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On the Mechanism of the Formation of Rearrangement Products in the Addition of Arenesulfenyl Chloride and 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione to Benzonorbornadienes

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On the basis of product and rate studies the similarity in the electrophilic addition of phenyltriazolediones (PTAD) and the arenesulfenyl chlorides **10** and **11** to benzonorbornadienes **1**, **8**, and **9**, giving the rearrangement products **2** and **6**, respectively, is being recognized. In analogy to the established mechanism involving three-center electrophilic attack for the arenesulfenyl chloride reaction, the PTAD reaction is proposed to proceed via the aziridinium ion **4** as intermediate. The lack of trapping, of regioselectivity and of formation of addition product in the case of PTAD is interpreted in terms of electronic and steric effects on the dipolar aziridinium species. – An X-ray analysis of the addition product **17**, derived from **9** and **11**, is reported.

Über den Mechanismus der Bildung von Umlagerungsprodukten bei der Addition von Arensulfenylchlorid und 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion an Benzonorbornadiene

Aufgrund von Produkt- und Geschwindigkeitsuntersuchungen wurde ein ähnliches Verhalten von Phenyltriazoldion (PTAD) und den Arensulfenylchloriden **10** und **11** bei der elektrophilen Addition an die Benzonorbornadiene **1**, **8** und **9** festgestellt, wobei die Umlagerungsprodukte **2** bzw. **6** entstehen. In Analogie zu dem gesicherten Mechanismus eines elektrophilen 3-Zentren-Angriffs bei der Reaktion der Arensulfenylchloride wird für die PTAD-Reaktion ein Ablauf über das Aziridinium-Ion **4** als Zwischenstufe vorgeschlagen. Daß dennoch im Fall des PTAD weder Regioselektivität noch Abfangreaktionen und auch kein Additionsprodukt ohne Umlagerung beobachtet werden konnten, wurde mit Hilfe elektronischer und sterischer Effekte am dipolaren Aziridinium-Molekül gedeutet. – Die Röntgenstrukturanalyse des aus **9** und **11** erhaltenen Additionsprodukts **17** wird mitgeteilt.

Of the numerous cycloaddition modes of triazolediones (TAD) with organic substrates, the most recently discovered[1] is the formation of skeletal rearrangement products, as illustrated for benzonorbornadiene [eq. (1)]. Rearranged urazole **2** bespeaks involvement of a carbenium ion center at the C-2 position via *exo*-attack of PTAD at the C-3

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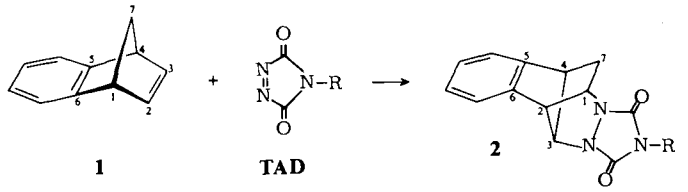
position and subsequent *Wagner-Meerwein* 1,2-shift of the $C^1 - C^6$ bond with dipolar collapse at the C-1 position.

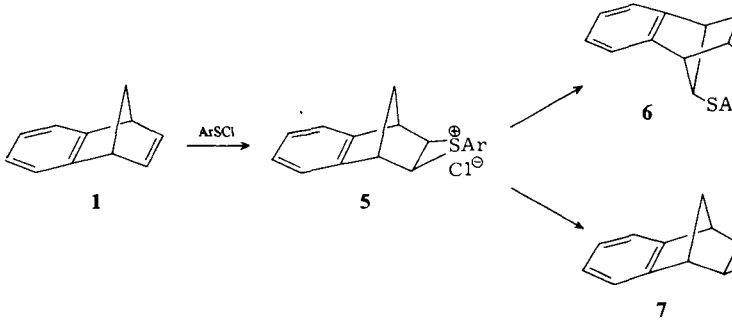


1 TAD 2 (1)

The relevant mechanistic question in this cycloaddition is whether an open or cyclic dipolar species, **3** and **4**, respectively, is engaged in this rearrangement as bona fide intermediate. Recently[2] it was proposed that aziridinium ions similar to **4** might be involved in the ene-reaction and [2 + 2]-cycloaddition of TAD with olefins. On the other hand, in the [2 + 2]-cycloaddition of TAD to enol ethers 1,4-dipoles similar to **3** have been proposed[3] as reaction intermediates. Consequently, it was of interest to assess which type of intermediate dominates in the electrophilic addition of TAD with benzonorbornadienes **1** leading to the rearranged urazoles **2**.

3 4

A number of electrophilic additions with bicycloalkenes are known[4] which engage skeletal rearrangements akin to that of eq. (1), but the mechanistically best studied are the reactions of arenesulfenyl halides[5]. As illustrated for benzonorbornadiene, with 2,4-dinitrobenzenesulfenyl chloride[6] the rearranged sulfide **6** [eq. (2)] results, while with *p*-toluenesulfenyl chloride[7] the unrearranged sulfide **7** is produced [eq. (2)]. However, for both cases bridged sulfur intermediates ranging from the ionic episulfonium species **5** to a covalent sulfurane are likely[5].



1 5 6 7 (2)

It appeared to us, therefore, that this established „onium" reaction [eq. (2)] of arenesulfenyl halides might serve as mechanistic model in the elucidation of whether aziridinium ions such as **4** play a role in this TAD reaction [eq. (1)]. In view of the lack of

pertinent kinetic data on the relative reactivities and product partitioning between rearrangement (sulfide **6**) and addition (sulfide **7**), we undertook a systematic mechanistic study of the reaction of the benzonorbornadienes **1**, **8**, and **9** with the arenesulfenyl chlorides **10** and **11**. Here is was of interest to compare the substituent effects on the relative rates and product partitioning of the arenesulfenyl chloride and 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) reaction with the benzonorbornadienes. The results of this investigation are reported herein.

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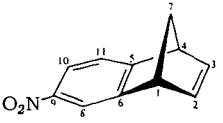

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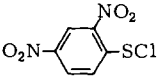

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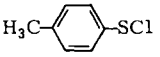

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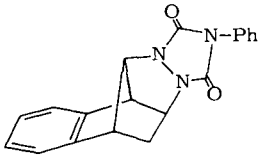
Results

Product Studies

For the derivatives of benzonorbornadienes **1**, **8**, and **9** investigated here, PTAD gives rearranged urazoles **12**, **13**, and **14**, while the arenesulfenyl chlorides **10** and **11** give rearrangement products **6** and addition products **7**. The proportion of rearrangement and addition products depends on the electronic character of the benzonorbornadiene **1** and of the arenesulfenyl chlorides **10** and **11** (Table 1). Thus, for the electron-rich dimethoxybenzonorbornadiene **8** predominantly rearrangement products are formed with both arenesulfenyl chlorides **10** and **11**. On the other hand, with the electron-deficient nitrobenzonorbornadiene **9** only addition products are formed with both arenesulfenyl chlorides. More interesting is the unsubstituted benzonorbornadiene **1** in that with *p*-toluenesulfenyl chloride (**11**) both rearrangement and addition products are produced, of which addition predominates over rearrangement, i. e. product ratio **15** to **16** is ca. 76:14. However, with 2,4-dinitrobenzenesulfenyl chloride (**10**) predominantly rearrangement is observed.



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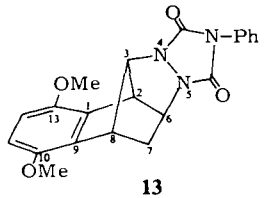

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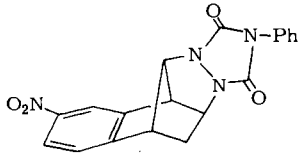

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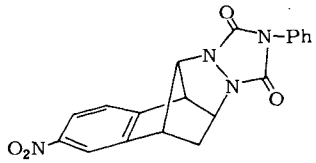

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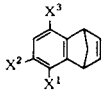
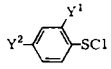
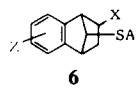
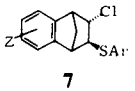
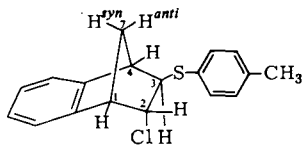
Table 1. Distribution of Rearrangement Products **6** and Addition Products **7** in the Reaction of Benzonorbornadienes **1**, **8**, and **9** with Arenesulfenyl Chlorides **10** and **11**

Reactants							Product Yields[a]	
							Rearrangement[b] 	Addition 
	X^1	X^2	X^3		Y^1	Y^2	**6**	**7**
8	MeO	H	MeO	**10**	NO_2	NO_2	63% (60 °C)[c]	–
8	MeO	H	MeO	**11**	H	Me	73% (**22**)	–
1	H	H	H	**10**	NO_2	NO_2	43% (**20**); 29% (**21**)[d]	–
1	H	H	H	**11**	H	Me	14% (**16**)	76% (**15**)[e]
9	H	NO_2	H	**10**	NO_2	NO_2	–	69% (**18**); 10% (**19**)[f]
9	H	NO_2	H	**11**	H	Me	–	71% (**17**)

[a] Absolute yields; determined by ^{1}H NMR (400 MHz); accurate within 5% of stated value. – [b] X is usually Cl, but when acetic acid is used as solvent, X can be OAc. – [c] *N. S. Zefirov, I. V. Bodrikov, N. K. Sadovaya, V. N. Moleva,* and *A. M. Magerramov,* Zh. Org. Khim. **12**, 2474 (1976) [Chem. Abstr. **86**, 139686x (1977)]. – [d] Ref.[6]; product yields from this work. – [e] Ref.[7]; product yields from this work. – [f] 400 MHz ^{1}H NMR clearly reveals a mixture of products **18** and **19**.

From this latter example, i. e. benzonorbornadiene (**1**) as substrate, it is clearly evident that the more electron-deficient arenesulfenyl chloride **10** promotes rearrangement, while the more electron-rich arenesulfenyl chloride **11** promotes addition. On the other hand, from the benzonorbornadiene substrates **8** and **9** we learn that for the electron-rich **8** only rearrangement, but for the electron-deficient **9** only addition ensues, irrespective of the electronic nature of the arenesulfenyl chloride. Therefore, we conclude that the best combination for rearrangement is to choose an electron-rich substrate, e. g. the dimethoxybenzonorbornadiene **8**, and an electron-deficient arenesulfenyl chloride, e. g. the 2,4-dinitro derivative **10**.

A few comments are in order concerning the structure assignment of the rearrangement and addition products **6** and **7**, respectively. For this purpose 400 MHz ^{1}H NMR was most definitive. As a model system we present the ^{1}H NMR spectra (Figure 1) of the rearrangement product **16** and addition product **15**, since they are derived from the same substrate/arenesulfenyl chloride pair, i. e. benzonorbornadiene (**1**) and *p*-toluenesulfenyl chloride (**11**). Important for the assignment are the protons H^1 to H^4 and H^7, but particularly proton H^2, which is juxtaposed to the chloride substituent.



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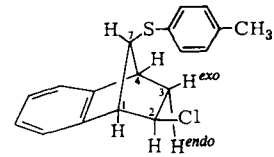

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The chemical shift ordering for the rearrangement product **16** is $H^2 > H^7 > H^1 > H^4 > H^{3\text{-}exo} > H^{3\text{-}endo}$. Most characteristic is the H^2 proton which appears as a doublet of doublets at $\delta = 3.85$. Double resonance experiments reveal that the H^2 is coupled to

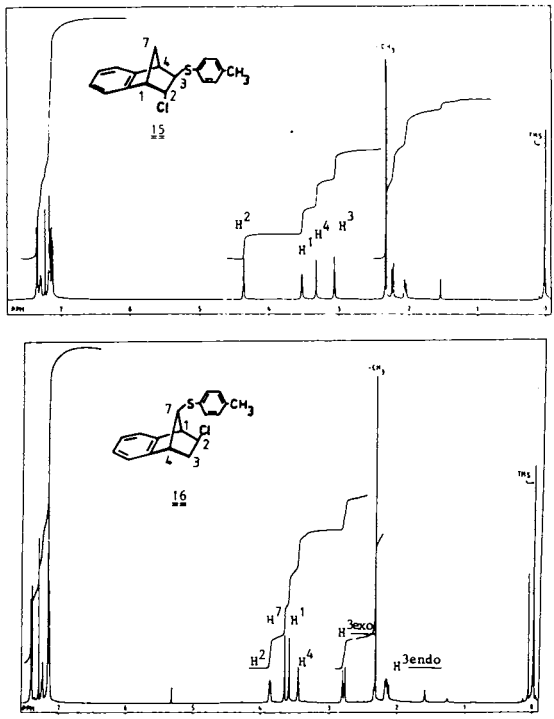
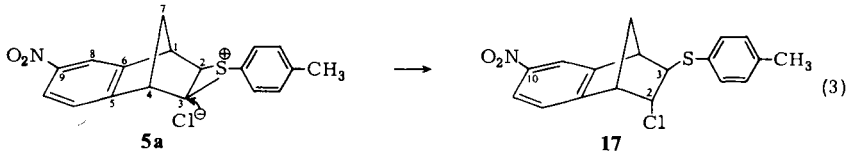


Figure 1. 400 MHz ^{1}H NMR spectra of the $H^1 - H^4$ and H^7 protons of **15** and **16**

$H^{3\text{-}endo}$ by a larger coupling constant ($J_{2,3\text{-}endo}$ = 7.5 Hz) and to $H^{3\text{-}exo}$ by a smaller coupling constant ($J_{2,3\text{-}exo}$ = 4 Hz), giving rise to a doublet of doublets. This fact and the lack of coupling between H^1 and H^2 confirm the *endo*-position of H^2 and consequently also the *exo*-position of chlorine. The structure is further corroborated by means of the $H^{3\text{-}exo}$ proton, which appears as a doublet of triplets at δ = 2.78. This pattern results from a large geminal coupling ($J_{3\text{-}exo,3\text{-}endo}$ = 13 Hz) and further coupling with H^2 and H^4 ($J_{2,3\text{-}exo} \approx J_{3\text{-}exo,4}$ = 4 Hz). The $H^{3\text{-}endo}$ proton shows a doublet of doublets with 13 and 7.5 Hz couplings.

For the addition product **15** the chemical shift ordering of the structurally useful protons is $H^2 > H^1 > H^4 > H^3 > H^{7\text{-}anti} > H^{7\text{-}syn}$, confirming the results already described by *Martin* and *Koster*[7]. Our chemical shifts differ slightly from theirs since we used $CDCl_3$ instead of CCl_4 as solvent. Again, characteristic is the $H^{2\text{-}exo}$ proton at δ = 4.34, which appears as triplet due to coupling by H^3 ($J_{2\text{-}exo,3\text{-}endo}$ = 4 Hz) and by H^1 ($J_{1,2\text{-}exo}$ = 4 Hz), as confirmed by double resonance. Similarly, the H^3 proton appears as a triplet (coupling by H^2 and $H^{7\text{-}syn}$) at δ = 3.04. An additionally useful feature for the spectral differentiation of the isomeric structures **15** and **16** are the methylene protons at the 7- and the 3-positions, respectively. For example, in **16** the chemical shifts are at δ = 2.14 and 2.78 and possess a geminal coupling of 13 Hz, while in **15** the chemical shifts are at δ = 2.04 and 2.22 with a geminal coupling of 10 Hz.

Although ^1H NMR was extremely helpful in deciphering the structures of the rearrangement and addition products **6** and **7**, respectively, it was of little help in determining the regioselectivity of the addition products **17**, **18**, and **19**, derived from the unsymmetrical 9-nitrobenzonorbornadiene (**9**). Fortunately, useful crystals of addition product **17**, derived from **9** and *p*-toluenesulfenyl chloride (**11**), could be grown for X-ray analysis. The perspective drawing of the crystal structure of **17** is shown in Figure 2. Consequently, nucleophilic attack by chloride ion takes place preferentially at the C-3 position of the episulfonium ion **5a** [eq. (3)].



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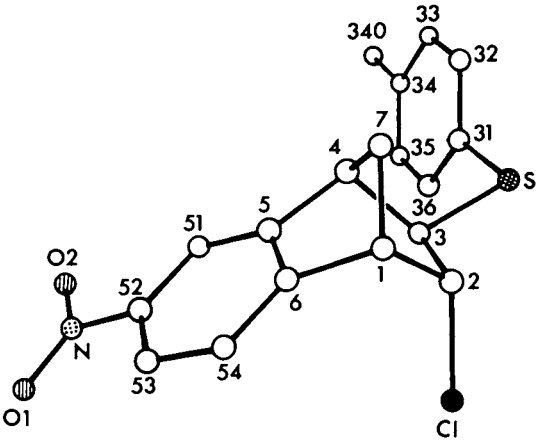
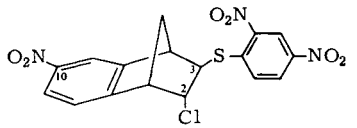


Figure 2. Perspective drawing of **17** with the labeling of the atoms corresponding to Tables 3 and 4

In the case of 9-nitrobenzonorbornadiene (**9**) with 2,4-dinitrobenzenesulfenyl chloride (**10**), a 9:1 mixture of addition products **18** and **19** is formed. In analogy to the addition product **17**, we assign the major isomer to **18** and the minor one to **19**.



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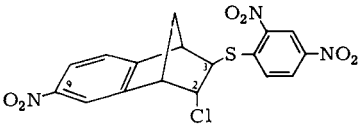

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A similar structural problem is encountered in the PTAD cycloaddition to 9-nitrobenzonorbornadiene (**9**). The 100 MHz ^{13}C NMR spectrum shows that a mixture of the isomeric rearrangement products **14** and **14a** in ca. equal proportion is formed. So far we could not separate this isomeric mixture by means of chromatography. However, it

is quite evident that the nitro group exerts a minimal differentiation in the regioselectivity of the electrophilic attack by PTAD on unsymmetrical benzonorbornadienes.

Rate Studies

The kinetic data is given in Tab. 2 for the arenesulfenyl chlorides **10** and **11** and for PTAD. For lack of solubility of the 2-*endo*-chloro-3-*exo*-(2,4-dinitrophenylthio)-9-nitrobenzonorbornene (**19**) in CCl_4 or CH_2Cl_2, acetic acid had to be used as solvent. In view of the slow rates, **10** and PTAD were run under pseudo-first-order conditions. The consumption of electrophile was followed spectrometrically, utilizing the arenesulfenyl chromophore at 425 and 390 nm and the triazoledione chromophore at 545 nm.

Table 2. Absolute Rate Constants of the Arenesulfenyl Chloride (ArSCl) and 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) with Benzonorbornadienes

Electrophile		Bicyclic Olefin				
Type	Conc. (mol/l × 10^3)	Type	Conc. (mol/l × 10^3)	Solvent	Temp. [°C]	k_{obs} [a] ($mol^{-1} \cdot s^{-1} \cdot 10^2$)
10	1.54	**8**	19.2	AcOH	40.0	8.13 ± 0.07
10	1.54	**1**	33.0	AcOH	40.0	6.63 ± 0.06
10	1.54	**9**	12.4	AcOH	40.0	0.01 ± 0.001
10	1.54	c,d)	13.4	AcOH	40.0	2.62 ± 0.11
11	3.66	**8**	3.66 [b]	CCl_4	20.0	1300 ± 30
11	3.66	**1**	3.66 [b]	CCl_4	20.0	231 ± 3
11	18.1	**9**	18.1 [b]	CCl_4	20.0	12.8 ± 0.2
11	18.1	c,e)	18.1	CCl_4	20.0	245 ± 8
PTAD	7.39	**8**	1.64	CH_2Cl_2	40.0	0.126 ± 0.002
PTAD	8.86	**1**	3.32	CH_2Cl_2	40.0	0.116 ± 0.003
PTAD	7.40	**9**	2.21	CH_2Cl_2	40.0	0.051 ± 0.004
PTAD	7.40	c,f)	5.96	CH_2Cl_2	40.0	0.230 ± 0.002

[a] Average of at least three independent runs. – [b] Run under second-order conditions, all others under pseudo-first-order conditions. – [c] Norbornene as substrate. – [d] *N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov, I. V. Bodrikov,* and *V. R. Kasrtashov,* Tetrahedron **31**, 2948 (1975). – [e] *H. Kwart* and *R. K. Miller,* J. Am. Chem. Soc. **78**, 5678 (1956). – [f] Ref.[1].

Several facts clearly stand out about the rate data of Table 2. For each electrophile the reactivity order among the benzonorbornadiene is **8** > **1** > **9**, i. e. the more electron-rich 8,11-dimethoxybenzonorbornadiene (**8**) reacts fastest and the more electron-deficient 9-nitrobenzonorbornadiene (**9**) slowest. In fact, reasonable *Hammett* correlations are obtained when lg k/k_0 is plotted against substituent constants (σ)[8], affording reaction constants (ρ) −1.13 (r = 0.993), −0.78 (r = 0.945), and −0.23 (r = 0.998) for **10**, **11**, and PTAD, respectively.

With respect to the reactivity of the electrophiles, we observe large differentiation. The relative order for the electron-rich olefin **8** ist **11** > **10** > PTAD, roughly in steps of hundred. Thus, *p*-toluenesulfenyl chloride (**11**) is ca. 10000-fold more reactive than PTAD in its electrophilic attack on **9**. Mechanistically more significant, a good linear correlation is obtained when the relative rates (lg k) of PTAD are plotted against those

of 2,4-dinitrobenzenesulfenyl chloride (**10**) and against *p*-toluenesulfenyl chloride (**11**), affording the respective slopes of 0.24 (r = 0.969) and 0.30 (r = 0.948). Quite evidently, the arenesulfenyl chloride is a much more selective electrophile (ca. 1000-fold differentiation in relative rates with the benzonorbornadienes **1**, **8**, and **9**) than PTAD (ca. 3-fold differentiation).

Discussion

The mechanistic question that we initially posed is concerned with whether similar type of intermediates intervene in the electrophilic reaction of triazolediones and arenesulfenyl chlorides, leading to the rearranged products **2** [eq. (1)] and **6** [eq. (2)], respectively. If an analogy between relative reactivities and product distributions can be established between these two rearrangements, a *bridged* species such as the aziridinium ion **4** rather than an open species such as the 1,4-dipole **3** should be then the more likely intermediate in the triazoledione rearrangement [eq. (1)]. This is based on the fact that in the arenesulfenyl chloride rearrangement [eq. (2)] *bridged* sulfur species are the accepted intermediates[5]. Both rearrangements involve initial rate-determining three-center attack by the electrophile.

While the analogy is far from perfect, we do experience considerable resemblance between these two reactions. Thus, we interpret this to mean that cyclic intermediates, i. e. aziridinium ions **4** and episulfonium ions **5**, account best for the observed facts. For example, the relative rate data (Table 2) support this hypothesis. Despite the great difference in the selectivities of these two electrophiles towards the substituted benzonorbornadienes **1**, **8**, and **9**, i. e. ca. 1000-fold for 2,4-dinitrobenzenesulfenyl chloride (**10**) and ca. 100-fold for *p*-toluenesulfenyl chloride (**11**) versus only ca. 3-fold for PTAD, their relative rates (lg k) correlate linearly against one another. This similar relative response of these two reactions to the electronic character of the substituents of the benzonorbornadiene substrate suggest similar electronic structures for the activated complexes[9]. In analogy to the three-center attack leading to bridged sulfur intermediates for arylsulfenyl chlorides[5], we postulate a three-center attack also for the PTAD rearrangement leading to the aziridinium ion **4**[2].

There exist, however, several differences in these two reactions concerning product distributions which need to be rationalized in terms of the proposed intermediates. For example, while the arenesulfenyl chloride leads to rearrangement and addition products **6** and **7**, respectively (Table 1), PTAD affords only rearranged urazoles **2** with the benzonorbornadienes. While in acetic acid as solvent rearranged acetates are formed in the arenesulfenyl chloride reaction, such external trapping is not observed for PTAD in acetic acid. Finally, while arenesulfenyl chlorides show a pronounced regioselectivity in the addition reaction with 9-nitrobenzonorbornadiene (**9**), PTAD forms about equal amounts of rearranged urazoles **14** and **14a** with **9**.

Closer inspection of the cyclic structures of the aziridinium and episulfonium ion intermediates **4** and **5**, respectively, clearly brings out some important differences. Thus, **4** is a dipolar species in which the proximate negative charge compensates to a large measure the positively charged aziridinium atom[10]. In contrast, for an ion pair such as **5** the chloride ion can readily separate from the positively charged episulfonium

atom. Consequently, the carbon atoms of the aziridinium ring in the dipolar species **4** are considerably less positively charged than those of the episulfonium ring of **5**.

For one thing this implies that the electronic demand on the substituent of the benzonorbornadiene is being much less taxed in the aziridinium ion **4** than in the episulfonium ion **5**. Therefore, the much more pronounced selectivity of arenesulfenyl chloride (ca. 100- to 1000-fold) than that of PTAD (ca. 3-fold) can be readily accounted for in terms of the proportionally larger charge separation in the transition state. The fact that solvent effects are significant in arenesulfenyl chloride reactions[5c] and essentially negligible in PTAD reactions[11] nicely corroborates this interpretation.

Charge separation arguments alone do not, however, explain the ability of arenesulfenyl chloride electrophiles to give both rearrangement and addition products with benzonorbornadienes (Table 1), while PTAD gives only rearrangement. Clearly, electron donors (ED) on the benzo ring in the benzonorbornadienes and electron acceptors (EA) on the arene ring of the arenesulfenyl chlorides, promote rearrangement over addition (Table 1). Presumably such push-pull conditions on the charge distribution in the episulfonium ion optimize neighboring group participation by the benzo ring and the species is already partly along the rearrangement coordinate.

To bring the present mechanistic implications on firmer grounds, a substrate is required which gives both rearrangement and addition products for both types of electrophiles, i. e. PTAD and arenesulfenyl chloride. Unfortunately, despite extensive searching, such a substrate could not be found so far. For example, while dibenzobarrelene gives both rearrangement and [2 + 2]-cycloaddition products with PTAD[12], with arenesulfenyl chlorides only *trans*-addition is observed[13].

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Experimental Part

Boiling and melting points are uncorrected. – Infrared spectra: Beckman Acculab 4 spectrometer. – ^{1}H NMR spectra: 60 MHz Hitachi-Perkin-Elmer R 24 B spectrometer, 90 MHz Varian EM-390 spectrometer or 400 MHz Bruker WM 400 spectrometer. – ^{13}C NMR spectra: 100.61 MHz Bruker WM 400 spectrometer. – Mass spectra: Varian MAT CH 7 spectrometer. – The elemental analyses were kindly run for us by Prof. Dr. *G. Maier's* staff at the Universität of Gießen. – Commercial reagents and solvents were purified according to literature procedures to match reported physical and spectral data. Known compounds used in this research were either purchased from standard suppliers or prepared according to the literature procedures and purified to match the reported physical and spectral data. Only the experimental details of hitherto unknown compounds are provided.

General Procedure of the Arenesulfenyl Chloride Reaction with Benzonorbornadienes

A 50-ml, round-bottomed flask was charged with 0.5 – 1.0 mmol of the benzonorbornadiene and 0.5 – 1.0 mmol of arenesulfenyl chloride in 20 – 50 ml of solvent (acetic acid or dichloromethane). The reaction mixture was allowed to stir magnetically at 20 – 40 °C until completion (ca. 10 – 20 min), as judged by the disappearance of the red color of the arenesulfenyl chloride. The solvent was roto-evaporated (ca. 20 °C at 10 torr) and the crude product purified by repeated

column chromatography on silica gel (ca. 20:1 adsorbant to substrate) and dichloromethane/pentane as eluant. Final purification for analytical samples was achieved either by distillation or recrystallization. In those cases in which separation of isomers was impossible, product composition was assessed by ^{1}H NMR at 400 MHz and ^{13}C NMR at 100.64 MHz, comparing the spectral data with known, analogous structures. The specific details on the individual systems are summarized below.

2-exo-Chloro-7-anti-(2,4-dinitrophenylthio)benzonorbornene (**20**) was obtained in 43% yield (30 mg; 0.08 mmol), m. p. 173–174°C (from dichloromethane/pentane) as first eluate in the reaction of 50 mg (0.35 mmol) of benzonorbornadiene (**1**) and 50 mg (0.21 mmol) of 2,4-dinitrobenzenesulfenyl chloride (**10**) in 20 ml of acetic acid at 40°C for 2 h. – IR (KBr): 3080, 2980, 1600, 1510, 1340, 1300, 1090, 1050, 760, 730 cm^{-1}. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 2.26 (dd, *J* = 13.5 and 7.5 Hz, 1H, 3-*endo*-H), 2.67 (dt, *J* = 13.5 and 4.4 Hz, 1H, 3-*exo*-H), 3.67 (m, 1H, 4-H), 3.80–3.84 (m, 2H, 1-H and 7-H), 3.92 (dd, *J* = 7.5 and 4 Hz, 1H, 2-H), 7.15–7.32 (m, 4H, benzo), 7.71 (d, *J* = 9 Hz, 1H, 6-H of ArS), 8.36 (dd, *J* = 9 and 2 Hz, 5-H of ArS), 9.04 (d, *J* = 2 Hz, 3-H of ArS). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 37.37 (t), 48.77 (d), 56.32 (d), 57.27 (d), 60.96 (d), 121.52, 121.68, 121.76, 126.90, 127.30, 127.37, 127.90, 143.18, 144.24, 145.04, 145.72, 145.97.

$C_{17}H_{13}ClN_2O_4S$ (376.8) Calc. C 54.19 H 3.48 N 7.43 Found C 54.15 H 3.30 N 7.37

2-exo-Acetoxy-7-anti-(2,4-dinitrophenylthio)benzonorbornene (**21**) was obtained in 29% yield (20 mg, 0.05 mmol), m. p. 170–171°C (from dichloromethane/pentane) as second eluate in the reaction of 50 mg (0.35 mmol) of benzonorbornadiene (**1**) and 50 mg (0.21 mmol) of 2,4-dinitrobenzenesulfenyl chloride (**10**) in 20 ml of acetic acid at 40°C for 2 h. – IR (CCl_4): 3100, 2980, 2940, 1745, 1600, 1530, 1340, 1230 cm^{-1}. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 2.10 (dd, 1H, 3-*endo*-H), 2.18 (s, 3H, CH_3CO), 2.36 (dt, 1H, 3-*exo*-H), 3.62 (m, 1H, 4-H), 3.74 (m, 1H, 1-H), 3.81 (m, 1H, 7-H), 4.74 (dd, *J* = 7.5 and 3 Hz, 1H, 2-H), 7.15–7.35 (m, 4H, benzo), 7.73 (d, *J* = 9 Hz, 1H, 6-H of ArS), 8.38 (dd, *J* = 9 and 2 Hz, 1H, 5-H of ArS), 9.04 (d, *J* = 2 Hz, 1H, 3-H of ArS). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 21.08 (q), 34.09 (t), 47.65 (d), 53.08 (d), 61.05 (d), 75.49 (d), 121.39, 121.57, 121.68, 122.48, 126.93, 127.15, 127.30, 127.67, 141.63, 144.19, 146.17, 170.49 (s). – MS (70 eV): *m/e* = 400 (7%, $M^{\oplus}$), 43 (100%, $CH_3C{\equiv}O^{\oplus}$).

$C_{19}H_{16}N_2O_6S$ (400.4) Calc. C 57.00 H 4.03 N 7.00 Found C 56.90 H 3.89 N 6.78

2-exo-Chloro-7-anti-(p-tolylthio)benzonorbornene (**16**) was obtained in 10–15% yield together with 85–90% yield of the known addition product **15** (determined by ^{1}H NMR at 400 MHz using the characteristic resonance at δ = 3.85 of the hydrogen at C-2 in the case of **16** and δ = 4.34 of the hydrogen at C-2 in the case of **15**) in the reaction of 0.14 g (0.98 mmol) of benzonorbornadiene (**1**) and 0.16 g (0.96 mmol) of *p*-toluenesulfenyl chloride (**11**) in 30 ml of dichloromethane at 20°C for 10 min. Repeated PLC on silica gel using petroleum ether as eluant and Kugelrohr distillation (ca. 230°C at 0.1 torr) enabled isolation of the pure rearrangement product **16**, which crystallized on standing, m. p. 95–96°C. – IR (CCl_4): 3080, 3020, 2980, 2940, 1510, 1480, 1300, 1280, 1130, 1060, 1005 cm^{-1}. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 2.14 (dd, *J* = 13 and 7.5 Hz, 1H, 3-*endo*-H), 2.31 (s, 3H, CH_3), 2.78 (dt, *J* = 13 and 4 Hz, 1H, 3-*exo*-H), 3.44 (m, 1H, 4-H), 3.56 and 3.62 (m, 2H, 1-H and 7-H), 3.85 (ddd, *J* = 7.5, 4, and 1 Hz, 1H, 2-H), 7.1–7.4 (m, 8H, benzo and ArS). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 21.02 (q), 37.01 (t), 49.72 (d), 56.78 (d), 58.20 (d), 65.54 (d), 121.45 (d), 121.60 (d), 126.66 (d), 127.24 (d), 129.85 (d), 131.70 (d), 133.46 (s), 135.04 (s), 144.53 (s), 146.32 (s).

$C_{18}H_{17}ClS$ (300.9) Calc. C 71.86 H 5.70 Found C 71.35 H 5.62

2-exo-Chloro-8,11-dimethoxy-7-anti-(p-tolylthio)benzonorbornene (**22**) was obtained in 73% yield (20 mg, 0.06 mmol), b. p. 210–220°C at 0.1 torr (by Kugelrohr distillation) in the reaction

of 156 mg (0.77 mmol) of 8,11-dimethoxybenzonorbornadiene (**8**) and 120 mg (0.77 mmol) of *p*-toluenesulfenyl chloride (**11**) in 50 ml of dichloromethane at 20°C for 15 min. The product crystallized on standing, m. p. 86–87°C. – IR (CCl_4): 3080, 3000, 2940, 2900, 2870, 2840, 1610, 1500, 1465, 1440, 1260, 1080 cm^{-1}. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 2.14 (dd, *J* = 12 and 8 Hz, 1H, 3-*endo*-H), 2.30 (s, 3H, CH_3), 2.74 (dt, *J* = 12 and 4 Hz, 1H, 3-*exo*-H), 3.51 (m, 1H, 4-H), 3.64 and 3.86 (m, 2H, 1-H and 7-H), 3.72 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.84 (m, 1H, 2-H), 6.58 (s, 2H, benzo), 7.10 and 7.36 (AA'BB', 4H, ArS). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 19.99 (q), 35.34 (t), 45.03 (d), 52.83 (d), 54.94 (q), 54.98 (q), 56.81 (d), 64.42 (d), 109.05 (d), 109.86 (d), 128.76 (d), 130.73 (d), 132.14 (s), 132.33 (s),134.23 (s), 135.91 (s), 146.59 (s), 146.86 (s).

$C_{20}H_{21}ClO_2S$ (360.9) Calc. C 66.56 H 5.86 Found C 66.53 H 5.80

2-endo-Chloro-10-nitro-3-exo-(p-tolylthio)benzonorbornene (**17**) was obtained in 71% yield (850 mg, 2.5 mmol), m. p. 162–164°C (from dichloromethane/pentane) in the reaction of 650 mg (3.5 mmol) of 9-nitrobenzonorbornadiene (**9**) and 700 mg (4.4 mmol) of *p*-toluenesulfenyl chloride (**11**) in 30 ml of dichloromethane at 20°C for 10 min. – IR (KBr): 3090, 2980, 2950, 1600, 1510, 1340, 1300, 1010, 960, 810, 800 cm^{-1}. – ^1H NMR ($CDCl_3$; 90 MHz): δ = 2.10 (d of m, 1H, 7-*syn*-H), 2.33 (d of m, 1H, 7-*anti*-H), 2.33 (s, 3H, CH_3), 3.03 (t, *J* = 3 Hz, 1H, 3-H), 3.43 (broad s, 1H, 4-H), 3.66 (m, 1H, 1-H), 4.40 (t, *J* = 3 Hz, 1H, 2-H), 7.20 and 7.45 (AA'BB', 4H, ArS), 7.46 (d, 8-H). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 21.08 (q), 46.75 (t), 49.92 (d), 51.68 (d), 57.98 (d), 62.78 (d), 116.29 (d), 122.39 (d), 125.03 (d), 130.06 (d), 130.31 (s), 132.12 (d), 137.92 (s), 147.36 (s), 150.60 (s).

$C_{18}H_{16}ClNO_2S$ (345.6) Calc. C 62.50 H 4.66 N 4.05 Found C 62.63 H 4.41 N 4.20

2-endo-Chloro-3-exo-(2,4-dinitrophenylthio)-10-nitrobenzonorbornene (**18**) *and 2-endo-Chloro-3-exo-(2,4-dinitrophenylthio)-9-nitrobenzonorbornene* (**19**) were obtained as a 90:10 mixture in 79% yield (950 mg, 2.25 mmol), as determined by 400 MHz ^1H NMR and HPLC on a LiChroprep Si 60 (5–20 μm) column and dichloromethane/ethyl acetate (2:1) as eluant, in the reaction of 550 mg (2.94 mmol) of 9-nitrobenzonorbornadiene (**9**) and 690 mg (2.94 mmol) of 2,4-dinitrobenzenesulfenyl chloride (**10**). The spectral data of the major isomer **18** are: IR (KBr): 3090, 2990, 2950, 1600, 1520, 1348 cm^{-1}. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 2.14 (broad d, *J* = 10.5 Hz, 1H, 7-*syn*-H), 2.22 (broad d, *J* = 10.5 Hz, 1H, 7-*anti*-H), 3.53 (t, *J* = 3 Hz, 1H, 3-H), 3.67 (broad s, 1H, 4-H), 3.83 (m, 1H, 1-H), 4.91 (t, *J* = 3 Hz, 1H, 2-H), 7.65 (d, *J* = 8.0 Hz, 1H, 8-H), 7.95 (d, *J* = 9.5 Hz, 1H, 6-H of ArS), 8.17 (dd, *J* = 8.0 and 2.0 Hz, 1H, 9-H), 8.47 (d, *J* = 2.0 Hz, 1H, 11-H), 8.59 (dd, *J* = 9.5 and 2.5 Hz, 1H, 5-H of ArS), 8.92 (d, *J* = 2.5 Hz, 1H, 3-H of ArS). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 46.55 (t), 48.74 (d), 50.96 (d), 54.41 (d), 61.64 (d), 117.19 (d), 121.13, 122.43, 125.32, 127.99, 129.59, 143.28, 144.13, 145.01, 146.77, 146.90, 150.80. – MS (70 eV): *m/e* = 421 (5%, $M^{\oplus}$), 386 (2%, $M^{\oplus}$ – Cl), 161 (83%, $C_9H_7NO_2^{\oplus}$), 115 (100%, $C_9H_7^{\oplus}$).

$C_{17}H_{12}ClN_3O_6S$ (421.6) Calc. C 48.39 H 2.87 N 9.96 Found C 48.12 H 2.65 N 9.73

General Procedure of the 4-Phenyl-4H-1,2,4-triazole-3,5-dione (PTAD) Reaction with Benzonorbornadienes

A 50-ml, round-bottomed flask was charged with 0.7 mmol of the benzonorbornadiene and 1.4 mmol of PTAD in 20 ml of dichloromethane. The reaction mixture was allowed to stir magnetically at 20°C until discoloration of the characteristic red color of PTAD (ca. 2 days). The solvent was roto-evaporated (ca. 20°C at 10 torr) and the crude product purified by column chromatography on silica gel (ca. 20:1 adsorbant to substrate) and dichloromethane as eluant. Final purification of the rearranged urazoles for analytical samples was achieved by repeated fractional recrystallization. The specific details on the individual systems are summarized below.

10,13-Dimethoxy-N-phenyl-4,5-diazatetracyclo[7.4.0.0^{2,6}.0^{3,8}]trideca-9,11,13-triene-4,5-dicarboximide (**13**) was obtained in 63% yield (177 mg, 0.5 mmol), m. p. 209–210°C (from ethanol) in the reaction of 150 mg (0.7 mmol) of 8,11-dimethoxybenzonorbornadiene (**8**) and 250 mg (1.4 mmol) of PTAD in 20 ml of dichloromethane at 20°C for 2 days. – IR (KBr): 3000, 2940, 2900, 2820, 1770, 1720, 1600, 1500, 1460, 1400, 1280, 1260, 1130 cm^{-1}. – ^{1}H NMR ($CDCl_3$; 60 MHz): δ = 1.40 (dm, *J* = 14 and 6 Hz, 1H, 7-*endo*-H), 2.15 (dm, *J* = 14 and 6 Hz, 1H, 7-*exo*-H), 3.70 (s, 6H, OCH_3), 3.80 (m, 2H, 8-H and 2-H), 4.52 (m, 2H, 3-H and 6-H), 6.51 (s, 2H, benzo), 7.30 (m, 5H, ArN). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 34.39 (t), 42.70 (d), 49.98 (d), 55.86 (q), 56.17 (q), 58.41 (d), 77.22 (d), 110.22 (d), 111.67 (d), 125.50 (d), 128.30 (d), 129.17 (d), 131.79 (s), 135.18 (s), 146.89 (s), 149.97 (s), 156.26 (s), 156.59 (s).

$C_{21}H_{19}N_3O_4$ (377.1) Calc. C 66.83 H 5.08 N 11.13 Found C 66.37 H 4.87 N 11.28

12-Nitro-N-phenyl-4,5-diazatetracyclo[7.4.0.0^{2,6}.0^{3,8}]trideca-9,11,13-triene-4,5-dicarboximide (**14**) *and 11-Nitro-N-phenyl-4,5-diazatetracyclo[7.4.0.0^{2,6}.0^{3,8}]trideca-9,11,13-triene-4,5-dicarboximide* (**14a**) were obtained as a ca. 1:1 mixture in 80% yield (670 mg, 1.9 mmol) in the reaction of 200 mg (1.07 mmol) of 9-nitrobenzonorbornadiene (**9**) and 400 mg (2.30 mmol) of PTAD in 30 ml of dichloromethane at 20°C for 3 days. – IR (KBr): 3060, 3000, 1780, 1720, 1600, 1525, 1500, 1405, 1350, 1240, 1140, 1070, 900, 840, 830, 780, 770, 730 cm^{-1}. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 1.42 and 1.45 (ddd, *J* = 12.5, 5, and 1.5 Hz, 1H, 7-*endo*-H), 2.30 and 2.32 (dd, *J* = 12.5 and 6 Hz, 1H, 7-*exo*-H), 3.76 and 3.79 (m, 1H, 2-H), 3.84 and 3.86 (m, 1H, 8-H), 4.66 and 4.67 (m, 1H, 6-H), 4.76 and 4.78 (m, 1H, 3-H), 7.40–8.40 (m, 8H, Ar). – ^{13}C NMR ($CDCl_3$; 100.61 MHz): δ = 33.95, 34.17, 46.00, 46.07, 52.76, 52.92, 58.03, 58.07, 76.67, 76.99, 115.76, 119.53, 121.07, 122.99, 123.99, 124.79, 125.29, 128.50, 129.20, 131.29, 137.52, 143.27, 147.35, 147.80, 152.95, 156.01, 156.10, 156.45, 156.53. – MS (70 eV): *m/e* = 362 (55%, $M^{\oplus}$), 243 (8%, $M^{\oplus}$ – C_7H_5NO), 119 (100%, $C_7H_5NO^{\oplus}$).

$C_{19}H_{14}N_4O_4$ (362.3) Calc. C 62.98 H 3.90 N 15.46 Found C 62.74 H 3.79 N 14.94

Table 3. Positional and Thermal Parameters (Å^2) of **17**[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl	0.87382(4)	0.35254(7)	0.0354 (1)	0.0730(5)	0.0569(4)	0.0601(3)	-0.0011(3)	-0.0257(3)	-0.0027(4)
S	0.73725(3)	0.24799(6)	0.54760(9)	0.0465(3)	0.0508(4)	0.0517(3)	-0.0147(3)	0.0071(3)	-0.0052(3)
N	0.4938 (1)	0.3410 (2)	0.2522 (3)	0.050 (1)	0.069 (2)	0.057 (1)	0.001 (1)	0.013 (1)	0.004 (1)
O(1)	0.4885 (1)	0.3657 (3)	0.4097 (3)	0.083 (2)	0.126 (2)	0.055 (1)	-0.005 (1)	0.025 (1)	-0.004 (1)
O(2)	0.4563 (1)	0.2732 (2)	0.1736 (3)	0.069 (1)	0.102 (2)	0.084 (2)	-0.013 (1)	0.021 (1)	-0.031 (1)
C(1)	0.7044 (1)	0.5175 (2)	0.8501 (3)	0.049 (1)	0.032 (1)	0.052 (1)	-0.003 (1)	0.003 (1)	-0.008 (1)
C(2)	0.7469 (1)	0.4027 (2)	0.8311 (3)	0.042 (1)	0.039 (1)	0.042 (1)	-0.002 (1)	-0.0001(9)	-0.005 (1)
C(3)	0.6999 (1)	0.3081 (2)	0.7471 (3)	0.043 (1)	0.034 (1)	0.039 (1)	-0.0051(9)	0.0004(9)	-0.0048(9)
C(4)	0.6376 (1)	0.3836 (2)	0.7107 (3)	0.044 (1)	0.043 (1)	0.037 (1)	-0.002 (1)	-0.0012(9)	-0.003 (1)
C(5)	0.6094 (1)	0.4068 (2)	0.8927 (3)	0.042 (1)	0.037 (1)	0.041 (1)	-0.0021(9)	-0.0018(9)	0.002 (1)
C(6)	0.6507 (1)	0.4897 (2)	0.9789 (3)	0.047 (1)	0.034 (1)	0.046 (1)	-0.004 (1)	0.001 (1)	-0.002 (1)
C(7)	0.6670 (1)	0.5091 (2)	0.6707 (3)	0.051 (1)	0.045 (1)	0.047 (1)	0.008 (1)	0.002 (1)	0.004 (1)
C(31)	0.6764 (1)	0.1439 (2)	0.4743 (3)	0.046 (1)	0.037 (1)	0.044 (1)	-0.009 (1)	0.002 (1)	0.004 (1)
C(32)	0.6467 (1)	0.1610 (2)	0.3088 (3)	0.060 (2)	0.041 (1)	0.052 (2)	-0.001 (1)	-0.004 (1)	0.007 (1)
C(33)	0.6021 (1)	0.0774 (3)	0.2452 (4)	0.064 (2)	0.059 (2)	0.064 (2)	-0.013 (1)	-0.019 (1)	0.008 (1)
C(34)	0.5843 (1)	-0.0226 (3)	0.3445 (4)	0.051 (2)	0.057 (2)	0.080 (2)	-0.022 (2)	0.000 (1)	-0.007 (1)
C(35)	0.6136 (2)	-0.0382 (3)	0.5095 (4)	0.078 (2)	0.049 (2)	0.072 (2)	-0.001 (1)	0.012 (2)	-0.014 (2)
C(36)	0.6596 (1)	0.0431 (3)	0.5735 (4)	0.069 (2)	0.052 (2)	0.048 (1)	0.001 (1)	-0.002 (1)	-0.004 (1)
C(51)	0.5572 (1)	0.3571 (2)	0.9793 (3)	0.039 (1)	0.042 (1)	0.047 (1)	-0.002 (1)	-0.002 (1)	-0.001 (1)
C(52)	0.5472 (1)	0.3963 (2)	0.1532 (3)	0.042 (1)	0.049 (1)	0.045 (1)	0.003 (1)	0.004 (1)	0.007 (1)
C(53)	0.5860 (1)	0.4806 (3)	0.2384 (3)	0.060 (2)	0.054 (2)	0.041 (1)	-0.010 (1)	0.002 (1)	0.008 (1)
C(54)	0.6394 (1)	0.5281 (2)	0.1503 (3)	0.058 (2)	0.045 (1)	0.051 (1)	-0.012 (1)	-0.001 (1)	-0.003 (1)
C(340)	0.5359 (2)	-0.1138 (4)	0.2703 (6)	0.081 (3)	0.091 (3)	0.131 (4)	-0.034 (3)	-0.006 (2)	-0.033 (2)

[a] U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots 2U_{12}hka^*b^* + \cdots)]$; the standard deviations are given in parentheses.

Rate Measurements

The rate of arenesulfenyl chloride and triazoledione (TAD) consumption was monitored by UV-VIS spectrophotometry, using a Cary 17 instrument, which was equipped with a thermostated cell block. Temperature control of the matched set of 1-cm pathlenght cells was maintained within 0.01 °C by means of Colora Ultrathermostat K 5. The disappearance of the absorption of the arenesulfenyl chloride chromophore, 390 nm (ε = 469) for the *p*-methyl and 425 nm (ε = 545) for the 2,4-dinitro derivative, and of the PTAD chromophore at 545 nm (ε = 151) was followed with time. Most runs were conducted under pseudo-first-order conditions, determining the rate constants from the semilogarithmic dependence of concentration with time. In some runs also second-order kinetics was employed, extracting the rate constants from the inverse dependence of concentration with time. After demonstrating in the initial runs that good linearity was achieved out to over 90% of reaction, most of the rate data was acquired up to two halflives. For the actual runs separate stock solutions of the arenesulfenyl chloride, of the PTAD and of the olefin were prepared in the desired solvent, aliquots transferred with standardized pipettes into a calibrated volumetric flask and diluted to the final volume with the same solvent to achieve the desired concentration. Temperature equilibration of the cell was allowed for at least 30 min prior to charging and rate measurement. The kinetic data was processed on a Tektronix 4051 desk computer including least square analysis. The results are collected in Table 2.

X-ray Crystallography of 2-endo-Chloro-10-nitro-3-exo-(p-tolylthio)benzonorbornene (**17**)*)

The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.7 × 0.7 × 0.7 mm on a Syntex-P3 four-circle diffractometer. Measurement of

Table 4. Bond Lengths (pm) and Angles (deg) for **17**[a)]

Bond lengths (pm)							
N - O(1)	122.2(3)	C(1) - C(2)	154.6(3)	C(5) - C(6)	139.9(3)	C(31) - C(32)	139.0(3)
N - O(2)	122.0(3)	C(1) - C(6)	151.0(3)	C(5) - C(51)	137.8(3)	C(31) - C(36)	138.5(4)
N - C(52)	146.7(3)	C(1) - C(7)	154.4(3)	C(6) - C(54)	138.0(3)	C(32) - C(33)	138.0(4)
Cl - C(2)	179.0(2)	C(2) - C(3)	154.9(3)	C(51) - C(52)	139.6(3)	C(33) - C(34)	138.4(4)
S - C(3)	182.0(2)	C(3) - C(4)	154.9(3)	C(52) - C(53)	137.6(4)	C(34) - C(35)	138.2(4)
S - C(31)	177.8(2)	C(4) - C(5)	151.6(3)	C(53) - C(54)	139.2(4)	C(34) - C(340)	151.1(5)
		C(4) - C(7)	154.1(3)			C(35) - C(36)	138.4(4)

Angles (°)					
C(3) - S - C(31)	100.8(1)	C(3) - C(4) - C(5)	104.9(2)	C(31) - C(32) - C(33)	120.0(2)
O(1) - N - O(2)	122.8(3)	C(3) - C(4) - C(7)	100.9(2)	C(32) - C(33) - C(34)	121.7(3)
O(1) - N - C(52)	118.6(2)	C(5) - C(4) - C(7)	100.5(2)	C(33) - C(34) - C(35)	117.9(3)
O(2) - N - C(52)	118.7(2)	C(4) - C(5) - C(6)	106.9(2)	C(33) - C(34) - C(340)	120.5(3)
C(2) - C(1) - C(6)	108.2(2)	C(4) - C(5) - C(51)	132.1(2)	C(35) - C(34) - C(340)	121.5(3)
C(2) - C(1) - C(7)	98.3(2)	C(6) - C(5) - C(51)	120.8(2)	C(34) - C(35) - C(36)	121.2(3)
C(6) - C(1) - C(7)	101.0(2)	C(1) - C(6) - C(5)	106.2(2)	C(31) - C(36) - C(35)	120.4(2)
C(1) - C(2) - C(3)	103.8(2)	C(1) - C(6) - C(54)	132.2(2)	C(5) - C(51) - C(52)	116.5(2)
C(1) - C(2) - Cl	114.0(2)	C(5) - C(6) - C(54)	121.5(2)	N - C(52) - C(51)	118.0(2)
C(3) - C(2) - Cl	113.3(2)	C(1) - C(7) - C(4)	94.3(2)	N - C(52) - C(53)	118.4(2)
C(2) - C(3) - C(4)	102.7(2)	S - C(31) - C(32)	119.1(2)	C(51) - C(52) - C(53)	123.6(2)
S - C(3) - C(4)	114.1(2)	S - C(31) - C(36)	122.0(2)	C(52) - C(53) - C(54)	119.1(2)
S - C(3) - C(2)	108.3(2)	C(32) - C(31) - C(36)	118.8(2)	C(6) - C(54) - C(53)	118.4(2)

a) The standard deviations are given in parentheses.

*) Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (West Germany). These data are available with quotation of the registry number CSD 50551, the authors, and the reference to this publication.

intensities: ω-scan, 1° range Mo-K_α, 2Θ maximum = 55°. The intensities of 3915 reflections were measured, 3244 of them with $F > 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 427 strong reflections were determined and on the resulting *E*-map approximate position of all non-hydrogen atoms could be determined. Positional and thermal parameters could be refined by anisotropic least squares cycles to $R = 0.050$. The position of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements..

Addition product **17** crystallizes in the monocyclic space group $P2_1/a$ (No. 14) with a = 2054.0(7), b = 1102.3(4), c = 752.1(3) pm and β = 90.09(3)°. The unit cell contains $Z = 4$ formula units, the density was calculated to be 1.354 Mg · m^{-3}. All atomic parameters are listed in Table 3. The labeling of the atoms can be seen in Figure 2. Bond distances and bond angles are summarized in Table 4.

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