electron-withdrawing groups on the observed $E_p$ values (Table I) is also manifest in the corresponding experimental p$K_a$ values.

As observed by other workers, oxidation of pyrrole (1) results in the deposition of "pyrrole black" at the working electrode. Similarly, the 2,5-diunsubstituted pyrroles **3**, **10**, and **11** deposit "metallic" conducting polymers at the working electrode, but 3-methylpyrrole-4-carboxylic acid (**9**) forms a soluble yellow polymer that fails to adhere to the electrode surface. No other pyrroles gave evidence of polymer formation, indicating that unsubstituted 2- *and* 5-positions are required for manifestation of this phenomenon.

## Experimental Section

Pyrroles **1**–**117** used in this study were available from synthetic work carred out over the past 20 years in Liverpool and Davis. Synthetic origins of the majority of the pyrroles are obvious and are published; specific details in particular examples are available by writing to K.M.S. Acetonitrile was dried by refluxing over calcium hydride, then distilled, and stored over 3-Å molecular sieves. The supporting electrolyte tetra-*n*-butylammonium perchlorate (Kodak) was vacuum dried at 60 °C before use.

A three-compartment electrochemical cell was used, with a main compartment of 20-mL capacity; the cell included a reference electrode (Ag/$AgNO_3$, a silver wire in 0.1 M $AgNO_3$ in acetonitrile; potential 0.337 V vs. the aqueous saturated calomel electrode), a platinum counterelectrode, and a platinum wire working electrode. The last was cleaned in 10 M nitric acid and then heated four times in a flame to incandescence prior to each run. Voltammetric measurements were made with a PAR Model 175 programmer and a PAR Model 173 potentiostat/galvanostat attached to a PAR Model RE0074 XY recorder. Sample solutions consisted of 2 mM pyrrole in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate, and measurements were performed with a scan rate of 100 mV/s.

**Acknowledgment.** We thank the National Science Foundation (CHE-81-20891) and National Institutes of Health (HL 22252) for support of this research. Leave of absence (for H.D.T.) from Yarmouk University, Jordan, is also gratefully acknowledged. We are grateful to Professor W. H. Fink for assistance with the least-squares computation and to the reviewers for helpful comments.

**Registry No.** **1**, 109-97-7; **2**, 636-41-9; **3**, 616-43-3; **4**, 634-97-9; **5**, 3757-53-7; **6**, 3284-51-3; **7**, 87462-15-5; **8**, 89909-39-7; **9**, 64276-66-0; **10**, 2199-49-7; **11**, 89909-40-0; **12**, 89909-41-1; **13**, 4868-30-8; **14**, 54474-51-0; **15**, 13219-76-6; **16**, 4513-93-3; **17**, 2199-44-2; **18**, 40236-19-9; **19**, 954-92-7; **20**, 42419-19-2; **21**, 51089-83-9; **22**, 31896-88-5; **23**, 51671-83-1; **24**, 51089-80-6; **25**, 51644-01-0; **26**, 89909-42-2; **27**, 2199-46-4; **28**, 50634-31-6; **29**, 61538-85-0; **30**, 33317-06-5; **31**, 517-22-6; **32**, 42781-37-3; **33**, 2199-47-5; **34**, 1925-61-7; **35**, 31896-92-1; **36**, 4758-64-9; **37**, 32900-45-1; **38**, 13219-71-1; **39**, 89909-43-3; **40**, 4989-24-6; **41**, 13219-74-4; **42**, 4868-32-0; **43**, 37531-54-7; **44**, 20303-31-5; **45**, 54278-10-3; **46**, 31837-62-4; **47**, 69366-55-8; **48**, 51089-69-1; **49**, 53365-82-5; **50**, 89909-44-4; **51**, 89909-45-5; **52**, 56015-18-0; **53**, 3750-36-5; **54**, 5866-63-7; **55**, 859-38-1; **56**, 50622-67-8; **57**, 4989-24-6; **58**, 69912-10-3; **59**, 89909-46-6; **60**, 2386-26-7; **61**, 2386-28-9; **62**, 89909-47-7; **63**, 52459-55-9; **64**, 89909-48-8; **65**, 37013-86-8; **66**, 31695-39-3; **67**, 40515-73-9; **68**, 6122-77-6; **69**, 40593-29-1; **70**, 40593-48-4; **71**, 37538-31-1; **72**, 31837-66-8; **73**, 50296-60-1; **74**, 53700-91-7; **75**, 89909-49-9; **76**, 32900-47-3; **77**, 89909-50-2; **78**, 6122-78-7; **79**, 52648-98-3; **80**, 52649-02-2; **81**, 2199-58-8; **82**, 89909-51-3; **83**, 6250-80-2; **84**, 18818-25-2; **85**, 89909-52-4; **86**, 87462-14-4; **87**, 6339-66-8; **88**, 89909-53-5; **89**, 52459-25-3; **90**, 965-20-8; **91**, 5866-53-5; **92**, 31897-11-7; **93**, 951-64-4; **94**, 978-24-5; **95**, 89909-54-6; **96**, 89909-55-7; **97**, 965-19-5; **98**, 942-74-5; **99**, 51089-73-7; **100**, 89909-56-8; **101**, 89909-57-9; **102**, 51089-77-1; **103**, 31837-46-4; **104**, 2199-60-2; **105**, 89909-58-0; **106**, 52649-06-6; **107**, 32900-44-0; **108**, 16132-27-7; **109**, 5408-12-8; **110**, 89909-59-1; **111**, 57745-26-3; **112**, 81972-01-2; **113**, 89909-60-4; **114**, 89909-61-5; **115**, 89909-62-6; **116**, 89909-63-7; **117**, 89909-64-8.

# Addition Reactions to *syn*- and *anti*-Sesquinorbornenes Involving Ionic Mechanisms. The Role of Tetracyanoethylene

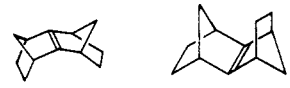
Paul D. Bartlett,* Antonius A. M. Roof, Ravi Subramanyam, and William J. Winter

*Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129*

*Received July 19, 1983*

Addition of bromine or of acids to *anti*-sesquinorbornene is more rapid and less readily reversible than that to the syn isomer, whereas other addition reactions proceeding by concerted or free-radical mechanisms show a small rate advantage for *syn*-sesquinorbornene and no reversibility. Tetracyanoethylene (TCNE) does not undergo cycloaddition with *syn*- or *anti*-sesquinorbornene, nor can any dipolar ion from TCNE and sesquinorbornene be trapped by methanol, as in the case of TCNE and vinyl ethers.[18] However, under the conditions of such experiments TCNE catalyzes the addition of methanol to yield sesquinorbornyl methyl ether, or of water to yield sesquinorbornanol, the TCNE undergoing no apparent chemical change. From a comparative study of TCNE and *p*-toluenesulfonic acid it is concluded that the TCNE reaction is an example of acid catalysis, probably by the complex between TCNE and the alcohol or water. *syn*-Sesquinorbornene adds methanol in $CD_3CN$, reaching an equilibrium constant of about 2.04 ± 0.14 L/mol at ~30 °C, and adds water in $CD_3CN$ with the lower equilibrium constant of about 0.54 ± 0.05 L/mol at ~30 °C. *anti*-Sesquinorbornene in similar additions shows an equilibrium more favorable to addition by about 3 orders of magnitude. These reactions are discussed in light of the general character and behavior of the sesquinorbornenes. A new route to *anti*-sesquinorbornene is described that gives better yields than the former electrolytic preparation.

The sesquinorbornenes, syn (**1**)[1] (SSNB) and anti (**2**)[2] (ASNB), have some special properties that make them useful in the study of reaction mechanisms at the double bond. These properties include very low reactivity toward



1 2

singlet oxygen as compared to the related olefin biadamantylidene; exclusive cis addition; exclusive exo attack

(1) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R.; *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218.
(2) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

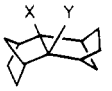
0022-3263/84/1949-1875$01.50/0 

on ground-state *syn*-sesquinorbornene,[1,3-5] but preferred endo attack on *syn*-sesquinorbornene in the excited state.[6]

**Reactivities of the Sesquinorbornene Isomers.** In a number of reactions proceeding by concerted or free-radical mechanisms, *syn*-sesquinorbornene is more reactive than the anti isomer by up to an order of magnitude.[3,7]

Toward another class of reagents, the sesquinorbornenes present a rather different picture. Compounds 3–8, rep-

3, X = Y = Br
5, X = H; Y = Br
7, X = H; Y = Cl
9, X = H; Y = OH
11, X = H; Y = $OCH_3$



4, X = Y = Br
6, X = H; Y = Br
8, X = H; Y = Cl
10, X = H; Y = OH
12, X = H; Y = $OCH_3$

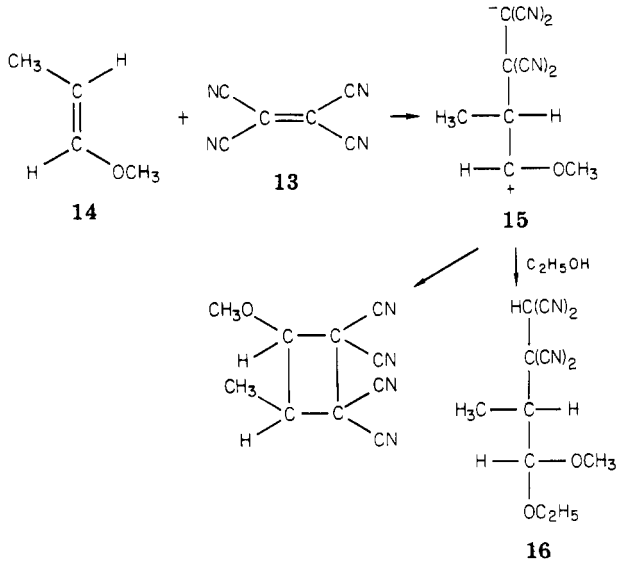
resenting the isomeric adducts of bromine, HBr, and HCl, to *syn*- and *anti*-sesquinorbornenes, were all prepared and characterized by their NMR spectra. In each case an equimolar mixture of 1 and 2, in reaction with addition reagent less than equivalent to one of them, yielded the anti adduct (4, 6, 8) without any detectable amount of the syn adduct in a reaction at temperatures from 0 to 25 °C. Nevertheless, in the absence of anti isomer, the syn isomer 1 also reacted rapidly with bromine or with the acidic reagents to yield products 3, 5, and 7, stable at room temperature.

The large competitive advantage of 2 over 1 at temperatures where the adducts of both are stable shows that the reactivity difference being measured is a kinetic phenomenon. However, independently of this, it is found that the hydrobromide, hydrochloride, and dibromide of *syn*-sesquinorbornene are thermally unstable at high temperature. For example, the adducts to 2 survive vapor chromatography involving temperatures up to 250 °C, but under the same conditions the syn adducts partly decompose directly to 1. A mixture of SSNB dibromide and ASNB, stable at room temperature, yields some of the anti dibromide upon injection on a VPC column (zone temperature 250 °C).

Thus reagents adding by an ionic mechanism, among which molecular bromine must be included,[8-11] show a mechanistic mobility that distinguishes them from a number of other reagents, tempered by a notably greater exothermicity of addition in the case of the anti as compared to the syn isomer of sesquinorbornene. All these characteristics appear reasonable in view of the unfavorable interaction of the four *endo*-ethylene hydrogens in any adduct of SSNB, part of which interaction is also present in the SSNB cation, but largely relieved in the olefin.

**Tetracyanoethylene.** Another stepwise reaction whose facility is generally associated with ability to form ionic centers is the (2 + 2) cycloaddition of olefins with tetracyanoethylene (TCNE, 13).[12-15,19]

Scheme I. Dipolar Cycloaddition Mechanism with TCNE[18]




This reaction occurs with sterically activated cyclic olefins[13,15a,16] and with other olefins having electron-donor substituents[14,16,17] as in 14 (Scheme I); the reaction is greatly accelerated by ionizing solvents. A convincing piece of evidence for the zwitterionic intermediate 15 in the TCNE–vinyl ether addition is the successful trapping of this intermediate with alcohols[18] to yield 16.

Following this lead, we observed that TCNE in anhydrous acetonitrile as solvent in the temperature range of 25 to 80 °C gave no reaction in 48 h with either *syn*- or *anti*-sesquinorbornene. Indeed, no reagent with branching at the unsaturated carbon atoms has yet been observed to add to the sesquinorbornene double bond, and it is probable that the flanking bridges impose hindrance on such an addition. It was thus of interest to see whether any product analogous to 16 would result from alcohol trapping.

To our surprise, the treatment of *anti*-sesquinorbornene with TCNE in methanol resulted in high yields of a product that proved to be *anti*-sesquinorbornyl methyl ether, 12. Careful search revealed no product of zwitterion trapping analogous to 16. Omission of the TCNE resulted in no reaction; however, its catalytic role could be assumed by *p*-toluenesulfonic acid under otherwise identical conditions.

Similarly, *syn*-sesquinorbornene with TCNE in methanol yielded *syn*-sesquinorbornyl methyl ether, 11.

TCNE was added to solutions of the sesquinorbornenes and water in nitromethane and in acetonitrile as common solvents to test for a similar addition of water. Again addition was seen, and again toluenesulfonic acid could

(3) Bartlett, P. D.; Blakeney, A. J.; Combs, G. L.; Galloy, J.; Roof, A. A. M.; Subramanyam, R.; Watson, W. H.; Winter, W. J.; Wu, C. In "Stereochemistry and Reactivity of Systems Containing $\pi$ Electrons"; Watson, W. H., Ed. Verlag Chemie: Deerfield Beach, FL, 1983; Chapter 3.
(4) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.
(5) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.
(6) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520.
(7) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J., paper in preparation.
(8) Roberts, I.; Kimball, G. D. *J. Am. Chem. Soc.* **1937**, *59*, 947.
(9) Williams, G.; Trans. *Faraday Soc.* **1941**, *37*, 749.
(10) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc. D.* **1969**, 907.
(11) Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *J. Am. Chem. Soc.* **1974**, *96*, 3565.
(12) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117 and references cited there.
(13) Erden, I. *Tetrahedron Lett.* **1983**, *24*, 2047.
(14) Masilamani, D.; Reuman, M. E.; Rogić, M. M. *J. Org. Chem.* **1980**, *45*, 4602.
(15) Ciganek, E.; Linn, W. J.; Webster, O. W. In "The Chemistry of the Cyano Group"; Rappoport, Z., Ed.; Interscience: New York, 1970; Chapter 9, (a) pp 453–456 and references cited there; (b) p 466.
(16) Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1959**, *81*, 667.
(17) (a) Steiner, G.; Huisgen, R. *J. Am. Chem. Soc.* **1973**, *95*, 5056. (b) Huisgen, R.; Grashey, R.; Sauer, J. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; Chapter 11.
(18) (a) Huisgen, R.; Schug, R.; Steiner, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 80, 81. (b) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.
(19) Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611.

Table I. Conditions of the *syn*-Sesquinorbornene Equilibrium Measurements (30 °C)

| run | catalyst, mg | $(SSNB)_0$, mg | $(ROH)_0$,[a] mg | $(ROMe)_0$,[a] mg | $(H_2O)_0$, mg | (MeOH), mg | $CD_3CN$, g |
|---|---|---|---|---|---|---|---|
| | | | Runs in $CD_3CN$ | | | | |
| 1 | TCNE, 11.2 | 46.1 | | | 90 | | 1.20 |
| 2 | TCNE, 8.7 | | 23 | | 92 | | 1.20 |
| 3 | TCNE, 9.0 | 47.2 | | | | 98.2 | 1.66 |
| 4 | TCNE, 6.0 | | | 40.1 | | 73 | 1.20 |
| 5 | TCNE, 5.0 | | | 65 | | 32 | 1.6 |
| 6 | TsOH, 13.5 | 46.5 | | | 49.4 | | 1.21 |
| 7 | TsOH, 6.9 | 45.8 | | | | 77 | 1.93 |
| 8 | TsOH, 6.9 | 45.8 | | | | 197 | 1.98 |
| | | | Runs in $CD_3NO_2$ | | | | |
| 9 | TsOH, 5 | 50.6 | | | 103 | | 1.8 |
| 10 | TsOH, 5 | 50.6 | | | | 155 | 1.8 |

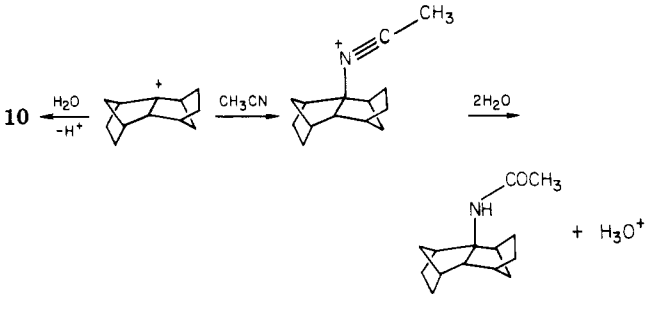
[a] R = sesquinorbornyl.

Table II. Equilibrium Measurements in Additions to *syn*-Sesquinorbornene (30 °C)

| run | (SSNB), M | (ROH),[a] M | (ROMe),[a] M | $(H_2O)$, M | (MeOH), M | $K$, $M^{-1}$ |
|---|---|---|---|---|---|---|
| | | | Runs in $CD_3CN$ | | | |
| 1 | 0.066 | 0.1174 | | 3.059 | | 0.58 |
| 2 | 0.0294 | 0.0544 | | 3.335 | | 0.56 |
| 3 | 0.0352 | | 0.0906 | | 1.319 | 1.95 |
| 4 | 0.0346 | | 0.0974 | | 1.472 | 1.93 |
| 5 | 0.085 | | 0.112 | | 0.069 | 1.98 |
| 6 | 0.0694 | 0.113 | | 3.36 | | 0.49 |
| 7 | 0.0378 | | 0.0765 | | 0.885 | 2.28 |
| 8 | 0.0194 | | 0.0886 | | 2.228 | 2.06 |
| | | | Runs in $CD_3NO_2$ | | | |
| 9 | 0.0733 | 0.1186 | | 3.35 | | 0.48 |
| 10 | 0.027 | | 0.154 | | 2.614 | 2.18 |

[a] R = sesquinorbornyl.

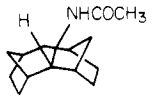
be substituted for TCNE as catalyst. When acetonitrile was used as solvent, the product alcohols **9** and **10** were




18

accompanied by the amides **19** and **18**, respectively, in greater amount from *anti*- than from *syn*-sesquinorbornene. These amides are presumably formed by interception of some of the sesquinorbornyl cation by the solvent. The formation of **18** and **19** was strictly dependent on the presence of TCNE or toluenesulfonic acid. The formation of these amides makes acetonitrile an unfavorable solvent for the preparation of the sesquinorbornanols. Our reference sample of **9** was prepared by reduction of the epoxide **17** (see Experimental Section).


17




19

However, under the conditions of the SSNB equilibrium measurements (shorter time intervals), the amounts of amide formed were too small to perturb the hydration equilibrium measurements.

The smallest amount of TCNE used, 1 mol % relative to the ASNB, in acetonitrile, brought about more than 98% reaction of the olefin within 3 days to form a mixture of alcohol **10** (54%) and amide **18** (44%) (by $^{13}C$ NMR).

**Equilibrium Studies.** For the addition of water and of methanol to SSNB, catalyzed by *p*-toluenesulfonic acid or by TCNE, a series of reactions at room temperature were carried out, leading to the equilibrium data of Tables I and II. The conditions were as described in the Experimental Section for the preparation of the alcohol and methyl ether from the sesquinorbornenes, but $^{13}C$ NMR analysis using $CD_3CN$ or $CD_3NO_2$ was repeated until the composition of the reaction mixture no longer changed. In calculating this composition a comparison was made with the $^{13}C$ NMR integrals obtained from standard mixtures of SSNB and **9** or **11**.

The additions to *anti*-sesquinorbornene are so much less reversible that the equilibrium could not be satisfactorily measured by this method. We could conclude only (by VPC) that the equilibrium constant $K$ = (alcohol)/(olefin)$(H_2O)$ is larger by about 3 orders of magnitude for the anti than for the syn reaction.

The equilibrium measurements for the addition reactions to SSNB were confirmed by following the catalytic dissociation of SSNB alcohol and methyl ether to the equilibrium mixture. However, this involved an observation that tells us something about the mechanism. In the "forward" reaction, starting with SSNB, methanol, and TCNE in dry acetonitrile-$d_3$, equilibrium was reached within 24 h. In contrast, when corresponding amounts of SSNB methyl ether and TCNE were dissolved in dry acetonitrile, although colors appeared corresponding to TCNE charge-transfer complexes, $^{13}C$ NMR showed *no* appearance of sesquinorbornene over a period of 2 days. At this point 32 mg of dry methanol was added, and within

17 h NMR showed that the dissociation process had reached equilibrium. Accordingly, in the dissociation runs of Tables I and II, the formation of catalyst from TCNE was assured by adding some of the appropriate ROH (water or methanol) to the dry solution containing TCNE.

The significance of this observation is that the Lewis acid–base complex formed from $SSNBOCH_3$ and TCNE does not of itself initiate the C–O or C–H cleavage process which might be the key step in establishing that equilibrium. Since this result is accomplished by the presence of the methanol–TCNE pair, it is highly probable that the efficient catalyst is the proton acid $(TCNE)CH_3OH$, whose presence assures the rapid protonation at C and at O that brings about the forward and reverse reactions, respectively.

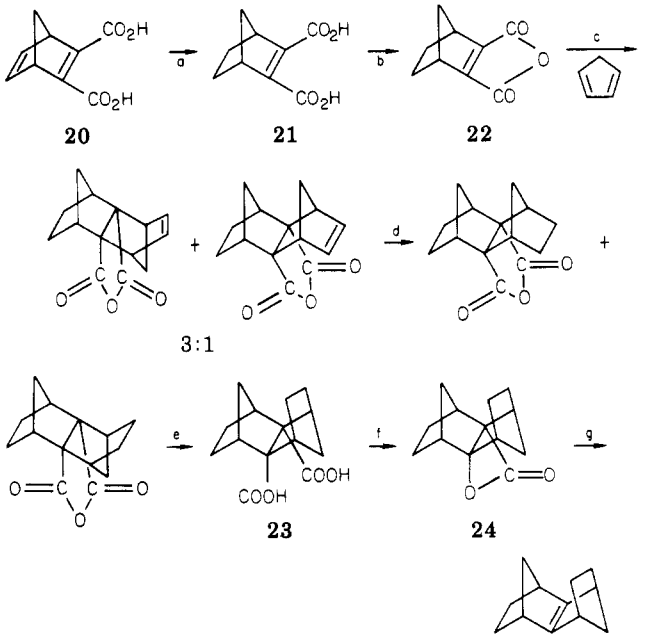
Although long exposure to methanol or water causes reaction with TCNE,[20] to yield acidic products, the apparent nonconsumption of TCNE in the present reactions suggests that the effective initial process may be a reversible interaction between TCNE and either methanol or water. The fact that these catalytic reactions can be paralleled by the use of *p*-toluenesulfonic acid as catalyst (see Tables I and II) indicates that any strongly acidic hydration product of TCNE may initiate the addition of ROH to the double bond. The first and most reversible acidic interaction product would be a donor–acceptor complex in which TCNE is a Lewis acid and ROH a Lewis base.

**Mechanistic Considerations.** Our initial working hypothesis that the catalytic function of TCNE originates in an interaction between it and **1** or **2** now seems improbable. None of the behavior of a dipolar ion is here observed—neither closure to a cycloadduct nor formation of a trapping product with methanol. It is also in accord with the stereochemical character of the sesquinorbornenes that the formation of such a fully substituted dipolar ion should be strongly, perhaps prohibitively, hindered. If there were still a strong, single-electron donor–acceptor affinity between SSNB and TCNE, we should expect detectable ESR signals at some point following their interaction, and none is observed, whether hydroxy compounds are present or not. We are forced to conclude that the catalysis by TCNE is the result of initial interaction between this reagent and the hydroxy compound that is being added to the double bond.[15b,20]

In a separate study of the reactions of TCNE with the three isodicyclopentadiene isomers,[21] catalytic additions of water and methanol have also been observed. The acid-catalyzed reactions of the isodicyclopentadienes are independent of the cycloaddition of TCNE.

**Equilibrium Differences in Addition Reactions to *syn*- and *anti*-Sesquinorbornenes.** From previous discussions[2,3,5,6] of the steric interactions in the sesquinorbornenes, it is clear that exo saturation of the double bond in SSNB brings about a crowding between the ethylene bridges that exceeds anything of the kind in either olefin or in the saturation product of *anti*-sesquinorbornene. This effect, which appears in some rather diverse reactions, offers a consistent explanation of the greater reversibility of addition to *syn*- than to *anti*-sesquinorbornene. However, this reversibility of additions to SSNB cannot be observed in the more exothermic reactions such as diimide hydrogenation, phenylazide addition, or peracid epoxidation, and in the cases now studied the observation of reversibility depends on favorable conditions for generating the cationic intermediate.

Scheme II[a]




[a] (a) $H_2$, Pd/C; (b) $Ac_2O$, reflux; (c) reflux in benzene; (d) $H_2$, Pd/C; (e) 1, KOH/EtOH, 2, removal of "syn-anhydride", 3, $H^+$; (f) $Pb(OAc)_4$ in dry benzene, $N_2$ 5–7 h, 80 °C; (g) heat (neat or in solution, ca. 150 °C).

## Experimental Section

Commercial samples of TCNE (**13**) were purified by repeated sublimation (3–4 times). Anhydrous methanol, acetonitrile, and acetonitrile-$d_3$ were obtained by distilling the solvents over Mg turnings and $CaH_2$, respectively. Nitromethane and nitromethane-$d_3$ were dried over $P_2O_5$ and distilled. $^1H$ NMR spectra were run on a Varian EM-390 spectrometer; $^{13}C$ NMR spectra were run on a JEOL FX-60 spectrometer. Vapor-phase chromatography was performed on a Perkin-Elmer Sigma 3 machine using a 6-ft nickel column packed with 5% SE-30 on Chromosorb W-AW, 60–80 mesh. Mass spectral analyses were performed on a Finnigan OWA 1020 GC-MS-DS equipped with the same SE-30 column mentioned above. Melting points are uncorrected and were taken on a Thomas Hoover capillary melting point apparatus. *syn*-Sesquinorbornene (**1**) was prepared as described in the literature.[1]

*anti*-Sesquinorbornene was prepared by the following new method, which, because of higher yields, has replaced the original electrolytic preparation[2] (Scheme II).

**2,5-Norbornadiene-2,3-dicarboxylic Acid (20).** To a solution of 25 g of 95% acetylenedicarboxylic acid (0.208 mol) in 200 mL of anhydrous ether was added dropwise 18 mL of freshly distilled cyclopentadiene (0.217 mol) over a period of 20 min at room temperature under a nitrogen atmosphere. The reaction mixture, which warmed slightly after a short period of time, was stirred overnight at room temperature. Evaporation of the solvent in vacuo and trituration of the residue in petroleum ether gave 33.5 g of diacid **20** (85%), which was then crystallized from water. The melting point was 163–164 °C; $^1H$ NMR (acetone-$d_6$) $\delta$ 12.1–12.2 (2 H, br s), 6.85–6.95 (2 H, m), 4.05–4.20 (2 H, m), 2.0–2.4 (2 H, m); $^{13}C$ NMR (acetone-$d_6$) 166.5, 157.6, 143.1, 73.3, 55.0 ppm.

**2-Norbornene-2,3-dicarboxylic Acid (21).** A total of 33 g of diacid **20** (0.183 mol) was dissolved in ethyl acetate (150 mL) and absolute ethanol (25 mL) in a Parr hydrogenation bottle. The mixture was treated with 5% palladium on carbon (1.0 g) and subjected to hydrogen gas with continuous shaking. After the uptake of 1 equiv of $H_2$ the hydrogenation was terminated. Filtration through a bed of Celite and evaporation of the solvents in vacuo gave 29 g of diacid **21**[2] (88%): $^1H$ NMR (acetone-$d_6$) $\delta$ 11.7 (2 H, br s), 3.4–3.5 (2 H, m), 1.75–2.1 (3 H, m), 1.4–1.65

(20) Middleton, W. J.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2788. Middleton, W. J.; Little, E. L.; Coffman, D. D.; Engelhardt, V. A. *Ibid.* **1958**, *80*, 2795.

(21) Bartlett, P. D.; Wu, C. *J. Org. Chem.*, following paper in this issue.

(1 H, m), 1.1–1.35 (2 H, m); $^{13}C$ NMR (acetone-$d_6$) 166.4, 148.4, 46.8, 46.7, 25.1 ppm.

The four-step conversion of norbornene-2,3-dicarboxylic acid **21** to *anti*-sesquinorbornane-4a,8a-dicarboxylic acid (**23**) consists of the following adaptations of procedures previously described,[2] following the formation of the anhydride **22**.

**Cycloaddition of 2-Norbornene-2,3-dicarboxylic Anhydride (22) to Cyclopentadiene in Benzene.** Five grams (0.031 mol) of 2-norbornene-2,3-dicarboxylic anhydride [$^1H$ NMR ($CDCl_3$) $\delta$ 3.35–3.5 (m, 2 H), 1.9–2.15 (m, 3 H), 1.55–1.70 (m, 1 H), 1.15–1.40 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) 160.0, 159.2, 52.6, 40.5 and 25.0 ppm] was dissolved in ca. 20 mL of dry benzene, and, while the solution was refluxing, 6 mL of freshly distilled cyclopentadiene was added dropwise over a period of ca. 1 h ($N_2$ atmosphere). The reaction mixture was stirred under reflux for another 3 h, after which the heating was discontinued.

After cooling, the solvent was removed under reduced pressure. A liquid residue was obtained, about 5 mL of ether was added to form a homogeneous solution, and the solution was kept in the refrigerator for several hours. Then crystals were formed which were filtered off (2.95 g, mainly anti isomer). To the filtrate was added about 5 mL of petroleum ether after which a solid could be separated (2.76 g; mixture of anti and syn isomers). The ratio of anti/syn isomer in this experiment was 3:1. The yield was ca. 80%.

**Anti Diacid 23.** Contrary to the earlier procedure,[2] the catalytic reduction of the reaction mixture was performed prior to the alkaline hydrolysis. This sequence leads to the diacid **23**, which can be purified by column chromatography using 100 g of alumina and using ethyl acetate as eluent.

**Oxidative Decarboxylation of Diacid 23.** To a solution of 4.0 g of diacid **23** (0.016 mol) in anhydrous benzene (250 mL) was added 15.6 g of fresh lead tetraacetate (0.035 mol), and the mixture was stirred mechanically at room temperature for ca. 10 min, while being purged with nitrogen. Then the mixture was heated at 80 °C for several hours until the evolution of carbon dioxide stopped. The reaction mixture was allowed to cool and then filtered, after which ca. 50 mL of water was added, which caused the formation of a brown solid. This solid was filtered off by using a sintered glass funnel. The aqueous layer was separated from the benzene layer, the latter being washed with dilute $NaHCO_3$ and 3 times with water. The benzene solution was dried over $MgSO_4$, and the solvent was evaporated, leaving ca. 2 g of a yellowish oily liquid. Injection on VPC (6 ft. 5% SE-30 on Chromosorb WAW, DMCS treated, 60/80 mesh; He flow 30 mL/min; $T_1$ = 100 °C, $t_1$ = 1 min, ramp rate 39 °C/min, $T_2$ = 225 °C, $t_2$ = 5 min) showed a number of components, viz., ASNB, a broad peak (decomposition?) at higher retention time and three smaller peaks. Column chromatography using neutral silica gel and methylene chloride as eluent gave $\beta$-lactone **24**, a yellowish liquid; IR (neat) 2950, 2865, 1800, 1460, 1290, 1215, 1055, 905, 835, 730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) no acidic proton absorption, 2.35–2.8 (4 H, m), 1.1–2.1 (12 H, series of m); $^{13}C$ NMR ($CDCl_3$) 172.7 (s), 89.9 (s), 73.0 (s), 43.9 (t), 42.9 (d), 39.4 (t), 38.9 (d), 38.2 (d), 36.4 (d), 27.7 (t), 25.1 (t), 24.4 (t), 22.7 (t); MS (70 eV), *m/e* 160 (M – 44), 132, 117, 104. This compound decomposes upon VPC injection, giving ASNB and a broad peak at higher retention time. On heating **24**, either in solution (*m*-dichlorobenzene at 145 °C) or neat, there is a clean decarboxylation with formation of ASNB (**2**). The olefin was then purified by column chromatography using petroleum ether as eluent; yield ca. 1 g (40%).

***syn*-Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodecan-2-ol (9).** To a solution of *syn*-sesquinorbornene epoxide (**17**; 176 mg, 1 mmol) in 5 mL of anhydrous ethylenediamine was added ca. 30 mg of lithium in small portions (4 equiv) under a nitrogen atmosphere. The mixture was heated at 50 °C until the solution remained bluish purple (after several color changes). This took ca. 1 h; 1 mL of water was added to the cooled reaction mixture, then ca. 25 mL of ether was added and the ether layer washed three times with water. After the ether layer was dried over $MgSO_4$, the solvent was evaporated, leaving 155 mg of the alcohol (87%): mp 99–100 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.0–2.6 (m, 4 H), 0.66–2.0 (series of m, 14 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 86.2, 59.6, 49.2, 45.7, 40.7, 24.6, 23.5; mass spectrum, *m/e* 178, 160, 150, 104, 67.

***anti*-Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodecan-2-ol (10).** A solution of 15 mL of acetonitrile containing 0.09 g of ASNB (**2**, 0.56 mmol), 0.07 g of TCNE (0.55 mmol), and 0.3 mL of water was held at reflux for 1 h. VPC analysis showed that all of the ASNB had disappeared and that there were two products, alcohol **10** and amide **18**. The products were separated, after removal of the solvent, by column chromatography (neutral silica gel) using pentane: ether (1:1, v/v) as eluent; 0.026 g of **10** (26%): mp 79–81 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.2–2.5 (d, 4 H), 1.6–2.2 (m, 7 H), 1.55 (s, 1 H); 1.0–1.5 (m, 6 H) (the peak at 1.55 ppm disappeared on adding $D_2O$ to the sample); $^{13}C$ NMR ($CDCl_3$) $\delta$ 86.7, 59.0, 49.9, 42.3, 41.5, 40.2, 37.1, 36.9, 30.1, 24.4, 24.2, 23.0; mass spectrum, *m/e* 178, 160, 150, 110, 68. Elution with methylene chloride gave 0.095 g of the amide **18** (56%): IR ($CHCl_3$) 3400, 1640 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 5.8 (br s, 1 H), 2.86 (br s, 1 H), 2.74 (br s, 1 H), 2.27 (br s, 1 H) 2.0 (d, 1 H), 1.90 (s, 3 H), 1.0–1.8 (series of m, 13 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.3 (s), 69.9 (s), 60.1 (d), 46.7 (d), 41.4, 40.7, 40.1, 36.6, 36.4, 34.2, 30.1, 26.2, 24.6, 23.8; mass spectrum, *m/e* 219 ($M^+$), 191 ($M^+$ – 28), 160, 151, 132, 123, 81, 67, 43 (base).

**Preparation of 2-Methoxy-*syn*-tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]-dodecane (11).** To a solution of 69.5 mg of **1** and 15 mg of *p*-toluenesulfonic acid in 1.64 mL of $CD_3CN$ was added 140 mg of methanol. The $^{13}C$ NMR showed that after ca. 1.5 h, 81% of the methyl ether had formed. Then ca. 20 mg of 2,6-lutidine was added to neutralize the acid. The solvent was removed and the residue was purified by column chromatography (silica gel, eluent petroleum ether). Early fractions contained some **1**, and almost pure **11** was obtained in later fractions by using petroleum ether/ether (1:1, v/v): IR (neat) 3000, 2940, 2860, 2000, 1460, 1065, 935, 725 $cm^{-1}$, $^1H$ NMR ($CDCl_3$) $\delta$ 3.14 (s, 3 H), 2.5–2.7 (br m, 2 H), 2.2–2.4 (br m, 2 H), 1.55–2.15 (series of m, 5 H), 1.05–1.50 (series of m, 5 H), 0.75–1.0 (m, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 91.3 (s), 57.8 (d), 50.8 (q), 45.0 (t), 42.6 (d), 40.4 (d), 24.6 (t), 24.2 (t); mass spectrum, *m/e* 192 ($M^+$), 164 ($M^+$ – 28), 104, 91, 67. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.26; H, 10.74.

**Preparation of *anti*-Sesquinorbornene *cis*-4a,8a-Dibromide (4).** A solution of bromine (0.06 mL, 0.0011 mol) in $CCl_4$ (5 mL) was added dropwise to a solution of ASNB (0.144 g, 0.0009 mol) in $CCl_4$ (10 mL) at room temperature. As the bromine solution was added, the chracteristic reddish brown color was instantly discharged. The reaction mixture was evaporated in vacuo, and then coevaporation was performed with ethyl ether to yield a solid, yellow residue.

Residue analysis by VPC indicated that no ASNB remained and that a new compound was present. The sample was purified by column chromatography (2 ft × $^1/_2$ in. column, 25 g of neutral silica gel) by elution with ethyl ether to yield dibromide as a white crystalline compound (0.085 g, 30%): mp 170–190 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 3.0–2.9 (br s, 2 H), 2.5–2.4 (br s, 3 H), 2.1–1.1 (m, 10 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 87.8, 57.0, 45.0, 41.9, 34.3, 29.7, 26.1.

***syn*-Sesquinorbornene *cis*-4a,8a-dibromide (3)** was prepared according to the above procedure and has been reported by Paquette et al.[22] Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 45.17; H, 5.04.

**Addition of Hydrogen Bromide to ASNB: 6.** A sample of ASNB (52.2 mg, 0.32 mmol) in dry diethyl ether (20 mL) was purged with nitrogen for 10 min and then cooled to 0 °C. Anhydrous HBr gas was bubbled through the solution for 5 min (the mixture became yellow). The solvent and excess HBr were evaporated in vacuo followed by dissolution of the residue in $CH_2Cl_2$ and reevaporation.

Without further purification the residue was found to contain one major product (95%), *anti-cis*-4a-hydro-8a-bromosesquinorbornane (**6**): $^1H$ NMR ($CDCl_3$) $\delta$ 2.9–1.1 (various multiplets); $^{13}C$ NMR ($CDCl_3$) $\delta$ 88.4, 61.3, 54.3, 45.1, 43.1, 42.7, 36.7, 35.4, 32.0, 29.0, 26.3, 23.3.

**Addition of Hydrogen Bromide to SSNB: 5.** A solution of SSNB (53.4 mg, 0.333 mmol) in dry diethyl ether (20 mL) was treated with anhydrous HBr in the same manner as described above for ASNB and gave *syn-cis,exo*-4a-hydro-8a-bromosesquinorbornane (**5**): $^1H$ NMR ($CDCl_3$) $\delta$ 3.1–0.80 (various multiplets); $^{13}C$ NMR ($CDCl_3$) $\delta$ 93.4, 61.4, 53.7, 49.1, 42.8, 26.5, 24.1.

(22) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. soc.* **1980**, *102*, 3303.

**Addition of Hydrochloric Acid to ASNB.** A three-necked, 25-mL round-bottomed flask was flushed with nitrogen for 15 min and charged with ASNB (0.171 g, 0.0011 mol). Anhydrous ether (10 mL) was added and stirring was initiated under an $N_2$ atmosphere. A gas inlet tube was immersed below the solvent level and dry HCl gas was bubbled through the solution for 10 min. Then the mixture was purged with $N_2$ for 10 min to remove excess HCl. The ether layer was extracted with 10% $NaHCO_3$ and dried with $MgSO_4$. GC analysis indicated one major product (8): $^1H$ NMR ($CDCl_3$) $\delta$ 2.63–2.26 (br d) 2.20–1.03 (complex multiplet); $^{13}C$ NMR ($CDCl_3$) $\delta$ 88.2, 61.0, 53.0, 44.3, 42.6, 41.9, 37.0, 36.7, 29.4, 28.7, 26.0, 23.3.

**Addition of Hydrochloric Acid to SSNB: 7.** SSNB (84 mg, 0.5 mmol) was dissolved in ca. 16 mL of ether and treated with a stream of HCl (anhydrous) gas for 1.5 h. The saturated solution was stirred at room temperature for 18 h. After the mixture was neutralized with saturated aqueous $NaHCO_3$, the organic layer was dried with $MgSO_4$ and analyzed by VPC. The major product observed was monochloro compound (7); $^{13}C$ NMR ($CDCl_3$) $\delta$ 91.6, 60.8, 52.0, 47.6, 42.0, 26.0, 23.7 (plus peaks for unreacted SSNB).

**Competitive Reaction with Bromine.** A solution of ASNB (50 mg) and SSNB (49.8 mg, 0.622 mmol total olefin) in $CCl_4$ (5 mL) was flushed with nitrogen and cooled to 0 °C. Then, 1.5 mL of 0.0996 M $Br_2$ (0.269 mmol) in $CCl_4$ was added to the mixture in one portion. After 15 min at 0 °C (note: the reddish brown bromine color disappeared immediately upon addition to the olefins), the mixture was evaporated in vacuo and the residue analyzed by $^{13}C$ NMR ($CDCl_3$). The first spectrum indicated approximately 50% disappearance of ASNB and *no* conversion of SSNB to dibromide. Clearly, ASNB had been converted to *anti-cis*-4a,8a-dibromosesquinorbornane (4): $^{13}C$ NMR ($CDCl_3$) $\delta$ 87.84, 56.98, 45.09, 41.97, 34.37, 29.75, 26.11.

The sample was then treated in the same manner with an additional portion (0.5 mL) of 0.0996 M $Br_2$ in $CCl_4$. Workup and analysis by $^{13}C$ NMR showed that 90% of ASNB had been converted to 4 while SSNB remained unreacted. Upon the addition of a third portion of $Br_2$ (0.5 mL of 0.0996 M solution), all of the ASNB was present as dibromide 4 and a small portion of SSNB had been converted to *syn-exo,cis*-4a,8a-dibromosesquinorbornane (3): $^{13}C$ NMR ($CDCl_3$) $\delta$ 92.0, 55.7, 48.8, 25.9.

**Competitive Hydrobromination of ASNB and SSNB.** HBr gas from a lecture bottle was bubbled through a solution of ASNB (109.0 mg, 0.68 mmol) and SSNB (111.1 mg, 0.69 mmol) in 2 mL of $CDCl_3$. After a short while the addition of HBr was stopped and $^{13}C$ NMR showed that only the HBr adduct to ASNB had formed, leaving SSNB and some unreacted ASNB. Successive additions of HBr depleted the anti olefin, while the syn isomer was still present, along with *anti-cis*-4a-hydro-8a-bromosesquinorbornane.

**Competitive Hydrochlorination of ASNB and SSNB.** A mixture of ASNB (30.2 mg, 0.188 mmol) and SSNB (30.3 mg, 0.189 mmol) in dry ether (5 mL) was flushed with nitrogen and cooled to 0 °C. Then, 0.5 equiv (based on the total amount of olefin) of HCl (0.35 mL of a 0.548 M solution in diethyl ether) was added to the reaction mixture in one portion. The solution was warmed to room temperature over 5 min and then the solvent was evaporated in vacuo.

Residue analysis by $^{13}C$ NMR ($CDCl_3$) gave peaks at $\delta$ 60.8, 53.0, 44.2, 42.8, 41.7, 36.9, 36.6, 29.3, 28.5, 25.9, and 23.2 (note: peak at 88.2 not visible due to low concentration) for *anti-cis*-4a-hydro-8a-chlorosesquinorbornane (7) and peaks at $\delta$ 151.6, 50.2, 42.8, and 25.2 for unreacted SSNB.

**Preparation of 2-Methoxy-*anti*-tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]-dodecane (12) Using *p*-Toluenesulfonic Acid.** To a solution of ca. 40 mg of ASNB (2) in acetonitrile was added ca. 5 mg of *p*-toluenesulfonic acid and ca. 50 $\mu$L of methanol. The mixture was stirred for half an hour, after which injection on VPC showed that no olefin was present. The solvent was removed in vacuo, and the methyl ether 12 was isolated from the residue, by using column chromatography (silica gel, eluent petroleum ether/ether, 1:1, v/v): $^1H$ NMR ($CDCl_3$) $\delta$ 3.1 (s, 3 H), 2.1–2.7 (m, 3 H), 1.0–2.1 (m, 14 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 92.5, 58.0, 51.8, 42.1, 41.0, 39.8, 38.6, 36.9, 36.4, 30.3, 24.4 (2 peaks), 23.7; mass spectrum, *m/e* 192, 164, 160, 67. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found C, 81.07; H, 10.32.

**Acknowledgment.** We thank the Robert A. Welch Foundation and the National Science Foundation for support.

**Registry No.** 1, 73321-28-5; 2, 73679-39-7; 3, 89824-44-2; 4, 89726-60-3; 5, 89824-42-0; 6, 89726-58-9; 7, 89824-43-1; 8, 89726-59-0; 9, 74387-82-9; 10, 89824-46-4; 11, 74387-85-2; 12, 89824-45-3; 13, 670-54-2; 17, 75765-77-4; 18, 89726-61-4; 20, 15872-28-3; 21, 16508-04-6; 22, 19479-86-8; 23, 73654-77-0; 24, 89746-15-6; $H_2O$, 7732-18-5; MeOH, 67-56-1; *anti*-(*cis*-4a,8a-dicarboxy)sesquinorbornane anhydride, 73654-75-8; *syn*-(*cis*-4a,8a-dicarboxy)sesquinorbornane anhydride, 73679-38-6; hydrogen bromide, 10035-10-6; hydrchloric acid, 7647-01-0; *p*-toluenesulfonic acid, 104-15-4; acetylenedicarboxylic acid, 142-45-0.

# Reactions of Tetracyanoethylene (TCNE) with the Three Isodicyclopentadiene Isomers

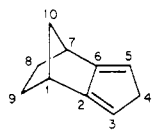
Paul D. Bartlett* and Chengjiu Wu

*Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129*

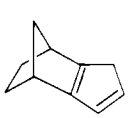
*Received November 16, 1983*

Each of the isodicyclopentadiene isomers 1–3 yields two characteristic cycloadducts with tetracyanoethylene (TCNE). One of these (11) is a (2 + 2) cycloadduct; the other five are reversibly formed Diels–Alder adducts. In the presence of water, TCNE induces a side reaction of hydration of diene isomer 3. TCNE and *N*-phenyltriazolinedione provide unusual examples of initial reaction with diene 1 on its exo face.

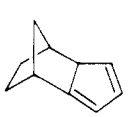
The synthetic possibilities of isodicyclopentadiene have recently been expanded by the discovery that not only the original isomer 1 but also diene isomers 2 and 3 can undergo controlled reactions with dienophiles to produce characteristic tetracyclo ring systems.[1-3] Tetracyanoethylene (TCNE) is of interest not only as one of the most reactive dienophiles[4] but also because under special con-




1



2



3

(1) Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491.
(2) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.
(3) Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

0022-3263/84/1949-1880$01.50/0 