π^* orbitals,[33] this insertion mechanism is probably confined to substrates in which the π^* orbitals of the double bond are not sterically accessible to the nucleophile HOMO which are thus free to interact with the π^* orbital of the carbon-halogen bond.

Experimental Section

All new compounds have correct elemental analyses which were performed by the Laboratoire de Microanalyse du C.N.R.S. de Lyon. The structures and optical purities are unambiguously deduced from the ^1H NMR spectrum measured on a Varian T60, Brucker, 90, or Cameca 250 MHz spectrometer (see Figures 1-4). The optical rotations were measured on a 141 M Perkin-Elmer polarimeter.

Starting Materials. The (+)- and (-)-methyl-β-chloro-β-(2-methylnaphthyl)acrylate (**1a**)[6,9] and methyl-β-chloro-β-(2-naphthyl)methacrylate (**1b**)[9] and (pyridine)cobaloxime(I)[5a] are known compounds.

Reactions with Lithium Dimethylcuprate. Under an atmosphere of dry nitrogen and at -5 °C is added 6 mL of an ethereal 0.67 M solution of CH_3Li (4 mmol) to 20 mg of CuI covered with 3 mL of dry ether. After 15 min, the Gilman test becomes negative and the ethereal solution of the copper reagent becomes limpid and has a light yellow color. After this solution is cooled to -20 °C, 315 mg (2.2 mmol) of acrylate **1a** is added. The clear solution becomes brown and a yellow precipitate is formed. After 1 h, dry air is bubbled into the solution and water is added. After the usual workup and purification on TLC, 160 mg (50%) of (*E*)-methyl-β-(2-methylnaphthyl)crotonate is obtained (see Table I). When the reaction is attempted with the methylacrylic ester **1b**, under the same condition, even after leaving the reaction mixture several hours, only the unchanged starting material **1b** is recovered.

Reactions with (Pyridine)cobaloxime(I) (2). The reaction was carried out under nitrogen. To a solution of 464 mg (4 mmol) of dimethylglyoxime in 15 mL of MeOH was added 476 mg (2 mmol) of $CoCl_2 \cdot 6H_2O$. After the cobalt salt had dissolved, 0.16 mL of pyridine followed by 0.50 mL of NaOH (8 N) were added. After 20 min, the reaction mixture turned brown. Subsequently 0.25 mL of NaOH (8 N) and 261 mg (1 mmol) of the reagent **1a** was added under hydrogen. The equivalent volume of hydrogen was absorbed (22.4 mL) in about 5 h; the solution had then turned orange-brown. Water was added, and after filtration, the orange solid was washed with water and diethyl ether and dried under vacuum. Complex **3a** was identified by its NMR spectrum (Table I) and its elemental analysis; yield 88%.

Preparation of Complexes 3b-d. The alkenyl(aquo) cobaloxime **3** (L = H_2O) was prepared by the same procedure as for complex **3a**. This complex was dissolved in MeOH and an equimolar amount of α-methylbenzylamine (**3c**) or (-)-α-methylbenzylamine (**3d**) or $P(OCH_3)_3$ (**3b**) was added. After the solution was stirred for 10 min, the orange solution turned brown. The solvent was removed, and the product was purified by chromatography on silica gel (Mallinkrodt CC7) with CH_2Cl_2-acetone (2:1).

Compounds **3b-d** were identified by their NMR spectra.

Reaction with NaI. In a 25-mL single-necked flask filled with a condenser protected by a $CaCl_2$ drying tube, a mixture of 500 mg (2 mmol) of ester **1a** and 300 mg (2 mmol) of dried sodium iodide was dissolved in 6 mL of anhydrous acetone. The mixture was refluxed for 5 days. After the usual workup, the partially racemized ester **1a** was recovered. By using anhydrous DMF instead of acetone and heating the mixture for 5 days we obtained a similar result. Likewise, after heating the ester with a 15-fold excess of dimethylamine in benzene solution in a sealed tube for 1 week at 80 °C, only the racemized starting material **1a** was recovered.

Acknowledgment. We acknowledge the constructive criticisms of Professor Z. Rappoport (Jerusalem).

Registry No. 1a, 89414-95-9; **1b**, 89414-96-0; **1c**, 89414-97-1; (±)-**1c**, 89414-98-2; (-)-**1c**, 89414-99-3; **3a**, 89414-92-6; **3b**, 89414-93-7; **3c**, 89414-94-8; **3d**, 89496-32-2.

(33) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953. Apeloig, Y., unpublished results, see footnote 14 in ref 28.

On the Mechanism of the Cycloaddition of 1,2,4-Triazoline-3,5-diones with Bicycloalkenes Leading to Rearranged Urazoles

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Abstract: On the basis of product and kinetic data the intervention of an aziridinium ion (mechanism C) is postulated in the formation of rearranged urazole during the cycloaddition of triazolinediones (TAD) with benzonorbornadiene, norbornenes, and related bicycloalkenes. The cycloaddition follows the second-order rate law, first order in each component. It exhibits typically low activation enthalpies and large negative activation entropies. The relative rates and product formation are insensitive to free radical conditions (initiators, scavengers, light) and exhibit a pronounced steric effect. Modest charge transfer from the olefin (nucleophilic partner) to the TAD (electrophilic partner) is detected in the activated complex (small negative ρ values for the Hammett plot of substituted benzonorbornadienes, linear dependence of relative rates with ionization potentials of benzonorbornadiene, small positive ρ values for the Hammett plot of substituted TADs, linear correlation between relative rates and half-wave reduction potentials of TADs, moderate dipole moment of the activated complex relative to reactants and products, and a small solvent effect). No charge-transfer complexes can be detected by UV-vis spectrophotometry, and trapping experiments for 1,4-dipolar intermediates failed. The relative rates of TAD cycloaddition correlate with the relative rates of arenesulfenyl chloride addition, a process for which a three-center mechanism has been established.

In the preparation of azoalkanes for mechanistic and synthetic purposes, the formation of urazoles via cycloaddition of 1,2,4-triazoline-3,5-diones (TAD) and their subsequent hydrolysis has played an important role.[2] Besides the common (4 + 2)-cycloaddition mode of TAD, homo-Diels-Alder reaction, and (2 + 2)-cycloaddition to π bonds and strained σ bonds, numerous

(1) Doctoral Dissertation, University of Würzburg, July 1983.

(2) (a) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762-779. (b) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99-150.

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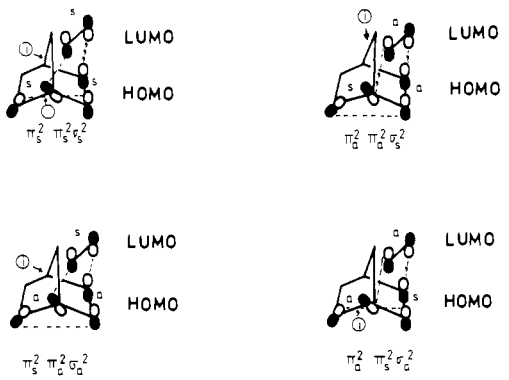
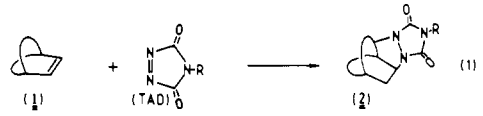
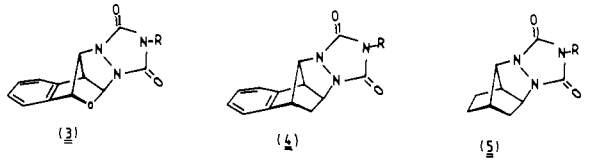


Figure 1. The possible allowed transition states for the cycloaddition of triazolinedione (LUMO) and norbornene (HOMO). The circled i indicates an improbable bonding interaction on steric and geometrical grounds.

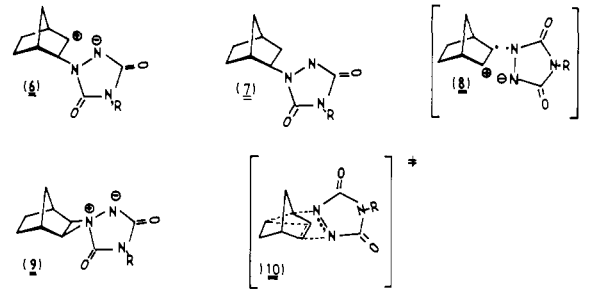
examples have been recently documented[3] in which bicyclic alkenes **1** afford rearranged urazoles **2** (eq 1). The first example[4] of this



novel cycloaddition of TAD constitutes the formation of the rearranged urazole **3** in the reaction of 2,3-benzo-7-oxanorbornadiene with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Other examples, which are the subject of this mechanistic investigation, are the rearranged urazoles **4** and **5**, respectively derived from benzonorbornadiene and norbornene.[3a]



In view of the skeletal rearrangement that is embodied in this transformation, a plausible mechanism is to postulate electrophilic addition of TAD, affording the 1,4-dipole **6** (mechanism A), as illustrated for the reaction of norbornene and PTAD generating urazole **5**. Wagner–Meerwein shift and collapse of the resulting 1,5-dipole would explain formation of the rearranged urazole **5**. A possible alternative path could involve formation of the 1,4-diradical **7**. Subsequent skeletal rearrangement and collapse of

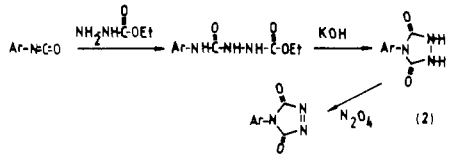


the resulting 1,5-diradical would also generate the rearranged urazole **5**. Since 2-norbornyl radicals are quite sluggish in undergoing skeletal rearrangements,[5] the likelihood of this mechanism is questionable. However, since PTAD is prone to form stabilized radical intermediates,[6] a plausible mechanistic alternative is electron transfer, preceded by charge transfer, to give the radical pair **8** (mechanism B), which on collapse at the radical sites would generate the 1,4-dipole **6**. Subsequently, this intermediate proceeds onto the rearranged urazole **5** via mechanism A. Finally, a likely mechanism, especially in view of recent observations on the ene reaction of PTAD,[7] is formation of the aziridinium ion intermediate **9** (mechanism C). Either direct rearrangement of the aziridinium dipole **9** or ring opening to the 1,4-dipole **6** and subsequent rearrangement would afford the urazole **5**. The possibility of the fully concerted process involving the activated complex **10** can be excluded. Orbital symmetry considerations require for this (2 + 2 + 2)-cycloaddition either all suprafacial components or one suprafacial and two antarafacial components. None of these are feasible on steric and geometric grounds (Figure 1).

It was the purpose of the present investigation to define the slow step of this novel cycloaddition reaction of TAD, by distinguishing between the plausible mechanistic alternatives A, B, and C, involving the 1,4-dipole **6**, the radical ion pair **8**, and the aziridinium ion **9**, respectively. For this purpose, kinetic and product studies including solvent effects, dipole moments, activation parameters, substitutent effects, ionization potentials, reduction potentials, trapping experiments, etc. were to be employed. Herein we report the results and their mechanistic interpretations.

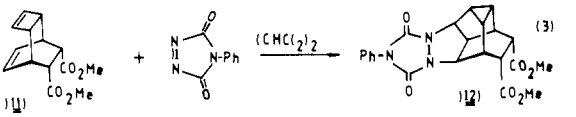
Results

Starting Materials. The substituted PTADs were prepared following the procedure for PTAD (eq 2), by adding ethyl hydrazinecarboxylate to the aryl isocyanates, followed by potassium hydroxide catalyzed cyclization of the resulting arylcarbethoxysemicarbazides into the corresponding arylurazoles and oxidation to the aryltriazolinediones with dinitrogen tetroxide. The yields, physical constants, spectral data, and elemental analyses for the new compounds are given in the Experimental Section. The known compounds matched the reported physical and spectral data.



The alkenes used in this investigation were all known compounds. They were prepared according to literature procedures and purified to match the reported physical data.

Rearranged Urazoles. All the rearranged urazoles except **12** (eq 3) are known compounds,[3a,8] and their physical and spectral data matched those reported. The full characterization of **12** is given in the Experimental Section.



Product Balance. The quantitative yields in the TAD cycloaddition were established for the rearranged urazoles **4** and **5** using ^{1}H NMR. For this purpose the 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) was employed, using the *N*-methyl group in the rearranged urazoles as ^{1}H NMR probe. The respective chemical shifts of the *N*-methyl groups in the rearranged urazoles **4** and **5** are located at δ 3.08 and 3.02. In $CDCl_3$ as solvent at 40 °C after 10 h all MTAD was consumed, and by calibrated ^{1}H NMR 91%

(3) (a) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806. (b) Adam, W.; De Lucchi, O. *Tetrahedron Lett.* **1981**, *22*, 929. (c) Adam, W.; De Lucchi, O.; Erden, I. *Angew. Chem.* **1979**, *91*, 512. (d) Adam, W.; De Lucchi, O.; Hill, K. *J. Am. Chem. Soc.* **1982**, *104*, 2934. (e) Adam, W.; De Lucchi, O.; Hill, K. *Chem. Ber.* **1982**, *115*, 1982. (f) Adam, W.; Arias, L. A.; De Lucchi, O. *Tetrahedron Lett.* **1982**, *23*, 399. (g) Adam, W.; De Lucchi, O. *Ibid.* **1981**, *22*, 3501.

(4) Sasaki, T.; Kanematsu, K.; Uchide, M. *Tetrahedron Lett.* **1971**, 4855.

(5) (a) Davies, D. I.; Cristol, S. J. *Adv. Free-Radical Chem.* **1965**, *1*, 155. (b) Rüchardt, C. *Angew. Chem.* **1970**, *82*, 845. (c) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, p 333.

(6) Hall, J. H.; Bigard, W. E.; Fargher, J. M.; Jones, M. L. *J. Org. Chem.* **1982**, *47*, 1459.

(7) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.

(8) Adam, W.; Carballeira, N.; Scheutzow, D.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1984**, *117*, 1139.

Table I. Second-Order Rate Constants for the TAD Cycloaddition with Olefins 13–19 at 40 °C

entry	olefin	TAD	[olefin], M	[TAD] × 10^3, M	solvent	$k_2 \times 10^3$,[a] $M^{-1}\ s^{-1}$	k_{rel}
1	13	PTAD	0.234	5.50	CH_2Cl_2	0.30 ± 0.04	0.26
2	14	MTAD	0.129	77.0	$CHCl_3$	0.91 ± 0.02	
3	14	PTAD	0.116	8.86	CH_2Cl_2	1.16 ± 0.03	1.0
4	14	MTAD[b,c]	0.310	77.0	$CDCl_3$	0.92 ± 0.05	
5	15	PTAD	0.112	5.86	CH_2Cl_2	1.73 ± 0.05	1.5
6	16	PTAD	0.298	5.75	CH_2Cl_2	2.38 ± 0.01	2.1
7	16	PTAD[b]	0.273	273	CH_2Cl_2	2.25 ± 0.20	
8	17	PTAD	0.135	7.40	CH_2Cl_2	2.66 ± 0.08	2.3
9	18	PTAD	0.073	7.46	CH_2Cl_2	13.1 ± 0.4	11.3
10	19	PTAD[b]	0.269	269	CH_2Cl_2[d]	234 ± 4	202

[a] Average of three independent runs. [b] Run under second-order conditions; all others under pseudo-first-order conditions using excess olefin. [c] Run by ^1H NMR following the *N*-methyl resonance of the urazole; all others run by spectrophotometry by monitoring the 525–545-nm absorption of the TAD. [d] Contains ca. 3% ether.

Table II. Second-Order Rate Constants for the Cycloaddition of Substituted TADs and Substituted Benzonorbornadienes and Norbornene in Methylene Chloride at 40 °C

entry	olefin	TAD	[olefin], M	[TAD] × 10^3, M	$k_2 \times 10^3$,[a,b] $M^{-1}\ s^{-1}$
1	21	PTAD	0.088	7.40	0.506 ± 0.044
2	22	PTAD	0.082	7.39	1.26 ± 0.02
3	14	PTAD (*p*-Me)	0.103	1.06	1.08 ± 0.02
4	14	PTAD	0.116	8.86	1.16 ± 0.03
5	14	PTAD (*m*-Cl_3)	0.103	8.42	2.76 ± 0.05
6	14	PTAD (*p*-NO_2)	0.103	9.61	5.42 ± 0.04
7	16	PTAD (*p*-Me)	0.218	5.08	1.51 ± 0.04
8	16	PTAD	0.298	5.75	2.38 ± 0.01
9	16	PTAD (*m*-CF_3)	0.215	8.16	5.26 ± 0.01
10	16	PTAD (*p*-NO_2)	0.232	5.36	8.37 ± 0.15

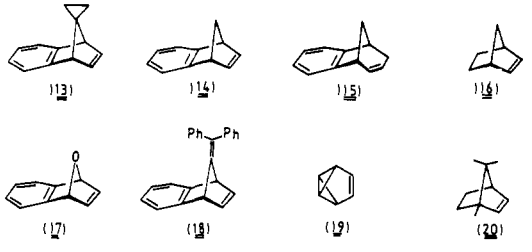
[a] Determined spectrophotometrically by following the 525–545-nm absorption of the PTAD under pseudo-first-order conditions in olefin. [b] Average of three independent runs.

of urazole **4** was formed. However, urazole **5** was formed only in 50% yield under these conditions. An undefined polymeric material was isolated to the extent of ca. 50% yield (by gravimetry), and its ^1H NMR revealed mainly aliphatic resonances in the norbornane region.

Kinetics. Most of the kinetic runs were performed under pseudo-first-order conditions (excess olefin), following the consumption of the TAD spectrophotometrically by utilizing their characteristic 525–545-nm absorption in the visible region. Good first-order plots were obtained over several half-lives, but most runs were taken only out to 2 half-lifes. As a check on the results, a few control runs were made under second-order kinetic conditions at equimolar concentrations of the olefin and TAD. Again good second-order plots were obtained. The directly determined second-order rate constants and those calculated from the pseudo-first-order data matched well within the experimental error (cf. Table I, entries 2 and 4 for olefin **14** and entries 6 and 7 for olefin **16**). In the pseudo-first-order run, a concentration dependence of the olefin showed that it followed first-order kinetics.

As an additional check the kinetics of benzonorbornadiene (**14**) were determined with ^1H NMR, by monitoring the appearance of the *N*-methyl resonance of the urazole at δ 3.08 with time. Again within experimental error the same second-order rate constants were obtained (cf. Table I, entries 2 and 4).

The second-order rate constants for the olefinic substrates **13–19** are collected in Table I. Some interesting features emerge from these kinetic data. By far the slowest substrate is the benzonorbornadiene **13** (cf. Table I, entry 1). Clearly, exo attack[9] of the TAD is hindered by steric effects of the spirocyclopropane group in olefin **13**. In fact, bornene (**20**) is completely inert toward TAD cycloaddition even in refluxing 1,2-dichloroethane.[3e] In substrate **18** steric effects appear to be minimized, so that it is one of the most reactive benzonorbornadienes (cf. Table I, entry 9). Presumably the flat benzhydrylidine group in **18** provides less steric encumbrance than the methylene bridge in **14**.



Also a larger ring system such as the bicyclo[3.2.1]octadiene skeleton in **15** appears to provide easier access for the TAD since this substrate reacts slightly faster than benzonorbornadiene **14** (cf. Table I, entries 3 and 5). Ring strain can hardly be responsible for the enhanced reactivity. Moreover, the increased rate of cycloaddition of the oxa-substituted benzonorbornadien **17** (cf. Table I, entry 8) cannot derive from steric interactions. A lone pair on oxygen is generally considered to occupy more space than a hydrogen atom so that we would have expected **17** to react slower than **14**. Electronic factors must play a role here. Possibly the nucleophilic oxygen provides some complexation for the incoming electrophilic TAD and thereby helps bring the two reactants together. Electronic factors appear also to be involved in the greater reactivity of norbornene **16** vs. benzonorbornadiene **14** (Table I, entries 3 and 6). The electron-withdrawing nature of the benzo group appears to deactivate **14** toward attack by the electrophilic TAD.

By far the most reactive substrate is benzvalene (**19**) reacting 20 times faster than the fastest benzonorbornadiene, namely **18** (cf. Table I, entries 9 and 10). Undoubtedly the great strain in benzvalene gives rise to this great reactivity toward TAD cycloaddition.

Substitutent Effects. To understand electronic effects in this cycloaddition, the rates of the benzonorbornadienes **14**, **21**, and **22** with *p*-methyl-, *m*-(trifluoromethyl)- and *p*-nitro-substituted

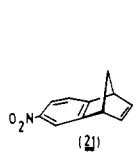
(9) In principle endo attack is possible, but unlikely on stereoelectronic grounds, at least for norbornene; cf.: Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171. Rondon, N. G.; Paddon Row, P.; Caranella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436. Burkert, U. *Angew. Chem.* **1981**, *53*, 171. Spanget-Larson, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435.

Table III. Second-Order Rate Constants for the Cycloaddition of PTAD to Norbornene (16) in Various Solvents

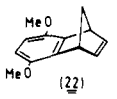
entry	solvent	[olefin], M	[PTAD] × 10^3, M	temp, °C	$k_2 \times 10^3$,[a,b] M^{-1} s^{-1}	E_T[c]
1	acetone	0.217	6.42	50	0.290 ± 0.001	42.2
2	ethyl acetate	0.157	12.5	50	0.312 ± 0.004	38.1
3	tetrahydrofuran	0.234	13.0	50	0.327 ± 0.011	37.4
4	dimethylformamide	0.240	6.30	50	0.453 ± 0.037	43.8
5	acetonitrile	0.260	9.29	50	0.623 ± 0.007	46.0
6	toluene	0.374	12.9	50	0.775 ± 0.042	33.9
7	*o*-dichlorobenzene	0.373	6.27	40	1.57 ± 0.01	38.1
8	methylene chloride	0.298	5.75	40	2.38 ± 0.01	41.1
9	chloroform	0.294	9.21	40	3.05 ± 0.04	39.1

[a] Determined spectrophotometrically by following the 525–545-nm absorption of PTAD under pseudo-first-order conditions in olefin. [b] Average of three independent runs. [c] Values taken from ref 10.

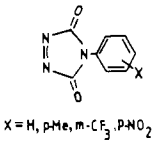
triazolinediones were investigated. The results are summarized in Table II. Clearly, electron-withdrawing groups on the ben-



(21)



(22)



zonorbornadienes, e.g., the nitro derivative **21**, slow down the rate of cycloaddition, while electron-donating groups, e.g., the dimethoxy derivative **22**, speed up the rate (cf. Table II, entries 1, 2, and 4). In fact, a good linear Hammett plot is obtained for these few data points, giving a reaction constant $\rho = -0.23$ ($r = 0.998$). To obtain a linear Hammett plot, the sum of the substituent constants, i.e., $(\sigma_m + \sigma_p)$, had to be used for the 6-nitro group in **21**. Similarly, for the two methoxy substituents in **22** $2(\sigma_m + \sigma_p)$ was used to approximate the required but unavailable σ_o value by the σ_p value. Thus, the olefin serves as nucleophilic partner, accumulating partial positive charge in the transition state of this cycloaddition. In this context it is of interest to mention that the relative rates (log k_2) of the olefins **14**, **16**, **21**, and **22** (cf. Table II, entries 4, 8, 1, and 2) give a resonable linear correlation with a slope of −0.64 ($r = 0.941$) against the reported ionization potentials.[10] The respective ionization potentials (IP) are 9.27, 8.98, 9.93, and 9.17 eV and were determined by photoelectron spectroscopy.[10] The nucleophilic role that the olefin partner plays in this cycloaddition with PTAD is clearly evident from this correlation.

As might be expected, the triazolinedione serves as electrophilic partner. Thus, an electron-donating substitutent on the *N*-phenyl group, e.g., the *p*-methyl-substituted PTAD (cf. Table II, entry 3 for **14** and entry 7 for **16**), slows down the rate, while electron-withdrawing groups, e.g., the *m*-(trifluoromethyl)- and *p*-nitro-substituted PTADs (cf. Table II, entries 5 and 6 for **14** and entries 9 and 10 for **16**), accelerate the reaction. Good linear Hammett plots are obtained for these few data points, giving reaction constants $\rho = +0.79$ ($r = 0.990$) and $\rho = +0.78$ ($r = 0.992$) for benzonorbornadiene (**14**) and norbornene (**16**), respectively. Thus, the positive ρ values convincingly demonstrate that PTAD acts as electrophilic partner, accumulating partial negative charge in the transition state for this cycloaddition. In fact, excellent linear plots are obtained when the relative rates (log k_2) of the olefins **14** and **16** are plotted against the half-wave reduction potentials ($E_{1/2}$) of the various PTADs. The respective slopes are +5.11 ($r = 0.989$) and +5.54 ($r = 0.996$), clearly exhibiting the electrophilic character of the PTADs in this cycloaddition. The $E_{1/2}$ values were determined in acetonitrile at 20–25 °C with use of a silver chloride reference electrode (cf. Experimental Section). The respective values are 0.089 ± 0.002, 0.105 ± 0.005, 0.179 ± 0.002, and 0.210 ± 0.001 V for *p*-methylphenyl-, phenyl-, *m*-(trifluoromethyl)phenyl-, and *p*-nitrophenyl-substituted triazolinediones.

Solvent Effects. Since the dependences of the ionization potentials of the olefins and the reduction potentials of the PTADs on the cycloaddition rates exhibit charge transfer from the olefin to the PTAD, it was important to test solvent effects. This kinetic data is displayed in Table III for several solvents, ranging from polar aprotic solvents such as acetonitrile and dimethylformamide to aromatic solvents such as toluene and *o*-dichlorobenzene and halogenated solvents like methylene chloride and chloroform. Protic polar solvents such as ethanol and acetic acid could not be employed, because under the conditions of cycloaddition PTAD reacts faster with these solvents than with the olefin.

Several points become immediately apparent from the second-order rate constants k_2 (Table III) for the PTAD–olefin reaction leading to rearranged urazoles. First of all, the k_2 values show that in polar aprotic solvents such as acetone, dimethylformamide, and acetonitrile (Table III, entries 1, 4, and 5) the rates are slower than those in toluene (Table III, entry 6) or methylene chloride (Table III, entry 8). In fact, in the halogenated solvents *o*-dichlorobenzene, methylene chloride, and chloroform (Table III, entries 7, 8, and 9) the rates are fastest. Furthermore, the total range in rates is only about 10-fold, i.e., acetone (Table III, entry 1) the slowest and chloroform (Table III, entry 9) the fastest. Besides this exceedingly small solvent effect, no obvious linear correlation can be recognized between the relative rates and solvent parameters such as the E_T values.[11]

Activation Parameters. To exclude the possibility that the insignificant and erratic solvent effects could stem from acquiring the rate data accidentally near the isokinetic temperature,[12] the rates were run as a function of temperature. The data are given in Table IV. The activation parameters for the norbornene–PTAD cycloaddition show typical bimolecular values (cf. Table IV, entries 10–13), i.e., low activation enthalpies ($\Delta H^{\ddagger}$) and very negative activation entropies ($\Delta S^{\ddagger}$).

More significant, however, are the activation data for the benzonorbornadiene–PTAD cycloaddition in acetonitrile, toluene, and methylene chloride. In that order $\Delta H^{\ddagger}$ decreases by almost 9 kcal/mol, i.e., acetonitrile highest (cf. Table IV, entries 1–3) and methylene chloride lowest (cf. Table IV, entries 7–9). This trend is offset in part by a corresponding decrease in the activation entropies by about 21 eu, i.e., acetonitrile (cf. Table IV, entries 1–3) least negative and methylene chloride (cf. Table IV, entries 7–9) most negative. In fact, an excellent linear correlation ($r = 0.998$) is obtained when the $\Delta H^{\ddagger}$ values are plotted against the $\Delta S^{\ddagger}$ values for these three solvents. The isokinetic temperature, i.e., the slope of this plot, was $\beta = 120$ °C or at least 75 °C above the temperature at which these rate data were acquired. Therefore, the small solvent effect in this cycloaddition is not an artifact of operating near the isokinetic point.

The validity of isokinetic relationships has been seriously questioned due to the large experimental errors in the activation parameters.[12] Applying the rigorous statistical analysis established for this purpose,[12b] our data gave the parameters $S_{00} = 423$, $S_0 = 368$, $S_\infty = 658$, and $S_s = 567$.[13] Since $S_0 < S_{00}$ for the above

(10) Santiago, C.; McAlduff, E. J.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6149.

(11) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.

(12) (a) Exner, O. *Prog. Phys. Org. Chem.* **1973**, *10*, 411. (b) Exner, O. *Collect. Czech. Chem. Commun.* **1972**, *37*, 1425.

(13) We thank Professor Dr. O. Exner for processing our rate data by his statistical method.

Table IV. Activation Parameters for the Cycloaddition of PTAD to Benzonorbornadiene (14) and Norbornene (16) in Acetonitrile, Toluene, and Methylene Chloride

entry	olefin	solvent	[olefin], M	[PTAD] × 10^3, M	temp, °C	$k_2 \times 10^3$,[a,b] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ at 298 K, kcal/mol
1	14	acetonitrile	0.189	9.72	45	0.105 ± 0.015			
2	14	acetonitrile	0.189	9.72	50	0.198 ± 0.019	17.9 ± 1.0	−20.4 ± 3.0	24.0
3	14	acetonitrile	0.189	9.72	55	0.257 ± 0.010			
4	14	toluene	0.090	9.60	45	0.328 ± 0.026			
5	14	toluene	0.090	9.60	50	0.460 ± 0.016	15.5 ± 1.0	−26.0 ± 1.0	23.3
6	14	toluene	0.090	9.60	55	0.696 ± 0.019			
7	14	methylene chloride	0.166	8.86	20	0.380 ± 0.015			
8	14	methylene chloride	0.166	8.86	30	0.611 ± 0.022	9.5 ± 1.5	−41.9 ± 5.0	22.0
9	14	methylene chloride	0.166	8.86	40	1.16 ± 0.03			
10	16	methylene chloride	0.307	5.54	20	0.495 ± 0.015			
11	16	methylene chloride	0.307	5.54	25	0.670 ± 0.030	11.4 ± 1.0	−34.9 ± 1.0	21.8
12	16	methylene chloride	0.307	5.54	30	0.937 ± 0.008			
13	16	methylene chloride	0.307	5.54	35	1.29 ± 0.01			

[a] Determined spectrophotometrically by following the 525–545-nm absorption of PTAD under pseudo-first-order conditions in olefin. [b] Average of three independent runs.

data, according to the empirical rules the isokinetic relationship obtains for the benzonorbornadiene–PTAD cycloaddition.

Dipole Moments. The small solvent effect in the olefin–PTAD cycloaddition leading to rearranged urazoles could fortuitously arise from similar trends in ground-state and transition-state solvation. Not only would this account for the small solvent effects, but it would also explain their erratic nature of not correlating with any solvent parameter. It was, therefore, of interest to estimate the degree of charge transfer in this cycloaddition by evaluating the dipole moment of the activated complex. For this purpose the Laidler–Eyring equation (eq 4) was used, in which

$$\ln k_2/k_0 = \frac{1}{k_B T}\left\{[\phi_A + \phi_B + \phi_{\ddagger}] - \left(\frac{\epsilon - 1}{2\epsilon - 1}\right)\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} + \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right]\right\} \quad (4)$$

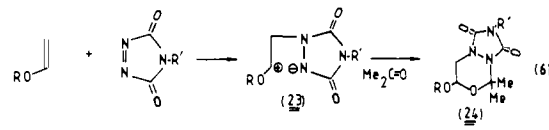
the subscripts A, B, and ‡ stand for reactants and activated complex, respectively. From the slope of a plot of the relative rates $\ln k_2/k_0$ vs. the solvent parameter $(\epsilon - 1)/(2\epsilon + 1)$ one can evaluate $\mu_{\ddagger}$, the dipole moment of the activated complex, provided the dipole moments of the reactants are known.

Unfortunately, the lack of a solvent effect in the cycloaddition rates precludes using eq 4 in this way. However, since for the present cycloaddition the solvent effect is negligible, the slope of such a plot is essentially zero. Under these conditions, eq 4 reduces to the simple expression of eq 5.[14] Since the measured dipole

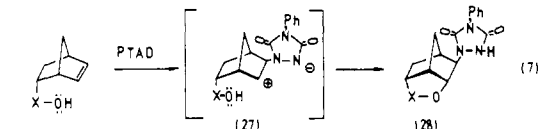
$$\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} \simeq \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \quad (5)$$

moments are 0.62, 2.9, and 2.8 D respectively for benzonorbornadiene (**14**), PTAD, and urazole **4** (cf. Experimental Section),[15] we estimate from these data $\mu_{\ddagger} = 4$ D for the activated complex using eq 5. The volume parameters r_A^3, r_B^3, and $r_{\ddagger}^3$ were approximated by the respective molecular weights. In view of the quite polar molecules involved in this cycloaddition, the dipole moment and thus charge transfer in the transition state is only moderate. The small solvent effect on the cycloaddition rates is, therefore, not surprising.

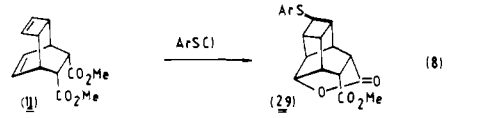
Trapping Experiments. To test whether long-lived intermediates intervene in this cycloaddition, a number of trapping experiments were conducted. For example, in the cycloaddition of PTAD to enol ethers in acetone the adduct **24** was isolated, presumably formed by trapping of the 1,4-dipole **23** with acetone (eq 6).[16] Consequently, we also ran the cycloaddition of both benzonorbornadiene (**14**) and norbornene (**16**) with PTAD in acetone, but only urazoles **4** and **5** respectively were obtained. No trapping products similar to **24** were detected.



In view of this unsuccessful intermolecular trapping, a few intramolecular trapping experiments were attempted. For example, the 2-*endo*-carboxy- and the 2-*endo*-hydroxymethylnorbornenes (**26** and **25**, respectively) were used for this purpose. It was hoped that the internal hydroxy nucleophile would trap the cationic center leading to urazole **28** (eq 7). Unfortunately,



neither norbornene **25** nor **26** reacted with PTAD even in refluxing *sym*-tetrachloroethane for 48 h. Finally, as shown already in eq 3, reaction of substrate **11** with PTAD afforded only the rearranged urazole **12** and no intramolecular trapping product such as **29**, reported to be formed in the reaction of arenesulfenyl chloride with **11** (eq 8).[17]



It is clear from these few attempts that whatever intermediates might intervene in the cycloaddition of PTAD and olefins they are too short-lived for intermolecular trapping by acetone or intramolecular trapping by carbomethoxy nucleophiles. If intermediates are involved in this cycloaddition, they appear to be distinct from the 1,4-dipoles trapped in the (2 + 2)-cycloaddition of PTAD with enol ethers.[16]

Control Experiments. A number of control experiments concerning the products and kinetics needed to be conducted in helping to define the mechanism of this cycloaddition. For example, the possibility had to be probed whether urazole **30**, initially formed via (2 + 2)-cycloaddition of PTAD to norbornene (**16**), rearranged under the reaction conditions to the urazole **5** (eq 9). Urazole

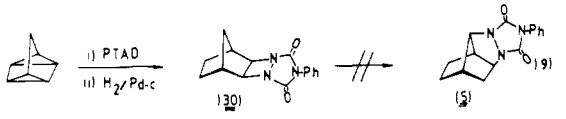
(14) Huisgen, R. *Pure Appl. Chem.* **1980**, *52*, 2283.
(15) We thank Dr. H. Huber, Universität München, for allowing us to measure these dipole moments in his laboratory.
(16) (a) Turner, S. R.; Guilbault, L. J.; Butler, G. B. *J. Org. Chem.* **1971**, *36*, 2838. (b) Hall, J. H.; Jones, M. L. *Ibid.* **1983**, *48*, 822.
(17) (a) Giese, B.; Daub, C. *Chem. Rev.* **1977**, *110*, 1101. (b) Zefirov, N. S.; Kirin, V. N.; Kozmin, A. S.; Bodrikov, I. V.; Potekhin, K. A.; Kurkutova, E. N. *Tetrahedron Lett.* **1978**, 2617.

Table V. Control Experiments on the Rates of the Cycloaddition of Benzonorbornadiene (14) and Norbornene (16) with PTAD

entry	olefin	solvent	temp, °C	additive	$k_{obsd} \times 10^4$,[a] s^{-1}
1	14	CH_2Cl_2	40	none	1.25 ± 0.02
2	14	CH_2Cl_2	40	$h\nu$[b]	1.52 ± 0.03
3	14	CH_2Cl_2	40	HCl (g)	0.85 ± 0.01
4	14	CH_2Cl_2	40	AcOH	0.80 ± 0.01
5	14	CH_2Cl_2	40	$LiClO_4$	0.86 ± 0.01
6	14	CH_2Cl_2	40	$CuSO_4$	1.91 ± 0.02
7	14	CH_2Cl_2	40	Et_3N	PTAD dec
8	14	CH_2Cl_2	40	$AlCl_3$	14 polymerized
9	16	CH_2Cl_2	40	N_2 (g)[c]	11.8 ± 0.3
10	16	CH_2Cl_2	40	O_2 (g)[d]	11.6 ± 0.2
11	16		40	H_2O	PTAD dec
12	16		40	*t*-BuOH	PTAD dec
13	16	CH_2Cl_2	40	$AlCl_3$	16 polymerized
14	16	CH_2Cl_2	40	CuCl	PTAD complexes
15	16	CH_2Cl_2	40	$FeSO_4$	12.1 ± 0.2
16	16	toluene	75	none	56.7 ± 0.2
17	16	toluene	75	$(PhCO_2-)_2$	53.1 ± 0.2
18	16	toluene	75	$(Me_2C(CN)N=)_2$	56.7 ± 0.2
19	16	toluene	90	none	PTAD dec

[a] Pseudo-first-order rate constants measured at olefin concentrations of ca. 0.3 M by following the rate of PTAD consumption spectrophotometrically at 525–545 nm. [b] Sample was irradiated at 500–600 nm with a sodium street lamp. [c] Saturated with nitrogen gas. [d] Saturated with oxygen gas.

30 was prepared according to literature[18] via cycloaddition of PTAD to quadricyclane and subsequent catalytic reduction. On heating even up to 400 °C urazole **30** was perfectly stable.



The kinetic control experiments are summarized in Table V, in which the effects of a number of conditions and additions were tested on the rate. Since radical intermediates have been shown to be involved in PTAD cycloadditions,[6,19] most of these control experiments were run to assess whether this cycloaddition reaction is sensitive to radical conditions. Thus, the reaction rate is not affected by visible light (cf. Table V, entries 1 and 2), by molecular oxygen (cf. Table V, entries 9 and 10), by transition-metal ions such as cupric sulfate (cf. Table V, entries 1 and 6) and ferrous sulfate (cf. Table V, entries 9 and 15), nor by free radical initiators, e.g., benzoyl peroxide and azobisisobutyronitrile (cf. Table V, entries 17 and 18).

Unfortunately, the stable free radical galvinoxyl[20] has too strong absorption in the region were PTAD absorbs so that the rate of reaction could not be monitored spectrophotometrically. However, after the required time the reaction mixture of benzonorbornadiene (**14**) and PTAD in the presence of galvinoxyl was worked up and about the same yield of the urazole **4** was isolated as in the absence of galvinoxyl. Had galvinoxyl scavenged any free radical intermediates that were responsible for the formation of the rearranged urazole **4**, this product could not have been obtained under these conditions.

In addition to these free radical tests, a number of other additions were examined. Thus, Brønsted acids such as hydrogen chloride and acetic acid (cf. Table V, entries 3 and 4) do not dramatically affect the reaction rate. However, strong Lewis acids such as aluminum chloride (cf. Table V, entries 8 and 13) promote fast polymerization of the olefins. Electrolytes such as lithium perchlorate (cf, Table V, entry 5) do not exhibit a dramatic rate effect. Protic nucleophiles such as water and *tert*-butyl alcohol and amine bases such as triethylamine (cf. Table V, entries 11, 12, and 7) destroy the triazolinedione. Finally, at temperatures of 90 °C and above the decomposition of PTAD competes efficiently with cycloaddition (cf. Table V, entry 19), so that the reaction temperatures must be kept below 80 °C.

In view of the observation that charge-transfer complexes are formed between polyalkoxybenzenes and PTAD,[19] attempts were made to detect such complexes in the cycloaddition of benzonorbornadiene **14** and PTAD. Even under the highest possible concentrations of PTAD, the absorption spectra were superimposable in the presence and absence of olefin **14**. Since the rate of cycloaddition is not instantaneous under these conditions ($t_{1/2}$ ca. 50 min) and since no detectable amounts of charge-transfer complex are observed, it appears that such complexes are not formed in the reaction between PTAD and **14**.

Mechanistic Discussion

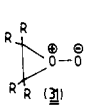
The mechanism for the formation of the rearranged urazoles **4** and **5** in the cycloaddition of TAD to strained olefins must account for the following experimental facts: (1) The rate law is overall second order, first order each in the alkene and the TAD, as expected for a bimolecular cycloaddition. (2) The activation parameters are typical for bimolecular reactions, i.e., relatively low activation enthalpies ($\Delta H^{\ddagger}$) but large and negative activation entropies ($\Delta S^{\ddagger}$). (3) The relative rates and product formation do not respond to free radical conditions[6] since neither initiators (benzoyl peroxide, azobisisobutyronitrile) nor scavengers (galvinoxyl) nor irradiation with visible light[19] cause detectable effects. (4) The relative rates exhibit a strong steric effect due to substitution at the methylene bridge in benzonorbornadiene (**14**) and norbornene (**16**). (5) In the activated complex modest charge transfer from the alkene (nucleophilic partner) to the TAD (electrophilic partner) occurs as substantiated by the following experimental observations: (a) The relative rates of substituted alkenes correlate linearly with the corresponding Hammett σ values, affording a small but negative reaction constant (ρ), and they correlate linearly with the ionization potentials (IP) of these alkenes. (b) The relative rates of substituted PTADs correlate linearly with the corresponding Hammett σ values, affording a small but positive reaction constant (ρ), and they correlate linearly with the half-wave reduction potentials ($E_{1/2}$) of the PTADs. (c) The measured dipole moments are 0.62, 2.9, and 2.8 D for benzonorbornadiene, PTAD, and urazole **4**, respectively, and the estimated dipole moment for the activated complex is only ca. 4 D. (d) No significant solvent effect can be registered on the relative rates; in fact, the rates are faster in nonpolar than in polar solvents and follow an isokinetic relationship with β = 120 °C. (6) The relative rates of PTAD cycloaddition correlate linearly with the relative rates of arenesulfenyl chloride addition[8] for the same set of alkenes. (7) No dipolar intermediates can be trapped either inter- or intramolecularly. (8) No charge-transfer complexes[19] can be observed between PTAD and benzonorbornadiene (**14**).

(18) (a) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5668–5669. (b) Olsen, H. *Ibid.* **1982**, *104*, 6836–6838.
(19) Hall, J. H. *J. Org. Chem.* **1983**, *48*, 1708.
(20) Adam, W.; Chiu, W. T. *J. Am. Chem. Soc.* **1971**, *93*, 3687.

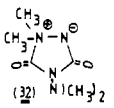
The three plausible mechanisms which need to be scrutinized now in terms of these experimental facts are formation of the 1,4-dipolar ion **6** (mechanism A), the radical ion pair **8** via electron-transfer process, preceded with charge transfer (mechanism B), and the aziridinium ion **9** (mechanism C). The activation parameters (fact 2) are not typical for electron transfer (mechanism B) involving PTAD.[19] More definitive, the lack of response of the rates toward free radical conditions (fact 3) and the small charge transfer (fact 5) in the activated complex speak against mechanism B, i.e., electron transfer. Solvent effects[21] and substitutent effects[22] are typically very large for electron-transfer reactions. Besides, no charge-transfer absorption (fact 8) could be detected.

Fact 5 can also not be reconciled in terms of formation of the 1,4-dipole **6** (mechanism A). For most reactions in which bona fide 1,4-dipoles of this type have been documented, solvent and substituent effects are very large and in the expected order, i.e., faster rates in polar solvents.[23]

This leaves us with mechanism C, i.e., formation of the aziridinium ion **9**. Such an unusual species was first postulated[7] for the ene reaction of TAD, in analogy to the perepoxide intermediate **31** proposed for the ene reaction of singlet oxygen on the basis of the small solvent effect and particularly the deuterium isotope effects. Related dipolar species of TAD have been documented,[24] for example, **32**, for which even a crystal structure[25] is available. Thus, the aziridinium ion **9** is a plausible reactive intermediate in the cycloaddition of PTAD and alkenes leading to rearranged urazoles **2**.

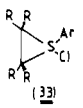


(31)

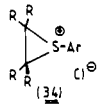


(32)

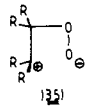
All experimental facts collected here are in reasonable accord with the aziridinium ion mechanism. The linear correlation between the relative rates of PTAD and arenesulfenyl chloride addition for the same set of olefinic substrates (fact 6) is indicative that similar transition states are involved in these two reactions.[8] Since a three-center attack by arenesulfenyl chloride on the olefin, involving a spectrum of intermediates ranging from the sulfurane **33** to the sulfonium ion **34**, has been established,[26] most likely a three-center attack by PTAD on the olefin leading to the aziridinium ion **9** (mechanism C) also obtains in the PTAD–olefin cycloaddition. Such an exo attack would be expected to be subject to steric effects caused by substituents on the methylene bridge (fact 4).



(33)



(34)



(35)

In view of the dipolar structure of the aziridinium ion **9**, one might expect large charge separation in the activated complex of mechanism C. This would be clearly in conflict with fact 5, i.e., small solvent and substituent effects. However, for the related case of the perepoxide **31** and its corresponding 1,4-dipole **35**, theoretical work[27] reveals that charge separation in the perepoxide **31** is much less than in the 1,4-dipole **35**. For example, the dipole moment of **31** is less than one-half of that of **35**, i.e., 5 and 12 D, respectively. Thus, we also expect for the aziridinium ion **9** much less charge separation than in the 1,4-dipole **6**. Presumably the proximity of the charges in the aziridinium ion **9** is responsible for charge cancellation. Consequently, the small solvent and substituent effects and the moderate dipole moment for the activated complex (fact 5) can be reconciled in terms of the aziridinium ion mechanism.

It is unfortunate that the trapping experiments (fact 7) were negative. Apparently the aziridinium ion **9** transposes swiftly into the rearranged urazole **5**, instead of opening up into the 1,4-dipole **6** and becoming trapped, as in the case of the cycloaddition of PTAD to enol ethers (eq 6).[16] In fact, in view of the small solvent effect in the latter reaction, it is likely that also here an aziridinium ion is formed in the slow step. Subsequently, fast ring opening would lead to the 1,4-dipole, which in the absence of acetone affords the (2 + 2)-cycloadduct and/or polymer. In the presence of acetone the trapping product **24** (eq 6) is formed in addition to polymer.

On the basis of the kinetic and product data presented in this study, the intervention of an aziridinium ion (mechanism C) in the cycloaddition of PTAD to olefins leading to rearranged urazoles (eq 1) is postulated. Rigorous proof would entail independent synthesis of such reaction intermediates and showing that they rearrange to urazoles.

Experimental Section

Instrumentation. The melting points are uncorrected and were determined on a Reichert Thermovar melting point apparatus. Quantitative weighings were performed on a Mettler H20T analytical balance. Infrared spectra and all quantitative infrared data were determined on a Perkin-Elmer 157G spectrophotometer or on a Beckman Acculab 4. The 60-MHz ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer Model R-24B NMR spectrometer or on a Varian EM-360. The 90-MHz ^{1}H NMR spectra were recorded on a Varian EM-390 or on a Bruker HFX 90 spectrometer. The 400-MHz ^{1}H NMR and the 100.6-MHz ^{13}C NMR spectra were run on a Bruker WM 400. The ultraviolet spectra and all quantitative UV–vis data were acquired on a Cary 17 or on a Beckman DB-GT spectrophotometer. The mass spectra were measured on a Varian MAT CH7. The elemental analyses were either carried out in house or were kindly run for us by Professor G. Maier's staff of the Universität Giessen. The half-wave reduction potentials were measured on a Princeton applied research polarograph Model 170, and the capacitance measurements for the dipole moments were acquired on a WTW dipole meter Model DM01.

Preparation of the Arylcarboethoxysemicarbazides. Into a 500-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a pressure-equalizing dropping funnel, and a reflux condenser, fitted with a $CaCl_2$ drying tube, was placed a solution of 0.15 mol of ethyl hydrazinecarboxylate in 250 mL of dry benzene. The solution was cooled by means of an ice bath, and 0.15 mol of the substituted phenyl isocyanate was added over a period of 45 min. After complete addition, the ice bath was removed and the mixture was stirred at ca. 20–25 °C for 2 h and then heated under reflux for 2 h. The suspension was allowed to cool to ca. 20–25 °C and the 4-substituted-1-carbethoxysemicarbazide collected on a Büchner funnel, washed with benzene, and dried at 100 °C and 10–15 torr. The observed physical constants matched those reported for the known semicarbazides.

Preparation of the 4-Arylurazoles. Into a 250-mL Erlenmeyer flask were placed 60 mL of 4 M aqueous potassium hydroxide and 0.10 mol of the corresponding 4-substituted-1-carbethoxysemicarbazide. The solution was warmed on a steam bath under magnetic stirring for 2 h, cooled, and acidified with concentrated hydrochloric acid until pH 2. The resulting precipitate was collected by suction filtration and dried at 70 °C and 10 torr for 3 h. The observed physical constants matched those reported for the known urazoles.

Preparation of the 4-Aryl-1,2,4-triazoline-3,5-diones. Into a 500-mL, round-bottomed flask were placed 200 mL of methylene chloride and 0.050 mol of the corresponding urazole together with 0.25 g of anhydrous sodium sulfate. The solution was cooled to 0 °C and dinitrogen tetraoxide (N_2O_4) was bubbled through at a moderate rate for ca. 30 min. The reaction mixture was filtered, the solvent roto-evaporated (20 °C and 10 torr), and the resulting colored product purified by sublimation at 110 °C and 0.1 torr. The observed physical constants matched those reported for the known triazolinediones. The data for the new ones are given below.

4-(*p*-Methylphenyl)-1,2,4-triazoline-3,5-dione. This substance was obtained in 51% yield (6.24 g, 33.0 mmol), mp 165–166 °C dec (red granular solid), in the reaction of 11.5 g (60 mmol) of 4-(*p*-methyl-

(21) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Mattes, S. L.; Farid, S. *Ibid.* **1982**, *15*, 80.
(22) Freeman, F. *Chem. Rev.* **1975**, *75*, 439.
(23) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.
(24) (a) Bettinetti, G. F.; Capretti, L. *Gazz. Chim. Ital.* **1965**, *95*, 33. (b) Ried, W.; Lim, S. H. *Liebigs Ann. Chem.* **1973**, 1141. (c) Bethäuser, W.; Regitz, M.; Theis, W. *Tetrahedron Lett.* **1981**, *22*, 2535. (d) Korobitsyna, I. K.; Rodina, L. L.; Lorkina, A. V. *Zh. Org. Khim.* **1982**, *18*, 1119–1120.
(25) Zürm, V.; Schwarz, W.; Rozdzinski, W.; Schmidt, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 81.
(26) (a) Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. (b) Schmid, G. H.; Garratt, D. G. *Tetrahedron Lett.* **1983**, *24*, 5299.
(27) Harding, L. B.; Goddard, W. A., III, *J. Am. Chem. Soc.* **1980**, *102*, 439.

phenyl)urazole with gaseous N_2O_4, according to the above procedure. ^1H NMR (CCl_4) (60 MHz) δ 2.50 (s, 3 H, CH_3), 7.4 (br s, 4 H, Ar); IR (KBr) ν 3040 (w), 2920 (w), 1850 (w), 1770 (s), 1519 (s), 1404 (s), 1196 (m), 1180 (m), 1160 (s), 1031 (m), 910 (m), 830 (m) cm^{-1}; vis (CH_2Cl_2) λ_{max} 540 nm, ϵ_{max} 139. Anal. Calcd for $C_9H_7N_3O_2$ (189.2): C, 57.14; H, 3.73; N, 22.21. Found: C, 56.90; H, 3.60; N, 22.14.

4-(*m*-(Trifluoromethyl)phenyl)-1,2,4-triazoline-3,5-dione. This substance was obtained in 80% yield (3.89 g, 16 mmol), mp 86–87 °C (red granular solid), in the reaction of 6.13 g (25 mmol) of 4-(*m*-(trifluoromethyl)phenyl)urazole with gaseous N_2O_4 according to the above procedure. ^1H NMR (CCl_4) (60 MHz) δ 7.6–7.9 (br s, 4 H, Ar); IR (KBr) ν 3100 (w), 1785 (s), 1770 (w), 1510 (m), 1470 (m), 1405 (m), 1340 (s), 1170 (s), 1140 (s), 1080 (m), 900 (m), 810 (m), 750 (s), 700 (s) cm^{-1}; vis (CH_2Cl_2) λ_{max} 540 nm, ϵ_{max} 160. Anal. Calcd for $C_9H_4F_3N_3O_2$ (243.1): C, 44.46; H, 1.66; N, 17.28. Found: C, 44.69; H, 1.67; N, 17.42.

Reaction of Triazolinedione (TAD) with Olefins. A 50-mL, round-bottomed flask was charged with 0.70 mmol of the olefin and 1.4 mmol of the TAD in 20 mL of methylene chloride. The reaction mixture was stirred magnetically at 20 °C until disappearance of the characteristic red color of the TAD (ca. 48 h). 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) using methylene chloride as eluant. Final purification of the rearranged urazoles for analytical samples was achieved by repeated fractional recrystallization from ethanol. The observed physical constants matched those of the reported rearranged urazoles. Urazole **12** is a new compound and its data are described below.

***N*-Phenyl-9,10-bis(methoxycarbonyl)-2,3-diazapentacyclo-[6.4.0.0^{4,12}.0^{5,7}.0^{6,11}]dodeca-2,3-dicarboximide (12).** Urazole **12** was obtained in 58% yield (1.00 g, 2.36 mmol), mp 249–250 °C (whilte plates from ethanol), in the reaction of 1.00 g (4.03 mmol) of dimethyl *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-dien-7,8-dicarboxylate (**11**) with 1.00 g (5.71 mmol) of PTAD in 30 mL of 1,1,2,2-tetrachloroethane at 80 °C for 48 h. ^1H NMR ($CDCl_3$) (400 MHz) δ 1.2 (br q, $J_{1,7}$ = 1 and $J_{5,7}$ = $J_{6,7}$ = $J_{7,8}$ = 6.5 Hz, 1 H, H_7), 1.6 (m, $J_{6,7}$ = 6.5 and $J_{5,6}$ = $J_{6,11}$ = 4.5 Hz, 1 H, H_6), 1.9 (m, $J_{5,7}$ = 6.5, $J_{5,6}$ = 4.5, and $J_{4,5}$ = 3.5 Hz, 1 H, H_5), 2.7 (br q, $J_{1,12}$ = 7 and $J_{4,12}$ = $J_{11,12}$ = 6 Hz, 1 H, H_{12}), 2.8 (m, $J_{11,12}$ = 6, $J_{6,11}$ = 4.5, $J_{10,11}$ = 3.5, and $J_{7,11}$ = 0.5 Hz, 1 H, H_{11}), 3.0 (br d, $J_{7,8}$ = 6, $J_{8,9}$ = 1.5, and $J_{1,8}$ = 1 Hz, 1 H, H_8), 3.08 (dd, $J_{9,10}$ = 10.5 and $J_{8,9}$ = 1.5 Hz, 1 H, H_9), 3.34 (dd, $J_{9,10}$ = 10.5 and $J_{10,11}$ = 3.5 Hz, 1 H, H_{10}), 3.68 (s, 3 H, CO_2Me), 3.72 (s, 3 H, CO_2Me), 4.8 (br d, $J_{1,12}$ = 7 and $J_{1,7}$ = $J_{1,8}$ = 1 Hz, 1 H, H_1), 4.87 (dd, $J_{4,12}$ = 6 and $J_{4,5}$ = 3.5 Hz, 1 H, H_4), 7.3–7.6 (m, 5 H, ArN). ^{13}C NMR ($CDCl_3$) (100.61 MHz) δ 14.35 (d), 19.87 (d), 21.99 (d), 30.94 (d), 36.12 (d), 40.49 (d), 43.75 (d), 44.68 (d), 52.05 (q), 52.17 (q), 56.84 (d), 61.20 (d), 125.36 (d), 127.91 (s), 129.03 (d), 132.15 (s), 154.39 (s), 154.75 (s), 171.95 (s), 173.65 (s); IR (KBr) ν 3040 (m), 3010 (m), 2980 (w), 2960 (m), 1750 (s), 1710 (s), 1500 (m), 1410 (s), 1350 (m), 1280 (m), 1225 (m), 1200 (m), 1030 (m), 935 (m), 760 (m), 745 (m) cm^{-1}; MS (70 eV) *m/e* 423 (100%, M^+), 392 (8%, M^+ - OMe), 364 (3%, M^+ - CO_2Me), 304 (3%, M^+ - PhNCO), 214 (14%), 129 (36%), 128 (15%), 119 (21%, $PhNCO^+$), 115 (11%), 91 (16%), 59 (14%, CO_2Me^+). Anal. Calcd for $C_{22}H_{21}N_3O_6$ (423.4): C, 62.41; H, 5.00; N, 9.92. Found: C, 62.37; H, 4.84; N, 9.92.

Product Balance in the Cycloaddition of MTAD with Benzonorbornadiene (14). Calibration curves were prepared for the authentic MTAD and urazole **4** by integrating their respective *N*-methyl resonances (sharp singlets at δ 3.04 and 3.08 at 60 MHz) of separate stock solution in $CDCl_3$ ranging from 0.070 to 0.130 M in concentration. Linear plots between peak height (in cm) of the *N*-methyl singlets and concentration (in M) of each substance were obtained, whose slopes were respectively 19.7 ± 0.2 cm/M (r = 0.998) and 21.3 ± 0.2 cm/M (r = 0.997) for MTAD and urazole **4**. Separate stock solutions of 87.8 mg (0.78 mmol) of MTAD and 110 mg (0.78 mmol) of benzonorbornadiene (**14**) each in 3 mL of spectrograde $CDCl_3$ was prepared in a 3-mL volumetric flask and 0.5 mL of each stock solution pipetted into a NMR tube. At the beginning of the reaction the peak area of the *N*-methyl singlet at δ 3.04 of the MTAD was integrated, affording a value of 2.50 ± 0.10 cm (average of four independent measurements). At the end of the reaction (ca. 10 h) the peak area of the *N*-methyl singlet at δ 3.08 of the urazole **4** was integrated, affording a value of 2.50 ± 0.10 cm (average of four independent measurements). From the authentic calibration curves the respective concentrations of MTAD and urazole **4** were extrapolated to be 0.129 and 0.117 M, corresponding to a ca. 91% yield of urazole **4**.

A similar determination of the product balance for the reaction of norbornene (**16**) with MTAD gave an ca. 50% yield of urazole **5**. The remainder was undefined polymeric product.

Kinetics. The ^1H NMR rates were run under equimolar conditions of the MTAD and olefin by monitoring simultaneously the disappearance of the *N*-methyl singlet of the MTAD at δ 3.04 and the appearance of the *N*-methyl singlet of the urazole at δ 3.08. For this purpose equimolar stock solutions of the MTAD and olefin were prepared in $CDCl_3$ and 0.5 mL of each stock solution pipetted into the NMR tube. The tube was placed into a constant temperature bath adjusted to 40.0 ± 0.2 °C by means of a Colora Ultrathermostat K5 and periodically (ca. 30-min intervals) transferred after cooling to 0 °C into the probe of the Bruker HFX 90 spectrometer, which was kept at 0 °C. The relative concentrations of disappearing MTAD and appearing urazole were monitored in terms of their respective peaks areas of the *N*-methyl singlets by means of electronic integration. Each peak area was integrated at least three times. The rate profiles of relative peak heights (relative concentrations) vs. time followed second-order kinetics. The second-order rate constants (k_2) are summarized for MTAD and the olefins **14** and **16** in Table I.

Table VI. Dipole Moment Data of Benzonorbornadiene (14), Urazole 4, and PTAD in Benzene at 25 °C[a]

substrate	$(\Delta\epsilon/\gamma)_\infty$	$(\Delta d/\gamma)_\infty$	$P_{2\infty}$, mL mol^{-1}	R_D, mL mol^{-1}	μ_D,[a] D
14	6.827 ± 0.034	0.239	53.4	45.5	0.62
4	11.210 ± 0.010	1.086	240.0	82.9	2.8
PTAD	12.033 ± 0.039	0.703	215.3	45.5	2.9

[a] Accurate within 5% of listed value.

The spectrophotometric rates were acquired by monitoring the disappearance of the n,π^*-absorption maximum of the TAD in the visible region at ca. 525–540 nm. The rate profiles of absorbance vs. time were determined on a Cary 17 UV–vis spectrophotometer, equipped with a thermostated cell block, kept constant to within ±0.01 °C by means of a Colora Ultrathermostat K5. Matched cells of 1.0-cm path length were used. Before recording the rate profiles of absorbance vs. time on the chart-strip recorder, the sample was allowed to equilibrate for ca. 20 min.

For the second-order rates equimolar concentrations of the TAD and the olefin were prepared in the appropriate solvent, allowed to equilibrate at the appropriate temperature for 30 min, and equal aliquots pipetted directly into the thermally equilibrated cell. The rate profile followed typical second-order kinetics. The second-order rate constants are given for PTAD and the olefins **14** and **16** in Table I.

For the pseudo-first-order rates stock solutions of the olefin and TAD in a 50:1 molar ratio were prepared in the appropriate solvent, thermostated at the appropriate temperature, and equal aliquots pipetted into the thermostated cell. The rate profile followed typical pseudo-first-order kinetics. The second-order rate constants for the various TADs and olefins in the various solvents at the various temperatures are collected in Tables I–V.

Cyclic Voltammetry. The half-wave reduction potentials of the TADs were determined by cyclic voltammetry. Platinum was the working electrode and Ag/AgCl/CH_3CN the reference electrode. Solutions in acetonitrile at 0.01–0.02 M in the TAD and 0.02–0.04 M in tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte were prepared and the reversible cyclic voltammograms recorded. The E_{pc} - E_{pa} and (i_{pa}/i_{pc}) values were 97 (1.0), 90 (1.0), 100 (0.9), and 140 (1.0) for *p*-methylphenyl-, phenyl-, *m*-trifluorophenyl-, and *p*-nitrophenyl-substituted triazolinediones, respectively.

Dipole Moments. For the determination of the dipole moments, the simplified Debye equation[28] was used (eq 10), where μ is the dipole moment in Debye, $P_{2\infty}$ the molar polarization, and R_D the molar refraction. In benzene as solvent, the molar polarization is given by eq

$$\mu = 0.01281[(P_{2\infty} - R_D)T]^{1/2} \quad (10)$$

11, where M_2 is the molecular weight of the compound for which the dipole moment is to be measured, $(\Delta\epsilon/\gamma)_\infty$ the slope of the dielectric constant of the medium vs. the molar fraction function, and $(\Delta d/\gamma)_\infty$ the slope of the density of the medium vs. the molar fraction function. For

$$P_{2\infty} = 14.710(\Delta\epsilon/\gamma)_\infty + 0.3413M_2 - 30.55(\Delta d/\gamma)_\infty \quad (11)$$

the determination of the $(\Delta\epsilon/\gamma)_\infty$ values different solutions of the substrate in question were prepared in benzene (ϵ 2.2726) and the dielectric constants of these solutions measured at 25 °C. For each substrate about five independent measurements were carried out. The plots of dielectric constant vs. molar fraction gave excellent straight lines. For the determinations of the $(\Delta d/\gamma)_\infty$ values the densities of each of the above solutions were measured at 25 °C by means of a pycnometer. For each substrate ca. five points were taken, resulting in good straight lines. The molar refractions (R_D) were calculated from the literature values.[28] In

(28) Hedestrand, G. *Z. Phys. Chem., Abt. B* **1929**, *2*, 428.

Table VI the experimental data are summarized for benzonorbornadiene (**14**), urazole **4**, and PTAD.

Control Experiments. Thermal Stability of Urazole 30: A 50-mg (0.24 mmol) sample of urazole **30** was sublimed at 0.1 torr through a hot tube kept at ca. 400 °C. The urazole **30** was recovered unchanged.

Acetone Trapping: A sample of 0.30 g (2.10 mmol) of benzonorbornadiene (**14**) was allowed to react with 0.37 g (2.1 mmol) of PTAD in 50 mL of absolute acetone as solvent at ca. 30 °C for 3 days. Only rearranged urazole **4** was detected as product.

Galvinoxyl Trapping: A sample of 0.20 g (2.0 mmol) of norbornene (**16**) was allowed to react with 0.15 g (0.86 mmol) of PTAD in the presence of 0.15 g (0.36 mmol) of galvinoxyl in 30 mL of methylene chloride at ca. 25 °C. Only rearranged urazole **5** was detected as product.

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Multiply Bonded Dimetal Complexes Containing Bis(diphenylphosphino)methane Bridges: Complexes Possessing Rhenium–Rhenium Double Bonds and a Tungsten–Tungsten Single Bond

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Abstract: The quadruply bonded dirhenium(III) complex $(n\text{-}Bu_4N)_2Re_2Cl_8$ reacts with bis(diphenylphosphino)methane (dppm) in dichloromethane to produce the complex $Re_2Cl_6(dppm)_2$ (I). The structurally analogous complex $Re_2Cl_6(Ph_2Ppy)_2$ (II) has been isolated from the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and Ph_2Ppy in acetonitrile. When primary alcohols (ROH) are used as solvents, $(n\text{-}Bu_4N)_2Re_2Cl_8$ reacts with dppm to form the alkoxide complexes $Re_2Cl_5(OR)(dppm)_2$ (R = CH_3, IIIa; R = CH_2CH_3, IIIb; R = $CH_2CH_2CH_3$, IIIc). When the quadruply bonded complex $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ is used in place of $(n\text{-}Bu_4N)_2Re_2Cl_8$, then the reaction with dppm in methanol yields $Re_2Cl_4(dppm)_2$, while with diethyl ether as the solvent $Re_2Cl_5(dppm)_2$ is formed. All of the preceding complexes exhibit well-defined electrochemical properties. Electrolysis of dichloromethane solutions of $Re_2Cl_4(dppm)_2$, containing an excess of Cl^-, at a potential of +0.60 V vs. SCE first generates $Re_2Cl_5(dppm)_2$, which is in turn converted to $Re_2Cl_6(dppm)_2$. This potential (+0.60 V) is sufficient to oxidize $Re_2Cl_4(dppm)_2$ to its monocation and, following the conversion of the latter to $Re_2Cl_5(dppm)_2$ upon its reaction with Cl^-, also to convert $Re_2Cl_5(dppm)_2$ to $[Re_2Cl_5(dppm)_2]^+$, which in turn reacts with Cl^-. The complexes I and IIIb have been structurally characterized by X-ray crystallography and shown to have structures which conform to the notion that these molecules possess rhenium–rhenium double bonds as predicted by Hoffmann. Using the bidentate ligand bis(diphenylphosphino)amine (dppa), we have prepared the complexes $Re_2Cl_6(dppa)_2$, $Re_2Cl_4(dppa)_2$, and $Re_2Cl_4(PMePh_2)_2(dppa)$ and the $[ReCl_2(dppa)_2]^+$ cation (either as the Cl^- or PF_6^- salt). The spectroscopic and electrochemical properties of the dirhenium species show a very close similarity to those of their dppm analogues, implying a close similarity of structure. To further explore the influence of replacing a terminal Cl ligand by OR on the M–M bond length we have also examined the structure of $W_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_6Cl_2$ and compare it with that of $W_2(\mu\text{-}OEt)_2(OEt)_4Cl_4$. Again the OR for Cl replacement causes a lengthening of the M–M bond. $Re_2Cl_6(dppm)_2$ crystallizes in the monoclinic space group $C2/c$ with cell parameters a = 23.083 (3) Å, b = 10.866 (3) Å, c = 23.253 (5) Å, β = 124.25 (2)°, Z = 4. The structure of $Re_2Cl_5(OC_2H_5)(dppm)_2$ was solved and refined in the orthorhombic space group $Pn2_1a$ with cell parameters a = 24.099 (8) Å, b = 18.225 (4) Å, c = 12.565 (4) Å. $W_2(O\text{-}i\text{-}Pr)_8Cl_2$ forms monoclinic crystals in space group $C2/m$ with a = 17.706 (4) Å, b = 12.034 (2) Å, c = 9.727 (2) Å, β = 123.74 (2)°, Z = 2.

Four important types of substitution reactions that can occur in the reaction chemistry of the octahalodirhenium(III) anion, $[Re_2X_8]^{2-}$, are as follows: (1) simple substitution where the quadruple bond is retained; (2) nonreductive substitution where the multiple bond is retained but is reduced to an order lower than 4; (3) reductive substitution where the multiple bond is retained but is of an order lower than 4; and (4) substitution where complete disruption of the metal–metal bond occurs. Tertiary phosphine complexes, in particular, comprise some of the best defined and most thoroughly studied examples of these types of substitution reactions.[2]

Recently we renewed our interest in the nature of the substitution products that arise when bidentate bridging ligands are used because of the range of interesting derivatives that are formed upon reacting the $[Re_2Cl_8]^{2-}$ anion with the Ph_2Ppy ligand.[3] One such derivative was of stoichiometry $[ReCl_3(Ph_2Ppy)]_n$ and was isolated from the reaction of $[Re_2Cl_8]^{2-}$ with Ph_2Ppy in acetonitrile.[3b] Its spectroscopic and electrochemical properties indicated that it bore a close structural relationship to the previously reported

(1) (a) Purdue University. (b) Texas A&M University.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; and references therein.

(3) (a) Barder, T. J.; Tetrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 4090. (b) Barder, T. J.; Cotton, F. A.; Powell, G. L.; Tetrick, S. M.; Walton, R. A. *Ibid.* **1984**, *106*, 1323.

0002-7863/84/1506-2882$01.50/0