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Electrophilic Additions to a 1,3 Hydrogen-Shifted Isomer of Hexamethylbenzvalene†

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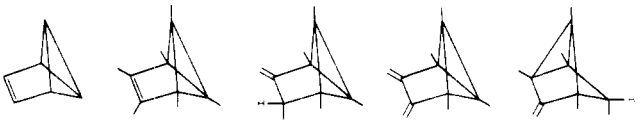
The chemical behavior of 1,2,4,5,6-pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane toward several electrophiles has been investigated. This 1,3 H-shifted isomer of hexamethylbenzvalene reacted with several uniparticulate electrophiles to unexpectedly give in good yield tricyclic [4.3.0.0^{1,5}] compounds which constitute a class of hitherto unknown di-cis-fused cyclopropanes.

During the last decade an increasing interest in small ring-containing compounds has developed. Some of these are of theoretical interest, and others are important in synthetic routes or as intermediates in reactions. Small-membered rings are also known to have a tremendous effect on reaction rates and reaction pathways if compared to larger ring-containing or acyclic compounds. Growing fields of interest are cyclopropane-containing biodegradable insecticides (e.g., pyrethrines[1-3]) and cyclobutane-containing pheromones.[4] Other recent research efforts focus on the possibility of reversible solar energy storage in strained polycyclic organic molecules.[5-9]

Among the multitude of small-ring polycycles, benzvalene (1) is one of the most intriguing ones. This highly strained



1 2 3 4 5

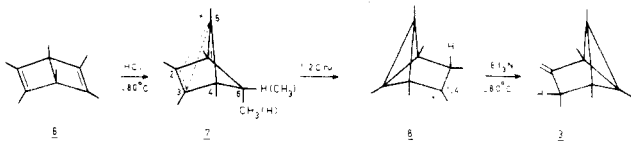
compound contains about 250 kJ/mol more energy than benzene.[8,10] Though easily obtainable,[11] 1 is not a stable compound and it slowly converts to benzene at room temperature.[12] The stability of strained molecules can frequently be improved by substituents on the carbon skeleton; e.g., perfluorohexamethylbenzvalene[13,14] is quite stable. On the other hand, hexamethylbenzvalene (2) has not yet been synthesized in an unequivocal way, although claims for its observation have been made.[14,15]

Some years ago the synthesis of 1,2,4,5,6-pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane (3) was reported, although at that time the tricyclic [2.2.0.0^{2,6}] structure 5 was assigned to the compound obtained.[16] Compound 3, which is a 1,3 H-shifted isomer of hexamethylbenzvalene, combines two reactive centers, an exocyclic double bond and a bicyclobutane group, which are both known to react with electrophiles; a bicyclobutane moiety has a reactive central bond with high p character (calculations[17] indicate this bond to be sp^{24}, and from ^{13}C NMR studies of a bicyclobutane derivative[18] a value of sp$^{10.4}$ has been derived). We were especially interested in the chemical reactivity (toward electrophilic species) of compound 3 because of the fact that the reactive centers are strongly coupled electronically. In this respect, reference is made to the recently[19] disclosed high reactivity of the bicyclobutane bridged diene 4, which has been ascribed to the orbital interactions between the bicyclobutane and the diene fragments.

† This publication is dedicated to Professor E. Havinga for his contributions to chemistry.

Results and Discussion

Synthesis and Structure of Compound 3. Using hexamethyl(Dewar benzene) (6) as starting material, 1,2,4,5,6-



6 7 8 3

pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane (3) can be obtained in good yield (90%) by a protonation–deprotonation sequence at low temperatures using HCl and Et_3N, respectively.[16]

Originally, the isomeric 1,2,4,5,6-pentamethyl-3-methylenetricyclo[2.2.0.0^{2,6}]hexane (5) was proposed[16] to be formed by proton abstraction from the $C_{2,3}$ methyl groups of ions 7 (exo–endo mixture, 3:1[20]). Generally speaking,[21] either tricyclic[2.2.0.0^{2,6}] or tricyclic[3.1.0.0^{2,6}] structures can be obtained by reaction of ions of type 7 with nucleophiles and bases. The proof of structure 3 is based on elemental analysis, spectroscopic data (^{1}H and ^{13}C NMR, MS, and IR), and chemical transformations; of special importance is the observation of long-range couplings in the ^{1}H NMR spectrum between the vinylidene protons and the single proton. Computer simulation[22] of the spectrum gave values of −1.75 and −1.95 Hz for the long-range coupling constants, in agreement with literature values for similar couplings over four bonds (in structure 5 the coupling implies five bonds). Unequivocal proof for structure 3 was provided by an independent synthesis of 3 from 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (4) by reduction with diimide. Diimide

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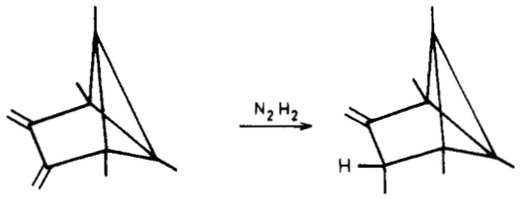
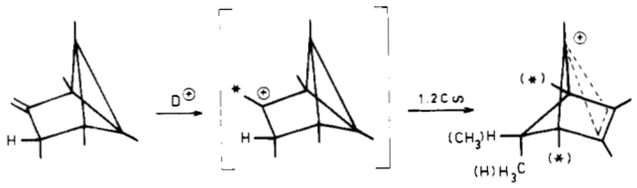


4 3

is known to give a specific 1,2-cis reduction in a concerted reaction, and rearrangements are avoided.[23] Blank experiments proved that both **3** and **4** were stable under the conditions used for generating the diimide. Also, the Birch reduction of **4** leads to **3**.[24]

Chemical Reactivity of 3 Toward Electrophiles. I. Protonation of 3. As a model reaction for the reactivity of **3** toward electrophiles, the protonation of **3** was studied. When **3** is treated with $HFSO_3$, an exo–endo equilibrium mixture of ions **7** is formed. When the reaction is carried out with $DFSO_3$,



3 8* 7*

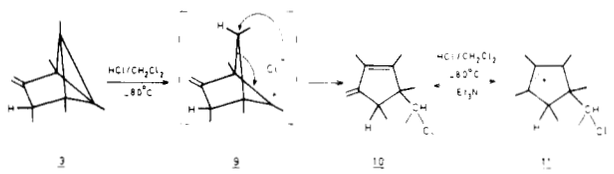
* = CH_2D

(*) = CH_3/CH_2D

the deuterium is selectively incorporated at the bridgehead methyl groups, in agreement with an initial attack at the carbon–carbon double bond followed by a 1,2 C-shift. This contrasts with the low temperature protonation of **3** with HCl/CH_2Cl_2 to afford **10** (see Scheme I), which was reported a few years ago[21] and which is interpreted by initial attack of the electrophile at the bicyclobutane moiety. According to the ab initio calculations performed by Lehn and Wipff[25] on the preferred way of attack of a proton on a bicyclobutane group, it is assumed that in the first instance **9** is formed, which immediately reacts further to **10**, which with an excess of acid is protonated to **11**. The nature of the acid (read electrophile) appears therefore to determine the center of attack at compound **3**. It is of interest to note that the uniparticulate[26] electrophiles studied prefer the same pathway of attack at compound **3** as $HFSO_3$, viz., attack at the carbon–carbon double bond. These novel reactions are discussed below.

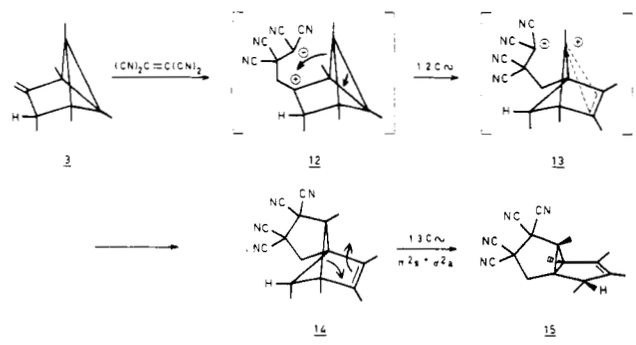
II. Reaction of 3 with Tetracyanoethylene. In a preliminary publication[27] the mode of reaction of compound **3** with tetracyanoethylene was described. At room temperature a 1:1 adduct was isolated to which structure **15** (see Scheme II) was assigned using X-ray techniques.[28] On NMR spectroscopic examination of the reaction at lower temperatures, it was found that prior to the formation of **15** an intermediate adduct **14** is formed. Kinetic measurements revealed the rate of reaction **3** → **14** to be dependent on solvent polarity, indicating the occurrence of an ionic process, whereas the rate of reaction **14** → **15** proved to be independent of solvent polarity, supporting a concerted sigmatropic process. Other evidence

Scheme I



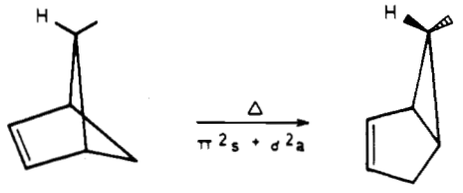
3 9 10 11

Scheme II



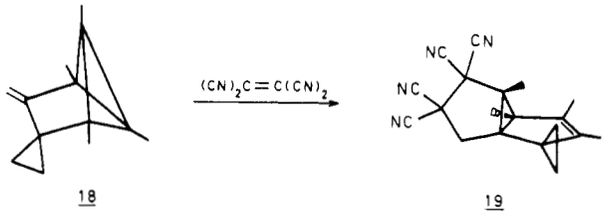
3 12 13 14 15

for this mechanism depends on the competition principle;[29] when the reaction of **3** with tetracyanoethylene was carried out in methanol, several methanol addition products are formed.[30] If **14** was formed in methylene chloride followed by replacing the methylene chloride by methanol (at temperatures below 0 °C), this compound converted upon warming up to **15** without giving methanol-trapping products. These data for the reaction of **3** to **14** are in agreement with the zwitterionic mechanism commonly assumed for the reaction of tetracyanoethylene with alkenes.[31] In our case, the zwitterionic intermediate **12** gives a similar 1,2 C-shift as observed in the protonation reaction (with $HFSO_3$) of **3**, in which the nonclassical zwitterion **13** is formed, which subsequently, after nucleophilic attack on the backside[32] of the three-center bond, gives ring closure to **14**. This sequence is followed by a concerted reaction from **14** to **15** which, according to the Woodward–Hoffmann rules,[33] has to proceed with inversion of configuration of the migrating C atom, which is indeed observed. This process is comparable with the reaction **16** → **17** described by Roth and Friedrich.[34]

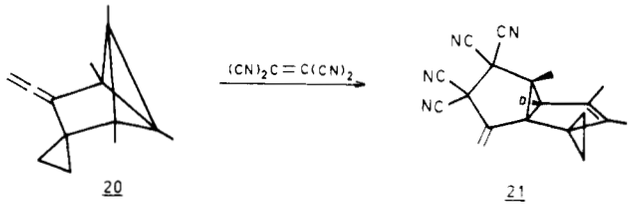


16 17

Compound **15** was the first reported example of the di-cis-fused cyclopropane-containing tricyclic[4.3.0.$0^{1,5}$] system. Two other examples have very recently been reported[35] in the formation of **19** from **18** and **21** from **20**, in which a similar reaction pathway is expected to be followed as in the present case.

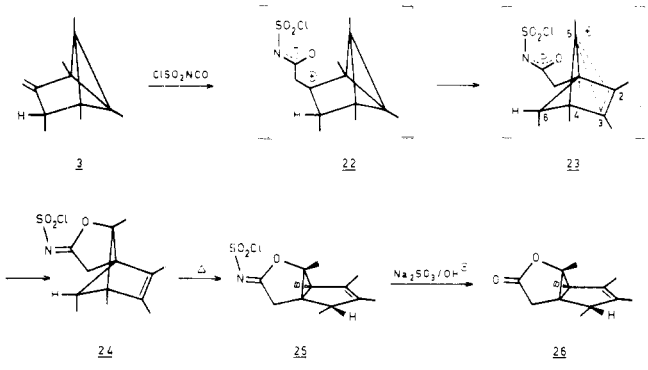


18 19

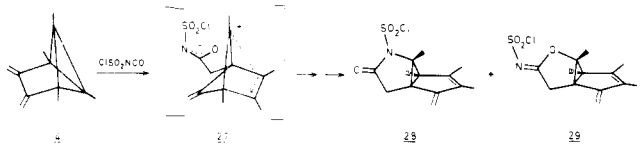


20 21

Scheme III



Scheme IV



III. Reaction of 3 with Chlorosulfonyl Isocyanate. Chlorosulfonyl isocyanate is a very reactive uniparticulate electrophile, first reported by Graf in 1952.[36] Reaction of this species with compound **3** yielded, after workup at room temperature, a product to which structure **25** (see Scheme III) is assigned. Similar to the tetracyanoethylene addition, NMR spectroscopic measurements confirmed the formation of an intermediate adduct **24,** which upon warming up exclusively reacts further to **25.** Compound **25** had to be kept under an inert atmosphere because of its reaction with moist air, but it could easily be converted into the more easily handled lactone **26** by treatment with Na_2SO_3/OH^-.[37]

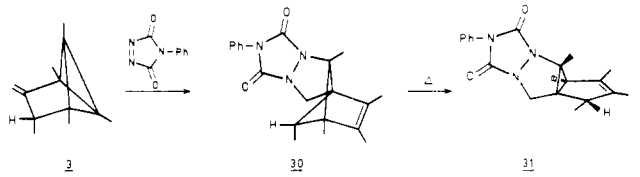
The addition of chlorosulfonyl isocyanate to **3** proceeds via the initial formation of zwitterion **22.** According to Malpass,[38] 1,4 dipoles should be considered to be primary intermediates in the addition of chlorosulfonyl isocyanate to olefines, giving [2 + 2] products under kinetic control and sometimes rearrangement products under thermodynamic control. In this case, the driving force for the occurring rearrangement is the formation of the resonance-stabilized ion **23,** which subsequently undergoes ring closure to **24.**

Another special feature of the addition of chlorosulfonyl isocyanate to **3** drew our attention; in compounds **24** and **25** ring closure has taken place via the O atom, whereas in most cases[39] ring closure takes place via the N atom to form the thermodynamically more stable product (~30 kJ/mol more stable[40]). This phenomenon is, in our opinion, caused by steric hindrance; considering intermediate **23,** it is obvious that the bulky $-SO_2Cl$ group approaches the rest of the molecule when ring closure via the N atom occurs. Indeed, molecular model studies show in the N ring-closed product interference of the $-SO_2Cl$ group with the CH_3 group at C_5 and the H atom at C_6. Such an interference is absent in the observed O ring-closed product **24.**

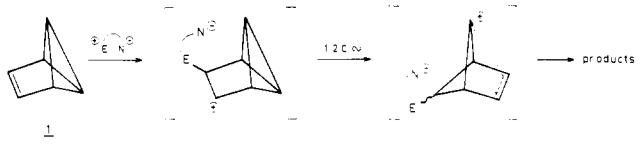
It is of interest to observe that the addition of chlorosulfonyl isocyanate to diene **4**[41] gives reaction products (**28** and **29**) (see Scheme IV) similar to compound **25;** this contrasts with the reported [2 + 4] cycloadditions of **4** with other uniparticulate electrophiles such as tetracyanoethylene[42] and 4-phenyl-1,2,4-triazoline-3,5-dione. Noteworthy is the fact that ring closure of intermediate **27** occurs both via the N atom and O atom, which may be due to reduced steric hindrance for N ring closure of intermediate **27** if compared to that of **23** (absence of the H atom at C_6).

IV. Reaction of 3 with Other Uniparticulate Electrophiles. One of the most powerful dienophiles, often reacting

Scheme V

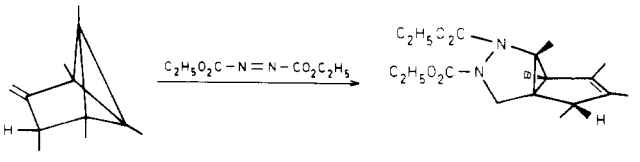


Scheme VI



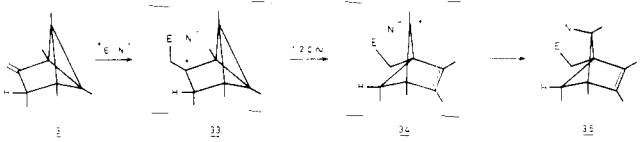
faster than tetracyanoethylene[43,44] in Diels–Alder reactions, is 4-phenyl-1,2,4-triazoline-3,5-dione. With compound **3** it reacts similarly to, though more slowly than, tetracyanoethylene and chlorosulfonyl isocyanate. At ~10 °C, an intermediate adduct **30** (see Scheme V) is formed which, upon warming the solution to room temperature, slowly rearranges to **31.** In this case the intermediate **30** could easily be isolated as a white solid, stable at room temperature, which rearranges quantitatively to **31** when heated to its melting point (~110 °C).

Dienophiles less reactive than the mentioned ones give also a [4.3.0.$0^{1,5}$] tricyclic compound upon reaction with **3.** With diethyl azo carboxylate, after refluxing for 8.5 h in acetonitrile, the 1:1 adduct **32** is obtained.



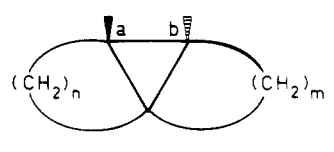
Conclusions

As shown above, compound **3** reacts smoothly with (uniparticulate) electrophiles with initial formation of cation **33,** which rearranges, without being observed, via a 1,2 C-shift to the [2.1.1]hexenyl cation **34,** leading to the observed intermediate products (**35**).



A similar sequence has been observed in the reaction of benzvalene with electrophiles (see Scheme VI) such as 4-phenyl-1,2,4-triazoline-3,5-dione[45] and chlorosulfonyl isocyanate.[46]

The rearrangement of cations **33** to the resonance-stabilized [2.1.1]hexenyl cations **34** seems characteristic for these ions. The formed compounds **35** convert, in a $_{\pi}2_s + {}_{\sigma}2_a$ fashion, to products containing a di-cis-fused cyclopropane unit. These compounds were discussed by Gassman[47] a number of years ago. He concluded that twisting would cause the di-cis-fused



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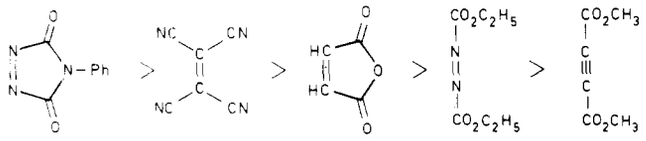
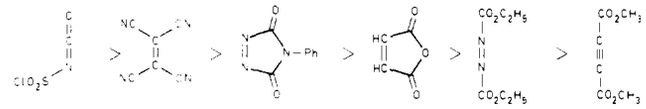
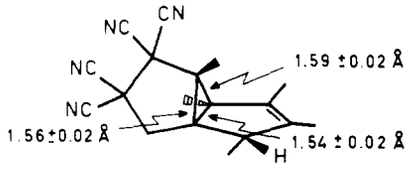
Scheme VII



Scheme VIII



cyclopropane to have a very reactive (a–b) bond (see **36**), a so called twist-bent σ bond, at least when $m,n \leq 4$. Hitherto, only a few examples of these compounds are known.[48] In 1965 Kropp[49] and more recently Ruppert and White[50] reported syntheses of such compounds with $m = 4$ and $n = 4$ or 3. The presently reported compounds (**15, 19, 21, 25, 26, 28, 29, 31, 32**) have $n,m = 3$, although some of them contain one or two heteroatoms in one five-membered ring. In contrast to Gassman's expectations, however, these compounds turn out to be quite stable toward acid. It is fair to say, however, that this lack of special reactivity is possibly due to these compounds being highly substituted. This is in agreement with the lack of reactivity of adduct **15** toward a second equivalent of tetracyanoethylene,[51] whereas cyclopropanes[52] and vinylcyclopropanes[53] (compound **15** being a substituted vinylcyclopropane) are known to react with this dienophile. Unfortunately, the X-ray analysis of **15** does not give a decisive answer, as it does not show much difference (in view of the reported error) between the three cyclopropane bonds, which seem to be rather long if compared to the bond length in cyclopropane (1.514 Å);[54] substitution is known[54] to have a large effect on bond lengths in cyclopropanes.



15

Finally, a qualitative comparison between the reactivity of the dienophiles in normal Diels–Alder reactions and in the electrophilic reaction with **3** can be drawn. The reactivity in Diels–Alder reactions[55] is shown in Scheme VII, and the reactivity toward **3**[56] is shown in Scheme VIII. The only difference between these orders is the interchange of tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione; the former possibly has more electrophilic character, which may be less important in the concerted Diels–Alder reaction than in the stepwise electrophilic addition to **3**.

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi Perkin-Elmer R24B, a Jeol C-60 HL, or a 100-MHz Varian XL-100. ^{13}C NMR spectra were recorded on a Varian XL-100. The chemical shifts are given in ppm downfield from internal tetramethylsilane. Unless otherwise stated, the NMR spectra were recorded in deuteriochloroform as solvent. Infrared spectra were recorded on a Unicam SP 200 and mass spectra on an AEI MS 902 spectrometer. Elemental analyses were performed in the analytical section of this department. Melting points, taken in a silicon oil bath, are uncorrected. All solvents were purified by common methods.

Synthesis of 1,2,4,5,6-Pentamethyl-3-methylenetricyclo-[3.1.0.0^{2,6}]hexane (3).[57] A solution of 25.0 g (0.15 mol) of hexamethyl(Dewar benzene) in 1.4 L of methylene chloride was cooled to −80°C in a nitrogen atmosphere. Under vigorous stirring, 7.3 g (0.20 mol) of dry hydrogen chloride gas was condensed into the solution and stirring was continued for 1.5 h at temperatures between −75 and −80 °C (note: all hexamethyl(Dewar benzene) has to be dissolved). The solution was cooled to −85 °C, and under vigorous stirring 30 g (0.30 mol) of triethylamine was rapidly added through a dropping funnel. After being stirred for 1 h at temperatures between −75 and −85 °C, the solution was allowed to warm up to room temperature and an excess of methyl iodide (to remove free amine) was added. Evaporation of the solvent afforded a solid residue which was extracted with pentane (~300 mL). The pentane solution was washed with water (2 × 50 mL), dried over magnesium sulfate, and evaporated. The crude product (yellow oil) was distilled from a Widmer flask, affording 22.5 g (0.14 mol, 90%) of compound **3**, bp 70–75 °C/50 mm.

Reaction of Diene 4 with Diimide. To a solution of 0.4 g (2.5 mmol) of diene **4** in 20 mL of pyridine was added, in a nitrogen atmosphere, 1.3 g (6.7 mmol) of potassium azodiformate. A solution of 0.8 mL (16 mmol) of acetic acid in 2 mL of water was added dropwise. After being stirred for 4 h at room temperature, an extra amount of 10 mL of water was added and the mixture was refluxed during 10 min. Workup by pentane extraction afforded a mixture of **3** and **4**. Both compounds were separated by column chromatography (Al_2O_3, activity II–III, 20 cm, ether), affording 100 mg (0.6 mmol, 24%) of **3**.

Reaction of 3 with $HFSO_3$ and $DFSO_3$. A NMR tube with 0.1–0.2 mL of acid ($HFSO_3$ or $DFSO_3$) was cooled to −70 °C, followed by condensation of SO_2ClF to a volume of ~0.6 mL. At this temperature (−70 °C) little portions of **3** were added. ^{1}H NMR spectra were recorded between −60 and −70 °C. Comparison of these spectra with each other and with spectra quoted in ref 20 proved D incorporation in the bridgehead methyl groups of ions **7**.

Synthesis of 15. To a suspension of 790 mg (6.2 mmol) of freshly sublimated (100 °C/12 mm) tetracyanoethylene in 10 mL of chloroform, in a nitrogen atmosphere, was added a solution of 1000 mg (6.2 mmol) of **3** in 20 mL of chloroform. After being stirred for 1 h at room temperature, evaporation of the solvent afforded 1750 mg (6.0 mmol, 97%) of compound **15** (slightly colored solid), which was recrystallized from cyclohexane: mp 123–124 °C; ^{1}H NMR 1.06 (d, J = 7 Hz, 3 H), 1.35 (s, 3 H), 1.60 (broad s, 9 H), 2.51 (q, J = 7 Hz, 1 H), 2.90 and 3.16 (AB q, J_{AB} = 14 Hz, 2 H) ppm; ^{13}C NMR 11.4 (CH_3), 11.6 (CH_3), 11.6 (CH_3), 12.4 (CH_3), 15.6 (CH_3), 39.6 (CH_2), 43.1 (C), 45.6 (CH), 46.8 (C), 48.3 (C), 48.8 (C), 52.8 (C), 111.6 (CN), 112.1 (CN), 112.7 (CN), 114.1 (CN), 133.6 (sp^2 C), 138.8 (sp^2 C) ppm; IR 2240 (CN), 1660 (C=C) cm^{-1}; mass spectrum parent peak at m/e 290. Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.5; H, 6.3; N, 19.3. Found: C, 74.4; H, 6.2; N, 19.4.

Observation of Intermediate 14. In a NMR tube at −60 °C an acetone-d_6 solution of equimolar quantities of **3** and tetracyanoethylene (freshly sublimated) was prepared. On warming up the solution to −20 °C in the NMR cavity, the formation of **14** was observed: ^{1}H NMR (in acetone-d_6) 0.95 (d, J = 6 Hz, 3 H), 1.20 (s, 3 H), 1.48 (s, 3 H), 1.77 (broad s, 6 H), 3.05 and 3.15 (AB q, J_{AB} = 13 Hz, 2 H), 3.40 (q, J = 6 Hz, 1 H) ppm; ^{13}C NMR (in acetone-d_6) 6.5 (CH_3), 8.2 (CH_3), 10.5 (CH_3), 10.5 (CH_3), 16.0 (CH_3), 38.0 (CH_2), 48.0 (C), 52.6 (C), 58.6 (C), 64.2 (CH), 71.8 (C), 84.6 (C), 111.2 (CN), 112.0 (CN), 112.8 (CN), 113.2 (CN), 133.0 (sp^2 C), 146.0 (sp^2 C) ppm.

Upon further warming up this solution to room temperature, compound **14** converted quantitatively to compound **15**.

Synthesis of 25. A stirred solution of 3760 mg (23.2 mmol) of **3** in 45 mL of methylene chloride, in a nitrogen atmosphere, was cooled to −60 °C. To this solution was added a solution of 3252 mg (23.2 mmol) of chlorosulfonyl isocyanate in 35 mL of methylene chloride dropwise. After being stirred for 0.5 h at −60 °C, the solution was allowed to warm up to room temperature. Evaporation of the solvent afforded a purple oil. Crystallization from ether/pentane yielded 5880 mg (19.5 mmol, 84%) of **25** as a white solid, mp 105–106 °C, which decomposes upon exposure to (moist) air: ^{1}H NMR 1.10 (d, J = 7 Hz, 3 H), 1.14 (s, 3 H), 1.49 (s, 3 H), 1.60 (broad s, 6 H), 2.48 (q, J = 7 Hz, 1 H), 3.16 and 3.53 (AB q, J_{AB} = 20 Hz, 2 H) ppm; ^{13}C NMR 7.3 (CH_3), 9.2 (CH_3), 11.3 (CH_3), 11.4 (CH_3), 16.0 (CH_3), 33.3 (CH_2, ABX), 34.8 (C), 42.3 (C), 43.5 (CH), 82.0 (C), 130.4 (sp^2 C), 137.2 (sp^2 C), 182.8 (C=N) ppm; IR 1630 (C=N), 1390 and 1190 (SO_2) cm^{-1}; mass spectrum parent peaks at m/e 303, 305 and 204 ($M^+ - SO_2Cl$).

Observation of Intermediate 24. In a NMR tube at −60 °C a methylene chloride solution of equimolar quantities of **3** and chlorosulfonyl isocyanate was prepared. An immediate reaction occurred, and adduct **24** was observed: ^{1}H NMR (in CH_2Cl_2) 0.88 (d, J = 6 Hz, 3 H), 1.01 (s, 3 H), 1.40 (s, 3 H), 1.70 (broad s, 6 H), 2.70 (broad s, 2 H), 2.95 (q, J = 6 Hz, 1 H) ppm; ^{13}C NMR (in CH_2Cl_2) 8.3 (CH_3), 10.3 (CH_3), 10.8 (CH_3), 11.4 (CH_3), 13.6 (CH_3), 31.3 (CH_2), 58.1 (C), 58.9 (C), 66.4 (CH), 93.5 (C), 131.2 (sp^2 C), 141.4 (sp^2 C), 174.7 (C=O) ppm.

Upon warming up this solution above −50 °C, compound **24** converted quantitatively to compound **25.**

Synthesis of 26. An emulsion of 2000 mg (6.6 mmol) of adduct **25** in 20 mL of ether was added to a solution of 10 g of sodium sulfite in 100 mL of water. The mixture was made alkaline by addition of 1 g of potassium hydroxide and stirred for 4 h at room temperature. The ether layer, containing **26** and ~30% of hexamethylbenzene, was separated, dried over sodium sulfate, and evaporated. Column chromatography of the oily residue (Al_2O_3, 10 cm, pentane/ether) yielded 710 mg (3.5 mmol, 53%) of **26** as a clear oil. Purification by several sublimations (80 °C/11 mm) afforded white crystalline **26:** mp 46.5–47.5 °C; ^{1}H NMR (in CCl_4) 1.02 (d, J = 7 Hz, 3 H), 1.12 (s, 3 H), 1.27 (s, 3 H), 1.56 (broad s, 6 H), 2.20 (q, J = 7 Hz, 1 H), 2.30 and 2.75 (AB q, J_{AB} = 18 Hz, 2 H) ppm; ^{13}C NMR 7.1 (CH_3), 9.3 (CH_3), 11.0 (CH_3), 11.2 (CH_3), 16.1 (CH_3), 29.7 (CH_2, ABX), 33.9 (C), 42.3 (C), 43.2 (CH), 71.9 (C), 131.0 (sp^2 C), 135.5 (sp^2 C), 175.7 (C=O) ppm; IR 1790 cm^{-1} (lactone); mass spectrum parent peak at m/e 206, exact mass at m/e 206.130, calcd for $C_{12}H_{18}O_2$ m/e 206.131.

Synthesis of 31. In a nitrogen atmosphere a solution of 3.24 g (20.0 mmol) of **3** in 50 mL of methylene chloride was added to a solution of 3.80 g (21.7 mmol) of freshly sublimated (80 °C/0.05 mm) 4-phenyl-1,2,4-triazoline-3,5-dione in 100 mL of methylene chloride. The mixture was refluxed during 2 h, washed with 50 mL of 2 N sodium hydroxide and 50 mL of water, dried over magnesium sulfate, and evaporated to afford 6.6 g (19.6 mmol, 98%) of **31** as a slightly yellow oil (NMR pure). Further purification by crystallization from acetone/petroleum ether (40–60 °C) resulted in white crystalline **32:** mp 120.5–121.0 °C; ^{1}H NMR 1.06 (d, J = 7 Hz, 3 H), 1.07 (s, 3 H), 1.43 (s, 3 H), 1.59 (broad s, 6 H), 2.50 (q, J = 7 Hz, 1 H), 3.95 (broad s, 2 H), 7.42 (m, 5 H) ppm; ^{13}C NMR 8.2 (CH_3), 9.3 (CH_3), 10.9 (CH_3), 11.0 (CH_3), 15.3 (CH_3), 42.5 (CH_2), 42.9 (CH), 44.2 (C), 44.9 (C), 49.3 (C), 124.9 (arom. CH), 127.4 (arom. CH), 128.5 (arom. CH), 130.9 (sp^2 C), 131.4 (arom. C), 136.1 (sp^2 C), 149.8 (C=O), 152.5 (C=O) ppm; IR 1770 (C=O), 1710 (C=O), 1610 (C=C) cm^{-1}; mass spectrum parent peak at m/e 337. Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.2; H, 6.9; N, 12.5. Found: C, 70.9; H, 6.8; N, 12.4.

Observation of Intermediate 30. In a NMR tube at −40 °C a $CDCl_3$ solution of equimolar quantities of **3** and freshly sublimated 4-phenyl-1,2,4-triazoline-3,5-dione was made. On warming up the solution to 5 °C in the NMR cavity, the formation of **30** was observed: ^{1}H NMR 0.92 (d, J = 6 Hz, 3 H), 1.11 (s, 3 H), 1.35 (s, 3 H), 1.71 (broad s, 6 H), 3.10 (q, J = 6 Hz, 1 H), 3.55 and 3.75 (AB q, J_{AB} = 10 Hz, 2 H), 7.4 (m, 5 H) ppm; ^{13}C NMR 8.7 (CH_3), 10.1 (CH_3), 11.1 (CH_3), 11.7 (CH_3), 11.8 (CH_3), 41.8 (CH_2, ABX), 57.5 (C), 67.2 (CH), 68.9 (C), 89.6 (C), 125.4 (arom. CH), 127.6 (arom. CH), 128.8 (arom. CH), 129.5 (arom. C), 131.8 (sp^2 C), 143.3 (sp^2 C), 150.3 (C=O), 150.3 (C=O) ppm.

Upon further warming up this solution, compound **30** converted quantitatively to compound **31.**

Synthesis of 32. In a nitrogen atmosphere a solution of 1000 mg (6.2 mmol) of **3** and 1100 mg (6.3 mmol) of diethyl azo carboxylate in 15 mL of acetonitrile was refluxed during 8.5 h. Evaporation of the solvent and column chromatography (Al_2O_3, 17 cm, pentane/ether) of the oily residue afforded 1.80 g (5.4 mmol, 87%) of **32** as a clear liquid. Further purification was achieved by short-path distillation: bp 100–120 °C/0.05 mm; ^{1}H NMR 1.05 (d, J = 8 Hz, 3 H), 1.10 (s, 3 H), 1.23 (s, 3 H), 1.27 (t, J = 7 Hz, 6 H), 1.55 (broad s, 3 H), 1.72 (s, 3 H), 2.40 (q, J = 8 Hz, 1 H), 3.40 (d, J = 12 Hz, 1 H), 4.18 (q, J = 7 Hz, 4 H), 4.20 (d, J = 12 Hz, 1 H) ppm; ^{13}C NMR 9.3 (CH_3), 10.5 (CH_3), 11.2 (CH_3), 11.6 (CH_3), 14.4 (CH_3, 2×), 15.6 (CH_3), 43.8 (CH), 44.3 (C), 47.0 (C), 48.6 (C), 53.7 (CH_2), 61.7 (CH_2–O), 62.4 (CH_2–O), 131.8 (sp^2 C), 136.4 (sp^2 C), 156.3 (C=O), 157.2 (C=O) ppm; IR 1700–1750 cm^{-1} (ester); mass spectrum parent peak at m/e 336, exact mass at m/e 336.208, calcd for $C_{18}H_{28}N_2O_4$ m/e 336.205.

Reaction of Di-Cis-Fused Cyclopropane Compounds with Acid. Compounds **15, 31,** and **32** were treated several days, at room temperature, with a 15-fold excess of F_3CCOOH in benzene; according to ^{1}H NMR spectra, no reaction occurred. Compound **26** under these conditions slowly reacted, probably caused by attack at the lactone function. Compound **32** also gave no reaction after refluxing for 2 h in a mixture of 20 mL of p-dioxane, 20 mL of water, and 15 mL of concentrated sulfuric acid.

Registry No.—3, 65501-17-9; **4,** 50590-86-8; **6,** 7641-77-2; **14,** 65703-25-5; **15,** 60221-50-3; **24,** 68813-29-6; **25,** 68813-30-9; **26,** 68813-31-0; **30,** 68813-32-1; **31,** 68813-33-2; **32,** 68843-15-2; diimide, 3618-05-1; fluorosulfuric acid, 7789-21-1; fluorosulfuric-d acid, 29171-24-2; tetracyanoethylene, 670-54-2; chlorosulfonyl isocyanate, 1189-71-5; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4; diethyl azo carboxylate, 1972-28-7.

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