The Chemistry of Cyclopropenones

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I. Introduction

In the fourteen years that cyclopropenones have been available for laboratory investigations, a considerable volume of information has accumulated in numerous publications scattered throughout the chemical literature. Their known chemical behavior, and their great potential for further applications in organic synthesis, makes a review of the chemistry of the cyclopropenones particularly opportune.

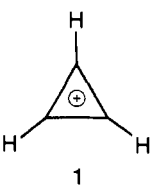
This review has been organized by discussing initially their physical properties, important features in the understanding of their chemical activity, and then the procedures used for their synthesis. Though at first sight their reactions appear to be extremely varied and complex, they may be arbitrarily classified as decarbonylation reactions, oxidation reactions, substitution reactions, and addition reactions. It is in this last area that the great bulk of the reactions of cyclopropenones fall, and they may be further divided according to the nature of the reactant and the site of reaction on the three-membered ring.

As would be anticipated, cyclopropenones have been utilized in the growing area of cycloaddition reactions. The wealth of chemistry stemming from these reactions, and the considerable potential for future development, suggested their separate classification, and they have been considered in terms of whether the cycloaddition occurs across the C=O, C=C, or C—CO bond of the cyclopropenone ring.

Earlier reviews of cyclopropenones have always been part of a wider consideration of cyclopropane, cyclopropene (1966, 1972), and cyclopropenyl cation chemistry. These topics are not discussed in this present review which covers the available literature to January 1973.

The development of cyclopropenone chemistry provides an interesting illustration of the judicious application of theoretical MO calculations to predicting the characteristics of as yet unknown ring systems. The development of the $(4n + 2)$ π-electron rule by Hückel[1] in 1931 was of paramount importance to the theory of cyclic, unsaturated systems, and it may be stated as follows: Planar, monocyclic systems with trigonally hybridized atoms containing $(4n + 2)$ π electrons possess a characteristic electronic stability. In addition to providing an explanation on the basis of quantum theory for the special properties of benzene ($n = 1$), it allowed predictions to be made regarding the stability of systems that had not yet been synthesized.[2]

The tropylium ion[3-5] provided confirmation of Hückel's rule for $n = 1$, and it may be predicted similarly that the cyclopropenyl cation (**1**), which has two π electrons in a field of three carbon atoms, should have the stability characteristic of aromatic systems. Quantum mechanical calculations showed[6] that the delocalization energy of 1 was 2β, and the synthesis by Breslow[7,8] of the first member of this class of compounds, the symmetrical triphenylcyclopropenylium salt (**2**), confirmed the stability



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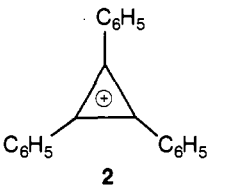

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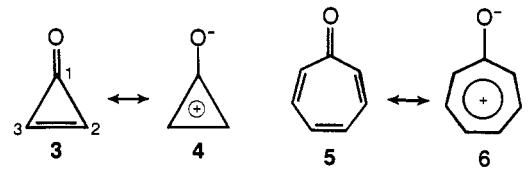
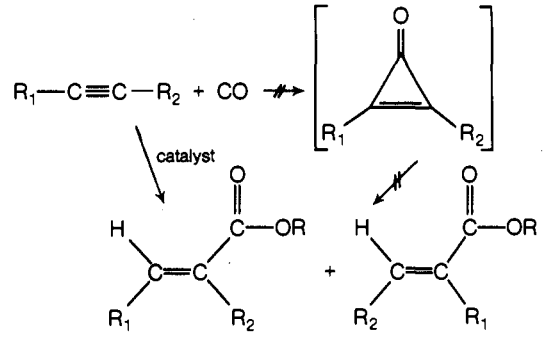
of these substances. Subsequent molecular orbital calculations[9] for a variety of cyclopropenyl systems including cyclopropenone (**3**) and its charge-delocalized form 4 gave calculated values of 1.36β for the delocalization energy of cyclopropenone and 6.15β for its diphenyl derivative, indicating that cyclopropenones should be aromatic, being the analogs in the two π-electron system of tropone (**5**) in the six π system. Taking into account ring strain, cyclopropanones would be expected to be more

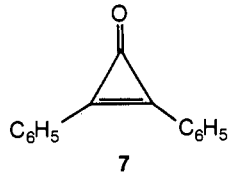


3 4 5 6

stable than the highly strained cyclopropenones, but it was only recently that the first member of the cyclopropanone series was fully characterized.[10,143] They had been detected previously only as reaction intermediates.[11-16] An earlier suggestion that cyclopropenones were intermediates in the catalytic carbonylation of acetylenes which, in the presence of water or alcohols, leads to acrylic acids or acrylates,[17] shown below, has since been found to be incorrect.[18,19]



The independent synthesis of diphenylcyclopropenone (**7**) in 1959 by Breslow and coworkers,[20] and by Vol'pin



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et al.[21] (sections IV.A,B), and its relative thermal stability provided verification of the utility and importance of the Hückel theory in making experimental predictions. These early experiments provided a stimulus for the study of cyclopropenone chemistry which has resulted in many, varied, synthetic routes to this ring system, a better understanding of their physical characteristics, and, more recently, demonstrations of their wide utility in organic synthesis. The recent synthesis of the parent cyclopropenone (section IV.A.4) provides further stimulus for the study of this ring system and is a fitting climax to the early synthetic efforts.

II. Nomenclature

The numbering of the cyclopropenone ring system is as in **3**. This numbering system complies with current IUPAC and *Chemical Abstracts* nomenclature; however, in the latter, the numbering is omitted and derivatives of the cyclopropenone ring system are simply named by the appropriate substituents being suffixed to cyclopropenone.

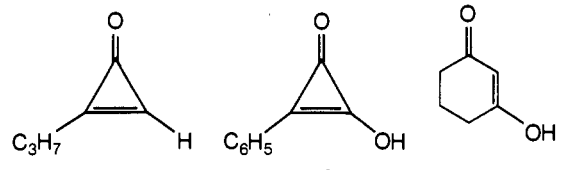
III. Physical Characteristics

The charge delocalized form (**6**) is considered to make a substantial contribution to the ground state of tropone (**5**). Cyclopropenones may be considered in an analogous fashion **3** and **4**, and their physical properties should provide some indication of the validity of this assumption.

A. Basicity

In comparison with α,β-unsaturated ketones, cyclopropenones are more basic, though tropone (determined by infrared spectroscopy)[22,23] is less basic. Estimates of the basicity of diphenyl-[24] (**7**), di-*n*-propyl-[34] (**8**), dicyclopropyl-,[174] methyl-[26] (**9**), and dimethylcyclopropenone[26] (**10**) have been made by determination of the half-protonation point, and the Hammett H_0 values are, respectively, −2.5, −1.9, −1.2, −5.0, and −1.5. A comparison of diphenyl- and di-*n*-propylcyclopropenone showed that the di-*n*-propylcyclopropenone was the more basic; it was extracted completely from an equal volume of carbon tetrachloride with 12 *N* HCl and was extracted 50% with 6 *N* acid. On the other hand, diphenylcyclopropenone was extracted only 50% with 12 *N* acid.[27] The relative basicities of a series of disubstituted cyclopropenones have been investigated and percentages of extraction by concentrated HCl indicated that the dialkylcyclopropenones were the most strongly basic. Introducing conjugation with the cyclopropenone ring by aromatic or olefinic substitution lowered the relative basicity, and a similar effect was observed when chlorine was substituted for certain olefinic hydrogens on the olefinic substituent. For example, *trans*-2-phenyl-3-styrylcyclopropenone was extracted 40% by concentrated HCl, but *trans*-2-phenyl-3-(1-chlorostyryl)-cyclopropenone was only extracted 10% under the same conditions. These results indicated that conjugation with the cyclopropenone ring, or substitution of an electron-withdrawing substituent, destabilized the positive charge in the resultant cyclopropenylium salt.[28]

In *n*-propylcyclopropenone (**11**), a facile base-catalyzed exchange of the ring hydrogen has been observed.[26,29] The acidity of this proton was considered to be due in part to hybridization effects, as indicated by the nmr chemical shift and ^{13}C coupling constant for this proton (section III.C.3). The acidity of the enolic hydroxyl hydrogen atom in cyclic α- and β-diketones is well known;[30] e.g., 3-hydroxycyclohex-2-enone (**13**) has a pK_a of 5.25, and it would be anticipated that phenylhydroxycyclopropenone (**12**) would be a strong acid. It has been shown[30] to have a pK_a of 2.0 ± 0.5, agreeing well with the predicted[31,32] value of 2.0.



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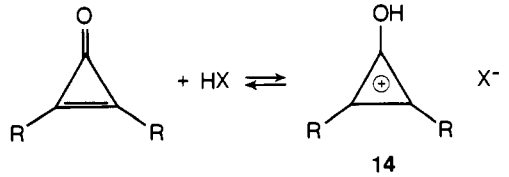
The high basicity of the cyclopropenones is also reflected in their ready conversion into hydroxycyclopropenylium salts (ref 21, 22, 33, 34) **14**. The structure of the salts **14** was determined from the disappearance of the two diagnostic cyclopropenone bands (section III.C.1) in the infrared spectrum and the appearance of an OH band and a band assignable[56,144] to the cyclopropenylium system at 1400–1430 cm^{-1}.



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B. Dipole Moments

The high dipole moments (ref 21, 24, 33, 34–38) ob-

served for several cyclopropenones are strong evidence in favor of the polarization of the carbonyl group. The dipole moment of diphenylcyclopropenone (**7**) has been reported as 5.08 D[21,33,35] and 5.14 D,[24,36] and for di-*n*-propylcyclopropenone (**8**), dicyclopropylcyclopropenone, and cycloheptenocyclopropenone (**15**), the values were 4.78, 4.58, and 4.66 D, respectively.[36,174] The calculated dipole moment (4.43 D) compared reasonably well with the observed value for diphenylcyclopropenone[38] (**7**), and a comparison of the above values with those observed for benzophenone (3.0 D), tropone (4.3 D), and trimethylamine oxide (5.03 D) indicates that in cyclopropenones considerable polarization of the molecule must occur. Theoretical studies related to the above topics have been described.[60,62-65]

C. Spectra

1. Infrared Spectra

Two bands in the infrared spectrum in the regions 1800–1875 and 1600–1660 cm^{-1} are present in all cyclopropenones (ref 20, 22, 24, 26, 27, 33, 39-50, 93, 145) except unsubstituted cyclopropenone[150] (**3**) and are considered diagnostic for the cyclopropenone nucleus. Cyclopropenone has bands at 1864 and 1833 cm^{-1}, but not in the 1600-cm^{-1} region. There has been controversy in the literature over the assignment of these bands. According to the solvent dependency of the positions of the bands, the 1800–1875-cm^{-1} band originated from a ring vibration, while the band between 1600 and 1660 cm^{-1} was assigned to a carbonyl stretching mode.[44,45,48] However, substitution of ^{18}O in some cyclopropenones affected the higher energy transition more strongly.[48] This indicates that a reversal of the original assignment should be made, but a more likely interpretation is that the two modes (carbonyl stretch and olefin stretch) are coupled[26,48,50] and considerable mixing of the two frequencies occurs. On this basis specific assignments are open to question. If there is validity to these assignments, then the occurrence of the carbonyl band at such a low wavenumber suggests a high degree of single-bond character in the C=O bond, and hence a considerable contribution of the charge delocalized form **4** to the ground state of cyclopropenones. Cyclopropanone itself absorbs[51] at 1825 cm^{-1} in support of the above assumptions.

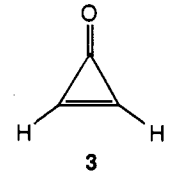
The carbonyl and double bond absorption bands were not present in the infrared spectra of the hydroxycyclopropenylium salts **14**, but the appearance of a broad OH band at 2976 cm^{-1} and a transition at 1420 cm^{-1} due to the cyclopropenylium system is consistent with the ionic structure of these cyclopropenone derivatives (ref 22, 23, 33, 52, 53). Thus the appearance of two absorptions in the regions 1800–1875 and 1600–1660 cm^{-1} may be considered to be indicative of the presence of a cyclopropenone nucleus.

2. Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of dialkylcyclopropenones showed only strong end absorption for the $\pi \rightarrow \pi^*$ transition whose maximum lies below 175 nm. This was detected only in methylene chloride solution.[34] These results confirmed predictions made from molecular orbital calculations that the relatively high-energy cyclopropene antibonding orbital causes $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions to occur only at low wavelengths.[34] The spectrum of diphenylcyclopropenone[24] (**7**) resembled that of simple diphenylcyclopropenes,[54] but recently a new absorption band of **7** in cyclohexane was observed at 362 nm (ϵ 1150). This was assigned tentatively to an intramolecular charge-transfer band.[45] Cyclopropenone (**3**) absorbed at 276 nm (ϵ 31), identified as the $n \rightarrow \pi^*$ transition, and the $\pi \rightarrow \pi^*$ maximum was observed below 190 nm.[156]

3. Nuclear Magnetic Resonance Spectra

With the synthesis of mono-substituted cyclopropenones and cyclopropenone itself, definitive evidence for the aromatic character of these compounds was obtained from their nmr spectra. The chemical shifts of the ring protons in cyclopropenone (**3**) (δ 9.08),[42,150] *n*-propylcyclopropenone (**11**) (δ 8.68),[26] methylcyclopropenone (**9**) (δ 8.66),[26] and *n*-pentylcyclopropenone (**16**) (δ 8.47)[36]



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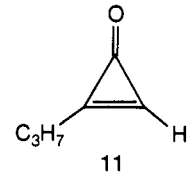

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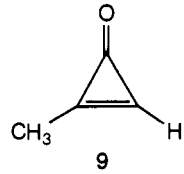

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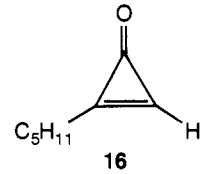

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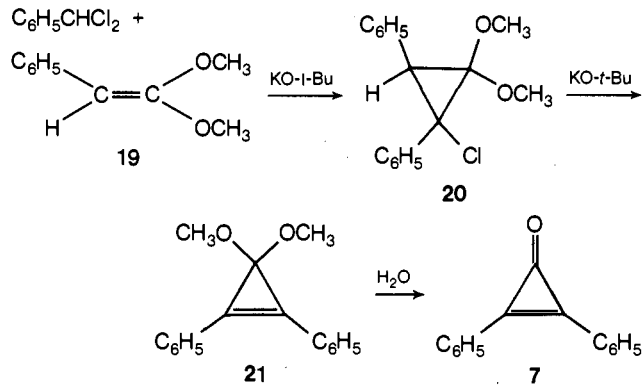
indicate that a considerable ring current is present in the molecule. These chemical shifts should be compared with those at δ 6.66 for the proton of 1,1,2-trimethylcyclopropene[55] and δ 10.42 for the di-*n*-propylcyclopropenyl cation.[56] This shows that the cyclopropenone ring has a larger deshielding effect than a cyclopropene ring but less than that of a cyclopropenyl cation. However, some consideration of the magnetic anisotropy of the carbonyl group should be made in discussing these relative chemical shifts.[26] ^{13}C nmr signals (in $CDCl_3$) relative to TMS at −155.1 ppm (C_1) and −158.3 ppm (C_2) are also of interest in this respect.[175]

The small shift of the ring proton ($\Delta\nu = 0.21\delta$) observed when the spectrum of **16** was determined in CF_3CO_2H–CCl_4 indicated that there is a high degree of polarization of the carbonyl group even in $CDCl_3$.[57] The ^{13}C–H coupling constants of cyclopropenone (**3**) ($J(^{13}C$–H) = 230 Hz) and of methylcyclopropenone (**9**) ($J(^{13}C$–H) = 213 Hz) were of the same order of magnitude as that observed in 1,1,2-trimethylcyclopropene[55] ($J(^{13}C$–H) = 218 Hz) and in the diethylcyclopropenyl cation[58] ($J(^{13}C$–H) = 228 Hz). These results may reflect a large s contribution to the carbon hybrid orbital.[26]

Prior to the synthesis of unsubstituted cyclopropenones, nmr spectra of dialkylcyclopropenones were used to identify structural features. In di-*n*-propylcyclopropenone (**8**), the separation between the signals for the methylene proton resonances α to the cyclopropenone ring and methylene protons β to the ring was 0.85 ppm, a value similar to that observed in corresponding covalent cyclopropenes. However, the difference in chemical shift of these methylene protons was not as large as those observed for alkyl cyclopropenylium salts (1.27–1.30 ppm).[56] In addition the influence of the long-range anisotropy effects of the carbonyl group may cause a fortuitous cancelling of the downfield shift of these α-methylene protons.[50]

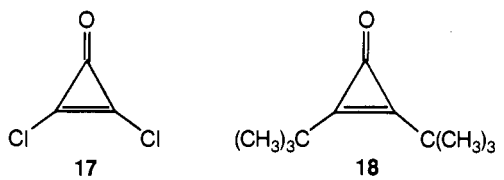
TABLE I. Arylphenylcyclopropenones Prepared by Cyclopropene Ketal-Potassium *tert*-Butoxide Route[20,66]

Aryl group	% yield	Mp, °C
C_6H_5	80	121–121.5
p-ClC_6H_4	43	147
m-ClC_6H_4	46	112
o-ClC_6H_4	4	104–105
p-$CH_3OC_6H_4$	26	104
m-$CH_3OC_6H_4$	25	80
o-$CH_3OC_6H_4$	3	94–96
p-$CH_3C_6H_4$	27	131
o-$CH_3C_6H_4$	28	127
o-FC_6H_4	~0.5	109–110



4. Mass Spectra

Very little study has been made of the fragmentation patterns of cyclopropenones, the reported spectra being all extremely simple. The molecular ion was not observed in the mass spectrum of diphenylcyclopropenone[154] (**7**) or diphenylcyclopropenethione[155] (**252**). Instead, an initial loss of CO or CS was observed, followed by a fragmentation pattern very similar to that of diphenylacetylene. There is no evidence to date to enable a decision to be made as to whether this initial loss of CO or CS is thermally induced or electron-impact induced. Dichlorocyclopropenone[59] (**17**) yielded a spectrum consisting of the molecular ion and five major fragment ions corresponding to the loss of Cl, Cl_2, CO, COCl, and C_2ClO. The mass spectrum of di-*tert*-butylcyclopropenone (**18**), with the exception of the molecular ion at m/e 166, was very similar to that of di-*tert*-butylacetylene, a not unexpected feature because of the stability of the latter molecule.



IV. Synthesis of Cyclopropenones

There are four main synthetic routes to cyclopropenones, and three involve the hydrolysis of 3,3-disubstituted cyclopropene derivatives in which the substituents may be either halogen or alkoxy groups. The fourth, and more general method, is a modified Favorskii reaction involving ring closure of α,α'-dibromo ketones.

A. Synthesis from 3,3-Disubstituted Cyclopropenes

1. Cyclopropene Ketal Route

Diphenylcyclopropenone (**7**) was first synthesized[20] by the addition of phenylchlorocarbene to phenylketene acetal (**19**), a procedure which probably gives the cyclopropane **20** as the initial product. Additional base converts **20** into the cyclopropene ketal **21** by a β-elimination of hydrogen chloride, followed by hydrolysis to diphenylcyclopropenone (**7**). This reaction has been employed in the synthesis of various arylphenylcyclopropenones utilizing the appropriate arylidene chloride.[66] p-Nitrobenzylidene chloride failed to give the corresponding cyclopropenone (see also section IV.A.2), and very low yields were obtained with some ortho-substituted derivatives (Table I).

2. Carbene-Insertion Route

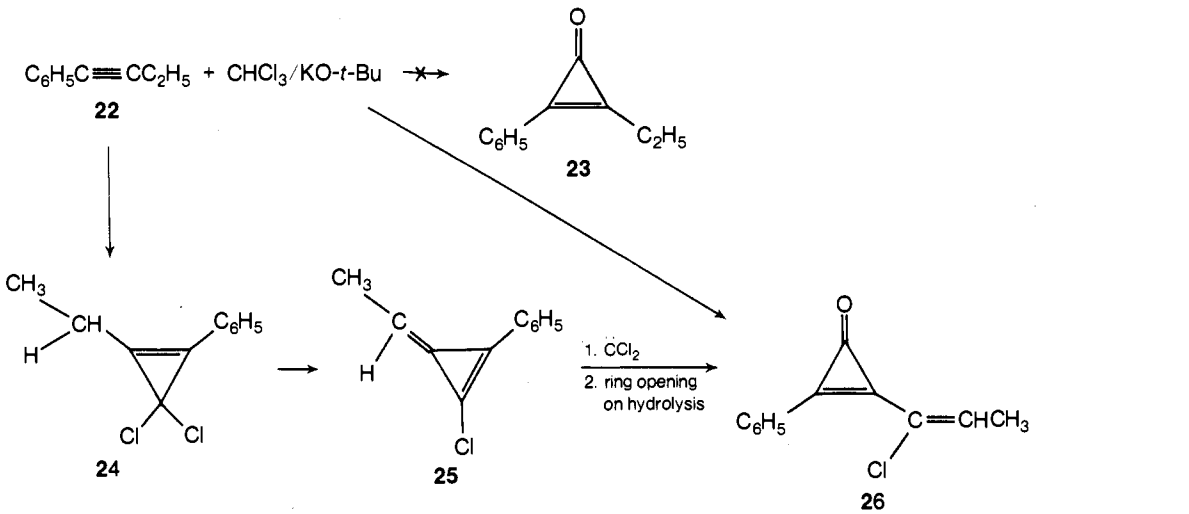
A simpler synthesis of cyclopropenones is based on the addition of dihalocarbene to acetylenes (ref 21, 26–30, 33, 34, 39, 41, 67–77). The intermediate 3,3-dihalocyclopropenes are usually not isolated under the reaction conditions employed, hydrolysis giving the final products as cyclopropenones.

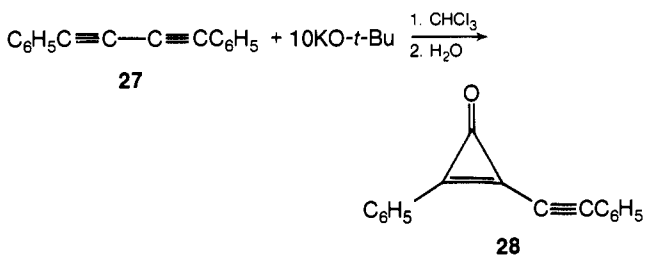
Concurrently with the initial isolation of diphenylcyclopropenone (**7**) by Breslow,[20] Vol'pin also synthesized **7** by the reaction of diphenylacetylene and bromoform in the presence of potassium *tert*-butoxide,[21,33] a reaction which clearly involves a carbene intermediate. The synthesis of **7** was also accomplished from diphenylacetylene, methyl trichloroacetate, and sodium methoxide.[39]

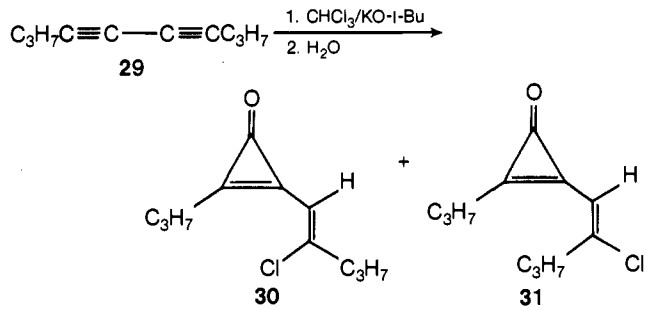
$$C_6H_5C{\equiv}CC_6H_5 + CHBr_3 \xrightarrow[2.\ H_2O]{1.\ KO\text{-}t\text{-}Bu} \mathbf{7}$$

Both dipropylacetylene and di-*tert*-butylacetylene react with sodium trichloroacetate in a similar fashion to form the corresponding cyclopropenones.[27,67] However, with 1-ethyl-2-phenylacetylene (**22**), the expected 2-ethyl-3-phenylcyclopropenone (**23**) was not obtained, 2-(1-chloropropen-1-yl)-3-phenylcyclopropenone (**26**) being isolated instead.[69] This compound may arise from initial dichlorocarbene attack on the triple bond to form **24**, followed by loss of HCl by base-catalyzed removal of the methylene proton α to the ring and rearrangement to **25**. Additional attack of dichlorocarbene, rearrangement, and ring opening on hydrolysis would yield **26**. On reaction of **22** with sodium trichloroacetate in dimethoxyethane at 80°, however, 2-ethyl-3-phenylcyclopropenone (**23**) was obtained.[69] Analogous products were isolated in the reaction of benzylphenylacetylene with ethyl trichloroacetate and either sodium methoxide[41] or potassium *tert*-butoxide.[70]

Dehmlow has studied extensively the addition of dichlorocarbene to a series of alkynes[28] and alkenynes.[68,71] A tenfold excess of potassium *tert*-butoxide in chloroform (nitrogen atmosphere) with the diacetylene **27** gave, after hydrolysis, a small amount of 2-phenyl-3-phenylethynylcyclopropenone (**28**). The analogous dipropyldiacetylene (**29**) under the same reaction conditions gave instead 2-propyl-3-(2-chloro-*trans*-1-penten-1-yl)cyclopropenone (**30**) and the corresponding cis derivative **31** in a 5:2 ratio.[68] Evidently the exocyclic acetylene analog of **28** is formed, but further addition of HCl across the triple bond yielded **30** and **31**. Aromatic and aliphatic tri- and tetraynes, and alkynes with electron-withdrawing substituents, did not give the expected cyclopropenones.[28,69] The addition of dichlorocarbene to the double or triple bond of alkenynes was found to be dependent upon the substituents attached to the system.[71] For example,

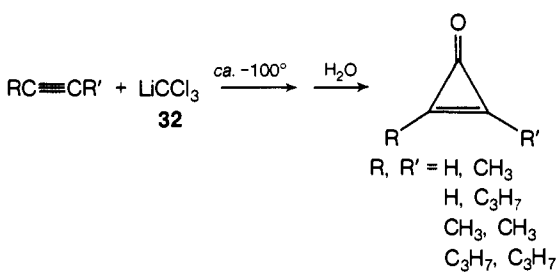






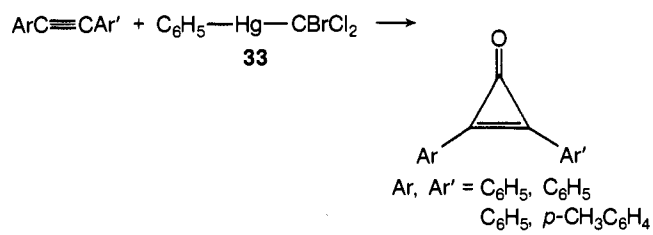
trans-1,4-diphenyl-1-buten-3-yne gave an addition product of dichlorocarbene across the triple bond, whereas 2-methyl-1-penten-3-yne yielded the addition product to the double bond.

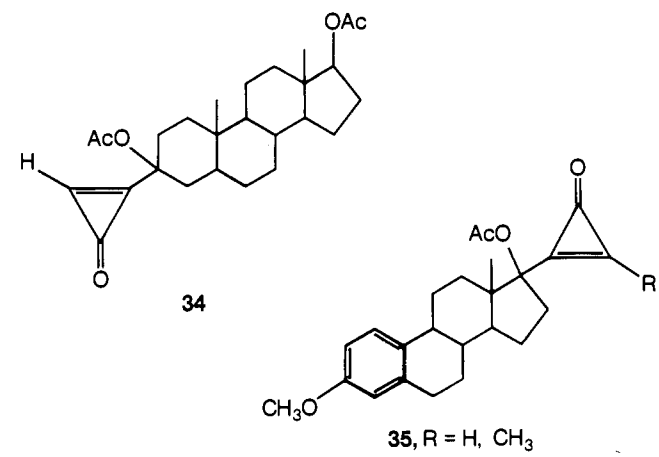
Lithium trichloromethide (**32**) as the dichlorocarbene source and various acetylenes also produced cyclopropenones after hydrolysis.[26,29] An attempt to prepare cyclopropenone (**3**) itself from acetylene by this method was unsuccessful.[26]



The use of phenyl(bromodichloromethyl)mercury (**33**) as the dichlorocarbene donor has also led to the synthesis of diarylcyclopropenones.[72] Unsymmetrical diarylcyclopropenones or diarylcyclopropenones containing base-sensitive functional groups may be prepared by this method. Analogous reactions could not be realized with dialkylacetylenes.

The addition of difluorocarbene to steroidal acetylenes has been reported.[73,74] Thus (3,17β-diacetoxy-5α-androstan-3α-yl)cyclopropenone (**34**) and (17β-acetoxy-3-methoxyestra-1,3,5(10)-trien-17α-yl)cyclopropenone (**35**) were prepared following hydrolysis of the intermediate difluorocyclopropene.





The synthesis of phenylhydroxycyclopropenone (**12**) was accomplished by the reaction of 2-phenyltetrachloropropene (**36**) or 1-phenyl-2,3,3-trichlorocyclopropene (**38**) with potassium *tert*-butoxide.[30,75,77] The former reaction was postulated to involve a vinyl carbene intermediate **37**. Subsequent ring closure and concomitant

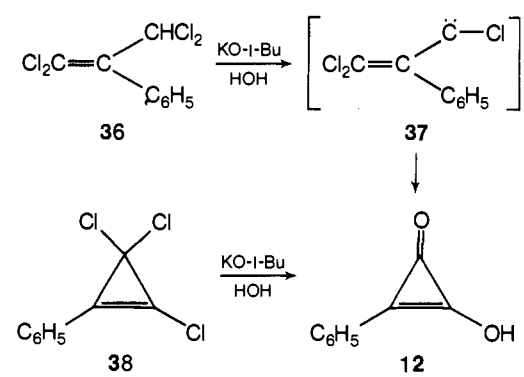
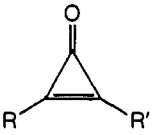
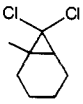


TABLE II. Aryl- and Alkylcyclopropenones Prepared by Carbene-Insertion Procedures



Substituents					
R	R′	Method[a]	Yield, %	Mp or bp (mm), °C	Ref
C_6H_5	C_6H_5	A	20–30	119–121	24, 33
C_6H_5	C_6H_5	B	6	119–121	24
C_6H_5	C_6H_5	E	63	120–122	72
C_6H_5	C_6H_5	F	40	114–117	34
C_6H_5	$C(Cl)=CHCH_3$	A	8	119.5–120.5	28, 69
C_6H_5	$C(Br)=CHCH_3$	A	4	117–118	28
C_6H_5	$C(Cl)=CHC_6H_5$ (isomer A)	A	3	97	28, 70
	(isomer B)	A	5	117	28
C_6H_5	$C\equiv CC_6H_5$	A	6	92	28, 68
C_6H_5	$CH=CHC_6H_5$ (cis)	A	23	80	28
	(trans)	A	10	98–99	28
C_6H_5	p-$NH_2C_6H_4$	A	6	192	28
C_6H_5	$C(Cl)=CHOCH_3$	A	31	152	28
C_6H_5	$CH(OC_2H_5)_2$	A	15	46	28
C_6H_5		A	11	122	71
C_6H_5	$CH=C(CH_3)_2$	A	3.5	106	71
C_6H_5	$C(Cl)=CH(CH_2)_2CH=CH_2$ (isomer A)	A	4	150 (0.1)	71
	(isomer B)	A	7	52	71
n-C_3H_7	$CH=C(Cl)$-n-C_3H_7 (isomer A)	A	7	100–120 (0.1)	28, 68
	(isomer B)	A	1.5	120 (0.1)	28, 68
n-C_3H_7	$C(Cl)=CH-C_2H_5$ (isomer A)	A		90 (0.1)	28
	(isomer B)	A		95 (0.1)	28
$C(CH_3)_3$	$CH=CHC(CH_3)_3$	A	47	55	28
$C(CH_3)_3$	$C\equiv CC(CH_3)_3$	A		65 (0.1)	28
$C(CH_3)_3$	$CH=C(Cl)C(CH_3)_3$	A	12	86	28
$C(CH_3)_3$	$C(Cl)=CH(CH_2)_2CH=CH_2$ (isomer A)	A	0.7	90 (0.1)	71
	(isomer B)	A	9.5	100 (0.1)	71
$SC(CH_3)_3$	$SC(CH_3)_3$	A	4	79	28
C_6H_5	$CH_2C_6H_5$	B		108–109	41
n-C_3H_7	n-C_3H_7	B	8.9	80 (0.7)	34
n-C_6H_{13}	C_2H_5	B	5	140 (0.5)	28
$C(CH_3)_3$	$C(CH_3)_3$	B	0.6	61–61.5	67
H	$C_{21}H_{27}O_3$ (**35**)	B		147–148	74
CH_3	$C_{21}H_{27}O_3$ (**35**)	B		168–170	74
H	$C_{23}H_{35}O_4$ (**34**)	B		132–134	73
n-C_3H_7	n-C_3H_7	C	19	80 (0.7)	26, 29
CH_3	CH_3	C	12	54–58 (0.7)	26, 29
H	n-C_3H_7	C		40 (2)	26, 29
H	CH_3	C	20	57 (2)	26, 29
C_6H_5	OH	D	18	244–245	30, 75
C_6H_5	p-$CH_3C_6H_4$	E	79	129.5–131.5	72

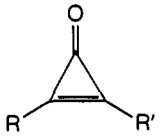
[a] (A) potassium *tert*-butoxide/$CHCl_3$ ($CHBr_3$); (B) sodium trichloroacetate; (C) lithium trichloromethide; (D) intermolecular carbene insertion/KO-*t*-Bu; (E) phenyl(bromodichloromethyl)mercury; (F) phenylchlorocarbene.

solvolysis would afford **12**, isolated in a 10% overall yield. Under these conditions **38** gave **12** in 18% overall yield.

3. *Trichlorocyclopropenylium Ion Route*

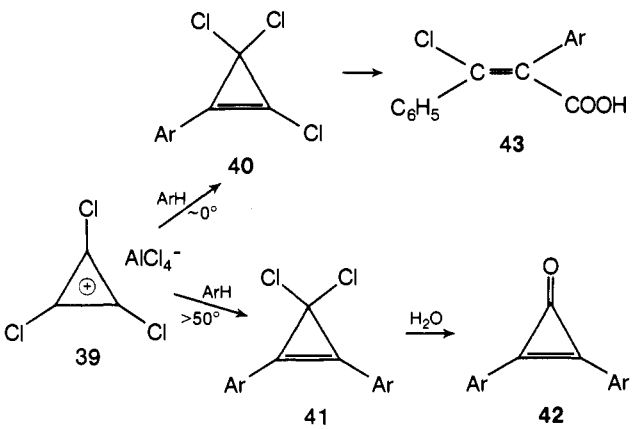
The reaction of trichlorocyclopropenium tetrachloroaluminate (**39**) with benzene derivatives *via* a Friedel-Crafts pathway provides aryltrichlorocyclopropenes (**40**) or *gem*-dichlorodiarylcyclopropenes (**41**). The latter may be readily converted into the corresponding diarylcyclopropenones **42**.[78-81] The electrophilic substitution into the benzene ring results in mono- or disubstitution products for aromatic hydrocarbons containing weakly activating substituents (alkyl, halogen). With strongly activating substituents present in the benzene ring, the cyclopropenone is not formed, but instead the reaction continues replacing all three halogens of **39** yielding triarylcyclopro-

TABLE III. Symmetrical and Unsymmetrical Disubstituted Cyclopropenones Prepared from Trichlorocyclopropenium Ion

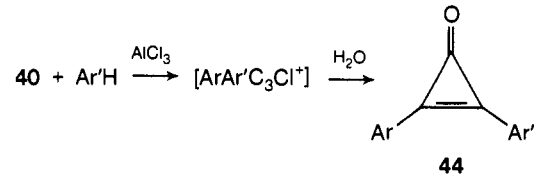


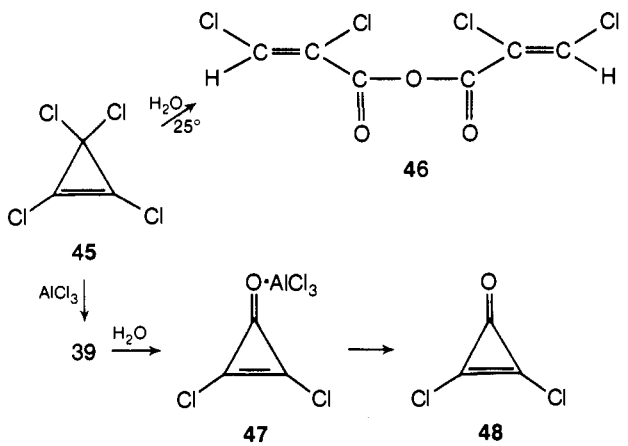
Substituents				
R	R′	Yield, %	Mp, °C	Ref
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	45	179–181	80
p-HOC_6H_4	p-HOC_6H_4	10	222–226 dec	80
3,5-$(CH_3)_2$-4-OH-C_6H_2	3,5-$(CH_3)_2$-4-OH-C_6H_2	100	268 dec	80
3,5-$(i\text{-}Pr)_2$-4-OH-C_6H_2	3,5-$(i\text{-}Pr)_2$-4-OH-C_6H_2	82	209–211 dec	80
3,5-$(t\text{-}Bu)_2$-4-OH-C_6H_2	3,5-$(t\text{-}Bu)_2$-4-OH-C_6H_2	48	215 dec	79, 80
p-FC_6H_4	C_6H_5	44	111–113	81
p-FC_6H_4	p-$CH_3C_6H_4$	20	141–142	81
p-FC_6H_4	Mesityl	10	135–137	81
p-FC_6H_4	p-FC_6H_4	48	184–185	78
Cl	Cl		−6	59

penylium ion salts.[80] 1-Aryl-2,3,3-trichlorocyclopropene (**40**) may be hydrolyzed with ring opening, affording as the major product 2-aryl-3-chloroacrylic acid (**43**). The mechanism of the hydrolysis is not known but may proceed through an arylhalocyclopropenone.[81]



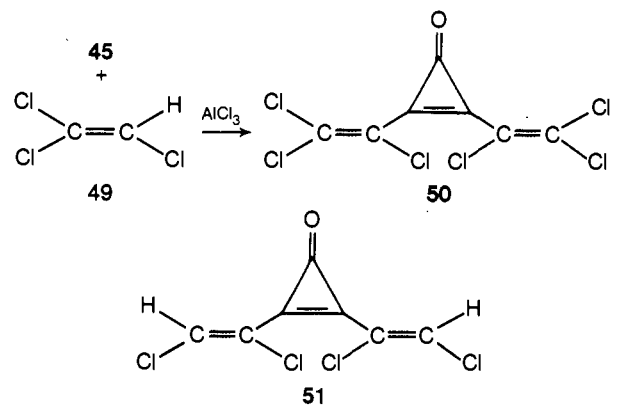
An attempt was also made to isolate phenylhydroxycyclopropenone (**12**) from the hydrolysis of **40** (Ar = Ph), but only with varied success (yields from 0 to 12%) could they isolate a compound with properties identical with those previously reported.[30] 1-Aryl-2,3,3-trichlorocyclopropene (**40**) was found to undergo further reaction with a second aromatic hydrocarbon, and the products, isolated after an aqueous reaction work-up procedure, were diarylcyclopropenones. The synthesis of diarylcyclopropenones may thus be accomplished stepwise, and an advantage of this procedure is in the synthesis of unsymmetrically substituted cyclopropenones **44**.[81] Tetrachlorocyclopropene (**45**), which is converted into **39** on reaction with aluminum chloride, was thought to be a likely possibility to give dichlorocyclopropenone (**48**) on hydrolysis. The synthesis of **48** was initially unsuccessful, with only a ring-opened anhydride **46** being isolated on hydrolysis.[172] However, a very slow hydrolysis of **39** suspended in methylene chloride produced an aluminum complex **47** from which dichlorocyclopropenone (**48**) was isolated as a dangerously unstable liquid[59] (Table III).





4. *Tetrachlorocyclopropene Route*

The reaction of 1,1,2-trichloroethylene (**49**), aluminum chloride, and tetrachlorocyclopropene (**45**) gave bis(trichlorovinyl)cyclopropenone (**50**) in 47% yield.[27] Reaction with *cis*- or *trans*-1,2-dichloroethylene under the same reaction conditions produced 17 or 5%, respectively, of bis(1,2-dichlorovinyl)cyclopropenone (**51**). No reaction was observed with tetrachloroethylene.

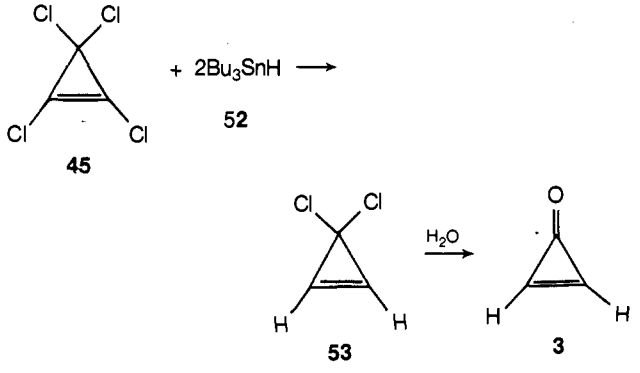


The synthesis of the parent ketone, cyclopropenone (**3**), was unsuccessful by the methods used to prepare substituted derivatives,[26,33,82] and by the modified Favorskii reaction (section IV.B). Breslow and coworkers (ref 42, 83, 150, 156) succeeded in synthesizing cyclopropenone itself (**3**) by the reaction of **45** with 2 equiv of tri-*n*-butyltin hydride (**52**) in paraffin oil at room temperature. This produced a volatile mixture of chlorocyclopropenes

TABLE IV. Cyclopropenones Prepared by the Modified Favorskii Reaction

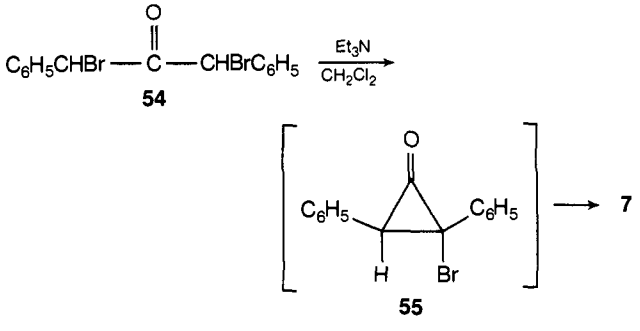
Substituents R	Substituents R′	Yield, %	Mp or bp (mm), °C	Ref
C_6H_5	C_6H_5	45	119–121	24, 40
n-C_3H_7	n-C_3H_7	9.2	66–68 (0.3)	34
n-C_4H_9	n-C_4H_9	12.4	96–99 (0.4)	34, 40
R = R′ =	$-(CH_2)_5-$	56	44–51	34, 40
R = R′ =	$-(CH_2)_9-$	8	120–124 (0.04)	34
C_6H_5	$N(C_2H_5)_2$		120–130 (0.001)	34
$C(CH_3)_3$	$C(CH_3)_3$	36	61–61.5	43a, 67
		52		43b
C_6H_5	C_2H_5	44	25	28
C_6H_5	$CH_2C_6H_5$	23	68	28
C_6H_5	CH_3		72–73	84
p-$CH_3OC_6H_4$	CH_3		97–98	84
H	n-C_5H_{11}	10–15		57

containing 3,3-dichlorocyclopropene (**53**) (nmr: δ 8.0), 1,3-dichlorocyclopropene, and mono- and trichlorocyclopropene isomers. Cautious hydrolysis and distillation afforded cyclopropenone (**3**) as a colorless liquid (bp 30° (0.45 Torr)) in 41–65% overall yield from tetrachlorocyclopropene (**45**). The availability of this product has led recently to the determination[175] of its microwave spectrum, and it was found to have an electric dipole moment of $|\mu| = (4.39 \pm 0.06) \times 10^{-18}$ esu along the a principal inertial axis.

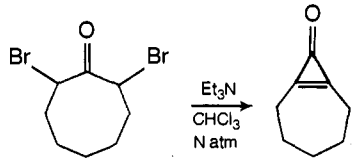


B. Synthesis by a Modified Favorskii Reaction

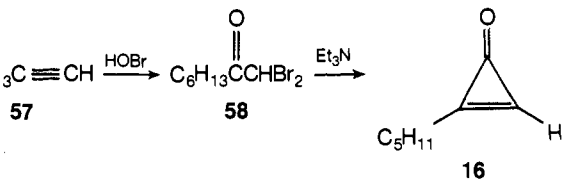
The most efficient procedure for obtaining cyclopropenones on a preparative scale is the elimination of HBr from α,α'-dihalo ketones by a modified Favorskii reaction (ref 24, 34, 36, 40, 43, 57, 67, 84, 85). It has been established[16] that the Favorskii reaction of α-halo ketones proceeds through an intermediate with the symmetry of a cyclopropenone. Thus treatment of di(α-bromobenzyl) ketone (**54**) with triethylamine caused elimination of HBr from the intermediate cyclopropanone **55** producing diphenylcyclopropenone in 45% overall yield from dibenzyl ketone.[24,40] The reaction has been extended to prepare

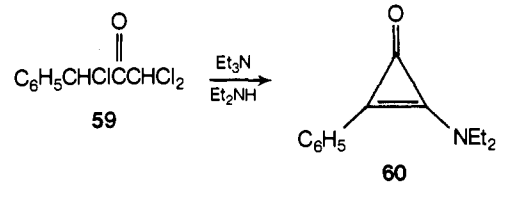


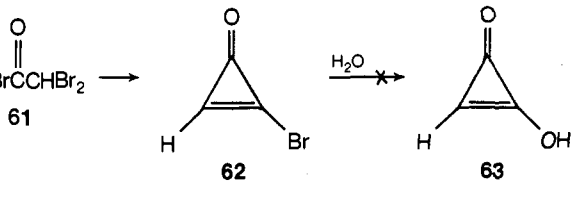
dialkylcyclopropenones such as dibutyl-,[40] dipropyl-,[34] di-*tert*-butyl-,[43,67] methylphenyl-,[84] and methyl-*p*-methoxyphenylcyclopropenone[84] (Table IV). Interestingly, the reaction was also applied to dibromocyclooctanone (**56**) and resulted in a 50% yield of the cycloheptenocyclopropenone[40] (**15**). Cycloundecenocyclopropenone was prepared in a similar manner in 8% yield. Benzocyclopropenone, another ring-fused system, is known only as a transient intermediate in the oxidation of 3-aminobenzotriazin-4-ones[173a] or from the photochemical decomposition of lithium 3-*p*-tolysulfonylamino-1,2,3-benzotriazin-4(3*H*)-one.[173b]



Monosubstituted cyclopropenones have been prepared by a modification of the above procedures.[57] Thus oct-1-yne (**57**) was converted by hypobromous acid into 1,1-dibromooctan-2-one (**58**), treatment of which with triethylamine gave *n*-pentylcyclopropenone (**16**). The attempted synthesis of cyclopropenone (**3**) by these methods proved unsuccessful.[40] An attempt to prepare phenylhydroxycyclopropenone (**12**) by dehydrochlorination of a mixture of trichlorophenylacetones (**59**) also failed, but when dehydrochlorination was carried out in the presence of diethylamine, some phenyldiethylaminocyclopropenone (**60**) was isolated.[34] The synthesis of hydroxycyclopropenone (**63**), the three-membered analog of tropolone, was also attempted by this route. The modified Favorskii reaction of 1,3,3-tribromoacetone (**61**) with various bases in numerous solvents was expected to give the bromocyclopropenone **62** which could be hydrolyzed to **63**. However, all attempts at this reaction resulted solely in the formation of the normal Favorskii, ring-opened product, β-bromoacrylic acid.[85]





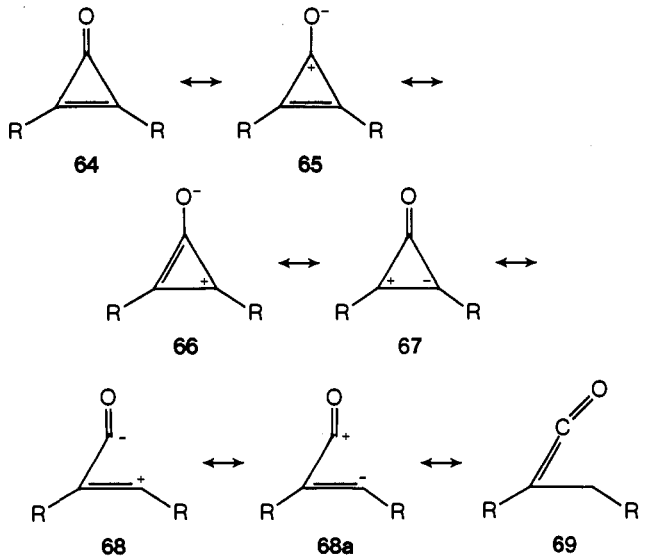


V. Reactions of Cyclopropenones

In recent years the importance of cyclopropenones in organic chemistry has been demonstrated by their utilization in a wide variety of organic reactions. These reactions may be classified into four categories: decarbonyla-

tion reactions, addition reactions, oxidation reactions, and substitution reactions.

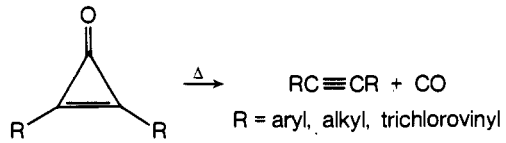
The addition reactions are especially important since the sites of the addition are threefold: to the carbonyl group; to the double bond; or to carbons 2 and 3 of the cyclopropenone nucleus. These reactions are often accompanied by rearrangements, usually with opening of the three-membered ring in either a stepwise or a concerted manner. The variety of reactions for such a simple system may reflect to some extent contributions from the canonical forms **64–69**.



64 **65** **66** **67** **68** **68a** **69**

A. Decarbonylation

The loss of carbon monoxide from cyclopropenones may be induced by pyrolysis (ref 20, 24, 26, 27, 34, 39, 40, 67, 81, 86, 87), photolysis (ref 67, 79, 88, 163), or by catalytic decarbonylation techniques (ref 18, 89, 90). Diphenylcyclopropenone (**7**) on heating at 130–140° lost carbon monoxide and diphenylacetylene was identified in the residue.[20] At higher temperatures, the conversion

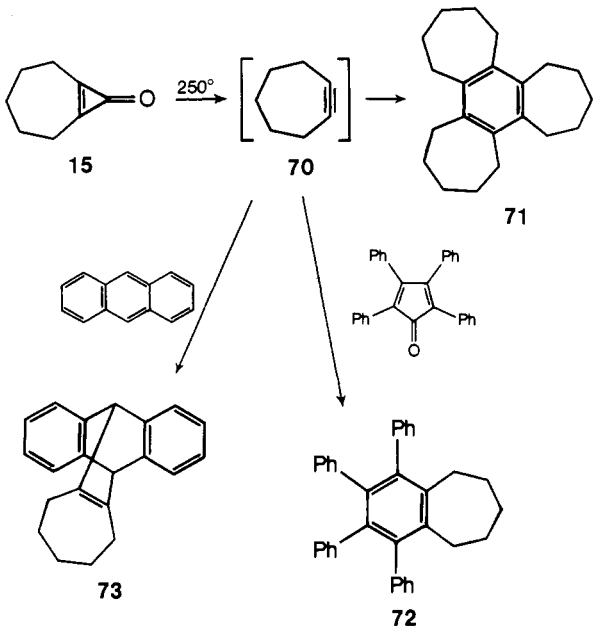


$$\xrightarrow{\Delta} RC{\equiv}CR + CO$$

R = aryl, alkyl, trichlorovinyl

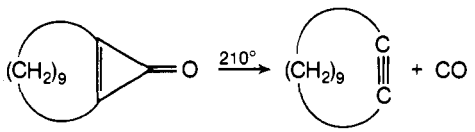
was more efficient.[24] A dimer of the original ketone has also been isolated from the pyrolysis at lower temperatures (section V.B.4.a). *p*-Fluorotolan was obtained similarly from the pyrolysis of the corresponding di(*p*-fluorophenyl)cyclopropenone.[81]

Thermolysis of dialkylcyclopropenones required higher temperatures than the corresponding diaryl compounds. Whereas **7** was 90% destroyed after **7** min at 190–191° (nitrogen atmosphere), di-*n*-propylcyclopropenone (**8**) was only 18% destroyed under the same reaction conditions.[27,39] These results have been interpreted as not necessarily signifying a greater stabilizing effect for the propyl substituents than for the phenyl groups, but rather they may reflect a greater stabilization by the phenyl groups of the transition state involved in the decomposition.[27] Propyne, carbon monoxide, and a dimer of methylcyclopropenone were obtained from the thermolysis[26] of di-*n*-propylcyclopropenone. This reaction has been extended with very interesting results to cycloheptenocyclopropenone (**15**).[34,40] After a high-temperature (250°) thermolysis of **15**, carbon monoxide and a 15% yield of tris(cyclohepteno)benzene (**71**), presumably arising from the intermediate cycloheptyne **70**, were isolated. Pyrolysis of **15** in the presence of tetracyclone afforded 1,2-cyclohepteno-3,4,5,6-tetraphenylbenzene (**72**), and with anthracene, a 1:1 adduct **73** was obtained. In contrast,



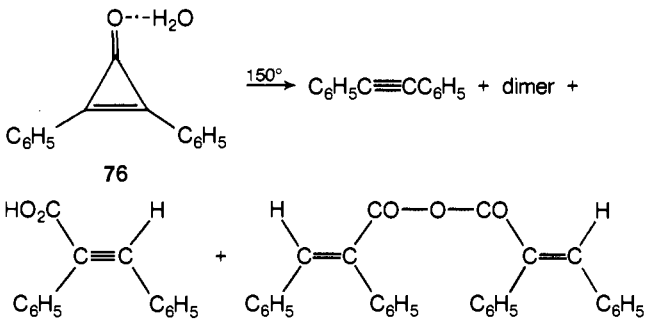
15 **70** **71** **73** **72**

cycloundecenocyclopropenone (**74**) at 210° afforded[34] 95% of cycloundecyne (**75**). Only under reduced pressure and at 320–327° did di-*tert*-butylcyclopropenone (**18**) undergo pyrolysis.[67] The products obtained were found to be di-*tert*-butylacetylene and carbon monoxide.



74 **75**

Heating the monohydrate **76** of **7** at 150° afforded tolan, the cyclic dimer, and other ring-opened products (section V.B.2).[87] Photolysis of diphenylcyclopropenone[88] (**7**) and bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone[79] (**236**) gave the corresponding acetylenes in good yield, a behavior also noted for cyclopropenone itself.[163]



76

The reaction of diphenylcyclopropenone (**7**) with nickel,[18,89] iron,[90] and cobalt[90] carbonyls was investigated as an alternative route to possible intermediates in the carbonylation of acetylenes. The catalytic decarbonylation of **7** by nickel carbonyl in benzene yielded diphenylacetylene and tetracyclone, whereas similar treatment of tolan gave hexaphenylbenzene along with tetracyclone, indicating that **7** is not an intermediate in the carbonylation of diphenylacetylene.[89] Triiron dodecacarbonyl, diiron nonacarbonyl, and dicobalt octacarbonyl reacted

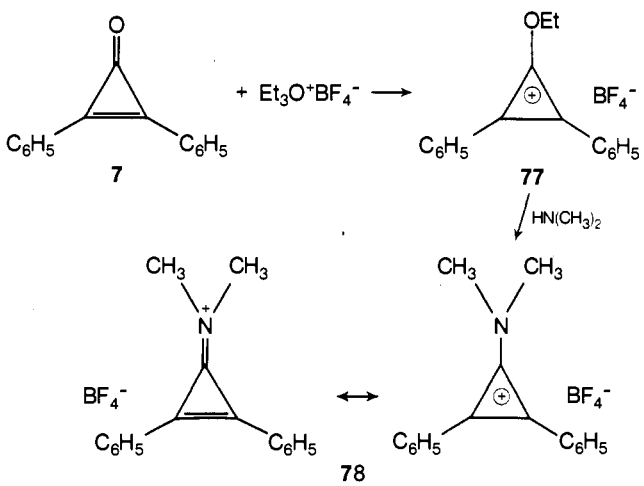
similarly with cyclopropenones to give decarbonylation products.[90]

B. Addition Reactions

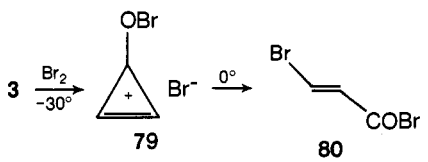
Addition reactions of cyclopropenones are numerous and quite varied for such a simple system. Electrophilic reagents attack the electron-rich carbonyl group and nucleophilic addition reactions occur at any carbon of the three-membered ring, a possible consequence of the delocalization of the partial positive charge over the ring. Many interesting cycloaddition reactions of cyclopropenones have been reported recently and these represent a logical development of the early chemistry of cyclopropenones. Various cyclopropenones which form complexes with metals are described in this section.

1. Electrophilic Additions at the Carbonyl Group

The formation of hydroxycyclopropenylium salts (**14**) by protonation of the carbonyl group has been described above. Alkylation of **7** by triethyloxonium fluoroborate (Meerwein's reagent) produced ethoxydiphenylcyclopropenyl fluoroborate[24,91] (**77**) which, with dimethylamine, was converted into the very stable 1,2-diphenyl-3-dimethylaminocyclopropenyl fluoroborate (**78**). Meerwein's reagent added[163] in a similar fashion to cyclopropenone (**3**).

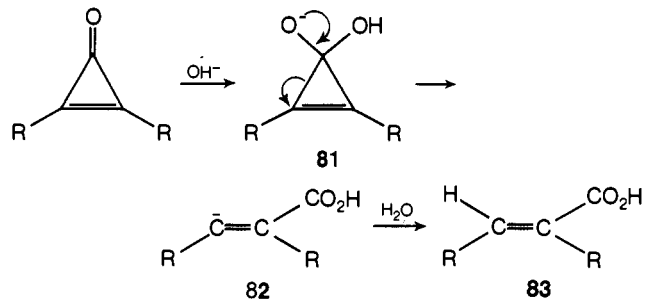


Bromine in $CDCl_3$ at $-30°$ reacted[163] with cyclopropenone giving the corresponding bromide salt **79** which, on warming to 0°, was converted into *trans*-β-bromoacryloyl bromide (**80**). This reaction indicated that bromine, a so-called double bond reagent, reacted successively with the carbonyl group and with the single bond of cyclopropenone without addition to the double bond.[163]

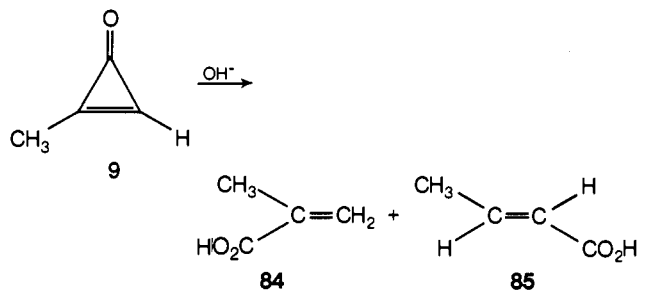


2. Nucleophilic Additions at the Carbonyl Group

Hydrolysis of cyclopropenones with sodium or potassium hydroxide solution gave the corresponding, ring-opened α,β-unsaturated acids **83** (ref 24, 26, 27, 33, 34, 39, 40, 66, 87, 92). Presumably the addition of hydroxide ion to the carbonyl group initiated the reaction, followed by collapse of the intermediate **81** in a fashion similar to the ring opening of cyclopropenone intermediates in the Favorskii rearrangement.[25] Protonation of the anion **82** would complete the process.

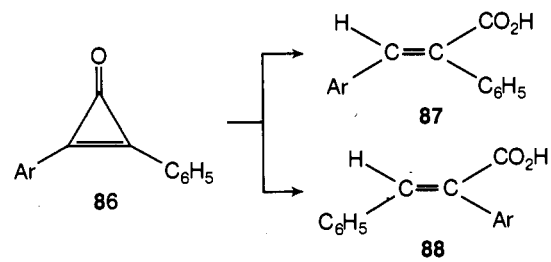


Dialkylcyclopropenones are more stable to base than diarylcyclopropenones,[27,39] a property analogous to their thermal stability (section V.A). Diphenylcyclopropenone was 90% cleaved after 3 min at 31° in 0.1 *N* ethanolic sodium hydroxide solution, whereas di-*n*-propylcyclopropenone (**8**) was recovered completely unchanged after 1 hr under the same hydrolysis conditions. Analogous to the decarbonylation of cyclopropenones (section V.A), this difference may be attributed to the phenyl groups exerting a greater stabilization of the hydrolysis transition state.[27] Treatment of methylcyclopropenone (**9**) with excess 0.05 *N* aqueous sodium hydroxide solution resulted in cleavage to a 3:1 mixture of methacrylic (**84**) and crotonic (**85**) acids.[26] Preferential cleavage to methacrylic

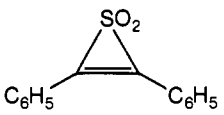


acid is consistent with the relative stabilities of the two possible intermediate carbanions. Thus the rate-controlling step in the base-catalyzed cleavage of cyclopropenones could be either the attack of OH^- forming **81** or subsequent formation of the carbanion **82.**

In examining the electronic and steric factors governing this cleavage, Bird[66] synthesized a series of arylphenylcyclopropenones (**86**) which, upon hydrolysis in 1 *M* methanolic potassium hydroxide solution, gave a mixture of the two isomeric acids, **87** and **88.** The amounts of **87** and **88** isolated reflected their relative rates of formation, and a linear Hammett-type correlation between log [**87**]/[**88**] and the appropriate σ constants were obtained with σ values from −0.268 to +0.373 yielding $\rho = 0.75$. This indicated that the intermediate **81** would undergo preferential cleavage to yield the more stable of the two possible carbanion species **82.** Ortho substituents resulted in preferential cleavage to the 2-phenyl-3-arylacrylic acid (**87**), irrespective of the electronic properties of the substituent. Presumably, this was due to the steric interaction of the substituent and the acid carbonyl group.



Comparison of the rates of cleavage by alkoxide ions of diphenylcyclopropenone (**7**) and diphenylthiirene 1,1-dioxide (**89**) showed **89** to be hydrolyzed 5000 times faster.[141] This reversal of the rate of the usual base attack on a carbonyl group rather than on a sulfonyl group may be attributed to the marked conjugative stabilization of **7** in contrast to the slight resonance stabilization of **89**.



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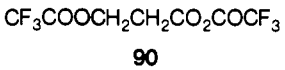

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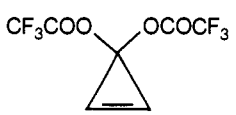

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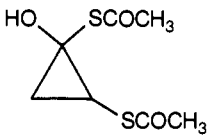
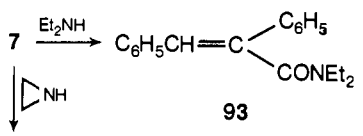


92

In trifluoroacetic acid cyclopropenone was found to be moderately stable but on gentle warming it formed a product assigned structure **90**. However, in trifluoroacetic anhydride the ketal **91** was obtained. In thiolacetic acid a cyclopropane derivative **92** in which two thiolacetic acid moieties have added across both the carbon–carbon double bond and the carbonyl group was formed.[163]

The action of nitrogen nucleophiles on the carbonyl group of cyclopropenones also led to ring-opened products. Addition of diethylamine to **7** gave **93** in good yield.[94] Similarly, 2 mol of aziridine reacted with **7** to form a ring-opened product **94**, presumably from an azetidinone intermedite **142** (section V.B.4.b), and only 2% of a 1:1 product **95**. In contrast, aziridine and 2-ethyl-3-



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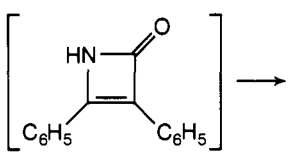

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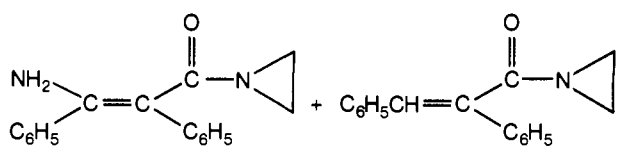
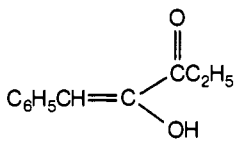


94 **95**

phenylcyclopropenone (**96**) produced a nitrogen-free hydrolysis product **97**, and **96** with diethylamine gave **97** and the expected product **98**.[92] The action of aqueous ammonia on **96** resulted in **99**, the product from ring fission and subsequent oxidation.[92] Treatment of **7** with liquid ammonia gave α-phenyl-β-amino-*trans*-cinnamaldehyde (**100**), possibly by the mechanism shown.[101]

The reaction of thioamides with diphenylcyclopropenone (**7**) led to *N*-(2-phenylcinnamoyl)thioamides (**101**), which underwent further ring closure to form 1,3-thiazin-4-ones **102** or **103**,[153] depending on the availability of enolizable hydrogens.

The reaction of **7** with phenylmagnesium bromide afforded, after appropriate work-up, a 50% yield of triphenylcyclopropenyl perchlorate (**105**). The dimeric ether[24,39] **104** was found to be an intermediate in this reaction. However, the reaction of **7** with cyclopentadienylmag-



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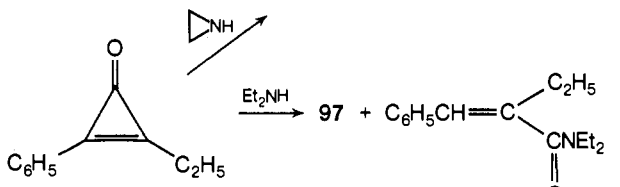
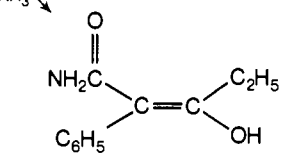


96 **98**



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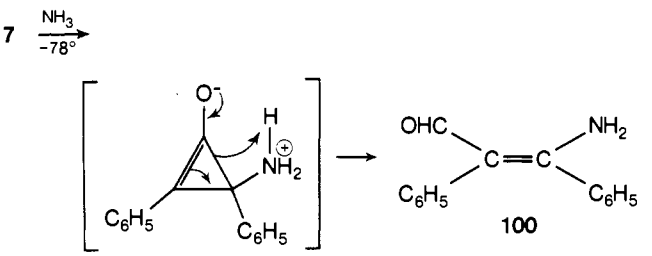

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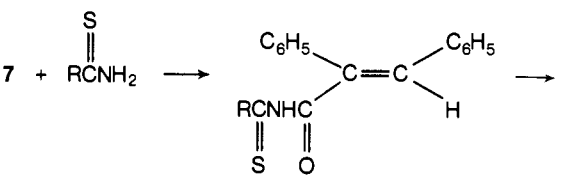

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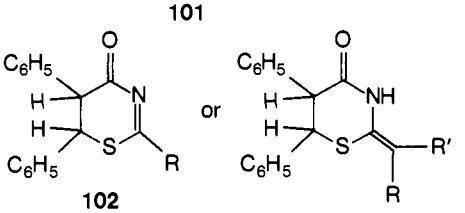
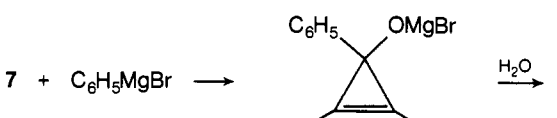
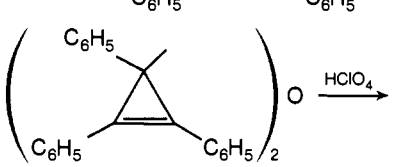


102 **103**





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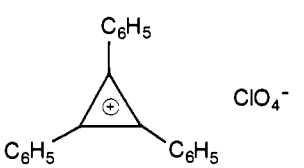


105

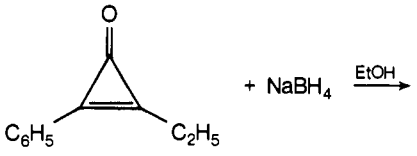
nesium bromide did not give the expected tertiary carbinol **106** but resulted in the formation of tetraphenylcyclo-

pentadienone (**107**), tetraphenyl-*p*-benzoquinone (**108**), and tetraphenylpyrocatechol (**109**) in 1, 2, and 8% yields, respectively.[96] The addition of a mixture of metallic magnesium and iodine was found to increase the yields of these products.[96] Their formation was attributed to the formation of an unstable pinacol intermediate which undergoes rearrangement to the benzene derivatives. This mechanism has been reevaluated[97] and, on the basis of product analysis and reassignment of the structure of **109** to tetraphenylresorcinol (**114**), a radical anion mechanism was proposed. After formation of **110** and subsequent dimerization to the pinacolate **111**, it was postulated that rearrangements to prismane (**112**) and Dewar benzenes (**113**), followed by final ring opening, would give the products obtained. Cyclopropenone (**3**) has been reported recently to react with methylmagnesium iodide to give 30–50% yields of 2-methylresorcinol (**117**), analogous products being obtained with other Grignard reagents.[164] As 2 equiv of cyclopropenone was used, it was suggested that conjugate addition gave an intermediate **115** which added to a second molecule of cyclopropenone giving **116** which then underwent subsequent cyclization and rearrangement to **117**. Polymeric materials only have been isolated from the reaction of cyclopropenone with organolithium reagents, lithium dimethylcopper or lithium aluminum hydride.[164] A particularly interesting reaction is the conversion of cyclopropenone into hydroquinone with 1% sodium amalgam.[164]

The addition of alkyl(or phenyl)lithium to di-*tert*-butylcyclopropenone (**18**), followed by hydrolysis, gave an oil which, on treatment with perchloric acid, resulted in the isolation of 3-alkyl(or phenyl)-1,2-di-*tert*-butylcyclopropenyl perchlorate[43,67] (**118**). The conjugate addition of phenyllithium to **7** gave, after hydrolysis, an 18% yield of a product represented by structure **120**. The proposed ketene intermediate **119** was detected spectroscopically at −70°.[99] This reaction thus appears to occur across the carbon–carbon bond.

Lithium aluminum hydride (*ca.* −20 or −70°) or H_2/Pt in *cold* alcohol reduced both the carbonyl group and the double bond to give 1,2-diphenylcyclopropan-3-ol.[21,23] The ease of reduction of not only the carbonyl group but also the double bond of diphenylcyclopropenone by lithium aluminum hydride was explained by the attack of the hydride ion on the positively charged carbon atoms of the three-membered ring.[33]

Reduction of ethylphenylcyclopropenone (**96**) by sodium borohydride in ethanol yielded compounds **122**, **123**, and **124**.[92] These products were presumably formed from a common intermediate **121**, followed by either further reduction or the attack of solvent.



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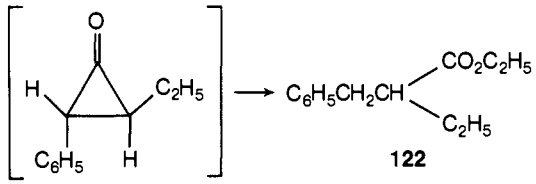
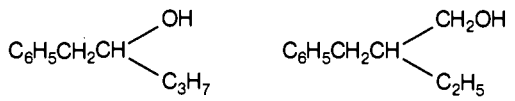


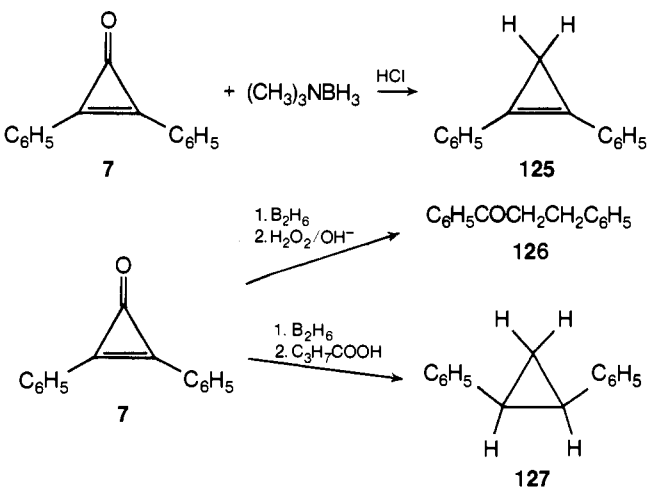
121 122



123 124

Selective reduction of the carbonyl group of diphenylcyclopropenone (**7**) was recently accomplished.[148] Reaction of **7** with trimethylamine-borane and subsequent treatment of the reduction medium with anhydrous HCl afforded 1,2-diphenylcyclopropene (**125**) in a 90% yield.

The reaction of **7** with diborane was studied with reaction work-up under both oxidizing and reducing conditions.[161] Hydroboration of **7** with excess diborane and oxidation with H_2O_2/OH^- gave, as the main product, benzylacetophenone (**126**) in 55-65% yield. The hydroboration of **7**, followed by protonation with butyric acid, yielded 1,2-*cis*-diphenylcyclopropane (**127**) in 45-50% yield. A common intermediate, a cyclopropenyl cation, was thought to be involved, and deuterioborane was used to obtain evidence in support of the proposed mechanism.

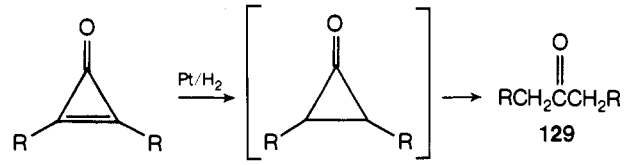


7 125 126 7 127

Polarographic reduction of **7** gave a polarogram with two waves resulting from both the reduction of the C=O and C=C functions. The half-wave potentials were $E_{1/2} = -1.91$ and -1.56 V, respectively,[98] and no conclusion could be reached regarding the order of the reduction.

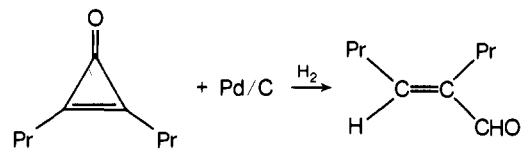
3. *Additions at the Carbon–Carbon Double Bond*

Catalytic hydrogenation (Pt/H_2) at room temperature of cyclopropenone[156] (**3**) and diphenyl-[24] (**7**), di-*n*-propyl,[34] (**8**), and di-*tert*-butylcyclopropenone[67] (**18**) gave, after consumption of 2 mol of hydrogen, the corresponding disubstituted ketones **129**. The postulated cyclopropanone intermediate, **128**, however, eluded spectroscopic detection and probably underwent reduction and ring fission faster than the cyclopropenone itself.[24] Palladium-on-carbon hydrogenation of the di-*n*-propyl derivative (**8**) gave



128 129

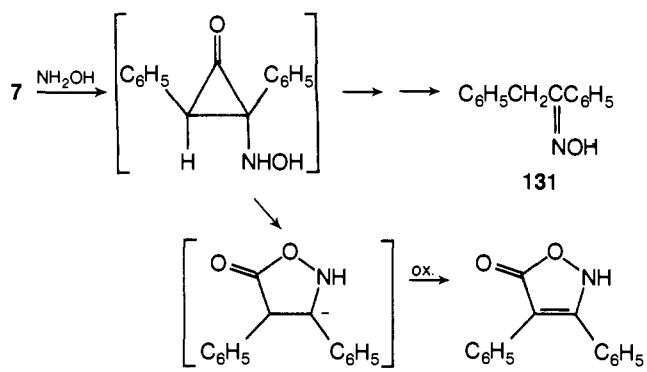
2-propyl-2-hexenal (**130**), a product accountable in terms of the addition of 1 mol of hydrogen across the -C–CO-



8 130

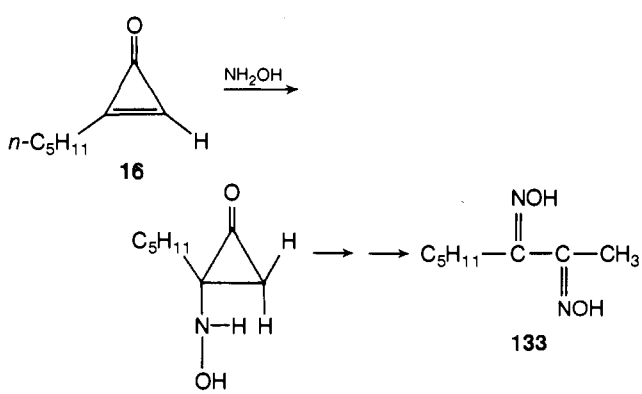
bond[34] and subsequent ring opening. Differentiation between these two reduction pathways was not possible since both procedures afforded minor reduction products. The addition of hydrogen in the presence of Pd/C to *n*-pentylcyclopropenone (**16**) gave *n*-hexyl methyl ketone as the major product.[57]

The reaction of **7** with hydroxylamine yielded 3,4-diphenylisoxazolone (**132**) and desoxybenzoin oxime (**131**).



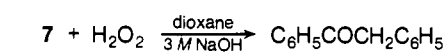
131 132

Their formation may be attributed to an oxidation process, but the exact mechanism is unknown.[24] Conjugate addition of hydroxylamine to the carbon-carbon double bond is presumably the first step. This is followed by a ring enlargement process and subsequent oxidation. *n*-Pentylcyclopropenone (**16**) gave a good yield of *n*-pentylmethylgloxime (**133**) by an equally tentative mechanism.[57]



16 133

The reaction of diphenylcyclopropenone (**7**) with alkaline hydrogen peroxide produced desoxybenzoin (**134**).[100]



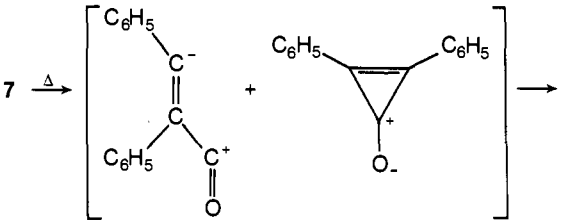
134

4. Cycloadditions of Cyclopropenones

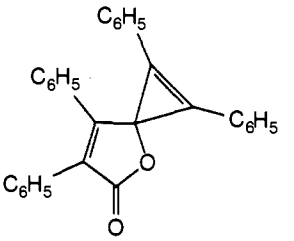
The most recent chemistry of cyclopropenones involves the utilization of these compounds in cycloaddition reactions with a wide variety of substrates. These additions have been found to occur across the C=O, C=C, or the 2—3 (C—CO) bond of the cyclopropenone ring.

a. Dimerization of Cyclopropenones

In the thermolysis of cyclopropenones, decarbonylation resulted (section E.1) and, depending on the temperature of the thermolysis, a dimeric product could also be isolated. Thus the pyrolysis of **7** gave a dimer,[24,87,102] assigned a spirolactone structure (**137**), possibly formed *via* a [2 + 3] cycloaddition of the intermediates[49] **135** and **136**. Alternatively dimerization of the radical interme-

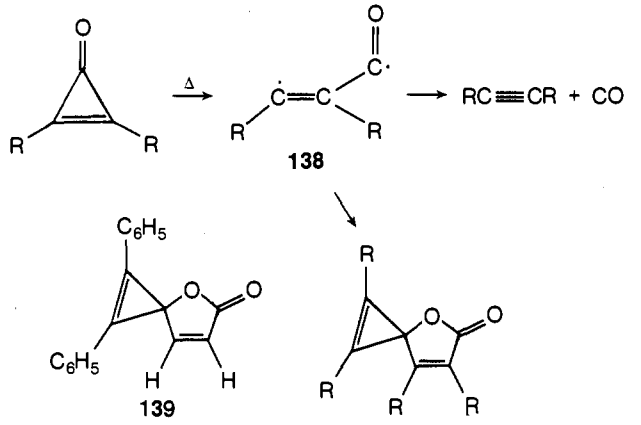


135 **136**



137

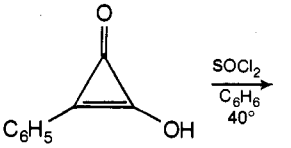
diate **138**, which also may be the precursor to the accompanying acetylene and which could undergo reaction with any suitable trapping agent, has been suggested[32] as a possible pathway. The dimer **137** was stable under these thermolysis conditions and thus could not be considered a precursor to the acetylene.[24] Analogous dimeric cyclopropenones have also been obtained from methylcyclopropenone[26,29] (**9**), dichlorocyclopropenone[59] (**17**), and cyclopropenone itself.[163] It is particularly interesting that cyclopropenone and diphenylcyclopropenone formed the codimer **139**. It is interesting to note that two additional



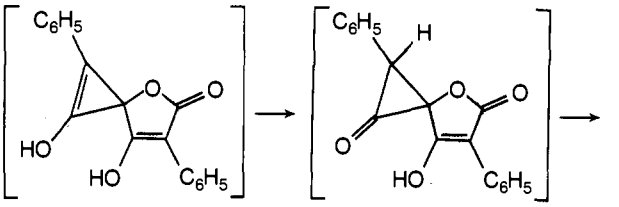
138 **139**

dimers of **7** have been reported,[103] but structural elucidation is still incomplete.[103]

Phenylhydroxycyclopropenone (**12**), which appeared to be an associated dimer in dioxane,[75] formed a dimeric pulvinic acid lactone (**141**) *via* oxidation of the dimer **140** which was isolated from the reaction of **12** with thionyl



12



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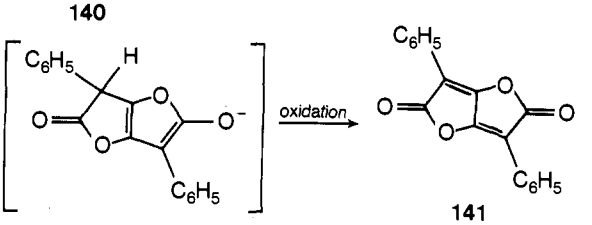
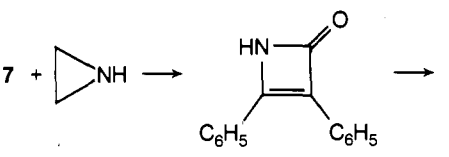


141

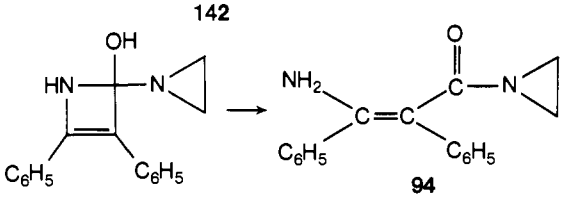
chloride.[30] The methyl ether of **12** on pyrolysis also gave a dimer[30] analogous to the dimer **137**, formed from the pyrolysis of diphenylcyclopropenone (**7**).[24]

b. Ring Expansion to a Four-Membered Ring

The azetinone **142** has been postulated as the intermediate in the formation of the ring-opened product **94** from the reaction of diphenylcyclopropenone and aziridine. It

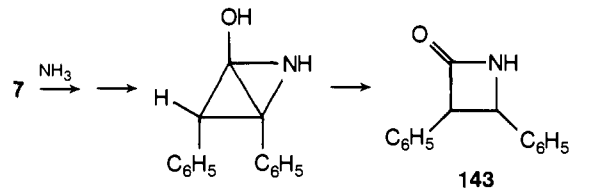


142



94

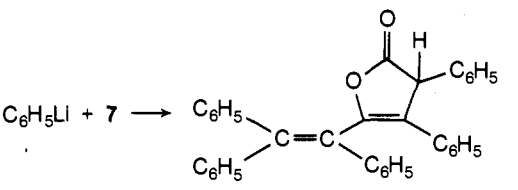
is presumably formed by insertion of nitrene into the 2-3 bond of diphenylcyclopropenone.[94] The saturated azetidinone **143** has been isolated in the ring expansion of **7** with ammonia at room temperature.[104]



143

c. Reaction *via* a Ketene Intermediate

The inverse addition of phenyllithium to diphenylcyclopropenone (**7**) gave an adduct **144**, possibly formed by

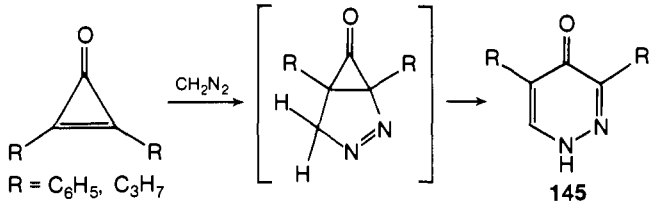


144

the addition of a second mole of **7** to an intermediate primary adduct.[99] This reaction pathway should be contrasted with that previously described for phenyllithium.

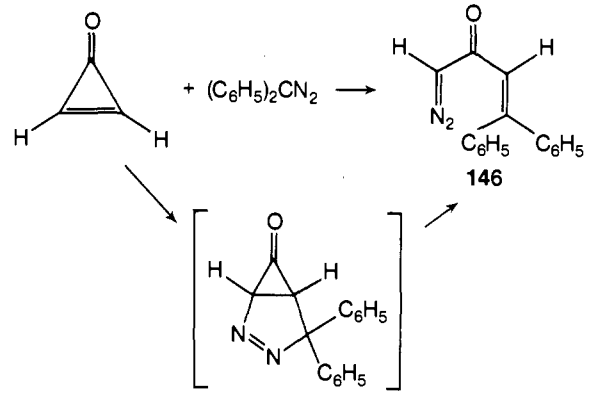
d. 1:1 Cycloadducts

(1) Cycloaddition across the C=C Bond. i. Diazo Compounds. Diazomethane, acting as a 1,3-dipole, was found to add across the C=C bond of substituted cyclopropenones to give, after rearrangement of the cyclopropanone intermediate, 3,5-disubstituted 4-pyridazones[24,105] (**145**). These were formed even when the cyclopropenone was coordinated with a Lewis acid.[24]



145

Similarly, cyclopropenone (**3**) reacted with diphenyldiazomethane, resulting in formation of the diazo ketone **146**, in 28% yield.[156] Benzoyldiazomethane gave an analogous product.[164]

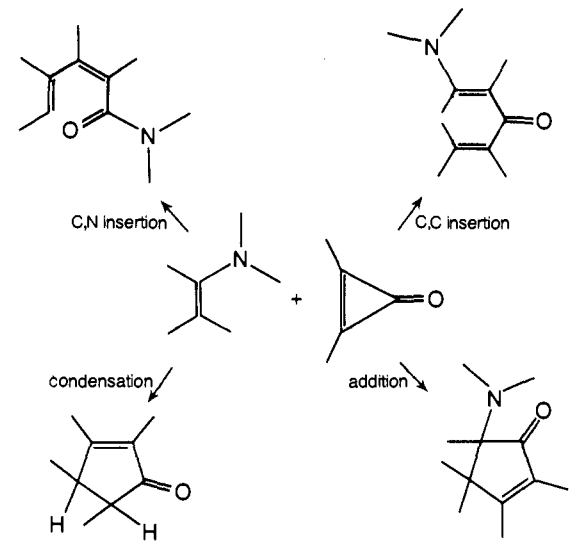


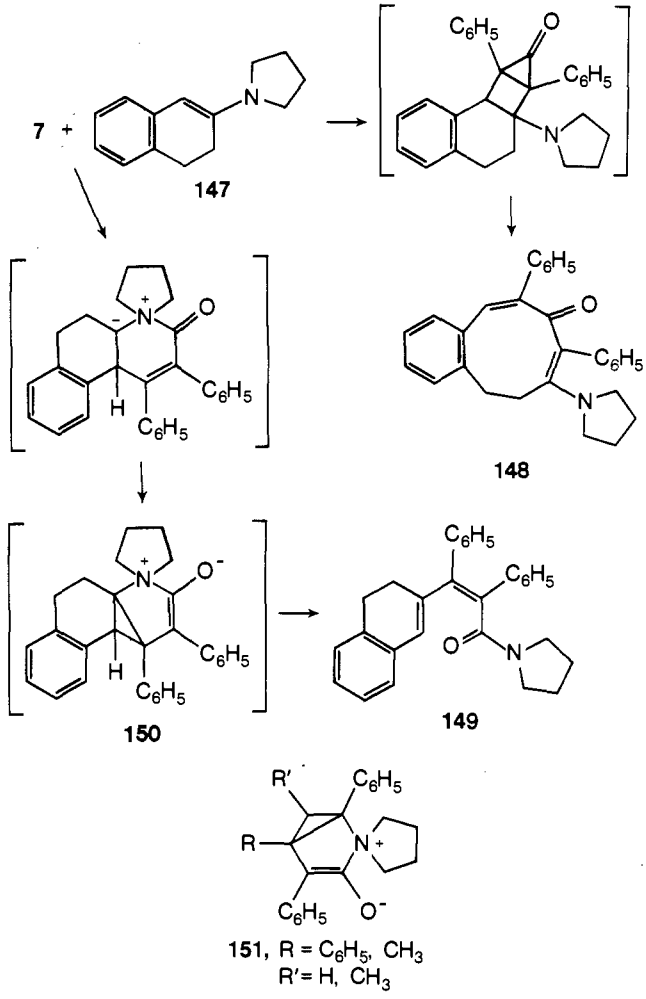
146

ii. Enamines and Ynamines. The outcome of the reactions of cyclopropenones with enamines has attracted much interest in the recent literature. A reinterpretation of the results obtained by Ciabattoni and Berchtold[102,106] and those by Sauer and Krapf[107] involving the reactions of various enamines with diphenylcyclopropenone or its thione derivative, has been advanced in a series of articles[165-168] from which a general reaction scheme may be postulated. Whereas the earlier work[102,106,107] suggested that the course of the reaction of an enamine with a cyclopropenone proceeded with initial cycloaddition across the C=C bond followed by rearrangement of the resultant cyclopropanone intermediate to yield one type of product, a C,C insertion product, the reevaluation of this work has led to postulation of four separate pathways, such as is illustrated in the general Scheme I.

For example, the reaction of 2-(*N*-pyrrolidino)-3,4-dihydronaphthalene (**147**) with **7** was previously reported[102,106] to have yielded 4,5-benzo-2,9-diphenyl-8-(*N*-pyrrolidino)cyclonona-2,4,8-trienone (**148**), a product which would arise from C,C addition and ring opening of the cyclopropanone intermediate. A reinterpretation[166] of the spectral data for this compound has led to assigning its structure as **149**, a product resulting from a novel C,N insertion. This pathway is rationalized with a reaction scheme in which an "acylide" intermediate **150** is postulated as the primary adduct. Recently, stable pyrrolidinium betaine intermediates, **151**, from pyrrolidinyl enamines and cyclopropenones were reported to have been isolated.[169]

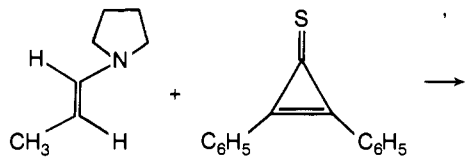
SCHEME I



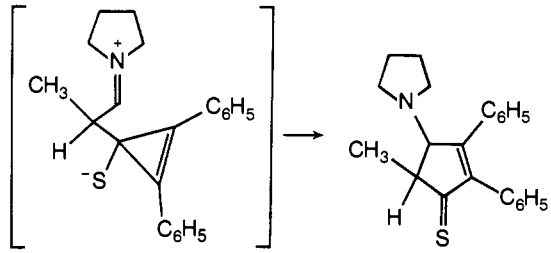


151, R = C_6H_5, CH_3
R' = H, CH_3

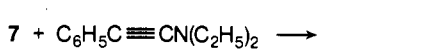
Diphenylcyclopropenethione (**252**) and 1-(*N*-pyrrolidino)prop-1-ene (**152**) gave[121] an addition-type product (see Scheme I) with addition occurring across the C-CS bond and formation of 2,3-diphenyl-5-methyl-4-(*N*-pyrrolidino)-2-cyclopentenethione (**154**) *via* the intermediate **153**. Diphenylcyclopropenone (**7**) underwent reaction with the ynamine **155** giving 2,4,5-triphenyl-4-cyclopentene-1,3-dione (**156**), presumably through an initial [2 + 2] cycloadduct and subsequent hydrolysis.[108]



152 252



153 154



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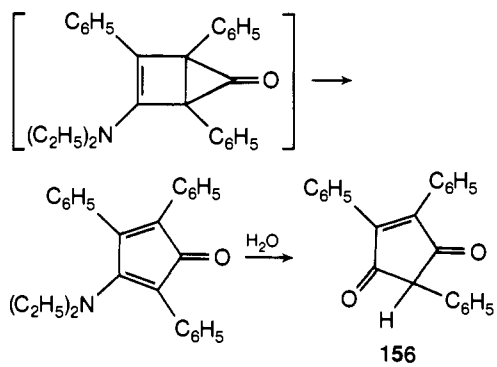
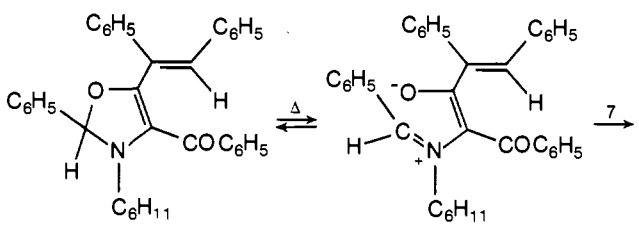


156

iii. Δ^4-Oxazolines. Δ^4-Oxazolines **157**, isolated from cycloadditions of **7**[111] (see cycloadditions to C=O), reacted with **7** across the C=C of the cyclopropenone ring with subsequent loss of carbon monoxide from the initial adduct **158** to give[109] the substituted furan **159**.



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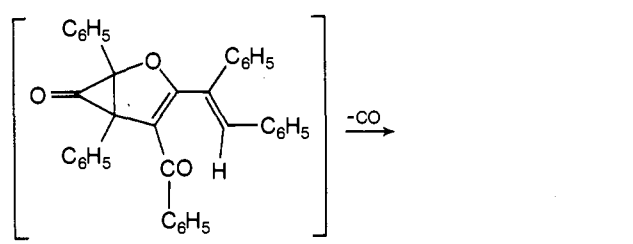

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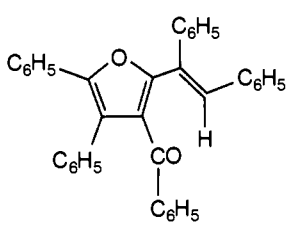
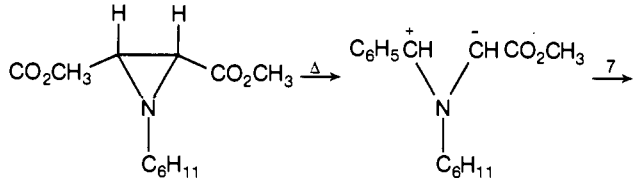
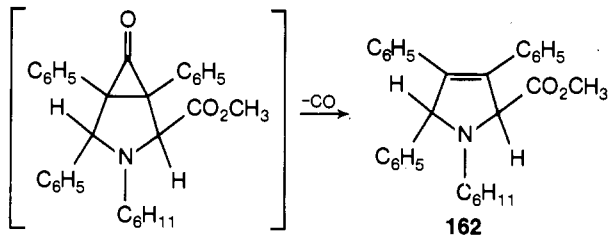


159

iv. Aziridines. 3-Carbomethoxy-1-cyclohexyl-2-phenylaziridine (**160**) reacted with **7** to give[114] the *trans*-3-pyrroline **162**. The reaction was rationalized as a [2 + 3] cycloaddition of the azomethine ylide **161** to the C=C bond of **7**, followed by decarbonylation.[114]

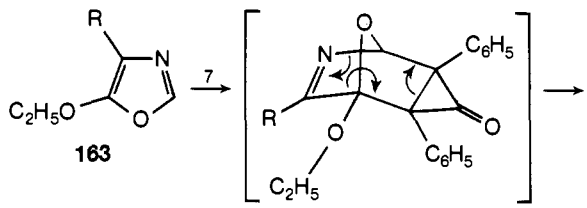


160 161

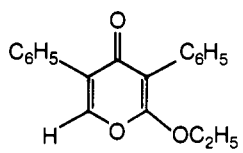


162

v. Oxazoles. The oxazoles **163** (R = H or CH_3) on heating with **7** gave none of the 1:1 adduct **164** but formed the γ-pyrone **165** by irreversible elimination of hydrogen cyanide or acetonitrile from the initial cycloadduct **164**. If addition across the C–CO bond had occurred,

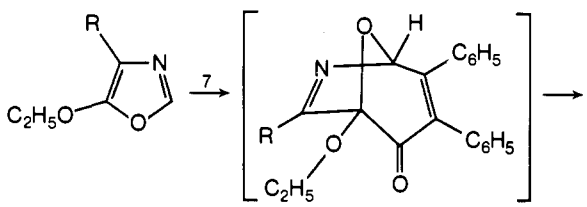


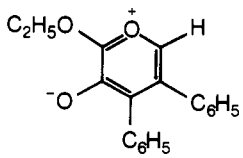
163 164



165

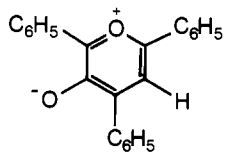
then elimination of RCN or HCN from the initial cycloadduct would result in the formation of a pyrylium betaine represented as **166**. The known pyrylium betaine[142] **167**





166

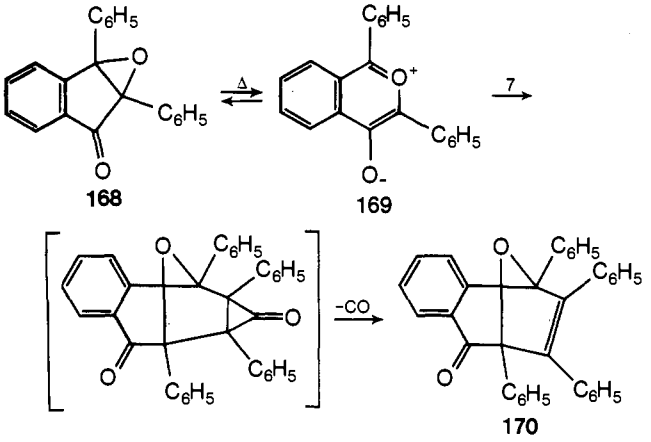
is deep red, whereas **165** was reported as colorless. The chemical shift of the 6-H in the pyrone **165** at δ 7.65



167

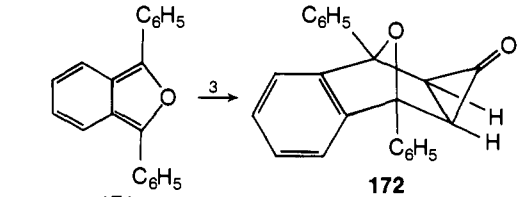
might suggest the aromatic structure **166**, but inspection of the literature[151] shows that the 6-H proton in 4*H*-pyran-4-one compounds does indeed resonate in this chemical shift region.

vi. Heteroaromatic Betaines. The reaction of 2,3-diphenylindenone oxide (**168**) with diphenylcyclopropenone (**7**) afforded[149] the adduct **170**. The cycloadduct was formed presumably from 1,3-cycloaddition across the carbon–carbon double bond of **7** with **168**, the latter reacting *via* its thermally induced tautomer **169**, followed by concomitant elimination of carbon monoxide. The adduct **170** was also obtained from the reaction of **168** and diphenylacetylene. Similar results were observed with anhydro-3-hydroxy-2,4,6-triphenylpyrylium hydroxide (**167**) and diphenylcyclopropenone.[170]

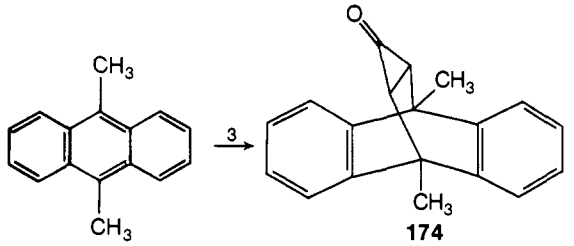


168 **169** **170**

vii. Diene Systems. In contrast to diphenylcyclopropenone, cyclopropenone itself has given two stable 1:1 adducts where addition has occurred across the C=C with 1,3-diphenylisobenzofuran (**171**) and 9,10-dimethylanthracene (**173**). These products, represented by **172** and **174**, are unique in containing a ring-fused cyclopropanone moiety.[156]

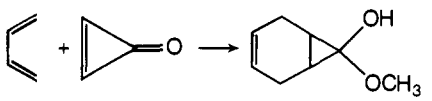


171 **172**



173 **174**

Cyclopropenone has also been found to react readily with tetracyclone, the complex reaction products depending on the solvent used. It also reacted with butadiene in methanol affording the hemiketal **175**, and with 6,6-dimethylfulvene (**176**) the tetracyclic product **178** was formed,[164] presumably *via* the initial 1:1 adduct **177**.



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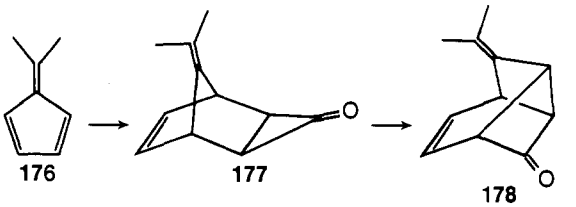
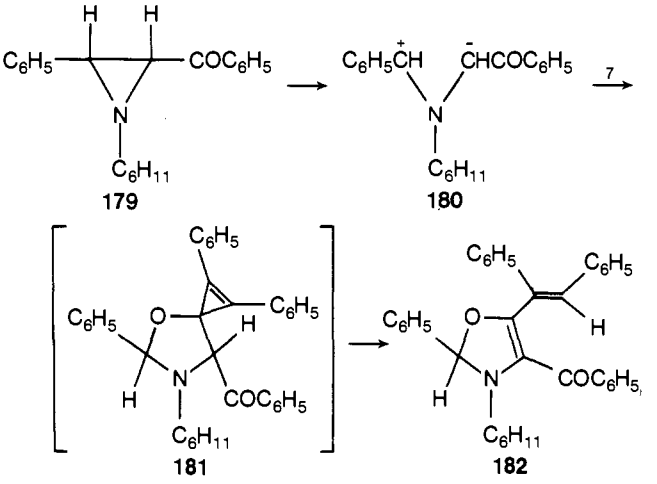
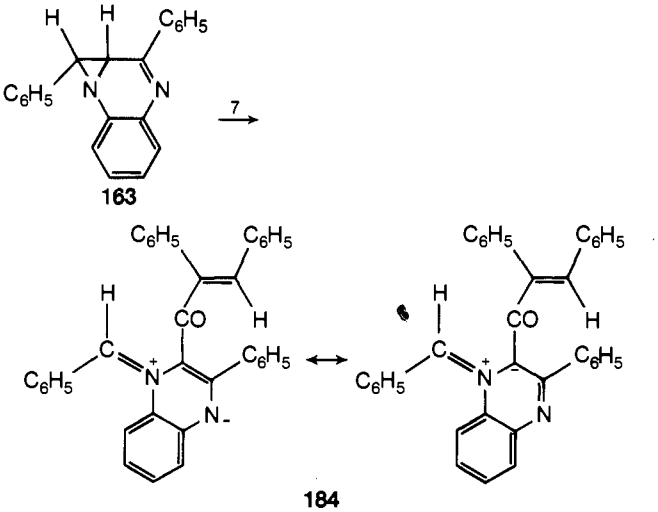


176 **177** **178**

(2) Cycloaddition across the C=O Group. 1,3-Dipolar cycloaddition to the azomethine ylide **180**, generated thermally from *cis*- or *trans*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (**179**), occurred across the C=O bond of diphenylcyclopropenone (**7**) and yielded[110,111] the 4-aroyl-4-oxazoline **182** by rearrangement of the initial 1:1 adduct **181**. The tricyclic aziridine **183** and **7** reacted similarly to give the zwitterionic ylide[111] **184**.



179 **180** **181** **182**

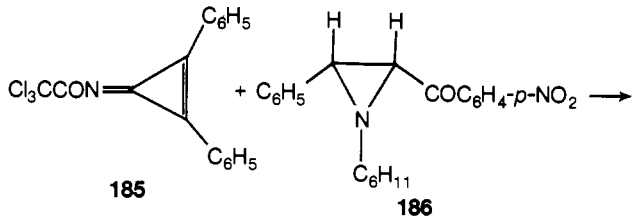


163 **184**

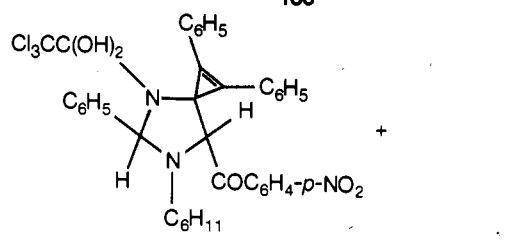
N-Trichloroacetyldiphenylcyclopropenimine (**185**), derived from **7** (section VI.A), reacted in a thermal [2 + 3] cycloaddition with the aziridine **186** yielding two products. These were identified as **187**, the 1:1 adduct with 1 mol of H_2O analogous to the intermediate **181** proposed above, and **188**. The latter was postulated to arise from the base-catalyzed elimination of the aroyl group of **187**.[112]

The addition of 3,3-pentamethylenediaziridine (**189**) to **7** gave a mixture of two isomeric 1:1 adducts. These have been described as **192**, a rearranged product, and **191**, both of which readily separated from the reaction mixture.[113] These products are mechanistically available from the common intermediate **190**.

(3) Cycloaddition across the C—CO Bond. In those cycloaddition reactions in which the product isolated con-



185 186



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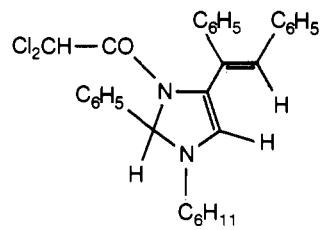
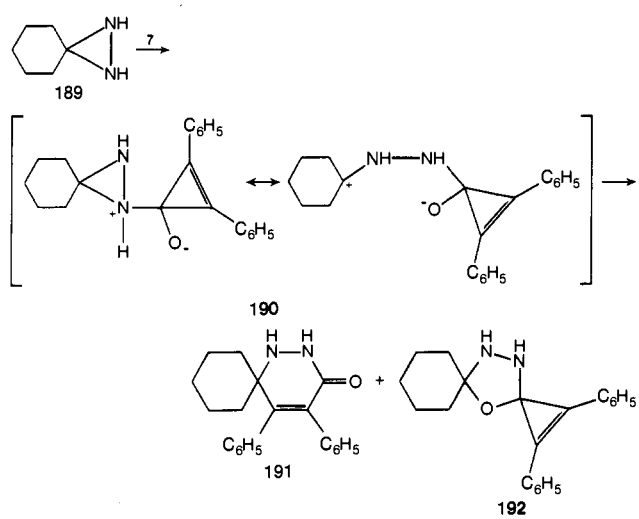


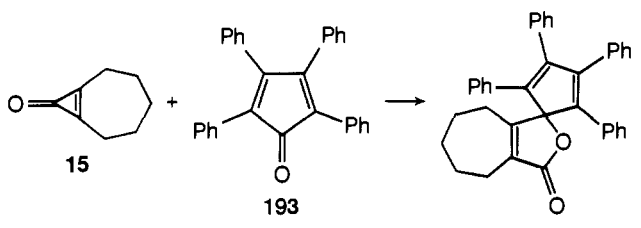
188



189 190 191 192

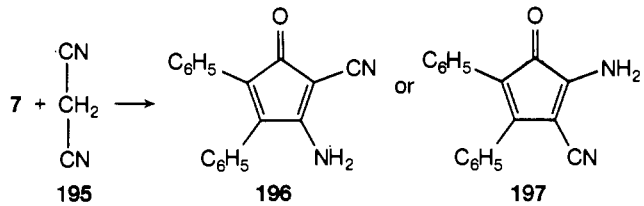
tained the cyclopropenone moiety as a ring-opened structure with newly formed bonds to carbons 2 and 3 of the original ring, it is most likely that the products originated from either an initial nucleophilic attack at the carbon atom or by a Michael-type addition to the C=C bond. This would then be followed by a rearrangement in which ring opening across the 2,3-bond occurred with subsequent ring closure yielding the cycloadduct. No data are available for determining the actual processes by which these changes occur.

i. Miscellaneous Reactions. A 1:1 adduct **194** has been isolated[34] from the pyrolysis of cycloheptenocyclopropenone (**15**) in the presence of tetracyclone (**193**). The formation of a product of this structure may be rationalized most reasonably in terms of an initial addition across the C–CO bond.



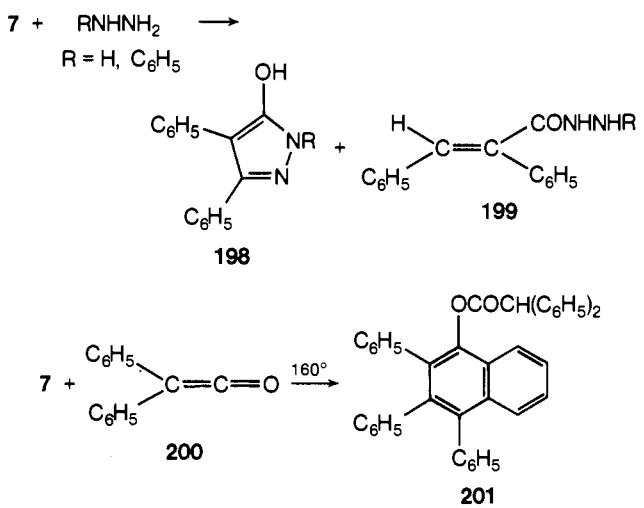
15 193 194

Similarly, in the reaction of diphenylcyclopropenone (**7**) with malononitrile (**195**) seven products were obtained, one of which was tentatively assigned[95] structure **196** or its isomer **197**.

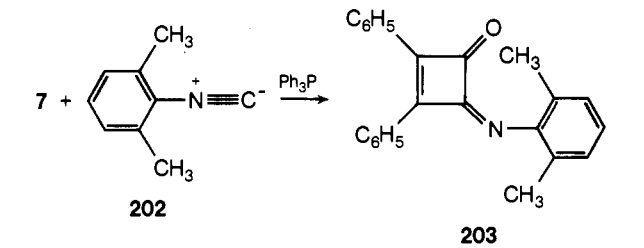


195 196 197

Reaction of **7** with either hydrazine or phenylhydrazine gave ring-expanded products **198** from addition, ring closure, and oxidation processes.[95] A ring-opened product **199** was also obtained when hydrazine was used as the reactant. Two moles of diphenylketene (**200**), minus the elements of carbon monoxide, was incorporated across the 2,3 bond of **7** giving 2,3,4-triphenyl-1-naphthyl diphenylacetate (**201**). Whereas 2 mol of 2,6-dimethylphenyl isocyanide (**202**) reacted with **7** through a bisketene intermediate[116] (section V.B.4.e), the same reaction in the presence of triphenylphosphine gave a 1:1 adduct **203** across the C–CO bond of the cyclopropenone.[117]



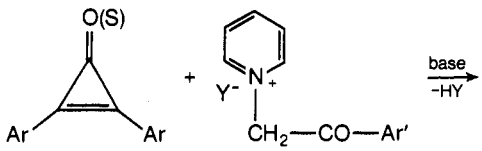
198 199 200 201



202 203

ii. Heteroaromatic Betaines and Ylides. Pyridinium betaines **204** were shown to undergo cycloaddition with diphenylcyclopropenone or its thione derivative. Either an initial attack on the carbonyl group of **7** by the betaine oxygen atom or a Michael addition of the methylene anion to the C=C bond of **7**, followed by isomerization, may account for the formation of the 3,4,6-triaryl-2-pyrone[118] (**205**). 3,4,5,6-Tetraaryl-2-pyrones (**207**) may be synthesized from the reaction of **7** with sulfonium ylides **206**.[147] The analogous *N*-iminopyridinium ylides **208** reacted[119] similarly with **7** to give the corresponding 1,3-oxazine derivatives **209**. Diphenylcyclopropenethione (**252**) also underwent cyclization with the pyridinium im-

ines, **208**, with formation[159] of analogous 6*H*-1,3-oxazine-6-thiones **210**. The compound **210** (R = C_6H_5) could be converted into **209** (R = C_6H_5), by reaction with *m*-chloroperbenzoic acid. Mechanistic pathways considered for the formation of **205** also apply above. It is unlikely that the cycloadditions involved acetylnitrenes or acylcarbenes generated from the corresponding pyridinium *N*-ylides as ethyl azidoformate was found to be unreactive toward diphenylcyclopropenone.[120]



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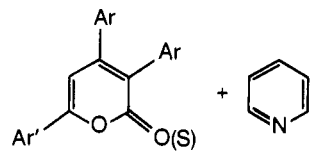

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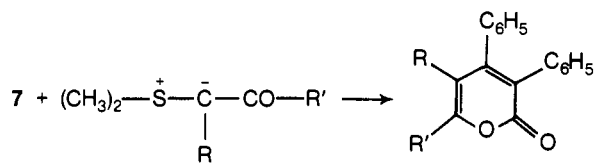
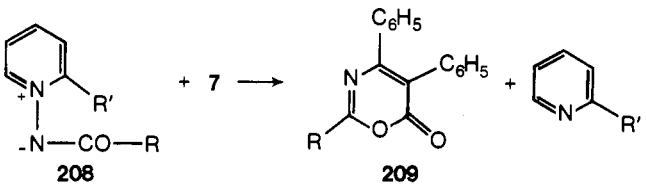
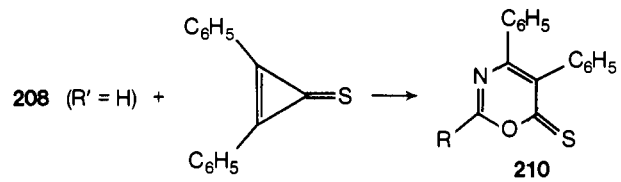


206 **207**

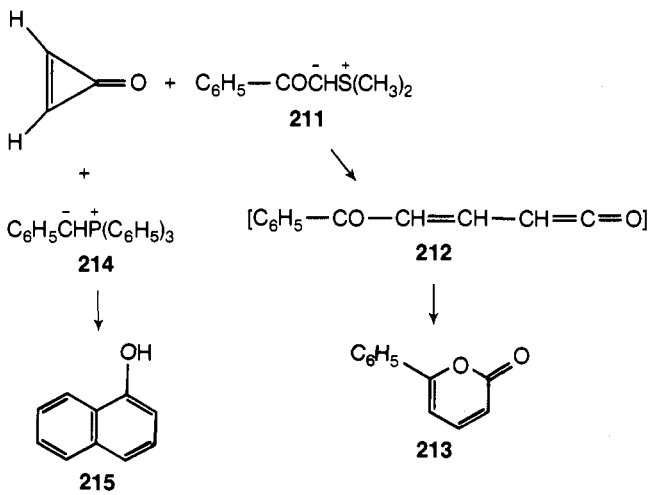


208 **209**



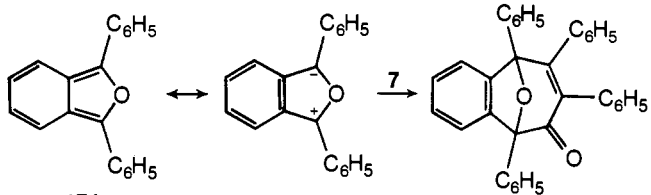
252 **210**

Cyclopropenone and the sulfur ylide **211** were found to give 6-phenyl-2-pyrone (**213**) at −78° in CH_2Cl_2. The ketene **212** was suggested as an intermediate in this reaction.[163] With benzylidene triphenylphosphorane (**214**), a similar ketene intermediate was postulated to explain the formation of 1-naphthol (**215**) as the final product.[163]



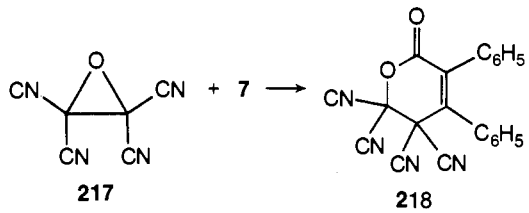
211 **214** **212** **213** **215**

1,3-Diphenylisobenzofuran (**171**) may, to some extent, be regarded as a potential 1,3 dipole of the carbonyl ylide type, and it was found[114] to react with **7** to give a [2 + 3] cycloadduct, **216**, across the C–CO bond of **7**, in contrast to the reaction of cyclopropenone (**3**) and **171** described previously (section V.B.4.d.(1).vii).

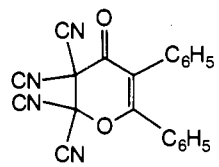


171 **216**

Tetracyanoethylene oxide (**217**) and **7** reacted readily[160] forming 3,4-diphenyl-5,5,6,6-tetracyano-5,6-dihydropyran-2-one (**218**) or its isomer, **219**. Spectral data were insufficient to distinguish between the two isomeric structures.

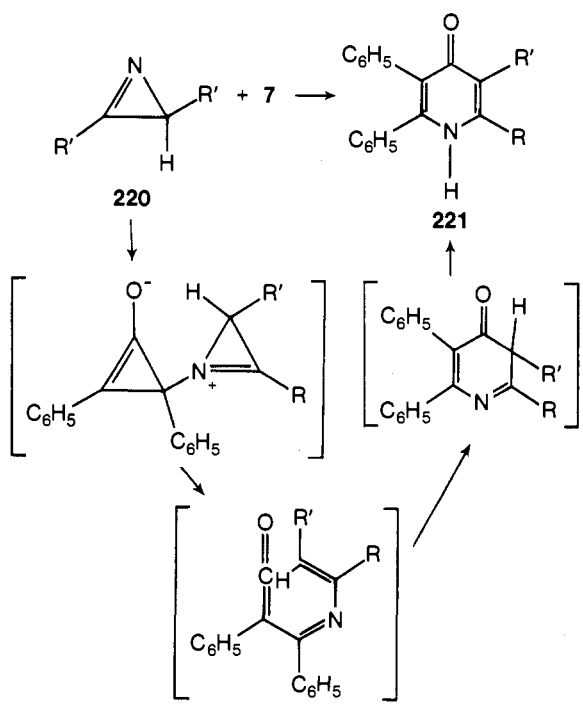


217 **218**



219

1-Azirines, **220**, reacted with **7** to produce 1:1 adducts shown to be 2,3-diphenyl-4-pyridones, **221**.[162] The 4-pyridones, **221**, may be postulated as arising from initial nucleophilic attack of the weakly basic azirine nitrogen on the electrophilic cyclopropenone ring, followed by an intramolecular Cope cyclization, as outlined below.

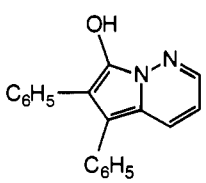


220 **221**

iii. Heteroaromatic Six-Membered Ring Systems Containing Nitrogen. In the recent investigation of cyclopro-

penones with heteroaromatic nitrogen compounds,[120] three types of cycloadducts were obtained. The first, 2:1 adducts, are described in the following section. The second, 1:1 adducts, were formed from an initial attack by an aza nitrogen on the carbonyl group of diphenylcyclopropenone (**7**), followed by cyclization to an adjacent carbon. The reaction of **7** and pyridazine proceeded readily to give a product which incorporated 1 equiv of **7** and was assigned the 5,6-diphenyl-7-hydroxypyrrolo[1,2-*b*]pyridazine structure **222** on the basis of a positive phenolic hydroxyl color test, spectral data, and the ready conversion into the 7-chloro and 7-ethoxy derivatives.

In contrast to the behavior of pyrazine itself (see following section V.B.4.e), 2,6-dimethylpyrazine and **7** afforded 1,3-dimethyl-7,8-diphenyl-6-hydroxypyrrolo[1,2-*a*]pyrazine (**223**), but the reason for this difference in reactivity is unknown. Structure **223** could also be smoothly converted into an imino ether with Meerwein's reagent. Similarly, 4-methyl-2,3-diphenyl-1-hydroxypyrrolo[1,2-*a*]quinoxaline (**224**), 1,2-diphenyl-3-hydroxypyrrolo[1,2-*a*]phthalazine (**225**), and 1,2-diphenyl-3-hydroxypyrrolo[1,2-c]quinazoline (**226**) were formed from ready reaction of **7** and 2-methylquinoxaline, phthalazine, and quinazoline, respectively. Both **225** and **226** were unreactive toward the addition of a second mole of **7** across the second imine function. The third type of adduct, in which addition of **7** occurred across the N=N bond, was isolated from 3,4-benzocinnoline. The adduct, 2,3-diphenyl-1-ketopyrazolo[1,2-*a*]cinnoline (**227**), was assigned this structure from its unreactivity as an enol toward phosphorus oxychloride, or trifluoroacetic acid, and from its spectral characteristics. The infrared spectrum showed a strong tertiary amidic carbonyl absorption at 1660 cm^{-1} and no OH absorption. A peri effect was observed in the nmr spectrum for H-12 which was deshielded (−1.4 ppm) by the carbonyl group.



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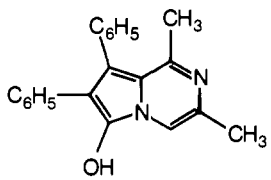

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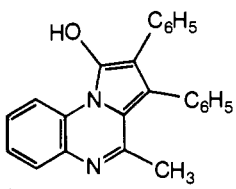

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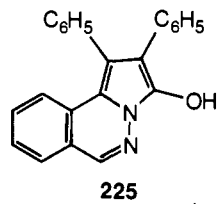

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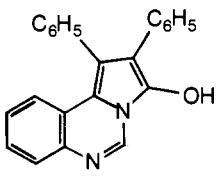

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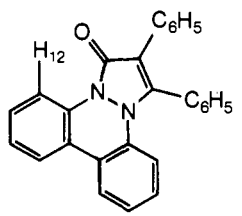
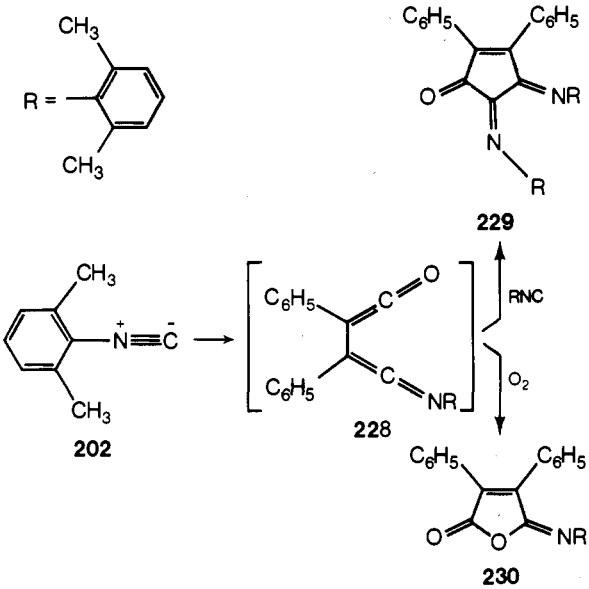


227

iv. 2:1 Cycloadducts. The reaction of **7** with 2,6-dimethylphenyl isocyanide (**202**) gave the ring-expanded products, 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenyl-2-cyclopenten-1-one (**229**) and a trace amount of *N*-(2,6-dimethylphenyl)diphenylisomaleimide (**230**). These were formed[116] presumably *via* a primary ring-opened intermediate **228** resulting from a Michael addition of the isocyanide to **7**.



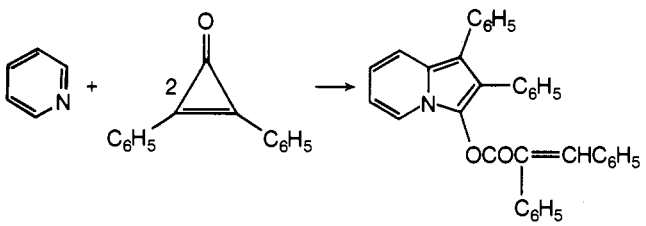
229

202

228

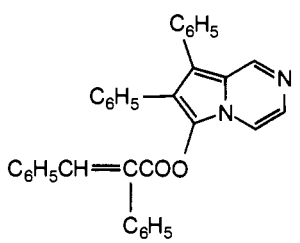
230

Diphenylcyclopropenone (**7**) reacted[24,95] with pyridine with 2 mol of **7** being incorporated into the final product which has now been shown[120] to be the 2:1 adduct **231**, the first type of cycloadduct mentioned in the previous sections on heteroaromatic nitrogen compounds. Other



231

2:1 adducts isolated from this class of reaction were **232** from pyrazine and **233** from isoquinoline.[120]



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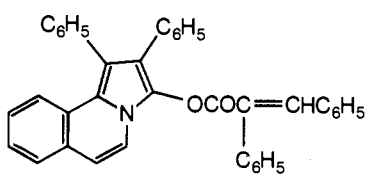
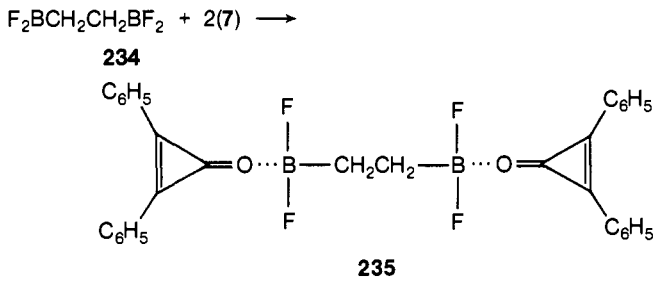


233

A 2:1 adduct **235** was also observed from the chelation of the bidentate Lewis acid **234** and **7**, the latter acting as the Lewis base.[122] Recently, more Lewis acid complexes of **7** with boron trifluoride and antimony pentachloride have been synthesized.[146]



235

5. *Metal Complexes with Cyclopropenones*

The formation of organometallic complexes from cyclopropenones and various metals has been examined (ref 18, 89, 90, 123, 124) extensively. The interaction of tetracarbonylnickel, $Ni(CO)_4$, with diphenylcyclopropenone (**7**) resulted in a complex in which three carbonyl ligands were replaced by 3 equiv of **7**.[18] The absence of the 1620-cm^{-1} band in the complex suggested that C=C coordination had occurred. However, recent studies of the infrared spectra of cyclopropenones (section III.C.1), and the synthesis of a series of complexes[123] of **7** with Zn(II), Co(II), Ni(II), Cu(II), Ru(III), Pt(II), and Pt(IV) and Pt(II) in which coordination occurred through the carbonyl oxygen, suggest that this initial hypothesis might be incorrect. Comparison with other oxygen donor ligands showed **7** to be as effective as the strongest donor, H_2O, in coordination with metals.[123] Some new cobalt and platinum complexes with **7** were similarly prepared.[125]

C. Oxidation of Cyclopropenones

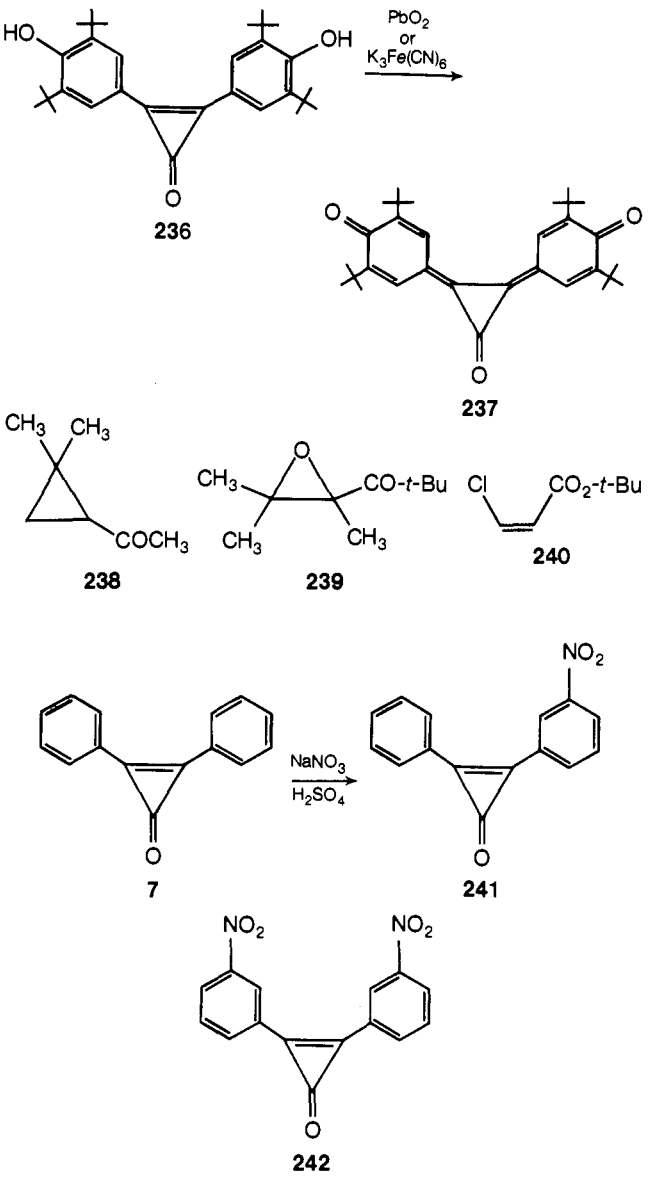
Two oxidations of cyclopropenones have been reported recently in the literature, and interesting products have been described. Treatment of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**236**) with lead dioxide or aqueous, basic potassium ferricyanide gave an intense purple, unstable solution (benzene, λ_{max} 542) from which **237** was isolated as a purple solid.[79] The peracid oxidation of di-*tert*-butylcyclopropenone (**18**) gave a 1:2.5:90:2 mixture of di-*tert*-butylacetylene, **238**, **239**, and (*t*-BuCO)$_2$, respectively. Similar treatment of **7** with *m*-chloroperbenzoic acid gave a 4:1:5 mixture of diphenylacetylene, benzophenone, and benzil.[126] *tert*-Butyl hypochlorite at room temperature in CH_2Cl_2 oxidized cyclopropenone to *cis*-*tert*-butyl β-chloroacrylate (**240**). Some of the trans isomer was also observed[163] but was thought to be the result of isomerization of **240**.

D. Substitution Reactions

1. *Nitration*

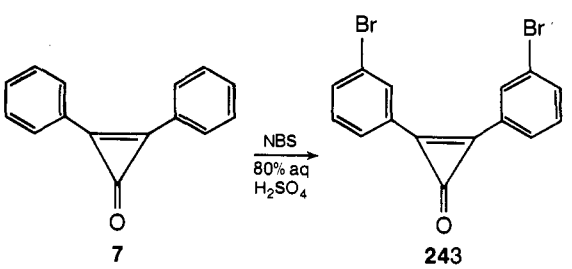
The failure[72] of nitrobenzylidene chlorides to form the nitro-substituted phenylcyclopropenones isolated from reaction between the appropriate acetylene and phenyl(bromodichloromethyl)mercury (**33**) (section IV.A.2) led to the direct nitration of **7** as an alternative route.[157]

The addition of a molar equivalent of sodium nitrate to a solution of **7** in sulfuric acid afforded a mononitrated product, **241**, in which meta orientation was assigned by photochemical decarbonylation to known 3-nitrodiphenylacetylene. Nitration in the meta position was expected, since **7** in acidic medium would be fully protonated and, in the resultant positive cyclopropenylium system, the charge could be delocalized effectively to the ortho and para positions in the phenyl substituents. Similarly, the use of 2 molar equiv of sodium nitrate gave dinitrodiphenylcyclopropenone (**242**) tentatively assigned as the 3,3′ isomer.



2. *Bromination*

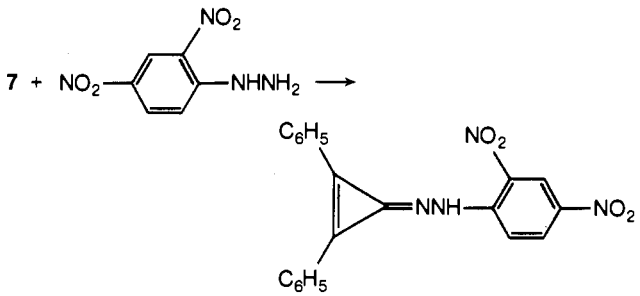
Failure to obtain the desired orientation of bromo substituents in the synthesis of a cyclopropenone was overcome by the bromination of **7** using *N*-bromosuccinimide. Whereas Tobey and West[78] obtained para-substituted diarylcyclopropenones from the electrophilic substitution of aromatic compounds by trichlorocyclopropenylium salts (section IV.A.3), treatment of a solution of **7** in 80% aqueous sulfuric acid with 2 molar equiv of *N*-bromosuccinimide gave[158] bis(*m*-bromophenyl)cyclopropenone (**243**). The meta orientation was assigned to the product on the basis of spectral data only, but nmr calculations for aromatic substitution patterns correlated well with the meta assignment.



VI. Derivatives of Cyclopropenones

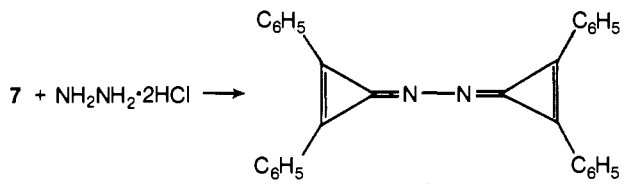
A. Iminocyclopropenones

The formation of a 2,4-dinitrophenylhydrazone, **244**, from **7** has been reported,[21] but it has not been possible



244

to duplicate this work.[24] Reaction in concentrated sulfuric acid–absolute ethanol mixture, or in diglyme, was reported[95] to have yielded **244**. Reaction of the ketone **7** and tosylhydrazine gave the tosylhydrazone.[127] Although anhydrous hydrazine gave[95] both the ring-opened product **199** and the cyclic product **198**, reaction of **7** with hydrazine dihydrochloride formed[127] only diphenylcyclopropenone azine (**245**). Other syntheses of cyclopropenimines were accomplished by reaction of several activated isocyanates[115,128] with diphenylcyclopropenone yielding **246**. This may be rationalized as an initial attack by the carbonyl oxygen atom on the heterocumulene, cyclization, and subsequent loss of CO_2.



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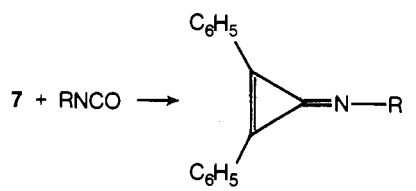
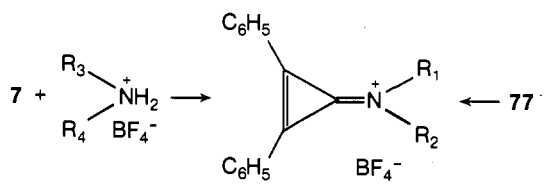


246, R = $CH_3C_6H_4SO_2$–
Cl_3CCO–
$ClSO_2$–
$C_6H_5SO_2$–

Addition of N-nucleophiles to **7** led to the protonated imines **247** (R_1 = H), which are easily converted into **246** with strong base.[91] Treatment of **7** with NH_4BF_4 gave a series of these cyclopropenylideneammonium salts (**247**), alternatively prepared from the ethyloxonium fluoroborate salt (**77**) and secondary amines.[84] It is interesting to recall that whereas hydroxylamine gave an oxime **131** and a cyclic oxidation product **132** in the reaction with **7**, hydroxylamine hydrochloride has been reported[129] to give the simple oxime **248**.



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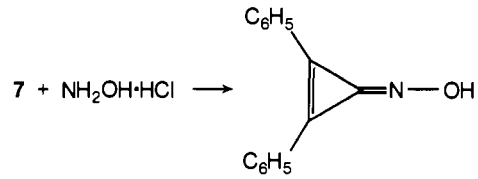

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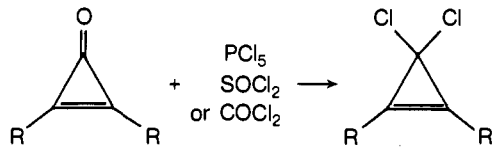
B. 3,3-Dichlorocyclopropenes

The reconversion of cyclopropenones into their precursors, 3,3-dichlorocyclopropenes (**249**), may be accomplished with phosphorus pentachloride,[129] thionyl chloride,[78] or phosgene.[91,130] Cycloaddition reactions of

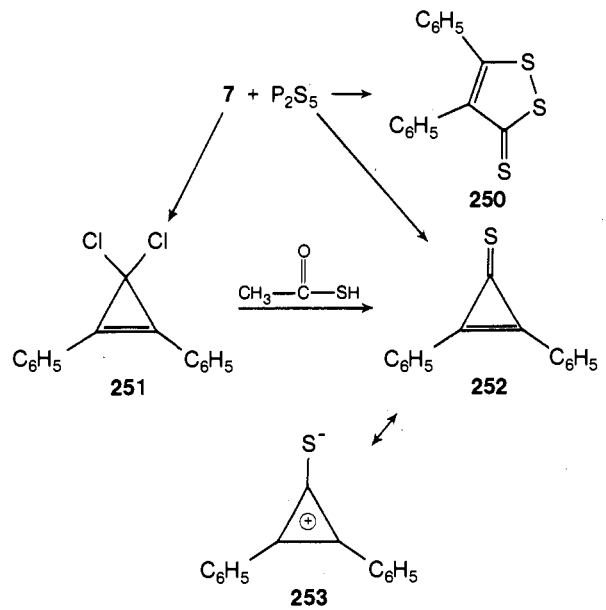


249

chlorocyclopropenes have been reported but the geminal dichlorocyclopropene was shown to be unreactive.[150]

C. Diphenylcyclopropenethione

Conflicting results have been obtained in the addition of P_2S_5 to **7**. 4,5-Diphenyltrithione (**250**) was reported as being isolated[131] in one instance, and diphenylcyclopropenethione (**252**) in another.[129] The latter has also been prepared in an alternative manner from the dichlorocyclopropene (**251**) and thioacetic acid.[91,132] Diphenylcyclopropenethione (**252**) has a dipole moment, μ = 5.8 D,[129]



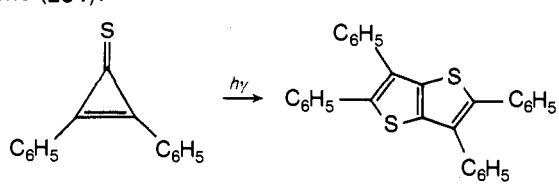
250

251

252

253

but recent X-ray studies show that the delocalized structure **253** is not supported by these data.[171] Whereas diphenylcyclopropenone (**7**) underwent decarbonylation upon photolysis (section V.A), photodimerization of diphenylcyclopropenethione was observed upon irradiation in benzene, affording 2,3,5,6-tetraphenylthieno[3,2-*b*]thiophene (**254**).[152]



254

However, in ethanol over 24 hr using a high-pressure Hg lamp, carbon monosulfide was eliminated, giving diphenylacetylene in 50% yield.[155]

D. Triafulvenes (Methylenecyclopropenes)

Methylenecyclopropene (**225**) is the simplest cross-conjugated cyclic system.[133] Its relationship to cyclopropenones was shown from the physical characteristics of its C-substituted derivatives, such as dipole moments[129,138] and calculated delocalization energies.[9] The simplest route to the methylenecyclopropenes would be expected to be the Wittig olefination of cyclopropenones, but it has been reported to be successful in only one instance. Thus, 1,2-diphenyl-4-ethoxycarbonylmethylenecyclopropene (**257**) was obtained from the reaction of **7** with triphenylphosphine-ethoxycarbonylmethylene[61,139] (**256**). Condensation of **7**,[129,138] dipropylcyclopropenone[140] (**8**), and di-*tert*-butylcyclopropenone[134] (**18**) with malononitrile also yielded the corresponding 1,1-dicyanomethylenecyclopropenes (**258**). The best method[160] for preparing 1,1-dicyanomethylenecyclopropene **258** (R = C_6H_5) was from the reaction of diphenylcyclopropenethione (**252**) and tetracyanoethylene oxide (**217**). The reaction possibly proceeded by the scheme outlined above in superior yields (67%).

Cyanoacetic acid and **7** gave[135] 4-cyano-4-(cyanoacetyl)-1,2-diphenyltriafulvene (**260**). Initial condensation of cyanoacetic acid would give the 4-cyano-4-carboxylic acid **259** which, followed by decarboxylation and electrophilic attack by $NC{=}CH_2CO^+$, would yield **260**. Tetrachlorocyclopentadiene condensed[102] with **7** to produce **261**.

Heterofulvenes were synthesized from the condensation of **7** with various heterocyclic nitrogen compounds.[136,137] The azapentatriafulvalenium salts **263** were prepared from **7**, and various indoles **262** and, in an analogous fashion, the salts **264** were obtained from 2-phenyl-7-methylindolizine; those represented by structure **265** were obtained from 2,4,5-triphenylpyrrole. From cycloheptenocyclopropenone (**15**) and 2-phenylindole, the salt **266** was isolated.

The reactions described above presumably involve electrophilic substitution at the most reactive position of the heterocyclic ring by the 3-hydroxy-1,2-diphenyl- or the 3-hydroxy-1,2-cycloheptenocyclopropenium cation, produced *in situ* from the cyclopropenone and HCl.[136]

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VII. References and Notes

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