cyclopropane: $-\Delta S°$ for its complex formation is in fact much smaller than the values observed for both monocyclic and bicylic cyclopropanes; it is also roughly equal to those observed for alkylbenzenes. The frequency shift for phenylcyclopropane is larger than for benzene.[8b] Hence, the cyclopropyl group appears to be an electron-donating group. This electron-donating ability of the cyclopropyl group seems to be smaller than that of the isopropyl group from the linear relation between the frequency shifts and the Hammett $\sigma_m + \sigma_p$ constants of the substituents on benzene ring.[33]

(33) E. Ōsawa, T. Kato, and Z. Yoshida, *J. Org. Chem.*, **32**, 2803 (1967).

The entropy contribution to the complex formation seems to be larger in the case of phenylcyclopropane than for isopropylbenzene, though the difference is small. This may suggest that there is a conjugation of the cyclopropyl group with the phenyl group, the degree of conjugation being smaller than the one of a vinyl group. This trend may correspond to the results observed in the dissociation constants,[34] the ultraviolet spectra,[2b,35] and the proton magnetic resonance spectra[4d] of the phenylcyclopropanes.

(34) H. Charton, *J. Chem. Soc.*, 1205 (1964).
(35) W. W. Robertson, J. F. Music, and R. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5260 (1950).

Cyclopropanones. XII. Cycloaddition Reactions of Cyclopropanones[1]

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Abstract: Some cycloaddition reactions of 2,2-dimethylcyclopropanone (**3**) and the alkylcyclopropanones (**2** and **4**) are reported. Cycloadditions of the $3 + 4 \rightarrow 7$ type are observed with cyclic conjugated dienes; however, $3 + 2 \rightarrow 5$ and $2 + 2 \rightarrow 4$ cycloadditions occur when **3** is treated with dipolarophiles. The scope and mechanisms of these reactions are discussed.

Cycloaddition reactions[6] have received wide attention because of their theoretical,[7] mechanistic,[8] and synthetic[9] importance. Huisgen[7a,b] has classified cycloadditions according to the number of new σ bonds formed, the ring size, and the number of ring members contributed by each addend. The Diels–Alder reaction is thus a $4 + 2 \rightarrow 6$ cycloaddition and most 1,3-dipolar cycloadditions are of the $3 + 2 \rightarrow 5$ type.[10]

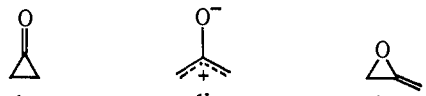
It is relatively rare for a single molecule (or class of molecules) to undergo more than one or two different types of cycloaddition reactions. We report here the cycloaddition reactions of some cyclopropanones and, in particular, 2,2-dimethylcyclopropanone (**3**), a molecule which undergoes an unusually large number of cycloaddition reactions under mild conditions.

Results

Preliminary accounts of this work have indicated the scope of cycloaddition reactions of some alkylcyclopropanones.[1a,11] Tautomers of the type **1a–c** must be considered in discussing the cycloaddition reactions of cyclopropanones. Although tautomers **1b** and **1c**

(1) (a) Part XI: N. J. Turro and J. R. Williams, *Tetrahedron Letters*, 321 (1969). (b) The authors thank the Air Force Office of Scientific Research (Grants AFOSR-66-1000 and AFOSR-68-1381) for their generous support of this work. A gift from the Upjohn Company is also gratefully acknowledged.
(2) Alfred P. Sloan Fellow, 1966–1970.
(3) National Science Foundation Trainee, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–1969.
(4) National Institutes of Health Postdoctoral Fellow (Grant 1-F2-GM-38, 274-01), 1967–1968.
(5) National Science Foundation Predoctoral Fellow, 1964–1967.
(6) For excellent general reviews of the definitions, classifications, and characteristics of cycloadditions see: (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **7**, 321 (1968); (b) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 739; (c) J. Hamer, "1,4-Cycloaddition Reactions," Academic Press, New York, N. Y., 1967; (d) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, Inc., New York, N. Y., 1967.
(7) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046, 4388 (1965); (b) K. Fukuii and H. Fujimoto, *Bull. Chem. Soc. Japan*, **40**, 2018 (1967); (c) L. Salem, *J. Am. Chem. Soc.*, **90**, 553 (1968); (d) M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1967); (e) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (f) R. B. Woodward, Special Publication No. 21, The Chemical Society, London, 1967; (g) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).
(8) (a) 1,3-Dipolar cycloadditions: R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963); *J. Org. Chem.*, **33**, 2291 (1968); *Bull. Soc. Chim. France*, 3431 (1965); ref 7f, p 51; (b) Diels–Alder: J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967); K. Alder and M. Schukmacher, *Fortschr. Chem. Org. Naturstoffe*, **10**, 21 (1953); (c) 1,2–1,2 cycloadditions: P. D. Bartlett, *Science*, **159**, 833 (1968); (d) cycloadditions of cyclopropanones and Favorskii intermediates: A. W. Fort, *J. Am. Chem. Soc.*, **84**, 4979 (1962); R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *ibid.*, 144 (1964); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc., C*, 473 (1967).
(9) (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. Forsch.*, **7**, 445 (1967); O. L. Chapman, "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 200.
(10) One must be careful not to confuse this nomenclature with that of Woodward and Hoffmann[7a] who have classified cycloadditions on the basis of the total number of π electrons involved in the ring-making step.
(11) (a) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **87**, 2774 (1965); (b) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966); (c) N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *ibid.*, **90**, 1926 (1968); (d) N. J. Turro and S. S. Edelson, *ibid.*, **90**, 4499 (1968).

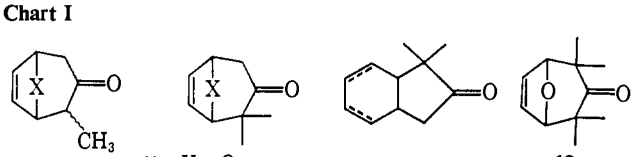
may not be expected to exist in measurably significant concentrations compared to **1a**, each of the tautomers may have sufficient reactivity to be important in reactions with particular substrates. Furthermore, the energy contents of **1b** and **1c** may be sufficiently comparable to **1a** that rapid interconversion of all three tautomers is conceivable.[12-14]



1a 1b 1c

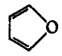
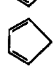
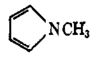
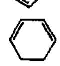
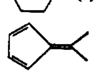
Reactions of Cyclopropanones with Conjugated Systems. Methylcyclopropanone (**2**), 2,2-dimethylcyclopropanone (**3**), and tetramethylcyclopropanone (**4**) undergo 4 + 3 → 7 cycloaddition reactions with certain cyclic conjugated dienes (Chart I and Table I). No comparable reactions of cyclopropanone (**1**) have been observed to date.

Chart I



10a, X = O; b, X = CH_2 11a, X = O; b, X = CH_2; c, X = NCH_3; d, X = CH_2CH_2; e, X = C=C$(CH_3)_2$ 12 13

Table I. Reactions of **2**, **3**, and **4** with Conjugated Dienes[a]

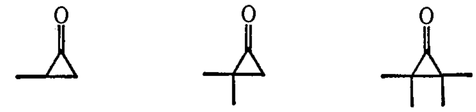
Cyclopropanone	Diene	Adduct(s)
2	 (5)	**10a**
2	 (6)	**10b**
3	5	**11a**
3	6	**11b**
3	 (7)	**11c**
3	 (8)[b]	**11d, 12**
3	 (9)	**11e**
4	5	**13**

[a] Reactions run at room temperature or in refluxing CH_2Cl_2 for 1-2 days. No reaction under these conditions was detected (nmr) for anthracene, thiophene, 1,3-butadiene, 1,3,5-cycloheptatriene, and cyclooctetraene. [b] Only tentatively identified.

Competition kinetics were run in order to compare the relative reactivities of cyclopropanones toward different dienes and to note the relative reactivities of two cyclopropanones toward the same diene. Compound **3** was found to react about ten times faster than **2** with furan, while **3** reacts about three times faster with cyclopentadiene than with furan.

(12) Theoretical calculations indicate that the energy content of **1b** should be comparable to that of **1a**.[13,14] Furthermore structure **1c** is calculated[14] to be of lower energy than **1a**. Thus, low-energy barriers may connect the interconversions of **1a**, **1b**, and **1c**.

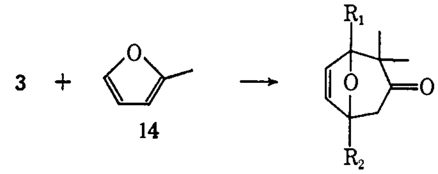
(13) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).
(14) R. Hoffman, *J. Am. Chem. Soc.*, **90**, 1475 (1968).



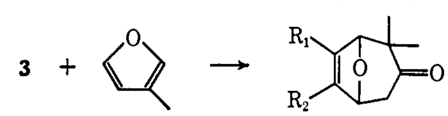
2 **3** **4**

The reactions of **3** with 2-methylfuran (**14**) and with 3-methylfuran (**16**) were studied in order to determine the directing ability of methyl on the orientation of addition. In both cases only a minor specificity was found (Chart II).

Chart II



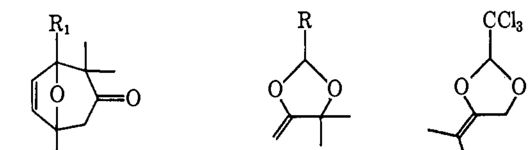
14 15a, $R_1 = CH_3$; $R_2 = H$; b, $R_1 = H$; $R_2 = CH_3$



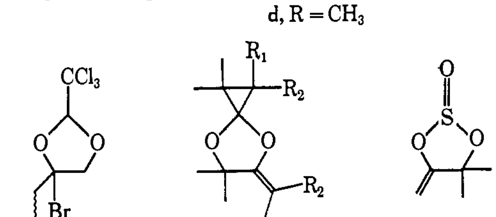
16 17a, $R_1 = CH_3$; $R_2 = H$; b, $R_1 = H$; $R_2 = CH_3$

Reaction of 3 with Dipolarophiles. Compound **3** was found to undergo 3 + 2 → 5 cycloaddition with aldehydes, SO_2 (**18**), and itself (Table II and Chart III). This reaction resembles 1,3-dipolar cycloaddition reactions.[8a,9a] Dimethylketene and 1,1-dimethoxyethylene, however, were found to undergo 2 + 2 → 4 cycloaddition to the carbonyl function of **3** to yield **25** and **26**, respectively.

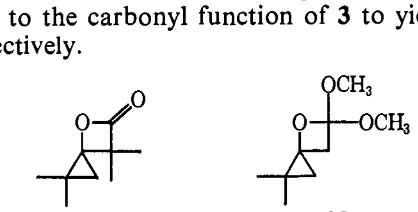
Chart III



19a, $R_1 = H$; $R_2 = CHO$; b, $R_1 = CHO$; $R_2 = H$ 20a, R = furyl; b, R = CCl_3; c, R = C_6H_5; d, R = CH_3 21



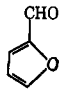
22 23a, $R_1 = R_2 = H$; b, $R_1 = R_2 = CH_3$ 24



25 26

Structural Assignments. Most of the 4 + 3 → 7 cycloadducts were characterized unambiguously on the basis of spectral data (Experimental Section), particularly the nmr data, which is summarized in Table

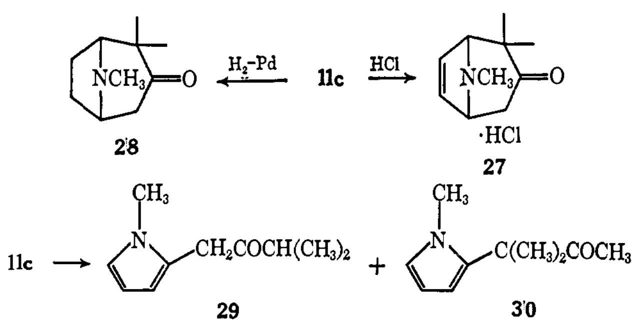
Table II. Reaction of 3 with Some Dipolarophiles[a]

Dipolarophile	Adduct(s)
	19b, 20a
CCl_3CHO	20b, 21
PhCHO	20c
CH_3CHO	20d
3	23a
SO_2	24
$(CH_3)_2C{=}C{=}O$	25
$(CH_3O)_2C{=}CH_2$	26

[a] Reactions run at room temperature or in refluxing CH_2Cl_2 for 1–2 days. No reaction under these conditions was observed (nmr) for bicycloheptadiene, CO_2, CS_2, N_2O, tetramethylallene, dimethylacetylene, phenyl isocyanate, phenylacetylene, maleic anhydride, tetracyanoethylene, 1,2-dicyanoethylene, phenyl azide, and diethyl azocarboxylate.

III. These data are quite consistent with the data for similar adducts studied by Fort[8d] and by Cookson.[8d] The tropinone derivative **11c** was characterized by formation of its HCl salt (**27**) and by hydrogenation to **28** (Chart IV). Attempts to isolate **11c** by preparative

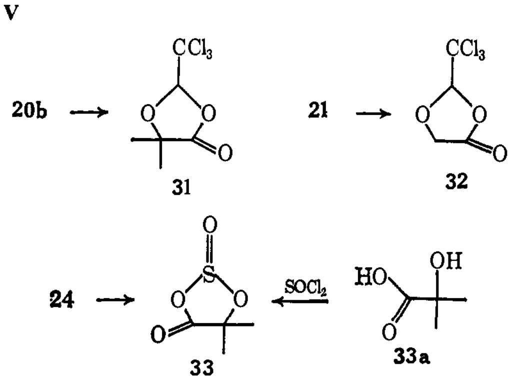
Chart IV



vapor phase chromatography resulted in formation of **29** and **30**.

The structures of the novel 3 + 2 → 5 cycloadducts **20b**, **21**, and **24** were confirmed by ozonolysis to the lactones **31**, **32**, and **33** (Chart V). The structure **33** was proved by synthesis from the α-hydroxy acid **33a** and thionyl chloride.

Chart V



The nmr spectra of adducts **20a**, **20b**, **30c**, **20d**, **23a**, and **24** all exhibited a characteristic doublet of doublets in the region from δ 3.70 to 4.66. The two doublets were separated by δ 0.33–0.50 and had coupling constants varying from 2.1 to 3.0 Hz. This doublet of doublets, which is attributed to the terminal methylene group, led to the characterization of **20a**, **20c**, **20d**,

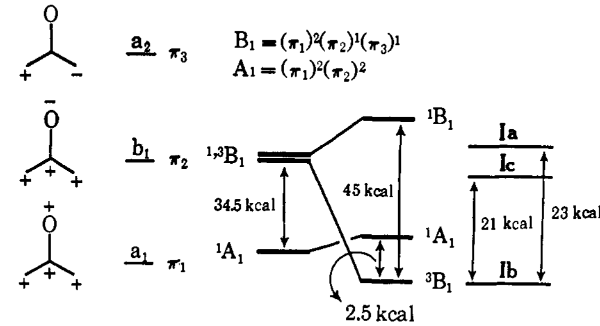
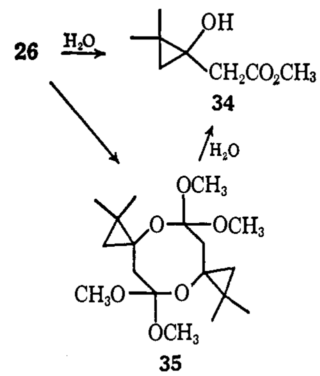


Figure 1. Orbital (left) and state (right) diagrams for **1b**. The symbols employed are those for C_{2v} symmetry with the XY plane being that of the molecule, which is assumed to be planar. Adapted from ref 14.

and **23a** by comparison to **20b** and **24**, which had been fully characterized by spectral and chemical means.

The novel ortho ester **26** was characterized by its hydrolysis to the cyclopropanol **34** (Chart VI). Compound **26** undergoes an unusual dimerization to **35**, whose structure was assigned on the basis of spectral properties and its hydrolyses to **34**.

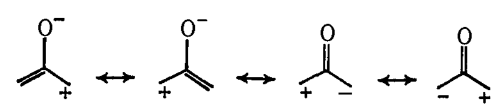
Chart VI



Attempted Reactions of 3 with Aromatic Compounds. No reaction between **3** and 1,4-diethoxybenzene, 1,4-dimethoxybenzene, 2,3,4-trimethoxy-N,N-dimethylaniline, or dimethylaniline could be detected (nmr). Only the decomposition of **3** was observed. Treatment of a solution of **3** in C_6H_6 with $BF_3 \cdot Et_2O$ also led to decomposition of **3**.

Discussion

The 4 + 3 → 7 and the 3 + 2 → 5 cycloaddition reactions of cyclopropanones seem to be best explained on the basis of an intermediate "bidentate 1,3 dipole" such as **1b**. Huisgen[8a] defines a 1,3 dipole as "a compound abc which undergoes 1,3 cycloadditions and is described by zwitterionic octet structures," *e.g.*



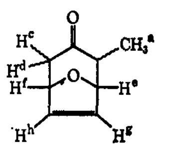
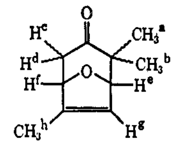
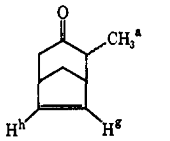
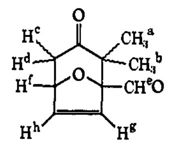
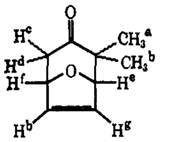
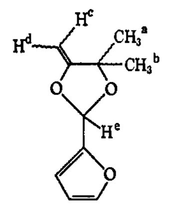
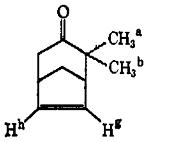
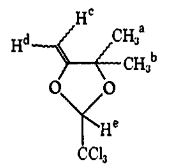
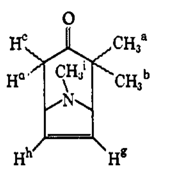
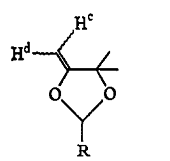
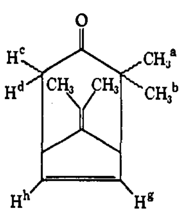
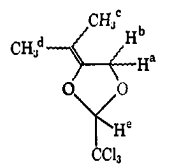
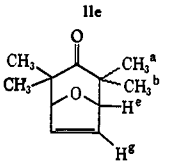
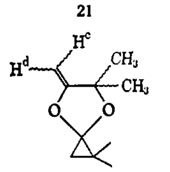
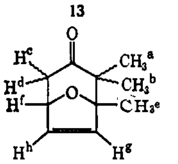
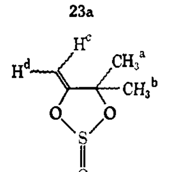
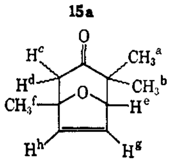
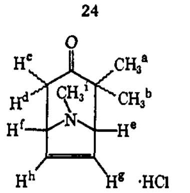
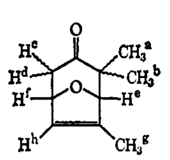
I II III IV

1b

If a transient such as **1b** is completely planar, then the four π MO's of **1b** may qualitatively correlated with those of trimethylene methane (Figure 1).[15]

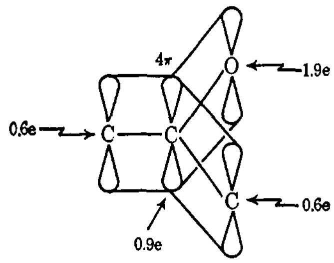
(15) J. D. Roberts, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1962, p 56.

Table III. Summary of Nmr Spectral Data

Compd	δ	Compd	δ
 10a	2 isomers: main isomer, a 0.88 (d, J = 6.8 Hz), c + d 2.37 (AB, $\Delta\nu_{AB}$ = 26.8 Hz, J_{AB} = 15.5 Hz, low-field half split J = 4.5 Hz, high-field half split J = 1.0 Hz), e 4.73 (d, J = 4.5 Hz), f 4.87 (d of t, J = 4.5 Hz, J = 1.0 Hz), g + h 6.08–6.37 (m);[a] minor isomer, a 1.22 (d, J = 7.2 Hz), e 4.54 (s), g + h 6.08–6.37 (m)[a]	 17b	a 0.95 (s), b 1.31 (s), c + d 2.43 (AB, $\Delta\nu_{AB}$ = 42.1 Hz, J_{AB} = 16 Hz, low-field half split J = 5 Hz), e 4.08 (s), f 4.78 (m), g 5.88 (m), h 1.86 (s)
 10b	2 isomers: main isomer, a 0.94 (d, J = 6.8 Hz), g + h 5.77–6.03 (m);[a] minor isomer, a 1.13 (d, J = 7.0 Hz), g + h 5.77–6.03 (m)[a]	 19b	a 1.11 (s), b 1.23 (s), c + d 2.59 (AB, $\Delta\nu_{AB}$ = 39.2 Hz, J_{AB} = 16 Hz, low-field half split J = 5 Hz, high-field half split J = 1.5 Hz), e 9.77 (s), f 5.13 (d of t, J = 5 Hz, J = 1.5 Hz), g + h 6.36 (AB, $\Delta\nu_{AB}$ = 7.75 Hz, J_{AB} = 6 Hz, low-field half split, J = 1.5 Hz)
 11a	a 0.91 (s), b 1.26 (s), c + d 2.41 (AB, $\Delta\nu_{AB}$ = 40.1 Hz, J_{AB} = 16 Hz, low-field half split J = 5.0 Hz, high-field half split J= 1.0 Hz), e 4.36 (s), f 4.89 (d of t, J = 5.0 Hz, J = 1.0 Hz), g + h 6.16–6.44 (m)[a]	 20a	a 1.42 (s), b 1.48 (s), c 3.82 (d, J = 2.5 Hz), d 4.24 (d, J = 2.5 Hz), e 6.13 (s)
 11b	a 1.00 (s), b 1.17 (s), g + h 5.95–6.25 (m)[a]	 20b	a 1.46 (s), b 1.57 (s), c 3.90 (d, J = 3 Hz), d 4.40 (d, J = 3 Hz), e 5.53 (s)
 11c	a 0.87 (s), b 1.23 (s), c + d 2.37 (AB, $\Delta\nu_{AB}$ = 34.8 Hz, J_{AB} = 16 Hz, low-field half split J = 4.5 Hz, high-field half split J = 2 Hz), g + h 5.97–6.25 (m),[a] i 2.24 (s)	 20c, R = C_6H_5 20d, R = CH_3	c 3.96 (d, J = 2.5 Hz), d 4.35 (d, J = 2.5 Hz) c 3.71 (d, J = 2.3 Hz), d 4.07 (d, J = 2.3 Hz)
 11e	a + b 1.07 (s), c + d 2.4 (m), g + h 6.15 (m)	 21	a + b 4.43–4.97 (m, appears to be AB quartet centered at 4.70 with $\Delta\nu_{AB}$ approximately 10.4 Hz and J_{AB} approximately 12 Hz; the quartet is complicated by further splitting), c 1.57 (s), d 1.75 (m), e 5.48 (s).
 13	a 0.86 (s), b 1.29 (s), e 4.23 (s), g 6.19 (s)	 23a	c 3.70 (d, J = 2.1 Hz), d 4.11 (d, J = 2.1 Hz)
 15a	a 0.94 (s), b 1.16 (s), c + d 2.39 (AB, $\Delta\nu_{AB}$ = 39.6 Hz, J_{AB} = 15.3 Hz, low-field half split J = 4.8 Hz, high-field half split J = 1.3 Hz), e 1.30 (s), f 4.80 (d of t, J = 4.8 Hz, J = 1.3 Hz), g + h 6.07 (AB, $\Delta\nu_{AB}$ = 4.08 Hz, J_{AB} = 5.7 Hz, low-field half split further)	 24	a 1.49 (s), b 1.87 (s), c 4.33 (d, J = 3.0 Hz), d 4.66 (d, J = 3.0 Hz)
 15b	a 0.88 (s), b 1.22 (s), c + d 2.32 (AB, $\Delta\nu_{AB}$ = 21.5 Hz, J_{AB} = 15.4 Hz), e 4.29 (d, J = 1.7 Hz), f 1.41 (s), g + h 6.04 (AB, $\Delta\nu_{AB}$ = 11.2 Hz, J_{AB} = 5.8 Hz, low-field half split J = 1.7 Hz)	 27	a 1.16 (s), b 1.79 (s), c 2.65 (d of d, J = 18 Hz, J = 2 Hz), d 4.05 (d of d, J = 18 Hz, J = 4 Hz), e 4.38 (s), f 4.53–4.75 (m), g + h 6.52 (m),[a] i 3.17 (s)
 17a	a 0.86 (s), b 1.20 (s), c + d 2.44 (AB, $\Delta\nu_{AB}$ = 34.5 Hz, J_{AB} = 16 Hz, low-field half split J = 5 Hz), e 4.23 (s), f 4.56 (d, J = 5 Hz), 1.81 (m), h 5.84 (m)		

[a] These multiplets all appear to be AB quartets with their chemical shifts ranging from 5.9 to 6.5, with $\Delta\nu_{AB}$ ranging from 3.0 to 4.5 Hz, and with J_{AB} ranging from 5 to 6 Hz. All the quartets are complicated by further splitting.

Burr and Dewar[13] have calculated the electron density of **1b** to be roughly as follows.



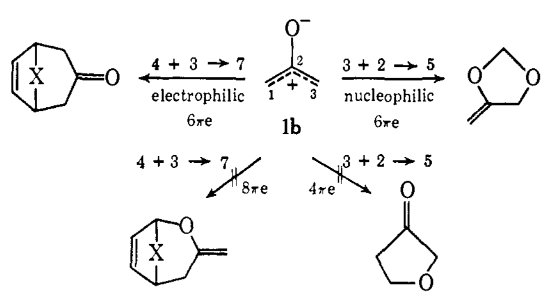
In resonance terminology major contributions should come from valence structures such as I and II above.

From Figure 1, the "zwitterion" representation of **1b** can be seen to be related to the highest filled orbital π_2. Thus, **1b** is isoelectronic with the allyl anion and the four π electrons of **1b** occupy pairwise the two lowest MO's π_1 and π_2. The greater electronegativity of oxygen over carbon causes the bulk of electron density in π_2 to be centered close to the oxygen atom.

The fact that the C_1–C_2–C_3 "dipole" carries roughly 2 electrons justifies the use of the *allylic cation* as a model to make orbital symmetry predictions for the electrocyclic reactions of **1b**. The C_1–C_2–O "dipole" on the other hand contains ~3.5 electrons and should be related to the allyl anion or radical, both of which possess the same symmetry properties as far as the highest filled MO is concerned.

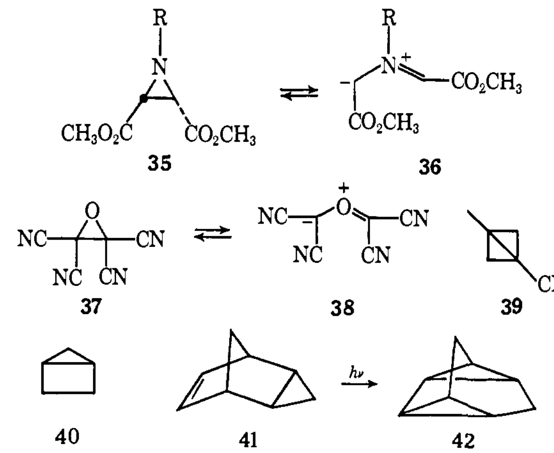
Orbital symmetry arguments[7] predict that the 4 + 3 → 7 ($C_1C_2C_3$) cycloaddition and the 3 + 2 → 5 (C_1C_2O) cycloadditions are allowed to be concerted. Correspondingly, the 3 + 4 → 7 (C_1C_2O) and the 3 + 2 → 5 ($C_1C_2C_3$) cycloadditions are forbidden to be concerted. These predictions assume that the $C_1C_2C_3$ system of **1b** is an electrophilic 2π-electron fragment and the C_1–C_2–O system is to be considered as a 4 π-electron nucleophilic fragment (Chart VII). The same conclusions, however, are derived from Longuet-Higgins level correlation diagrams.[16]

Chart VII



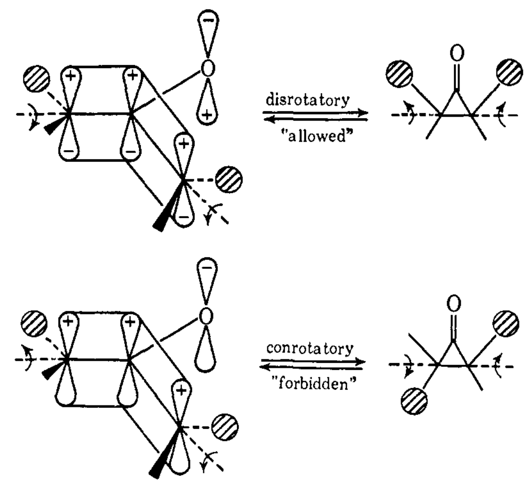
Other cycloadditions of a three-membered ring single bond to nonconjugated C=C bonds are known (Chart VIII).[17] The cycloaddition reactions of **35**[18] and **37**[19] may proceed *via* the open (4π electron) species **36** and **38**, respectively. The thermal 2 + 3 → 5 (4 electron) cycloadditions of **39**[20] and **40**[21] are formal violations of orbital symmetry selection rules. The corresponding photochemical cycloaddition reaction (*e.g.*, **41** → **42**)[22] is well established.[23]

Chart VIII



An interesting point, which may be testable when an optically active *cis–trans* isomeric pair of cyclopropanones is prepared, concerns the nature of the ring opening of **1a** to **1b** which should be a disrotatory, or 2π-electron opening (Chart IX). Since 2,2-dimethylcyclopropanone (for which ring opening generates a methyl hydrogen nonbonded interaction) reacts *faster* than methylcyclopropanone with furan, and cyclopropanone does not react at all with furan under comparable conditions, it may be that the ring opening is rate determining.

Chart IX



The ring opening of **1a** → **1a** may also be compared and correlated to the disrotatory opening of cyclopropyl cations to allyl cations,[24] a topic of considerable recent experimental[25] and theoretical[26] interest. In

(16) (a) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); (b) R. Hoffman and R. B. Woodward, *ibid.*, **87**, 2046 (1965).
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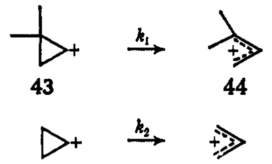
(21) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1517, 1524 (1968); *Chem. Commun.*, 391 (1965).
(22) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 3254 (1967).
(23) Review: H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).
(24) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 73, 5034 (1951).
(25) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedermann, *ibid.*, **87**, 4006 (1965); (b) C. H. DePuy, L. G. Schnack, and

this regard, it is significant that the 2,2-dimethylcyclopropyl cation (**43**) appears to ring open about 500 times faster than the cyclopropyl cation[24] (Chart X).

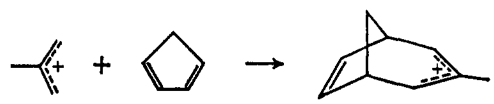
Chart X



43 44 45 46

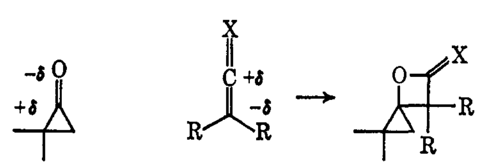
$k_1/k_2 \backsim 500$

It is also interesting to note that allylic cations have been found to undergo 3 + 4 → 7 ($2\pi + 4\pi$) cycloaddition.[17] A detailed calculation of the energy levels



and electronic states of **1b** indicates that the ground state of **1b** should be a triplet, but that a singlet state lies just a few kilocalories per mole above the ground state (Figure 1). This surprising result derived from the large singlet–triplet splitting of the degenerate B_1 configuration of **1b**, and results from the high degree of spatial overlap of π_2 and π_3. This calculation also places **1a** and **1c** at higher energies than **1b**. If the disposition of these relative levels should prove to be correct, then **1b** would have to react *via* its $^1A_1$ *excited* state in the cycloaddition reactions discussed here. The known rate of singlet–triplet interconversions are sufficiently fast to allow for rapid interconversion of $^3B_1$ and $^1A_1$.

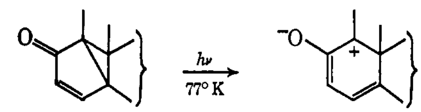
The two observed 1,2–1,2 cycloadditions across the C=O bond of **3** are formal, but not very surprising, violations of the Woodward–Hoffman cycloaddition rules. These are probably either one- or two-step polar additions initiated by nucleophilic attack on the extremely reactive carbonyl carbon.



All of the other cycloadditions fall into one of the two classes of symmetry allowed 4 + 3 → 7 or 3 + 2 → 5 reactions, except for the reaction of **3** and 1,3-cyclohexadiene which seems to produce a 3 + 2 → 5 ($2\pi + 2\pi$) adduct **12**.

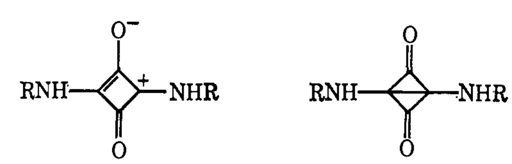
Some formal cycloaddition reactions of trimethylenemethane[27] have recently been reported,[28] but relatively little is known about the mechanisms of these reactions.

It is of interest to point out that a zwitterion related to **1b** has been proposed as an intermediate in the certain Favorskii rearrangements,[29] the reductive debromination of α,α^1-dibromo ketones[30] and the photochemical rearrangements of 2,5-cyclohexadienones,[31a–c] and other cross-conjugated dienones **13d–f**. Recently, a colored species believed to be **47**[32] was reported to be formed when lumisantanonin is irradiated at 77°K. Cyclopropenones[33] undergo a dimerization reaction formally related to formation of **23a** and **23b**.



47

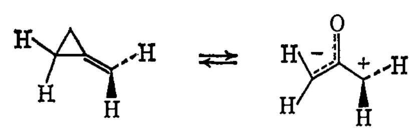
Finally, an interesting class of compounds (**48**) formally related to bicyclopropanones (**49**) may be prepared from squaric acid.[34]



48 **49**

Conclusion

It is possible to explain the 4 + 3 → 7 and 3 + 2 → 5 cycloadditions described here on the basis of a concerted or two-step reaction of the closed forms **1a** or **1c**. The correlation of product structures with those predicted from orbital symmetry arguments, the low orientational selectivity with methylfurans, and the fact that **3** reacts faster than **2** with furan seem to eliminate a rate-determining step involving **1a**. It is more difficult to find a strong argument against the participation of **1c** which is closely related to the twisted open form **1e**. However, the formation of two adducts of



1c 1e

3 and chloral can be used as evidence against structures related to **1c** if an overwhelming predominance of the form placing the positive charge on the tertiary carbon occurred.

Kinetic and stereochemical experiments to attempt to differentiate these possibilities are in progress.

J. W. Hausser, *J. Am. Chem. Soc.*, **88**, 3343 (1966); (c) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); (d) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (e) L. Ghosez, P. LaRoche, and G. Slinckx, *Tetrahedron Letters*, 2767 (1967).

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

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

(31) (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (b) K. Schaffner, *Advan. Photochem.*, 4, 81 (1966); (c) P. Kropp, *Org. Photochem.*, 1, 1 (1968); (d) J. K. Crandall and R. P. Haseltine, *J. Am. Chem. Soc.*, 90, 6251 (1968); (e) H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Letters*, 3635 (1968); (f) R. Noyoi and M. Kato, *ibid.*, 5075 (1968).

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(34) S. Skujins and G. A. Webb, *Chem. Commun.*, 598 (1968); G. Manecke and J. Gauger, *Tetrahedron Letters*, 3509 (1967); G. Maahs and P. Hegenberg, *Angew. Chem. Intern. Ed. Engl.*, **5**, 888 (1966); D. Farnum, *et al.*, *Tetrahedron Letters*, 5003 (1968).

Experimental Section

Infrared spectra were taken on a Perkin-Elmer 137 spectrometer or a Perkin-Elmer 421 grating spectrometer. Nuclear magnetic resonance spectra were taken on a Varian A-60 or A-60 A analytical high-resolution nmr spectrometer. Chemical shifts are reported in δ (ppm) from internal tetramethylsilane (δ 0.00) or from internal methylene chloride (δ 5.30) unless specified. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Vpc analyses were performed on an Aerograph Model A90P or Model 1200 gas chromatograph. The following liquid phases were used: 1,2,3-tris(2-cyanoethoxy)propane ($\beta\beta\beta$), Carbowax 20M (CWX 20M), SE 30. Chromosorb P (chrom P) and acid-washed, dimethyldichlorosilane-treated Chromosorb W (a/w dmcs chrom W) were used as solid supports. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Unless specified, yields are based on nmr integrations of product absorption *vs.* methylene chloride. All commercial chemicals used were reagent quality.

Preparation of Dimethylketene.[35] A ketene generator[36] was used to generate dimethylketene. After isobutyric anhydride was placed in the boiler, the system was evacuated to 2–3 mm and the anhydride was heated to reflux. After refluxing started, the filaments were turned on and maintained at a dull red glow. The output of the generator was fed directly into a series of three traps. The first trap was maintained at 0°, the second at −78°, and the third at −195°. After enough material had collected in trap two, the filaments and heater were turned off, and the system was flushed with N_2. Trap two was removed and the crude dimethylketene was flash distilled from room temperature to −78°. High-purity dimethylketene was the result. The material in the other traps was decomposed with MeOH. *Caution:* Oxygen must be kept away from the dimethylketene because it forms a highly explosive peroxide!!

Preparation of 2,2-Dimethylcyclopropanone (3). A cold (−78°) CH_2Cl_2 solution of CH_2N_2 was added to a twofold excess of dimethylketene (−78°). The mixture was stirred during the addition and then vacuum distilled. The distillation apparatus was flushed with N_2 whenever the distillation was interrupted. During the distillation the pot was maintained at 10–20°, the column at −10–0° and the condenser and receiver at −78°. Aliquots were removed periodically for nmr analysis. The distillation was continued until the excess dimethylketene had been removed and the resulting CH_2Cl_2 solution of **3** was at the proper concentration. Excess CH_2Cl_2 usually had to be added during the distillation. This method usually gave a CH_2Cl_2 solution of **3** of greater than 90% purity with tetramethyl-1,3-cyclobutanedione, 2,2-dimethylcyclobutanone and 3,3-dimethylcyclobutanone being the main impurities. The purity could be improved by further distillation (flash or column), but this resulted in a lower yield of **3**. The usual yield of **3** (based on CH_2N_2) is greater than 65%.

2-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (10a). A dilute (2–3%) CH_2Cl_2 solution of **2** (15 ml) was mixed with 5 ml of purified furan (~69 mmoles). After 4 days at room temperature, evaporation of the solvent followed by preparative vpc (5 ft × 3/8 in., 22% CWX 20M, chrom P, 200°, 120 cc of He/min) led to the isolation of a mixture of the two isomers of **10a**: ir, $\nu_{max}^{CCl_4}$ 1717 cm^{-1}; nmr (CCl_4–TMS), δ 0.88 (d, 2.4 H, J = 6.8 Hz), 1.22 (d, 0.6 H, J = 7.2 Hz), 1.85–2.91 (m, 3 H), 4.54 (s, 0.2 H), 4.73 (d, J = 4.5 Hz), 4.87 (d of t, J = 4.5 Hz and J = 1.0 Hz) (the combined integration of the last two peaks is 1.8 H), 6.08–6.37 (m, 2 H); the multiplet from δ 1.85–2.91 appears to contain an AB quartet centered at 2.37 with $\Delta\nu_{AB}$ = 26.8 Hz, J_{AB} = 15.5 Hz (low-field half split further J = 4.5 Hz, high-field split further, J = 1.0 Hz); the multiplet from δ 6.08–6.37 appears to be an AB quartet centered at 6.23 with $\Delta\nu_{AB}$ ~ 3 Hz and J_{AB} ~ 6 Hz (this AB quartet is complicated by further splitting); mass spectrum (75 eV), *m/e* (relative intensity) 138 (M$^+$, 35), 123 (4), 110 (6), 109 (5), 95 (16), 83 (7), 82 (83), 81 (100), 70 (10), 68 (18), 67 (15), 57 (19), 56 (24), 55 (20), 54 (34), 53 (36), 51 (15), 50 (10), 44 (15), 43 (14), 42 (15), 41 (29), 40 (15), 39 (61), 38 (12), 29 (31), 27 (68), 26 (16). *Anal.* Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.28; H, 7.53 Attempts to separate the two isomers with various vpc columns (CWX 20M, $\beta\beta\beta$, cyanosilicone, dioctyl phthalate, γ-methyl-γ-nitropimelonitrile) or by recrystallization failed.

2-Methylbicyclo[3.2.1]oct-6-en-3-one (10b). A dilute (2–3%) CH_2Cl_2 solution of **2** (15 ml) was mixed with 5 ml of cyclopentadiene (~61 mmoles). After 5 days at room temperature, evaporation of the solvent followed by preparative vpc (5 ft × 3/8 in., 22% CWX 20M, chrom P, 191 and 165°, 120 cc of He/min) led to the isolation of a mixture of the two isomers of **10b**: ir, $\nu_{max}^{CCl_4}$ 1720 cm^{-1}; nmr (CCl_4–TMS), δ 0.94 (d, ~ 2 H, J = 6.8 Hz), 1.13 (d, ~ 1 H, J = 7.0 Hz), 1.76–2.98 (m, 7 H) 5.77–6.03 (m, 2 H); the multiplet from δ 5.77–6.03 appears to be an AB quartet centered at approximately 5.90 with $\Delta\nu_{AB}$ ~ 4.2 Hz and J_{AB} ~ 5.5–6.0 Hz (the AB quartet is complicated by further splitting); mass spectrum (75 eV), *m/e* (relative intensity) 136 (M$^+$, 40), 135 (1.5), 122 (1), 121 (6), 118 (2), 117 (1), 108 (6), 107 (10), 94 (13), 93 (23), 92 (5), 91 (14), 80 (51), 79 (100), 79 (9), 77 (32), 66 (14), 65 (10), 53 (12), 51 (12), 41 (14), 40 (8), 39 (37), 26 (26). *Anal.* Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.40; H, 8.76. No attempt was made to separate the two isomers.

2,2-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (11a). A solution of **3** (1 mmole) in methylene chloride (5 ml) and furan (5 ml) were combined at room temperature. After 10 hr the cyclopropanone–furan adduct (**11a**) had formed in quantitative yield (nmr). Compound **11a** was isolated by preparative vpc on a 1-ft $\beta\beta\beta$ column at 130° and characterized by the following spectral properties: infrared, $\nu_{max}^{CCl_4}$ (cm^{-1}) 1720 (C=O), 1382, 1362 (*gem*-dimethyl); nmr (CCl_4–TMS), δ 0.91 (s, 3 H), 1.26 (s, 3 H), 2.41 (AB, 2 H, $\Delta\nu_{AB}$ = 40.1 Hz, J_{AB} = 16 Hz, (high-field half split further J = 1.0 Hz, low-field half split further J = 5.0 Hz), 4.36 (s, 1 H), 4.89 (d of t, J = 5.0 Hz, J = 1.0 Hz), 6.16–6.44 (m, 2 H, appears to be an AB quartet centered at δ 6.30 with J_{AB} ~ 6 Hz and $\Delta\nu_{AB}$ ~ 3.7 Hz; the multiplet is complicated by further splitting); mass spectrum (75 eV), *m/e* (relative intensity) 152 (M$^+$, 70), 137 (4), 124 (17), 109 (17), 95 (24), 84 (11), 83 (11), 82 (100), 81 (66), 71 (16), 70 (82), 69 (11) 68 (17), 54 (20), 53 (24), 43 (29), 42 (51), 41 (45), 39 (45), 27 (28). *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.05; H, 8.08.

2,2-Dimethylbicyclo[3.2.1]oct-6-en-3-one (11b). A mixture of 2 ml of cyclopentadiene (24.3 mmoles) and 5 ml of a CH_2Cl_2 solution of **3** (10.45 mmoles) was left at room temperature for 2 hr. After being stored overnight at −78°, the mixture was left at room temperature for another 2 hr. After the solvent was stripped off, preparative vpc (5 ft × 3/8 in., 22% CWX 20M, chrom P, 245°, 120 cc of He/min) led to the isolation of 0.53 g (35%) of **11b**: ir, $\nu_{max}^{CCl_4}$ 1714 cm^{-1}; nmr (CCl_4–TMS), δ 1.00 (s, 3 H), 1.17 (s, 3 H), 1.75–2.97 (m, 6 H), 5.95–6.25 (m, 2 H, appears to be an AB quartet centered at δ 6.1 with J_{AB} approximately 6 Hz and $\Delta\nu_{AB}$ ~ 4.5 Hz; the multiplet is complicated by further splitting); mass spectrum (75 eV), *m/e* (relative intensity) 150 (M$^+$, 94), 135 (5.7), 122 (9.1), 108 (47.3), 107 (57.2), 95 (11.1), 94 (16), 93 (100), 92 (9.9), 91 (44.2), 85 (20.4), 84 (90.8), 81 (11.7), 80 (65.4), 79 (87.8), 78 (19.7), 77 (11.7), 71 (17.3), 70 (69.5), 67 (31.6), 66 (34.0), 65 (18.4), 53 (19.4), 52 (8.7), 51 (16.0), 43 (26.2), 42 (26.6), 41 (53.7), 40 (12.3), 39 (15.4). *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.68; H, 9.40.

2,2,8-Trimethyl-8-azabicyclo[3.2.1]oct-6-en-3-one (11c). After being mixed and left at room temperature for 1 hr, a mixture of 3 ml of purified N-methylpyrrole (34 mmoles) and 25 ml of a CH_2Cl_2 solution of **3** (25 mmoles) was refluxed for 4 hr and then left at room temperature overnight. The solvent was stripped off and the residue was taken up in Et_2O. The Et_2O solution was extracted with five 10-ml portions of 1% aqueous HCl. The aqueous portions were combined, neutralized with aqueous NH_4OH, and extracted with several portions of Et_2O. These fractions were combined, dried with $MgSO_4$, and stripped of Et_2O. This resulted in the isolation of **11c**: $\nu_{max}^{CCl_4}$ 2770, 1701 cm^{-1}; nmr (neat–TMS), δ 0.87 (s, 3 H), 1.23 (s, 3 H), 2.24 (s, 3 H), 2.37 (AB, 2 H, $\Delta\nu_{AB}$ = 34.8 Hz, J_{AB} = 16 Hz, high-field half split J = 2 Hz, low-field half split J = 4.5 Hz), 3.16 (m, 1 H), 3.50–3.70 (m, 1 H), 5.97–6.25 (m, 2 H); the multiplet from δ 5.97 to 6.25 appears to be an AB quartet centered at 6.11 with $\Delta\nu_{AB}$ ~ 4.5 Hz and J_{AB} = 5–6 Hz (the multiplet is complicated by further splitting); mass spectrum (75 eV), *m/e* (relative intensity) 165 (M$^+$, 10.7), 122 (6.2), 95 (36.9), 94 (100), 44 (34.1).

Treatment of 3 with Cyclohexadiene. Tentative Identification of 2,2-Dimethylbicyclo[3.2.2]non-6-en-3-one (11d) and Δ^4- or Δ^6-2,2-Dimethyltetrahydro-2-indanone (12). A CH_2Cl_2 solution of **3** was mixed with at least a threefold excess of cyclohexadiene and was left at room temperature for several days. The solvent was then stripped off and the residue was worked up by vpc ($\beta\beta\beta$). This method left a lot to be desired because it was hard to get good separation and to collect reasonable amounts of products. In an attempt to remedy this, column chromatography (silica gel–cyclo-

(35) P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc., B*, 360 (1967).
(36) W. E. Hanford and T. C. Sauers, *Org. Reactions*, 3, 132 (1946).

hexane solvent) was tried, but this failed to give pure products. Two products were finally isolated in low yield by vpc.

The ir spectrum of the first had a carbonyl band at 1690 cm^{-1}. This is consistent with structure **11d**. The ir spectrum of the second had a carbonyl band at 1740 cm^{-1}. This is consistent with structure **12**. The nmr spectra of both products were uninformative.

2,2-Dimethyl-8-isopropylidenebicyclo[3.2.1]oct-6-en-3-one (11e). To a 1.18 *M* methylene chloride solution of dimethylcyclopropanone (17.0 ml, 20.5 mmoles) was added excess dimethylfulvene (7 ml) and the solution refluxed for 2 hr. The solvent was evaporated and the remaining oil distilled giving 2.80 g (72%) of the adduct **11e**: bp 111–115° (5.5 mm); ir (neat) (cm^{-1}) 3050 (C=CH), 1705 (C=O); nmr ($CDCl_3$), δ 1.07 (6 H, s), 1.71 (3 H, s), 1.73 (3 H, s) 2.4 (2 H, m), 3.05 (H, m), 3.4 (H, m), and 6.15 (2 H, m). The *gem*-dimethyl group α to the carbonyl in **11e** gave rise to singlets at δ 0.99 (3 H, s) and 1.07 (3 H, s) when the spectrum was measured using benzene as a solvent. In this solvent the isopropylidene gave rise to a singlet at δ 1.52 (6, H); mass spectrum (75 eV), *m/e* (relative intensity) 191 (7), 190 (48, M$^+$), 175 (7), 147 (14), 133 (11), 120 (79), 119 (30), 106 (30), 105 (100), 91 (39).

The adduct **11e** (320 mg) was dissolved in ethanol, 5% Pd–C was added, and it was reduced with hydrogen at atmospheric pressure. After 1 hr hydrogen uptake ceased (36.60 ml absorbed, 0.96 mole). The catalyst was filtered off and the solution was evaporated to yield 291 mg of 2,2-dimethyl-8-isopropylidenebicyclo[3.2.1]octan-3-one: ir, no C=CH, 1700 cm^{-1} (C=O); nmr ($CDCl_3$), 1.05 (6 H, s), 1.75 (3 H, s), 1.78 (3 H, s), 1.6 (4 H, m), 2.0–3.5 (4 H, m).

2,2,4,4-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (13). To a solution of **4** (*ca.* 10%) in pentane was added 5 ml of furan at −78°. The resulting solution was warmed to 25° and showed no infrared absorption at 1843 cm^{-1} characteristic of **4**. The solution was concentrated to an oil under vacuum and analyzed by vpc (5 ft × $^3/_8$ in., 22% CWX 20M, chrom P, 120 cc of He/min, 200°). This led to the isolation of **13**: ir, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS), δ 0.86 (s, 6 H), 1.29 (s, 6 H), 4.23 (s, 2 H), 6.19 (s, 2 H); mass spectrum (75 eV), *m/e* (relative intensity) 180 (M$^+$, 23), 166 (1), 165 (5), 137 (4), 111 (10), 110 (85), 109 (26), 96 (7), 95 (100), 84 (7), 81 (15), 79 (10), 70 (30), 69 (22), 67 (11), 53 (12), 43 (15), 42 (24), 41 (56), 40 (9), 39 (38). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.34; H, 9.09.

1,2,2-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (15a) and 1,4,4-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (15b). A solution of **3** (1 mmole) in methylene chloride (5 ml) and 2-methylfuran (5 ml) were combined at room temperature. After 10 hr **3** had reacted completely (nmr) to produce furan adducts **15b** and **15a** in a combined 85% yield (nmr) and a ratio of 1:1.[37] The adducts were separated by vpc on a 10-ft βββ column at 170°. Adduct **15a** had the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1715 cm^{-1}; nmr (CCl_4–TMS), δ 0.94 (s, 3 H), 1.16 (s, 3 H), 1.30 (s, 3 H), 2.39 (AB, 2 H, $\Delta\nu_{AB}$ = 39.6 Hz, J_{AB} = 15.3 Hz, low-field half split further J = 4.8 Hz, high-field half split further J = 1.3 Hz), 4.80 (d of t, 1 H, J = 4.8 Hz, J = 1.3 Hz), 6.07 (AB, 2 H, $\Delta\nu_{AB}$ = 4.08 Hz, J_{AB} = 5.7 Hz, low-field half split further); mass spectrum (75 eV), *m/e* (relative intensity) 166 (M$^+$, 28), 151 (3), 138 (2), 123 (9), 109 (13), 96 (92), 95 (100), 82 (28), 81 (43), 71 (11), 70 (37), 53 (24), 43 (47), 42 (33), 41 (44), 39 (28). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.14; H, 8.51.

Adduct **15b** had the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS), δ 0.88 (s, 3 H), 1.22 (s, 3 H), 1.41 (s, 3 H), 2.32 (AB, 2 H, $\Delta\nu_{AB}$ = 21.5 Hz, J_{AB} = 15.4 Hz), 4.29 (d, 1 H, J = 1.7 Hz), 6.04 (AB, 2 H, $\Delta\nu_{AB}$ = 11.2 Hz, J_{AB} = 5.8 Hz, low-field half split further J = 1.7 Hz); mass spectrum (75 eV), *m/e* (relative intensity) 166 (M$^+$, 36), 151 (11), 137 (8), 134 (10), 123 (20), 109 (23), 105 (23), 96 (22), 95 (18), 82 (13), 81 (25), 79 (10), 77 (13), 71 (10), 70 (100), 69 (9), 67 (15), 55 (10), 53 (15), 44 (57), 43 (39), 42 (37), 41 (42), 40 (16), 39 (29), 29 (14), 27 (18). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.43; H, 8.40.

2,2,7-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (17a) and 2,2,6-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (17b). A mixture of 22–23 ml of a CH_2Cl_2 solution of **3** (25–26 mmoles) and 2.2 ml of 3-methylfuran (24.8 mmoles) was refluxed for approximately 20 hr. After the solvent was stripped off, preparative vpc (10 ft × $^3/_8$ in. βββ, 170°, 120 cc of He/min) resulted in the isolation of **17a** and **17b**. Compound **17a** exhibited the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; uv, $\lambda_{max}^{CCl_4}$ 2930 Å (ε 38.3); nmr (CCl_4–TMS), δ 5.84 (m, 1 H), 4.56 (d, 1 H, J = 5 Hz), 4.23 (s, 1 H), 2.44 (AB, 2 H, J_{AB} = 16 Hz, $\Delta\nu_{AB}$ = 34.5 Hz, low-field half split further J = 5 Hz), 1.81 (m, 3 H), 1.20 (s, 3 H), 0.86 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 166 (M$^+$, 48.1), 123 (11.4), 109 (28.7), 96 (60.2), 95 (93.0), 82 (49.5), 81 (79.2), 71 (23.2), 70 (75.9), 53 (51.8), 43 (63.9), 42 (65.3), 41 (100), 39 (81.9). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.11; H, 8.42.

Compound **17b** exhibited the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; uv, $\lambda_{max}^{CCl_4}$ 2920 Å (ε 37.6); nmr (CCl_4–TMS), δ 5.88 (m, 1 H), 4.78 (m, 1 H), 4.08 (s, 1 H), 2.43 (AB, 2 H, J_{AB} = 16 Hz, $\Delta\nu_{AB}$ = 42.1 Hz, low-field half split further J = 5 Hz), 1.86 (s, 3 H), 1.31 (s, 3 H), 0.95 (s, 3 H), singlet at 1.86 and high-field peak of AB quartet coincide; mass spectrum (75 eV), *m/e* (relative intensity) 166 (M$^+$, 47.7), 123 (12.7), 109 (38.4), 96 (100), 95 (50.5), 82 (19.0), 81 (51.6), 53 (43.3), 43 (46.6), 42 (63.5), 41 (94.6), 39 (83.9). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.00; H, 8.36.

Compounds **17a** and **17b** were formed in approximately equal amounts.

1-Formyl-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (19b) and 2-(2-Furyl)-5,5-dimethyl-4-methylene-1,3-dioxolane (20a). After being left at room temperature for 2 days, a mixture of 2.5 ml of a CH_2Cl_2 solution of **3** (5.4 mmoles) and 2 ml of furfural (24 mmoles) was subjected to preparative vpc (5 ft × $^3/_8$ in., 22% CWX 20M, chrom P, 215°, 200 cc of He/min). This resulted in the isolation of **19b** and **20a**. The spectral properties of **19b** are ir, $\nu_{max}^{CCl_4}$ 1702, 1688 cm^{-1}; nmr (CCl_4–TMS), δ 9.77 (s, 1 H), 6.36 (AB, 2 H, J_{AB} = 6 Hz, $\Delta\nu_{AB}$ = 7.75 Hz, low-field half split J = 1.5), 5.13 (d of t, J = 5 Hz, J = 1.5 Hz), 2.59 (AB, 2 H, J_{AB} = 16 Hz, $\Delta\nu_{AB}$ = 39.2 Hz, low-field half split J = 5 Hz, high-field half split J = 1.5 Hz), 1.23 (s, 3 H), 1.11 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 180 (M$^+$, 3.4), 152 (5.1), 111 (9.2), 110 (100), 109 (61.8), 97 (5.6), 96 (28.5), 95 (33.4), 94 (18.1), 81 (19.8), 70 (38), 59 (67.8), 44 (23.9), 43 (48.1), 42 (23.6), 41 (37.2), 32 (33.1), 31 (40.9), 29 (14.0). The spectral properties of **20a** are ir $\nu_{max}^{CCl_4}$ 1730, 1710 cm^{-1}; nmr (CCl_4–TMS) δ 7.43 (m, 1 H), 6.28–6.53 (m, 2 H), 6.13 (s, 1 H), 4.24 (d, 1 H, J = 2.5 Hz), 3.82 (d, 1 H, J = 2.5 Hz), 1.48 (s, 3 H), 1.42 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 180 (3.1), 165 (2.5), 97 (100), 96 (24.8), 95 (36.8), 94 (83.2), 84 (23.0) 73 (35.2), 71 (13.4), 70 (18.9), 69 (31.6), 59 (49.5), 57 (14.1), 56 (24.2), 52 (15.7), 43 (69.5), 42 (23.2), 41 (65.3), 39 (41.8). Both the ir spectrum and mass spectrum of **20a** are complicated by the presence of furfural as an impurity. Attempts to further purify **20a** by vpc met with failure because **20a** decomposed on the column.

Treatment of 3 with Benzaldehyde and with Acetaldehyde. 5,5-Dimethyl-4-methylene-2-phenyl-1,3-dioxolane (20c) and 2,5,5-Trimethyl-4-methylene-1,3-dioxolane (20d). In both cases, a mixture of excess aldehyde and several milliliters of a CH_2Cl_2 solution of **3** was left at room temperature for several days. The reactions were monitored by nmr and this indicated the formation of **20c** and **20d**. Attempts to isolate **20c** by preparative vpc (5 ft. × $^3/_8$ in., 22% CWX 20M, chrom P, 210°, He 200 cc/min) failed because **20c** decomposed on the column. No attempt was made to isolate **20d**.

The nmr spectrum of **20c** had a doublet of doublets of 3.96 and 4.35 (J = 2.5 Hz) and the spectrum of **20d** had a doublet of doublets at 3.71 and 4.07 (J = 2.3 Hz).

5,5-Dimethyl-4-methylene-2-trichloromethyl-1,3-dioxolane (20b) and 4-Isopropylidene-2-trichloromethyl-1,3-dioxolane (21). After being left at room temperature overnight, a mixture of 3 ml of CCl_3CHO (30.9 mmoles) and 40 ml of a CH_2Cl_2 solution of **3** (21 mmoles) was refluxed gently for 24 hr. After removal of the excess chloral by filtration through a short silica gel column (CH_2Cl_2 solvent), removal of the solvent followed by preparative vpc (6 ft × $^3/_8$ in., 20% SE 30, chrom P, 185–190°, 200 cc of He/min) resulted in the isolation of 785 mg (16%) of **20b** and 80 mg (1.5%) of **21**. Compound **20b** exhibited the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1695, 1382, 1366 cm^{-1}; nmr (CCl_4–TMS), δ 5.53 (s, 1 H), 4.40 (d, 1 H, J = 3 Hz), 3.90 (d, 1 H, J = 3 Hz), 1.57 (s, 3 H), 1.46, (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 230 (M$^+$, 3.7), 215 (1.7), 113 (83.8), 103 (11.8), 86 (56.3), 85 (43.7), 84 (82.4), 83 (15.1), 82 (11.6), 69 (22.5), 67 (100), 59 (10.8), 57 (16.4), 56 (89.2), 55 (10.0), 51 (37.4), 49 (98.6), 48 (15.4), 47 (28.4), 44 (49.6), 43 (62.4), 42 (27.9), 41 (79.7), 39 (31.1). *Anal.* Calcd for $C_7H_9O_2Cl_3$: C, 36.31; H, 3.92; Cl, 45.95. Found: C, 36.15; H, 3.99; Cl, 46.65.

Compound **21** exhibited the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1730 cm^1; nmr (CCl_4–TMS) δ 5.48 (s, 1 H), 4.43–4.97 (m,

(37) In one experiment **15a** and **15b** were formed in the ratio of 58:42 as measured by vpc. Thermal conductivity corrections were not made.

2 H), 1.74 (m, 3 H), 1.57 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 230 (M^+, 10.3), 113 (32.7), 86 (37.4), 85 (28.5), 84 (68), 67 (100), 56 (22.2), 51 (23.5), 49 (83.3), 47 (16.5), 44 (18.1), 43 (21.2), 42 (14.2), 41 (46.1), 40 (14.2), 39 (18.1).

4-Bromo-4-bromomethyl-5,5-dimethyl-2-trichloromethyl-1,3-dioxolane (22). A CH_2Cl_2 solution of Br_2 was slowly added to a CH_2Cl_2 solution of **20b**. Decolorization of the Br_2 was rapid at first and then gradually slowed down. Addition was stopped when decolorization became fairly slow. At that time, an nmr spectrum indicated that most of **20** was gone and that **22** had formed. Compound **22** had the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1388, 1369 cm^{-1}; nmr (CH_2Cl_2), δ 5.62 (s, 1 H), 3.94 (AB, 2 H, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 11.8 Hz), 1.70 (s, 3 H), 1.55 (s, 3 H).

1,1,6,6-Tetramethyl-5-methylene-4,7-dioxaspiro[2.4]heptane (23a). A mixture of 4 ml of a CH_2Cl_2 solution of **3** (6.65 mmoles) and 1 ml of 1,1-dichloro-2,2-difluoroethylene (~12 mmoles) was heated at 80–100° for 20 hr in an evacuated sealed tube. Evaporation of the solvent and preparative vpc (6 ft × 3/8 in., 20% SE 30, chrom P, 107°, 150 cc of He/min) then resulted in the isolation of **23a**: ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS), δ 0.65 (AB, 2 H, J_{AB} = 6 Hz, $\Delta\nu_{AB}$ = 6.17 Hz), 1.08 (s, 3 H), 1.14 (s, 3 H), 1.34 (s, 3 H), 1.43 (s, 3 H), 3.70 (d, 1 H, J = 2.1 Hz), 4.11 (d, 1 H, J = 2.1 Hz); mass spectrum (75 eV), *m/e* (relative intensity) 168 (M^+, 9), 153 (3), 87 (10), 86 (19), 83 (49), 69 (24), 68 (100), 67 (94), 59 (18), 56 (26), 55 (25), 53 (29), 43 (16), 42 (17), 41 (59), 40 (15), 39 (30).

5-Isopropylidene-1,1,2,2,6,6-hexamethyl-4,7-dioxaspiro[2.4]heptane (23b). A solution of **4** in methylene chloride was prepared as described previously[38] and concentrated to a volume of *ca.* 15 ml. Triglyme (20 ml) was added to the concentrated solution of **4**, the solution was cooled to −130° and the system was evacuated to 0.1 mm. All material volatile at 0° was distilled into a small receiver. The resulting solution contained **4** (infrared, 1843, 1823 cm^{-1}), tetramethylethylene (infrared, 1455 cm^{-1}), and a small amount of dimethylketene (infrared, 2130 cm^{-1}). The solution was analyzed by vpc (4-ft βββ 165°) after 1 week at 25° and contained one major component with the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1710 cm^{-1} (rel weak); nmr, δ 0.98 (s, 3 H), 1.03 (s, 3 H), 1.23 (s, 3 H), 1.58 (s, 3 H); mass spectrum *m/e* (75 eV), 224 (M^+).

5,5-Dimethyl-4-methylene-2-oxo-1,3-dioxa-2-thiolane (24). To 100 ml of 0.47 *M* 2,2-dimethylcyclopropanone (47 mmoles) in methylene chloride at −78° was added 4 ml of sulfur dioxide (89.5 mmoles). The solution was kept at −78° for 1 hr and at room temperature for 30 min. Evaporation of the solvent *in vacuo* gave the adduct **24** (7.0 g, 67% by nmr): ir ν_{max}^{neat} 3110 cm^{-1} (C=CH), 1670 cm^{-1} (OC=C); nmr, (neat), 1.49 (3 H, s), 1.87 (s, 3 H), 4.33 (1 H, d, J = 3.0 Hz), 4.66 (1 H, d, J = 3.0 Hz); mass spectrum (75 eV), *m/e* (relative intensity) 148 (M^+, 3), 84 (24), 69 (20), 56 (68), 48 (20). *Anal.* Calcd for $C_5H_8O_3S$: C, 40.55; H, 5.41. Found: C, 40.18; H, 5.33.

1,1,6,6-Tetramethyl-5-oxo-4-oxaspiro[2.3]hexane (25). To a 10% solution of dimethylketene (*ca.* 30 mmoles) in methylene chloride was added an ether solution (50 ml) of diazomethane (*ca.* 15 mmoles). The infrared spectrum of the resulting solution showed intense peaks at 1830 (**3**) and 2130 (dimethylketene) cm^{-1}. After 1 hr methanol (5 ml) was added and the solution was warmed to room temperature. The absorption at 1830 cm^{-1} remained on addition of more methanol or oxygen, but vanished on treatment with sodium methoxide. The reaction mixture was concentrated under vacuum and analyzed by vpc on a 1-ft βββ on Teflon column. The major product was collected and identified as adduct **25** by the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1830 cm^{-1}; nmr (CCl_4), δ 0.59 (d, A of AB, J = 7 cps, 1 H), 0.75 (d, B of AB, J = 7 cps, 1 H), 1.10 (s, 3 H), 1.25 (s, 3 H), 1.29 (s, 3 H), 1.38 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 154 (M^+, 1.5), 139 (1.0), 126 (1.0), 110 (8), 95 (13), 70 (100), 67 (10), 56 (15), 42 (45), 41 (33), 39 (20).

Spiro[4,4-dimethoxyoxetane-2,1′-(2′2′-dimethylcyclopropane)] (26). 1,1-Dimethoxyethylene, 2.29 g (26.0 mmoles), was added to 15 ml of 1.66 *M* dimethylcyclopropanone (25 mmoles) in methylene chloride at −78°. After 3 hr at room temperature, the solvent was evaporated *in vacuo* to yield 4.24 g (90% by nmr) of the adduct **26** as an oil; ir (CCl_4), no OH, no C=O; nmr (CH_2Cl_2), δ 0.47 (2 H, AB, $\Delta\nu_{AB}$ = 12.0 Hz, J = 6.8 Hz), 0.97 (3 H, s), 1.12 (3 H, s), 2.73 (2 H, AB, $\Delta\nu_{AB}$ = 9.1 Hz, J = 11.5 Hz), 3.31 (3 H, s), and 3.33 (3 H, s): mass spectrum (75 eV), *m/e* (relative intensity) 172 (24, M^+), 157 (57), 143 (25), 141 (24), 130 (18), 125 (12), 115 (88), 88 (82), 85 (15) 84 (12), 83 (21), 82 (11), 81 (30), and 43 (100) *inter alia*. The instability of **26** precluded analysis.

Preparation of the Hydrochloride of 11c. A portion of **11c** was dissolved in MeOH and methanolic HCl was added until the pH was ~1–2. Evaporation of the MeOH, followed by recrystallization from 2-butanone led to the isolation of **27**: ir, ν_{max}^{KBr} 1720 cm^{-1}; nmr ($CDCl_3$–TMS), δ 1.16 (s, 3 H), 1.79 (s, 3 H), 2.65 (d of d, 1 H, J = 18, 2 Hz), 3.17 (s, 3 H), 4.05 (d of d, 1 H, J = 18, 4 Hz), 4.38 (s, 1 H), 4.53–4.75 (m, 1 H), 6.52 (m, 2 H, appears to be AB with J_{AB} ~ 6 Hz and $\Delta\nu_{AB}$ ~ 3.7 Hz; the multiplet is complicated by further splitting); 11.23–13.06 (1 H); mass spectrum (75 eV), *m/e* (relative intensity) 165 (M^+ − HCl, 4.0), 122 (3.6), 108 (13.3), 95 (27.8), 94 (100), 81 (16.1), 80 (13.5), 42 (48.3), 41 (27.2), 39 (27.2), *Anal.* Calcd for $C_{10}H_{16}NOCl$: C, 59.55; H, 8.00; N, 6.95; Cl, 17.58. Found: C, 59.31; H, 8.08; N, 6.75; Cl, 17.61.

Vpc Treatment of 11c. **11c** (9.3 mg) (5.6 × 10^{-5} mole if 100% pure), and 3.7 mg of 2-methylcyclohexanone (3.3 × 10^{-5} mole internal standard) were dissolved in CH_2Cl_2 and 1 ml of solution was made up. Preparative vpc (6 ft × 3/8 in., SE 30 20%, chrom P, 180°, He 150 cc/min) led to the isolation of a mixture of **29** and **30** (**29**:**30** = 6:1 nmr, **29**:**30** = 5:1 vpc). The vpc yield of **29** + **30** was 48% (uncorrected).

2,2,8-Trimethyl-8-azabicyclo[3.2.1]octan-3-one (28). **11c** (1.07 g, 6.5 mmoles if pure) was dissolved in several milliliters of MeOH. A spatula full of Pd–C was added and the mixture was hydrogenated at atmospheric pressure and room temperature until H_2 uptake ceased (H_2 uptake 110.2 ml; calculated for 6.5 mmoles, 145 ml). The Pd–C was removed by filtration, and the mixture was stored at −78° for 4 days.

Since an nmr spectrum of the crude reaction mixture indicated the possible presence of some olefinic protons, more catalyst was added and further reduction was attempted. Only 7 ml of H_2 were taken up. The catalyst was filtered off and the reaction mixture was stored overnight at −78°. The solvent was stripped off and the residue was filtered through base-washed alumina using CH_2Cl_2 as a solvent. Evaporation of the CH_2Cl_2 followed by preparative vpc of the residue (6 ft × 3/8 in., 20% SE 30, chrom P, 197°, 120 cc of He/min) led to the isolation of **28** (340 mg, 31%): ir, ν_{max}^{neat} 2780, 1706 cm^{-1}; nmr ($CDCl_3$), δ 1.00 (s, 3 H), 1.29 (s, 3 H), 1.35–2.24 (m, 5 H), 2.35 (s, 3 H), 2.58–3.07, (m, 2 H), 3.17–3.48 (m, 1 H); mass spectrum (75 eV), *m/e* (relative intensity) 167 (M^+, 19.6), 124 (2.7), 110 (2.5), 96 (19.1), 83 (14.0), 82 (100), 81 (19.6), 42 (25.6), 41 (13.4). *Anal.* Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.61; H, 10.38; N 8.54.

N-Methyl-2-(3-methyl-2-oxobutyl)pyrrole (29) and N-Methyl-2-(1,1-dimethyl-2-oxopropyl)pyrrole (30). In a typical reaction, 8.5 ml of N-methylpyrrole (97 mmoles) was mixed with 3.5 ml of CH_2Cl_2. The mixture was cooled to −78° in a test tube sealed with a serum cap and 5 ml of a CH_2Cl_2 solution of **3** (9.7 mmoles) was added. After 48 hr at −78°, the solvent was stripped from the reaction mixture and preparative vpc (6 ft × 3/8 in., 20% SE 30, chrom P, 175°, 120 cc of He/min) of the residue resulted in the isolation of adducts **29** and **30**. An attempt to isolate **29** and **30** from the reaction mixture by recrystallization from *n*-pentane at −78° failed. The ratio of **29**:**30** was 5:1 (vpc). Compound **29** exhibited the following spectral properties: ir, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS), δ 6.43 (t, 1 H, J = 2 Hz), 5.88 (m, 2 H), 3.56 (s, 2 H), 3.4 (s, 3 H), 2.7 (sep, 1 H, J = 7 Hz), 0.97 (d, 6 H, J = 7 Hz); mass spectrum (75 eV), *m/e* (relative intensity) 165 (M^+, 13.3), 94 (100). Compound **30** exhibited the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1706 cm^{-1}; nmr (CCl_4–TMS), δ 6.45 (t, 1.2 H, J = 2 Hz), 5.98 (m, 2.2 H), 3.4 (s, 2.5 H), 1.87 (s, 2.8 H), 1.43 (s, 6 H); mass spectrum (75 eV), *m/e* (relative intensity) 165 (11.0), 122 (100).

5,5-Dimethyl-4-oxo-2-trichloromethyl-1,3-dioxolane (31) and 4-Oxo-2-trichloromethyl-1,3-dioxolane (32). **20b** (111 mg) was dissolved in 5 ml of CH_2Cl_2. The solution was cooled to −78° and ozone was passed through it until it turned blue (excess ozone). After the mixture warmed to room temperature, the solvent was stripped off and the resulting residue was dissolved in a mixture of 1 ml of MeOH and 1 ml of Me_2S. The mixture was left at room temperature for about 1 hr after which the solvent was blown off with N_2. The residue was dissolved in benzene and the mixture was washed with H_2O. The benzene was then stripped off and the residue was taken up in CH_2Cl_2. Drying with $MgSO_4$, filtration, and evaporation of the CH_2Cl_2 resulted in the isolation of lactone **31**. Similar treatment of **21** resulted in the isolation of lactone **32**. Compound **31** exhibited the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1820 cm^{-1}; nmr (CH_2Cl_2), δ 5.78 (s, 1 H), 1.58 (s, 3 H), 1.51 (s, 3 H); mass spectrum (75 eV), *m/e* (relative intensity) 217

(38) N. J. Turro and W. B. Hammond, *Tetrahedron*, 24, 6017, 6029 (1968).

($M^+ - 15$, 0.1%), 115 (23.6), 87 (44.7), 59 (100), 43 (42.1), 41 (21.8), 39 (17.7). Compound **32** had the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1840 cm^{-1}; nmr (CCl_4–TMS), δ 5.85 (s, 1 H), 4.48 (AB, 1.9 H, $\Delta\nu_{AB}$ = 10 Hz, J_{AB} = 14 Hz); both the singlet and the AB quartet exhibit some second-order splitting.

α-Hydroxyisobutyric Acid Anhydrosulfite (33). Ozone was bubbled through a solution of **24** (300 mg) in 25 ml of methylene chloride at −78° until a bluish color appeared. The excess ozone was blown away and evaporation of the solvent yielded the partially hydrolyzed anhydrosulfite **33**. This anhydrosulfite was identical with authentic material prepared from α-hydroxyisobutyric acid and thionyl chloride;[39] ir (CH_2Cl_2), no OH, 1815 (C=O), 1380 and 1365 cm^{-1} [$(CH_3)_2C<$]; nmr (CH_2Cl_2), δ 1.57 (3 H, s), 1.74 (3, H, s).

Methyl (1-Hydroxy-2,2-dimethylcyclopropyl)acetate (34). To 2.14 g (11.2 mmoles) of ortho ester **26** (90% by nmr) dissolved in pentane was added five drops of water and the mixture was shaken. Evaporation of the solvent afforded 1.51 g (85% by nmr) of the cyclopropanol **34**: ir ($CDCl_3$) (cm^{-1}), 3600, 3550 (free and intramolecular assoc OH, respectively), 3068 (CH, cyclopropyl), 1730 (C=O); nmr ($CDCl_3$), δ 0.43 (2 H, AB, $\Delta\nu_{AB}$ = 14.5 Hz, J = 5.5 Hz), 1.04 (3 H, s), 1.27 (3 H, s), 2.70 (2 H, AB, $\Delta\nu_{AB}$ = 14.0 Hz, J = 17.0 Hz), 3.49 (1 H, s, from D_2O) and 3.73 (3 H, s); mass spectrum (75 eV), m/e (relative intensity) 158 (7, M^+), 143 (56), 140 (12), 127 (4), 125 (5), 111 (8), 88 (11), 86 (63), and 84 (100) *inter alia*.

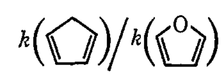
Similarly, one drop of water added to dimer **35** (120 mg) in pentane afforded 93 mg (84%) of **34**.

1,1,8,8-Tetramethyl-5,5,11,11-tetramethoxy-4,10-dioxadispiro-[2.3.2.3]dodecane (35). Ortho ester **26** (2.1 g) in hexane was kept at room temperature and crystals were slowly deposited. After 2 weeks the solution was cooled to −20° and the crystals were filtered off and washed with cold pentane. Recrystallization from pentane afforded 0.82 g (39%) of dimer **35**: mp 121–124°; ir (CCl_4), no OH, no C=O; nmr ($CDCl_3$), δ 0.87 (4 H, AB, $\Delta\nu_{AB}$ = 19.2 Hz, J = 5.5 Hz), 1.06 (6 H, s), 1.23 (6 H, s), 2.39 (4 H, AB, $\Delta\nu_{AB}$ = 21.8 Hz, J = 16.0 Hz), 3.17 (6 H, s), and 3.22 (6 H, s); mass spectrum (75 eV), m/e (relative intensity) 344 (0.4, M^+), and 155 (100) *inter alia*. *Anal.* Calcd for $C_{18}H_{32}O_6$: C, 62.77; H, 9.36. Found: C, 62.74; H, 9.17.

(39) E. Blaise and A. Montagne, *Compt. Rend.*, **174**, 1553 (1922).

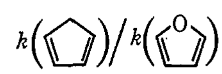
Treatment of 3 with a Mixture of Furan and 2-Methylfuran. In each of four test tubes were placed 0.5 ml of a 2.09 M CH_2Cl_2 solution of **3**, 0.90 ml of 2-methylfuran (10 mmoles), and 0.72 ml of furan (10 mmoles). After being cooled to 77°K, evacuated, degassed once, and sealed, the tubes were heated at 40–50° for 48 hr. Vpc analysis (5 ft × 0.25 in., 25% $\beta\beta\beta$, chrom P, 158°, 60 cc of He/min) then indicated that the 2-methylfuran reacted about 1.25 times as fast as furan with **3**.

Treatment of 3 with a Mixture of Furan and Cyclopentadiene. A. A mixture of 50 μl of a CH_2Cl_2 solution of **3** (0.1045 mmole), 82.5 μl of cyclopentadiene (1 mmole), and 72 μl of furan (1 mmole) was left at room temperature in a sealed (serum cap) tube for 3 days. Vpc analysis (5 ft × 3/8 in., 22% CWX 20M, chrom P, 233°, 120 cc of He/min) indicated that



$$= 2.9 \pm 3$$

B. Cyclopentadiene (0.825 ml, 10 mmoles), 0.72 ml of furan (10 mmoles), and 0.104 ml of cyclohexanone (1 mmole internal standard) were mixed in a test tube and the tube was sealed with a serum cap. After cooling the tube to −78°, 0.5 ml of a CH_2Cl_2 solution of **3** (1.05 mmoles) was added and the tube was allowed to warm to room temperature. Aliquots were taken every 10 min and analyzed by vpc (5 ft × 3/8 in., 22% CWX 20M, chrom P, 220°, He 60 cc/min). This indicated that



$$= 2.51 \pm 0.08$$

Treatment of Furan with a Mixture of 3 and 2. To 7 ml of furan were added 1 ml of a CH_2Cl_2 solution of **2** (0.96 mmole) and 0.71 ml of a CH_2Cl_2 solution of **3** (0.96 mmole) and the resulting mixture was left standing at room temperature overnight. Vpc analysis (5 ft × 1/8 in., 5% SE 30, 60–80 a/w dmcs chrom W, 100°, He 40 cc/min) then showed that

$$k(\mathbf{3})/k(\mathbf{2}) = 13 \pm 2$$

Treatment of Cyclopentadiene with a Mixture of 3 and 2. A mixture of **3** and **2** was treated with cyclopentadiene as described above for furan and **3** was found to react faster than **2**. The reaction was "messy" and no quantitative data could be obtained from it.