

Cyclopropanones

NICHOLAS J. TURRO¹

Department of Chemistry, Columbia University, New York, New York 10027

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The chemistry² and theory³ of small-ring compounds have been studied extensively. Nevertheless, before 1965 no unambiguous synthesis or characterization of cyclopropanones, one of the simplest classes of organic compounds, was known. Lipp⁴ and Roberts,⁵ however, provided strong evidence that cyclopropanone is an intermediate in the formation of cyclobutanone from ketene and diazomethane at -70° . Both Kende⁶ and Davidson⁷ found evidence to indicate that cyclopropanone could be prepared and survive long enough to be examined spectrally. Although the attempts to isolate cyclopropanone failed,⁸ products formed which were characterized as cyclopropanone adducts.⁴

Since many reactions are known which appear to proceed *via* a cyclopropanone intermediate (*e.g.*, Favorskii rearrangements,⁹ *vide infra*), it seemed possible that under appropriate conditions these reactive molecules could be isolated.⁸ Indeed, in 1965–1966, with the preparation of tetramethylcyclopropanone (**8**)^{10–12} and 2,2-dimethylcyclopropanone (**6**)¹³ by Hammond⁸ at Columbia, this class of compounds became accessible to detailed study.

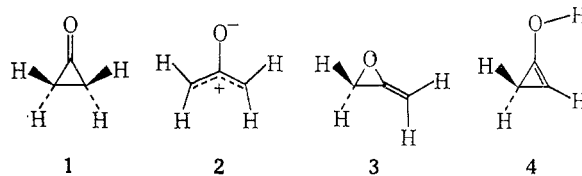
Cyclopropanone¹⁴ itself was successfully prepared both by Hammond⁸ and by Schaafsma¹⁵ and Professor

Table I
Spectral Properties^a of Cyclopropanones

Cyclopropanone	Ir (C=O), cm ⁻¹	Uv, Å	Nmr, ^c ppm
1	1813	3100 3300 (sh)	1.65 (s)
5	1822 1850	3300	1.9 (m, 1) 1.0–1.4 (m, 4)
6	1815	3400	1.5 (m, 1) 1.40 (s, 6)
8	1843 ^b 1823 ^b	3400	1.20 (s, 2) 1.19 (s)

^a Methylene chloride solvent. ^b Doublet collapses to singlet at 1825 cm⁻¹ in pentane. ^c TMS external standard.

DeBoer¹⁶ at the University of Amsterdam and characterized (Table I) in 1966. Spectral data¹⁷ and a microwave analysis¹⁸ leave no doubt that the classical closed three-ring ketone best describes cyclopropanone. That this would be so is not completely obvious since predictions based on qualitative, theoretical, and thermodynamic considerations did not really allow an unequivocal choice between the closed form **1** and the tautomers **2**, **3**, and **4**.



The energy contents of **1**, **2**, and **3**, in particular, may be comparable;¹⁹ if so, several important consequences follow: (a) a measurable concentration of **2** or **3** may exist in mobile equilibrium with **1**, (b) **2** or **3** may be crucial reactive intermediates in some reactions of **1**, and (c) appropriate substitution or environmental effects of the three-membered ring may shift the equilibrium to favor forms such as **2** or **3**.

Several cyclopropanone derivatives have now been prepared, *e.g.*, **5**, **6**, **8**, **10**, **11**, **12**, and **15**. We shall consider the preparations and reactions of cyclopropanones and attempt, using available evidence, to formulate generalizations concerning structure–reactivity relations for these compounds.

(16) S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim.*, **85**, 1170 (1966).

(17) N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017 (1968).

(18) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 1072 (1968).

(19) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

(1) (a) Alfred P. Sloan Foundation Fellow, 1966–1970. (b) The generous support of this work by the Air Force Office of Scientific Research (Grants AFOSR-66-1000 and AFOSR-68-1381) is gratefully acknowledged.

(2) Review: R. A. Raphael in "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1953, p 11.

(3) Review: W. A. Bennett, *J. Chem. Educ.*, **44**, 17 (1967); J. P. Pete, *Bull. Soc. Chim. France*, 357 (1967).

(4) P. Lipp and R. Koster, *Ber.*, **64**, 2823 (1931); P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932).

(5) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

(6) A. Kende, Ph.D. Dissertation, Harvard University, 1956.

(7) W. D. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

(8) Review: W. B. Hammond, Ph.D. Dissertation, Columbia University, 1967.

(9) Review: A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(10) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **87**, 2774 (1965).

(11) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964); H. C. Richey, J. M. Richey, and D. C. Claggett, *ibid.*, **86**, 3906 (1964); I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965); *Can. J. Chem.*, **43**, 3165 (1965).

(12) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2612 (1965); R. C. Cookson, M. J. Nye, and G. Subrahmayan, *Proc. Chem. Soc.*, 144 (1964).

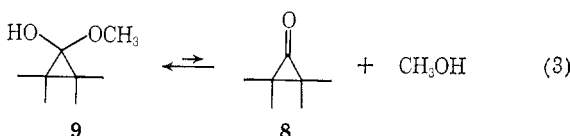
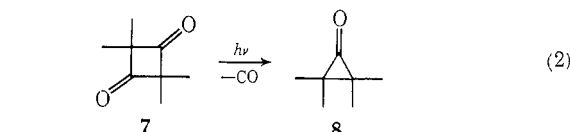
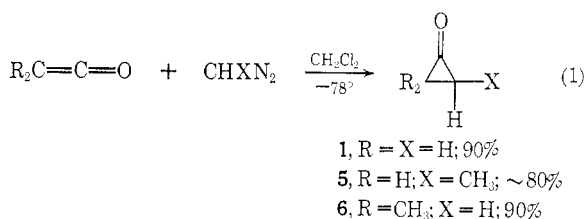
(13) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966).

(14) N. J. Turro and W. B. Hammond, *ibid.*, **88**, 3672 (1966).

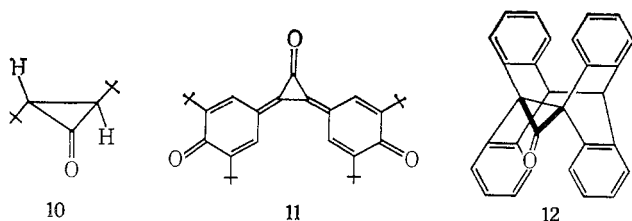
(15) S. E. Schaafsma, Ph.D. Dissertation, University of Amsterdam, 1968.

Preparation of Cyclopropanones

The high degree of reactivity expected of cyclopropanones from the work of Lipp⁴ and Kende⁶ and the apparent sensitivity of these compounds to acids and bases require that mild and neutral conditions be employed for the preparation of cyclopropanones. To date, three routes of limited generality have been developed: (a) the "ring expansion" reaction resulting from the addition¹⁷ of a diazo compound to a ketene, *e.g.*, eq 1; (b) the photoelimination¹⁰ of CO, *e.g.*, eq 2; and (c) the extraction of cyclopropanone from its equilibrium^{17,30} with a labile adduct, *e.g.*, eq 3.

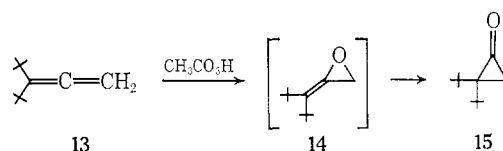


The cyclopropanone **11** was prepared by a reversible oxidation of the corresponding diarylcyclopropenone.²¹ *trans*-2,3-Di-*t*-butylcyclopropanone (**10**) is the first cyclopropanone to have been prepared under Favorskii rearrangement conditions (*vide infra*).²²



Photochemical closure of 9,9'-dianthracylcarbinol²³ followed by oxidation with MnO₂ yields the stable cyclopropanone **12**. The same compound is formed by irradiation of 9,9'-dianthracylketone.²⁴

An extremely interesting preparation of the stable 2,2-di-*t*-butylcyclopropanone (**15**) has been reported.²⁵ The allene oxide **14** is a rational intermediate and primary product from the peracid treatment of **13**.



1,3 ring closures, which have been so successful for the preparation of cyclopropanes,² have only found success in the preparation of **10** which appears to be a special case because of its unusual stability toward nucleophiles. Oxidation of cyclopropanols under mild neutral conditions (*viz.*, **12**) merits further attention. Research is presently in progress to develop versatile and general cyclopropanone syntheses.

Structure of Cyclopropanone and Its Tautomers

The spectral properties of **1** in the vapor phase and in solution demonstrate that the molecule possesses the closed-ring structure.¹⁷ Table II summarizes the bond

Table II
Bond Lengths of Cyclopropanone and Some Model Compounds^{18,28}

Molecules	Bond distances, Å
	$r(\text{CO})$, 1.18
	$r(\text{C}_1\text{C}_2)$, 1.49
	$r(\text{C}_2\text{C}_3)$, 1.58
	$r(\text{CC})$, 1.54
	$r(\text{CO})$, 1.21
H ₂ CO	$r(\text{CO})$, 1.21
H ₂ CCO	$r(\text{CC})$, 1.33
	$r(\text{CO})$, 1.15
(CH ₃) ₂ CO	$r(\text{CO})$, 1.22

distances of **1** as revealed from its microwave spectrum.¹⁸ It should be noted that **1** possesses a rather short CO distance and a long C₂C₃ distance. This indicates a reactive carbonyl function (*cf.* formaldehyde and ketene) and a weak C₂C₃ bond, *i.e.*, the conversion of **1** → **2** may proceed with a low activation energy. More will be said about these points below.

The high value of the CO stretching frequency of cyclopropanone is consistent with its short CO bond length (Table II). The large bathochromic shift of the n, π^* absorption maximum of cyclopropanone¹⁷ relative to acetone probably results from the higher ground-state energy of cyclopropanones relative to acetone and a greater stabilization of the excited state by the movement of electronic charge toward the strained and abnormally electronegative carbonyl carbon.

The cyclopropane ring of **1** is expected to imbue this ketone with special properties. The three-membered ring itself has been long known to possess properties similar to those of unsaturated molecules (*e.g.*, capacity to undergo addition reactions and to "conjugate" to double bonds).³ These properties are generally considered to arise from "ring strain" of cyclopropanes.^{2,3}

(20) N. J. Turro, W. B. Hammond, P. A. Leermakers, and H. T. Thomas, *Chem. Ind.* (London), 990 (1965).

(21) D. C. Zecker and R. West, *J. Am. Chem. Soc.*, **89**, 152 (1967).

(22) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

(23) F. D. Greene and N. M. Weinschenker, *ibid.*, **90**, 506 (1968).

(24) N. J. Turro and D. S. Weiss, unpublished results.

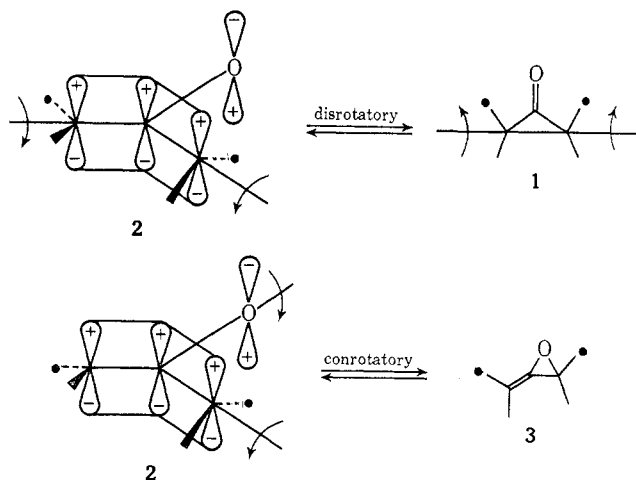
(25) J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90**, 7292 (1968).

(26) Y. Yukawa, "Handbook of Organic Structural Analysis," W. A. Benjamin, Inc., New York, N. Y., 1965, p 510 ff.

In valence bond terminology this "strain" results because the cyclopropane bonds are not hybridized in a manner so that the C-C bond direction can coincide with the direction of the greatest overlap of electronic orbitals of the bond. Since bond strengths parallel the degree of orbital overlap, cyclopropane bonds are weaker relative to "normal" C-C bonds.

A second feature which will be important because it tends to facilitate the rupture of the C₂C₃ bond of **1** is the possibility of resonance stabilization ($E_{\text{res}} \sim 40$ kcal) of the transition state for bond breaking as **1** passes to **2**.

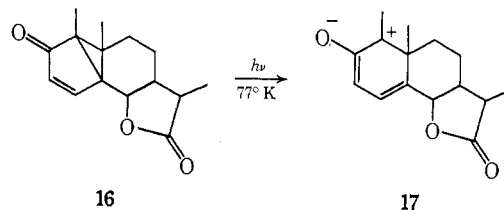
Orbital symmetry arguments predict that the ring opening of **1** → **2** should occur by a disrotatory motion of the methylene hydrogens.²⁷ It would be of some interest, therefore, to see if an appropriate optically active *cis*-2,3-disubstituted cyclopropanone is racemized faster than it rearranges to the *trans* isomer (a process which could require considerable activation if compounds related to **2** are intermediates, since allylic resonance of **2** is destroyed), since this result would imply reversible preformation of the dipolar ion which possesses a plane of symmetry. The allene oxide formed from a *cis*-cyclopropanone should be *cis* with respect to the epoxide oxygen as shown. At Columbia work is presently in progress to test these interesting possibilities.



Zwitterions related to **2** have been proposed as intermediates in the photochemical reactions of cyclohexadienones²⁸ and the reductive debromination of α, α' -dibromo ketones.^{29, 30} Recently, a colored species, believed to be the zwitterion **17**, was formed upon irradiation of lumisantonin³¹ (**16**).

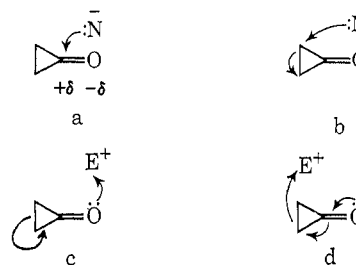
Reactivity of Cyclopropanones

Numerous possibilities exist for nucleophilic or electrophilic attack on structures **1**–**4**. We shall con-

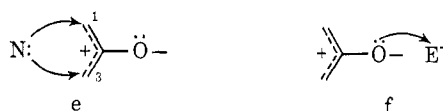


cern ourselves mainly with structures **1** and **2**, since evidence to date does not require involvement of **3**³² and **4**.

Two sites for nucleophilic attack (the carbonyl carbon, route a, or ring carbon attack, route b) or electrophilic attack (routes c and d) on **1** must be considered.



Should the tautomer **2** be involved in a similar reaction, nucleophilic attack probably would occur only on the C₁ and C₃ ring carbons and electrophilic attack would be directed to the alkoxide-like oxygen atom (e and f, respectively).



One might expect the reactivity of cyclopropanones toward nucleophiles and electrophiles to be intermediate between that of a formal "2-ring" ketone (e.g., ketene) and that of cyclobutanone. In fact, in its chemistry **1** appears to have a much closer analogy to ketene than to cyclobutanone.

Two main modes of driving force are expected to direct the rates and types of reactions of **1**: (a) conversion of a highly strained sp² center on a small ring to a sp³ center (I strain);³³ (b) relief of ring strain and gain of resonance energy in going from **1** to **2** or a transition state that involves a species resembling **2**.

As a result of their severe strain energies, cyclopropanones possess large amounts of energy waiting to be released. Experimentally, "strain" manifests itself as low activation energies for reaction. Many reactions of cyclopropanones proceed smoothly at or near room temperature. Every bond in a cyclopropanone ring system is labile and the carbonyl group is exceptionally reactive.

Reactions of Cyclopropanones with Alcohols, Acids, and Organic Bases

Both ring-opened and ring-closed products result when cyclopropanones are treated with nucleophiles or

(27) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(28) Review: P. Kropp, *Org. Photochem.*, **1**, 1 (1968).

(29) H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966).

(30) H. E. Zimmerman and D. S. Crumine, *ibid.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5615 (1968).

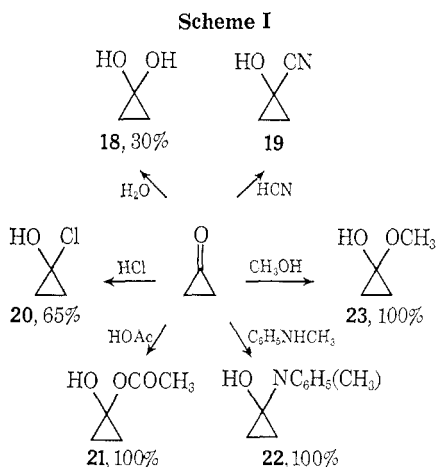
(31) M. Fisch and F. E. Richards, *ibid.*, **90**, 1547, 1553 (1968).

(32) For a recent attempt to prepare allene oxide see J. K. Crandall and W. H. Machleder, *Tetrahedron Letters*, 6037 (1966).

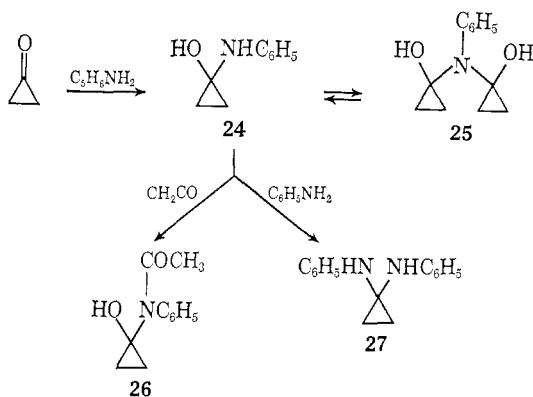
(33) H. C. Brown, R. S. Fletcher, and R. B. Johanner, *J. Am. Chem. Soc.*, **73**, 212 (1951); H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

electrophiles.^{34,35} Which of these reactions predominates depends on the cyclopropanone structure and also on the structure of the acid or base employed.

Some reactions of cyclopropanone with HX molecules are listed in Scheme I. In these cases, carbonyl adducts are formed in good yield and little ring opening occurs.^{34,36}



Addition of aniline to **1** yields a mixture of the mono- and bisadducts **24** and **25**.^{34,37} After several days, in the presence of excess aniline, 1,1-dianilincyclopropane (**26**) forms.



Dimethylamine shows similar reactivity to aniline with **1**. Methylamine,³⁸ however, yields polycyclic products.

Wasserman and Clagett^{39,40} have found that treatment of the acetoxy ketal or the hemiketal of cyclopropanone with lithium aluminum hydride or aniline results in formation of cyclopropanol and **26**, respectively. Thus it appears that the cyclopropanone is leached out of equilibrium with these reagents. Al-

(34) N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6029 (1968).

(35) W. J. M. Van Tilborg, S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim.*, **86**, 419, 651 (1967).

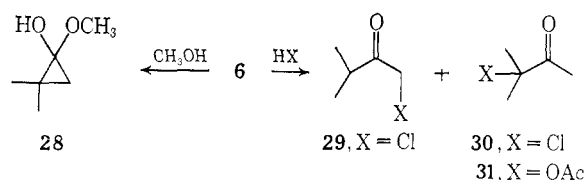
(36) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **89**, 1028 (1967).

(37) N. J. Turro and W. B. Hammond, *Tetrahedron Letters*, 3085 (1967).

(38) W. J. M. Van Tilborg, S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim.*, **86**, 417 (1967).

(39) H. H. Wasserman and D. C. Clagett, *J. Am. Chem. Soc.*, **88**, 5368 (1966).

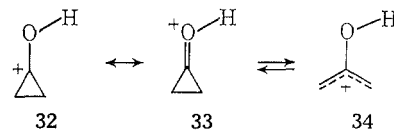
(40) H. H. Wasserman and D. C. Clagett, *Tetrahedron Letters*, 341 (1964).



though addition of CH_3OH to **6** yields the hemiketal **28** quantitatively, HCl or HOAc and **6** yield only ring-opened products.^{34,41}

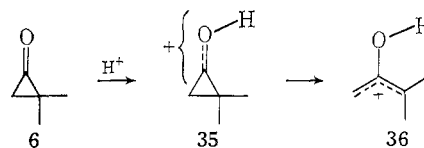
There has been considerable interest in the solvolyses of cyclopropyl compounds because of the extreme sluggishness of this small ring system toward nucleophilic substitution. The facility of substitution reactions of cyclopropanone carbonyl adducts indicates that the attachment of a saturated oxygen atom stabilizes the cationic center generated in these reactions.

Interestingly, **21** is apparently in mobile equilibrium with cyclopropanone and acetic acid since addition of CH_2CO to **21** yields cyclopropanone and acetic anhydride. Olah⁴² has found that the nmr of **1** in strong acid indicates the formation of an equilibrium mixture of protonated cyclopropanone and protonated dipolar ion. The resistance of cyclopropanone to ring opening by HCl or CH_3COOH may be attributed to the strong contribution of resonance form **33** which localizes the



bulk of the electronic deficiency on oxygen rather than on carbon.

Since **6**, on the other hand, yields only ring-opened products when treated with acidic reagents, one may conclude that the ring opening of **6** (via **35**) to the 1,1-dimethylallyl cation **36** (which is more stable than the unsubstituted cation $32 \leftrightarrow 33$) is fast compared to attack by the gegenion or that the latter reaction is reversible.



Cycloaddition Reactions of Cyclopropanones

Cycloaddition reactions⁴³ have received wide attention because of their theoretical,⁴⁴ mechanistic,⁴⁵ and

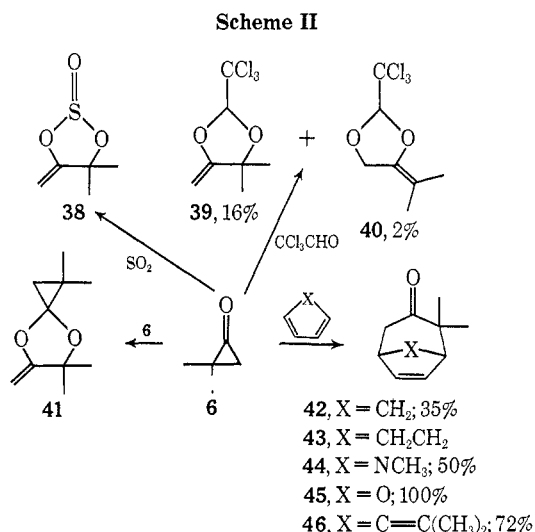
(41) R. B. Gagosian and N. J. Turro, unpublished results.

(42) G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **90**, 938 (1968).

(43) General reviews of cycloadditions: R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **7**, 321 (1968); R. Huisgen, R. Grashey, and J. Sauer in "Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 739.

(44) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046, 4388 (1965); L. Salem, *ibid.*, **90**, 553 (1968); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(45) (a) 1,3-Dipolar cycloadditions: R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963); (b) Diels-Alder: J. Sauer, *ibid.*, **6**, 16 (1967); (c) 1,2:1,2-cycloadditions: P. D. Bartlett, *Science*, **159**, 833 (1968); (d) photochemical cycloadditions: A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience Publishers, New York, N. Y., in press.



synthetic importance.⁴⁶ Cycloadditions have been classified according to the number of new σ bonds formed, the ring size, and the number of ring members contributed by each addend.⁴³ In this terminology, the Diels–Alder reaction is a $4 + 2 \rightarrow 6$ cycloaddition and the dimerization of tetrafluoroethylene to octafluorocyclobutane is a $2 + 2 \rightarrow 4$ cycloaddition. Recently, cycloadditions have been classified according to whether they are allowed to be concerted by orbital symmetry selection rules,⁴² which state that thermal cycloadditions are generally allowed (*i.e.*, may involve the simultaneous conversion of two π bonds into two σ bonds) when the total number of π electrons involved in the cycloadditions = $4n + 2$. Steric factors and polarization effects are not explicitly considered in these rules, so that other arguments for determining the mechanisms of cycloadditions may also be invoked in appropriate cases.

Although cycloaddition appears to be a general reaction of cyclopropanones,⁴⁷ only 2,2-dimethylcyclopropanone has been studied extensively.⁴⁸ This molecule undergoes $3 + 4 \rightarrow 7$ (six π electron), $3 + 2 \rightarrow 5$ (six π electron), and $2 + 2 \rightarrow 4$ (four π electron) cycloadditions (Scheme II). The first two types of cycloaddition are best explained in terms of an intermediate “bidentate 1,3 dipole” such as **2**. If the transient **2** is completely planar, then the four π molecular orbitals of **2** may be qualitatively correlated to those of trimethylenemethane⁴⁹ (Figure 1).

Burr and Dewar⁵⁰ calculate the electron density at

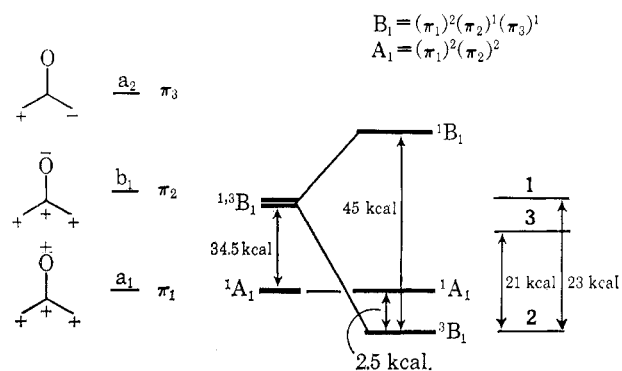
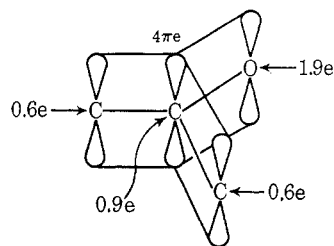
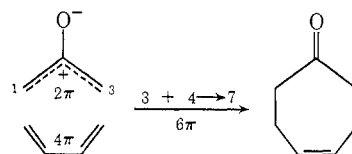


Figure 1. Orbital (left) and state (right) diagrams for **2**. The symbols employed are those for C_{2v} symmetry with the XY plane being that of the molecule, which is assumed to be planar, (adapted from ref 19).

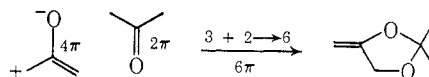
the various unsaturated atoms of **2** to be



On the basis of this analysis, when making orbital symmetry predictions, we can consider **2** to be an allyl cation fused to an oxyanion or to be an enolate anion fused to a carbonium ion. Such reasoning leads to the prediction that the $C_1C_2C_3$ (two π electron) group should be electrophilic and attack four π electron systems in concerted cycloadditions, *viz.*



On the other hand, the C_1C_2O group contains between three and four electrons and should be nucleophilic and attack (electron poor) two π systems, *viz.*



A quantitative calculation¹⁹ yields the same conclusions concerning the types of symmetry allowed cycloadditions of **2** (*vide infra*). However, a detailed calculation of the energy levels and electronic states of **2** indicates that the ground state of **2** should be a triplet, but with a singlet state (presumably the reactive state in the cycloadditions discussed here) just a few kilocalories higher in energy (Figure 1). This surprising result derives from the large singlet–triplet splitting of the B_1 states of **2**. This splitting is comparable to the singlet triplet splittings of π, π^* states of ethylenes⁵¹ and probably results from the high degree of spatial overlap

(51) N. J. Turro, “Molecular Photochemistry,” W. A. Benjamin Co., New York, N. Y., 1965.

(46) (a) 1,3-Dipolar cycloadditions: R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); (b) Diels–Alder: J. Sauer, *ibid.*, **5**, 211 (1967); (c) 1,2:1,2-cycloadditions: J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962); (d) photochemical cycloadditions: R. Steinmetz, *Fortschr. Chem. Forschung*, **7**, 445 (1967); O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 200 (1967).

(47) To date cyclopropanone has not been induced to undergo any cycloaddition reactions. The polymerization of **1** is quite fast and generally competes effectively with cycloaddition.

(48) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Am. Chem. Soc.*, in press.

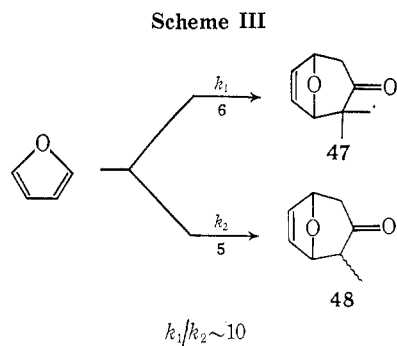
(49) For recent work on trimethylenemethane see: P. Dowd, *ibid.*, **88**, 2587 (1966); P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); **90**, 2175 (1968); W. Borden, *Tetrahedron Letters*, 259 (1967).

(50) J. G. Burr, Jr. and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

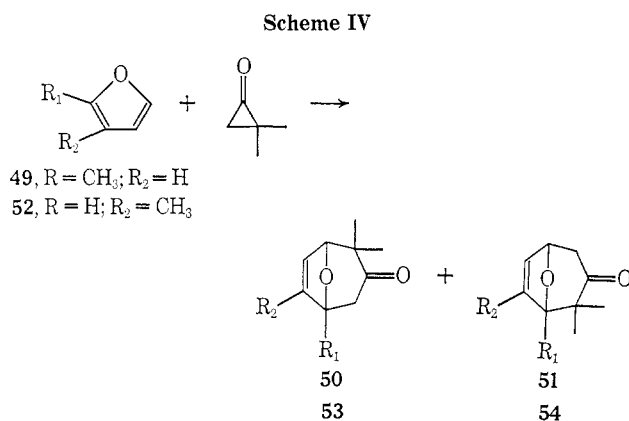
of the π_2 and π_3 orbitals. This calculation also places both **1** and **3** at higher energy than **2**. Should the 3B_1 state, in fact, lie below but close to the 1A_1 state of **2**, then these cycloadditions, if concerted, are *excited state* reactions of **2**.

It is not known yet whether these cycloaddition reactions^{52,53} involve a fast preequilibrium between **6** and its dipolar tautomer **6D** by the rate-determining addition of **6D** to the diene or whether formation of **6D** is rate determining. One can test the possibility that **6** and other cyclopropanones may add directly to dienes and carbonyls without passing through a dipole ion, by using an optically active cyclopropanone as substrate.

The rate of addition⁴⁸ of **6** to furan is about ten times faster than the addition of **5** to furan (Scheme III).



However, very little orientational selectivity is observed when **6** reacts with 2- or 3-methylfuran (Scheme IV).



Both results seem consistent with concerted addition of **6** to the dienes involved.⁵² The faster rate of reaction of **6** implies either a faster ring opening of **6** to a dipolar ion (*vide infra*) or a higher steady-state concentration of dipolar ion in the case of **6**. It should be noted that the related disrotatory ring opening of cyclopropyl cations,^{27,53} a topic of considerable recent experimental^{54,55} and theoretical interest,⁵⁶ occurs much faster for **55** than for **57**.

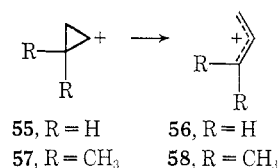
(52) N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Am. Chem. Soc.*, **90**, 1926 (1968).

(53) N. J. Turro and S. S. Edelson, *ibid.*, **90**, 4499 (1968).

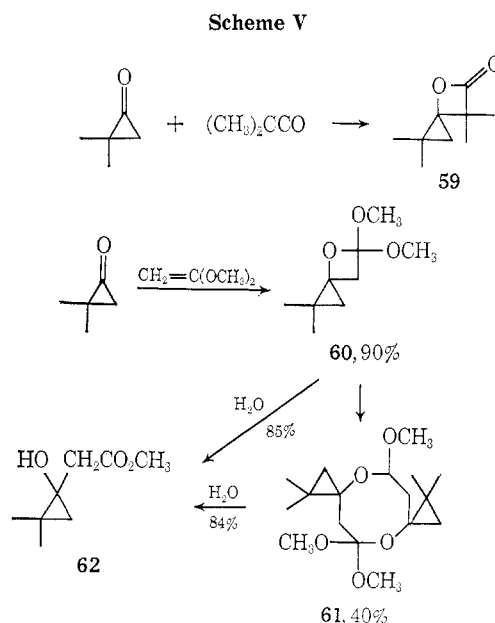
(54) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *Tetrahedron*, **88**, 3343 (1966).

(55) P. von R. Schleyer, G. W. Van Dine, U. Schollkolf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966); J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(56) W. Kutzelnigg, *Angew. Chem. Intern. Ed. Engl.*, **6**, 813 (1967); *Tetrahedron Letters*, 4965 (1967).



In addition to the six π electron cycloadditions which **6** undergoes, cycloadditions to the C=O bond of **6** have been found with dimethylketene and 1,1-dimethoxyethylene (Scheme V). Although the addition of ketenes to



C=O bonds is well known, this type of cycloaddition to form **60** appears to be unique.⁵⁷ The novel ortho ester **60** also undergoes an unusual dimerization to yield **61**. Both **60** and **61** may be converted to the cyclopropanol **62**.

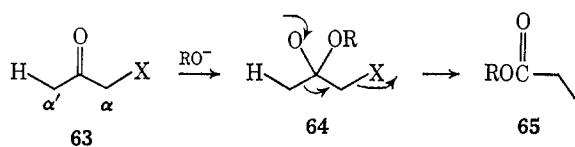
The 2 + 2 \rightarrow 4 cycloadditions which occur across the C=O bond of **6** are formal, but not very surprising, violations of orbital symmetry selection rules for cycloaddition. These additions are probably either one- or two-step polar additions which are initiated by nucleophilic attack on the highly reactive cyclopropanone carbonyl carbon.

The Cleavage of Cyclopropanones by Strong Base. The Favorskii Rearrangement

The Favorskii reaction is a base-induced skeletal rearrangement of α -halogenated ketones to carboxylic acid derivatives which has proven to be a reliable and important route to derivatives of highly branched cyclic carboxylic acids and 1-substituted cycloalkanecarboxylic acids and for the contraction of specific rings in steroids.⁹ Two mechanisms are required to explain available data: (a) a "semibenzylic" rearrangement⁵⁸ induced by attack of base on the carbonyl carbon to

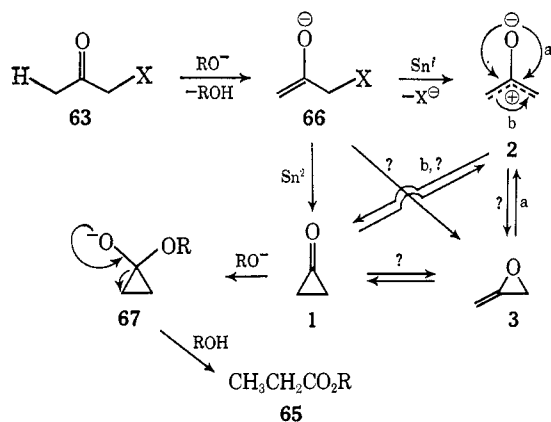
(57) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949). Ketenes react with ketene acetals at the C=C not the C=O bond: R. Scarpati and D. Sica, *Gazz. Chim. Ital.*, **92**, 107 (1962).

(58) J. M. Conia and J. Salaun, *Bull. Chim. Soc. France*, 1957 (1964); C. Rappe and L. Knutsson, *Acta Chim. Scand.*, **21**, 163 (1967).



form an intermediate such as **64** which then rearranges to product; this mechanism is favored when the α' position has a nonacidic,⁵⁹ hindered, or otherwise inaccessible hydrogen atom;⁶⁰ (b) α' -hydrogen abstraction by base followed by formation of an intermediate cyclopropanone or its corresponding dipolar tautomer; attack, by base, on the cyclopropanone then leads to rearranged products (Scheme VI). Numerous ques-

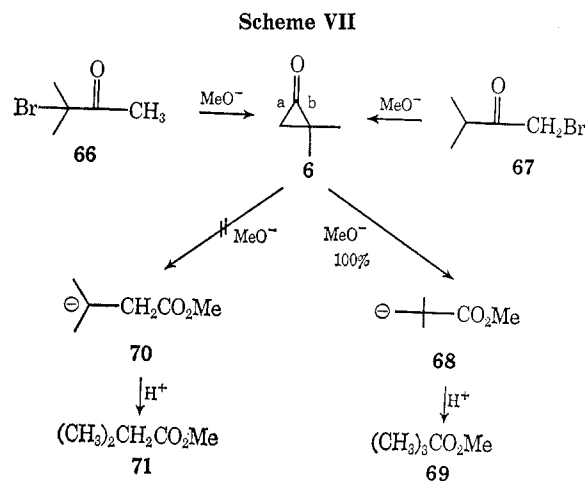
Scheme VI



tions about the details of the elementary steps of Scheme VI exist: (a) Does the anion **66** collapse to **1** or **2** or both? (b) Can **2**, if formed, collapse to **1** or will it be attacked more rapidly by base? (c) Does an equilibrium exist between **1** and **2** under Favorskii conditions?

Stork and Borowitz,⁶¹ in a classic study, showed that, under appropriate experimental conditions, Favorskii rearrangements can be stereospecific, thus ruling out the general occurrence of intermediates such as **2** as precursors to cyclopropanones. However, more recent work has shown that in polar solvents a nonstereospecific rearrangement and formation of products expected from a dipolar species occur.^{62,63}

We have found strong evidence for a common intermediate in the rearrangement⁶⁴ of the α -bromo ketones **66** and **67** to methyl trimethylacetate (**69**). Treatment of either **66** or **67** with NaOMe results in formation of only one rearranged ester, **69**, the same exclusive product formed when **6** is treated with base¹³ (Scheme VII). No evidence for the occurrence of a dipolar species was obtained. Indeed, it was found that the α -



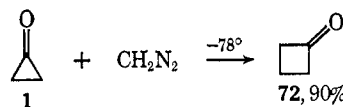
substitution products formed (often considered characteristic products of the dipolar tautomer) derive from attack of base on the starting ketone.⁶⁴

The specificity of ring opening of **6** by base is striking. The ester **69** is formed in nearly quantitative yield and the isomeric cleavage product **71** is formed in less than 1% yield if it is formed at all. The direction of cleavage is expected to be governed by both electronic and steric factors. In the case of **6**, the energy of the transition states for cleavage can be correlated to the stabilities of the carbanions formed by ring opening. Thus, cleavage of bond a by base yields the primary carbanion **68**, while cleavage of bond b yields the tertiary carbanion **70**. Thus, the transition-state energies for cleavage parallel the stabilities⁶⁵ of carbanions **68** and **70**.

Cases are known, however, for which steric factors can modify the rule for cleavage given above (at least for presumed cyclopropanones generated under Favorskii conditions).⁶⁶ Research is under way at Columbia in collaboration with Professor Rappe of Uppsala University which should help to elucidate the factors determining the direction of ring opening.

Miscellaneous Reactions of Cyclopropanones

Addition of excess diazomethane to cyclopropanones results in facile conversion to cyclobutanones.^{17,67}



Thermal decarbonylations of cyclopropanones⁶⁸ are expected to occur in a stepwise, nonconcerted fashion. Although the appropriate labeled cyclopropanones for testing this hypothesis have not been made, hot-tube pyrolysis of **6** yields isobutylene as an important volatile

(59) A. C. Cope, M. E. Synerholm, and E. S. Graham, *J. Am. Chem. Soc.*, **72**, 5228 (1950); **73**, 4702 (1951).

(60) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *ibid.*, **90**, 514 (1968).

(61) G. Stork and I. J. Borowitz, *ibid.*, **82**, 4307 (1960).

(62) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965).

(63) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **87**, 3258 (1965).

(64) N. J. Turro, R. B. Gagosian, C. Rappe, and L. Knutsson, unpublished results.

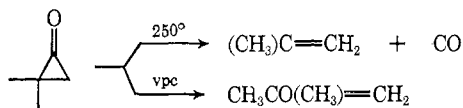
(65) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(66) C. Rappe and L. Knutsson, *Acta Chem. Scand.*, **21**, 2205 (1967).

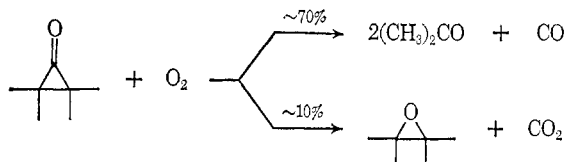
(67) J. M. Conia and J. Salaun, *Bull. Chim. Soc. France*, 1957 (1964).

(68) For related reactions and discussions see: J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).

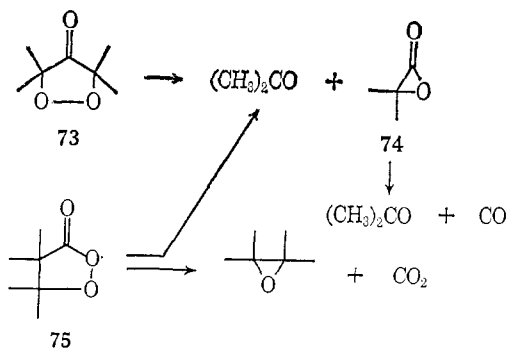
product. Vpc pyrolysis of **6**, however, yields methyl isopropenyl ketone. A related reaction was found to occur for **8** during vpc analysis.



The reaction of **8** with oxygen is particularly intriguing. The products formed are tetramethylethylene oxide, acetone, CO, and CO₂. The stoichiometry for this reaction is approximately as follows.

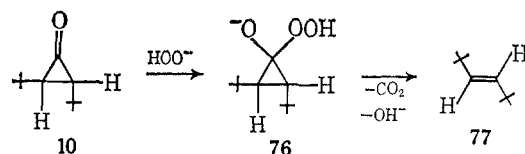


Two possible intermediates in the formation of the products are the peroxides **73** and **75**. It is interesting to note that either may decompose to products *via* the α -lactone **74**. A search for the occurrence of this molecule is presently under way.



Treatment of cyclopropanones with H₂-Pt yields ketones derived from hydrogenolysis of the C₂-C₃ bond.^{22,69} Finally, the reaction of **10** with basic H₂O₂

(69) N. J. Turro and J. R. Williams, unpublished results.



yields the olefin **77**, possibly *via* the mechanism shown. A similar reaction may obtain in the synthesis of olefins from α -halogeno ketones.⁷⁰ Addition of LiAlH₄ to cyclopropanones results in formation of cyclopropanols.¹⁰

Conclusion

Cyclopropanone chemistry has already provided a number of interesting avenues for synthetic and mechanistic studies. The synthesis of substituted cyclopropanones, especially those capable of undergoing *cis-trans* isomerization, should prove of great use in examining the problem of the structure of dipolar ions such as **2**. Synthetic efforts directed toward preparation of allene oxides should be performed so that the place of this tautomer on the reaction surfaces relating **1** and **2** can be elucidated. Much remains to be done in the way of kinetic and other physical measurements of cyclopropanones, *i.e.*, rates of addition of nucleophiles to the C=O group, rates of proton removal from **1**, rates of cycloadditions, etc. Hopefully these studies will help to formulate an understanding of the great reactivity of small rings and to test current theories concerning the bonding in small rings. The high energy content of **1** essentially assures us that a wealth of novel, exciting, interesting, and, hopefully, useful chemistry of cyclopropanones awaits future discovery.

It is my great pleasure to acknowledge the contributions of Willis B. Hammond to much of the work reported here. The experimental and intellectual skills and perseverance of Dr. John R. Williams, Mr. Simon S. Edelson, Mr. Robert B. Gagosian, and Mr. Thomas Darling are also warmly acknowledged.

(70) F. D. Green, quoted in J. E. Baldwin and J. H. I. Cardellia, *Chem. Commun.*, 558 (1968).