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Diels–Alder Cycloadditions of a Bicyclobutane Bridged Diene. Acid and Thermal Stability of Benzvalene Derivatives as a Function of Substituents

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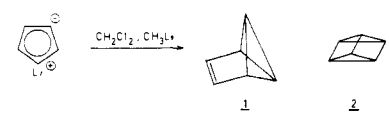
Abstract. Diels–Alder cycloadditions of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**5**) with a variety of dienophiles have been investigated. Depending on the dienophile used derivatives of benzvalene, of benzene, or of homofulvene are isolated. The benzene derivatives are formed from the corresponding benzvalenes via a thermal reaction, whereas the homofulvene derivatives result from an acid-catalyzed rearrangement. Benzene derivatives are the exclusive reaction products when the cycloadditions are carried out in the presence of silver perchlorate/sodium carbonate. The rates of cycloaddition are enhanced by Lewis acid catalysis of Ag thereby providing a useful synthetic approach for tetraline derivatives. The reaction of benzvalene derivatives with acid has been investigated in detail. The conclusion is reached that both the acid lability as well as the preferred pathways of the rearrangement depend on the nature of the substituents. The acid and thermal stability of benzvalene derivatives is enhanced by the presence of strongly electron-withdrawing groups at the C=C double bond of the benzvalene skeleton.

Among the multitude of interesting chemical structures derivable from the unit -CH- used *n* times, that of benzvalene (**1**), a $(CH)_6$ isomer, is one of the most fundamental and intriguing. Benzvalene is thus a valence bond isomer of benzene;[1] the molecule was first discussed by Hückel in 1937.[2] The parent benzvalene (**1**) was first synthesized[3,4] in the late 1960s by ultraviolet irradiation of liquid benzene. Through photochemical routes a few corresponding benzvalene derivatives have been prepared.[5,6] The yields from these photochemical methods are usually small and as a consequence the study of the chemical properties of benzvalene and its derivatives has not been extensive. In 1971 Katz and co-workers[7] reported an efficient synthesis of the parent benzvalene (**1**), which is depicted below. Since then, microwave studies[8] and calculations[9] of benzvalene have been performed and some interesting chemistry, culminating in the synthesis[10] of the parent prismane (**2**), have been reported.[11]



1 2

Benzvalenes are highly strained molecules. The heat of the reaction **1** → benzene has recently[12] been measured and found to be 67.54 kcal/mol.[13] At room temperature, benzvalene (**1**) reverts quantitatively to benzene with a half-life of about 10 days.[12,15] The strain energy of prismane (**2**) was calculated[14]

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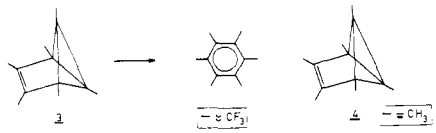
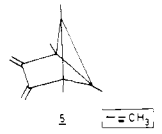
to be 107.6 kcal/mol. In contrast to benzvalene (**1**) prismane is stable at room temperature.[10,15] Obviously, the strain energy of these molecules is not directly related to their readiness to rearrange. The stability of these compounds is governed above all by the lack of a symmetry-allowed[16] or stabilized biradical pathways to their thermodynamically much more stable aromatic valence isomer benzene. There is, however, another factor which largely determines the stabilities of highly strained molecules: the nature of the substituents on the carbon skeleton. For example, perfluorohexamethylbenzvalene (**3**)[6]



is very stable at room temperature[17,18] and rearranges into the corresponding perfluorohexamethylbenzene with an energy of activation of 40 kcal/mol.[17] In contrast hexamethylbenzvalene (**4**), although mentioned and claimed as unobserved intermediate,[19] has not been isolated at room temperature[17] nor to our knowledge identified properly.

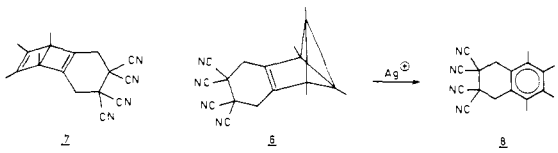
Subject and Aims. In 1973 Hogeveen and Kwant[20] reported the synthesis of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**5**). This molecule combines two highly



reactive moieties: the diene and the bicyclobutane part. In view of this bifunctionality the question arose how **5** would behave toward dienophiles. Cycloadditions of reactive dienophiles with bicyclobutane[21] and other strained molecules[22,23] have been reported. The Diels–Alder cycloaddition to the diene moiety of **5** would offer a unique opportunity to synthesize methylated benzvalene derivatives. It was of interest to know how their stability would be influenced by the dienophile used.

Results and Discussion

Reaction of 5 with Tetracyanoethylene (TCNE). It was already found that **5** reacts very smoothly with tetracyanoethylene to give the benzvalene derivative **6**.[20] Silver ion catalyzed rearrangements of derivatives of bicyclo[1.1.0]butane have been investigated extensively and the mechanism[24-26] and preparative aspects[27] of this intriguing skeletal reorganization have been discussed in detail. Extrapolating these results, one should expect that the TCNE adduct **6** would rearrange to its



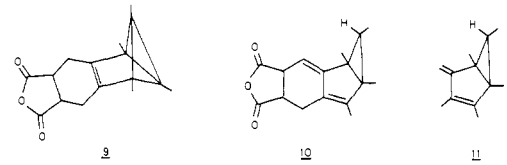
valence isomer **8** in the presence of silver ions. Indeed, upon treatment with a catalytic amount of silver perchlorate (20 mol %) **6** is converted quantitatively to **8.** Compound **8** was also obtained from the thermal[20] rearrangement of **6.**

Reaction of 5 with Maleic Anhydride (MAA). Among the many dienophiles used in Diels–Alder cycloadditions, maleic anhydride is among the more reactive ones and is from a synthetic point of view probably the most useful one. Maleic anhydride reacts smoothly with the diene **5** at room temperature in chloroform or methylene chloride solution, but the isolated reaction product is not the expected benzvalene derivative **9.** Instead the homofulvene derivative **10** was formed in a yield of over 80%. Homofulvene derivatives[28] have been encountered as reaction products from cyclopentadienylcarbinyl derivatives

Table I. 100-MHz ^{1}H NMR Parameters of **10**

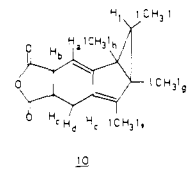
Proton	Chemical shift[a]	Coupling constants, Hz
H_a	5.09	J_{ab} = 3.2, J_{ac} = 0.6
H_b	3.70	J_{bc} = 8.2, J_{ba} = 3.2
H_c	3.45	J_{cb} = 8.2, J_{ce} = 6.7, J_{cd} = 2, J_{ca} = 0.6
H_d	2.94	J_{de} = 16.5, J_{dc} = 2, J_{df} = 0.4
H_e	2.21	J_{ed} = 16.5, J_{ec} = 6.7, J_{ef} = 2
$(CH_3)_f$	1.76	J_{fe} = 2, J_{fd} = 0.4
$(CH_3)_g$	1.04[b]	s
$(CH_3)_h$	1.01[b]	s
$(CH_3)_i$	0.92	J_{ij} = 6.5
H_j	0.6	J_{ji} = 6.5

[a] Data are given in parts per million (downfield from internal Me_4Si). [b] The assignment of these methyl groups may be reversed.



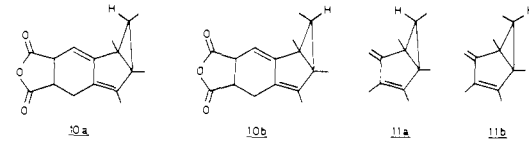
on treatment with base[29] or solvolysis[30] under basic conditions, Homofulvene **11** was obtained by quenching with base the intermediate cations that arise from the reaction of hexamethyl(Dewar benzene) with acids.[20b,31,32] The same compound was found to be a side product in the photochemical isomerization of hexamethyl(Dewar benzene).[33]

The structure assignment of **10** rests on elemental analysis and spectral data. The ultraviolet spectrum shows a maximum at λ 264 nm (ε 12 500), which is in agreement with reported data on related compounds.[28,29,33] The 100-MHz ^{1}H NMR spectrum of **10** was analyzed by decoupling and INDOR experiments and computer simulation. The data are compiled in Table I according to the numbering convention below.



The carbon-13 spectrum fits equally well with the proposed structure. It shows two singlets for the carbonyl carbons at 171.7 and 173.2 ppm. The four alkene carbons appear as three singlets at 156.2, 150.7, and 121.2 ppm and one doublet at 102.2 ppm (J_{CH} = 166 Hz). In the alkane region six carbon signals are observed: two singlets at 38.1 and 29.4, one triplet at 19.0 (J_{CH} = 130 Hz), and three doublets at 42.6 (J_{CH} = 142 Hz), 39.8 (J_{CH} = 140 Hz), and 38.3 ppm (J_{CH} = 164 Hz). The latter one, with the characteristic[34] coupling constant of 164 Hz, is the cyclopropane carbon. The resulting four methyl groups carbons resonate at 12.9 (q, J_{CH} = 125 Hz), 9.9 (q, J_{CH} = 128 Hz), 9.6 (q, J_{CH} = 128 Hz), and 7.3 (q, J_{CH} = 121 Hz).

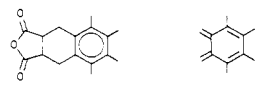
Two more questions remain both concerning the stereochemistry of **10.** First, the hydrogen on the cyclopropane ring in **10** can be in the endo position **10a** or in the exo position **10b.**



Both parent compounds **11a** and **11b** have been prepared.[29,31-33] The chemical shifts of the relevant methyl groups were found to be 0.66 and 0.92 ppm. The first one (0.66 ppm)

was assigned[32] to the parent compound with the methyl group in the endo position (**11b**). This relative upfield shift is due to the shielding effect of the double bonds. In **10** the methyl group is found at 0.96 ppm which corresponds with structure **10a.** In addition the chemical shift of the hydrogen on the cyclopropane ring in **10** (0.6 ppm) is in good agreement with the shift found for the corresponding hydrogen in the parent compound **11a** (0.64 ppm). Hence, we can conclude that the hydrogen on the cyclopropane ring in **10** is in the endo position. The second stereochemical question concerns the position of the anhydride group which can be anti or syn with respect to the cyclopropane ring. Unfortunately, addition of a shift reagent ($Eu(DPM)_3$) to a solution of **10** in deuteriochloroform did not cause linear shifts and decomposition of **10** occurs. Owing to the instability of **10** toward Lewis acids we have made no further efforts to solve this problem.

When the reaction of **5** and maleic anhydride was followed in the NMR cavity at suitable temperatures, e.g., from 10 to 40 °C, no indication could be found for the formation of the benzvalene derivative **9**. On the other hand, there is obviously a close relationship between structures **9** and **10.** More direct evidence for the intermediacy of **9** comes from the following observation. When the reaction of maleic anhydride with diene **5** was carried out in the presence of a catalytic amount of silver perchlorate (20 mol %) and an excess of sodium carbonate[35] compound **12,** the aromatic valence isomer of **9,** was isolated

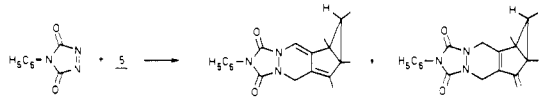


12 13

in an almost quantitative yield. Reaction of maleic anhydride and **5** in the presence of sodium carbonate affords **10.** The homofulvene derivative **10** is unaffected under silver perchlorate/sodium carbonate conditions, whereas the TCNE adduct **6** very rapidly isomerizes to **8.**

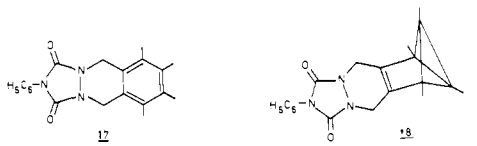
These observations strongly suggest but still do not prove the intermediacy of **9**. One could argue that action of Ag upon diene **5** would lead to the highly reactive *o*-xylylene[36] derivative **13** which then reacts with maleic anhydride to form **12.** *o*-Xylylene derivatives have been found to be useful intermediates for the preparation of naphthalenes, tetralins, and some polycyclic quinones.[37] However, diene **5** itself is not affected by the combination silver perchlorate/sodium carbonate under the reaction conditions used.

Reaction of 5 with 4-Phenyl-1,2,4-triazoline-3,5 dione (14, PTAD). The most powerful dienophile[39,40] known at this moment is 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD),[38,39] In Diels–Alder cycloadditions with dienes[39,40a,h] PTAD reacts in most cases much faster than tetracyanoethylene (TCNE). When diene **5** was treated with PTAD[41] at room temperature a mixture of **15** (46%) and **16** (54%) was obtained in an es-



14 5 15 16

sentially quantitative yield. The two isomeric homofulvene derivatives were separated and purified by column chromatography and crystallization. When the reaction was carried out in the presence of silver perchlorate and sodium carbonate the aromatic compound **17** was isolated quantitatively. The



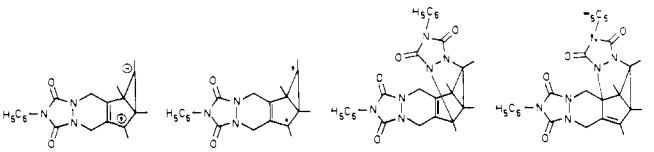
17 18

homofulvene derivatives **15** and **16** were not affected under these conditions. Hence these observations strongly suggest the intermediacy of the benzvalene derivative **18.**

The extreme reactivity of PTAD allows spectroscopic confirmation of this suggestion. Addition of PTAD to a solution of diene **5** in deuterioacetone at −70 °C leads to rapid decolorization of the azo compound. The ^1H NMR spectrum, taken at −70 °C, showed the complete disappearance of **5** and only four signals at 7.55 (aromatic H), 3.76 (4 H), 1.53 (6 H), and 1.14 ppm (6 H) which is fully consistent with structure **18,**[42] the normal Diels–Alder cycloaddition product. On warming up (−30 °C) the homofulvene derivatives **15** and **16** are slowly formed in the same ratio as before. However, when a solution of **18,** prepared at −70 °C, was poured rapidly into a stirred, ice-cold mixture of 2 N sodium hydroxide and ether unrearranged **18** was obtained quantitatively after workup. At room temperature in deuteriochloroform solution **18** rearranges slowly ($\tau_{1/2}$ = 2 days) not into the isomeric homofulvenes **15** and **16,** but into its aromatic valence isomer **17.** Treatment of purified **18** with silver perchlorate or silver perchlorate/sodium carbonate affords instantaneously **17.** The structure assignment of **18** was confirmed by elemental analysis and further spectral data. The carbon-13 spectrum of **18** shows the same features as the one of the TCNE adduct **6.**

Treatment of a solution of **18** with silver perchlorate/sodium carbonate at −70 °C affords the aromatic valence isomer **17.** This means that the Ag-catalyzed valence isomerization is faster than the rearrangement leading to the homofulvene derivatives **15** and **16,** which is in accordance with the proposed intermediacy of the MAA adduct **9** in the reaction of **5** with maleic anhydride.

Isolation of a Diadduct. Addition of a solution of diene **5** in chloroform to an excess of PTAD (**14**) in acetone affords an adduct which is made up of two molecules of PTAD and one molecule of diene **5,** according to elemental analysis and mass spectrum. This diadduct is also formed when **18** is treated with an excess of PTAD. Hence, we can conclude that this diadduct arise from a reaction of **18** and PTAD. Breaking one of the side bonds of the bicyclobutane moiety in **18** may lead to the dipolar species **20** or to the biradical **21**. Capturing of the species **20**



20 21 22 23

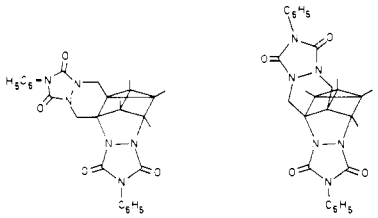
and **21** by a second molecule of PTAD would in principle lead to **22** and **23.** The ^1H NMR spectrum shows, besides the multiplet for the phenyl protons at 7.50 ppm (10 H), eight absorption peaks in the region 3.0–5.5 ppm (4 H), INDOR experiments demonstrate that these lines belong to two AB systems, one centered at 4.5 (J = 13 Hz), the other at 3.7 ppm (J = 13 Hz). In the high-field region four distinct singlets are observed at 1.79, 1.37, 1.22, and 1.20 ppm (all 3 H). These data are not in disagreement with structures **22** and **23** and exclude more symmetrical ones. The carbon-13 spectrum shows besides the carbonyl and phenyl carbons six singlets, two triplets, and four quartets. The six singlets appear at 72.7, 69.1, 57.1, 36.0, 34.3, and 34.1 ppm, which means that no alkene carbons are present. Therefore structures **22** and **23** must be excluded. Similarly the possibility of a [2 + 2] addition of PTAD to one of the homofulvene derivatives **15** and **16** can be rigorously ruled out. The ^{13}C and ^1H NMR spectra fit quite well with structures **24** and **25,** but do not allow us to distinguish unambiguously between these structures.[44]

Reaction of 5 with Other Dienophiles. Synthesis of Tetralin Derivatives. The findings with the very reactive dienophiles prompted us to examine the reaction of **5** with some other di-

Table II. Formation of Tetralin Derivatives[a]

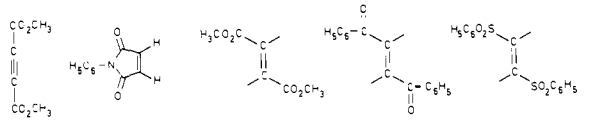
Dienophile	$AgClO_4$/ Na_2CO_3[c] yield,[b] %	Thermally yield,[b] %	Conditions
TCNE	100	0	20 °C, 15 min
PTAD[41]	95	0	20 °C, 4 h
MAA	95	0	20 °C, 2 h
26	50	8	20 °C, 17 h
27	90	12	20 °C, 23 h
28	12	6	20 °C, 48 h
	84	70	61 °C, 24 h
29	51	36	20 °C, 24 h
	77	70	61 °C, 3 h
30	18	12	20 °C, 23 h
	87	80	61 °C, 24 h
Methyl acrylate	90[d]	0	20 °C, 5 h
Acrylonitrile	85[d]	0	20 °C, 35 h

[a] The results of the previously described reactions have been included. [b] According to ^1H NMR. [c] 0.2 equiv of $AgClO_4$ and 2 equiv of Na_2CO_3 were used except for *d*. [d] 1 equiv of $AgClO_4$ and 10 equiv of Na_2CO_3 were used.



24 25

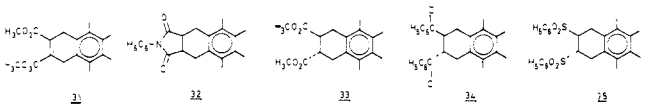
enophiles. A number of these must be reckoned to be reactive dienophiles:[46] dimethyl acetylenedicarboxylate (**26**), *N*-phenylmaleimide (**27**), dimethyl fumarate (**28**), *trans*-1,2-



26 27 28 29 30

bis(benzoyl)ethylene (**29**), and *trans*-1,2-bis(phenylsulfonyl)ethylene (**30**). The other two, acrylonitrile and methyl acrylate, are of moderate reactivity. The results are compiled in Table II.

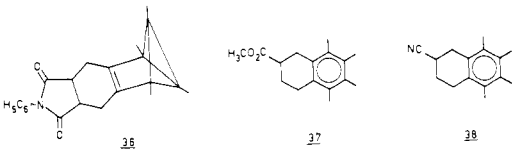
The reactive dienophiles all show a similar behavior toward **5**. The reaction is slow at room temperature and the aromatic valence isomers of the (likely initially formed) benzvalene derivatives are isolated. At elevated temperatures the cycloaddition reactions occur smoothly and aromatized products **31**–**35** (tetralin derivatives) are formed in good yields with the



31 32 33 34 35

stereochemistry shown.[46,47]

As anticipated, the tetralin derivatives are also the isolated reaction products when the reactions are carried out under silver perchlorate/sodium carbonate conditions. However, under the latter conditions the reactions are faster than in the absence of silver perchlorate/sodium carbonate. This effect is especially noteworthy in the reaction of *N*-phenylmaleimide **27** with **5**. After 23 h at room temperature **32** is formed in only 12% yield, whereas in the presence of silver perchlorate/sodium carbonate it is formed in 90% yield. Under both conditions the remaining starting material is observed to be unchanged. Since we can exclude the intermediacy of the *o*-xylylene derivative **13** under the conditions used the benzvalene derivative **36** is

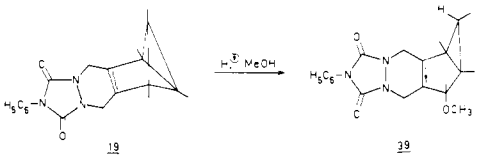


36 37 38

most probably the intermediate in the formation of **32**. Following the reaction in the NMR cavity did not give any indication for the intermediacy of **36**. Hence, we must conclude that the rearrangement of **36** to **32** is fast and the formation of **36** is rate limiting. Therefore the difference in rate cannot be ascribed to the action of Ag upon **36**. More probably Ag acts as a Lewis acid[49] and enhances, by complexation with an oxygen of the imide group, the dienophilicity of *N*-phenylmaleimide.

A solution of diene **5** in the moderate reactive dienophiles methyl acrylate or acrylonitrile showed no reaction after standing for several days at room temperature (see Table II). However, in the presence of silver perchlorate (1 equiv) and sodium carbonate (10 equiv) diene **5** reacts smoothly with methyl acrylate; after 5 h at room temperature compound **37** is formed in a yield of 90%.

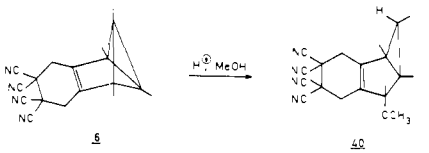
Homofulvene Formation. Reaction of Benzvalene Derivatives with Acid. The isolation of the PTAD adduct **18** as described before offers the opportunity to study this molecule under more closely controlled conditions. The method of isolation of **18** suggests strongly that the normally isolated homofulvene derivatives **15** and **16** result from an acid-catalyzed rearrangement. Indeed when a solution of **18** in deuteriochloroform was treated with a catalytic amount (10 mol %) of trichloroacetic acid at room temperature **15** and **16** were formed instantaneously in a ratio 45:55. When this reaction was carried out with methanol as solvent the methoxy compound **39** was ob-



19 39

tained as the main product. The same compound was formed when the reaction mixture of diene **5** and PTAD (**14**), prepared at −70 °C, was allowed to warm up to room temperature in the presence of excess methanol. Isolated PTAD adduct, once purified, did not react with methanol. A mixture of the two homofulvenes **15** and **16**, treated with acidified methanol (10 mol % of trichloroacetic acid), showed no methanol addition after workup: both isomers were recovered unchanged.

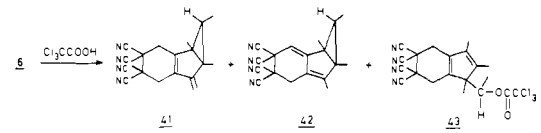
Similarly a solution of the TCNE adduct **6** in methanol gave upon addition of a catalytic amount of acid (10 mol %) a white precipitate identified as the methoxy compound **40**. The re-



6 40

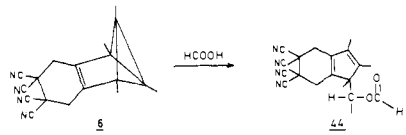
action proceeds very rapidly and **40** is formed in 95% yield. In methanol without acid **6** is stable under the conditions used. The ^1H NMR chemical shifts of the cyclopropyl hydrogens are 0.4 and 0.43 ppm in **39** and **40**, respectively. This is in good agreement with a stereochemical assignment in which the methoxy group is in a trans position with respect to the cyclopropane ring[50] and the hydrogen on the cyclopropane ring is in the endo position.[51]

When a solution of **6** in benzene is treated with trichloroacetic acid (10 mol %) at room temperature it takes 4 h to accomplish total conversion. The main products obtained are the homofulvene derivatives **41** and **42** in a 2:1 ratio.[52] However,



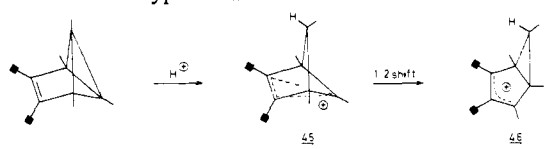
careful examination of the ^1H NMR spectrum reveals that yet another product was formed in 9% yield. This product turned out to be the cyclopentadiene derivative **43**. Treatment of a mixture of **41, 42,** and **43** with acidified methanol (10 mol % of trichloroacetic acid) did not give rise to any reaction. This means that formation of **41, 42,** and **43** is essentially irreversible under the reaction conditions used. Compounds **41** and **42**[52] could be separated and purified by column chromatography and crystallization.

Structure assignment of **41** and **42** rests on elemental analysis and the spectral data (see Experimental Section). The cyclopentadiene derivative **43** becomes the major reaction product (68%) when **6** is treated with 1 equiv of trichloroacetic acid. Similarly treatment of **6** with formic acid affords almost quantitatively (95%) the cyclopentadiene derivative **44.**



Compound **43** is obtained quantitatively when **6** or a mixture of **41** and **42** is heated in benzene during 24 h in the presence of 1.5 equiv of trichloroacetic acid.

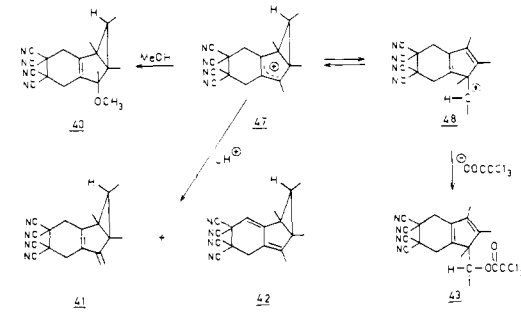
Mechanistic Aspects of the Acid-Catalyzed Rearrangement of Benzvalene Derivatives. Roughly speaking one can imagine two different modes in which a proton can attack a benzvalene molecule: attack at the double bond or, alternatively, attack at the bicyclobutane moiety. Attack at the double bond, which is observed in the reaction of benzvalene with other electrophiles,[10,11a,b] seems unlikely because in that case it is difficult to explain the exclusive product formation as far as the position of the hydrogen and the position of the substituents is concerned. Two modes in which a proton attacks a bicyclobutane ring have been proposed.[55,56] Attack at the back lobe of the bent central C–C bond[55] leads initially to a [2,1,1]hexenyl cation **45**.[57] This type of cation is known to convert readily via



a 1,2 shift into the more stable [3,1.0]hexenyl cation **46.** Attack on one of the side bonds of the bicyclobutane moiety[56] leads directly to cation **46.** In both mechanisms the proton ends up in the endo position,[58] which is actually observed in the reaction products.

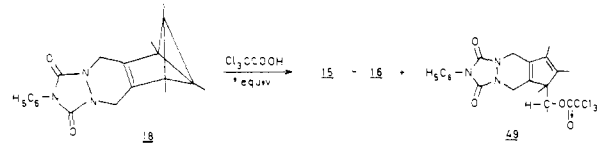
There is another argument, which suggests direct attack of a proton at the bicyclobutane moiety rather than attack at the double bond. Hogeveen and Kwant[59] have studied the relative reactivity of cyclopropanes and double bonds toward protonation. They concluded that protonation in hydrogen chloride/methylene chloride, a reaction medium comparable with ours, takes place preferentially at the cyclopropane ring. Since bicyclobutane is approximately 10^{10} as reactive as cyclopropane toward acid[60] this observation suggests that attack at the bicyclobutane ring is favored over attack at the double bond. Hence we believe that a proton attacks preferentially at the bicyclobutane moiety of the benzvalene derivatives.[61]

The [3.1.0]hexenyl cation is the key intermediate in the acid-catalyzed rearrangement of the benzvalene derivatives. It can lose a proton from two different positions to give homofulvene derivatives. When an effective nucleophile is present, for example, methanol, the ion is quenched to form a methoxy compound. It can also rearrange further to give a cyclopentadiene carbonium ion, which is subsequently trapped by the anion. This is pictured below for the TCNE adduct **6.**



A Comparison of the Acid-Catalyzed Rearrangements of 6 and 18. It attracts attention that **43** is formed (9% yield) from **6** upon treatment with a catalytic amount of trichloroacetic acid (10 mol %) whereas the corresponding cyclopentadiene derivative **49** could not be observed in the analogous reaction of **18.**

When the TCNE adduct **6** (0.5 mmol) was treated with 1 equiv of trichloroacetic acid in benzene (10 mL) for 5 min at room temperature, three products were formed: **41** (20%), **42** (12%), and **43** (68%). No starting material could be detected. Prolonged reaction time (16 h) raises the yield of **43** to 80% at the cost of mainly **41** (9%). The homofulvene derivative **42** is not affected within the limits of the experimental error. This is also true when a mixture of **41** and **42** is treated with 1 equiv of trichloroacetic acid for 16 h. Only **41** is converted into **43** (85%). Thus the formation of **42** is essentially irreversible under these conditions. On the contrary **41,** the isomer with the exocyclic double bond, is slowly converted into the thermodynamically more stable cyclopentadiene derivative **43.** The PTAD adduct **18** gave upon treatment with 1 equiv of trichloroacetic acid in benzene solution for 5 min at room temperature mainly the homofulvene derivatives **15** (39%) and **16** (44%). No starting material could be observed and besides **15** and **16** the cyclopentadiene derivative **49** was formed in only



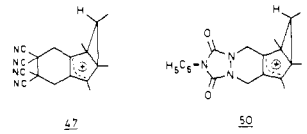
17% yielded. In the case prolonged reaction time (16 h) has a more radical effect than in the reaction of the TCNE adduct under these conditions, the cyclopentadiene derivatives **49** becoming the major product (70%). The remaining 30% consisted of **15** (17%) and unidentified material (13%); **16** could not be detected. Treatment of a 1:1 mixture of the homofulvene derivatives **15** and **16** with 1 equiv of trichloroacetic acid in benzene for 5 min at room temperature gives **15** (38%), **16** (44%), and **49** (18%). The same reaction for 16 h affords **49** (68%) and **15** (16%); unidentified material accounted for 16% and no **16** could be observed.

These experimental facts clearly indicate that the cyclopentadiene derivatives **43** and **49** are formed preferentially with respect to the corresponding homofulvene derivatives when the reactions are carried out under thermodynamically controlled conditions. However, there is a fundamental difference in the reaction with acid of the PTAD adduct **18** on the one hand, and the TCNE adduct **6** on the other hand. In the former reaction the kinetically favored products are the homofulvene derivatives **15** and **16** whereas in the latter reaction the thermodynamically favored and kinetically favored product is the same, viz., the cyclopentadiene derivative **43.** A reason may be found

Table III

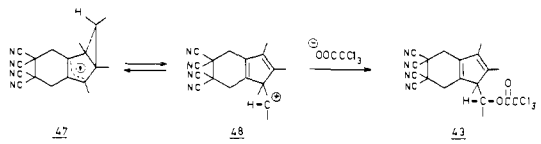
Conversion **18–17**			Conversion **6–8**		
Temp, °C	Solvent	k_1, s^{-1}	Temp, °C	Solvent	k_1, sec^{-1}
74	Chlorobenzene	1.9×10^{-3}	98	Chlorobenzene	8.5×10^{-3}
52	Chlorobenzene	1.4×10^{-4}	76	Chlorobenzene	8.5×10^{-4}
20	Deuteriochloroform	5.3×10^{-6}	66	Chlorobenzene	2.1×10^{-4}

in the influence of the substituents on the stability on the intermediate carbonium ions. If we look at the bicyclo[3.1.0]-hexenyl cations **47** and **50,** derived from the TCNE adduct **6**



47 **50**

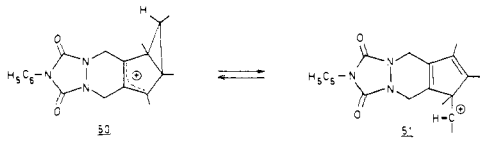
and the PTAD adduct **18,** respectively, one can argue that the positive charge in **47** is less effectively delocalized than in carbonium ion **50** owing to the strong electron-withdrawing cyano groups. If **47** rearranges to cation **48,** the electron-



47 **48** **43**

withdrawing cyano groups are further from the positive charge and their destabilizing influence becomes less.

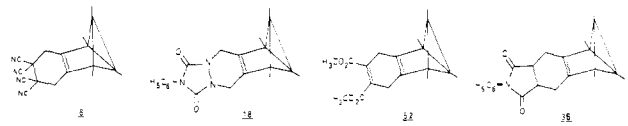
Homofulvene formation from **47** can successfully compete with cyclopentadiene formation **43** from **48** as soon as the concentration of the trichloroacetic acid anion becomes low. Hence, there must be an equilibrium between the carbonium ions **47** and **48** under the reaction conditions used. This equilibrium lies to the right so that formation of the cyclopentadiene derivative **43** occurs more effectively than the formation of the homofulvene derivatives **41** and **42.** On the contrary the equilibrium between carbonium ions **50** and **51** lies more to the



50 **51**

left, indicating that the influence of the urazole moiety on the [3.1.0]cation **50** is less destabilizing than that of the cyano groups in cation **47.** Hence, homofulvene formation occurs preferentially. Another indication for the less effective charge delocalization in cation **47** with respect to cation **50** may be found in the ratio in which the isomeric homofulvene derivatives are formed when the reaction is carried out under kinetically controlled conditions. In a kinetically controlled reaction one may anticipate that proton abstraction occurs at the methyl group adjacent to the carbon atom bearing the highest positive charge. Cation **47** gives rise, upon proton abstraction, to the isomeric homofulvene derivatives **41** and **42** in a ratio 2:1, whereas cation **50** affords **15** and **16** in a ratio close to 1:1. Hence one can conclude that the positive charge in **50** is more effectively delocalized than in the corresponding cation **47.** The experimental results indicate that the PTAD adduct **18** is much more labile to acid than the TCNE adduct **6.** However, one should be cautious in comparing these two reactions. The formation of a cyclopentadiene derivative, which is the kinetically favored product in the rearrangement of the TCNE adduct, involves a bimolecular process wherein trichloroacetic acid is consumed. On the other hand, the formation of homofulvene derivatives which are the kinetically favored products in the rearrangement of the PTAD adduct, is a bimolecular process in which the acid only plays a catalytical role. The concentration of trichloroacetic acid diminishes in the former reaction but remains unchanged in the latter. Hence, one cannot draw conclusions properly from these experiments. The following experiment gives a definite answer. A solution of the TCNE adduct **6** in benzene was treated with trichloroacetic acid (10 mol %) for 10 min. Then PTAD adduct **18** was added and the reaction mixture was stirred for another 10 min. After workup the ^1H NMR spectrum showed the complete conversion of the PTAD adduct. The TCNE was only partially (68%) converted. Thus, we can safely conclude that the PTAD adduct (**18**) is more sensitive to acid than the TCNE adduct (**6**).

Thermal Rearrangement of Benzvalene Derivatives. We have shown that the preferred pathways of the rearrangements of benzvalene derivatives as well as their acid lability depend on the nature of the substituents. Their thermal stability seems likewise to be determined by the substituents. For example, the TCNE adduct **6** and the PTAD adduct **18** are quite stable at room temperature, whereas the adducts **52** and **36** can neither



be isolated at room temperature nor observed by following the reaction in the NMR cavity. The aromatic valence isomers **31** and **32** are the only products detectable.

The rate constants of aromatization of the two isolated benzvalene derivatives **18** and **6** were determined by following the conversion as a function of time by means of NMR spectroscopy. The first-order constants are shown in Table III. From these data the Arrhenius energies of activation were determined as 23.4 ± 1 and 29.4 ± 1 kcal/mol for the conversions **18–17** and **6–8,** respectively. Therefore one can conclude that the thermal reactivity follows the same trend as the reactivity toward acids. Larger electron-withdrawing capacity of the substituents leads to an enhancement of stability. Reasoning along these lines provides a good circumstantial argument for accepting the intermediacy of the benzvalene derivatives **52** and **36** in the formation of **31** and **32.** A troublesome aspect in the arrangements of highly strained molecules is the possibility of glass surface catalysis.[64] In view of this we have studied the thermal rearrangement of the PTAD adduct **18** in a mixture of chlorobenzene and TMEDA[64] using ^1H NMR tubes carefully washed with ammonia and dried at 140 °C. At 68 °C the rate constant was found to be 8×10^{-4} s^{-1}, which is very close to the value obtained in pure chlorobenzene (7×10^{-4} s^{-1}). At 100 °C in pure TMEDA and PTAD adduct **18** rearranged at a rate too fast to be followed into its aromatic isomer **17.** Hence, we believe that the rearrangements of the benzvalene derivatives into their aromatic counterparts truly are thermal rather than catalyzed reactions. The impossibility of isolating benzvalene derivatives as **52** and **36** must be ascribed to their inherent instability. The fact that electron-withdrawing substituents, especially perfluoroalkyl groups,[15] enhance the stability of highly strained carbon skeletons is well known. All valence isomers of perfluorohexamethylbenzene have been isolated[6,69] and are found to be remarkably stable.[15,69] Perfluorohexamethylbenzvalene (**3**) is stable at room

temperatures whereas benzvalene (**1**) rearranges with a half-life of 10 days at room temperature.[3a,13] This means that the tetramethylbenzvalene derivatives described here, with the exception of the TCNE adduct **6**, are thermally less stable than benzvalene itself. Hence, we can conclude that methyl groups have a destabilizing effect on the benzvalene skeleton. This is in agreement with the unsuccessful efforts to isolate hexamethylbenzvalene.[15,70] In contrast two other hexamethylated valence isomers, hexamethylprismane[43] and hexamethyl(Dewar benzene),[73] are more stable than their parent compounds.

Experimental Section

General Remarks. Melting points (uncorrected) were determined on a Mettler FP 21 apparatus. Elemental analysis were performed in the analytical section of this department. Mass spectra were obtained on an AEI MS-902. Infrared spectra were recorded on a Perkin-Elmer 257 or a Perkin-Elmer 125 spectrophotometer. Ultraviolet spectra were taken with a Zeiss PMQ 11 or a Beckman DB-G spectrophotometer.

Proton magnetic resonance spectra were taken with 60-MHz Varian (Model A-60D) or Jeol C-60 HL spectrometers equipped with variable temperature probes with deuteriochloroform as solvent and tetramethylsilane as internal standard (unless otherwise stated). Chemical shifts are denoted in parts per million downfield from Me_4Si (δ 0).

A Varian XL-100 was used for the carbon-13 and 100-MHz proton spectra. Chemical shifts are given in parts per million downfield from Me_4Si.

Column chromatography was performed with Florisil (60–100 mesh, Fluka AG). All solvents were purified by common methods.

Synthesis of Diene 5 (See Ref 20). The synthesis of **5** can be carried out without any problem at a tenfold larger scale than has been reported.[20] Using 0.2 mol of hexamethyl(Dewar benzene) yields of over 60% are obtained. Compound **5** becomes yellow upon standing. Kept under nitrogen and stored at −30 °C **5** is stable for several months.

Synthesis of the TCNE Adduct 6. To a stirred solution of 4.8 g of diene **5** (30 mmol) in 100 mL of methylene chloride was added 4.0 g of tetracyanoethylene (TCNE) (31 mmol) in small portions over 30 min. After the solvent was removed in vacuo (bath temperature 30 °C) the resulting dark solid was redissolved in a small amount of methylene chloride and chromatographed over Florisil with ether. The eluate was concentrated until crystallization occurred. The crystals were collected on a Büchner funnel, washed with *n*-pentane/ether, and dried in vacuo at 25 °C affording 6 g of **6** (70%): ^{1}H NMR spectrum 3.12 (s, 4 H), 1.47 (s, 6 H), 1.16 ppm (s, 6 H); ^{13}C NMR spectrum ($CDCl_3$) 134.5 (s, alkene carbons), 110.8 (s, cyano carbons), 64.3 (s), 45.9 (s), 38.8 (s), 32.2 (t, J_{CH} = 140 Hz), 7.1 (q, J_{CH} = 125 Hz), and 4.4 ppm (q, J_{CH} = 125 Hz).

Neat samples of **6** rearrange into **8** at room temperature with a half-life of about 6 months. Stored at −30 °C **6** is stable for several months.

Reaction of 6 with Silver Perchlorate. Formation of 8.[20] To a solution of 288 mg of **6** (1 mmol) in 10 mL of chloroform was added 41 mg of silver perchlorate (0.2 mmol). The reaction mixture was stirred for 15 min at room temperature and was then quenched with 1 mL of a solution of sodium sulfide in water (0.75 mol/L). The resulting dark suspension was diluted with 9 mL of water. After separation the organic layer was once more extracted with 10 mL of water, dried over sodium carbonate, and filtered through Celite-535. The resulting clear solution was concentrated to leave 275 mg of a slightly yellow solid. The ^{1}H NMR spectrum showed the complete conversion of **6** into **8**; ultraviolet spectrum ($CHCl_3$) λ_{max} 274 nm (ϵ 404); ^{1}H NMR spectrum 3.71 (s, 4 H), 2.28 (s, 6 H), 2.22 ppm (s, 6 H).

The workup procedure as described in the preceding experiment was used in all silver-catalyzed reactions (unless otherwise stated).

Reaction of 5 with Maleic Anhydride. Isolation of the Homofulvene Derivative 10. To a stirred solution of 640 mg of diene **5** (4 mmol) in 10 mL of methylene chloride was added dropwise 420 mg of maleic anhydride (4.3 mmol) in 20 mL of methylene chloride in a nitrogen atmosphere. The reaction mixture was stirred for 3 h and then 20 mL of water was added. After stirring for 2 h the organic layer was separated and dried over sodium carbonate. Evaporation of the solvent in vacuo afforded 1.09 g of a yellow solid which consisted according to the ^{1}H NMR spectrum of 80% of **10**. This solid was transferred into a porous thimble which was placed into a Soxhlet extraction apparatus. Continuous extraction with *n*-pentane in a nitrogen atmosphere afforded after evaporation of the solvent in vacuo 850 mg of slightly yellow **10** (purity >90% according to ^{1}H NMR spectrum). The remaining 150 mg of yellow solid in the thimble could not be identified. Further purification of **10**, mp 117.5–119.0 °C dec, was accomplished by careful crystallization from *n*-pentane.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.03. Found: C, 73.7; H, 7.03.

Mass spectrum parent peak at *m/e* 258; IR spectrum inter alia 1839 and 1769 cm^{-1}. For the ultraviolet, ^{1}H NMR, and ^{13}C NMR spectra, see Table I and text. Compound **10** was also obtained when **5** was treated with freshly distilled (bp 90 °C, 15 mmHg) or freshly sublimed (20 °C, 0.06 mmHg) maleic anhydride (mp 52.2–52.4 °C) in dry benzene. Following the reaction in the NMR cavity at 40 °C gave no indication of the intermediacy of the benzvalene derivative **9**.

Reaction of 5 with Maleic Anhydride in the Presence of Silver Perchlorate and Sodium Carbonate. Synthesis of 12. To a solution of 640 mg of the diene **5** (4 mmol) in 30 mL of methylene chloride was added 166 mg of silver perchlorate (0.8 mmol) and 848 mg of sodium carbonate (8 mmol). To this suspension was added 588 mg of maleic anhydride (6 mmol). The mixture was stirred for 1 h at room temperature and then quenched with a sodium sulfide solution. After workup 927 mg of **12**, mp 260.9–262.6 °C, was obtained (90%). Crystallization from 96% ethanol furnished analytically pure **12**, mp 261.6–262.2 °C.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.03. Found: C, 74.2; H, 7.0.

Mass spectrum parent peak at *m/e* 258; IR spectrum inter alia 1830 and 1757 cm^{-1}; ultraviolet spectrum ($CHCl_3$) λ_{max} 274 nm (ϵ 300); ^{1}H NMR spectrum ($CDCl_3$) 3.53 (m, 4 H), 2.65 (m, 2 H), 2.22 ppm (broad s, 12 H).

Reaction of 5 with 0.5 Equiv of Maleic Anhydride in the Presence of Silver Perchlorate and Sodium Carbonate. To a stirred suspension of 160 mg of diene **5** (1 mmol), 41 mg of silver perchlorate (0.2 mmol), and 210 mg of sodium carbonate (2 mmol) in 10 mL of methylene chloride was added 50 mg of maleic anhydride (0.5 mmol). The reaction mixture was stirred for 1 h. After workup the ^{1}H NMR spectrum showed a conversion of **5** into **12** (50%). The remaining 50% of **5** was recovered unchanged.

Reaction of 10 with Silver Perchlorate and Sodium Carbonate. To a solution of 129 mg of **10** (0.5 mmol) in 5 mL of methylene chloride was added 21 mg of silver perchlorate (0.1 mmol) and 106 mg of sodium carbonate (1 mmol). The mixture was stirred at room temperature for 1 h. After workup the ^{1}H NMR spectrum showed only the presence of starting material **10**; no **12** could be detected.

Reaction of 6 with Silver Perchlorate and Sodium Carbonate. Under the conditions of the previous experiment the TCNE adduct **6** was completely converted into **8**.

Reaction of 5 with PTAD (14). Isolation of the Homofulvene Derivatives 15 and 16. To a stirred solution of 1.6 g of diene **5** (10 mmol) in 100 mL of ether at 0 °C in a nitrogen atmosphere was added dropwise (over 30 min) a solution of about 1.93 g of PTAD (**14**) (11 mmol) in 10 mL of acetone until the decolorization of PTAD became slow. The reaction mixture was then heated to 35 °C for 15 min. After addition of 40 mL of methylene chloride the reaction mixture was extracted twice with 50 mL of 2 N sodium hydroxide, washed with 50 mL of water, and dried over sodium carbonate. Evaporating the solvents in vacuo afforded 3.25 g of a slightly yellow solid which consisted according to the ^{1}H NMR spectrum of a mixture (>90%) of **15** (46%) and **16** (54%). The solid was partially dissolved in 100 mL of boiling ether and stirred for 2.5 h at room temperature during which time a white precipitate formed. The precipitate was collected on a Büchner funnel and dried in vacuo to give 1.68 g of a white solid which consisted according to the ^{1}H NMR spectrum mainly of **15** (80%) and a small amount of **16** (20%). Recrystallization from 96% ethanol provided 1.1 g of **15**, mp 183–184 °C. Another recrystallization from 96% ethanol afforded analytically pure **15**, mp 183.4–184 °C.

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.60; H, 6.31; N, 12.53. Found: C, 71.75; H, 6.1; N, 12.6.

Mass spectrum parent peak at *m/e* 335; IR spectrum (KBr) inter alia 1760, 1700, 1500, 1420, 1130 cm^{-1}; ultraviolet spectrum λ_{max} 307 nm (ϵ 22 000); ^{1}H NMR spectrum 7.48 (m, 5 H), 6.63 (broad s, 1 H), 4.42 (AB system, 2 H, J = 15 Hz), 1.78 (broad s, 3 H), 1.20 (s, 3 H), 1.13 (s, 3 H), 1.0 (dist d, 3 H, J = 6 Hz), 0.7 ppm (dist q, 1 H, J = 6 Hz); ^{13}C NMR spectrum 149.7 (s), 146.8 (s), 145.7 (s), 134.8

(s), 130.8 (s, phenyl carbon), 128.6 (phenyl carbon meta), 127.5 (phenyl carbon para), 125.0 (phenyl carbon ortho), 119.1 (s), 105.0 (d), 41.5 (t), 38.9 (s), 37.8 (d), 29.0 (s), 12.1 (q), 9.8 (q), 9.4 (q), and 7.5 ppm (q).

The filtrate was concentrated in vacuo, leaving 1.62 g of a yellow oil which consisted according to the ^{1}H NMR spectrum mainly of **16** (89%) and **15** (11%). This material was dissolved in a small amount of ether/methylene chloride and chromatographed over Florisil. Eluting with *n*-pentane afforded 80 mg of a yellow oil which was neglected. Further eluting with *n*-pentane/ether (1:1) provided 650 mg of **16** which was purified, mp 150.8–151.6 °C, by crystallization from *n*-pentane/ether.

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.60; H, 6.31; N, 12.53. Found: C, 71.4; H, 6.4; N, 12.6.

Mass spectrum parent peak at *m/e* 335; IR spectrum (KBr) inter alia 1770, 1710, 1620, 1500, 1420, and 1140 cm^{-1}; ultraviolet spectrum λ_{max} 255 nm (ϵ 11 200); ^{1}H NMR spectrum 7.5 (m, 5 H), 4.9 (broad s, 1 H), 4.8 (broad s, 1 H), 4.3 (m, 2 H), 4.2 (m, 2 H), 1.24 (s, 3 H), 1.16 (s, 3 H), 1.04 (dist d, 3 H, J = 6 Hz), 0.9 ppm (dist q, 1 H, J = 6 Hz); ^{13}C NMR spectrum 155.8 (s), 151.4 (s), 144.6 (s), 130.9 (s, phenyl carbon), 128.7 (phenyl carbon meta), 127.7 (phenyl carbon para), 125.7 (s), 125.0 (phenyl carbon ortho), 100.6 (t), 43.4 (t), 41.8 (t), 39.1 (d), 35.0 (s), 32.9 (s), 9.9 (q), 9.6 (q), and 7.1 ppm (q).

Reaction of 5 with PTAD (14) in the Presence of Silver Perchlorate and Sodium Carbonate. Formation of 17. To a stirred suspension of 480 mg of **5** (3 mmol), 125 mg of silver perchlorate (0.6 mmol), and 636 mg of sodium carbonate (6 mmol) in 20 mL of methylene chloride was added over 4 h 560 mg of PTAD (**14**) (3.2 mmol). After quenching as usual the organic layer was extracted twice with 2 N sodium hydroxide. Evaporation of the solvent afforded a slightly yellow solid (965 mg) which consisted according to the ^{1}H NMR spectrum of 95% of **17**. Recrystallization from 96% ethanol and a small amount of methylene chloride afforded analytically pure **17**, mp 182.2–182.6 °C, as white crystals (800 mg, 80%).

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.60; H, 6.31; N, 12.53. Found: C, 71.5; H, 6.4; N, 12.5.

Mass spectrum parent peak at *m/e* 335; IR spectrum (Nujol) inter alia 1775, 1720, and 1150 cm^{-1}; ^{1}H NMR spectrum 7.5 (m, 5 H), 4.73 (s, 4 H), 2.21 (s, 6 H), 2.28 ppm (s, 6 H).

Isolation of the PTAD Adduct 18. In a 50-mL three-necked bottle equipped with a mechanical stirrer, 1.6 g of diene **5** (10 mmol) was dissolved in 25 mL of dry ether. The solution was cooled under nitrogen to −80 °C and a solution of 2.1 g of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **14**, 12 mmol) in 10 mL of acetone was added dropwise over 15 min. After the addition the dark red reaction mixture was stirred for another 5 min at −80 °C and was then poured into a rapidly stirred mixture of 50 mL of 2 N sodium hydroxide solution, 50 g of ice, and 50 mL of ether. After stirring for 5 min the organic layer was separated, once more extracted with 50 mL of ice-cold sodium hydroxide solution, and washed with 50 mL of ice-cold water. The almost colorless organic layer was dried over sodium carbonate. Evaporation of the solvent in vacuo at 0 °C afforded 3.3 g of a white solid which consisted according to the ^{1}H NMR spectrum of >95% of **18**. This material was redissolved in 50 mL of dry ether. The solution was concentrated in vacuo at 0 °C until some crystallization occurred and then cooled at −30 °C for 1 h. The resulting precipitate was filtered and dried in vacuo to give 2.8 g of analytically pure **18** (8.4 mmol, 84%).

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.60; H, 6.31; N, 12.53. Found: C, 71.4; H, 6.1; N, 12.6.

Mass spectrum parent peak at *m/e* 335; IR spectrum inter alia 1765, 1710, 1600, and 1405 cm^{-1}; ^{1}H NMR spectrum 7.4 (m, 5 H), 4.15 (s, 4 H), 1.43 (s, 6 H), 1.04 ppm (s, 6 H); ^{13}C NMR spectrum ($CDCl_3$) 151.4 (s, C=O), 133.9 (s, alkene carbons), 130.2 (s, phenyl C), 128.8 (phenyl C, meta), 127.8 (phenyl C, para), 125.1 (phenyl C, ortho), 63.1 (s), 44.3 (s), 42.6 (t, J_{CH} = 145 Hz), 6.8 (q, J_{CH} = 125 Hz), 4.5 ppm (q, J_{CH} = 130 Hz).

Neat samples of **18** are stable for at least 1 month at −35 °C but rearrange at room temperature with a half-life of 10 days.

Pyrolysis of 18. A neat sample of **18** (33 mg, 0.1 mmol) was heated for 5 min at 100 °C and then dissolved in deuteriochloroform. The ^{1}H NMR spectrum showed the complete conversion to **17**.

Reaction of 18 with Silver Perchlorate. To a stirred solution of 167 mg of the PTAD adduct **18** (0.5 mmol) in 10 mL of benzene was added 11 mg of silver perchlorate (0.05 mmol) and 53 mg of sodium carbonate. The reaction mixture was stirred for 5 min and then 5 mL of sodium sulfide solution (10%) was added. The organic layer was separated, washed two times with 10 mL of water, and dried over sodium carbonate. After evaporation of the solvent the ^{1}H NMR spectrum showed the complete conversion of **18** into **17**. When the addition of sodium carbonate was omitted the same result was obtained.

Reaction of 18 with Silver Perchlorate–Sodium Carbonate at −70 °C. To a stirred solution of **18** (1 mmol) in 10 mL of ether and 5 mL of acetone at −70 °C was added 41 mg of silver perchlorate (0.2 mmol) and 212 mg of sodium carbonate. The reaction mixture was stirred for 15 min and then quenched with a sodium sulfide solution. After workup as usual the ^{1}H NMR spectrum showed the complete conversion of **18** into **17**. When sodium carbonate was omitted the same result was obtained.

Preparation of the Diadduct 24/25.[44] To a stirred solution of 1.05 g of PTAD (6 mmol) in 10 mL of acetone at 0 °C was added dropwise during 1 h a solution of 390 mg of **5** (2.4 mmol) in 50 mL of ether. After this addition the red color of PTAD had disappeared. The reaction mixture was then diluted with methylene chloride, extracted twice with 50 mL of 2 N sodium hydroxide, and washed with 50 mL of water. After drying over sodium carbonate the solvent was removed in vacuo. The resulting yellow solid (1.11 g) consisted of 70% of the diadduct. Pure, according to the ^{1}H NMR spectrum, diadduct, mp 242–243.5 °C, was obtained after one crystallization from 96% alcohol and a small amount of chloroform. Recrystallization of this material from methylene chloride/ether afforded analytically pure diadduct, mp 243.3–243.6 °C.

Anal. Calcd for $C_{28}H_{26}N_6O_4$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.9; H, 5.2; N, 16.3.

Mass spectrum peak at *m/e* 391 ($C_{28}H_{26}N_6O_4 - C_6H_5NCO$); IR spectrum (Nujol) inter alia 1765, 1725, 1713, and 1420 cm^{-1}; ^{1}H NMR spectrum 7.5 (m, 10 H), 4.5 (AB system, 2 H, J = 13 Hz), 3.7 (AB system, 2 H, J = 13 Hz), 1.79 (s, 3 H), 1.37 (s, 3 H), 1.22 (s, 3 H), 1.20 ppm (s, 3 H); ^{13}C NMR spectrum ($CDCl_3$) 154.8, 153.2, and 152.5 (all s, carbonyl carbons), 131.1 (s, phenyl carbon), 130.6 (s, phenyl carbon) 128.8 (phenyl carbon, meta), 128.0 (phenyl carbon, para), 125.0 (phenyl carbon, ortho), 72.2 (s), 69.1 (s), 57.1 (s), 44.6 (t, J_{CH} = 140 Hz), 39.5 (t, J_{CH} = 145 Hz), 36.0 (s), 34.3 (s), 34.1 (s), 12.5 (q, J_{CH} = 130 Hz), 6.5 (q, J_{CH} = 125 Hz), 5.3 (q, J_{CH} = 125 Hz), and 4.3 (q, J_{CH} = 125 Hz).

Reaction of 5 with Dimethyl Acetylenedicarboxylate (26). Synthesis of 31. To a stirred suspension of 640 mg of **5** (4 mmol), 166 mg of silver perchlorate (0.8 mmol), and 848 mg of sodium carbonate (8 mmol) in 5 mL of methylene chloride was added 710 mg of **26** (5 mmol) in 2 mL of methylene chloride. The reaction mixture was heated to reflux for 30 h. After workup as usual a yellow oil (1.3 g) was obtained which consisted according to the ^{1}H NMR spectrum of **31**, the excess of **26**, and a small amount (~5%) of unidentified products. Recrystallization from 35 mL of 96% ethanol afforded 1.0 g of analytically pure **31**, mp 157–158 °C (83%).

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.49; H, 7.34. Found: C, 71.4; H, 7.3.

Mass spectrum parent peak at *m/e* 302; IR spectrum (KBr) inter alia 1732, 1712, and 1670 cm^{-1}; ^{1}H NMR spectrum 3.86 (s, 6 H), 3.64 (s, 4 H), 2.24 (s, 6 H), and 2.20 ppm (s, 6 H).

Influence of Silver Perchlorate/Sodium Carbonate on the Reaction of Diene 5 and 26. To a stirred solution of 320 mg of **5** (2 mmol) in 5 mL of methylene chloride was added 284 mg of **26** (2 mmol). The mixture was stirred at room temperature for 17 h. After workup the ^{1}H NMR spectrum showed the presence of **31** in only 8% yield; the remaining starting materials were observed to be unchanged.

When the previous reaction was carried out in the presence of 83 mg of silver perchlorate (0.4 mmol) and 424 mg of sodium carbonate (4 mmol) compound **31** was formed in 50% yield, and the remaining starting materials (50%) were observed to be unchanged.

Reaction of 5 with *N*-Phenylmaleimide (27). Synthesis of 32. To a stirred suspension of 160 mg of **5** (1 mmol), 41 mg of silver perchlorate (0.2 mmol), and 216 mg of sodium carbonate (2 mmol) was added 171 mg of *N*-phenylmaleimide (1 mmol). The reaction mixture was stirred for 23 h at room temperature. After workup as usual the ^{1}H NMR spectrum showed the presence of **32** (90% yield); the remaining starting materials (10%) were observed to be unchanged. Analytically pure **32**, mp 180.2–182.0 °C, was obtained after recrystallization from 96% ethanol.

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.2; H, 7.0; N, 4.0.

Mass spectrum parent peak at *m/e* 333; IR spectrum (Nujol) inter alia 1710, 1600, 1390, and 1180 cm^{-1}; ^1H NMR spectrum 7.1 (m, 5 H), centered at 2.9 (complex m, 6 H), 2.22 (s, 6 H), 2.26 ppm (s, 6 H).

When this reaction was carried out in the absence of silver perchlorate and sodium carbonate for 23 h at room temperature only 12% of **32** was formed.

Reaction of 5 with Dimethyl Fumarate (28). Synthesis of 33. To a stirred suspension of 400 mg of **5** (2.5 mmol), 104 mg of silver perchlorate (0.5 mmol), and 530 mg of sodium carbonate (5 mmol) in 3 mL of chloroform was added 360 mg of dimethyl fumarate (2.5 mmol). The stirred reaction mixture was heated to reflux for 36 h. After dilution with methylene chloride the reaction mixture was worked up as usual affording 750 mg of a yellow oil which consisted mainly of **33** (84%). Recrystallization from 96% ethanol and a small amount of methylene chloride afforded 525 mg of **33,** mp 177–178.3 °C (1.7 mmol, 69%). Another recrystallization provided analytically pure **33**, mp 178.8–179.8 °C.

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.9; H, 8.0.

Mass spectrum parent peak at *m/e* 304; IR spectrum (KBr) inter alia 1730, 1430, 1190, 1153, and 1030 cm^{-1}; ^1H NMR spectrum 3.73 (s, 6 H), 2.84 (m, 6 H), 2.18 (s, 6 H), and 2.12 ppm (s, 6 H). When the previously described reaction is carried out in the absence of silver perchlorate and sodium carbonate **33** is formed in 70% yield and ~10% of the starting material is observed unchanged. At room temperature **5** reacted slowly with dimethyl fumarate at these concentrations (see Table II).

Reaction of 5 with *trans*-1,2-Bis(benzoyl)ethylene (29). Formation of 34. To a stirred suspension of 320 mg of **5** (2 mmol), 83 mg of silver perchlorate (0.4 mmol), and 424 mg of sodium carbonate (4 mmol) in 3 mL of chloroform was added 472 mg of **29**. The stirred reaction mixture was heated to reflux for 6 h. After dilution with methylene chloride the reaction mixture was worked up as usual affording 770 mg of a yellow oil which consisted mainly of **34** (86%). Recrystallization from 96% ethanol and a small amount of methylene chloride provided 600 mg of **34** as a white solid, mp 202–205 °C (1.52 mmol, 76%). Analytically pure **34,** mp 205–207 °C, was obtained after another crystallization from 96% ethanol/methylene chloride.

Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.82; H, 7.12. Found: C, 84.8; H, 7.2.

Mass spectrum parent peak at *m/e* 396; IR spectrum (KBr) inter alia 1670, 1210, and 700 cm^{-1}; ^1H NMR spectrum 7.9 (m, 10 H), 4.15 (m, 2 H), 3.1 (m, 4 H), 2.22 (s, 6 H), 2.10 ppm (s, 6 H).

For reactions at these concentrations in the absence of silver perchlorate and sodium carbonate and at room temperature at these concentrations, see Table II.

Reaction of 5 with *trans*-1,2-Bis(phenylsulfonyl)ethylene (30). Formation of 35. To a stirred suspension of 320 mg of **5** (2 mmol), 83 mg of silver perchlorate (0.4 mmol), and 424 mg of sodium carbonate (4 mmol) in 3 mL of chloroform was added 616 mg of **30** (2 mmol). The stirred reaction mixture was refluxed during 24 h. After dilution with chloroform the reaction mixture was worked up as usual affording 910 mg of a yellow oil which consisted mainly of **35** (87%). Recrystallization from a mixture of 96% ethanol and chloroform provided 750 mg of analytically pure **35,** mp 242.5–243.3 °C (1.6 mmol, 80%).

Anal. Calcd for $C_{26}H_{28}O_4S_2$: C, 66.63; H, 6.02; S, 13.68. Found: C, 66.4; H, 6.0; S, 13.5.

Mass spectrum parent peak at *m/e* 468; IR spectrum (KBr) inter alia 1300, 1135, and 740 cm^{-1}; ^1H NMR spectrum 8.10 (m, 10 H), 4.35 (m, 2 H), 3.35 (m, 4 H), 2.25 (s, 6 H), and 2.17 ppm (s, 6 H).

For reactions at these concentrations in the absence of silver perchlorate and sodium carbonate and at room temperature at these concentrations, see Table II.

Reaction of 5 with Methyl Acrylate. Formation of 37. To a stirred suspension of 320 mg of **5** (2 mmol) and 2.12 g of sodium carbonate (20 mmol) in 10 mL of methyl acrylate was added 414 mg of silver perchlorate (2 mmol). The mixture was stirred at room temperature for 5 h. After quenching with 5 mL of sodium sulfide solution and diluting with water the mixture was extracted twice with methylene chloride. The combined extracts were filtered and extracted twice more with water and dried over sodium carbonate. Evaporation of the solvent afforded 440 mg of a yellow oil which consisted of 90% of **37**. Recrystallization from 96% ethanol afforded pure **37,** mp 91.3–91.6 °C.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.02; H, 9.00. Found: C, 77.8; H, 9.1.

Mass spectrum parent peak at *m/e* 246; IR spectrum (Nujol) inter alia 1740 cm^{-1}; ^1H NMR spectrum 3.73 (s, 3 H), centered at 2.8 (m, 5 H), 2.22 (s, 6 H), 2.18 ppm (s, 6 H). These two singlets overlap a multiplet (2 H).

When the experiment was carried out in the absence of silver perchlorate no reaction took place under these conditions.

Reaction of 5 with Acrylonitrile. Formation of 38. To a stirred suspension of 480 mg of **5** (3 mmol) and 3.18 g of sodium carbonate (30 mmol) in 10 mL of acrylonitrile was added 621 mg of silver perchlorate (3 mmol). The reaction mixture was stirred for 35 h at room temperature. Working up as in the previous experiment afforded 560 mg of a slightly yellow solid which consisted according to the ^1H NMR spectrum of 85% of **38**. Washing with *n*-pentane–ether provided 410 mg of **38,** mp 152.8–153.9 °C (1.92 mmol, 64%). An analytically pure sample of **38,** mp 153.5–154.2 °C, was obtained by one recrystallization from 96% ethanol.

Anal. Calcd for $C_{15}H_{19}N$: C, 84.49; H, 9.45; N, 6.57. Found: C, 84.1; H, 9.1; N, 6.4.

Mass spectrum parent peak at *m/e* 213; IR spectrum (Nujol) inter alia 2280 cm^{-1} (C≡N); ^1H NMR spectrum complex m centered at 2.9 (5 H), 2.25 (s, 6 H), 2.19 ppm (s, 6 H). These two singlets overlap a multiplet (2 H).

When the experiment was carried out in the absence of silver perchlorate no reaction took place under these conditions.

Reaction of 18 with a Catalytic Amount of Trichloroacetic Acid. To a solution of 33.5 mg of the PTAD adduct **18** (0.1 mmol) in 0.1 mL of deuteriochloroform in a NMR tube was added at room temperature 0.2 mL of deuteriochloroform containing 1.6 mg of trichloroacetic acid (0.01 mmol). Immediately after the addition the tube was placed in the NMR cavity and the ^1H NMR spectrum was recorded. It shows only the presence (>90%) of **15** (45%) and **16** (55%), no starting material being detected.

Reaction of 18 with Acidified Methanol. Preparation of 39. To a solution of 1 g of **18** (3 mmol) in 50 mL of methanol, cooled to −5 °C, was added to a solution of 24.5 mg of trichloroacetic acid (0.15 mmol) in 5 mL of methanol. The mixture was stirred for 5 min and then poured into a mixture of 150 mL of 2 N sodium hydroxide solution and 150 mL of ether. After separation, the organic layer was extracted twice with 50 mL of 2 N sodium hydroxide solution, washed three times with 100 mL of water, and dried over sodium carbonate. The solvent was removed in vacuo leaving 1.1 g of a white solid which consisted according to the ^1H NMR spectrum of >90% of **39**. Fractional recrystallization from ether/*n*-pentane afforded analytically pure **39,** mp 125.9–127.4 °C dec.

Anal. Calcd for $C_{21}H_{25}N_3O_3$: C, 68.64; H, 6.86; N, 11.44. Found: C, 68.4; H, 6.9; N, 11.4.

Mass spectrum parent peak at *m/e* 367; IR spectrum (KBr) inter alia 1770, 1730, 1420, and 1070 cm^{-1}; ultraviolet spectrum (96% ethanol) no maxima (ϵ >1000) above 220 nm; ^1H NMR spectrum ($CDCl_3$) 7.55 (m, 5 H), 4.32 (m, 2 H), 4.03 (m, 2 H), 2.90 (s, 3 H), 1.30 (s, 3 H), 1.10 (s, 3 H), 1.03 (s, 3 H), 0.98 (distorted d, J = 7 Hz, 3 H), 0.43 (distorted q, J = 7 Hz, 1 H); ^{13}C NMR spectrum ($CDCl_3$) 152.2 (s, carbonyl carbon) 152.1 (s, carbonyl carbon), 143.1 (s, alkene carbon), 131.1 (s, phenyl carbon), 128.9 (d, phenyl C, meta), 127.8 (d, phenyl C, para), 125.1 (d, phenyl C, ortho), 125.1 (s, alkene carbon), 88.2 (s, $\underline{C}OCH_3$), 50.2 (q, OCH_3, J_{CH} = 145 Hz), 42.7 (t, J_{CH} = 145 Hz), 41.4 (t, J_{CH} = 145 Hz), 34.7 (s), 33.9 (s), 33.7 (d, J_{CH} = 160 Hz, cyclopropyl carbon), 20.5 (q, J_{CH} = 125 Hz), 9.5 (q, J_{CH} = 125 Hz), 6.7 (q, J_{CH} = 125 Hz), 4.8 ppm (q, J_{CH} = 125 Hz). One of the signals of the alkene carbons coincides with that of the ortho phenyl carbon (125.1). Addition of 1,1,1,3,3,3-hexafluoropropanol gave rise to an upfield shift (50 Hz) of this signal. The other alkene carbon at 143.1 ppm is shifted downfield (20 Hz).

Reaction of the TCNE Adduct 6 with Acidified Methanol. Preparation of 40. To a stirred solution of 864 mg of **6** (3 mmol) in 20 mL of methanol was added 35.6 mg of hydronium perchlorate (0.3 mmol) in 5 mL of methanol. This caused formation of a white precipitate. Stirring was continued for 15 min after which the white precipitate was collected on a Büchner funnel, washed with cold methanol, and dried in vacuo. This afforded 795 mg of **40** (2.5 mmol, 83%), pure according to ^1H NMR. Crystallization from ether and a small amount of methylene chloride furnished analytically pure **40,** mp 205.2–205.5 °C.

Anal. Calcd for $C_{10}H_{20}N_4O$: C, 71.23; H, 6.29; N, 17.49. Found:

C, 71.3; H, 6.3; N, 17.4.

Mass spectrum parent peak at *m/e* 320; IR spectrum inter alia 2260, 1060 cm^{-1}; ultraviolet spectrum (96% ethanol) no maximum above 220 nm; ^1H NMR spectrum ($CDCl_3$) 3.19 (m, 2 H), 2.98 (m, 2 H), 2.98 (s, 3 H), 1.25 (s, 3 H), 1.12 (s, 3 H), 1.01 (s, 3 H), 0.95 (distorted d, J = 6 Hz, 3 H), 0.45 ppm (distorted q, J = 6 Hz, 1 H); ^{13}C NMR spectrum ($CDCl_3$) 142.8 (s, alkene carbon), 126.1 (s, alkene carbon), 110.0–110.6 (four partially overlapping s, CN), 85.2 (s, -$\underline{C}OCH_3$), 50.3 (q, J_{CH} = 140 Hz, OCH_3), 38.3 (s), 38.2 (s), 35.6 (s), 35.0 (s), 33.6 (d, J_{CH} = 170 Hz, cyclopropyl carbon), 32.1 (t, J_{CH} = 150 Hz), 30.5 (t, J_{CH} = 150 Hz), 20.2 (q, J_{CH} = 125 Hz), 9.5 (q, J_{CH} = 125 Hz), 6.3 (q, J_{CH} = 125 Hz), 6.3 (q, J_{CH} = 125 Hz), 4.7 (q, J_{CH} = 125 Hz).

Addition of successive portions of shift reagents $Eu(dmp)_3$ or $Eu(fod)_3$ up to 20 mol % to solutions of **40** in deuteriochloroform gave only small shifts (max 0.1 ppm for the methyl group at 1.25 ppm) and no definite information about the stereochemical arrangement of **40** could be obtained from these experiments.

Preparation of the Homofulvene Derivatives 41 and 42. To a solution of 82 mg of trichloroacetic acid (0.5 mmol) in 100 mL of benzene was added 1.44 g of TCNE adduct **6** (5 mmol). The mixture was stirred for 4 h at room temperature and then poured into 50 mL of 2 N sodium hydroxide. After separation the organic layer was once more extracted with 50 mL of 2 N sodium hydroxide and twice washed with 50 mL of water. After drying over sodium carbonate the benzene was evaporated in vacuo leaving 1.4 g of a white solid. According to ^1H NMR this solid consisted of **41** (60%), **42** (31%), and **43** (9%). The solid was partially dissolved in 40 mL of boiling ether and then the flask was cooled to −25 °C for 1 h. The resulting white precipitate was collected on a Büchner funnel and dried in vacuo. This material (800 mg) consisted mainly of **41** (81%). Recrystallization from ether and a small amount of methylene chloride afforded pure **41,** mp 188.8–189.2 °C, as white crystals.

Anal. Calcd for $C_{18}H_{16}N_4$: C, 75.00; H, 5.59; N, 19.42. Found: C, 74.9; H, 5.6; N, 19.5.

Mass spectrum parent peak at *m/e* 288; IR spectrum (KBr) inter alia 2260 (CN), 1630, and 880 cm^{-1}; ultraviolet spectrum ($CHCl_3$) λ_{max} 260 nm (ϵ 9700); ^1H NMR spectrum 4.83 (AB system, olefinic hydrogens, 2 H), 3.22 (m, 2 H), 3.07 (m, 2 H), 1.18 (s, 3 H), 1.10 (s, 3 H), 0.99 (distorted d, J = 6 Hz, 3 H), 0.87 ppm (distorted q, J = 6 Hz, 1 H); ^{13}C NMR spectrum ($CDCl_3$) 156.5 (s, alkene carbon), 144.1 (s, alkene carbon), 125.1 (s, alkene carbon), 110.5 (four partially overlapping s, CN), 102.9 (t, J_{CH} = 155 Hz, alkene carbon), 38.6 (d, J_{CH} = 170 Hz, cyclopropyl carbon), 38.4 (s), 38.2 (s), 36.2 (s), 32.8 (s), 32.6 (t, J_{CH} = 140 Hz), 30.3 (t, J_{CH} = 140 Hz), 9.6 (q, J_{CH} = 125 Hz), 9.4 (q, J_{CH} = 125 Hz), 7.0 ppm (q, J_{CH} = 125 Hz).

The filtrate was concentrated and dissolved in 3 mL of methylene chloride. This solution was chromatographed over Florisil with methylene chloride as eluent. The first eluate was concentrated affording a white solid which consisted mainly of **42** (83%). Purified material, mp 181.1–182 °C, was obtained by repeated recrystallization from *n*-hexane and a small amount of methylene chloride.

Anal. Calcd for $C_{18}H_{16}N_4$: C, 75.00; H, 5.59; N, 19.42. Found: C, 74.35; H, 5.68; N, 19.10.

Mass spectrum parent peak at *m/e* 288; IR spectrum (KBr) inter alia 2260, 1625 cm^{-1}; ultraviolet spectrum ($CHCl_3$) λ_{max} 285 nm (ϵ 6800); ^1H NMR spectrum 5.13 (s, olefinic hydrogen, 1 H), 3.12 (broad s, 2 H), 1.87 (s, methyl group on the double bond, 3 H), 1.19 (s, 3 H), 1.13 (s, 3 H), around 1.04 ppm (complex absorption due to overlapping of the distorted doublet and quartet, 4 H); ^{13}C NMR spectrum ($CDCl_3$) 161.6 (s, alkene carbon), 159.6 (s, alkene carbon), 117.5 (s, alkene carbon), 110.8 (four partially overlapping s, CN), 97.9 (d, J_{CH} = 170 Hz, alkene carbon), 44.0 (d, J_{CH} = 170 Hz, cyclopropyl carbon), 40.6 (s), 39.8 (s), 32.8 (s), 32.6 (s), 30.5 (t, J_{CH} = 140 Hz), 12.8 (q, J_{CH} = 130 Hz), 10.0 (q, J_{CH} = 130 Hz), 8.5 (q, J_{CH} = 130 Hz), 7.1 ppm (J_{CH} = 130 Hz).

Preparation of Cyclopentadiene Derivative 43 from 6. To a solution of 492 mg of trichloroacetic acid (3 mmol) in 30 mol of benzene was added 576 mg of the TCNE adduct (2 mmol). The reaction mixture was heated to reflux during 24 h, and then poured into 25 mL of 2 N sodium hydroxide. After separation the organic layer was once more extracted with 25 mL of 2 N sodium hydroxide and twice washed with 25 mL of water. After drying over sodium carbonate the organic solvent was evaporated in vacuo leaving 900 mg of a white solid. The ^1H NMR spectrum showed **43** to be formed quantitatively. Analytically pure **43**, mp 182.6–183.0 °C, was obtained by recrystallization from benzene/ether.

Anal. Calcd for $C_{20}H_{17}O_2Cl_3$: C, 53.19; H, 3.80; N, 12.41; Cl, 23.54. Found: C, 53.0; H, 4.0; N, 12.5; Cl, 23.8.

Mass spectrum parent peaks at *m/e* 450 and 452 (chlorine isotopes); IR spectrum (KBr) inter alia 2260 (CN), 1720 (C=O), 1260 cm^{-1}; ultraviolet spectrum ($CHCl_3$) λ_{max} 269 nm (ϵ 4800);[53] ^1H NMR spectrum 4.96 (q, J = 8 Hz, 1 H), 3.03 (m, 4 H), 1.89 (s, 3 H), 1.79 (s, 3 H), 1.09 (s, 3 H), 0.88 ppm (d, J = 8 Hz, 3 H); ^{13}C NMR spectrum ($CDCl_3$) 159.0 (s, carbonyl carbon), 143.9 (s, alkene carbon), 134.0 (s, alkene carbon), 133.1 (s, alkene carbon), 132.7 (s, alkene carbon), 110.5 (four partially overlapping s, CN), 89.8 (s, CCl_3), 78.6 (d, J_{CH} = 140 Hz), 60.0 (s), 36.7 (s), 36.5 (s), 31.8 (t, J_{CH} = 140 Hz), 31.4 (t, J_{CH} = 140 Hz), 17.7 (q, J_{CH} = 130 Hz), 14.3 (q, J_{CH} = 130 Hz), 11.7 (q, J_{CH} = 125 Hz), 10.2 (q, J_{CH} = 125 Hz).

Preparation of Cyclopentadiene Derivative 43 from 41 and 42. To a solution of 241 mg of trichloroacetic acid (1.5 mmol) in 15 ml of benzene was added 173 mg of **41** (0.6 mmol) and 115 mg of **42** (0.4 mmol). The reaction mixture was heated to reflux during 24 h. After workup as usual the ^1H NMR spectrum showed the complete conversion into **43**.

Preparation of Cyclopentadiene Derivative 44. To 30 mL of formic acid was added 864 mg of the TCNE adduct (**6**). The reaction mixture was stirred for 10 min. After the addition of 100 mL of ether the mixture was poured into 200 mL of 2 N sodium hydroxide. After separation the organic layer was extracted twice with 100 mL of 2 N sodium hydroxide and washed twice with 100 mL of water. After drying over sodium carbonate the ether was evaporated in vacuo to leave 980 mg of a white solid. According to ^1H NMR **44** was formed quantitatively. An analytically pure sample, mp 195.4–196.2 °C, was obtained by crystallization once from 96% ethanol and a small amount of methylene chloride.

Anal. Calcd for $C_{19}H_{18}N_4O_2$: C, 68.25; H, 5.43; N, 16.75. Found: C, 68.1; H, 5.5; N, 16.7.

Mass spectrum parent peak at *m/e* 334; IR spectrum inter alia 2260 (CN), 1720 (C=O), 1190 cm^{-1}; ultraviolet spectrum λ_{max} 270 nm (ϵ 4500);[53] ^1H NMR spectrum 8.09 (s, 1 H), 5.12 (q, J = 6 Hz, 1 H), 3.26 (broad s, 4 H), 1.88 (s, 3 H), 1.82 (s, 3 H), 1.08 (s, 3 H), 0.89 (d, J = 6 Hz, 3 H); ^{13}C NMR spectrum ($CDCl_3$) 160.1 (d, J_{CH} = 230 Hz, carbonyl carbon),[54] 146.0 (s, alkene carbon), 133.7 (s, alkene carbon), 133.3 (s, alkene carbon), 132.0 (s, alkene carbon), 110.7–110.3 (four partially overlapping s, CN), 71.7 (d, J_{CH} = 145 Hz), 59.4 (s), 38.4 (s), 38.3 (s), 31.4 (t, J_{CH} = 140 Hz), 31.1 (t, J_{CH} = 140 Hz), 17.6 (q, J_{CH} = 125 Hz), 15.0 (q, J_{CH} = 125 Hz), 11.5 (q, J_{CH} = 125 Hz), 10.0 (q, J_{CH} = 125 Hz).

Preparation of Cyclopentadiene Derivative 49. To a solution of 730 mg of trichloroacetic acid (4.5 mmol) in 20 mL of benzene was added 1.0 g of the PTAD adduct **18** (3 mmol). The mixture was stirred for 18 h at room temperature and became yellow. It was then diluted with 40 mL of ether and poured into 50 mL of 2 N sodium hydroxide. After workup as usual the ^1H NMR spectrum showed the complete conversion of **18** into **49** (65%) and unidentified material (35%). The reaction products were dissolved in a small amount of methylene chloride and chromatographed over Florisil with ether. The first eluate was concentrated affording 500 mg of **49**. Analytically pure **49**, mp 180.2–180.5 °C, was obtained by crystallization from ether/*n*-hexane.

Anal. Calcd for $C_{22}H_{22}N_3O_4Cl_3$: C, 52.99; H, 4.44; N, 8.43; Cl, 21.33. Found: C, 53.1; H, 4.4; N, 8.6; Cl, 21.3.

Mass spectrum parent peaks at *m/e* 497 and 499; IR spectrum (KBr) inter alia 1770, 1740, 1420, 1230, and 680 cm^{-1}; ultraviolet spectrum ($CHCl_3$) λ_{max} 282 nm (ϵ 6300); ^1H NMR spectrum 7.5 (m, 5 H), 5.08 (q, J = 6 Hz, 1 H), 4.32 (broad s, 4 H), 1.93 (s, 3 H), 1.83 (s, 3 H), 1.27 (s, 3 H), 1.05 (d, J = 6 Hz, 3 H); ^{13}C NMR spectrum ($CDCl_3$) 160.8 (s, C=O), 152.1 (s, C=O), 143.1, 134.2, 133.7, and 132.0 (all s, four alkene carbons), 131.0 (s, phenyl), 128.7 (phenyl meta), 127.7 (phenyl para), 125.0 (phenyl ortho), 89.9 (s, $\underline{C}Cl_3$), 78.9 (d, J_{CH} = 142 Hz), 58.5 (s), 42.4 (t, J_{CH} = 140 Hz), 42.0 (t, J_{CH} = 140 Hz), 17.8 (q, J_{CH} = 125 Hz), 14.1 (q, J_{CH} = 125 Hz), 11.1 (q, J_{CH} = 125 Hz), 9.9 (q, J_{CH} = 130 Hz).

Difference in Acid Lability of 18 and 6. To a solution of 8.2 mg of trichloroacetic acid (0.05 mmol) in 10 mL of benzene was added 144 mg of TCNE adduct **6** (0.5 mmol). The reaction mixture was stirred for 10 min. Then 167 mg of PTAD adduct **18** (0.5 mmol) was added and stirring was continued for another 30 min. The reaction mixture was then poured into 10 mL of 2 N sodium hydroxide. After workup the ^1H NMR spectrum showed the complete conversion of **18** into the

homofulvene derivatives **15** (45%) and **16** (55%). The TCNE adduct **6** was converted into **43** (9%), **41** (37%), and **42** (21%). The remaining 33% was observed unchanged.

Kinetics of the Thermal Rearrangement of 18 and 6. Solutions of 0.15 mmol of **18** and **6** in 0.5 mL of chlorobenzene or tetramethylethylenediamine (TMEDA) were prepared in ^{1}H NMR tubes. The tube was then placed into the probe maintained at the appropriate temperature. Integration of the methylene protons of the benzvalene derivatives and their aromatic counterparts was performed at measured time intervals. Plots of $\ln a/a - x$ vs. time were linear to at least 75% conversion and the first-order rate constants (k) were determined. These values have an accuracy of about 5%. Plotting $\ln k$ against the reciprocal of the absolute temperature gave straight lines. From the slopes of these lines the energy of activation was calculated.

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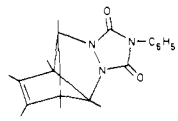

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of **19** at 40 °C the six methyl groups appear as three sharp singlets at 1.71 (6 H), 1.46 (6 H), and 0.85 ppm (6 H), which remain unchanged down to −70 °C. At −85 °C some line broadening is observed and at −95 °C the methyl signals are considerably broadened but are not resolved into separate peaks. Moreover, this broadening occurs for all three signals to an equal extent and must therefore be attributed to viscosity line broadening. These observations do not give any indication for inverting pyramidal conformations for the hydrazine nitrogens.
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Comparison of Diels–Alder Reactivity of a Bicyclobutane and of a Cyclobutane Bridged Diene

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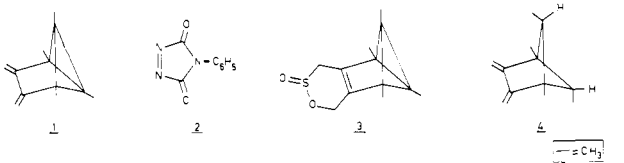
Abstract: Kinetic measurements reveal an unanticipated difference in the Diels–Alder reactivities of dienes bridged by small rings. The bicyclobutane bridged diene **1** is extremely reactive whereas the cyclobutane bridged diene **4** shows a remarkably low reactivity even toward highly reactive dienophiles. Theoretical approaches to explain the reactivity of dienes in Diels–Alder cycloadditions are applied to the dienes at hand. The orbital interactions between the small rings and unsaturated bridges in **1** and 4 and the corresponding Diels–Alder adducts have been examined. The results of ab initio calculations, performed by van Duynen and van der Ploeg, indicate that the HOMO of bicyclobutane has A_2 symmetry which leads to a repulsive interaction with the diene bridge in **1**. As a consequence, **1** has a high-lying HOMO which is confirmed by PES measurements. The reactivity of **1** is shown to be quantitatively in accordance with its HOMO energy. In contrast the reactivity of **4** is much lower than anticipated from its HOMO energy. This is attributed to the existence of repulsive interactions between the filled frontier orbitals of the cyclobutane ring and the ethylene bridge in the Diels–Alder adducts of **4**.

The Diels–Alder reaction,[1] discovered nearly half a century ago, has been the subject of numerous studies.[2-15] As far as the mechanism is concerned the Diels–Alder reaction is generally believed to occur via a concerted pathway.[16] This conclusion, based on experimental observations,[2,17] received a theoretical foundation from the principle of conservation of orbital symmetry as formulated by Woodward and Hoffmann[4] and was corroborated by calculations.[13,15,18] The reactivity of substrates in a Diels–Alder cycloaddition depends greatly on the structural features of the reaction components. In general, rates of addition are the same,[2] within an order of magnitude, in going from a polar to a nonpolar solvent except when the solvent acts as a specific catalyst.[2h] The reactivity of the diene component[2,19,20] depends on its structure and configuration, and on the nature of the substituents at the conjugated chain.[19,20] It is essential that the double bonds of the diene molecule have a coplanar cis configuration. Normally electron-donating groups increase the reactivity of the diene whereas an electron-acceptor group decreases it.[20] An increase in the volume of substituents[19] of the same type results in a decrease of the reactivity of the diene as well as of the dienophile.[2,19,20] Electron-attracting substituents on the carbon–carbon double bond of the dienophile normally increase the rate of the Diels–Alder reaction. This rule, originally proposed by Alder,[21] has been confirmed by many investigations.[22] A more quantitative treatment of reactivity can in principle be performed by using the quantum-mechanical theory of perturbation.[7,23] Especially frontier molecular orbital treatments,[3] which are a first approximation to a complete perturbation treatment of chemical reactivity, have been exceptionally useful for rationalizing substituent effects in cycloaddition reactions.[11,12,14] In this paper we wish to report the reactivity of a diene 2,3 bridged by a bicyclobutane ring (**1**) and a diene



2,3 bridged by a cyclobutane ring (**4**) and to explain the observed differences.

Kinetic Measurements and Discussion. One of the striking properties of the recently synthesized 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**1**)[24] is its high Diels–Alder reactivity. For example, this bicyclobutane bridged diene reacts at a rate too fast to measure with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **2**) even at −70 °C. Competition experiments, carried out at −70 °C, showed that **1** reacts only by a factor of 2–3 slower than cyclopentadiene

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