Proton and Carbon-13 Nuclear Magnetic Resonance Spectra of Para-Bisannelated Benzenes

Randolph P. Thummel* and Wutichai Nutakul

Department of Chemistry, University of Houston, Houston, Texas 77004

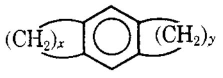
Received January 12, 1978

A complete proton and carbon-13 NMR analysis has been carried out for a series of benzo[1,2:4,5]dicycloalkenes where the fused cycloalkene portions contain all possible combinations of four-, five-, and six-membered rings. With decreasing size of the annelated rings the chemical shift of the unsubstituted aromatic carbon moves upfield and the bridgehead carbons move downfield. The aromatic proton chemical shift of the benzocyclobutene derivatives show anomalous behavior but the aromatic C–H coupling constant increases very consistently with decreasing size of the annelated rings. Comparison is made with the methylenecycloalkanes and interpretations are set forth in terms of local anisotropy effects as well as a rehybridization theory associated with bond angle distortions. CNDO/2 calculations lend support to these observations.

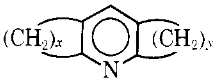
The chemical and physical properties of the benzocycloalkenes have been the subject of a variety of investigations.[1] These systems present a convenient means for studying the effect of regularly increasing steric strain on a simple aromatic nucleus without complicating or competing electronic perturbations. Manatt and Cooper have reported a detailed analysis of the ^{1}H NMR spectra of the benzocycloalkenes with particular regard to changes in proton–proton spin–spin couplings with changes in strain.[2] They conclude that although certain definite trends are present no direct correlation with "Mills-Nixon" type bond alternation can be made without more accurate structural information.

^{13}C NMR provides a more sensitive probe of nuclear shielding effects and affords a useful correlation to ^{1}H NMR data. An early report on the carbon chemical shifts of the benzocycloalkenes misassigned the unsubstituted aromatic carbons.[3] This situation was later corrected by two independent groups utilizing a variety of instrumental techniques as well as specifically deuterated or fluorinated derivatives.[4,5] General trends were pointed out in that the bridgehead carbon atom chemical shifts move downfield with increasing strain thus evidencing a deshielding effect. Similarly, the aromatic carbons ortho to the fused ring move upfield with increasing strain. Benzocyclopropene does not correlate well with its higher homologues and this behavior is attributed to the substantial shielding effect of the cyclopropene ring system.[6] Semiempirical[7] as well as ab initio[8] theoretical treatments have afforded some accordance with experimental results. It is still not clear, however, to what extent the observed shielding trends for strained aromatic systems depend upon changes in bond order, charge density, or rehybridization effects.[9]

In a recent paper we reported an interesting anomaly regarding the aromatic proton chemical shifts and ^{13}C–H coupling constants of the series of para-bisannelated benzenes **1–3.**[10] As the size of the rings fused to benzene is decreased the ^{13}C–H coupling constant is observed to increase (Table II). Such an increase has often been associated with an increase in s character of the bond in question.[11] This observation is consistent with a rehybridization theory set forth by Streitweiser[12] and also by Finnegan[13] in which it is claimed that for small ring fused benzocycloalkenes the bridgehead carbon rehybridizes to use orbitals of higher p character in bonding to the small ring. This leaves an orbital of higher s character to bond to the ortho carbon which results in an inductive polarization of the ortho aromatic C–H bond evidenced by the increased ^{13}C–H coupling constant. Such polarization should result in an increase in the acidity of the aromatic proton and therefore a lower field chemical shift. What is observed, instead, is a substantial shift to higher field from δ 7.08 for **3** to δ 6.64 for **1.** On the other hand, a similar study in the pyridine series **7–9** shows a consistent downfield shift for the aromatic proton from δ 7.02 for **9** to δ 7.30 for **7.**[14]

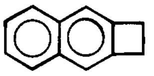


1, $x = 2; y = 2$
2, $x = 2; y = 3$
3, $x = 3; y = 3$
4, $x = 2; y = 4$
5, $x = 3; y = 4$
6, $x = 4; y = 4$

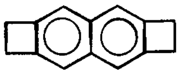


7, $x = 3; y = 3$
8, $x = 3; y = 4$
9, $x = 4; y = 4$

It therefore became of interest to extend the benzene study through the higher homologues **4–6,** thus providing a series consisting of all possibilities of para-bisannelated benzenes in which the fused rings contain four, five, or six carbon atoms. The analysis of trends resulting from strain effects on the NMR spectra should be more reliable than in the simple monoannelated series benzocyclobutene, indan, tetralin where only three molecules are available for comparison. Cyclopropene-fused analogues have been purposely omitted due to the complicating electronic features mentioned above. A parallel study comparing naphtho[*b*]cyclobutene (**10**) with the corresponding naphtho[*b*,*e*]dicyclobutene (**11**) has demonstrated that strain effects evidenced by the fusion of one small ring are amplified by the linear fusion of a second small ring.[15]



10



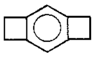
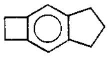
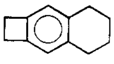
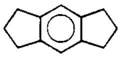
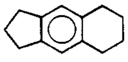
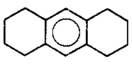
11

Assignment of Chemical Shifts

As compared to the benzocycloalkenes, the assignment of carbon resonances in the benzodicycloalkenes is considerably simplified by the additional degree of symmetry inherent in systems **1, 3,** and **6.** Benzo[1,2:4,5]dicyclobutene (**1**) shows only two aromatic and one aliphatic resonance. In the proton-coupled spectrum, the unsubstituted aromatic carbon splits into a doublet, assuring its identity. At the same time the bridghead aromatic carbon of **1** (B4) shows a four-line pattern due to long-range coupling (ca. 2.5 Hz) with the aromatic and benzylic protons. This same characteristic pattern appears clearly in the proton-coupled spectra of **2** and **4** assuring the assignment of their cyclobutene bridgehead carbons. The

0022-3263/78/1943-3170$01.00/0

Table I. Carbon-13 and Proton Chemical Shifts of Benzo[1,2:4,5]dicycloalkenes (in ppm Downfield from Me_4Si)[a]

	registry no.	carbons A	B4	B5	B6	4α	5α	5β	6α	6β	protons A	4α	5α	5β	6α	6β
 1	1610-51-1	117.3	143.4			29.3					6.64	2.99				
 2	60582-10-7	118.9	143.1	142.1		28.5	33.1	25.3			6.91	3.08	2.86	2.00		
 4	65957-33-7	122.9	142.9		135.6	29.2			30.0	23.3	6.68	3.04			2.67	1.69
 3	495-52-3	120.0		141.9			32.4	25.8			7.08		2.85	2.05		
 5	1624-25-5	124.8		141.5	134.7		32.5	25.7	29.6	23.6	6.91		2.82	2.01	2.74	1.76
 6	1079-71-6	134.1			129.3				28.9	23.4	6.74				2.67	1.74

[a] A = aromatic carbon or proton. B4, B5, B6 = bridgehead carbon fused to four-, five-, or six-membered ring. 4, 5, 6 (α or β) = α or β methylene carbon or proton in the four-, five-, or six-membered ring.

long-range coupling exhibited by cyclopentene and cyclohexene bridgehead carbons is more complex and less well resolved due to additional coupling with the nonbenzylic methylene protons. Further support for the assignment of bridgehead carbons in the unsymmetrically fused benzenes **2**, **4**, and **5** comes from the close analogy of their chemical shifts with the more symmetrical homologues **1**, **3**, and **6**. With no attempt being made to normalize relaxation time effects or to suppress the Nuclear Overhauser effect, the aromatic carbon is always found to be the most intense downfield peak even when statistically outnumbered 2:1 by the bridgehead carbons.

The aliphatic ring carbons of **1**, **3**, and **6** are also assigned with comparative ease. The benzylic methylene carbons appear at lower field than their nonbenzylic counterparts. Again, assignments for the unsymmetrically annelated systems were made by close analogy with their more symmetrical homologues.

The proton-coupled spectra showed downfield doublets for the aromatic C–H coupling and upfield triplets for the aliphatic methylenes. Of the aliphatic couplings, only those on the four-membered rings vary significantly from the range of 124–129 Hz. In all cases, fine structure resulting from long-range effects was observed but detailed analysis was not attempted at this time.

The ^1H NMR spectra were assigned with little difficulty. Each system showed one sharp aromatic singlet downfield. The cyclobutene methylene appeared as a slightly broadened singlet, while the remaining benzylic protons gave multiplets in the region of δ 2.67–2.86 and the nonbenzylic methylenes appeared at δ 1.69–2.05. Analysis of the proton–proton couplings was not carried out although J values of about 7.5 Hz were typical.

Table II. Aromatic ^{13}C–H Coupling Constants for Benzo[1,2:4,5]dicycloalkenes (in Hz ±0.4)[a]

compd	A	4α	5α	5β	6α	6β
1	160.2	138.4				
2	158.7	137.6	129.4	128.9		
4	157.3	136			124	126
3	155.1		127.5	126.6		
5	153.8		128.0	126.9	125.6	127.6
6	152.3				127.0	127.5

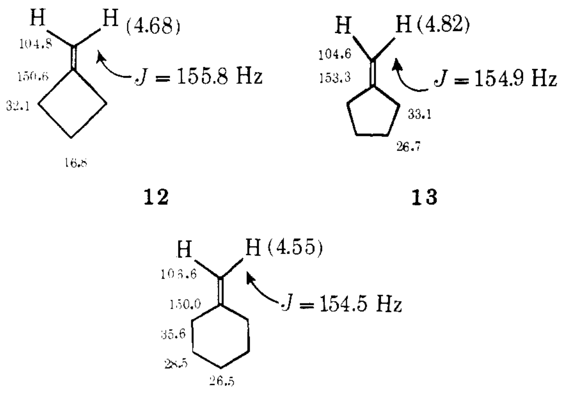
[a] A = aromatic carbon or proton. B4, B5, B6 = bridgehead carbon fused to the four-, five-, or six-membered ring. 4, 5, 6 (α or β) = α or β methylene carbon or proton in the four-, five-, or six-membered ring.

Discussion of NMR Data

The ^{13}C chemical shifts for the benzo[1,2:4,5]dicycloalkenes show very smooth and consistent trends throughout the homologous series (see Table I). The unsubstituted aromatic carbon (A) moves upfield with increasing strain from a value of 134.1 ppm for **6** to 117.3 ppm for **1**. Compound **4**, in which the annelated rings differ by two methylene units, is consistent in both the series **6** > **5** > **4** and **4** > **2** > **1** where one ring is held constant and the other is varied. The bridgehead carbon chemical shifts move downfield with decreasing size of the annelated ring from a high field value of 129.3 ppm for **6** to 143.4 ppm for **1**. The bridgehead carbons of a ring fused to one side of the benzene nucleus are even sensitive to changes in the ring fused to the other side. In the series **6, 5, 4**; **5, 3, 2**; and **4, 2, 1** small downfield shifts are observed for the bridgehead carbons of the ring whose size is held constant as the size of the other ring is decreased. It should be noted that the olefinic resonances of the series cyclohexene (δ 126.5), cyclopentene (δ 129.9), cyclobutene (δ 136.3) also move downfield with increasing strain[16] although the magnitude of the overall shift is somewhat less. The aliphatic methylene carbons do not show any very distinctive or characteristic variation, exhibiting chemical shifts that correlate reasonably well with those observed for the corresponding cycloalkenes.[16]

The aromatic proton chemical shifts for the series **1–6** show the lowest field peak at δ 7.08 for **3** and high field values of δ 6.64 for **1** and δ 6.75 for **6**. The unsymmetrical systems **2** and **5** fall in between, both showing a peak at δ 6.91 (Table II). Compound **4**, to which is fused both a four- and a six-membered ring, shows an aromatic resonance at δ 6.68, intermediate between the values observed for **1** and **6**.

The aromatic C–H coupling constant increases very consistently from a low value of 152.3 Hz for **6** to 160.2 Hz for **1**. These values may be compared with the J_{CH} value for durene (148.1 Hz) and that of benzene (159 Hz). To a first approxi-



12 **13**

14

Figure 1. NMR data for methylenecycloalkanes (in ppm, proton chemical shifts in parentheses).

mation one might attribute the observed increments in J_{CH} to a lessening of the alkyl inductive effect. The larger coupling constants also reflect the higher degree of s character associated with the bond in question. The same trend of increasing aromatic C–H coupling has been observed along the benzocycloalkene series increasing from a value of 155 Hz for tetralin to a value of 162 Hz for benzocyclobutene.[4]

Any attempt to analyze the chemical shift trends exhibited by the aromatic carbon and proton as well as the corresponding coupling between these atoms for the series of benzo[1,2:4,5]dicycloalkenes must confront a variety of potential influencing factors. As was already mentioned, there are rehybridization effects functioning in the σ framework. Anisotropy effects could result either from perturbations of the aromatic ring current or simply from factors involving the local environment of the C–H bond. Finally, geometric distortions of the benzene ring involving changes in bond lengths and angles could be important.

As was stated previously, rehybridization of the bridgehead carbon atom of a benzocycloalkene would cause the orbital used in bonding to the adjacent unsubstituted aromatic carbon to become higher in s character as the size of the fused ring is decreased from six carbons to four. According to Streitweiser, this effect would then cause the neighboring carbon to contribute an orbital higher in p character to preserve the C–C bond order.[12] Such rehybridization would therefore leave the aromatic C–H bond enriched in s character and polarized toward carbon. Such polarization might explain the higher field shift of this carbon atom with decreasing size of the fused rings on benzene. Also consistent with this model is the observed increase in the aromatic C–H coupling constant. The aromatic proton chemical shift moves downfield along the series **6, 5, 3,** again consistent with increasing polarization of the C–H bond, but then anomalously moves upfield in the cyclobutene-fused systems **1, 2,** and **4.**

A useful model for a portion of the benzocycloalkenes would be the methylenecycloalkanes **12–14** (Figure 1). The orientation of the vinylic hydrogens of these molecules with respect to the cyclic portion of the system should be quite similar to the orientation of the aromatic protons of **1–6** with respect to the fused rings. Although there appears to be little discernible trend or relationship between the ^{13}C chemical shifts of **12–14** with **1–6,** the vinylic ^{13}C–H coupling constant is seen to increase with decreasing ring size although much less dramatically than for the bisannelated compounds. Most noticeably, the proton chemical shifts show the same unusual behavior with a decided downfield shift apparent for methylenecyclopentane. Therefore the possibility cannot be ignored that this shift is partly attributable to a local anisotropy effect caused by the orientation of the small ring rather than any perturbation of the aromatic ring current.

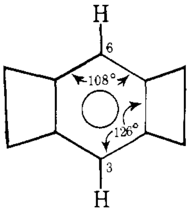


Figure 2. Aromatic bond angles in benzo[1,2:4,5]dicyclobutene (ref 17).

Table III. CNDO Calculated s-Orbital Overlap for Varying Benzene Geometries

internal C_a–C_b–C_c bond angle (θ), deg	$P^2_{C_b(s)H_b(s)}$	internal C_a–C_b–C_c bond angle (θ), deg	$P^2_{C_b(s)H_b(s)}$
108	0.3169	122	0.2625
112	0.3020	124	0.2535
116	0.2869	126	0.2447
120	0.2707		

An X-ray crystal study of **1** has shown a severe pinching effect to be imposed on the aromatic ring by the fused cyclobutene rings. This pinching results in an opening of the interior bridghead angle to 126° and a closing down of the interior angle at the unsubstituted aromatic carbon to 108°.[17] The net result of this distortion is to move carbons 3 and 6 and their attached hydrogens away from the geometric center of the molecule. Such a move should decrease the deshielding effect experienced by this proton and perhaps account for its upfield chemical shift.

To test the effect of these geometric distortions on a simple benzene nucleus, we carried out CNDO calculations for a set of model benzene systems in which the internal angles of a planar benzene ring were modified from 120° at all six carbons to the limiting values shown for the structure in Figure 2. All bond lengths were held constant with C–C equal to 1.39 Å and C–H equal to 1.09 Å. The square of the carbon-s hydrogen-s bond order should thus be proportional to s character and thereby related to the ^{13}C–H coupling constant for this same bond.[18] Table III presents the results of these calculations and demonstrates clearly that as an internal C_a–C_b–C_c benzene bond angle (θ) is compressed, the s character of the C_b–H_b bond increases substantially in very good accord with what is observed for compound **1.** The relationship between angle θ and $P^2_{C_b(s)H_b(s)}$ is almost linear. It will be of interest to design systems in which a proton is attached to the apical carbon of an expanded benzene bond angle to see if it exhibits an unusually small ^{13}C–H coupling constant.

Experimental Section

The preparation of benzodicycloalkenes **1–4** has been previously described.[10,15] Clemmensen reduction[19] of 6,7-trimethylene-1-tetralone[20] gave a 77% yield of 6,7-trimethylene-1,2,3,4-tetrahydronaphthalene (**5**), bp 90–95 °C (0.15 mm) (lit.[21] bp 125–126 °C (6 mm)). Similar Clemmensen reduction of 6,7-tetramethylene-1-tetralone[20] gave an 80% yield of 1,2,3,4,5,6,7,8-octahydroanthracene (**6**), bp 128–135 °C (0.3 mm), mp 73–74 °C (lit.[22] mp 73–74 °C). Methylenecyclobutane was prepared from pentaerythrityl tetrabromide according to the procedure of Roberts and Sauer.[23] Methylenecyclopentane was obtained from Chemical Samples Co., Columbus, Ohio 43220. Methylenecyclohexane was prepared by the Wittig reaction of methylenetriphenylphosphorane and cyclohexanone.[24]

^1H and ^{13}C NMR spectra were obtained at 32 °C for 5–10% solutions in $CDCl_3$ and chemical shifts in ppm are referred to internal Me_4Si. The proton spectra were measured at 100.06 MHz and the carbon-13 spectra were measured at 25.15 MHz with a flip angle of

20–40° and a 3–8 s delay time. All spectra were recorded on a Varian Associates XL-100 spectrometer equipped with a Nicolet TT-100 Data System and an NT-440 Multinuclear Probe. Slight deviations of the ^{13}C–H couplings for compounds **1–3** from earlier reported values[10] obtained from ^{13}C satellites in the ^{1}H NMR spectra are well within the range of experimental error.

Molecular Orbital Calculations were carried out using the CNDO/2 program (No. 141) from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We would also like to thank Mr. Steven Silber for his assistance in obtaining NMR spectra. The Varian XL-100 NMR spectrometer was obtained with a major equipment grant from the National Science Foundation.

Registry No.—**12**, 1120-56-5; **13**, 1528-30-9; **14**, 1192-37-6.

References and Notes

(1) For leading references see P. J. Garratt and D. N. Nicolaides, *J. Org. Chem.*, **39**, 2222 (1974), as well as ref 2 and 6 below.
(2) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **92**, 1605 (1970).
(3) E. L. Motell, D. Lauer, and G. E. Maciel, *J. Phys. Chem.*, **77**, 1865 (1973).
(4) H. Gunther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew Chem., Int. Ed. Engl.*, **12**, 762 (1973).
(5) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Am. Chem. Soc.*, **96**, 1595 (1974).
(6) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, **41**, 751 (1976).
(7) (a) C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 701 (1971); (b) M. Randic and Z. B. Maksic, *J. Am. Chem. Soc.*, **93**, 64 (1971).
(8) A. Streitweiser, P. H. Owens, R. A. Wolf, and J. E. Williams, *J. Am. Chem. Soc.*, **96**, 5448 (1974).
(9) See for example: (a) A. J. Jones, P. J. Garratt, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **12**, 241 (1973); (b) W. M. Beckenbaugh, S. R. Wilson, and P. A. Loeffler, *Tetrahedron Lett.*, 4821 (1972).
(10) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977).
(11) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).
(12) A. Streitweiser, Jr., G. Ziegler, P. Mowery, A. Lewis, and R. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
(13) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).
(14) R. P. Thummel and D. K. Kohli, *J. Org. Chem.*, **42**, 2742 (1977).
(15) R. P. Thummel and W. Nutakul, submitted for publication.
(16) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).
(17) J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B*, **25**, 978 (1969).
(18) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 1 (1970).
(19) L. F. Feiser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1968, p 1287.
(20) H. Christol, D. D. Koulodo, M. Mousseron, and F. Plenat, *Bull. Soc. Chim. Fr.*, 1576 (1960).
(21) S. Chandra and S. Gupta, *J. Indian Chem. Soc.*, **16**, 89 (1939).
(22) G. Schroeter, *Chem. Ber.*, **57B**, 2003 (1924).
(23) J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).
(24) G. Wittig and U. Schoellkopf, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 751.

Addition of Dichloroketene to Silyl Enol Ethers. Synthesis of Functionalized Cyclobutanones[1]

Larry R. Krepski and Alfred Hassner*

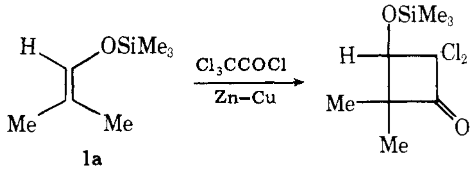
Department of Chemistry, University of Colorado, Boulder, Colorado 80302, and
Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

Received October 27, 1977

Dichloroketene, generated from trichloroacetyl chloride and activated zinc, has been found to react readily with silyl enol ethers. In most cases, good yields of 3-siloxy-substituted dichlorocyclobutanones could be isolated. The reaction appears to be both regio- and stereospecific. Mild acid hydrolysis of the siloxycyclobutanones afforded the corresponding 3-hydroxydichlorocyclobutanones. In some cases, cyclobutane ring opening or elimination to generate a dichlorocyclobutenone was observed. The silyl enol ethers derived from acetophenone and pinacolone, on the other hand, afforded only acyclic products from the dichloroketene. The possibility that these acyclic products may result from ring opening of initially formed cyclobutanones is discussed.

General Reaction Scheme. The cycloaddition of dichloroketene[2] to reactive olefins constitutes a convenient synthesis of cyclobutanones.[3] In view of the considerable synthetic utility of silyl enol ethers[4] as masked enols and our[5] own interest in these species, we investigated the reaction of dichloroketene with silyl enol ethers as a possible route to functionalized cyclobutanones.

When trichloroacetyl chloride was slowly added to a stirred mixture of the trimethylsilyl enol ether **1a** and activated zinc in dry ether, a mildly exothermic reaction occurred and a one to one adduct was obtained in 92% yield after workup. A strong high-frequency (1805 cm^{-1}) carbonyl absorption in the IR spectrum indicated cyclobutanone **2a** as the product of this cycloaddition (eq 1). Regiochemistry was assigned in accord with known examples of diphenylketene cycloadditions with enol ethers.[6] Several other silyl enol ethers were found to react smoothly with dichloroketene to afford good yields of substituted cyclobutanones (see Table I). The yields are generally higher than in cycloadditions of dichloroketene to simple olefins.



1a **2a** (1)

Hydrolysis of the trimethylsilyl group of the cycloadducts was readily accomplished by treating a tetrahydrofuran or methanol solution of the siloxycyclobutanone with dilute hydrochloric acid. As indicated in Table I, this afforded high yields of the hydroxy-substituted cyclobutanones (**3a–f**).

Generation of dichloroketene by the triethylamine dehydrohalogenation of dichloroacetyl chloride in the presence of silyl enol ethers did not lead to cycloadducts. For instance, in the case of **1b**, conversion to cyclopentanone appeared to be the major reaction, accompanied by minor amounts of **4** (eq

---

* Address correspondence to State University of New York at Binghamton.

0022-3263/78/1943-3173$01.00/0