

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

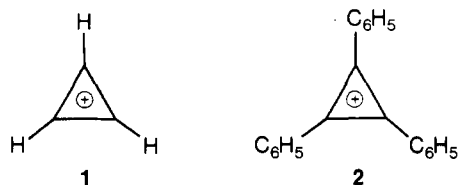
reactant and the site of reaction on the three-membered ring.

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.

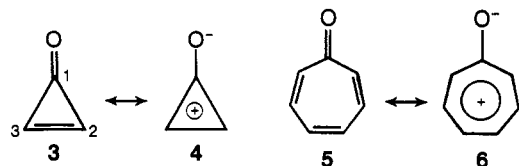
Earlier reviews of cyclopropenones have always been part of a wider consideration of cyclopropane, cyclopropene (1966, 1972), and cyclopropenyl cation chemistry. These topics are not discussed in this present review which covers the available literature to January 1973.

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 Hückel¹ 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

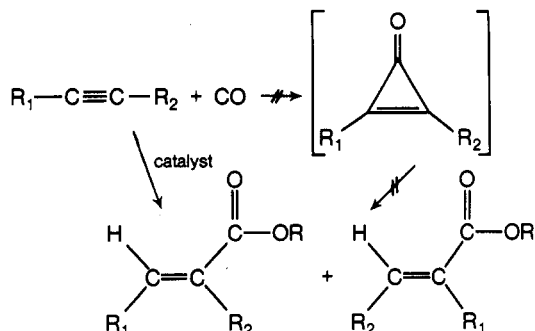
The tropylium ion³⁻⁵ provided confirmation of Hückel's rule for $n = 1$, and it may be predicted similarly that the cyclopropenyl cation (**1**), which has two π electrons in a field of three carbon atoms, should have the stability characteristic of aromatic systems. Quantum mechanical calculations showed⁶ 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 triphenylcyclopropenyl cation salt (**2**), confirmed the stability



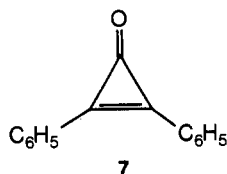
of these substances. Subsequent molecular orbital calculations⁹ for a variety of cyclopropenyl systems including cyclopropenone (**3**) and its charge-delocalized form **4** gave calculated values of 1.36β for the delocalization energy of cyclopropenone and 6.15β for its diphenyl derivative, indicating 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



stable than the highly strained cyclopropenones, but it was only recently that the first member of the cyclopropenone 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



*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.

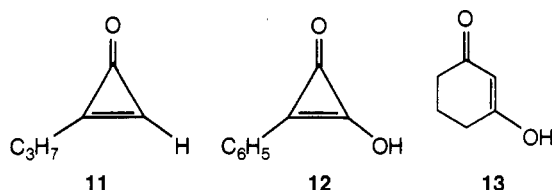
III. Physical Characteristics

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.

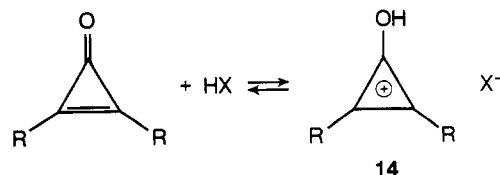
A. Basicity

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), dicyclopentyl-,¹⁷⁴ methyl-²⁶ (9), and dimethylcyclopropenone²⁶ (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 ¹³C 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 shown³⁰ to have a pK_a of 2.0 ± 0.5 , agreeing well with the predicted^{31,32} value of 2.0.



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 $1400-1430\text{ cm}^{-1}$.



B. Dipole Moments

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

served for several cyclopropenes 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 diphenylcyclopropenone³⁸ (**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 cyclopropenes 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 cyclopropenes (ref 20, 22, 24, 26, 27, 33, 39–50, 93, 145) except unsubstituted cyclopropenone¹⁵⁰ (**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 ¹⁸O in some cyclopropenes 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 cyclopropenes. Cyclopropanone itself absorbs⁵¹ 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 hydroxycyclopropenyl salts **14**, but the appearance of a broad OH band at 2976 cm⁻¹ and a transition at 1420 cm⁻¹ due to the cyclopropenyl 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.

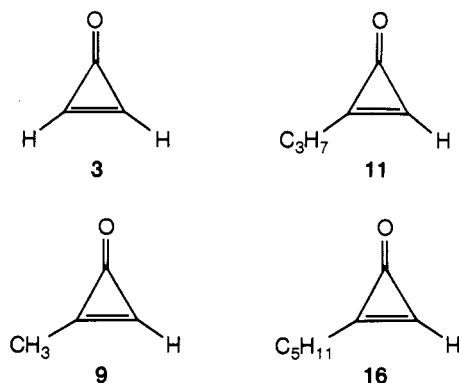
2. Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of dialkylcyclopropenes 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 diphenylcyclopropenone²⁴ (**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 cyclopropenes 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



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-trimethylcyclopropene⁵⁵ 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 ¹³C nmr signals (in CDCl₃) relative to TMS at -155.1 ppm (C₁) and -158.3 ppm (C₂) 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 CF₃CO₂H–CCl₄ indicated that there is a high degree of polarization of the carbonyl group even in CDCl₃.⁵⁷ The ¹³C–H coupling constants of cyclopropenone (**3**) ($J(^{13}\text{C}-\text{H}) = 230$ Hz) and of methylcyclopropenone (**9**) ($J(^{13}\text{C}-\text{H}) = 213$ Hz) were of the same order of magnitude as that observed in 1,1,2-trimethylcyclopropene⁵⁵ ($J(^{13}\text{C}-\text{H}) = 218$ Hz) and in the diethylcyclopropenyl cation⁵⁸ ($J(^{13}\text{C}-\text{H}) = 228$ Hz). These results may reflect a large *s* contribution to the carbon hybrid orbital.²⁶

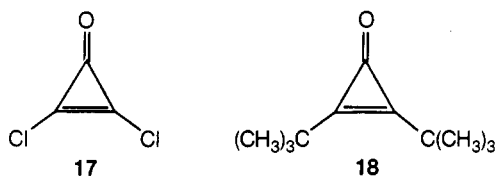
Prior to the synthesis of unsubstituted cyclopropenes, nmr spectra of dialkylcyclopropenes were used to identify structural features. In di-*n*-propylcyclopropenone (**8**), the separation between the signals for the methylene proton resonances α to the cyclopropenone ring and methylene protons β to 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 cyclopropenyl 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 ₆ H ₅	80	121-121.5
<i>p</i> -ClC ₆ H ₄	43	147
<i>m</i> -ClC ₆ H ₄	46	112
<i>o</i> -ClC ₆ H ₄	4	104-105
<i>p</i> -CH ₃ OC ₆ H ₄	26	104
<i>m</i> -CH ₃ OC ₆ H ₄	25	80
<i>o</i> -CH ₃ OC ₆ H ₄	3	94-96
<i>p</i> -CH ₃ C ₆ H ₄	27	131
<i>o</i> -CH ₃ C ₆ H ₄	28	127
<i>o</i> -FC ₆ H 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 diphenylcyclopropenone¹⁵⁴ (7) or diphenylcyclopropenethione¹⁵⁵ (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. Dichlorocyclopropenone⁵⁹ (17) yielded a spectrum consisting of the molecular ion and five major fragment ions corresponding to the loss of Cl, Cl₂, CO, COCl, and C₂ClO. 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.



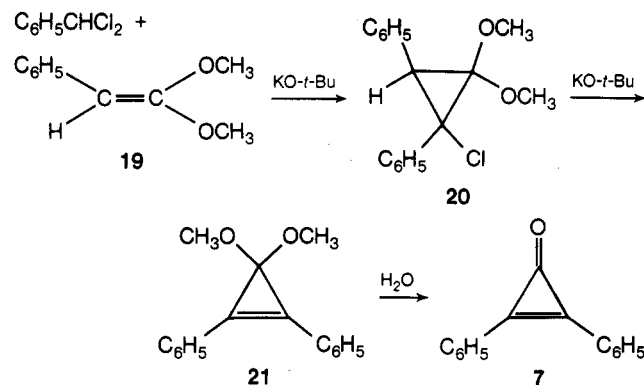
IV. Synthesis of Cyclopropenones

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

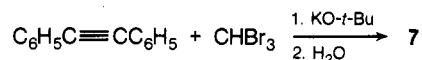
Diphenylcyclopropenone (7) was first synthesized²⁰ by the addition of phenylchlorocarbene to phenylketene acetal (19), a procedure which probably gives the cyclopropane 20 as the initial product. Additional base converts 20 into the cyclopropene ketal 21 by a β -elimination of hydrogen chloride, followed 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

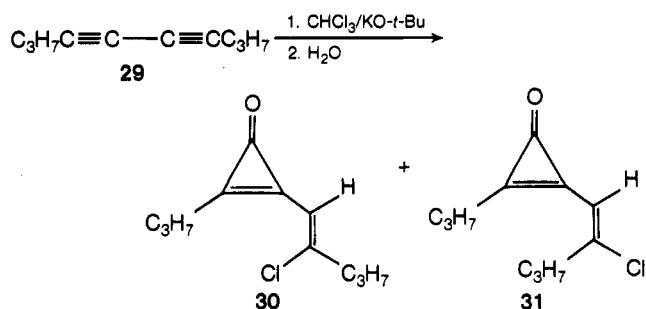
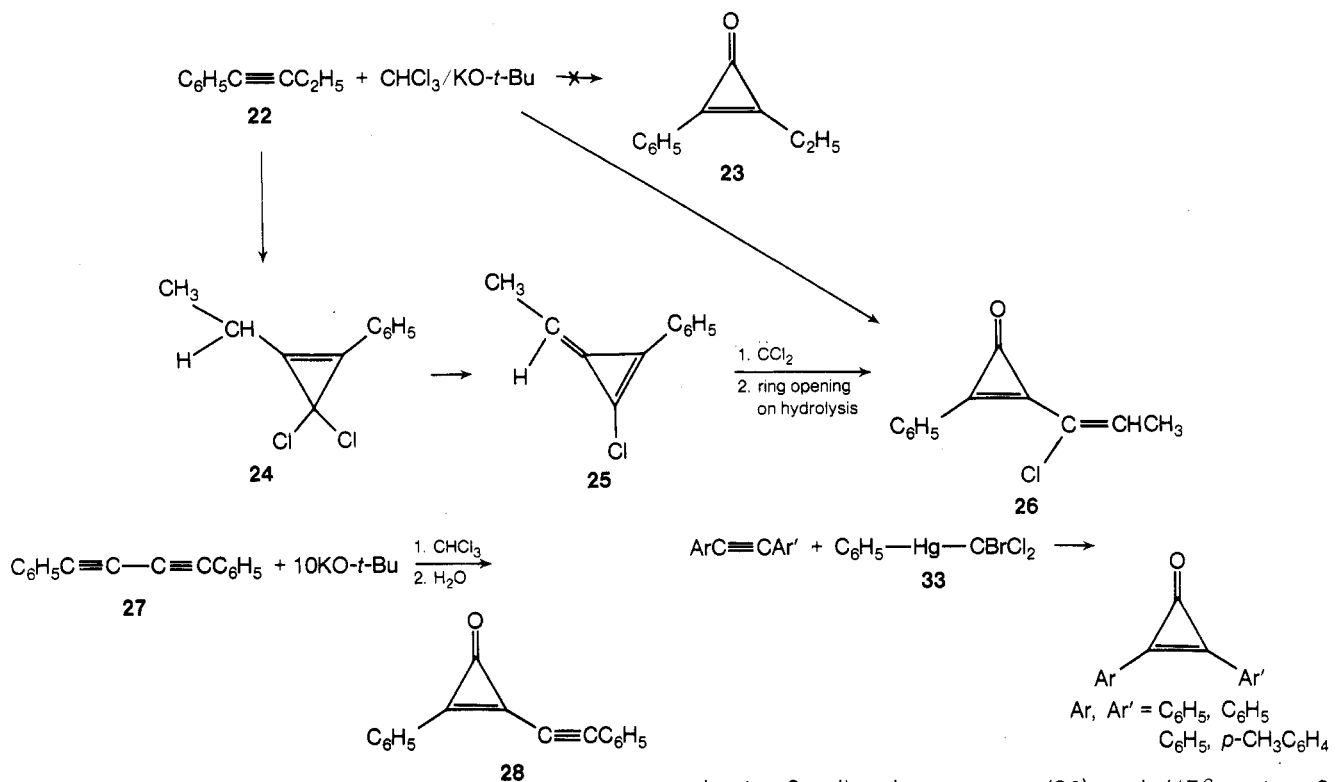
A simpler synthesis of cyclopropenones is based on the addition of dihalocarbene to acetylenes (ref 21, 26-30, 33, 34, 39, 41, 67-77). The intermediate 3,3-dihalo-cyclopropenes are usually not isolated under the reaction conditions employed, hydrolysis giving the final products as cyclopropenones.

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



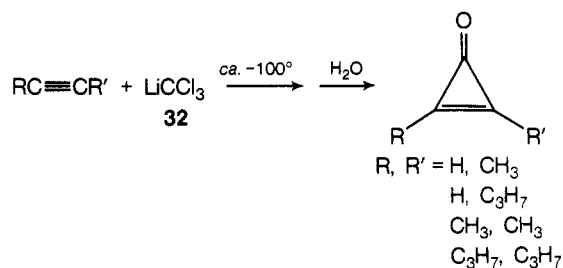
Both dipropylacetylene and di-*tert*-butylacetylene react with sodium trichloroacetate in a similar fashion to form the corresponding cyclopropenones.^{27,67} However, with 1-ethyl-2-phenylacetylene (22), the expected 2-ethyl-3-phenylcyclopropenone (23) was not obtained, 2-(1-chloropropen-1-yl)-3-phenylcyclopropenone (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 methoxide⁴¹ or potassium *tert*-butoxide.⁷⁰

Dehmlow has studied extensively the addition of dichlorocarbene to a series of alkynes²⁸ 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.⁶⁶ 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.

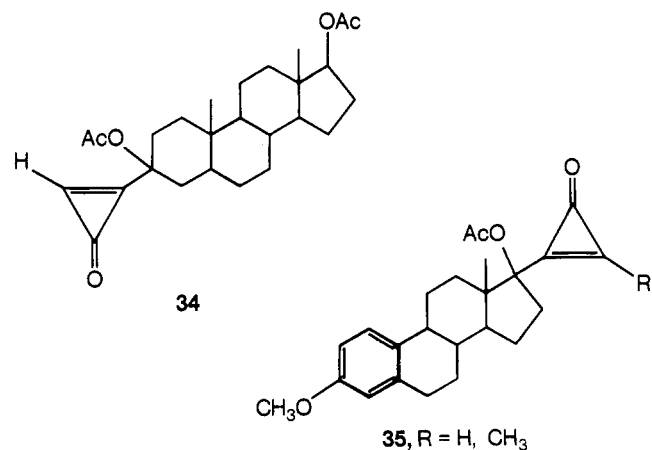
Lithium trichloromethide (**32**) as the dichlorocarbene source and various acetylenes also produced cyclopropanones after hydrolysis.^{26,29} An attempt to prepare cyclopropanone (**3**) itself from acetylene by this method was unsuccessful.²⁶



The use of phenyl(bromodichloromethyl)mercury (**33**) as the dichlorocarbene donor has also led to the synthesis of diarylcyclopropanones.⁷² Unsymmetrical diarylcyclopropanones or diarylcyclopropanones 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 (3,17 β -diacetoxy-5 α -an-

drostan-3 α -yl)cyclopropanone (**34**) and (17 β -acetoxy-3-methoxyestra-1,3,5(10)-trien-17 α -yl)cyclopropanone (**35**) were prepared following hydrolysis of the intermediate difluorocyclopropane.



The synthesis of phenylhydroxycyclopropanone (**12**) was accomplished by the reaction of 2-phenyltetrachloropropene (**36**) or 1-phenyl-2,3,3-trichlorocyclopropane (**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

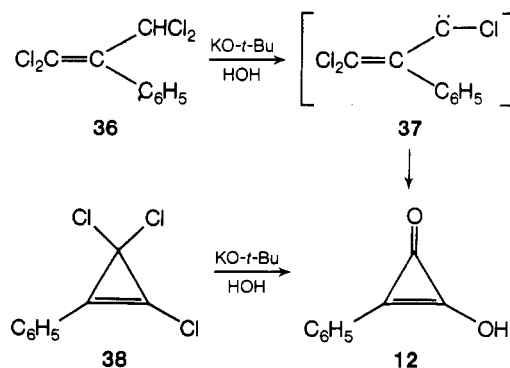
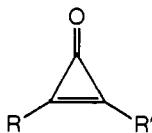


TABLE II. Aryl- and Alkylcyclopropenones Prepared by Carbene-Insertion Procedures



Substituents		Method ^a	Yield, %	Mp or bp (mm), °C	Ref
R	R'				
C ₆ H ₅	C ₆ H ₅	A	20-30	119-121	24, 33
C ₆ H ₅	C ₆ H ₅	B	6	119-121	24
C ₆ H ₅	C ₆ H ₅	E	63	120-122	72
C ₆ H ₅	C ₆ H ₅	F	40	114-117	34
C ₆ H ₅	C(Cl)=CHCH ₃	A	8	119.5-120.5	28, 69
C ₆ H ₅	C(Br)=CHCH ₃	A	4	117-118	28
C ₆ H ₅	C(Cl)=CHC ₆ H ₅	A	3	97	28, 70
	(isomer A)				
	(isomer B)	A	5	117	28
C ₆ H ₅	C≡CC ₆ H ₅	A	6	92	28, 68
C ₆ H ₅	CH=CHC ₆ H ₅	A	23	80	28
	(cis)				
	(trans)	A	10	98-99	28
C ₆ H ₅	<i>p</i> -NH ₂ C ₆ H ₄	A	6	192	28
C ₆ H ₅	C(Cl)=CHOCH ₃	A	31	152	28
C ₆ H ₅	CH(OC ₂ H ₅) ₂	A	15	46	28
C ₆ H ₅		A	11	122	71
C ₆ H ₅	CH=C(CH ₃) ₂	A	3.5	106	71
C ₆ H ₅	C(Cl)=CH(CH ₂) ₂ CH=CH ₂	A	4	150 (0.1)	71
	(isomer A)				
	(isomer B)	A	7	52	71
<i>n</i> -C ₈ H ₇	CH=C(Cl)- <i>n</i> -C ₈ H ₇	A	7	100-120 (0.1)	28, 68
	(isomer A)				
	(isomer B)	A	1.5	120 (0.1)	28, 68
<i>n</i> -C ₈ H ₇	C(Cl)=CH-C ₂ H ₅	A		90 (0.1)	28
	(isomer A)				
	(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≡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) ₂ CH=CH ₂	A	0.7	90 (0.1)	71
	(isomer A)				
	(isomer B)	A	9.5	100 (0.1)	71
SC(CH ₃) ₃	SC(CH ₃) ₃	A	4	79	28
C ₆ H ₅	CH ₂ C ₆ H ₅	B		108-109	41
<i>n</i> -C ₈ H ₇	<i>n</i> -C ₈ H ₇	B	8.9	80 (0.7)	34
<i>n</i> -C ₆ H ₁₃	C ₂ H 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 ₂₈ H ₃₅ O ₄ (34)	B		132-134	73
<i>n</i> -C ₈ H ₇	<i>n</i> -C ₈ H ₇	C	19	80 (0.7)	26, 29
CH ₃	CH ₃	C	12	54-58 (0.7)	26, 29
H	<i>n</i> -C ₈ H ₇	C		40 (2)	26, 29
H	CH ₃	C	20	57 (2)	26, 29
C ₆ H ₅	OH	D	18	244-245	30, 75
C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	E	79	129.5-131.5	72

^a (A) potassium *tert*-butoxide/CHCl₃ (CHBr₃); (B) sodium trichloroacetate; (C) lithium trichloromethide; (D) intermolecular carbene insertion/KO-*t*-Bu; (E) phenyl(bromodichloromethyl)mercury; (F) phenylchlorocarbene.

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

3. Trichlorocyclopropenyl Ion Route

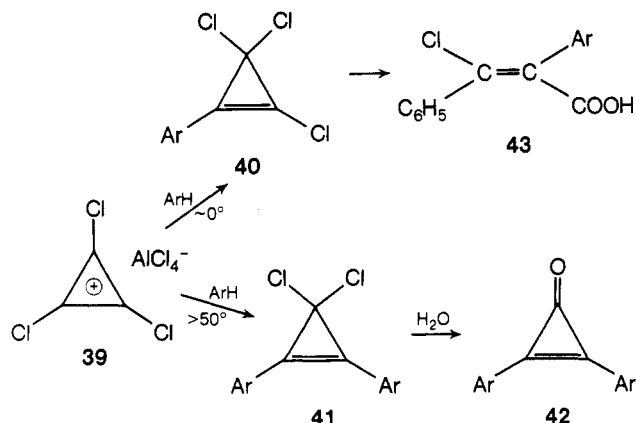
The reaction of trichlorocyclopropenium tetrachloroaluminate (**39**) with benzene derivatives via a Friedel-Crafts pathway provides aryltrichlorocyclopropenes (**40**) or *gem*-dichlorodaryl cyclopropenes (**41**). The latter may be

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 triaryl cyclopro-

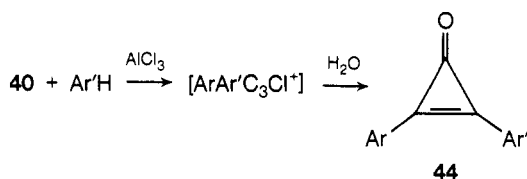
TABLE III. Symmetrical and Unsymmetrical Disubstituted Cyclopropanones Prepared from Trichlorocyclopropenium Ion

Substituents		Yield, %	Mp, °C	Ref
R	R'			
<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	45	179–181	80
<i>p</i> -HOC ₆ H ₄	<i>p</i> -HOC ₆ H ₄	10	222–226 dec	80
3,5-(CH ₃) ₂ -4-OH-C ₆ H ₂	3,5-(CH ₃) ₂ -4-OH-C ₆ H ₂	100	268 dec	80
3,5-(<i>i</i> -Pr) ₂ -4-OH-C ₆ H ₂	3,5-(<i>i</i> -Pr) ₂ -4-OH-C ₆ H ₂	82	209–211 dec	80
3,5-(<i>t</i> -Bu) ₂ -4-OH-C ₆ H ₂	3,5-(<i>t</i> -Bu) ₂ -4-OH-C ₆ H ₂	48	215 dec	79, 80
<i>p</i> -FC ₆ H ₄	C ₆ H ₅	44	111–113	81
<i>p</i> -FC ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	20	141–142	81
<i>p</i> -FC ₆ H ₄	Mesityl	10	135–137	81
<i>p</i> -FC ₆ H ₄	<i>p</i> -FC ₆ H ₄	48	184–185	78
Cl	Cl		–6	59

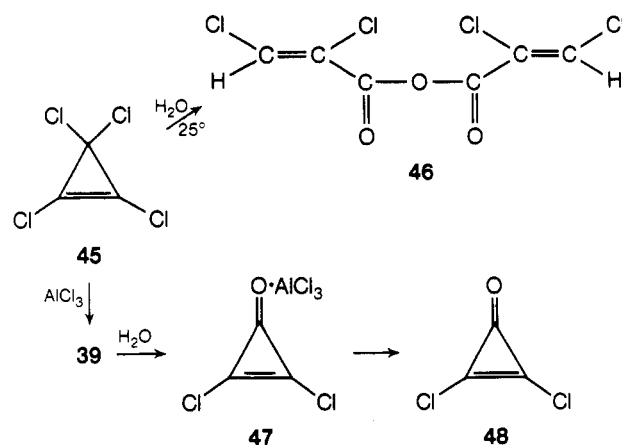
penylium ion salts.⁸⁰ 1-Aryl-2,3,3-trichlorocyclopropane (**40**) may be hydrolyzed with ring opening, affording as the major product 2-aryl-3-chloroacrylic acid (**43**). The mechanism of the hydrolysis is not known but may proceed through an arylhalocyclopropanone.⁸¹



An attempt was also made to isolate phenylhydroxycyclopropanone (**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-trichlorocyclopropane (**40**) was found to undergo further reaction with a second aromatic hydrocarbon, and the products, isolated after an aqueous reaction work-up procedure, were diarylcyclopropanones. The synthesis of diarylcyclopropanones may thus be accomplished stepwise, and an advantage of this procedure is in the synthesis of unsymmetrically substituted cyclopropanones **44**.⁸¹ Tetrachloro-

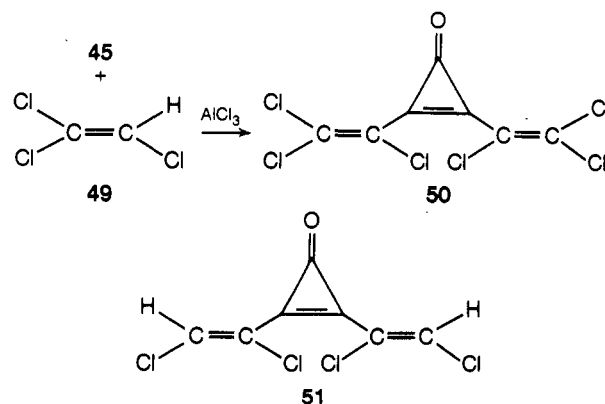


cyclopropane (**45**), which is converted into **39** on reaction with aluminum chloride, was thought to be a likely possibility to give dichlorocyclopropanone (**48**) on hydrolysis. The synthesis of **48** was initially unsuccessful, with only a ring-opened anhydride **46** being isolated on hydrolysis.¹⁷² However, a very slow hydrolysis of **39** suspended in methylene chloride produced an aluminum complex **47** from which dichlorocyclopropanone (**48**) was isolated as a dangerously unstable liquid⁵⁹ (Table III).



4. Tetrachlorocyclopropane Route

The reaction of 1,1,2-trichloroethylene (**49**), aluminum chloride, and tetrachlorocyclopropane (**45**) gave bis(trichlorovinyl)cyclopropanone (**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)cyclopropanone (**51**). No reaction was observed with tetrachloroethylene.

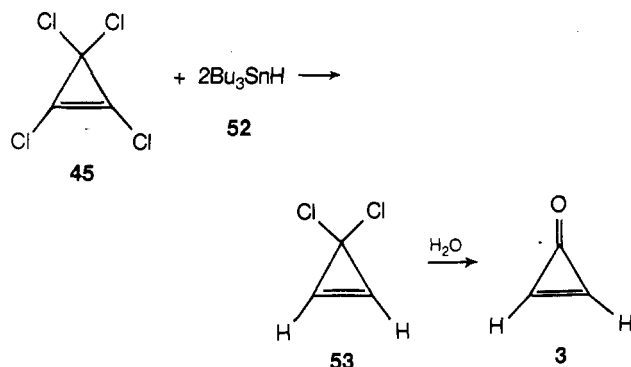


The synthesis of the parent ketone, cyclopropanone (**3**), was unsuccessful by the methods used to prepare substituted derivatives,^{26,33,82} and by the modified Favorskii reaction (section IV.B). Breslow and coworkers (ref 42, 83, 150, 156) succeeded in synthesizing cyclopropanone itself (**3**) by 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 chlorocyclopropanes

TABLE IV. Cyclopropenones Prepared by the Modified Favorskii Reaction

Substituents		Yield, %	Mp or bp (mm), °C	Ref
R	R'			
C ₆ H ₅	C ₆ H ₅	45	119–121	24, 40
<i>n</i> -C ₈ H ₇	<i>n</i> -C ₈ H ₇	9.2	66–68 (0.3)	34
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H 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 ₆ H ₅	N(C ₂ H ₅) ₂		120–130 (0.001)	34
C(CH ₃) ₃	C(CH ₃) ₃	36	61–61.5	43a, 67
		52		43b
C ₆ H ₅	C ₂ H ₅	44	25	28
C ₆ H ₅	CH ₂ C ₆ H ₅	23	68	28
C ₆ H ₅	CH ₃		72–73	84
<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃		97–98	84
H	<i>n</i> -C ₈ H ₁₁	10–15		57

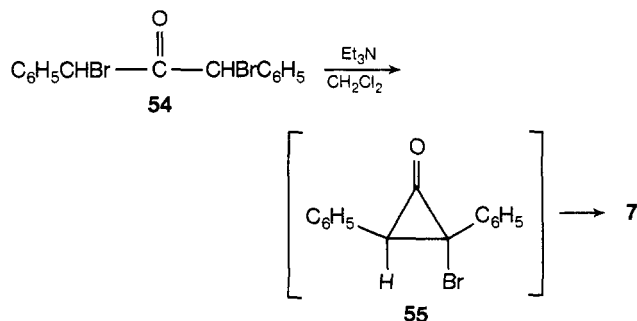
containing 3,3-dichlorocyclopropene (**53**) (nmr: δ 8.0), 1,3-dichlorocyclopropene, and mono- and trichlorocyclopropene isomers. Cautious hydrolysis and distillation afforded cyclopropenone (**3**) as a colorless liquid (bp 30°



(0.45 Torr)) in 41–65% overall yield from tetrachlorocyclopropene (**45**). The availability of this product has led recently to the determination¹⁷⁵ 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.

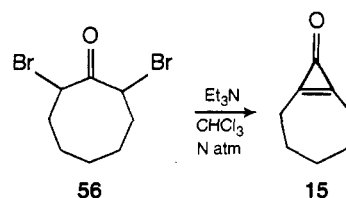
B. Synthesis by a Modified Favorskii Reaction

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 established¹⁶ 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 di-

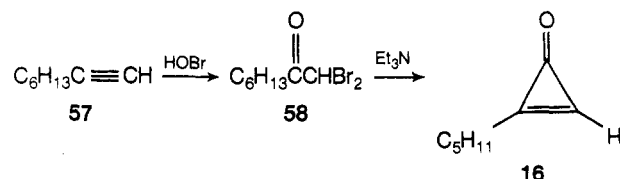


phenylcyclopropenone in 45% overall yield from dibenzyl ketone.^{24, 40} The reaction has been extended to prepare

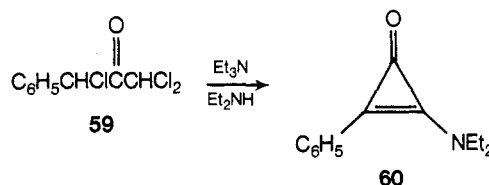
dialkylcyclopropenones such as dibutyl-,⁴⁰ dipropyl-,³⁴ di-*tert*-butyl-,^{43, 67} methylphenyl-,⁸⁴ and methyl-*p*-methoxyphenylcyclopropenone⁸⁴ (Table IV). Interestingly, the reaction was also applied to dibromocyclooctanone (**56**) and resulted in a 50% yield of the cycloheptenocyclopropenone⁴⁰ (**15**). 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}



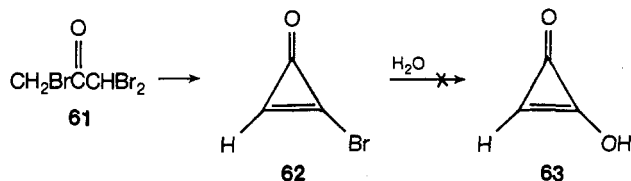
Monosubstituted cyclopropenones have been prepared by a modification of the above procedures.⁵⁷ Thus oct-1-yne (**57**) was converted by hypobromous acid into 1,1-dibromooctan-2-one (**58**), treatment of which with trieth-



ylamine 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 hydroxycy-



clopropenone (**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

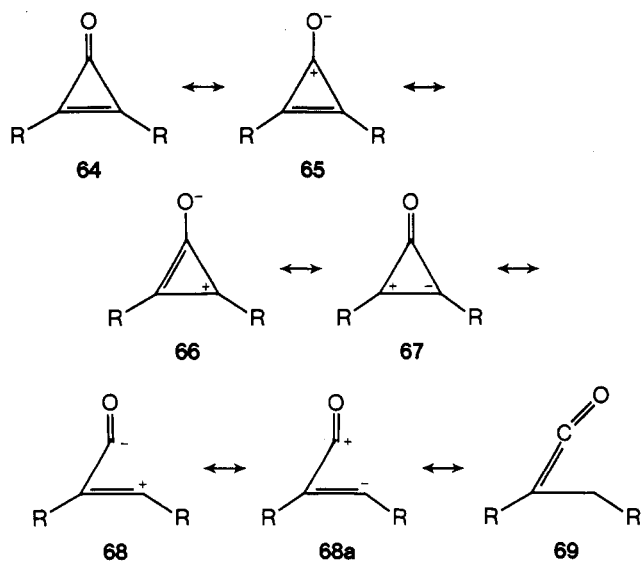


V. Reactions of Cyclopropenones

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-

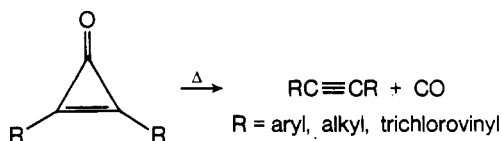
tion reactions, addition reactions, oxidation reactions, and substitution reactions.

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 cyclopropanone 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**.



A. Decarbonylation

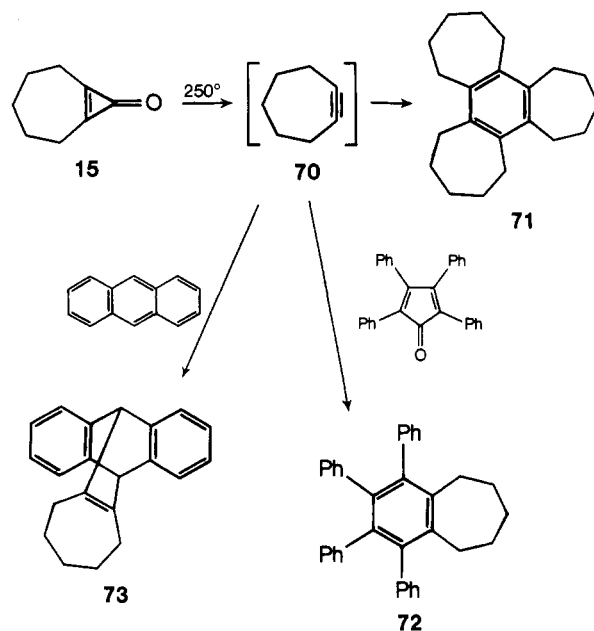
The loss of carbon monoxide from cyclopropanones may be induced by pyrolysis (ref 20, 24, 26, 27, 34, 39, 40, 67, 81, 86, 87), photolysis (ref 67, 79, 88, 163), or by catalytic decarbonylation techniques (ref 18, 89, 90). Diphenylcyclopropanone (**7**) on heating at 130–140° lost carbon monoxide and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



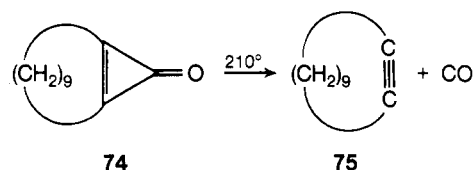
was more efficient.²⁴ A dimer of the original ketone has also been isolated from the pyrolysis at lower temperatures (section V.B.4.a). *p*-Fluorotolan was obtained similarly from the pyrolysis of the corresponding di(*p*-fluorophenyl)cyclopropanone.⁸¹

Thermolysis of dialkylcyclopropanones required higher temperatures than the corresponding diaryl compounds. Whereas **7** was 90% destroyed after 7 min at 190–191° (nitrogen atmosphere), di-*n*-propylcyclopropanone (**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 methylcyclopropanone were obtained from the thermolysis²⁶ of di-*n*-propylcyclopropanone. This reaction has been extended with very interesting results to cycloheptenocyclopropanone (**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,

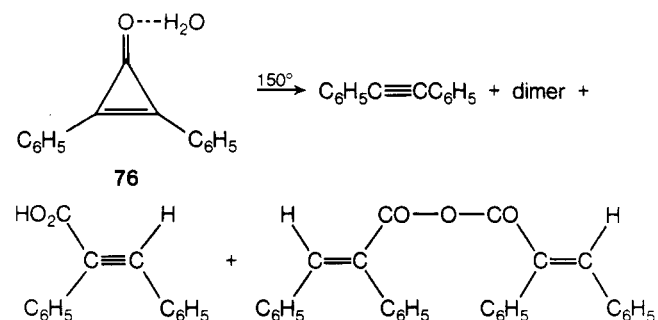


cycloundecenocyclopropanone (**74**) at 210° afforded³⁴ 95% of cycloundecyne (**75**). Only under reduced pres-



sure and at 320–327° did di-*tert*-butylcyclopropanone (**18**) undergo pyrolysis.⁶⁷ The products obtained were found to be di-*tert*-butylacetylene and carbon monoxide.

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 diphenylcyclopropanone⁸⁸ (**7**) and bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropanone⁷⁹ (**236**) gave the corresponding acetylenes in good yield, a behavior also noted for cyclopropanone itself.¹⁶³



The reaction of diphenylcyclopropanone (**7**) with nickel,^{18,89} iron,⁹⁰ and cobalt⁹⁰ 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

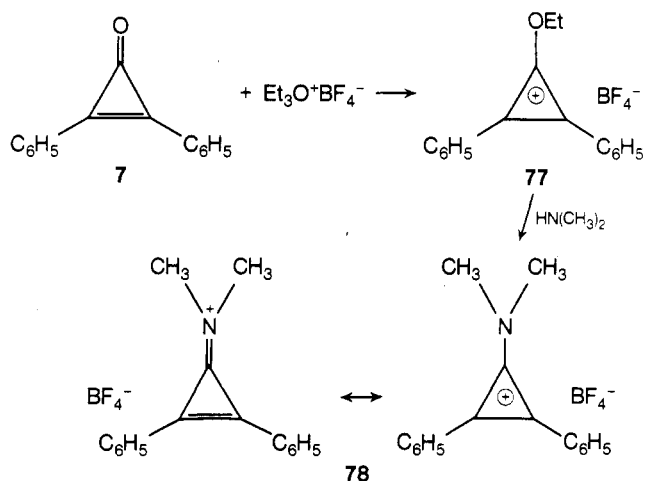
similarly with cyclopropanones to give decarbonylation products.⁹⁰

B. Addition Reactions

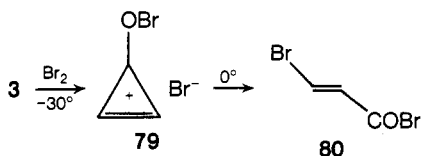
Addition reactions of cyclopropanones are numerous and quite varied for such a simple system. Electrophilic reagents attack the electron-rich carbonyl group and nucleophilic addition reactions occur at any carbon of the three-membered ring, a possible consequence of the delocalization of the partial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

1. Electrophilic Additions at the Carbonyl Group

The formation of hydroxycyclopropenylum salts (**14**) by protonation of the carbonyl group has been described above. Alkylation of **7** by triethyloxonium fluoroborate (Meerwein's reagent) produced ethoxydiphenylcyclopropenylum fluoroborate^{24,91} (**77**) which, with dimethylamine, was converted into the very stable 1,2-diphenyl-3-dimethylaminocyclopropenylum fluoroborate (**78**). Meerwein's reagent added¹⁶³ in a similar fashion to cyclopropanone (**3**).



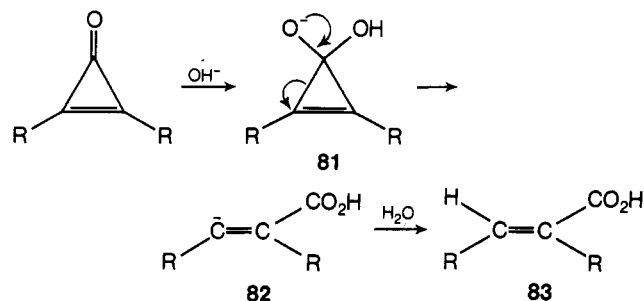
Bromine in CDCl_3 at -30° reacted¹⁶³ with cyclopropanone giving the corresponding bromide salt **79** which, on warming to 0° , was converted into *trans*- β -bromoacryloyl bromide (**80**). This reaction indicated that bromine, a so-called double bond reagent, reacted successively with the carbonyl group and with the single bond of cyclopropanone without addition to the double bond.¹⁶³



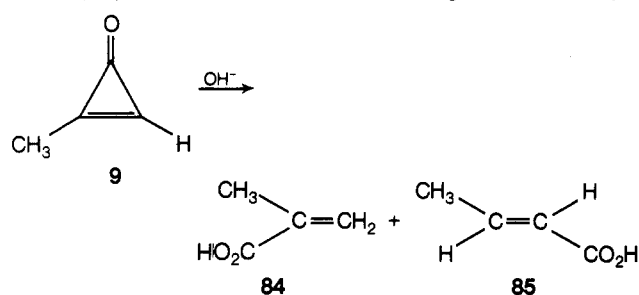
2. Nucleophilic Additions at the Carbonyl Group

Hydrolysis of cyclopropanones 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 cyclopropanone intermediates in the

Favorskii rearrangement.²⁵ Protonation of the anion **82** would complete the process.

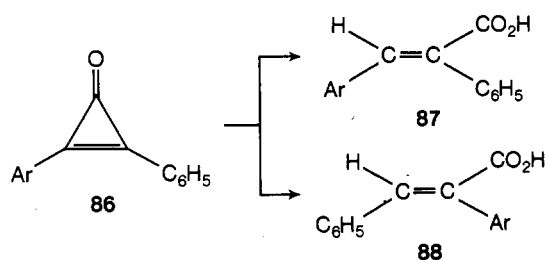


Dialkylcyclopropanones are more stable to base than diarylcyclopropanones,^{27,39} a property analogous to their thermal stability (section V.A). Diphenylcyclopropanone was 90% cleaved after 3 min at 31° in 0.1 *N* ethanolic sodium hydroxide solution, whereas di-*n*-propylcyclopropanone (**8**) was recovered completely unchanged after 1 hr under the same hydrolysis conditions. Analogous to the decarbonylation of cyclopropanones (section V.A), this difference may be attributed to the phenyl groups exerting a greater stabilization of the hydrolysis transition state.²⁷ Treatment of methylcyclopropanone (**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

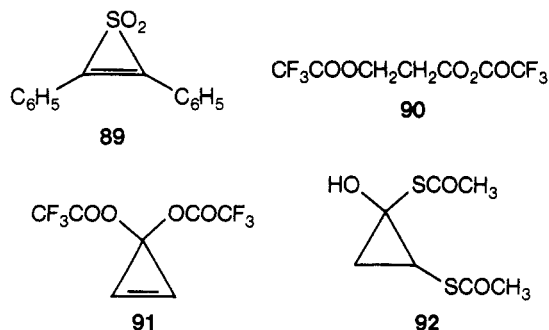


acid is consistent with the relative stabilities of the two possible intermediate carbanions. Thus the rate-controlling step in the base-catalyzed cleavage of cyclopropanones could be either the attack of OH^- forming **81** or subsequent formation of the carbanion **82**.

In examining the electronic and steric factors governing this cleavage, Bird⁶⁶ synthesized a series of arylphenylcyclopropanones (**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 $\log [\text{87}]/[\text{88}]$ 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.

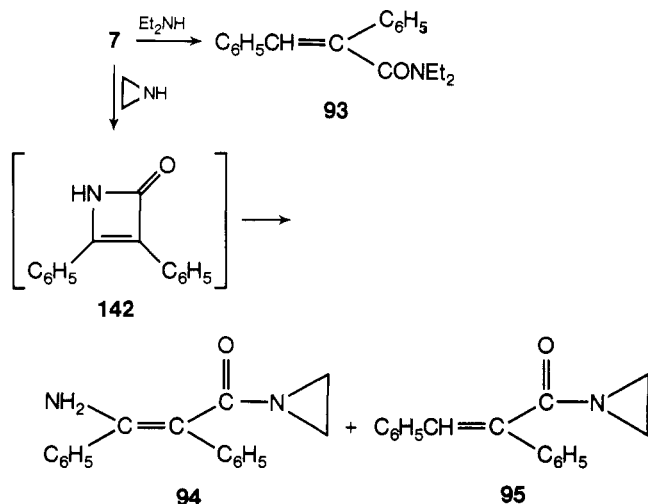


Comparison of the rates of cleavage by alkoxide ions of diphenylcyclopropanone (**7**) and diphenylthiirene 1,1-dioxide (**89**) showed **89** to be hydrolyzed 5000 times faster.¹⁴¹ This reversal of the rate of the usual base attack on a carbonyl group rather than on a sulfonyl group may be attributed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



In trifluoroacetic acid cyclopropanone 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 thioacetic acid a cyclopropane derivative **92** in which two thioacetic acid moieties have added across both the carbon-carbon double bond and the carbonyl group was formed.¹⁶³

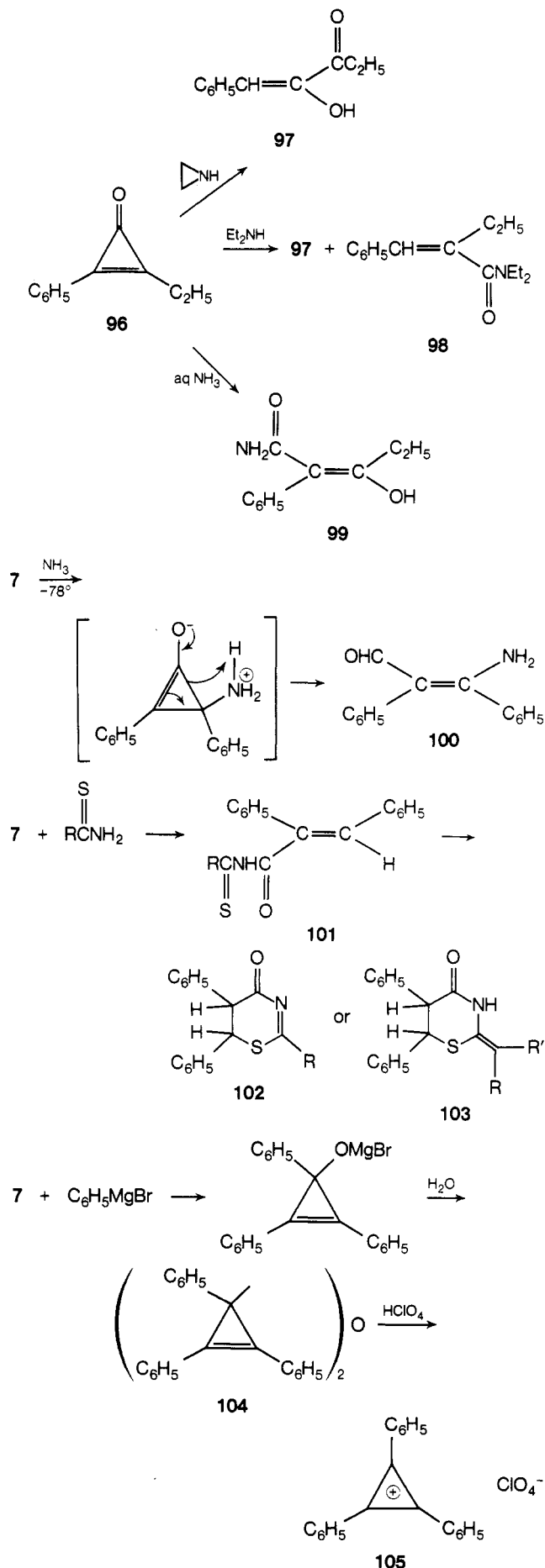
The action of nitrogen nucleophiles on the carbonyl group of cyclopropanones also led to ring-opened products. Addition of diethylamine to **7** gave **93** in good yield.⁹⁴ Similarly, 2 mol of aziridine reacted with **7** to form a ring-opened product **94**, presumably from an azetidione intermediate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



phenylcyclopropanone (**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

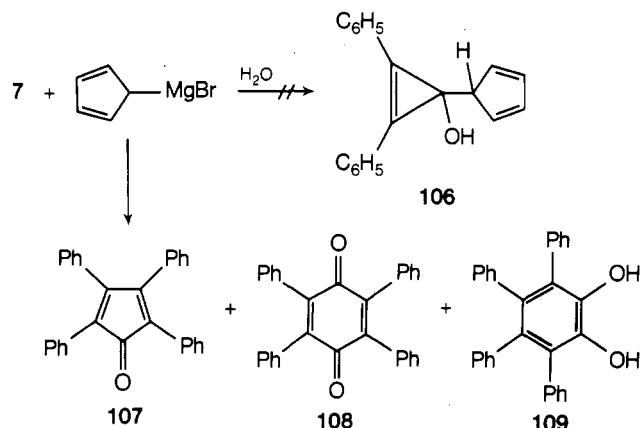
The reaction of thioamides with diphenylcyclopropanone (**7**) led to *N*-(2-phenylcinnamoyl)thioamides (**101**), which underwent further ring closure to form 1,3-thiazin-4-ones **102** or **103**,¹⁵³ depending on the availability of enolizable hydrogens.

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-

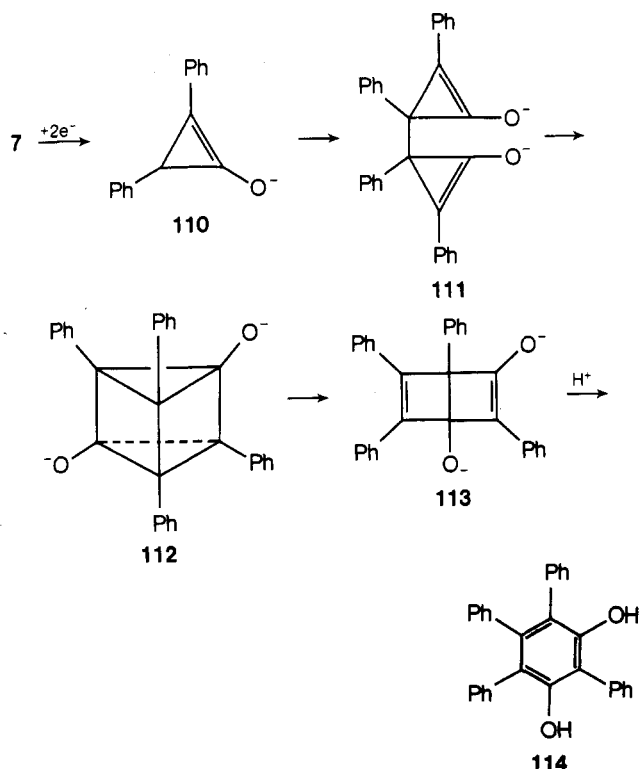


nesium bromide did not give the expected tertiary carbion **106** but resulted in the formation of tetraphenylcyclo-

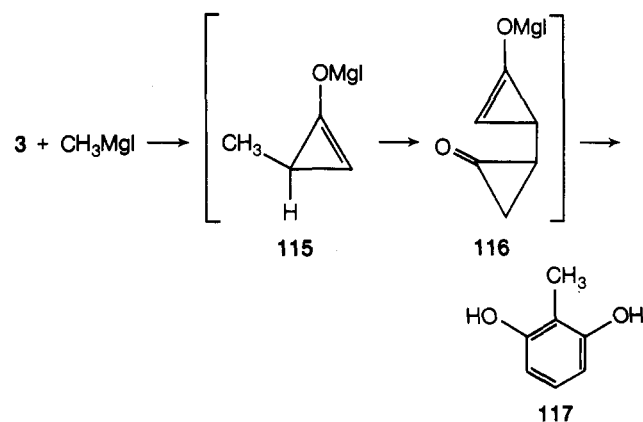
pentadienone (**107**), tetraphenyl-*p*-benzoquinone (**108**), and tetraphenylpyrocatechol (**109**) in 1, 2, and 8% yields, respectively.⁹⁶ The addition of a mixture of metallic mag-



nesium 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 reevaluated⁹⁷ 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. Cyclopropanone (**3**)

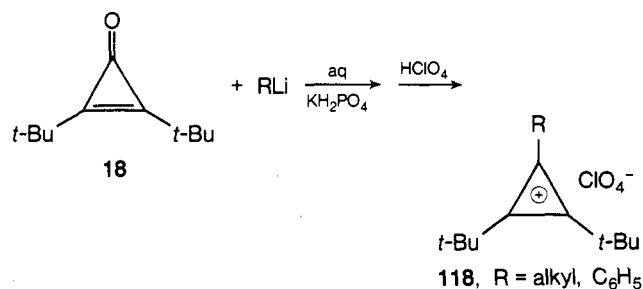


has been reported recently to react with methylmagnesium iodide to give 30–50% yields of 2-methylresorcinol (**117**), analogous products being obtained with other Grignard reagents.¹⁶⁴ As 2 equiv of cyclopropanone was used, it was suggested that conjugate addition gave an intermediate **115** which added to a second molecule of cyclopropanone giving **116** which then underwent subsequent cyclization and rearrangement to **117**. Polymeric materials only have been isolated from the reaction of

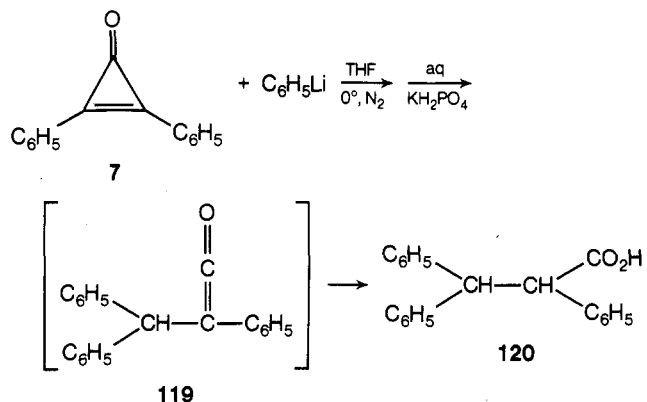


cyclopropanone with organolithium reagents, lithium dimethylcopper or lithium aluminum hydride.¹⁶⁴ A particularly interesting reaction is the conversion of cyclopropanone into hydroquinone with 1% sodium amalgam.¹⁶⁴

The addition of alkyl(or phenyl)lithium to di-*tert*-butylcyclopropanone (**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

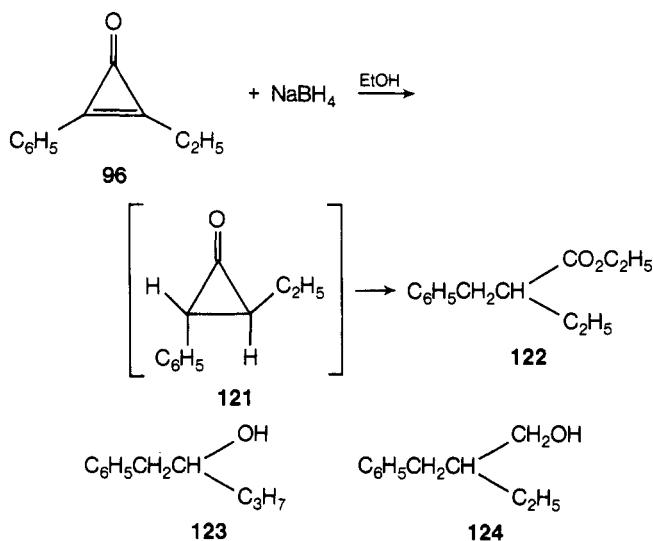


phenyllithium to **7** gave, after hydrolysis, an 18% yield of a product represented by structure **120**. The proposed ketene intermediate **119** was detected spectroscopically at -70° .⁹⁹ This reaction thus appears to occur across the carbon-carbon bond.



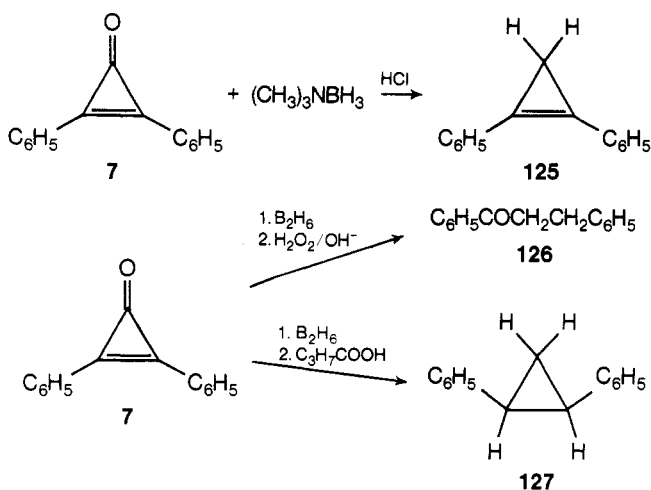
Lithium aluminum hydride (ca. -20 or -70°) or H_2/Pt in cold alcohol reduced both the carbonyl group and the double bond to give 1,2-diphenylcyclopropan-3-ol.^{21,23} The ease of reduction of not only the carbonyl group but also the double bond of diphenylcyclopropanone by lithium aluminum hydride was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

Reduction of ethylphenylcyclopropanone (**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.



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

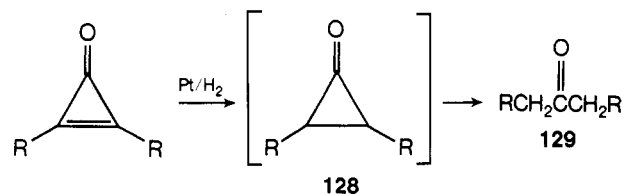
The reaction of **7** with diborane was studied with reaction work-up under both oxidizing and reducing conditions.¹⁶¹ Hydroboration of **7** with excess diborane and oxidation with $\text{H}_2\text{O}_2/\text{OH}^-$ gave, as the main product, benzylacetophenone (**126**) in 55–65% yield. The hydroboration 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.



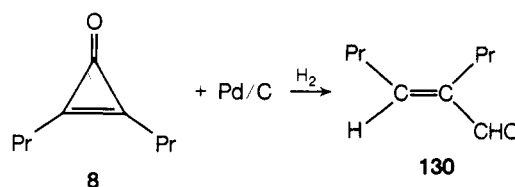
Polarographic reduction of **7** gave a polarogram with two waves resulting from both the reduction of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ functions. The half-wave potentials were $E_{1/2} = -1.91$ and -1.56 V, respectively,⁹⁸ and no conclusion could be reached regarding the order of the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

3. Additions at the Carbon-Carbon Double Bond

Catalytic hydrogenation (Pt/H_2) at room temperature of cyclopropanone¹⁵⁶ (**3**) and diphenyl-²⁴ (**7**), di-*n*-propyl,³⁴ (**8**), and di-*tert*-butylcyclopropanone⁶⁷ (**18**) gave, after consumption of 2 mol of hydrogen, the corresponding di-substituted ketones **129**. The postulated cyclopropanone intermediate, **128**, however, eluded spectroscopic detection and probably underwent reduction and ring fission faster than the cyclopropanone itself.²⁴ Palladium-on-carbon hydrogenation of the di-*n*-propyl derivative (**8**) gave

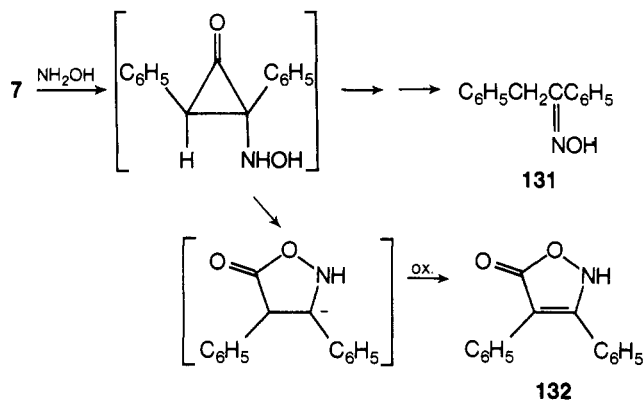


2-propyl-2-hexenal (**130**), a product accountable in terms of the addition of 1 mol of hydrogen across the $-\text{C}=\text{CO}-$

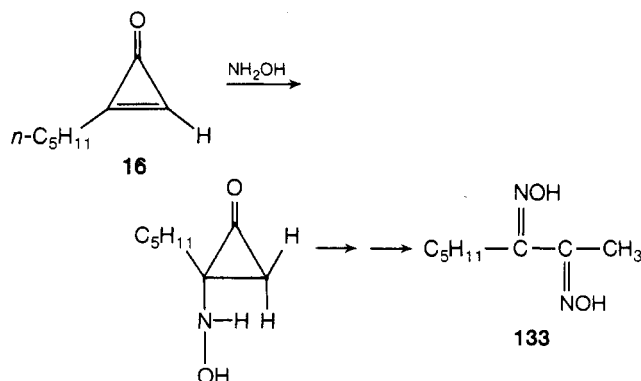


bond³⁴ and subsequent ring opening. Differentiation between these two reduction pathways was not possible since both procedures afforded minor reduction products. The addition of hydrogen in the presence of Pd/C to *n*-pentylcyclopropanone (**16**) gave *n*-hexyl methyl ketone as the major product.⁵⁷

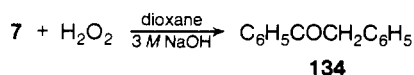
The reaction of **7** with hydroxylamine yielded 3,4-diphenylisoxazolone (**132**) and desoxybenzoin oxime (**131**).



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*-Pentylcyclopropanone (**16**) gave a good yield of *n*-pentylmethylgloxime (**133**) by an equally tentative mechanism.⁵⁷



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

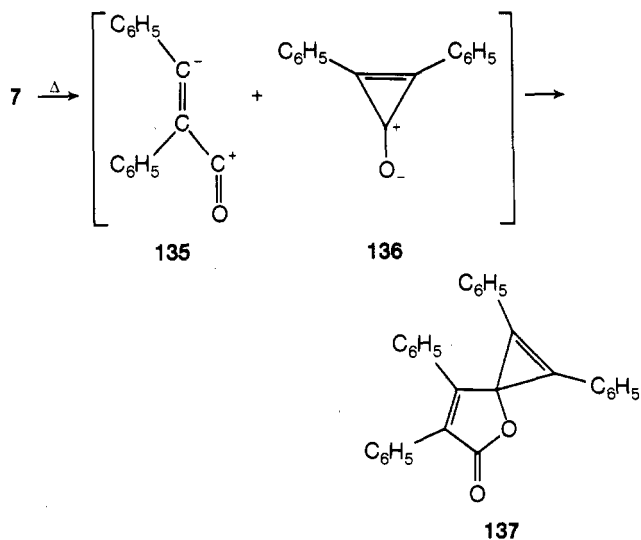


4. Cycloadditions of Cyclopropenones

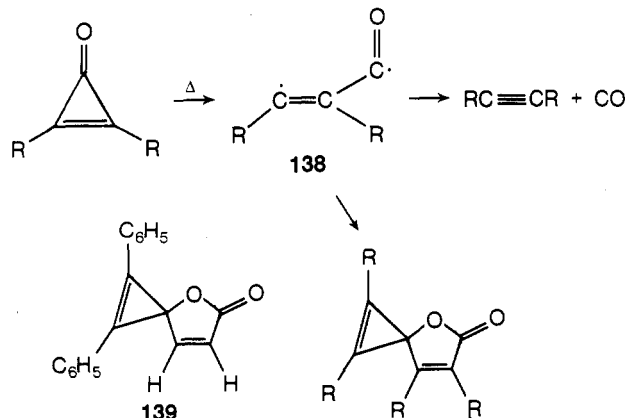
The most recent chemistry of cyclopropenones involves the utilization of these compounds in cycloaddition reactions with a wide variety of substrates. These additions have been found to occur across the C=O, C=C, or the 2-3 (C-CO) bond of the cyclopropenone ring.

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 spiro lactone structure (**137**), possibly formed via a [2 + 3] cycloaddition of the intermediates⁴⁹ **135** and **136**. Alternatively dimerization of the radical interme-

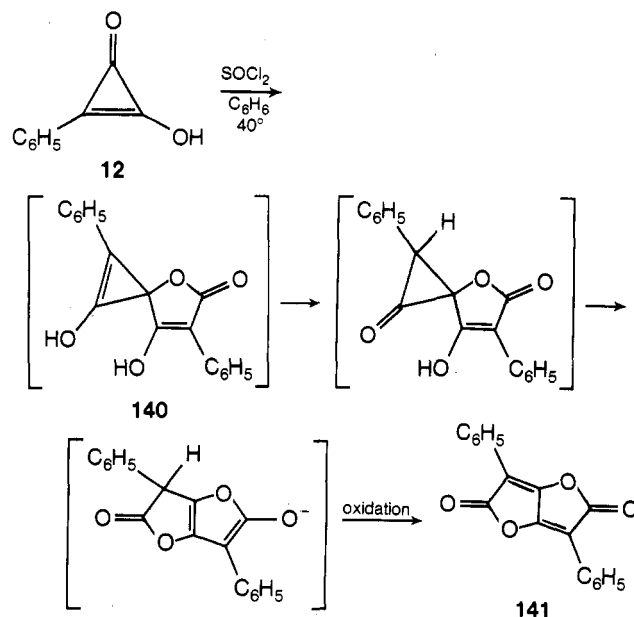


diate **138**, which also may be the precursor to the accompanying acetylene and which could undergo reaction with any suitable trapping agent, has been suggested³² as a possible pathway. The dimer **137** was stable under these thermolysis conditions and thus could not be considered a precursor to the acetylene.²⁴ Analogous dimeric cyclopropenones have also been obtained from methylcyclopropenone^{26,29} (**9**), dichlorocyclopropenone⁵⁹ (**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



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

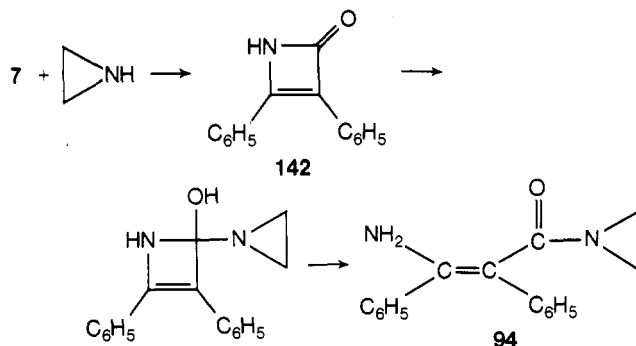
Phenylhydroxycyclopropenone (**12**), which appeared to be an associated dimer in dioxane,⁷⁵ formed a dimeric pulvinic acid lactone (**141**) via oxidation of the dimer **140** which was isolated from the reaction of **12** with thionyl



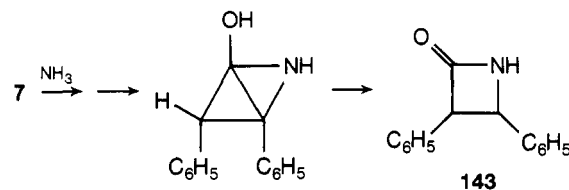
chloride.³⁰ The methyl ether of **12** on pyrolysis also gave a dimer³⁰ analogous to the dimer **137**, formed from the pyrolysis of diphenylcyclopropenone (**7**).²⁴

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 diphenylcyclopropanone and aziridine. It

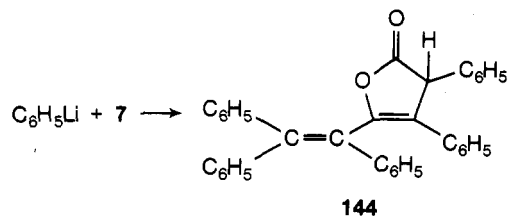


is presumably formed by insertion of nitrene into the 2-3 bond of diphenylcyclopropanone.⁹⁴ The saturated azetidione **143** has been isolated in the ring expansion of **7** with ammonia at room temperature.¹⁰⁴



c. Reaction via a Ketene Intermediate

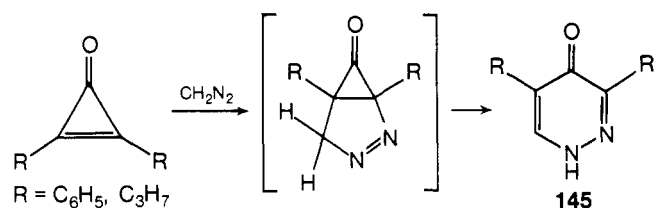
The inverse addition of phenyllithium to diphenylcyclopropanone (**7**) gave an adduct **144**, possibly formed by



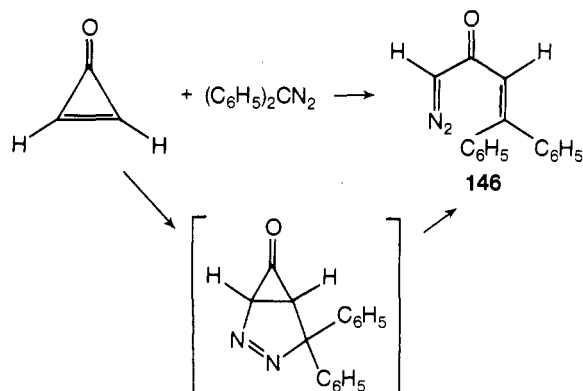
the addition of a second mole of **7** to an intermediate primary adduct.⁹⁹ This reaction pathway should be contrasted with that previously described for phenyllithium.

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 cyclopropanones to give, after rearrangement of the cyclopropanone intermediate, 3,5-disubstituted 4-pyridazines^{24,105} (**145**). These were formed even when the cyclopropanone was coordinated with a Lewis acid.²⁴



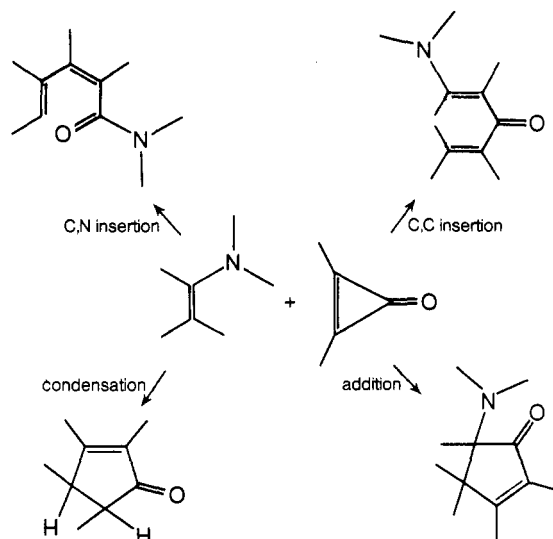
Similarly, cyclopropanone (**3**) reacted with diphenyldiazomethane, resulting in formation of the diazo ketone **146**, in 28% yield.¹⁵⁶ Benzyldiazomethane gave an analogous product.¹⁶⁴



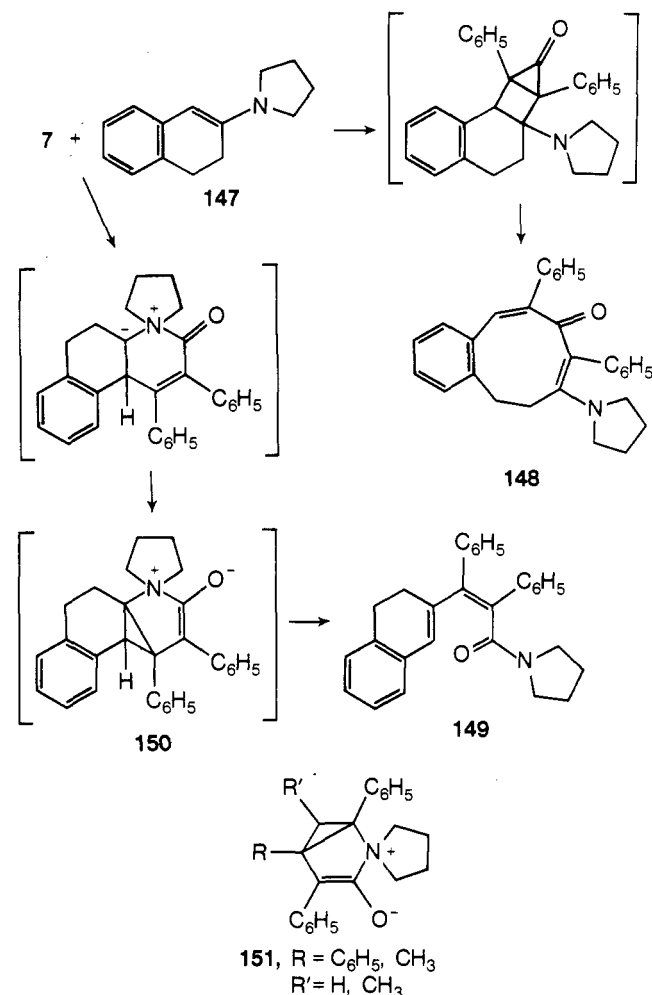
ii. *Enamines and Ynamines.* The outcome of the reactions of cyclopropanones with enamines has attracted much interest in the recent literature. A reinterpretation of the results obtained by Ciabattini and Berchtold^{102,106} and those by Sauer and Krapf¹⁰⁷ involving the reactions of various enamines with diphenylcyclopropanone or its thione derivative, has been advanced in a series of articles¹⁶⁵⁻¹⁶⁸ 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 cyclopropanone 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 (**7**) 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 reinterpretation¹⁶⁶ 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 pyrrolidiny enam-

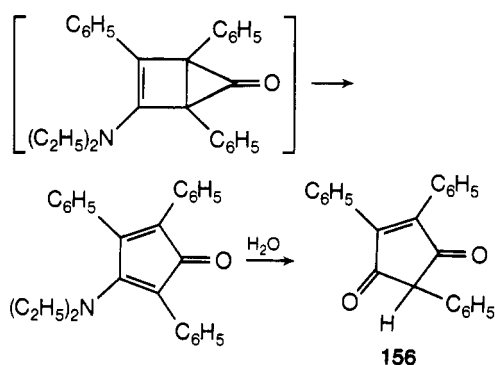
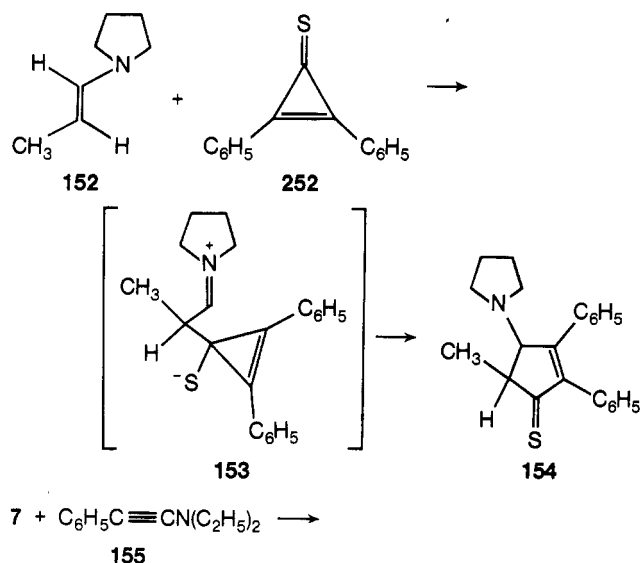
SCHEME I



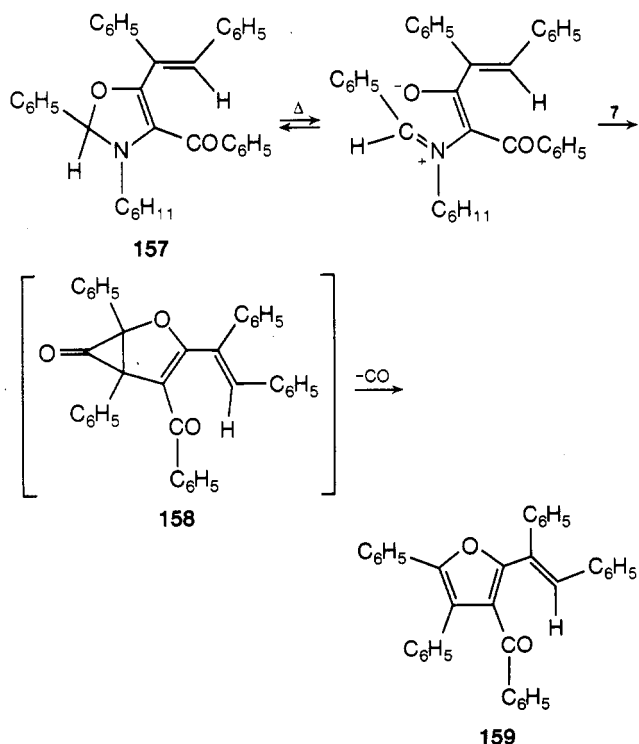
ines and cyclopropanones were reported to have been isolated.¹⁶⁹



Diphenylcyclopropanethione (**252**) and 1-(*N*-pyrrolidino)prop-1-ene (**152**) gave¹²¹ 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**. Diphenylcyclopropanone (**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

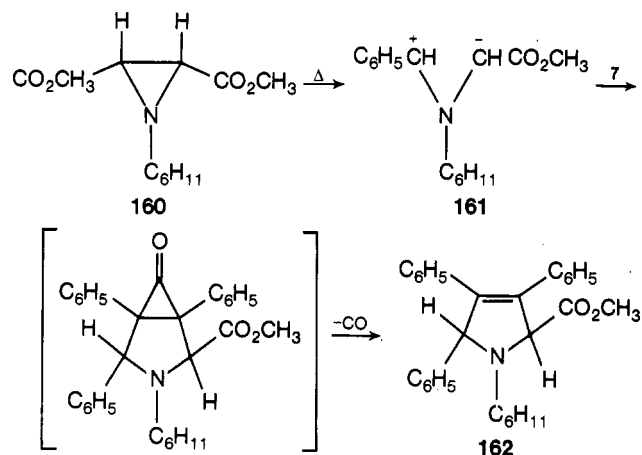


iii. Δ^4 -Oxazolines. Δ^4 -Oxazolines 157, isolated from cycloadditions of 7¹¹¹ (see cycloadditions to C=O), reacted with 7 across the C=C of the cyclopropenone ring with subsequent loss of carbon monoxide from the initial adduct 158 to give¹⁰⁹ the substituted furan 159.

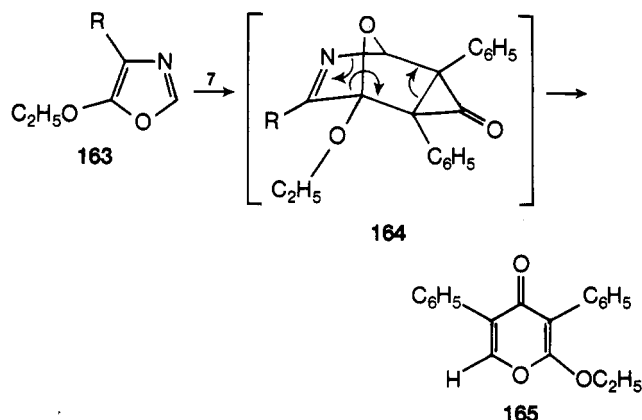


iv. Aziridines. 3-Carbomethoxy-1-cyclohexyl-2-phenylaziridine (160) reacted with 7 to give¹¹⁴ the *trans*-3-pyrro-

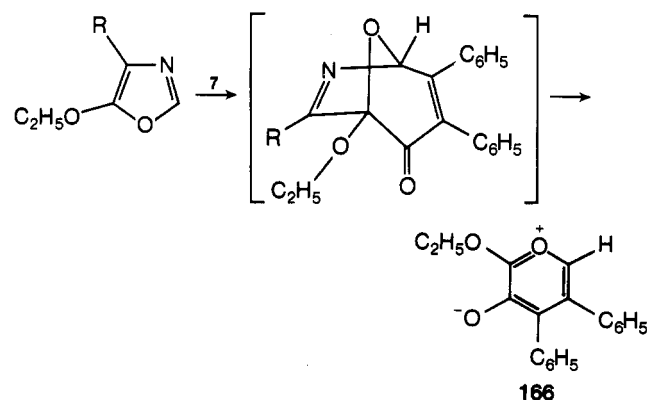
line 162. The reaction was rationalized as a [2 + 3] cycloaddition of the azomethine ylide 161 to the C=C bond of 7, followed by decarbonylation.¹¹⁴



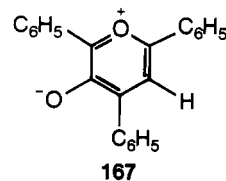
v. Oxazoles. The oxazoles 163 (R = H or CH₃) on heating with 7 gave none of the 1:1 adduct 164 but formed the γ -pyrone 165 by irreversible elimination of hydrogen cyanide or acetonitrile from the initial cycloadduct 164. If addition across the C-CO bond had occurred,



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 betaine¹⁴² 167

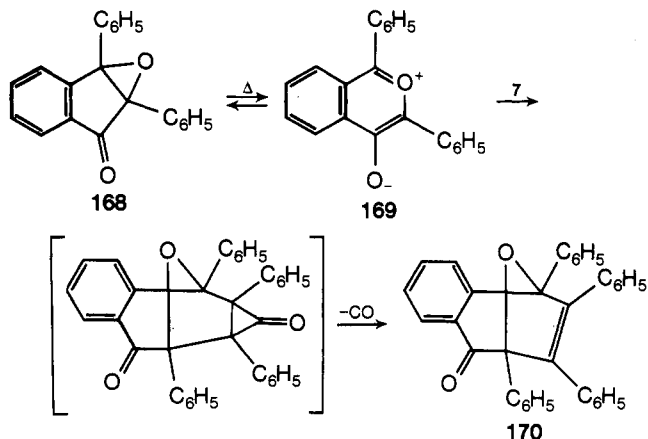


is deep red, whereas 165 was reported as colorless. The chemical shift of the 6-H in the pyrone 165 at δ 7.65

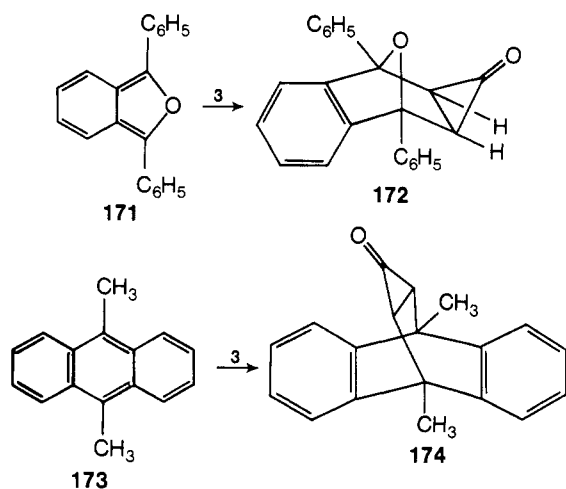


might suggest the aromatic structure **166**, but inspection of the literature¹⁵¹ shows that the 6-H proton in 4H-pyran-4-one compounds does indeed resonate in this chemical shift region.

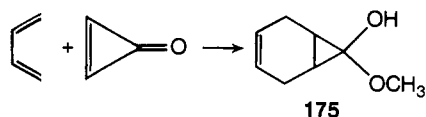
vi. Heteroaromatic Betaines. The reaction of 2,3-diphenylindenone oxide (**168**) with diphenylcyclopropenone (**7**) afforded¹⁴⁹ the adduct **170**. The cycloadduct was formed presumably from 1,3-cycloaddition across the carbon-carbon double bond of **7** with **168**, the latter reacting via its thermally 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



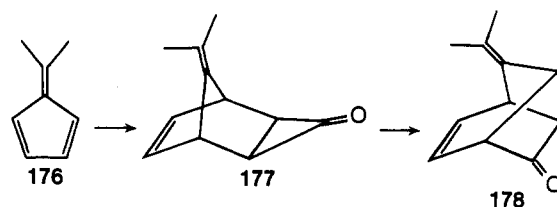
vii. Diene Systems. In contrast to diphenylcyclopropenone, cyclopropenone itself has given two stable 1:1 adducts where addition has occurred across the C=C with 1,3-diphenylisobenzofuran (**171**) and 9,10-dimethylanthracene (**173**). These products, represented by **172** and **174**, are unique in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



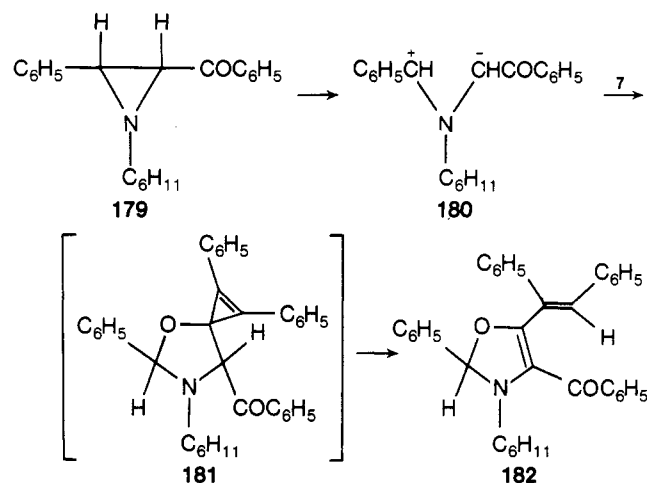
Cyclopropenone has also been found to react readily with tetracyclone, the complex reaction products depending on the solvent used. It also reacted with butadiene in methanol affording the hemiketal **175**, and with 6,6-di-



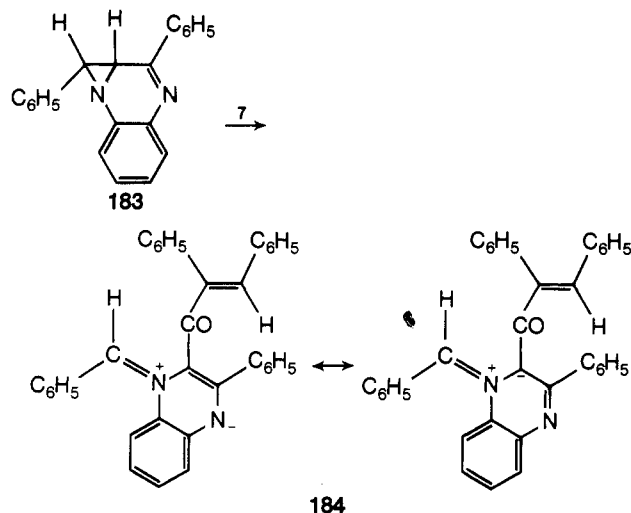
methylfulvene (**176**) the tetracyclic product **178** was formed,¹⁶⁴ presumably via the initial 1:1 adduct **177**.



(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-aryloxy-4-oxazoline **182** by rearrangement of the initial 1:1



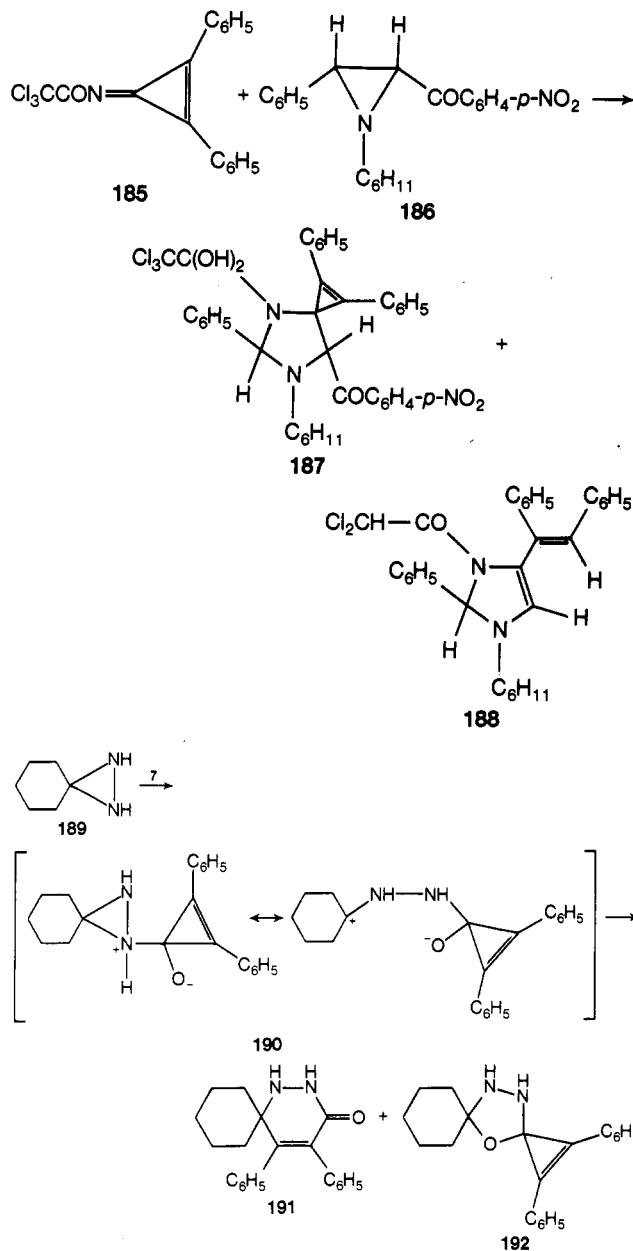
adduct **181**. The tricyclic aziridine **183** and **7** reacted similarly to give the zwitterionic ylide¹¹¹ **184**.



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 H₂O analogous to the intermediate **181** proposed above, and **188**. The latter was postulated to arise from the base-catalyzed elimination of the aryl group of **187**.¹¹²

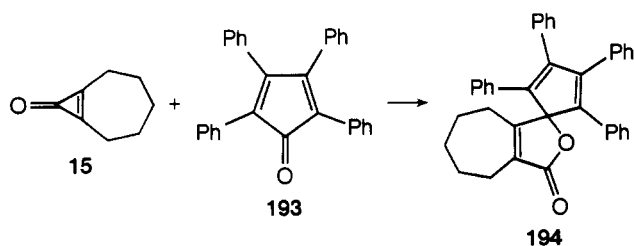
The addition of 3,3-pentamethylenediaziridine (**189**) to **7** gave a mixture of two isomeric 1:1 adducts. These have been described as **192**, a rearranged product, and **191**, both of which readily separated from the reaction mixture.¹¹³ These products are mechanistically available from the common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

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



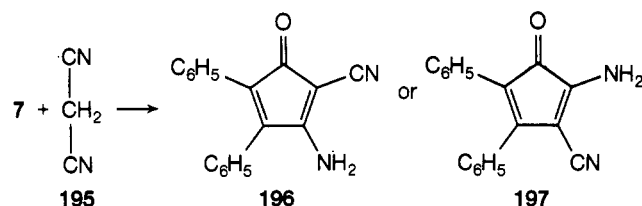
tained the cyclopropenone moiety as a ring-opened structure with newly formed bonds to carbons 2 and 3 of the original ring, it is most likely that the products originated from either an initial nucleophilic attack at the carbon atom or by a Michael-type addition to the C=C bond. This would then be followed 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 isolated³⁴ from the pyrolysis of cycloheptenocyclopropenone (**15**) in the presence of tetracyclone (**193**). The formation of a product of this structure may be ra-

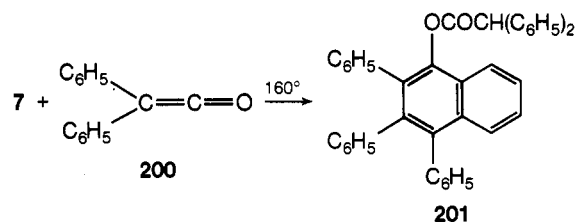
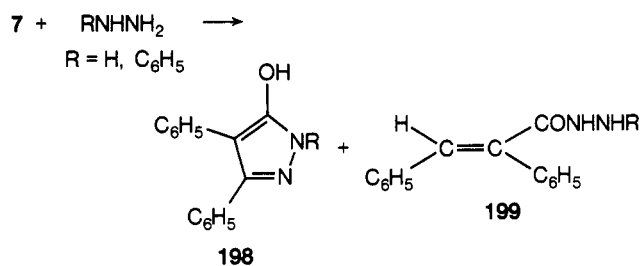


tionized most reasonably in terms of an initial addition across the C-CO bond.

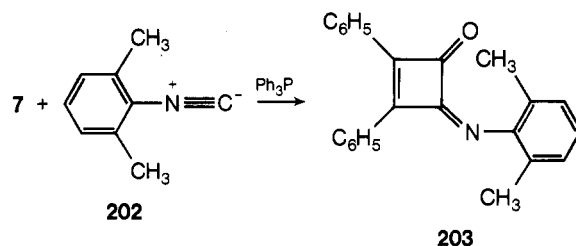
Similarly, in the reaction of diphenylcyclopropenone (**7**) with malononitrile (**195**) seven products were obtained, one of which was tentatively assigned⁹⁵ structure **196** or its isomer **197**.



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-dimethyl-

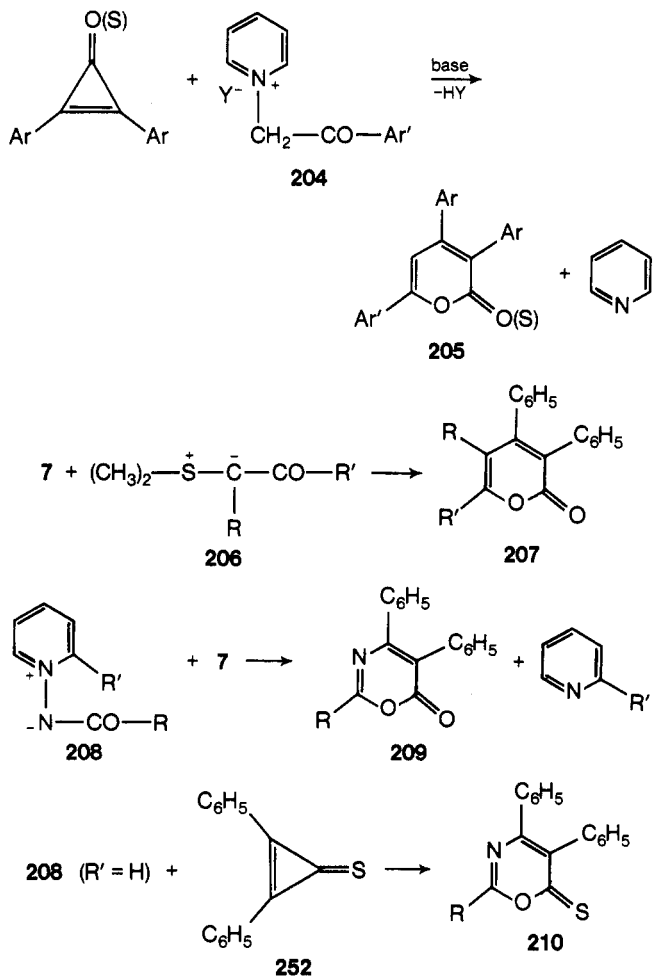


phenyl isocyanide (**202**) reacted with **7** through a bisketenone intermediate¹¹⁶ (section V.B.4.e), the same reaction in the presence of triphenylphosphine gave a 1:1 adduct **203** across the C-CO bond of the cyclopropenone.¹¹⁷

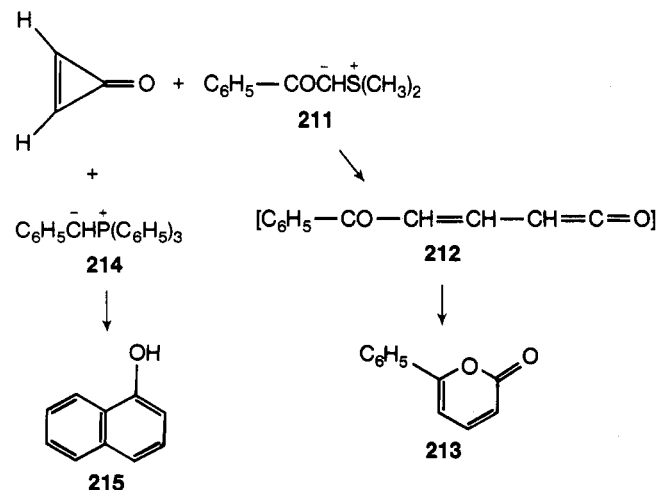


ii. Heteroaromatic Betaines and Ylides. Pyridinium betaines **204** were shown to undergo cycloaddition with diphenylcyclopropenone or its thione derivative. Either an initial attack on the carbonyl group of **7** by the betaine oxygen atom or a Michael addition of the methylene anion to the C=C bond of **7**, followed by isomerization, may account for the formation of the 3,4,6-triaryl-2-pyrone¹¹⁸ (**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** reacted¹¹⁹ similarly with **7** to give the corresponding 1,3-oxazine derivatives **209**. Diphenylcyclopropenethione (**252**) also underwent cyclization with the pyridinium im-

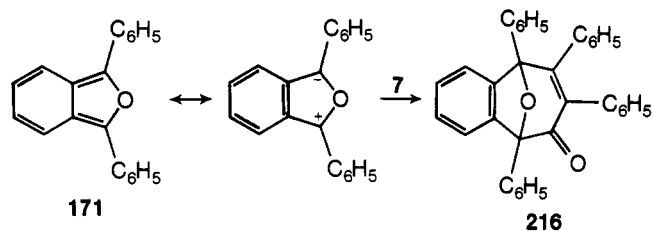
ines, **208**, with formation¹⁵⁹ of analogous 6*H*-1,3-oxazine-6-thiones **210**. The compound **210** ($R = C_6H_5$) could be converted into **209** ($R = C_6H_5$), by reaction with *m*-chloroperbenzoic acid. Mechanistic pathways considered for the formation of **205** also apply above. It is unlikely 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



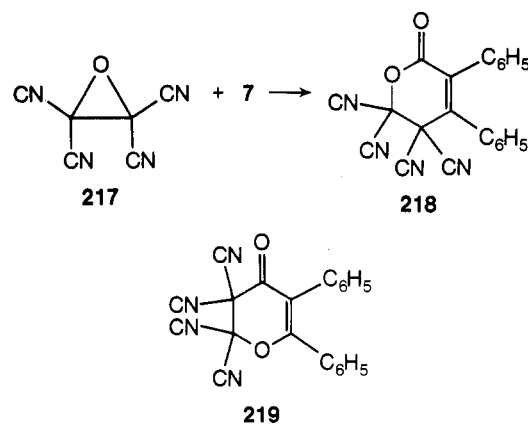
Cyclopropenone and the sulfur ylide **211** were found to give 6-phenyl-2-pyrynone (**213**) at -78° in CH_2Cl_2 . The ketene **212** was suggested as an intermediate in this reaction.¹⁶³ With benzylidene triphenylphosphorane (**214**), a similar ketene intermediate was postulated to explain the formation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



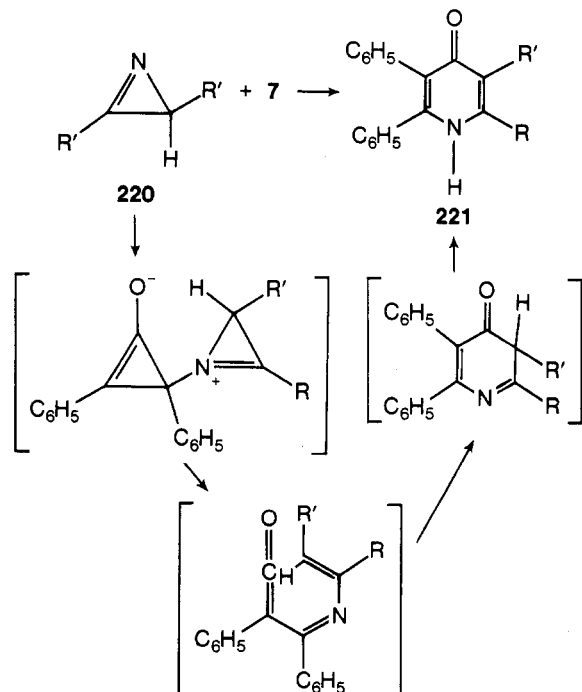
1,3-Diphenylisobenzofuran (**171**) may, to some extent, be regarded as a potential 1,3 dipole of the carbonyl ylide type, and it was found¹¹⁴ to react with **7** to give a [2 + 3] cycloadduct, **216**, across the C-CO bond of **7**, in contrast to the reaction of cyclopropenone (**3**) and **171** described previously (section V.B.4.d.(1).vii).



Tetracyanoethylene oxide (**217**) and **7** reacted readily¹⁶⁰ 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.



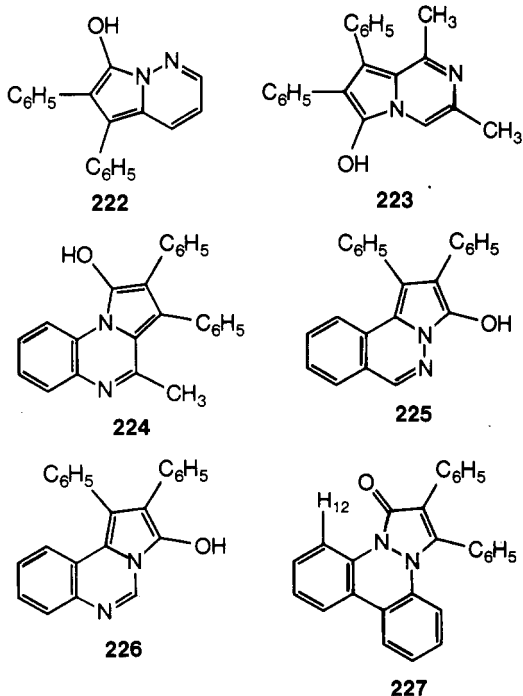
1-Azirines, **220**, reacted with **7** to produce 1:1 adducts shown to be 2,3-diphenyl-4-pyridones, **221**.¹⁶² The 4-pyridones, **221**, may be postulated as arising from initial nucleophilic attack of the weakly basic azirine nitrogen on the electrophilic cyclopropenone ring, followed by an intramolecular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



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

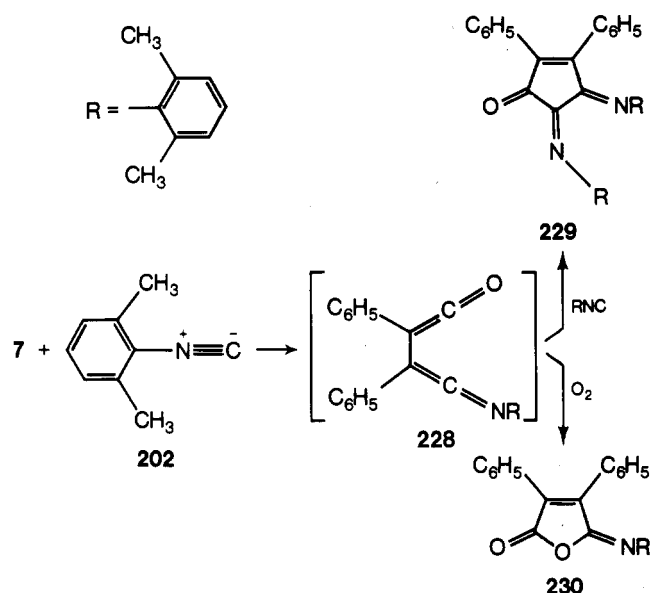
penones with heteroaromatic nitrogen compounds,¹²⁰ three types of cycloadducts were obtained. The first, 2:1 adducts, are described in the following section. The second, 1:1 adducts, were formed from an initial attack by an aza nitrogen on the carbonyl group of diphenylcyclopropanone (7), followed by 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.

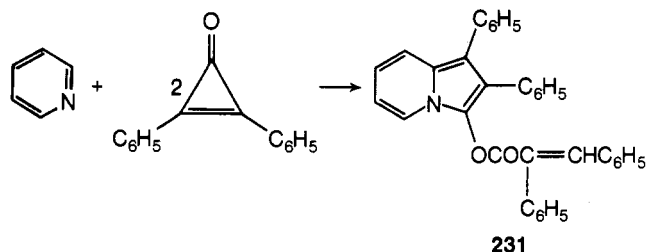


iv. 2:1 Cycloadducts. The reaction of 7 with 2,6-dimethylphenyl isocyanide (**202**) gave the ring-expanded products, 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenyl-2-cyclopenten-1-one (**229**) and a trace amount of *N*-(2,6-dimethylphenyl)diphenylisomaleimide (**230**). These

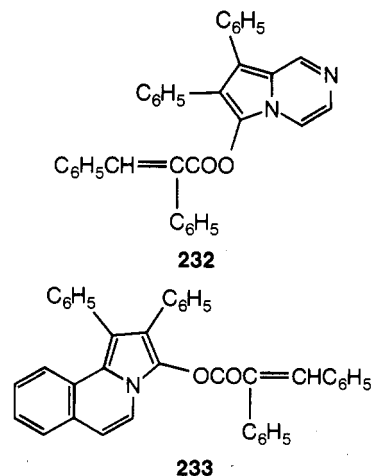
were formed¹¹⁶ presumably *via* a primary ring-opened intermediate **228** resulting from a Michael addition of the isocyanide to 7.



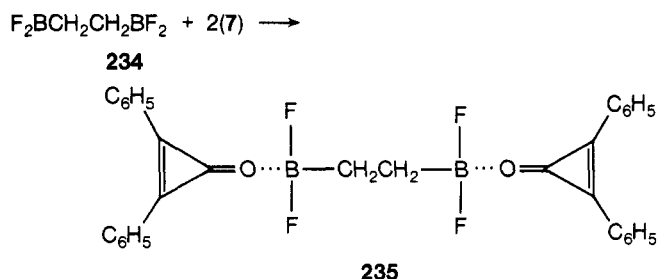
Diphenylcyclopropanone (7) reacted^{24,95} with pyridine with 2 mol of 7 being incorporated into the final product which has now been shown¹²⁰ to be the 2:1 adduct **231**, the first type of cycloadduct mentioned in the previous sections on heteroaromatic nitrogen compounds. Other



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



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



5. Metal Complexes with Cyclopropanones

The formation of organometallic complexes from cyclopropanones and various metals has been examined (ref 18, 89, 90, 123, 124) extensively. The interaction of tetracarbonylnickel, $\text{Ni}(\text{CO})_4$, with diphenylcyclopropanone (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 $\text{C}=\text{C}$ coordination had occurred. However, recent studies of the infrared spectra of cyclopropanones (section III.C.1), and the synthesis of a series of complexes¹²³ of 7 with $\text{Zn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Ru}(\text{III})$, $\text{Pt}(\text{II})$, and $\text{Pt}(\text{IV})$ and $\text{Pt}(\text{II})$ 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 Cyclopropanones

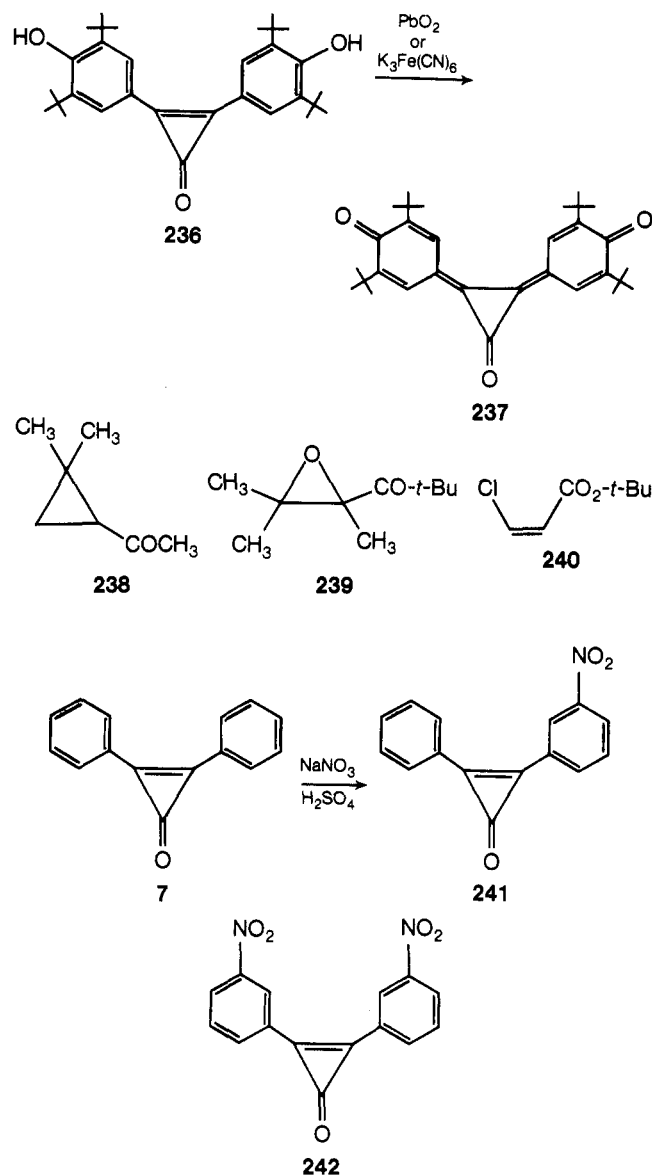
Two oxidations of cyclopropanones have been reported recently in the literature, and interesting products have been described. Treatment of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropanone (236) with lead dioxide or aqueous, basic potassium ferricyanide gave an intense purple, unstable solution (benzene, λ_{max} 542) from which 237 was isolated as a purple solid.⁷⁹ The peracid oxidation of di-*tert*-butylcyclopropanone (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 cyclopropanone to *cis*-*tert*-butyl β -chloroacrylate (240). Some of the *trans* isomer was also observed¹⁶³ but was thought to be the result of isomerization of 240.

D. Substitution Reactions

1. Nitration

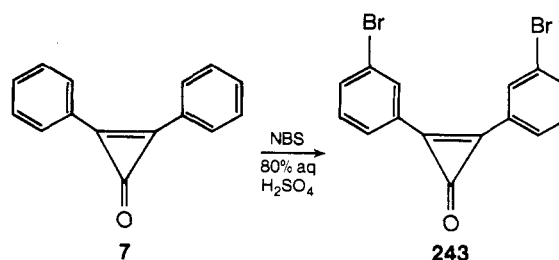
The failure⁷² of nitrobenzylidene chlorides to form the nitro-substituted phenylcyclopropanones isolated from reaction between the appropriate acetylene and phenyl-(bromodichloromethyl)mercury (33) (section IV.A.2) led to the direct nitration of 7 as an alternative route.¹⁵⁷

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 dinitrodiphenylcyclopropanone (242) tentatively assigned as the 3,3' isomer.



2. Bromination

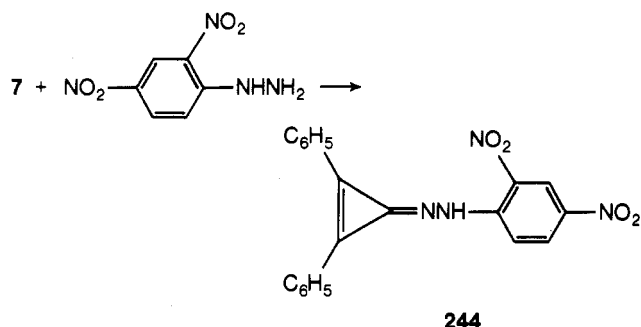
Failure to obtain the desired orientation of bromo substituents in the synthesis of a cyclopropanone was overcome by the bromination of 7 using *N*-bromosuccinimide. Whereas Tobey and West⁷⁸ obtained para-substituted diarylcyclopropanones from the electrophilic substitution of aromatic compounds by trichlorocyclopropenylium salts (section IV.A.3), treatment of a solution of 7 in 80% aqueous sulfuric acid with 2 molar equiv of *N*-bromosuccinimide gave¹⁵⁸ bis(*m*-bromophenyl)cyclopropanone (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.



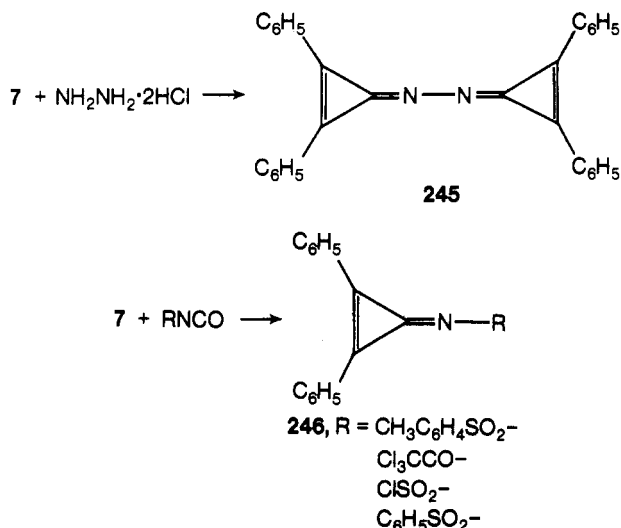
VI. Derivatives of Cyclopropenones

A. Iminocyclopropenones

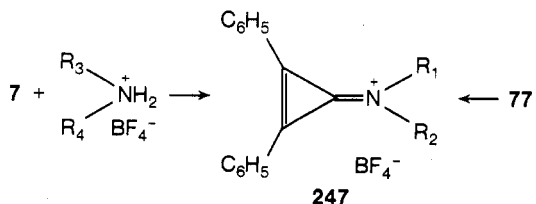
The formation of a 2,4-dinitrophenylhydrazone, **244**, from **7** has been reported,²¹ but it has not been possible



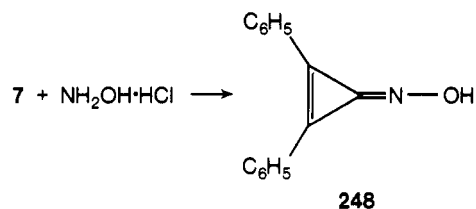
to duplicate this work.²⁴ Reaction in concentrated sulfuric acid-absolute ethanol mixture, or in diglyme, was reported⁹⁵ to have yielded **244**. Reaction of the ketone **7** and tosylhydrazine gave the tosylhydrazone.¹²⁷ Although anhydrous hydrazine gave⁹⁵ both the ring-opened product **199** and the cyclic product **198**, reaction of **7** with hydrazine dihydrochloride formed¹²⁷ 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 CO₂.



Addition of N-nucleophiles to **7** led to the protonated imines **247** (R₁ = H), which are easily converted into **246** with strong base.⁹¹ Treatment of **7** with NH₄BF₄ gave a series of these cyclopropenylideneammonium salts (**247**), alternatively prepared from the ethyloxonium fluoroborate salt (**77**) and secondary amines.⁸⁴ It is inter-

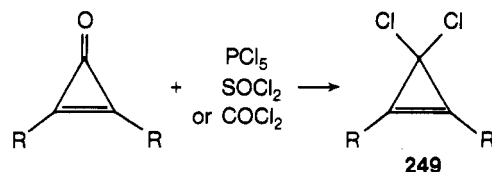


esting to recall that whereas hydroxylamine gave an oxime **131** and a cyclic oxidation product **132** in the reaction with **7**, hydroxylamine hydrochloride has been reported¹²⁹ to give the simple oxime **248**.



B. 3,3-Dichlorocyclopropenes

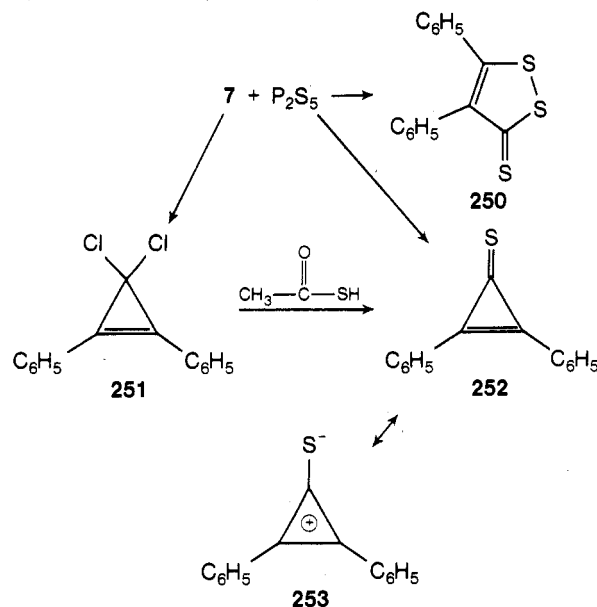
The reconversion of cyclopropenones into their precursors, 3,3-dichlorocyclopropenes (**249**), may be accomplished with phosphorus pentachloride,¹²⁹ thionyl chloride,⁷⁸ or phosgene.^{91,130} Cycloaddition reactions of



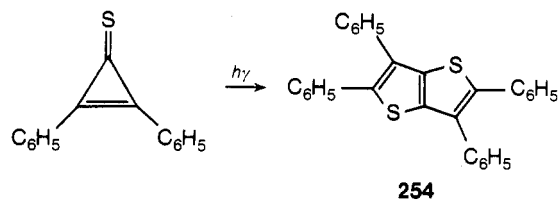
chlorocyclopropenes have been reported but the geminal dichlorocyclopropene was shown to be unreactive.¹⁵⁰

C. Diphenylcyclopropenethione

Conflicting results have been obtained in the addition of P₂S₅ to **7**. 4,5-Diphenyltrithione (**250**) was reported as being isolated¹³¹ 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



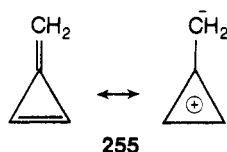
but recent X-ray studies show that the delocalized structure **253** is not supported by these data.¹⁷¹ Whereas diphenylcyclopropenone (**7**) underwent decarbonylation upon photolysis (section V.A), photodimerization of diphenylcyclopropenethione was observed upon irradiation in benzene, affording 2,3,5,6-tetraphenylthieno[3,2-*b*]thiophene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



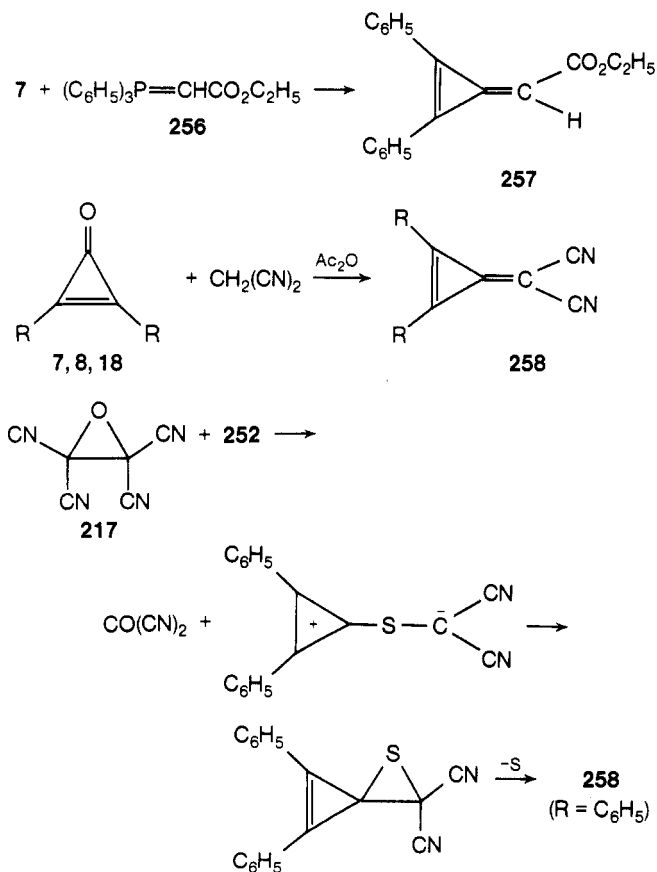
However, in ethanol over 24 hr using a high-pressure Hg lamp, carbon monosulfide was eliminated, giving diphenylacetylene in 50% yield.¹⁵⁵

D. Trifulvenes (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} dipropylcyclopropenone¹⁴⁰ (**8**), and di-*tert*-butylcyclopropenone¹³⁴ (**18**) with malononitrile also yielded the corresponding 1,1-dicyanomethylenecyclopropenes (**258**). The best method¹⁶⁰ for preparing 1,1-dicyanomethylenecyclopropene **258** (R = C₆H₅) was from the reaction of diphenylcyclopropenethione (**252**)



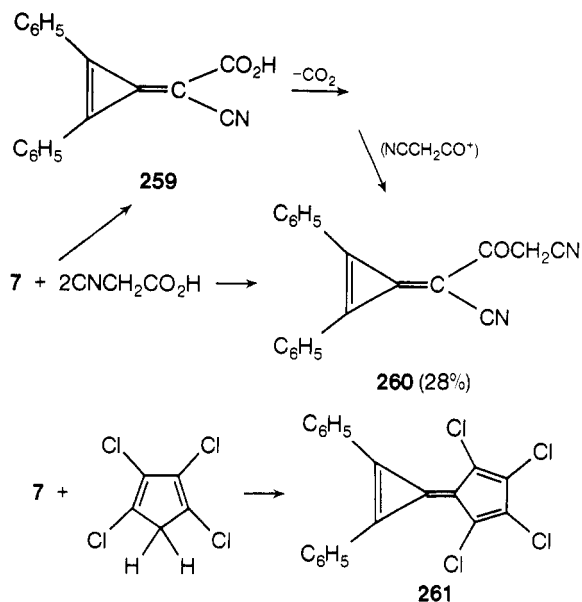
and tetracyanoethylene oxide (**217**). The reaction possibly proceeded by the scheme outlined above in superior yields (67%).



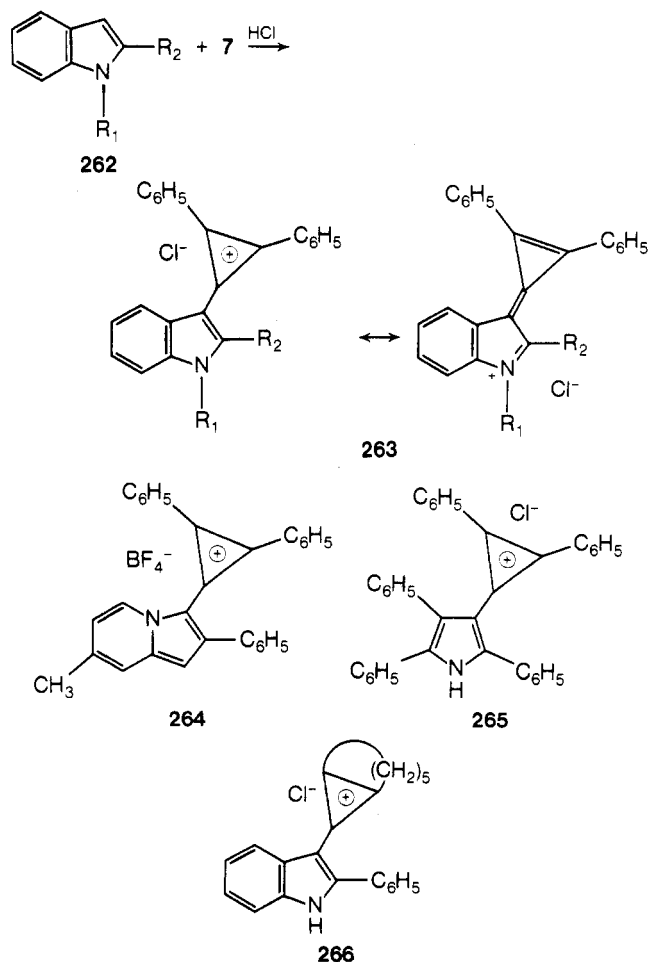
and tetracyanoethylene oxide (**217**). The reaction possibly proceeded by the scheme outlined above in superior yields (67%).

Cyanoacetic acid and **7** gave¹³⁵ 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 electro-

philic attack by NC=CH₂CO⁺, would yield **260**. Tetrachlorocyclopentadiene condensed¹⁰² with **7** to produce **261**.



Heterofulvenes were synthesized from the condensation of **7** with various heterocyclic nitrogen compounds.^{136,137} The azapentatriafulvenium 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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