Tetrahedron Vol 24, pp 6017 to 6028 Pergamon Press 1968 Printed in Great Britain

CYCLOPROPANONES—VIII

PREPARATION AND CHARACTERIZATION OF CYCLOPROPANONE, METHYLCYCLOPROPANONE, 2,2-DIMETHYLCYCLOPROPANONE AND TETRAMETHYLCYCLOPROPANONE[1,2,*]

N. J. Turro† and W. B. Hammond‡
Contribution from the Department of Chemistry, Columbia University New York,
New York 10027

(*Received in USA* 9 *April* 1968; *accepted for publication* 13 *May* 1968)

Abstract—The preparations of cyclopropanone (**1**), methylcyclopropanone (**2**), 2,2-dimethylcyclopropanone (**3**) and tetramethylcyclopropanone (**4**), are described. The spectral properties of these molecules demonstrate unambiguously the ring closed structure for cyclopropanones. The reactions of cyclopropanones with methanol, diazomethane and furan are employed as chemical means of characterization

INTRODUCTION

NUMEROUS alleged isolations of cyclopropanones previously reported in the literature have not withstood the criteria of reproducibility or the scrutiny of spectral analyses.§

On the other hand, a large body of experimental work strongly implicates cyclopropanones as intermediates in various reactions such as the preparation of cyclopropenones,[4a] the Favorskii rearrangement,[4b] and the reactions of cyclopropanone derivatives.[4c]

Thus, at the advent of this work, there appeared to be no general and useful methods available for the preparation of cyclopropanones. This family of molecules had evaded unequivocal characterization, even though cyclopropanones were invoked as reaction intermediates before the turn of the century.[5]

The syntheses and characterization of cyclopropanones is of importance because the physical and chemical manifestations of the unique strain involved in these systems should lead to a better understanding of bonding in small ring compounds. In addition, the expected reactivity of these compounds makes them attractive intermediates for organic syntheses. There has not been universal acceptance of the ring closed form as the equilibrium structure of cyclopropanones. Burr and Dewar,[6] for example, have proposed that the energy content of the open "dipolar" form‖[7] of cyclopropanone (**5**) might be comparable to that of cyclopropanone itself.

---

[*] The generous support of this research by the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant NSF-GP-4280) is gratefully acknowledged

[†] Alfred P. Sloan Fellow 1966–1968.

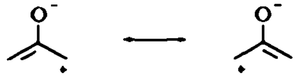
[‡] National Science Foundation Predoctoral Fellow, 1964–1967.

[§] For example, the reported oxidation of a bicyclic cyclopropanol to a cyclopropanone[3a] was shown to be incorrect.[3b] Similarly the structure proof of the alleged cyclopropanone from the degradation of material believed to be the active principle of the cockroach sex attractant[3c] has been questioned.[3d]

[‖] The dipolar form **5** is completely planar and possesses a π-orbital system related to trimethylene methane.[7]

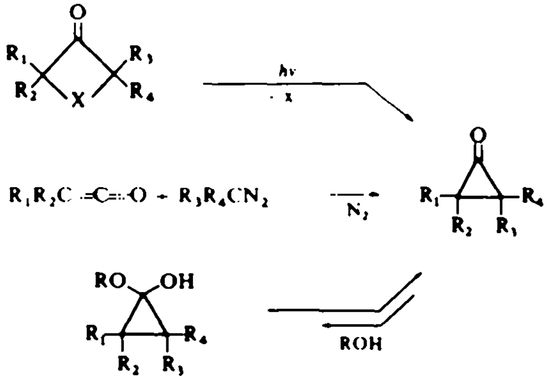
Hoffmann[8] has come to similar conclusions on the bases of extended Hückel calculations. Furthermore, the chemistry of α-bromoketones in basic medium (Favorskii rearrangement conditions) may be rationalized by assuming that a dipolar ion[9] either precedes cyclopropanone formation[10] or that the ion is in equilibrium with the cyclopropanone.[11-13] Finally, the 1,3-cycloadditions of cyclopropanones to dienes[14] and olefins[15] are most easily explained in terms of a dipolar ion intermediate.[16]

1



5 5

Synthesis of cyclopropanones. Because of their high reactivity, especially toward nucleophiles, the use of mild neutral, non-nucleophilic solvents is required for preparation of simple cyclopropanones.[16] Three general schemes which we have employed are (a) photolytic elimination of a small molecule[17] (b) addition of diazo compounds to ketenes,[18] (c) extraction of a cyclopropanone from an equilibrium.[4c, 19]

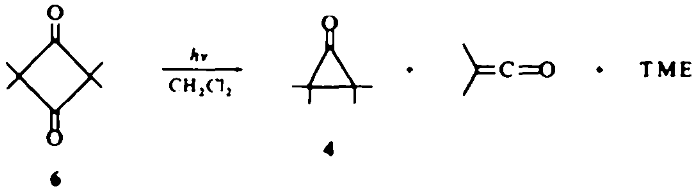


*Photolysis of cyclobutane-*1,3*-diones.* The photodecarbonylation of cyclic ketones is a general reaction[20] if the (presumed) biradical intermediate is resonance stabilized and undergoes rapid loss of CO. Thus, photodecarbonylation[17] of the readily available tetraalkylcyclobutane-1,3-diones[21] offers a potential path to tetraalkylcyclopropanones.

Irradiation[17,22-24,*] of tetramethylcyclobutane-1,3-dione, **6**, in methylene chloride results in rapid evolution of carbon monoxide ($\Phi = 0{\cdot}30$)[17] and formation of tetramethylcyclopropanone, **4**. The formation of **4** is easily monitored by IR spectroscopy, the photolysis being terminated when the characteristic carbonyl doublet of **4** (1843 and 1823 cm^{-1}) reaches a constant intensity (10–20% conversion of **6**). Some dimethyl ketene and tetramethyl ethylene[17] are also formed. Higher conversions are precluded by the secondary photodecarbonylation of **4** to tetramethylethylene (TME).

---

[*] Hanovia 450-watt immersion photolysis reactor, aqueous nickel sulfate filter (transmission maximum 3200Å). Some care should be taken to avoid excessive contact of the photosate with air, since **4** undergoes rapid oxidation.[17]



6

4

Cooling of the photosate (−78) removed most of the unreacted dione by recrystallization. Vacuum distillation of the supernatant liquid (10°/20 mm) afforded a 10–15% solution of 4 along with minor amounts of TME and 6 (NMR). The spectral properties of methylene chloride solutions of 4 produced in this manner are given in Table 1.

TABLE 1. SPECTRAL PROPERTIES[a] OF CYCLOPROPANONES 1, 2, 3 AND 4

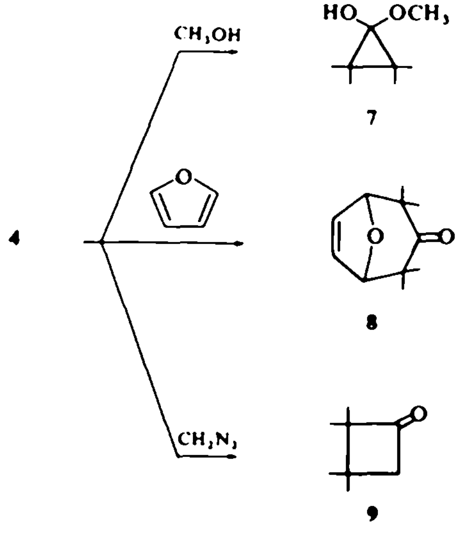
Cyclopropanone	IR (C=O)	UV	NMR[c]
1	1813 cm^{-1}	3100 Å ($\varepsilon \sim 23$) 3300 Å (sh)	δ 1·65 (s)
2	1822 cm^{-1} 1850 cm^{-1}	3300 Å ($\varepsilon \sim 18$)	δ 1·9 (m, 1) δ 0·9 1·7 (m, 5)
3	1815 cm^{-1}	3400 Å ($\varepsilon \sim 27$)	δ 1·40 (s, 6) δ 1·20 (s, 2)
4	1843 cm^{-1}[b] 1823 cm^{-1}[b]	3400 Å ($\varepsilon \sim 20$)	δ 1·19 (s)

[a] Methylene chloride solvent.

[b] Doublet collapses to singlet at 1825 cm^{-1} in pentane

[c] TMS external standard

Compound 4 was found to react quantitatively with methanol to yield the hemiketal[17,22] 7. In refluxing furan, 4 yields the adduct 8 in good yield. Reaction of 4 with diazomethane yields 2,2,3,3-tetramethylcyclobutanone 9.



7

8

9

Tetramethycyclopropanone is stable for weeks in methylene chloride at −78°, but is destroyed in several hours at 25°. The ketone apparently polymerizes to yield a mixture of dimers and higher oligomers.[25]

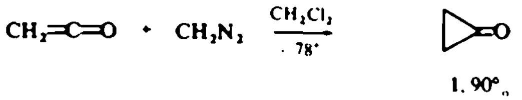
Irradiation of 2,2-dimethylcyclobutane-1,3-dione,[26] **10**, 2,4-dimethyl-2,4-diphenylcyclobutane-1,3-dione,[26] **11**, and tetraphenylcyclobutane-1,3-dione,[15] **12**, results in formation of the corresponding cyclopropanones, but in low yields (IR). Instead a number of complex photoreactions occur.[25, 26]

The photolytic elimination of carbon monoxide thus appears to be of limited synthetic value for the preparation of cyclopropanones.*

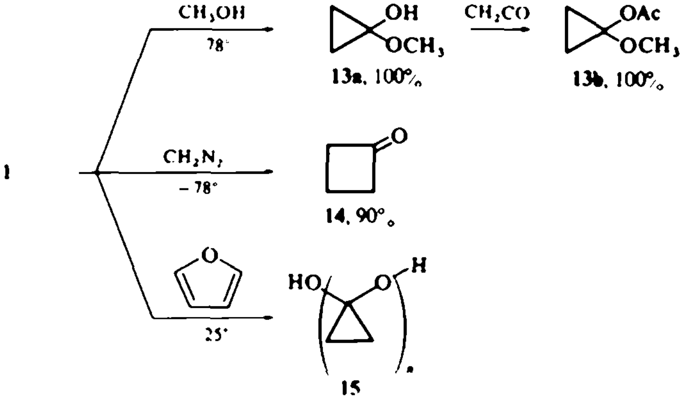
Addition of diazomethanes to ketenes. Evidence exists[28] that the addition of diazomethane to ketene yields cyclopropanone, at least as a transient intermediate. We have verified and extended these results.[18, 29]

A cold methylene chloride (−78°) solution of diazomethane[30, 31] was added to a 4–6 fold excess of ketene at −130°. Nitrogen was rapidly evolved. The excess ketene was removed (−78°) on a conventional vacuum line,[25] and the remaining solution was then flash distilled and maintained at −78°. It was possible, in this manner, to prepare 0·4 to 0·8M methylenechloride solutions of **1**. The spectral properties of **1** are listed in Table 1.

Cyclopropanone reacts quantitatively with methanol to yield the hemiketal **13a**. Addition of diazomethane to **1** yields cyclobutanone in good yield. Attempts to add furan to **1** at −78° were unsuccessful. At room temperature rapid polymerization of **1** occurs to the exclusion of adduct formation.



1, 90%

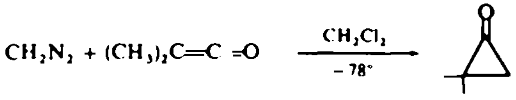


Addition of a cold (−78°) methylene chloride solution of diazomethane to a 4–5 fold excess of cold (−78°) dimethyl ketene in methylene chloride results in formation of 2,2-dimethylcyclopropanone **3** in excellent yield. The excess dimethyl ketene is removed by vacuum distillation. The resulting methylene chloride solution, after

---

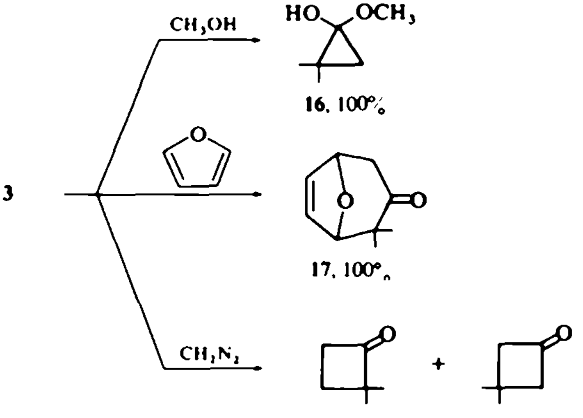
* Attempts to eliminate molecules other than CO has lead to similar results.[27]

flash distillation, contains only a few percent impurities (NMR). Spectral properties of **3** are given in Table 1.



3, 90%

2,2-Dimethylcyclopropanone (**3**) reacts quantitatively with methanol to yield the hemiketal **16**. Furan and diazomethane react with **3** to yield the adduct **17** and the cyclobutanones **18**, respectively.



16, 100%

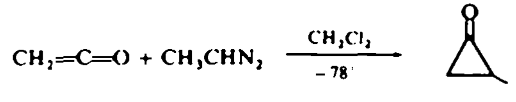
17, 100%

18a, 25% **18b**, 75%

2,2-Dimethylcyclopropanone possesses moderate stability at room temperature (20% solution in CH_2Cl_2 shows a half life of several days) and is stable for months at -78.

Addition of diazoethane[32] to ketene, in the manner described above, yields methylcyclopropanone, **2**. The spectral properties of distilled methylene chloride solutions of **2** are listed in Table 1. The NMR integration indicates some impurities are present.

Analogous[25, 26] to **3** and **4**, methylcyclopropanone reacts with methanol, furan and diazomethane.

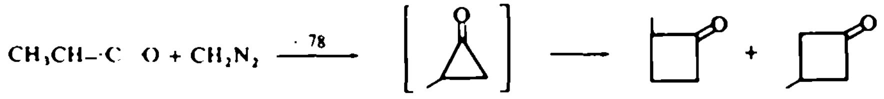


2

Methylcyclopropanone in methylene chloride is moderately stable at room temperature ($t_{1/2}$ = several hr).

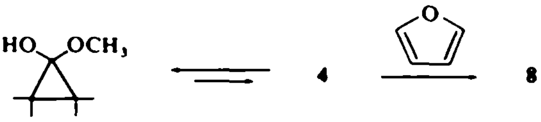
Attempts to make methylcyclopropanone from methylketene[32] and diazomethane have been unsuccessful so far because of the rapid polymerization of the ketene.

However, 2- and 3-methylcyclobutanones were isolated, which indicates that methyl cyclopropanone was formed.



Attempts to prepare cyclopropanones derived from methylchloroketene[33] also have been unsuccessful. It appears that this ketene must be trapped *in situ* and was not isolable, in our hands, even at − 110°.

Extraction of cyclopropanones from an equilibrium. The hemiketals of cyclopropanones are presumable in mobile equilibrium with the corresponding cyclopropanone.[19, 34] The position of the equilibrium is far in favor of the hemiketal, such that no C—O stretch is observable when the IR spectra of hemiketals are measured. However, cyclopropanones are enormously more reactive than their hemiketals towards many reagents. Thus, addition of appropriate reagents should utilize the cyclopropanone from its equilibrium with the hemiketal. Several examples of the effect are known.[34] The most convincing evidence for a free cyclopropanone in equilibrium with its hemiketal is probably the reaction of the methylhemiketal of **4** with furan which yields the furan adduct **8**.



DISCUSSION

We have described three potentially general syntheses of cyclopropanones. Of these methods, the addition of diazoalkanes to ketenes at low temperatures is the most promising.

The data in Table 1 coupled with the reactions of cyclopropanones leaves little doubt that these compounds are best represented as ring closed structures rather than the dipolar species. However, the dipolar structure nicely rationalizes the formation of adducts with furan and other dienes,[15, 1c] although the addition of the C_2—C_3 *single* bond to a diene may occur in a concerted fashion.[35, *]

The position of the infrared C=O stretching frequency of cyclopropanone may be predicted from consideration of the known frequencies of 6, 5, 4 and 2-ring ketones. Extrapolation from these numbers (Table 2) yields a value of 1815 cm^{-1} (5·52 μ) for the expected position of the C=O band for **1**. This is also in good agreement with the value of 1815 cm^{-1} assigned to cyclopropanone produced by the photolysis of CH_2N_2 in a nitrogen matrix (77°K) containing ketene.[36]

The NMR spectra of cyclopropanones **1**–**4** seem unexceptional. Compound **3** was found to possess a J^{13}_{CH} coupling of 160 c/s, a value consistent with a cyclopropane structure.[37]

---

[*] The three carbon system of the dipolar ion is considered as an allyl cation attached to an alkoxy anion.

TABLE 2. CO STRETCHING FREQUENCIES OF CYCLIC KETONES $(CH_2)_nCO$

n	$\nu(C{=}O)$
1[a]	2130 cm^{-1}
2 (calc.)	~1815 cm^{-1}
2[b] (found)	1813 cm^{-1}
3[c]	1775 cm^{-1}
4[c]	1740 cm^{-1}
5[c]	1710 cm^{-1}

[a] L. G. Drayton and H. W. Thompson, *J. Chem. Soc.* 1416 (1958).

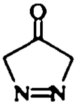
[b] This work.

[c] D. H. Wiffin and H. W. Thompson, *J. Chem. Soc.* 1005 (1946).

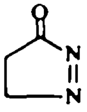
The UV spectrum of the cyclopropanones **1**–**4** all show an n,π* transition near 3300 Å. It is interesting to note that this band falls between that of ketenes[38a] and alkyl ketones[38b] (3800–3400 Å) *but is closer to the value for ketenes*. A formal analogy of the properties of ketenes and cyclopropanones is possible. Indeed, the chemistry of cyclopropanone is much more similar to that of ketene than it is to that of cyclobutanone.

Definitive evidence[39] for the ring-closed form of cyclopropanone in the vapor phase has been obtained from the microwave spectrum of **1**.

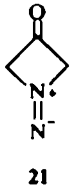
The mechanism of the photochemical formation of **4** has been discussed.[17] Although the addition of diazomethane to ketenes is formally a simple methylene transfer reaction, the mechanism is far from clear since the decomposition of azo compounds to yield carbenes generally requires either high temperature, or a catalyst.[30] Although 1,3-cycloadditions of diazomethane and ketene to yield **19**, **20** or **21** may occur, that any of these compounds should spontaneously evolve nitrogen requires documentation. Indeed, compound **22** was found* to be exceedingly stable to thermolysis.



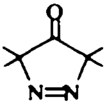
19



20

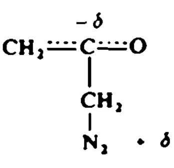


21



22

It may be, therefore, that a zwitterion intermediate such as **23** is formed.



$$\overset{-\delta}{CH_2 \cdots C \cdots O}\quad CH_2N_2^{+\delta}$$

23

* See footnote * on page 6020

It should also be pointed out that the addition of diazomethane to heterocumulenes may be a general method of generating small ring carbonyl compounds.[40]

EXPERIMENTAL

IR spectra were taken on a Perkin Elmer 137 spectrometer or a Perkin Elmer 421 grating spectrometer. NMR spectra were taken on a Varian A-60 or A-60A Analytical High Resolution NMR Spectrometer. Chemical shifts are reported in δ (ppm) from internal TMS (δ 0·00) or from internal CH_2Cl_2 (δ 5·30) unless specified. Mass spectra were taken on a Hitachi Perkin Elmer RMU-6D Mass Spectrometer. VPC was performed on an aerograph A90P gas chromatography. Elemental Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Unless specified, yields are based on NMR integrations of product absorption versus CH_2Cl_2. All commercial chemicals were reagent quality.

Preparation of cyclopropanone (**1**). Ketene was prepared by pyrolysis of acetone in a ketene generator[41a] and was collected at −130° (pentane: liq. N_2 slurry). One bulb to bulb distillation on the high vacuum line (−78° to −130°) gave essentially pure ketene which was stored at −78° until needed.

Ketene was measured for reactions by distilling a sample into a receiver graduated in ml and connected to a conventional vacuum line. In one example ketene (2 ml at −130°) was distilled into a calibrated tube and then into a receiver containing methanol (2 g) and CH_2Cl_2 chloride (5 ml). The receiver was removed from the line under N_2 and maintained at −95° (acetone: liq. N_2 slurry) until the highly exothermic reaction was over.[42]* By measuring the ratio of MeOH to AcOMe in the final solution by NMR the weight of ketene measured can be calculated (ca 13 mmoles per ml).

Diazomethane was prepared by a modified procedure of Closs and Coyle.[31] Best results were obtained as follows.

To a rapidly stirred mixture of CH_2Cl_2 (75 ml) and KOH (25 g) dissolved in water (to make 50 ml) and cooled to 0° was added N-methylnitrosourea[41b] (10 g, 0·1 mole). Addition took about 5 min. As soon as the solid had dissolved the two phase system was freeze dried by cooling to −78°. The organic layer was decanted from the solid aqueous phase and stored at −78° over KOH pellets. The diazomethane soln was standardized by the benzoic acid method[41b,c] and found to be 1·0 to 1·2M in diazomethane.

Ketene (ca. 65 mmoles) was distilled into an elongated flat bottom reaction vessel containing a stirring bar. The reaction vessel and ketene were removed from the vacuum line at −130° and treated with a cold (−78°)* CH_2Cl_2 soln (70 ml) of diazomethane[31] (1·0 to 1·5 moles, 20–30 mmoles). Rapid reaction occurs as evidenced by the rapid evolution of N_2 and disappearance of the yellow color of diazomethane. The reaction vessel was connected to the vacuum line and the ketene[41a] removed at −78°.

When the pressure in the system was reduced to less than 1 mm, the soln of cyclopropanone was flash distilled into a receiver cooled to −195°. The resulting soln of cyclopropanone can be stored at −78° for several days and contains **1** in concentrations of 0·5 to 0·8M.† The yield of **1** varies from 50 to 70% based on diazomethane. Cyclopropanone shows the following spectral properties: IR $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3045 (cyclopropane CH), 1813 (C=O stretch, strained); NMR (CH_2Cl_2) δ 1·65 (s), ultraviolet $\lambda_{max}^{CH_2Cl_2}$ 310 mμ ($\varepsilon \sim 23$), 330 mμ (sh, $\varepsilon \sim 15$).

Polymerization of **1** *to polycyclopropanone* (**15**). A soln of **1** in methylene chloride on warming to room temperature produces a polymeric material which can be isolated as a white solid by evaporation of the solvent. The polymer possesses the following properties: infrared $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 1130 (C–O stretch), 1050, 980 and 950 (cyclopropanone C–C stretch); NMR (CH_2Cl_2) δ 0·9 (broad singlet); molecular weight, 3000–4000.‡

Preparation of 1-*hydroxy*-1-*methoxycyclopropane* (**13a**) *and* 1-*methoxy*-1-*acetoxycyclopropane* (**13b**). A cold (−95°) soln of ketene (40 mmoles) in CH_2Cl_2 (5 ml) was treated with diazomethane (10 mmoles)

---

* *CAUTION*: At higher temperatures (−78°) and without dilution, ketene and methanol can react violently.

Ketene has a vapor pressure of ca. 50 mm at −78°. Once the air was removed from the vacuum system, the system was isolated from the pump and the ketene was allowed to distill into traps at −95°, −130°, and −195°. Efficient stirring of the ketene, cyclopropanone solution makes this process faster.

† The concentration of **1** was measured by converting a sample to its hemiketal with methanol and integrating the area of the hemiketal peak (δ 0·8) relative to methylene chloride (δ 5·30).

‡ The authors are grateful to Dr. Eugene Magat, of the E. I. duPont Company for this measurement. This compares favorably with the value found in ref 40.

in CH_2Cl_2 (10 ml) at −95°. An NMR spectrum at −50° of the resulting soln showed an 89% yield of cyclopropanone (s, δ 1·65). Addition of one equivalent of MeOH to the NMR tube converted **1** quantitatively to **13a** (s, δ 0·8). Upon warming, **13** slowly (5 min) disappeared while a new broad absorption developed at δ 1·1 also in quantitative yield. No AcOMe could be detected in the NMR (5% or more could have easily been observed). The remaining soln was treated with MeOH (0·44 ml, 11 mmoles) for 1 hr at −78 then warmed to 25°. The resulting soln was concentrated and analyzed by VPC on a 4 ft. 20% 1,2,3-triscyanoethoxypropane on Chromosorb P (βββ) column at 150° (1 ml/sec flow of He): this is the standard flow rate in the following sections. The major product (retention time 3 min) was collected and identified as **13b** by the following spectral properties: IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 2883 (CH_3O–), 1740 (C=O), 1240 (acetate); NMR (CCl_4) δ 1·08 (broad s, 4H), 2·09 (s, 3H), 3·48 (s, 3H), mass spec, m/e (%), 115 (3), 88 (12), 71 (7), 57 (13), 43 (100, Ac^+) 28 (22).

Reaction of **1** *with diazomethane; cyclobutanone* (**14**). Cyclopropanone (6·1 mmoles in 11 ml CH_2Cl_2) was reacted with diazomethane (8·8 mmoles) in CH_2Cl_2 (8 ml) at −95. After warming to room temp and removing the solvent by distillation, **14** was obtained in 90% yield (estimated by VPC on a 10 ft, 20% βββ column at 115° using cyclopentanone as an internal standard)

Unsuccessful attempts to prepare 1,4-adducts of **1**. Compound **1** (5 mmoles) in CH_2Cl_2, 10 ml) was allowed to react with furan (50 ml) overnight at 25°. The NMR showed a broad singlet at δ 0·9 to 1·0 (polymer). The concentrated soln was resolved into many components on a 4 ft. 20% βββ column at 155°. Only one component was present in sufficient quantity to identify as propionyloxyacetone by comparison with a known sample.

When acetyl chloride was added to inhibit polymerization no furan adduct was detected after 3 days. Slow polymerization of **1** occurred during this time. Similar results were obtained with cyclopentadiene.

Preparation of methylcyclopropanone (**2**). In a typical preparation, ethylnitrosourea* (5 g 43 mmoles) was added to a magnetically stirred mixture of CH_2Cl_2 (40 ml) and KOH aq (12·5 g in enough water to make 25 ml) cooled to 0°. The resulting mixture was cooled to −78° and the red soln of diazoethane decanted from the frozen aqueous layer and stored at −78° over KOH pellets.†

To ketene (8 ml, 100 mmoles) at −130° was added diazoethane (21 ml) prepared as described above. N_2 was evolved and the soln faded to a pale orange. The excess ketene was removed at −78° on the high vacuum line and the resulting soln flash distilled to give an 0·4M soln of **2** in CH_2Cl_2 (NMR). **2** showed the following spectral properties: IR $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 1822, 1850 (strained, C=O); NMR (CH_2Cl_2) δ 1·85–2·1 (m, 1H), 0·9–1·8 (complex, 3·3–3·9H); UV $\lambda_{max}^{cyclohexane}$ 330 mμ. On addition of methanol the UV and IR absorptions disappeared. The NMR of the resulting hemiketal **2** showed a complex absorption at δ 1·05 and a multiplet at δ 0·3 in the relative areas of (6·2–7·3 to 1). The methyl hemiketal of **2** was formed in 85 to 95% yield.

Preparation of 2,2-dimethylcyclopropanone (**3**).‡ Dimethylketene was prepared by pyrolysis of tetramethyl-1,3-cyclobutanedione over a hot filament in an apparatus described by Hanford and Sauer.[18] The dimethylketene was collected and stored at −78°. It was stable at −78° for prolonged periods of time and dimerized only slowly at 0°. The product collected from the generator contained as much as 10% tetramethylethylene along with lesser amounts of higher boiling materials. One contaminant appeared to be 2,4-dimethyl-1-penten-3-one from the NMR of crude product. The receiver for the dimethylketene was connected directly to the high vacuum line and the material was distilled into the system as it was needed. The amount of dimethylketene used in a reaction was measured by distilling it into a cold finger of known volume at −78°. A weighed amount of methanol was then added and after warming slowly to room temp the ratio of remaining MeOH to methyl isobutyrate was measured by NMR (ca. 15 mmoles per ml at −78°).

Compound **3** was readily handled on a conventional vacuum line. Dimethylketene was stored on the line at −78°. In a typical preparation a reaction vessel was connected to the line and dimethylketene (2·1 g, 30 mmoles) was distilled into a calibrated cold finger. The dimethylketene was diluted with CH_2Cl_2 (5 ml) and the reaction vessel was removed from the line under N_2 at −78°. Addition of diazomethane (15 mmoles) in cold CH_2Cl_2 (−78°, 15 ml) produced immediate evolution of N_2 and **3** was found in high

---

* Ethylnitrosourea was prepared according to the procedure of *Org. Syn.*, Col. Vol II, p. 461, for methylnitrosourea. Ethylamine was substituted for methylamine.

† Diazoethane should be prepared fresh before use since it is known to be less stable than diazomethane.

‡ *CAUTION: Care must be taken to keep dimethylketene from contact with oxygen since it readily forms an explosive peroxide.*

yield (>90%, NMR). The resulting soln was transferred under N_2 to a round bottomed flask containing a magnetic stirrer and connected to the vacuum line. The system was evacuated to less than 0·1 mm and the excess dimethylketene removed by co-distillation with CH_2Cl_2 at −45° (chlorobenzene slurry). When the volume had been reduced to ca. 2 ml distillation was stopped and CH_2Cl_2 (5 to 10 ml) was added. The resulting soln of 3 contained small amounts of dimethylketene (δ 1·55), tetramethylene (δ 1·60), and dione **6** (δ 1·28).

Compound 3 shows the following spectral properties. IR, $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3050 (C—H stretch, cyclopropane), 1815 (C=O) stretch, strained, 1380 1387 (doublet, *gem*-dimethyl), NMR (CH_2Cl_2) δ 1·20 Pr (s, 6H), 1·40 (s, 2H); ultraviolet $\lambda_{max}^{CH_2Cl_2}$ 337 mμ (ε = 27)

C^{13} *Satellites of* 3. A soln of 3 prepared as described above and concentrated to ca. 2 ml, was distilled into two NMR tubes which were sealed. The first tube contained a soln of 3 (14 mole%) in CH_2Cl_2 and the second tube contained a 42 mole % soln of 3 in the same solvent (measured by NMR). The NMR at high amplitude of each tube showed small but reproducible peaks separated by 130 c/s and 160 c/s symmetrically disposed about the methyl and methylene hydrogens of 3 respectively. These peaks were assigned to the C^{13} satellites of 3.

Preparation of **16**: *1-methoxy-1-hydroxy-2,2-dimethylcyclopropanone*. Addition of excess MeOH to a soln of 3 produces the methyl hemiketal **16** of 3 in quantitative yield (analysis by NMR). **16** shows the following spectral properties: IR, $\lambda_{max}^{CCl_4}$ (cm^{-1}) 3330 (OH stretch), 2850 (—OMe), 1150 (C—O—C, broad); NMR (CH_2Cl_2) δ 0·47 (A of AB, J = 5 c/s, 1H), 0·55 (B of AB, J = 5 c/s, 1H), 1·12 (s, 3H), 1·17 (s, 3H), 3·41 (s, 3H), 3·85 (s, 1H); mass spec m/e 116 (M^+, $C_6H_{12}O_2$)

Preparation of 2,2-dimethylcyclobutanone (**18a**) *and 3,3-dimethylcyclobutanone* (**18b**). A CH_2Cl_2 soln (20 ml) of dimethylketene (10·6 mmoles) and diazomethane (17·4 mmoles) in CH_2Cl_2 (20 ml) were allowed to react at −78°. The IR showed peaks of ca. equal intensity at 1820 (3), 1785 (cyclobutanone) and 1720 (acetone) cm^{-1}. The soln remained yellow on addition of more diazomethane (8·7 mmoles in 10 ml of CH_2Cl_2). The resulting soln was concentrated by distillation through a short column and the residue was analyzed by VPC on a 10 ft βββ column at 100°. Two cyclobutanones **18a** and **18b** were formed in the ratio of 1:3 and were identified by their spectral properties: 2,2-dimethylcyclobutanone (**18a**):[42] IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 1785 (C=O), 1380, 1365 (*gem*-dimethyl); NMR (CCl_4) δ 1·68 (s, 6H), 1·78 (A of A_2B_2, 2H), 3·00 (B of A_2B_2, 2H); mass spec, m/e 98 (M^+, 23%), 70 (C_5H_{10}, 98%), 70 (metastable (98 83), 56 (98%), 55 (66%), 50·5 (metastable, 98 70), 43·3 (metastable, 70 55), 42 (71%), 41 (100%), 39 (50%), 30 (metastable, (56 41). 3,3-dimethylcyclobutanone (**18b**): IR $\lambda_{max}^{CCl_4}$ 1785 cm^{-1} (C=O); NMR (CCl_4) δ 1·38 (s, 6H), 2·73 (s, 4H); mass spec. m/e 98 (M^+, 3·3%), 83 (2%), 70 (79%), 56 (100%), 55 (36%), 42 (56%), 41 (61%), 39 (33%), 30 (metastable, 56–41).

Preparation of tetramethylcyclopropanone (4) *and its hemiketal*, 7. Compound 6 (50 g) in CH_2Cl_2 (250 ml) was irradiated for 4 hr* in a Pyrex vessel using a 450 watt Hanovia immersion lamp. The lamp was cooled by circulating a 50% $NiSO_4$ aq† through the Pyrex lamp jacket and a 20 ft copper heat exchange coil immersed in ice. After replacing the lamp jacket with a large stopper, the soln of 4 and 6 was cooled to −78° to precipitate most of the unphotolysed dione 6. The CH_2Cl_2 soln was separated from the solid dione by a siphon and concentrated to ca. 15 ml by slow vacuum distillation (200 mm) at ca. 10°. The remaining soln was flash distilled into a receiver at −78°.‡ This soln contained **4** along with small amounts of dione **6**, tetramethylethylene and dimethylketene. Compound **4** showed the following spectral properties: NMR, δ 1·09 (s); IR $\lambda_{max}^{CH_2Cl_2}$ 1843, 1823 cm^{-1} strained C=O; UV $\lambda_{max}^{CH_2Cl_2}$ 350 mμ. Addition of MeOH to **4** converted it rapidly to 7 identical with authentic material[17,34]

Preparation of the furan adduct **8**. To a soln of **4** (ca 10%) in pentene was added 5 ml of furan at −78°. The resulting soln was warmed to 25° and showed no IR absorption at 1843 cm^{-1} characteristic of **4**. The soln was concentrated to an oil under vacuum and analyzed by VPC on a 6 ft silicone gum rubber column at 75°. A product was isolated with retention time and IR spectrum identical to that of authentic 1:1 adduct (**8**).[22,24]

Preparation of **9**. A soln of **4** (ca. 7%) in toluene (15 ml) was treated with diazomethane until a yellow

---

* The formation of **4** was followed by infrared. **4** shows a characteristic doublet at 1843 and 1823 cm^{-1} which reaches a maximum concentration after 4 hours.

† This solution in pyrex transmits light between 300 and 340 mμ with a transmittance maximum at 320 mμ.

‡ All operations with **4** were done under a nitrogen atmosphere since **4** and dimethylketene are both sensitive to oxygen.

color persisted. The resulting soln was concentrated by distillation to a few ml and analysed by VPC on a 10 ft 1,2,3-tris-(β-cyanoethoxy) propane column (βββ) at 150°. The major product was identified as 9 by its spectral properties: IR, $\lambda_{max}^{CCl_4}$ (cm^{-1}), 1790 (C=O), 1390, 1378 (*gem*-dimethyl); NMR δ 1·05 (s, 3H), 1·18 (s, 3H), 2·72 (s, 1H); mass spec. *m/e* 126 (M^{+}), 84 ($C_6H_{12}^{+\cdot}$), 70 ($C_4H_6O^{+}$), 69 ($C_5H_9^{+}$), 56·7 (metastable 84→69). No 2,2,4,4-tetramethylcyclobutanone could be detected by VPC analysis on the crude reaction mixture[42]

Reaction of hemiketal 7 with furan to yield the adduct 9. Compound 7 (1 g) was refluxed in furan for one week and left at 25° for 4 days before removing the furan under vacuum. A small amount of 1:1 adduct of 4 and furan was isolated by prep. VPC on a 6 inch SE 30 column at 100° and identified by comparison of its retention time, infrared and mass spectrum with authentic material 9

REFERENCES

[1] Taken in part from the dissertation of W.B.H. submitted in partial fulfillment of the requirements for the Ph.D. degree, Columbia University, 1967

[2] Paper VII: N. J. Turro, S. S. Edelson, J. R. Williams and T. Darling, *J. Am. Chem. Soc.* **90**, 1926 (1968).

[3] [a] R. Jacquier and R. Fraisse, *Bull. Soc. Chim. Fr.* 559 (1956).
[b] J. E. Hodgkins and R. J. Flores, *J. Org. Chem.* **28**, 3356 (1963).
[c] M. Jacobson, M. Beroza and R. T. Yamamoto, *Science*, **139**, 48 (1963)
[d] J. Meinwald, M. Beroza and R. T. Yamamoto, *J. Org. Chem.* **30**, 1038 (1966)

[4] [a] R. Breslow, J. Posner and A. Krebs, *J. Am. Chem. Soc.* **85**, 234 (1963).
[b] A. S. Kende, *Org. Reactions* **11**, 261 (1960),
[c] H. H. Wasserman and D. C. Clagett, *Tetrahedron Letters* 341 (1964)

[5] L. Wolff, *Liebigs Ann.* **260**, 79 (1890); L. Wolff, *Chem. Ber.* **26**, 2220 (1893); L. Wolff, *Liebigs Ann.* **288**, 1 (1895); M. Conrad and R. Krieshgauer, *Chem. Ber.* **29**, 1047 (1896).

[6] J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.* 1201 (1954).

[7] J. D. Roberts, *Molecular Orbital Calculations*, p. 56. Benjamin, New York, N.Y. (1962)

[8] R. Hoffman, *J. Am. Chem. Soc.* **90**, 1475 (1968).

[9] J. Aston and J. Newkirk, *Ibid.*, **73**, 3900 (1951); A. W. Fort, *Ibid.* **82**, 4979 (1962).

[10] N. J. Turro and W. B. Hammond, *Ibid.* **87**, 3258 (1965)

[11] G. Stork and I. J. Borowitz, *Ibid.* **82**, 4307 (1960).

[12] H. O. House and W. F. Gilmore, *Ibid.* **83**, 3972, 3980 (1961).

[13] H. O. House and H. W. Thompson, *J. Org. Chem.* **28**, 164 (1963)

[14] N. J. Turro, W. B. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.* **87**, 2774 (1964)

[15] S. S. Edelson, J. Williams, T. Darling and N. J. Turro, unpublished results

[16] For evidence pertaining to this intermediate see Ref. 1c

[17] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers and G. F. Vesley, *J. Am. Chem. Soc.* **87**, 2613 (1965).

[18] W. B. Hammond and N. J. Turro, *Ibid.* **88**, 2880 (1966).

[19] H. H. Wasserman and D. C. Clagett, *Ibid.* **88**, 5368 (1966)

[20] For a review of these reactions see N. J. Turro, *Molecular Photochemistry*, p. 224. Benjamin, New York, 1965).

[21] R. H. Hasek, P. G. Gott and J. C. Martin, *J. Org. Chem.* **31**, 1931 (1966).

[22] H. C. Richey, J. M. Richey and D. C. Clagett, *J. Am. Chem. Soc.* **86**, 3906 (1964)

[23] I. Haller and R. Srinivasan, *Ibid.* **87**, 1144 (1965); *Canad. J. Chem.* **43**, 3665 (1965).

[24] R. C. Cookson, M. J. Nye and G. Subrahmanyan, *Proc. Chem. Soc.* 144 (1964).

[25] W. B. Hammond, Ph.D. Dissertation, Columbia University, New York, N.Y. (1967)

[26] W. B. Hammond, R. Southam and S. Edelson, unpublished results

[27] W. L. Mock, Ph.D. Dissertation, Harvard University, Cambridge, Massachusetts, 1965.

[28] P. Lipp, J. Buckremer and H. Seeles, *Liebigs Ann.* **499**, 1 (1932).

[29] N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.* **88**, 3672 (1966).

[30] B. Eistert, *Newer Methods of Organic Chemistry*. Interscience, New York, N.Y. (1908).

[31] C. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.* **87**, 4270 (1965).

[32] J. Jaz and E. Denis, *Bull. Soc. Chim. Belges* **75**, 845 (1966).

[33] W. T. Brady and B. M. Holifield, *Tetrahedron* **23**, 4251 (1967).

[34] N. J. Turro, W. B. Hammond, P. A. Leermakers and H. T. Thomas, *Chem. & Ind.* 990 (1965)

[35] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 2046 (1965).

[36] W. B. DeMore, H. O. Pritchard and N. Davidson, *J. Am. Chem. Soc.* **81**, 5874 (1959); see also, A. Kende, Ph.D. Dissertation, Harvard University, Cambridge, 1956, A. Ohno, D. J. Grosse and R. E. Davis, *Tetrahedron Letters* 952 (1968).

[37] N. Miller and D. E. Pritchard, *J. Chem. Phys.* **31**, 768, 1471 (1959).

[38] [a] G. C. Landry, *J. Chem. Phys.* **21**, 353 (1924), R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J. Chem. Soc.* 1533 (1933);
  [b] R. A. Holdroy and F. E. Blacet, *J. Am. Chem. Soc.* **79**, 4830 (1957);
  [c] N. J. Turro and R. M. Southam, unpublished results; E. M. Kosower, *J. Chem. Phys.* **38**, 2813 (1963).

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

[40] For example, see S. E. Schafsma, H. Steinberg and T. J. deBoer, *Rec. Trav. Chim.* **84**, 113 (1965), D. E. Mulligan and M. E. Jacox, *J. Chem. Phys.* **36**, 2911 (1962). J. C. Sheehan and P. T. Izzo, *J. Am. Chem. Soc.* **71**, 4059 (1949); S. Rossi and S. Maiorana, *Tetrahedron Letters* 263 (1966).

[41] [a] W. E. Hanford and J. C. Sauer, *Organic Reactions* 3, 136 (1946);
  [b] F. Arndt, *Org. Syn.* Col. Vol. II, 461 (1943);
  [c] F. Arndt, *Ibid.* Col. Vol. II, 165 (1943).

[42] J. M. Conia and J. Salaun, *Bull. Chem. Soc. Fr.* 1957 (1964)