 6 Hz), 2.3 (m, 3 H, J = 2 Hz), 1.9 (m, 3 H, J = 2 Hz), 1.6–0.7 (m, 7 H); IR (CCl_4) 1760, 1740, 1655 cm^{-1}; ^{13}C NMR δ 167.3, 132.6, 127.6, 66.5, 57.8, 30.5, 22.6, 19.0, 15.3, 13.6. Anal. Calcd for $C_{10}H_{15}Cl_2O_2$: C, 50.22; H, 6.76. Found: C, 50.36; H, 6.82.

Butyl 4,4-dichloro-2,3-diethyl-2-butenoate (7b): 80% yield; bp 110 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.2 (s, 1 H), 4.1 (t, 2 H, J = 6 Hz), 2.8–0.6 (m, 17 H); IR (neat) 1760, 1740, 1640 cm^{-1}. Anal. Calcd for $C_{12}H_{20}Cl_2O_2$: C, 53.93; H, 7.56. Found: C, 53.97; H, 7.60.

(*E*)- and (*Z*)-Butyl 4,4-dichloro-2,3-diphenyl-2-butenoate (7c) were separated by chromatography over silica gel (10% ethyl acetate in petroleum ether). The first fraction gave 60 mg of (*E*)-**7c** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.5, 7.2 (m, 10 H), 5.5 (s, 1 H), 4.1 (t, 2 H, J = 6 Hz), 1.7–0.6 (m, 7 H); IR (CCl_4) 1763, 1730 cm^{-1}. Anal. Calcd for $C_{20}H_{20}Cl_2O_2$: C, 66.19; H, 5.56. Found: C, 66.39; H, 5.65. The second fraction gave a mixture, and the third gave 75 mg of (*Z*)-**7c** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.15, 7.55 (m, 10 H), 6.6 (s, 1 H), 4.1 (t, 2 H, J = 6 Hz), 1.5–0.4 (m, 7 H); IR (CCl_4) 1715, 1680 cm^{-1}. Anal. Calcd for $C_{20}H_{20}Cl_2O_2$: C, 66.19; H, 5.56. Found: C, 66.32; H, 5.62.

Reduction of 2f (14). To a two-necked flask equipped with an addition funnel under argon was added 500 mg (2.4 mmol) of **2f** in 15 mL of anhydrous THF (described in general section) was added 18 mL (19.8 mmol) of a 1.1 M solution of $CrCl_2$[22] dropwise over 15 min. The resulting green solution is stirred for 12 h, and 100 mL of ether was added. The ether was washed successively with water, 5% $NaHCO_3$, and saturated NaCl and dried ($MgSO_4$). Removal of ether in vacuo yielded a pale yellow oil which crystallized upon standing. Recrystallization from ether at −78 °C gave white crystals (mp 52 °C) in 80% yield, the NMR, IR, and melting point, of which were identical with those of the compound reported previously:[23] ^{1}H NMR ($CDCl_3$) δ 7.5 (m, 5 H), 6.3 (s, 1 H), 3.5 (s, 2 H); IR (CCl_4) 1755, 1658 cm^{-1}.

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Registry No. **1**, 4591-28-0; **2a**, 72284-72-1; **2b**, 72284-71-0; **2c**, 17204-73-8; **2d**, 72284-70-9; **2e**, 86853-61-4; **2f**, 3470-35-7; **2g**,

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85973-82-6; **2h**, 85973-84-8; **2i**, 85973-83-7; **2j**, 72284-73-2; **3a**, 503-17-3; **3b**, 928-49-4; **3c**, 501-65-5; **3d**, 693-02-7; **3e**, 628-71-7; **3f**, 536-74-3; **3g**, 1066-54-2; **3h**, 6224-91-5; **3j**, 78-80-8; **4f**, 52784-31-3; **4g**, 62012-20-8; **5f**, 13866-28-9; **5g**, 85973-87-1; **6e**, 86853-62-5; **6f**, 86853-63-6; **6g**, 86853-64-7; (*E*)-**7a**, 86853-65-8; (*E*)-**7b**, 86853-66-9; (*E*)-**7c**, 86853-67-0; (*Z*)-**7c**, 86853-68-1; **7f**, 86853-69-2; **7f'**, 86853-70-5; **10**, 754-05-2; **13**, 86853-71-6; **14**, 38425-47-7; trichloroacetyl chloride, 76-02-8.

Structural Effects in Solvolytic Reactions. 44. Effect of Increasing Electron Demand on the Carbon-13 NMR Shifts in 1-Aryl-1-hydroxyethyl Carbocations. Deviations in the σ^{C^+}-$\Delta\delta C^+$ Plot for These Protonated Acetophenones Containing Strongly Electron-Withdrawing Substituents

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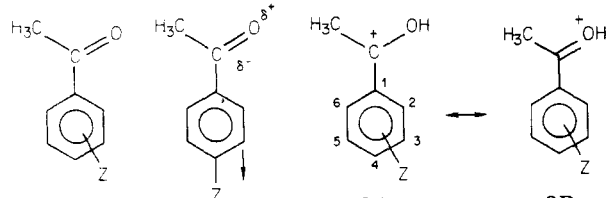
A series of meta- and para-substituted 1-aryl-1-hydroxyethyl carbocations were prepared by protonation of the corresponding acetophenones in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and the carbon-13 NMR shifts were measured at −70 °C. A plot of $\Delta\delta C^+$ shifts against the σ^{C^+} constants exhibits deviations from linearity for electron-demanding substituents. The deviation is attributed to more shielding of the cationic carbon center than that estimated by the σ^{C^+} constants. Previously, such shielding effects were observed for side-chain conjugated benzene derivatives containing electron-demanding substituents. For example, the carbonyl carbon atom in substituted acetophenones becomes more shielded on substitution with electron-demanding substituents. This was attributed to inductive π-polarization of the conjugating side chain. Accordingly, the present study establishes that the deviations observed for the ^{13}C shifts of the carbonyl carbon atom in acetophenones with electron-demanding substituents persist in the protonated acetophenones (1-aryl-1-hydroxyethyl carbocations).

It was recently reported that the inductive (field) effect contribution to the chemical shift of the first atom in a conjugating side chain was negative, leading to reverse substituent chemical shifts.[1] For example, in meta- and para-substituted acetophenones **1**, the carbonyl carbon atom becomes more shielded with electron-withdrawing substituents. This is contrary to the expectation that the electron-withdrawing substituents should withdraw electron density, decrease the shielding, and cause an increased chemical shift.



1 **2** **3A** **3B**

Brownlee and co-workers suggested that these reverse chemical shifts result from the interaction of the substituent dipole with the side-chain π-system.[1] This interaction is suggested to operate through the space of the molecular cavity, resulting in the polarization shown in **2**. The net result is that the inductive withdrawing substituent increases the electron density around the carbonyl carbon atom and hence increases the shielding to cause a reduced chemical shift. Brownlee and co-workers also reported that in the case of 1-aryl-1-hydroxyethyl carbocations normal chemical shifts (deshielding) are observed for electron-withdrawing substituents.[1] They suggested that the normal behavior [i.e., increased shifts (deshielding) for inductive withdrawing substituents] is observed for the C^+ carbon atom in 1-aryl-1hydroxyethyl cations **3** because of the absence of the conjugate double bond in the side chain. In that case, we would expect the $\Delta\delta C^+$ values observed for **3** to correlate linearly with the σ^{C^+} constants similar to the correlations observed for simple benzylic carbocations.[2-7] Accordingly, we decided to run the carbon-13 NMR spectra for the entire range of the 1-aryl-1-hydroxyethyl carbocations **3** [Z = *p*-OCH_3 to Z = 3,5-$(CF_3)_2$].

Table I. Comparison of the $\Delta\delta C^+$ Shifts[a] of 1-Aryl-1-hydroxyethyl Carbocations

	$\Delta\delta C^+$ [a]	
substit	concn H_2SO_4 (25 °C)	$SbF_5/FSO_3H/SO_2ClF$ [c] (−70 °C)
m-Br	−0.8 [b]	−1.1
m-CF_3	−1.6 [b]	−2.0
p-CF_3	−2.3 [b]	−3.1
3,5-Cl_2	−0.30 [c]	−2.2
3,5-$(CF_3)_2$	+0.9 [c]	−3.4

[a] $\Delta\delta C^+ = \delta C^+(Z = H) - \delta C^+(Z \neq H)$. [b] Data taken from ref 1. [c] Present work.

Results and Discussion

Several 1-aryl-1-hydroxyethyl cations **3** were studied by Olah and co-workers.[8] These authors prepared these ions by protonation of the corresponding acetophenones in

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