of BH_4^-, strongly suggests the participation of 8. In-cage transfer of hydrogen at this stage can explain the lack of a primary isotope effect.

Acrylonitrile quenches the borohydride reactions to a very small extent. It is likely that aryl radicals are formed when 7 fragments. In the case of 8, the caged radical pair may abstract a hydrogen from within the cage or diffuse into the solvent in the form of a radical. It is likely that acrylonitrile, which appears to be an inefficient quencher of the aryl radical generated from 1, has a lower rate of quenching than the rate of hydrogen transfer from the borohydride in 8 within the radical pair cage.

Experimental Section

General Procedures. Reagent grade acetonitrile (Baker Chemical Co.) was freshly distilled from phosphorus pentoxide, and its purity was greater than 99% by GLC analysis. Sodium borohydride and borodeuteride (Aldrich) were 99% and 98 atom %, respectively.

General Procedure for Photolysis. Irradiations of 1 were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å lamps. A steady stream of air was passed into the reactor to maintain a constant temperature of 40 °C. The photolysis samples (1 mL) were placed in quartz tubes (Ace Glass, 170 mm × 15 mm), each screwed to a nylon adapter bushing containg a Pyrex glass sliding stopper valve, and degassed through three or four freeze–pump–thaw cycles. The tubes were sealed under vacuum and irradiated at 254 nm for 6 min. Quantum yields of products were determined by using the potassium ferrioxalate[14] actinometer.

Product Analysis. The photolysis mixtures were analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with an FID with a 30 m × 0.25 mm DB-225 capillary column (J & W Scientific Inc.) and a Varian 4290 integrator. The column was held at 60 °C for 5 min and raised to 180 °C at a rate of 5 °C/min with an injection port temperature of 200 °C and detector temperature of 250 °C. Helium was used as carrier gas at 30 mL/min. The photoproducts were identified by comparing their retention times with those of commercially obtained authentic samples. The mass spectral analyses were carried out with a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph. Dodecane was used as an internal standard in the determination of yields of products.

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Registry No. 1, 608-93-5; $NaBH_4$, 16940-66-2.

Bicyclopropylidene: Cycloadditions onto a Unique Olefin

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Bicyclopropylidene (1) is capable of undergoing cycloadditions in at least six different modes, depending on the nature of the cycloaddend. In analogy to its [2 + 2] cyclodimerization, 1 adds in a [2 + 2] and [2 + 4] fashion to 1,3-dienes, most probably via diradical intermediates to a large extent. A concerted mode of formation is likely for at least fractions of the [2 + 4] cycloadducts **11**, **14**, **17**, and **45** and the [2 + 2] cycloadducts **22** and **23** of chloroketenes. 1 readily undergoes cycloaddition to electron-deficient olefins, both with σ- and π-electron-withdrawing groups, to give cyclobutane derivatives **18–20** and **24** via 1,4-diradical intermediates all retaining the two cyclopropyl groups of 1. Chlorosulfonyl isocyanate (CSI), *N*-phenyltriazolinedione (PTAD), and tetracyanoethylene (TCNE), all known for their propensity to form zwitterionic intermediates with electron-rich olefins, yield three types of products with 1 in different proportions. All three arise from the same type of initial 1,4-dipolar intermediates **25**, **29**, and **36** and ring closure yields **27** and **35**, while cyclopropyl to cyclobutyl ring enlargement and cyclopropylcarbinyl to homoallyl ring opening with subsequent closure lead to **32**, **40** and **31**, **41** respectively. The products **33**, **51**, and **59**, obtained from 1 upon photooxidation and ozonolysis, can also best be rationalized by assuming zwitterionic intermediates. This body of results helps to constitute a plausible and general scheme for the classification of various [2π]-cycloaddends according to their preferred reaction modes.

Cross-conjugated polyenes, such as fulvene and fulvalenes, can partake in diverse modes of cycloadditions (i.e., [2 + 2], [4 + 2], [6 + 2], [8 + 2], [14 + 2], etc.), depending on the nature of the olefinic reaction partner.[1-3] Normal monoalkenes, on the other hand, are confined to only two types of pericyclic reactions, namely, the [$_\pi 2_s + {}_\pi 2_a$] and [2 + 4] including the 1,3-dipolar cycloadditions.[4,5] Thermal cyclodimerizations of alkenes are rare, because the orbital symmetry conservation rules preclude a concerted [$2_s + 2_s$] reaction, and the [$2_s + 2_a$] transition state is energetically unfavorable; the relatively facile thermal cyclodimerizations of fluoroalkenes have been explained by a stepwise mechanism involving diradical intermediates which are stabilized by the fluoro substituents.[6,7] Methylenecyclopropane[8] and its 1,1-dihalo- and 1-halo-substituted derivatives[9a] as well as the cyclopropylidene-acetates[9b] behave in an entirely analogous manner: they all give head to head dimers upon heating, and the 1,1-dichloro derivative also cycloadds to 1,3-butadiene in a [2 + 2] mode. The role of the cyclopropane ring on the high propensity of methylenecyclopropanes to undergo cyclo-

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[‡] San Francisco State University.

(1) Dunn, L. C.; Chang, Y.-M.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 7095 and references cited therein.
(2) Prinzbach, H. *Pure Appl. Chem.* **1971**, *28*, 281.
(3) Erden, I.; Kaufmann, D. *Tetrahedron Lett.* **1981**, 215.
(4) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.
(5) Fleming, I. *Grenzorbitale und Reaktionen organischer Verbindungen*; Verlag Chemie: Weinheim, Germany, 1979.
(6) Sharts, C. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 871.
(7) Sharts, C. M.; Roberts, J. D. *Org. React. (N.Y.)* **1962**, *12*, 1.
(8) Binger, P. *Angew. Chem.* **1972**, *84*, 483; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433.
(9) (a) Dolbier, W. R., Jr.; Lomas, D.; Tarrant, P. *J. Am. Chem. Soc.* **1968**, *90*, 3594. Bottini, A. T.; Cabral, L. J. *Tetrahedron* **1978**, *34*, 3187; (b) de Meijere, A.; Wenck, H.; Seyed-Mahdavi, F.; Viehe, H. G.; Gallez, V.; Erden, I. *Tetrahedron* **1986**, *42*, 1291. Liese, Th.; Teichmann, S.; de Meijere, A. submitted for publication in *Synthesis*.

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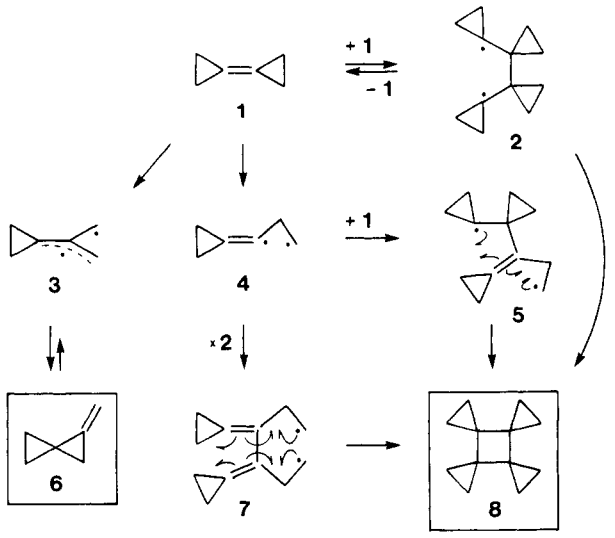
Scheme I



dimerizations and thermal [2 + 2] cycloadditions is not fully understood as yet. In view of the considerable double bond character of the cyclopropane ring, as evidenced by its chemical behavior[10] and explained by the various theoretical models describing its bonding properties,[11] it is probably more appropriate to draw parallels between methylenecyclopropanes and allenes, as the latter compounds likewise cyclodimerize readily.[12] Bicyclopropylidene (1)[13,14] is a unique olefin, combining the structural features of a tetrasubstituted ethylene and two methylenecyclopropane units. As unraveled by its He I photoelectron spectrum,[15a] **1** has a much higher HOMO energy than methylenecyclopropane. As the length of its symmetrically substituted central bond is significantly shorter than a regular $C(sp^2)=C(sp^2)$ double bond[15b] and the $^{13}C,^{13}C$ coupling constant is considerably larger,[15c] bicyclopropylidene (1) conforms to the predictions based on the bonding properties in methylenecyclopropane. The central C(sp)=C(sp) bond in **1** should impart properties which more closely resemble those of the central double bond in butatriene than of that in a simple tetrasubstituted ethylene. In this full account[16] we wish to report our observations that bicyclopropylidene (1) combines with numerous cycloaddends in such a variety of cycloadditions which no other alkene has previously been capable of.

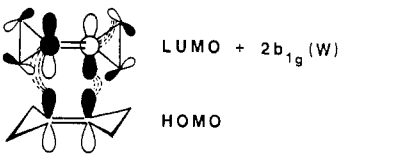


Figure 1. Concerted $[{}_{\pi}2_s + {}_{\pi}2_a]$ combination of two bicyclopropylidene molecules with HOMO–[LUMO + $2b_{1g}$(Walsh)] interaction.

Table I. Cycloadditions of Bicyclopropylidene (1) to 1,3-Dienes

diene	reaction conditions: T, °C	reaction conditions: t, h	products (rel yields, %): [2 + 2]	products (rel yields, %): [4 + 2]	total yields,[a] %
9	150	10		11 (>97)	16[b]
12	170	11	**13** (78)	14 (22)	50
15	180	12	**16** (92)	17 (8)	54

[a] Based on GLPC-isolated amounts. [b] In this reaction 1 was not consumed completely (50%).

Moreover, our results should contribute significantly to the growing body of experimental studies aimed at grouping cycloaddends according to their mode of cycloaddition.

Results

Cycloadditions of Bicyclopropylidene to Olefinic Hydrocarbons. Le Perchec and Conia[13] previously reported that **1** upon heating to 210 °C in a sealed tube, gives a 54.5:35:10.5 mixture of **6**, **8**, and **1**, respectively (Scheme I). A normal methylenecyclopropane rearrangement[17] after homolysis of the C_2–C_3 bond in **1** via the trimethylenemethane diradical **3** easily accounts for methylenespiropentane **6**. As to the cyclodimer **8**, the authors ruled out a thermal concerted [2 + 2] reaction for being orbital symmetry forbidden. Instead, they held the combination of two vinyl radicals **4** to **7** responsible for the formation of [4]rotane (**8**). It appears unlikely, however, that the diradical **7** would lead to **8** as the sole product, taking into account that three new rings have to be formed. If this cyclodimerization were to proceed stepwise, it is more probable that the diradical **4** would add onto **1** to form **5**, unless it were a regular olefin dimerization via a 1,4-diradical, in this case **2**. The latter would have to close only one ring, **5** in turn would have to close two rings to arrive at **8**. An attractive alternative would be a thermally allowed concerted $[{}_{\pi}2_s + {}_{\pi}2_a + {}_{\sigma}2_a]$ pericyclic reaction (see Figure 1). This description corrresponds to a concerted equivalent of the stepwise diradical pathway via the intermediate **5** (see Scheme I). **1** also undergoes cycloadditions with 1,3-dienes, and these showed an interesting dependence on the structure of the diene. Whereas cyclopentadiene (**9**) gave the [4 + 2] cycloadduct only, 1,3-cyclohexadiene (**12**) and 1,3-butadiene (**15**) led to mixtures of the [4 + 2] and [2 + 2] cycloadducts, with the proportion of the [2 + 2] adduct increasing in this order (Table I).

The products from each reaction were isolated by gas chromatography and identified mainly on the basis of their ^1H NMR spectra. The spectral data of **11** and **17** were identical with those of authentic materials prepared by independent syntheses.[18-20]

The observation that the overwhelming product from the cycloaddition of **1** to 1,3-butadiene (**15**) is **16** and the

(10) Cf.: de Meijere, A. *Angew. Chem.* **1979**, *91*, 867; *Angew. Chem., Int Ed. Engl.* **1979**, *18*, 809 and references cited therein.

(11) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179. Sugden, T. M. *Nature (London)* **1947**, *160*, 364. Schoeller, W. W. *Tetrahedron* **1973**, *29*, 929. Förster, Th. *Z. Phys. Chem. (Leipzig)* **1939**, *58*, 1343. Coulson, C. A.; Moffit, W. E. *J. Chem. Phys.* **1947**, *15*, 151; *Philos. Mag.* **1949**, *40*, 1.

(12) Cf.: Murray, M. In *Methoden der Organischen Chemie (Houben-Weyl)*; Thieme: Stuttgart; Vol. 5/2a, p 1067 ff and references cited therein. Hopf, H. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic: New York, 1982; p 525 ff.

(13) Le Perchec, P.; Conia, J.-M. *Tetrahedron Lett.* **1970**, 1587. Fitjer, L.; Conia, J.-M. *Angew. Chem.* **1973**, *85*, 345; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 332. Schmitt, A. H.; Schirmer, U.; Conia, J.-M. *Chem. Ber.* **1976**, *109*, 2588.

(14) Weber, W.; de Meijere, A. *Synth. Commun.* **1986**, *16*, 837.

(15) (a) Gleiter, R.; Haider, R.; Conia, J.-M.; Barnier, J.-P.; de Meijere, A.; Weber, W. *J. Chem. Soc., Chem. Commun.* **1979**, 130. (b) Traetteberg, M.; Simon, A.; de Meijere, A. *J. Mol. Struct.* **1984**, *118*, 333. (c) Seyed-Mahdavi, F.; Machinek, R.; Gleiter, R.; Flotow, A.; Spiekermann, M.; de Meijere, A., to be published.

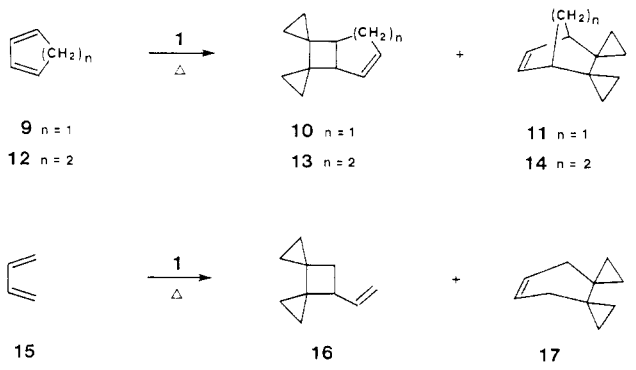
(16) (a) Cf. preliminary communications on cycloadditions of **1**, with 1,3-dienes: Kaufmann, D.; de Meijere, A. *Angew. Chem.* **1973**, *85*, 151; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 159. (b) With electron-deficient cycloaddends: Weber, W.; Erden, I.; de Meijere, A. *Angew. Chem.* **1980**, *92*, 387; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 387. (c) With singlet oxygen: Erden, I.; de Meijere, A.; Rousseau, G.; Conia, J.-M. *Tetrahedron Lett.* **1980**, 2501. (d) With monoenes under nickel(0) catalysis: Kaufmann, D.; de Meijere, A. *Chem. Ber.* **1984**, *117*, 3134.

(17) Cf.: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981, p 51 ff.

(18) An authentic sample of **11** was prepared from the Diels–Alder adduct of ethylenetetracarboxylic dianhydride to cyclopentadiene,[19] essentially following the procedure applied for **17**.[20]

(19) Sauer, J.; Schröder, B.; Mielert, A. *Chem. Ber.* **1967**, *100*, 315.

(20) Magrill, D. S.; Altmann, J.; Ginsburg, D. *Isr. J. Chem.* **1969**, *7*, 479.



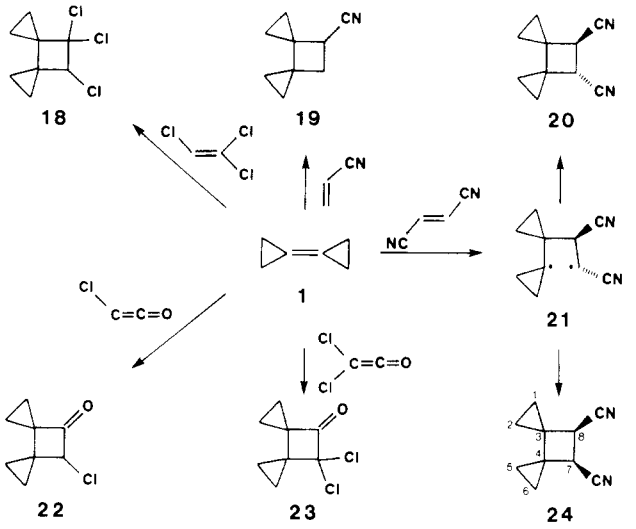
proportion of the [4 + 2] adduct increases in the order **15** < **12** ≪ **9** is in accord with the increasing diene reactivity in this series.[21] Whereas cyclopentadiene readily combines with most dienophiles at low temperatures, 1,3-butadiene, mainly owing to its predominant s-trans conformation, enters into [4 + 2] cycloadditions only at elevated temperatures. It is noteworthy that (dichloromethylene)-cyclopropane cycloadds to **15** exclusively in a [2 + 2] fashion,[9a] presumably by a stepwise mechanism involving 1,4-diradicals, while bicyclopropylidene (**1**) gives a significant fraction of the [4 + 2] product **17**. This seems to indicate that the latter may actually have been formed in a concerted process and that **1** has a general reaction trajectory leading to the transition state of the Diels–Alder addition.

Cycloadditions of 1 with Electron-Deficient Cycloaddends. Bicyclopropylidene (**1**) reacts with electron-deficient cycloaddends in three distinct ways, depending on the partner.[16b] Trichloroethylene and acrylonitrile cycloadded onto **1** at elevated temperatures yielding the corresponding [2 + 2] adducts **18** and **19**, respectively, (Scheme II). *trans*-Dicyanoethylene upon reaction with **1** gave rise to both the *trans*- (**20**) and the *cis*-7,8-dicyanodispiro[2.0.2.2]octane (**24**) in a ratio of 78:22, respectively. All of these [2 + 2] cycloadducts presumably arise via an intermediate 1,4-diradical like **21** in a stepwise manner. 1,4-Zwitterions in all these cases appear to be unlikely since attempts to capture them with dipolarophiles such as acetone and acetonitrile failed. The ring closure of the intermediate **21** leading to **20** and **24** proved to be reversible; when a GLPC purified sample of **20** was subjected to the cycloaddition conditions (190 °C, sealed tube, 2 h) an equilibrium mixture of the trans and the cis isomers **20** and **24** in a ratio of 78 ± 3%:22 ± 3%, respectively, was formed.

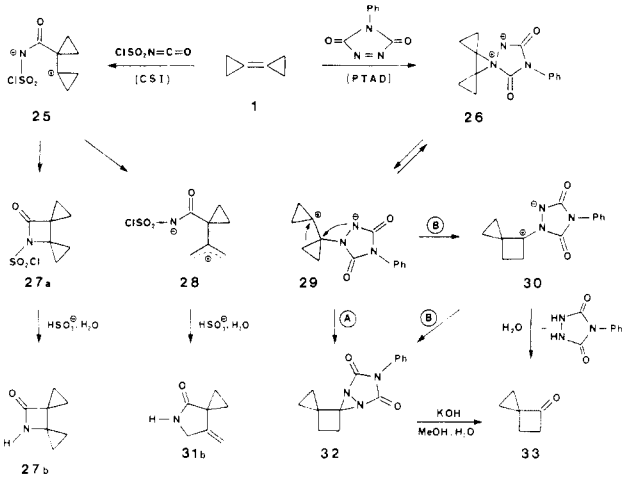
Chloro- and dichloroketene reacted readily with **1** in refluxing diethyl ether to provide the corresponding cyclobutanones **22** and **23** in high yields. Contrary to the previous cases, these cycloadducts of **1** most likely stem from a concerted [$_\pi 2_s + {}_\pi 2_a$] mode.[4] Dipolar cycloadditions of chlorinated ketenes to olefins involving zwitterionic intermediates are extremely rare.[22]

Chlorosulfonyl isocyanate (CSI) on the other hand, although a typical [2 + 2] cycloaddend with most monoalkenes, has previously exhibited cycloadditions via polar intermediates in cases where the structure of the substrate

Scheme II



Scheme III



permitted.[23,24] With **1**, CSI gave the expected β-lactam **27a** only as a minor product, the principal product being the γ-lactam derivative **31a** (Scheme III). Prior to chromatographic separation, both cycloadducts were converted to the corresponding lactams **27b** and **31b** by hydrolytic replacement of the sensitive SO_2Cl group. Although no intermediates were trapped with dipolarophiles, it is quite reasonable to assume a common zwitterionic intermediate (**25**) in the formation of **27** and **31**. Obviously, a rapid cyclopropyl to allyl cation rearrangement (**25** → **28**) precedes the ring-closure step. The alternative possibility, a cyclopropylmethyl to cyclobutyl cation rearrangement in **25** would have led to a carbonyl-substituted and thereby highly destabilized cyclobutyl cation and consequently did not occur here.

4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD), known for its high reactivity as a dienophile,[25] is also capable of undergoing dipolar cycloadditions with certain olefins with or without skeletal rearrangements.[26–29] A substituted

(21) Huisgen, R.; Grashey, R.; Sauer, J. In "The Chemistry of Alkenes" *Chemistry of Functional Groups*; Patai, S., Ed.; Interscience: London, 1964; Vol. 1, p 921.

(22) (a) For a discussion and an example of nonconcerted ketene cycloadditions, see: Al-Husaini, A. H.; Moore, H. W. *J. Org. Chem.* **1985**, *50*, 2595. (b) Erden, I.; Cauchon, G. unpublished results. (c) A zwitterion intermediate has been suggested in one dichloroketene addition to a vinylcyclopropane, although the result can also be explained with an alternative pathway. Cf.: Sarel, S.; Felzenstein, A.; Yovell, J. *Tetrahedron Lett.* **1975**, 4069.

(23) (a) For a review on CSI cycloadditions, see: Hassner, A.; Rasmussen, J. K. *Chem. Rev.* **1976**, *76*, 395. (b) Paquette, L. A.; Kirschner, S.; Malpass, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 3970. (c) Paquette, L. A.; Kirschner, S.; Malpass, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 4330. (d) Paquette, L. A.; Broadhurst, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 630.

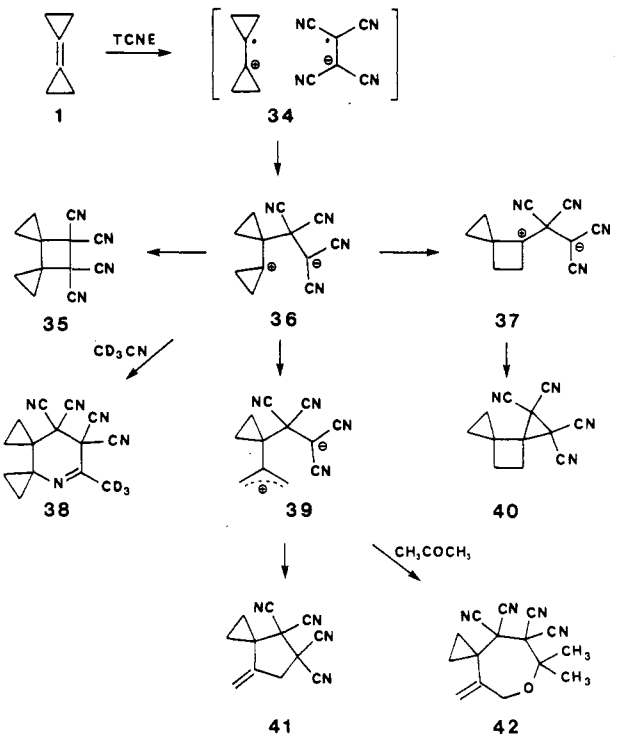
(24) (a) Barton, T. J.; Rogido, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 878. Barton, T. J.; Rogido, R. J. *Tetrahedron Lett.* **1972**, 3901. (b) Sarel, S.; Felzenstein, A.; Yovell, J. *Tetrahedron Lett.* **1976**, 451.

(25) Burrage, M. E.; Cookson, R. C.; Gupta, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325.

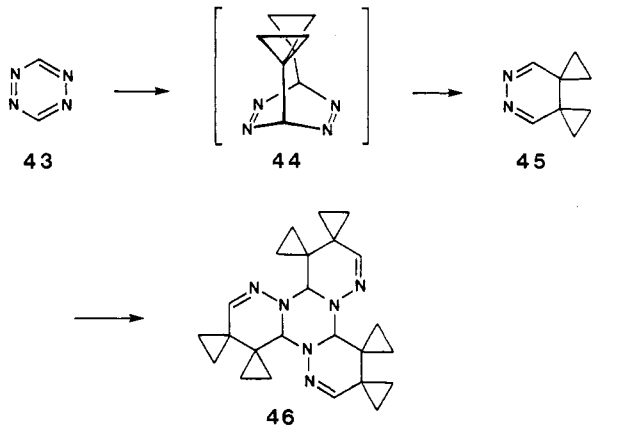
methylenecyclopropane has previously been reported to give a [2 + 2] cycloadduct with PTAD.[30] Bicyclopropylidene (1) reacted with PTAD at 0 °C to give a cycloadduct to which the unusual structure **32** was unequivocally assigned on the basis of its spectral data and chemical transformations. To the best of our knowledge, this mode of cycloaddition yielding a 1,2-diaziridine derivative is unprecedented in PTAD cycloadditions. The formation of **32** can readily be rationalized in terms of a dipolar attack of PTAD on 1, leading to the zwitterion **29**, which suffers a cyclopropylmethyl to cyclobutyl cation ring enlargement before or simultaneously with closure to **32** (Scheme III). From the reaction pattern of 1 with singlet oxygen (see below) it can be inferred that PTAD actually attacks 1 to give the aziridinium amide **26**[31,32] which equilibrates with **29**. In an attempt to prepare the corresponding 1,2-diaziridine, saponification of the urazole ring in **32** with KOH gave the known spiro[2.3]hexan-4-one (**33**).[33] Conclusive evidence for the intervention of zwitterionic intermediates as well as the timing of the ring closure step (route A or B in Scheme III) was provided by a trapping experiment: the cycloaddition of 1 with PTAD was carried out at 0 °C in wet acetone; gratifyingly, the sole product from this reaction was **33**, rather than **32**. Apparently, the cyclopropylmethyl to cyclobutyl cation rearrangement precedes the closure to the 1,2-diaziridine derivative **32** (route B in Scheme III). By contrast to the CSI addition to 1, this mode of rearrangement is the preferred one because the cyclobutyl cation **30** can be stabilized by the adjacent nitrogen atom through its resonance effect. In the presence of water, **30** is captured to give a hemiaminal-type adduct which readily converts to **33** and *N*-phenylurazole.

By contrast to the cycloadditions of 1 discussed so far, tetracyanoethylene (TCNE) did not react with bicyclopropylidene (1) in the presence of molecular oxygen, although formation of a deeply colored species, most probably a charge-transfer complex between TCNE and 1, was observed. However, cycloaddition was brought about under strict exclusion of oxygen (several freeze–pump–thaw cycles were necessary) to furnish a mixture of three compounds, which were partially separated by column chromatography on silica gel. The earlier fractions were composed of a 1:1 mixture of two adducts which on the basis of their distinctly separated signals in the ^{1}H NMR spectrum were identified as **35** and **40**. The component that eluted last was uncontaminated and its structure was readily elucidated as **41** (Scheme IV). Thus, all three types of cycloadducts described above for various electron-deficient cycloaddends were realized in the reaction of 1 with TCNE alone. While the propensity of TCNE to enter into dipolar cycloadditions with certain alkenes is well-known,[34,35] the unique behavior in this reaction must

Scheme IV



Scheme V



be due to a subtile peculiarity in the lifetime of or the electronic interactions in the 1,4-zwitterionic intermediate **36**, which most probably originates from the radical ion pair **34** formed by single electron transfer (SET) from the easily oxidized 1[36] to the oxidant TCNE. Indeed, the postulated initial 1,4-zwitterion **36** was trapped with CD_3CN to give **38** along with small amounts of **41** and **40**. With acetone, on the other hand, the rearranged 1,5-zwitterion **39** was captured to furnish the seven-membered heterocyclic ring **42**, accompanied by a small amount of **41** (Scheme IV).[37]

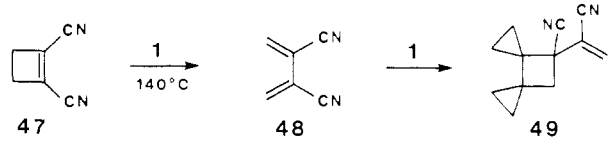
1,2,4,5-Tetrazine (**43**) and its derivatives are electron-deficient cycloaddends, which are well-known for their

(26) Erden, I.; de Meijere, A. *Tetrahedron Lett.* **1980**, 1837.
(27) Erden, I. *Chem. Lett.* **1981**, 263 and references cited therein.
(28) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.
(29) Smith, R. L.; Gream, G. E.; Meinwald, J. *J. Org. Chem.* **1977**, *42*, 927.
(30) (a) Pasto, D. J.; Chen, A. *J. Am. Chem. Soc.* **1971**, *93*, 2562; (b) Pasto, D. J.; Chen, F. T.-A. *Tetrahedron Lett.* **1973**, 713. (c) Pasto, D. J.; Wampfler, D. *Tetrahedron Lett.* **1974**, 1933.
(31) For a discussion of an aziridinium amide intermediate, see: Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.
(32) For a spectroscopic detection of an aziridinium amide intermediate, see: Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548.
(33) Denis, J. M.; Le Perchec, P.; Conia, J.-M. *Tetrahedron* **1977**, *33*, 399 and earlier papers cited therein.
(34) (a) Kaufmann, D.; de Meijere, A.; Hingerty, B.; Saenger, W. *Angew. Chem.* **1975**, *87*, 842; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 816. (b) Sarel, S.; Felzenstein, A.; Yovell, J. *J. Chem. Soc., Chem. Commun.* **1974**, 753. (c) König, B.; Kaufmann, D.; Näder, R.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1983**, 771.
(35) (a) Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659 and references cited therein. (b) Erden, I. *Tetrahedron Lett.* **1983**, *24*, 2047.
(36) 1 has a remarkably high HOMO energy as evidenced by its He I PE spectrum.[15a]
(37) By contrast to our findings, a zwitterionic intermediate had been regarded as unlikely in the cycloaddition of TCNE to certain methylenecyclopropanes as the rates of these cycloadditions were insensitive to changes in solvent polarity. Noyori, R.; Hayashi, N.; Katô, M. *J. Am. Chem. Soc.* **1971**, *93*, 4948.

facile [4 + 2] cycloadditions with inverse electron demand.[38] When bicyclopropylidene (1) was added to a dichloromethane solution of **43**,[39] the red color disappeared within 1.5 h at room temperature. The white crystalline product isolated with 86% yield was identified on the basis of its spectroscopic data (MS, IR, ^{1}H NMR, ^{13}C NMR) as a mixture of at least two stereoisomeric compounds of type **46**, trimers of the 8,9-diazadispiro[2.0.2.4]deca-7,9-diene (**45**) obviously formed via the normal [4 + 2]-cycloadduct **44** (Scheme V).

Apparently 1 undergoes [4 + 2] cycloadditions with inverse electron demand more readily than normal Diels–Alder reactions (see above). Several attempts to trap the monomeric **45**, which should be in an equilibrium with **46**,[38b] as a cycloadduct with a second molecule of **1**, were unsuccessful even at elevated temperatures in chloroform (70 °C) or toluene-d_8 (150 °C).

Finally, the reactivity of 1 toward 1,2-dicyanocyclobutene (**47**) was tested. Surprisingly, no reaction took place at 100 °C with this strained as well as electron-deficient olefin. Upon raising the temperature to 140 °C, the expected 1,1-dicyanobicyclo[2.2.0]hexane derivative was not formed, but the vinyldispiro[2.0.2.2]octane **49** derivative was isolated instead. Apparently, **47** underwent the

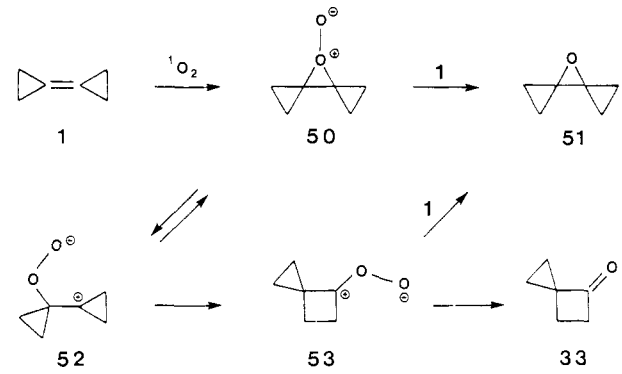


47 48 49

well-known electrocyclic ring-opening to 2,3-dicyanobutadiene (**48**)[40] at this temperature and then **1** attacked one of the double bonds in **48** to give the [2 + 2] adduct, probably via a diradical intermediate (see above).

Reaction of 1 with Singlet Oxygen ($^1O_2$). Previous studies have shown that methylenecyclopropanes are virtually inert toward singlet oxygen and certain derivatives react at an extremely slow rate.[41] In accord with this observation, epoxidation of methylenecyclopropane proceeds 74 times more slowly than that of methylenecyclopentane.[42] Lack of a significant release of strain energy in the epoxidation of methylenecyclopropane has been held responsible for this phenomenon. Moreover, a good correlation between the π-orbital energies, as indicated by the respective ionization potentials in the phtoelectron spectra (PES), and the rates of epoxidation of methylenecycloalkanes has been found.[42] The relatively low π-ionization potential of 8.93 eV[15] for **1** compared to that of a methylenecyclopropane (9.57 eV)[42,43] indicates a significantly higher HOMO in **1** which should more strongly interact with the LUMO of $^1O_2$. As an apparent consequence thereof, bicyclopropylidene (1) readily reacted with photochemically generated singlet oxygen (Na vapor lamp, tetraphenylporphyrin) at 30–35 °C.[16c] The progress of the reaction could be monitored by ^{1}H NMR spectroscopy. After complete consumption of **1** (~6 h with 200 mg of **1**) the solution was separated from the sensitizer and polymeric material by trap to trap distillation at 0 °C under reduced pressure, and the two new components[44] were identified as spiro[3.4]hexan-4-one (**33**) and 7-oxatrispiro[2.0.2.1]heptane (bicyclopropylidene epoxide, **51**) (ratio 6:10) on the basis of their spectroscopic data (Scheme VI). Methylenecyclopropane did not react with $^1O_2$ under these conditions, and **1** was totally inert toward $^3O_2$ in the absence of TPP or in the presence of the $^1O_2$-quencher diazabicyclooctane (DABCO). An authentic sample of the novel epoxide **51**[46] was prepared by epoxidation of **1** with *m*-chloroperoxybenzoic acid (*m*-CPBA) in the presence of solid sodium carbonate.[16c] In contrast to methylenecyclopropane, **1** reacted spontaneously with *m*-CPBA in dichloromethane solution even at 0 °C in 5 min. The product **51** isolated by flash distillation after careful removal of the solvent was identical with the major product from the photooxidation of **1**. The epoxide **51** is remarkably more stable toward lithium iodide than other oxaspiropentanes;[42,47] its isomerization could be effected only at 75 °C and gave spiro[2.3]hexan-4-one (**33**) as the sole product.

Scheme VI



A mechanism for the photooxidation of **1** that is consistent with the aforementioned results features a perepoxide intermediate **50** that should serve as an oxygen atom source. In the presence of unreacted **1** it would lead to two molecules of epoxide **51**. Alternatively, cleavage of **50** to the zwitterion **52** would be succeeded by a cyclopropylmethyl to cyclobutyl rearrangement to lead to the carbonyl oxide **53**, which could transfer an oxygen atom to **1** to give **33** along with **51** (Scheme VI).

Theoretical studies predict perepoxide intermediates as likely precursors of products resulting from photooxidation

(38) (a) Avram, M.; Dinulescu, J. G.; Marica, E.; Nenitzescu, C. D. *Chem. Ber.* **1962**, *95*, 2248. (b) Huber, F.-X.; Sauer, J.; McDonald, W. S.; Nöth, H. *Chem. Ber.* **1982**, *115*, 444 and references cited therein.

(39) 1,2,4,5-Tetrazine was prepared according to a procedure kindly provided by Prof. J. Sauer, University of Regensburg, West Germany. Cf. Sichert, H. Dissertation, Universität Regensburg, 1980.

(40) Bellus, D.; v. Bredow, K.; Sauter, H.; Weiss, C. *Helv. Chim. Acta* **1973**, *56*, 3004.

(41) (a) Frimer, A. A.; Farkash, T.; Sprecher, M. *J. Org. Chem.* **1979**, *44*, 989. (b) Rousseau, P.; Le Perchec, P.; Conia, J.-M. *Tetrahedron* **1976**, *32*, 2533; **1978**, *34*, 3475. (c) van den Heuvel, C. J. M.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 145.

(42) Aue, D. H.; Meshishnek, M. J.; Shellhamer, D. F. *Tetrahedron Lett.* **1973**, 4799.

(43) (a) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: New York, 1970. (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179.

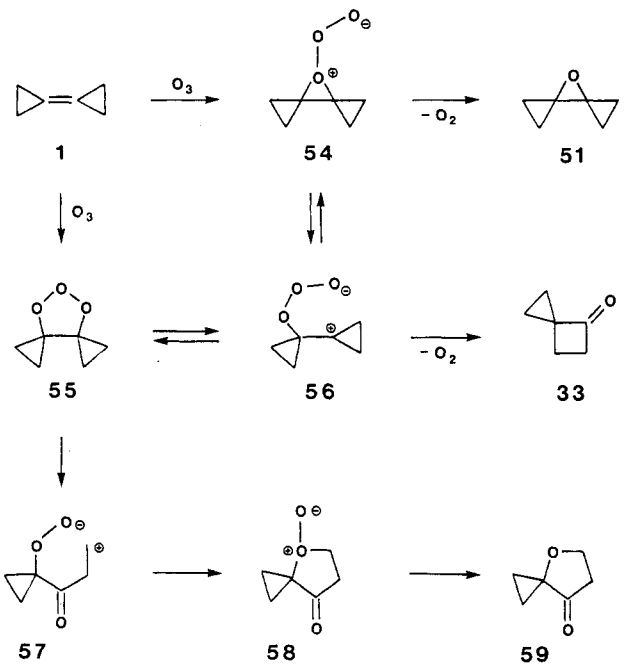
(44) According to independent studies of Prof. Dr. Th. J. de Boer and Dr. A. Hofland, Amsterdam, **1** upon photooxidation in CD_3CN with methylene blue as a sensitizer, in addition to **33** and **51**, also gave spiro[cyclopropane-1,2′-γ-butyrolactone] and spiro[cyclopropane-1,4′-γ-butyrolactone]. Both lactones, each isolated with 5% yield, probably arose from the 1,2,4,5-tetroxane dimer of the carbonyl oxide **53**. We thank Prof. de Boer and Dr. Hofland for communicating these results to us prior to publication. Cf. ref 45.

(45) Hofland, A. Thesis, University of Amsterdam, 1985.

(46) Prior to our work,[16c] **51** had only been suggested as a possible intermediate in the solvolytic rearrangement of 1,1′-bis(trimethylsiloxy)bicyclopropyl to **33**. Denis, J.-M.; Conia, J.-M. *Tetrahedron Lett.* **1972**, 4593. More recently, **51** was independently prepared by epoxidation of **1** with $KHSO_5$/acetone. Cf.: Hofland, A.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 350.

(47) Cf.: Salaün, J. R.; Conia, J.-M. *J. Chem. Soc., Chem. Commun.* **1971**, 1579. Salaün, J. R.; Champion, J.; Conia, J.-M. *Org. Synth.* **1977**, *57*, 36.

Scheme VII



of alkenes, such as 1,2-dioxetanes, allylic hydroperoxides, epoxides, etc.,[48] and there is good experimental evidence for their intermediacy.[49] Our results on the photooxidation of **1** indicate that indeed the perepoxide **50** was formed first and ring opened to the zwitterion **52**. This might be the general sequence in the photooxidation of electron-rich olefins and normally be followed by cyclization of the 1,4-zwitterion to a 1,2-dioxetane. In the case of **52** the cationic end of the 1,4-zwitterion happens to be an unstable cyclopropyl cation that suffers the observed rearrangement to the cyclobutyl cation **53**.[50] It is well understood that **1** does not undergo an ene reaction with $^1O_2$ since it would have to form a cyclopropene with a considerable increase in strain energy.

Reaction of 1 with 1,3-Dipolar Cycloaddends. The unusual mode of singlet oxygen addition to **1** encouraged the study of ozonolysis of **1** since ozone generally combines with alkenes in a 1,3-dipolar cycloaddition to give 1,2,3-trioxacyclopentanes (so-called primary ozonides). These intermediates are unstable, however, and in most cases give rise to fragmentation and recombination to 1,2,4-trioxolanes (ozonides).[51] The unique interplay between electronic and strain factors in **1** ought to influence its reaction pattern with ozone as well.

Upon passing a slow stream of dry ozone through a methylene chloride solution of **1** at −78 °C, a mixture of three products was obtained, irrespective of whether the ozonolysis mixture was worked up with or without addition of dimethyl sulfide. The ^1H NMR spectrum and gas chromatogram of the mixture clearly showed the presence of a 2:1 mixture of the epoxide **51** (22%) and the spirohexanone **33** (11%). The third and major component (67%)[52] was readily separated from **51** and **33** by preparative TLC. On the basis of its characteristic spectroscopic data its structure was assigned to be that of the 7-oxaspiro[2.4]heptan-4-one (**59**).[52] Both **33** and **51** could arise from the same intermediate, the epitrioxide **54** and the zwitterion **56** (Scheme VII). For the formation of **59** the primary ozonide **55** ought to be responsible by way of an O–O cleavage with concomitant or subsequent cyclopropane ring opening to **57**. Closure of **57** would ensue to give **58**, which would transfer an oxygen atom to **1** and yield **59** and **51**.

Table II. Tentative Classification of 2-Cycloaddends According to Their Modes of Cycloadditions with Alkenes (Based on Results in This and Previous Studies)

group	cycloaddend	cycloadd mode	rearrangement
I	trichloroethene, acrylonitrile, dicyanoethylene	via biradicals	none
II	ketenes	concerted [$_\pi2_s$ + $_\pi2_a$]	rare
III	CSI[a]	generally polar (1,4-zwitterions)	common
IV	TCNE[b]	polar (1,4-zwitterions)	mostly
V	$^1O_2$, PTAD[c]	perepoxide and its aza analogue, zwitterions	common
VI	O_3	usually but not exclusively concerted; zwitterions possible	rarely

[a] Chlorosulfonyl isocyanate. [b] Tetracyanoethylene. [c] 4-Phenyl-1,2,4-triazoline-3,5-dione.

Conclusion

The results presented in this report should constitute an important step toward establishing a general scheme of classifying $_\pi2$-cycloaddends according to their modes of cycloaddition. Bicyclopropylidene (**1**), owing to its electron-rich π-bond proved to be an ideal substrate for this type of study. Whereas it did not react with electron-rich alkenes, it readily entered into cycloadditions with virtually all types of electron-deficient cycloaddends. Even as important is the fact that **1** represents a sensitive probe for distinguishing between cycloadditions that involve zwitterionic intermediates and those that do not. This unique property of **1** arises from the facile rearrangements of 1,4- and 1,5-zwitterionic intermediates such as **25**, **29**, **36**, **52**, and **56**, respectively. Besides entailing a cyclopropyl cation that can ring open to an allyl cation, these intermediates are cyclopropyl carbinyl cations as well and thereby are also capable of rearranging to spiro [2.3]hexyl cations. The formation of unrearranged cyclobutane derivatives with dienes **9**, **12**, and **15** and the cycloaddends trichloroethylene, acrylonitrile, dicyanoethylene, 2,3-dicyano-1,3-butadiene (**48**) as well as the fact that these reactions occur at relatively high temperatures (180–190 °C) has to be interpreted in terms of stepwise cycloadditions via 1,4-biradicals. Therefore, these four cycloaddends should belong to the same group (see Table II).

Although they also lead to cyclobutane derivatives with **1** (in this case cyclobutanones) and do not show a tendency to give rise to rearranged products in general, chloro- and dichloroketene have to be regarded as a different group. They are typical [$_\pi2_s$ + $_\pi2_a$] cycloaddends that exhibit a concerted mode of cycloaddition. The low reaction temperatures (below or slightly higher than room temperature)

(48) (a) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (b) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. Denny, D. W.; Nickson, A. *Org. React. (N.Y.)* **1973**, *20*, 133. (c) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1975**, *97*, 3978.

(49) See the discussion in Schaap, A. P.; Zahlika, K. A. In *Singlet Oxygen*; Wassermann, H. H.; Murray, R. W., Eds.; Academic: New York, 1979; pp 174–242.

(50) An analogous cyclobutanone carbonyl oxide has been observed in the photooxidation of cyclopropylideneadamantane.[41c]

(51) Cf.: Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1978; Vol. I.

(52) A. Hofland and Th. J. de Boer have independently studied the ozonolysis of **1** and identified, in addition to **33**, **51**, and **59**, small amounts of 5-oxacyclohepta-1,2-dione and its enol tautomer.[45] We thank Dr. A. Hofland and Prof. Th. J. de Boer for communicating their results to us prior to publication.

at which they combine with 1 or most other alkenes testifies to a pericyclic process in their cycloadditions.

Chlorosulfonyl isocyanate (CSI) has occasionally been considered a good model for chloroketenes; however, our findings have once again underlined the distinctly polar character of this reactive heterocumulene which appears to favor zwitterionic processes. We therefore suggest to place CSI into a group by itself due to its extreme reactivity compared to other cycloaddends such as TCNE that likewise prefers zwitterionic intermediates but reacts with most alkenes at comparatively much higher temperatures.

TCNE has again proved to be unique in its reaction pattern with 1, as with many other alkenes, since it seems to embody the cycloaddition modes of several different cycloaddends such as CSI, PTAD, and $^1O_2$. The formation of all three types of products in its reaction with 1 puts TCNE (and probably DDQ also) into a transition group right between CSI, PTAD, and $^1O_2$ (Table II).

The similarities between PTAD and $^1O_2$ have been observed in several other systems previously. Their reactions with 1 constitute yet another example in this context. At the same time, our work has unveiled one facet of PTAD and $^1O_2$ cycloadditions that has quite often been postulated but never unequivocally proven: the formation of **51** renders the perepoxide formation a plausible pathway; a similar intermediate has also been postulated for PTAD[31] and recently been verified spectroscopically.[32] It now seems to be certain that these intermediates do equilibrate with their zwitterionic tautomers, and whenever the structure permits, as is the case with **52** from 1, rearrangements will occur. The formation of **51** and the unique 1,2-diaziridine derivative **32**, as well as the successful trapping experiment in the latter case are excellent indications that the aforementioned mechanistic pathways are indeed operative.

In spite of the relatively large body of experiments described in this study, it appears that the cycloaddition chemistry of bicyclopropylidene (1) is far from being a closed project. It is quite likely that some of our results will trigger new studies aimed at a better understanding of the factors underlying the varied mechanistic pathways involved in cycloaddition reactions.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 297 or 399 spectrophotometer, and mass spectra (MS) were recorded on a Varian MAT 311 instrument at 15 or 70 eV. ^1H NMR spectra were obtained with Bruker WM 270 (270 MHz), Varian EM 360 (60 MHz), HA 100 (100 MHz), and Perkin-Elmer (Model R 32) (90 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker WP 80 (20.17 MHz) spectrometer. The NMR data are reported in δ (ppm) relative to internal tetramethylsilane ($\delta = 0$) and chloroform ($\delta = 77.0$). Gas chromatographic analyses were carried out on a F+M Research Chromatograph Model 810 of Hewlett-Packard (carrier gas: N_2), a Siemens analytical gas chromatograph Model L 402, (carrier gas: H_2), and a GC 920 of Varian Aerograph (carrier gas: H_2). Elemental analyses were performed in-house in the microanalytical laboratory, University of Hamburg. Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this work were either purchased from standard suppliers or prepared according to published procedures.

Reaction of 1 with Cyclopentadiene (9). A 10 mL thick-walled glass tube containing 200 mg (2.50 mmol) of 1 and 1.0 g (15.1 mmol) of freshly distilled cyclopentadiene was sealed under nitrogen and heated at 150 °C for 10 h. Analysis of the product mixture by GLPC–MS combination (3% SE 30 and 3% Apiezon M columns) revealed that a single product with the molecular mass of 146 was formed. It was isolated by preparative GLPC (GC 920, 3-m 10% SE 30 on Chromosorb W; column temperature, 95 °C) to give 60 mg (16% yield) of dispiro[cyclopropane-1,2′-bicyclo[2.2.1]hept-5-ene-3′,1″-cyclopropane] (**11**), identical with an authentic sample in all respects:[18] ^1H NMR (100 MHz, CCl_4) δ 0.12 (m, 8 H), 1.80 (AB system, 2 H), 2.12 (m, 2 H), 6.20 (m, 2 H); MS (70 eV), m/e 146 (M^+). Found: C, 90.46; H, 9.70. Calcd for $C_{11}H_{14}$ (146.11): C, 90.36; H, 9.64.

Reaction of 1 with 1,3-Cyclohexadiene (12). A mixture of 1 (200 mg, 2.50 mmol) and 1,3-cyclohexadiene (1.0 g, 12.5 mmol) was heated in a thick-walled glass tube, sealed under nitrogen, at 170 °C for 11 h. Analysis of the resulting mixture by GLPC–MS combination showed that two adducts with the molecular mass 160 had been formed along with the dimer of **12**. These were separated from one another by preparative GLPC (GC 920, 3-m 10% SE 30 on Chromosorb W; column temperature, 100 °C) and characterized on the basis of their ^1H NMR data. Dispiro[cyclopropane-1,2′-bicyclo[2.2.2]oct-5-ene-3′,1″-cyclopropane] (**14**), isolated in 10% yield (40 mg), gave an ^1H NMR (100 MHz, $CDCl_3$) spectrum that was identical with that of an authentic sample synthesized by an independent route (see below): δ 0.05 (m, 8 H), 1.21 (m, 2 H), 1.53 (m, 2 H), 1.85 (m, 2 H), 6.34 (m, 2 H). Found: C, 89.79; H, 10.13. Calcd for $C_{12}H_{16}$ (160.27): C, 89.93; H, 10.07.

The major component proved to be dispiro[cyclopropane-1,7-bicyclo[4.2.0]oct-2′-ene-8,1″-cyclopropane] (**13**): ^1H NMR (100 MHz, CCl_4) δ 0.17 (m, 8 H), 1.53 (m, 2 H), 2.02 (m, 2 H), 2.63 (m, 1 H), 2.93 (m, 1 H), 5.52 (m, 1 H), 5.89 (m, 1 H). Found: C, 89.77; H, 10.07. Calcd for $C_{12}H_{16}$ (160.27): C, 89.93; H, 10.07.

A solution of 3.25 g (13.1 mmol) dispiro[cyclopropane-1,2′-bicyclo[2.2.2]octa-7′-ene-3′,1″-cyclopropane]-5′,6′-dicarboxylic acid[53] in 300 mL of anhydrous methanol was added to a suspension of 160 mg of prehydrogenated 10% Pd/C in 20 mL of anhydrous methanol. After the expected volume of hydrogen had been absorbed (45 min), the reaction mixture was filtered and the solvent rotary evaporated. The residue weighed 2.95 g (90%) and was pure enough for oxidative decarboxylation [^1H NMR (100 MHz, $CDCl_3/CH_2Cl_2$ (95:5)) δ 0.32 (m, 8 H), 1.40 (m, 2 H), 1.76 (mc, 4 H), 3.41 (m, 2 H); MS (70 eV), m/e 250 (M^+)].

To a magnetically stirred suspension of the hydrogenated dicarboxylic acid (2.70 g, 10.8 mmol) and 2.75 g (34.8 mmol) of pyridine in 100 mL of anhydrous acetonitrile was added under an atmosphere of nitrogen 5.26 g (11.9 mmol) of lead tetraacetate (90%, stabilized with 10% acetic acid). The mixture was warmed to 55 °C within 2 h, kept at this temperature for an additional 2 h, and then warmed to 65 °C for 3 h. The reaction mixture was diluted with 500 mL of 5% nitric acid and extracted with five 30-mL portions of *n*-pentane. The pentane solutions were washed with 50 mL each of 10% $NaHCO_3$ solution and water and then dried over anhydrous Na_2SO_4. The pentane was distilled over a 30-cm column. The white precipitate (starting material) was removed from the residue by filtration and the liquid separated by GLPC (3-m 10% SE 30; column temperature, 120 °C) to give 100 mg (6%) of **14** (see above).

Reaction of 1 with 1,3-Butadiene (15). A mixture of 1 (210 mg, 2.62 mmol) and 1,3-butadiene (1.30 g, 23.6 mmol) was placed in a thick-walled glass tube, and 10 mg of hydroquinone was added. The tube was sealed under nitrogen and heated at 180 °C for 12 h. After cooling to room temperature the product mixture was subjected to preparative gas chromatography (GC 920, 1.6-m 10% SE 30 on Chromosorb W; column temperature, 60 °C). The component with the shorter retention time was isolated in 49% (170 mg) yield and identified as 7-vinyldispiro[2.0.2.2]octane (**16**): ^1H NMR (100 MHz, CCl_4) δ 0.25 (m, 8 H), 2.26 (m, 2 H), 3.07 (m, 1 H), 4.79, 4.93, 5.85 (m, s, m, ABX system, 3 H). Found: C, 89.23; H, 10.50. Calcd for $C_{10}H_{14}$ (134.23): C, 89.47; H, 10.53. The second fraction (16 mg, 8%) was shown to be dispiro[2.0.2.4]dec-8-ene (**17**) on the basis that its spectroscopic data were identical with those of an authentic sample.[20,53]

Cycloaddition of Trichloroethylene to 1. A 20-mL thick-walled glass tube was charged with 400 mg of 1 (5 mmol) and 607 mg (5 mmol) of trichloroethylene. The tube was sealed under nitrogen and heated at 180 °C for 96 h. The products were isolated by preparative GLPC, and the first fraction identified as [4]rotane

(53) de Meijere, A. *Chem. Ber.* **1974**, *107*, 1702.

(8) through coinjection with an authentic sample[33] and ^{1}H NMR spectroscopy. The second fraction (181 mg, 18% yield) was 7,7,8-trichlorodispiro[2.0.2.2]octane (**18**): IR (film): 3080, 3000, 1421, 1391, 1262, 1047, 1028, 1010, 935, 914, 812, 724 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.29–1.27 (m, 8 H), 5.02 (s, 1 H). Found: C, 45.47; H, 4.27; Cl, 50.22. Calcd for $C_8H_9Cl_3$ (211.52): C, 45.43; H, 4.29; Cl, 50.28.

Cycloaddition of Acrylonitrile to 1. A mixture of 200 mg (2.5 mmol) of **1** and 530 mg (10 mmol) of acrylonitrile, sealed in a thick-walled glass tube under nitrogen, was heated at 190 °C for 2 h. According to the ^{1}H NMR spectrum of the crude product, the conversion of **1** to the cycloadduct was quantitative. Purification was achieved by GLPC (1.5-m 10% SE 30; column temperature, 120 °C) to give 324 mg (97.6%) of 7-cyanodispiro-[2.0.2.2]octane (**19**): mp 32 °C; ^{1}H NMR (100 MHz, CCl_4) δ 0.05–0.82 (m, 8 H), 2.43 (m, 2 H), 3.25 (dd, ^3J = 9 Hz, 1 H). Found: C, 81.15; H, 8.31; N, 10.43. Calcd for $C_8H_{11}N$ (133.20): C, 81.15; H, 8.32; N, 10.52.

Cycloaddition of *trans*-Dicyanoethylene to 1. In a thick-walled glass tube, sealed under nitrogen, a mixture of 200 mg (2.5 mmol) of **1** and 1.0 g (12.8 mmol) *trans*-dicyanoethylene was heated at 190 °C for 2 h. The product mixture was freed from excess dicyanoethylene by sublimation at 25 °C (0.01 Torr). The product sublimed at 60 °C (0.01 Torr) to yield 223 mg (57%) of a 78:22 mixture of *trans*-(**20**) and *cis*-7,8-dicyanodispiro-[2.0.2.2]octane (**24**). Attempted separation of the two isomers by GPLC (20-cm 10% SE 30; column temperature, 140 °C) resulted in the decomposition of the cis isomer **24**, thereby allowing the isolation of pure **20**: mp 88–89 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ [**20** + **24**] 0.15–0.89 (m, 8 H), 3.40 (s, 2 H), 3.53 (s, 2 H); ^{1}H NMR (100 MHz, $CDCl_3$) δ [**20**] 0.17–0.89 (m, 8 H), 3.53 (s, 2 H). Found: C, 76.05; H, 6.27; N, 17.66. Calcd for $C_{10}H_{10}N_2$ (158.21): C, 75.92; H, 6.27; N, 17.71.

Dichloroketene Addition to 1. A solution of 910 mg (5 mmol) of freshly distilled trichloroacetyl chloride in 50 mL of dry ether was added over 1.5 h to a stirred, refluxing mixture of 400 mg (5 mmol) of **1** and 1.0 g (0.015 g atom) of activated zinc in 50 mL of dry ether under a nitrogen atmosphere. The reaction mixture was stirred at reflux for additional 16 h after the addition was complete. The excess zinc was removed by filtration and washed with 10 mL of ether. The reaction solution was concentrated under reduced pressure (20 °C, 15 Torr) to $^1/_4$ of its original volume, and 20 mL of *n*-pentane was added. The almost colorless supernatant was decanted from the zinc salts and the solvent rotary evaporated. The residue was chromatographed on 10 g silica gel, eluting with *n*-pentane to give 528 mg (59%) of 8,8-dichlorodispiro[2.0.2.2]oct-7-one (**23**). Recrystallization from *n*-hexane furnished an analytically pure sample: mp 74–74.5 °C; IR (KBr) 3085, 3010, 2924, 1800, 1438, 1423, 1370, 1315 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.79 (m, 2 H), 1.02 (m, 2 H), 1.32 (m, 2 H), 1.56 (m, 2 H). Found: C, 49.14; H, 4.07. Calcd for $C_8H_8Cl_2O$ (191.06): C, 50.29; H, 4.22.

Chloroketene Addition to 1. The chloroketene addition to **1** was carried out in exactly the same manner as described for the dichloroketene addition, except dichloroacetyl chloride was used instead of trichloroacetyl chloride. Thus, from 100 mg (1.25 mmol) of **1**, 185 mg (1.25 mmol) of dichloroacetyl chloride, and 0.5 g (0.0075 mol) of activated zinc, 80 mg (63%) of 8-chlorodispiro[2.0.2.2]oct-7-one (**22**) was obtained after column chromatography on silica gel (10 g, *n*-pentane/CH_2Cl_2 = 5:1): mp 30–31 °C; IR (film) 3080, 3005, 2965, 1790, 1430, 1380, 1328, 912, 735 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.58 (m, 2 H), 0.73 (m, 2 H), 0.92 (m, 1 H), 1.00 (m, 1 H), 1.38 (m, 2 H), 4.90 (s, 1 H). Found: C, 61.27; H, 5.73; Cl, 22.56. Calcd for C_8H_9ClO (156.62): C, 61.36; H, 5.79; Cl, 22.64.

Chlorosulfonyl Isocyanate (CSI) Addition to 1. To a solution of 100 mg (1.25 mmol) of **1** in 10 mL of dichloromethane, stirred magnetically and cooled with an acetone–dry ice bath, was added a solution of 177 mg (1.25 mmol) of CSI in 10 mL of dichloromethane through a syringe within 20 min under a nitrogen atmosphere. After complete addition, the cooling bath was removed and the mixture stirred at 25 °C for 2 h. The solution was then poured into a mixture of 20 g of $NaHCO_3$ and 1.3 g of $Na_2S_2O_5$ in 50 mL of water. After the mixture was stirred at room temperature for 1 h, the two phases were separated, and the water layer was extracted with each 2 × 20 mL of CH_2Cl_2 and diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, the solvent was rotary evaporated (20 °C, 20 Torr), and the residue was chromatographed on 20 g of Florisil. Elution with ether/methanol (95:5) resulted in a clean separation of the two adducts. Dispiro[2.0.2.2]azetidin-8-one (**27b**), which was formed in 9.7% yield (15 mg), eluted first: mp 120–121 °C; IR (KBr) 3220, 3120, 3005, 1740, 1450, 1410, 1355, 1115, 978 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.59 (m, 2 H), 0.73 (m, 2 H), 0.93 (m, 2 H), 1.23 (m, 2 H), 5.83 (br s, 1 H). Found: C, 67.97; H, 7.20; N, 11.23. Calcd for C_7H_9NO (123.16): C, 68.27; H, 7.36; N, 11.37. The second fraction, isolated in 55% yield (85 mg) was spiro[cyclopropane-1,3′-(4-methylene-2-pyrrolidone)] (**31b**): mp 87–88 °C; IR (KBr) 3210, 3100, 3080, 3000, 2770, 1695, 1665, 1488, 1393, 1278 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.02 (m, 2 H), 1.49 (m, 2 H), 4.16 (m, 2 H), 4.56 (m, 1 H), 4.77 (m, 1 H), 6.90 (br s, 1 H). Found: C, 67.82; H, 7.16; N, 11.16. Calcd for C_7H_9NO (123.16): C, 68.27; H, 7.36; N, 11.37.

Reaction of 1 with 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). A 25-mL round-bottomed flask, equipped with a magnetic spin bar and a 10-mL pressure-equalizing addition funnel, was charged with 100 mg (1.25 mmol) of bicyclopropylidene (**1**) in 5 mL of CH_2Cl_2. The solution was cooled to 0 °C and a solution of 240 mg (1.25 mmol) of freshly sublimed PTAD in 5 mL of CH_2Cl_2 added dropwise. The red color of PTAD disappeared almost instantaneously upon additon. The resulting pale yellow solution was concentrated under reduced pressure and the residue chromatographed on 8 g of silica gel, by eluting with CH_2Cl_2. The cycloadduct was isolated in 83% yield (199 mg) as a white solid. Recrystallization from ethanol afforded an analytically pure sample of **32**: mp 228–230 °C; IR (KBr) 3065, 3000, 1760, 1725, 1500, 1400, 1260 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.80 (m, 4 H), 2.25 (dd, ^3J = 7.8, 8.6 Hz, 2 H), 3.18 (dd, ^3J = 7.8, 8.6 Hz, 2 H), 7.48 (m, 5 H); ^{13}C NMR (20.17 MHz, $CDCl_3$) δ 12.49, 23.27, 29.37, 29.76, 87.60, 125.58, 128.75, 129.27, 130.50, 151.07. Found: C, 65.86; H, 5.08; N, 16.41. Calcd for $C_{14}H_{13}N_3O_2$ (255.28): C, 65.87; H, 5.13; N, 16.46.

Reaction of 1 with PTAD in Wet Acetone. The reaction was carried out in exactly the same manner as described above except that CH_2Cl_2 was replaced by a 95:5 mixture of acetone/water (25 mL) as solvent. The resulting solution was diluted with 100 mL of water and extracted twice with 20-mL portions of *n*-pentane. The combined organic layers were dried over anydrous Na_2SO_4, and the solvent was distilled off through a 25-cm Vigreux column. The residue was flash distilled (2 Torr, 25 °C) to give 91 mg (76%) of spiro[2.3]hexan-4-one (**33**).[33]

Reaction of 1 with Tetracyanoethylene (TCNE) in Benzene. A solution of 100 mg (1.25 mmol) of **1** and 150 mg (1.25 mmol) of freshly sublimed TCNE in 5 mL of dry benzene was thoroughly degassed by applying six freeze–pump–thaw cycles and sealed under argon in a thick-walled glass tube. The mixture was then heated at 60 °C for 30 min; after cooling to room temperature, the solvent was rotary evaporated and the residue chromatographed on 15 g of silica gel, by eluting with CH_2Cl_2. Two well-separated components were isolated, the one eluting first being a 1:1 mixture of 7,7,8,8-tetracyanodispiro[2.0.2.2]octane (**35**) and 1,1,2,2-tetracyanodispiro[2.0.2.2]octane (**40**, 91.5 mg, 35%): mp 140–145 °C; IR (KBr) [**35** + **40**] 3020, 2260, 1428, 1110, 1070, 1050, 1030 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ [**35**] 0.85 (m, 4 H), 1.20 (m, 4 H); ^{1}H NMR (270 MHz, $CDCl_3$) δ [**40**] 0.67 (m, 2 H), 1.41 (m, 2 H), 2.39 (m, 2 H), 2.64 (m, 2 H). Found (**35** + **40**): C, 69.18; H, 3.85, N, 26.83. Calcd for $C_{12}H_8N_4$ (208.23): C, 69.22; H, 3.87; N, 26.91. The second fraction isolated in 45% (116.5 mg) yield was pure 6,6,7,7-tetracyano-4-methylenespiro-[2.4]heptane (**41**): mp 192–193 °C; IR (KBr) 3100, 3020, 2930, 2260, 1660, 1435, 1235, 1030 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.30 (m, 2 H), 1.57 (m, 2 H), 3.51 (m, 2 H), 4.81 (m, 1 H), 5.09 (m, 1 H). Found: C, 69.20; H, 3.86; N, 26.90. Calcd for $C_{12}H_8N_4$ (208.23): C, 69.22; H, 3.87; N, 26.91.

Reaction of 1 with TCNE in Acetone. The cycloaddition of **1** to TCNE in acetone was carried out in the same manner as described above except that the reaction time was 24 h at 100 °C. After rotary evaporation of the solvent, the residue was chromatographed on 20 g of silica gel. Elution with CH_2Cl_2 gave as the first fraction 40 mg (15%) of **41**. The second fraction (240 mg, 60%) was identified as 4-methylene-7,7-dimethyl-8,8,9,9-tetracyano-6-oxaspiro[2.6]nonane (**42**): mp 99–102 °C; IR (KBr)

3100, 3000, 2930, 2250, 1458, 1398, 1203, 1098, 1035 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.15 (m, 2 H), 1.64 (m, 2 H), 4.40 (m, 2 H), 5.56 (m, 1 H), 5.63 (m, 1 H). Found: 266.31014. Calcd for $C_{15}H_{14}N_4O$: 266.31028.

Reaction of 1 with TCNE in Acetonitrile-d_3. A solution of 100 mg (1.25 mmol) of **1** and 150 mg (1.25 mmol) of TCNE in 1 mL of CD_3CN was placed in an NMR tube and allowed to stand at room temperature (~23 °C) under an argon atmosphere. The progress of the reaction was monitored by ^1H NMR spectroscopy. Once all of the bicyclopropylidene (**1**) had been consumed (~12 days), the product mixture was chromatographed on 15 g of silica gel, by eluting with CH_2Cl_2/*n*-pentane (5:1). The earlier fractions gave 37 mg (15%) of a 1:1 mixture of **41** and **40**. The last fraction consisted of pure 8-(trideuteriomethyl)-9,9,10,10-tetracyano-7-azadispiro[2.0.2.4]dec-7-ene (**38**): mp 92–93 °C; IR (KBr) 3060, 3020, 2930, 2860, 2250, 1672, 1195, 1180, 1038 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80 (m, 2 H), 1.00 (m, 2 H), 1.29 (m, 4 H). Found: 252.30601. Calcd for $C_{14}H_8D_3N_5$: 252.30608.

Reaction of 1 with 1,2,4,5-Tetrazine (43).[39] To a solution of 164 mg (2.0 mmol) **43**[39] in 5 mL of dichloromethane was added 168 mg (2.1 mmol) of **1** at room temperature. Decolorization under N_2 evolution occurred within 1.5 h. The solvent was rotary evaporated and the white residue recrystallized from ether/pentane (1:1) to yield 231 mg (86%) of trimer **46** of 8,9-diazadispiro[2.0.2.4]deca-7,9-diene: IR (KBr) 3070, 3000, 2910, 1615, 1420, 1330, 1320, 1220, 1140, 1115, 1100, 1090, 1045, 1025, 965, 930, 925, 910, 875, 830, 790 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.10–1.03 (complex m, 24 H), 3.47, 3.62, 4.23, 6.09, 6.16, 6.20 (6 s, 1 H each); ^{13}C NMR (15.08 MHz, $CDCl_3$) δ 0.0, 5.7, 6.2, 6.7, 8.8, 9.3, 10.0, 10.6, 12.4, 13.3, 17.3, 19.4, 19.8, 21.0, 79.7, 84.6, 146.2, 146.9, 147.4; MS (70 eV), *m/e* (relative intensity) 402 (M^+, 34), 268 (21), 239 (61), 212 (36), 211 (30), 172 (21), 135 (85), 134 (94), 133 (85), 120 (22), 119 (60), 118 (20), 107 (50), 106 (69), 105 (50), 103 (22), 92 (32), 91 (100), 80 (27), 79 (87), 78 (90), 77 (85), 67 (20), 66 (29), 65 (89), 63 (36), 57 (29), 55 (22), 53 (53), 52 (86), 51 (86), 50 (76), 43 (20), 41 (77), 40 (24), 39 (88), 38 (20). Found: C, 71.48; H, 7.54; N, 20.92. Calcd for $C_{24}H_{30}N_6$ (402.54): C, 71.61; H, 7.71; N, 20.88.

Reaction of 1 with 1,2-Dicyanocyclobutene (47). A mixture of 260 mg (2.5 mmol) of 1,2-dicyanocyclobutene (**47**) and 200 mg (2.5 mmol) of **1** was heated at 100 °C for 12 h in a sealed thick-walled glass tube. The ^1H NMR spectrum of an aliquot showed that no reaction had taken place under these conditions. Repetition of the experiment at 140 °C gave, after 8 h, a dark viscous liquid, which was triturated with ether/*n*-pentane (1:1). The soluble portion of the product mixture was separated, the solvent rotary evaporated to give 263 mg (28%) of 7-cyano-7-(1-cyanovinyl)dispiro[2.0.2.2]octane (**49**) as a yellowish oil: IR (film) 3070, 2995, 2940, 2235, 1611, 1422, 1198, 1025, 1010, 950 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.12–0.8 (m, 8 H), 2.65 (d, ^2J = 13.5 Hz, A part of an AB system, 1 H), 2.72 (d, ^2J = 13.5 Hz, B part, 1 H), 5.88 (s, 1 H), 5.95 (s, 1 H). Found: C, 78.14; H, 6.49; N, 15.12. Calcd for $C_{12}H_{12}N_2$ (184.25): C, 78.23; H, 6.57; N, 15.21.

Singlet Oxygen Additon to 1. A solution of 200 mg (2.5 mmol) of **1** in 5 mL of $CDCl_3$ containing 4 mg of tetraphenylporphyrin (TPP) was placed into a 10-mL round-bottomed flask. The system was purged with dry oxygen and left under a slight positive oxygen pressure. The flask was irradiated by means of a 250-W sodium vapor lamp at 30–35 °C, while the solution was stirred with a magnetic stirring bar. The progress of the reaction was monitored by ^1H NMR. Within 6 h, singlet oxygenation was complete. The product mixture was separated from the sensitizer by trap-to-trap distillation (0 °C, 0.1 Torr), and the two components were identified as spiro[2.3]hexan-4-one (**33**) and 7-oxatrispiro[2.0.2.1]heptane (**51**) (ratio 6:10, combined yield 180 mg, 76%) on the basis that their ^1H NMR spectroscopic data were identical with those of authentic samples of **33**[33] and **51**.

In the absence of TPP or in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) no reaction was observed.

Epoxidation of 1. A 10-mL single-neck round-bottomed flask was charged with a solution of 100 mg (1.25 mmol) of **1** in 2 mL of dry CH_2Cl_2 and 200 mg of anhydrous Na_2CO_3. While the mixture was cooled in an ice–water bath and stirred magnetically, a solution of 215 mg (1.25 mmol) of *m*-chloroperoxybenzoic acid in 5 mL of dry CH_2Cl_2 was added through a 10-mL pressure-equalizing addition funnel. After the mixture was stirred for 5 min at 0 °C, the precipitate (*m*-chlorobenzoic acid) was filtered off, the filter cake rinsed with 10 mL of CH_2Cl_2, and the solvent distilled through a 25-cm Vigreux column. After the last traces of solvent were removed under reduced pressure (–15 °C, 15 Torr), the product was flash distilled at 0 °C (0.1 Torr) to give 115 mg (96%) of 7-oxatrispiro[2.0.2.1]heptane (**51**): IR (film) 3060, 2960, 1410, 1395, 1252, 1005, 910 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00 (m, 4 H), 1.31 (m, 4 H). Found: C, 74.91; H, 8.30. Calcd for C_6H_8O (96.13): C, 74.97; H, 8.32.

Lithium Iodide Catalyzed Rearrangement of 51. A mixture of 60 mg (0.63 mmol) of epoxide **51** and 10 mg of lithium iodide in 2 mL of $CDCl_3$ was heated in a sealed ampule at 75 °C for 1.5 h. The product, isolated in 75% yield (45 mg) by preparative GLPC (1.0-m 10% SE 30 on Chromosorb W; column temperature, 60 °C) was identical in all respects (^1H NMR, GLPC retention time, etc.) with an authentic sample of **33**.[33]

Ozonolysis of 1. A slow stream of dry oxygen was passed through an ozonator (Fischer Model 502), which was connected to a 10-mL two-necked round-bottomed flask, equipped with a gas inlet tube and an outlet, connected to a trap containing an aqueous solution of potassium iodide. The reaction flask was charged with 300 mg (3.75 mmol) of **1** in 3 mL of CH_2Cl_2 and cooled to –78 °C in an acetone/dry ice bath before the ozonator was turned on. The ozonolysis was terminated when the blue color of excess ozone persisted (~15–20 min). The reaction mixture was purged with dry argon and allowed to warm up to room temperature. The contents of the flask were then flash distilled (23 °C, 0.1 Torr) to give 152 mg of a product mixture which, according to its ^1H NMR spectrum, was composed of 22% **51**, 11% **33**, and a third compound (67%), which was separated from **33** and **51** by preparative TLC (SiO_2; CH_2Cl_2/*n*-pentane, 3:1). Its mass spectrum (*m/e* 112) indicated the presence of two oxygen atoms; its ^1H NMR and IR spectra permitted the assignment of its structure as 7-oxaspiro[2.4]heptan-4-one (spiro[cyclopropane-1,2′-tetrahydrofuran]-3-one) (**59**):[45,52] IR (film) 2960, 2925, 2860, 1742, 1240, 1090 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (m, 2 H), 1.29 (m, 2 H), 2.71 (t, ^3J = 7.2 Hz, 2 H), 4.22 (t, ^3J = 7.2 Hz, 2 H). Found: 112.13155. Calcd for $C_6H_8O_2$: 112.13156.

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Appendix

Structures of the Cycloadducts. The NMR and IR spectra as well as analytical data are reported in the Experimental Section.

In the [2 + 2] adducts the common structural feature is the system of two adjacent spirocyclopropane groups that give rise to characteristic multiplets in the δ 0.15–1.56 region of the ^1H NMR spectrum. In general, those protons facing the other spirocyclopropane group are upfield-shifted due to the diamagnetic anisotropy of the cyclopropane ring. For the acrylonitrile, dicyanoethylene, and TCNE adducts, the IR absorptions at 2240–2260 cm^{-1} due to the C≡N stretch vibration were of diagnostic value. The shift to lower wavenumbers by 10–15 cm^{-1} in the carbonyl absorption of the chloro- and dichloroketene adducts as compared to their counterparts without spirocyclopropane rings arises from the conjugative interaction of the cyclopropyl group with the adjacent carbonyl π-system. The minor product from the CSI addition to **1** was identified as the β-lactam **27b** mainly on the basis of its carbonyl absorption at 1740 cm^{-1}, characteristic for a β-lactam ring when the appropriate allowance is made for the conjugation with the spirocyclopropane group. The γ-lactam **31b**, formed as the major product, accordingly exhibits a carbonyl absorption at 1695 cm^{-1}. In the ^1H NMR spectrum of **31b** the *exo*-methylene hydrogens give

rise to two narrow multiplets at δ 4.56 and 4.77; the ring CH_2 group appears likewise as a narrow multiplet at δ 4.16. Double resonance experiments permitted unequivocal assignment of the structure as shown. The structure determination of the unusual PTAD adduct **32** has relied heavily on its ^1H and ^{13}C NMR data. The A_2B_2 pattern at δ 2.25 and 3.18 and the multiplet at δ 0.80 point to a spiro[2.3]hexane derivative; the spectrum is very similar to that of the spiro[2.3]hexan-4-one (**33**) except for the five-proton multiplet at δ 7.48 for the *N*-phenyl group. The symmetry in the molecule manifests itself in the ^{13}C NMR spectrum; four signals appear in the aliphatic region due to the cyclopropyl and cyclobutyl carbon atoms, whereas the quaternary carbon of the 1,2-diaziridine derivative absorbs at δ 87.6.

The major product from the photooxidation of **1** was the epoxide **51**, which was independently prepared from **1** by epoxidation. Its ^1H NMR displays a high symmetry in the molecule, with two sets of multiplets at δ 1.00 and 1.31, both of which appear as parts of an AA'BB' system.

The ^1H NMR spectrum of the ozonolysis product **59** indicates the presence of one spirocyclopropane group only, and shows two CH_2 groups which are adjacent to one another (two triplets with ^3J = 7.2 Hz each). The unusually low-field absorption for one of the CH_2 groups at δ 4.22 testifies to its neighboring an oxygen atom in the ring. The other CH_2 group absorbs at δ 2.71, a little lower than in a cyclopentanone ring. The strong absorption for the carbonyl group in the IR at 1742 cm^{-1} and those corresponding to the C–O stretch at 1090 and 1240 cm^{-1} as well as its mass spectrum confirm the assigned structure.

Registry No. **1**, 27567-82-4; **8**, 24375-17-5; **9**, 542-92-7; **11**, 40459-58-3; **12**, 592-57-4; **12** (dimer), 6143-79-9; **13**, 40459-60-7; **14**, 40459-59-4; **14** (5',6'-dicarboxylic acid), 111407-33-1; **14** (hydrogenated, 5',6'-dicarboxylic acid), 111291-54-4; **15**, 106-99-0; **16**, 40459-57-2; **17**, 24029-73-0; **18**, 73496-17-0; **19**, 73496-18-1; **20**, 73496-19-2; **22**, 73496-21-6; **23**, 73496-22-7; **24**, 73496-20-5; **27b**, 111291-55-5; **31b**, 111291-56-6; **32**, 73496-25-0; **33**, 20571-15-7; **35**, 73506-18-0; **38**, 73496-27-2; **40**, 73496-26-1; **41**, 73506-17-9; **42**, 73496-28-3; **43**, 290-96-0; **46**, 111323-53-6; **47**, 3716-97-0; **49**, 111291-57-7; **51**, 52952-63-3; **59**, 111291-58-8; CSI, 1189-71-5; PTAD, 4233-33-4; TCNE, 670-54-2; trichloroethylene, 79-01-6; acrylonitrile, 107-13-1; *trans*-dicyanoethylene, 764-42-1; trichloroacetyl chloride, 76-02-8; dichloroacetyl chloride, 79-36-7.

Regioselectivity of Nucleophilic Ring Opening in Substituted Phenanthrene 9,10-Imine and 9,10-Oxide. Molecular Orbital Theoretical Predictions and Experimental Results

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Hückel-type calculations of Wheland's π-localization energies were applied to the prediction of product distributions in the reactions of the model nucleophile N_3^- with various unsymmetrically substituted phenanthrene imines **1B** and oxides **1A**. Experimental work with 3-methyl-, 2-methoxy-, 3-methoxy-, and 3-chlorophenanthrene 9,10-imine as well as with the analogous oxides revealed excellent correlation between the observed product distribution and the calculated differences (magnitude and sign) in π-energies of the common ionic precursors of both the isomeric trans-azido alcohols **2Aa** and **2Ab** and the isomeric trans-azido amines **2Ba** and **2Bb**.

The observation that polycyclic arene oxides react with a variety of cellular nucleophiles awoke special interest in the stereo- and regioselectivity associated with the nucleophilic ring opening of these biologically important oxiranes.[1] By application of several model nucleophiles, trans attack has been established both by spectroscopic[2] and by X-ray diffraction analysis,[3] leading to isomeric products in ratios that could be predicted by MO theoretical calculations.[4,5]

Recently, it has been demonstrated that various polycyclic arene imines act in vitro similarly to arene oxides: they were found to bind to DNA[6] and other cellular constituents and to have exceptionally high mutagenic potencies[7-9] that are clearly related to the activities of the corresponding epoxides.[7] Therefore, we found it imperative to undertake a detailed study on the chemical transformations of the imines in the presence of typical nucleophilic reagents.[10]

In this paper we report a theoretical method for predicting the regioselectivity of attack of nucleophiles on both

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