Table V. Physical Properties of Di- and Monoalkylated Products 2 and 5

compd	mp, °C	IR (KBr) ν_{CN}, cm^{-1}	^{1}H NMR ($CDCl_3$/Me_4Si), δ	microanalysis found (calcd)		
				C	H	N
2a	59–60	2220	0.82 (t, J = 5 Hz, 6 H), 1.0–1.6 (m, 16 H), 1.7–2.6 (m, 6 H), 6.1–7.1 (br m, 1 H), 7.1–7.7 (m, 3 H), 8.0–8.4 (br m, 1 H)	for $C_{23}H_{33}N_3$ 78.82 (78.58)	9.35 (9.46)	12.07 (11.95)
2b	116–117	2230	1.20 (s, 6 H), 1.6–2.4 (m, 6 H), 7.00 (br s, 1 H), 7.38 (s, 3 H), 8.12 (br s, 1 H)	for $C_{15}H_{17}N_3$ 75.12 (75.28)	7.10 (7.16)	17.60 (17.56)
2c	220–221	2230	1.75 (br s, 6 H), 2.50 (d, J = 13 Hz, 2 H), 2.79 (d, J = 13 Hz, 2 H), 7.24 (s, 5 H)	for $C_{27}H_{25}N_3$ 83.07 (82.83)	6.53 (6.44)	10.62 (10.73)
2d	119–120	2230	1.50–2.10 (m, 6 H), 2.15 (d, J = 7 Hz, 4 H), 4.98 (dd, J = 17, 2 Hz, 2 H), 5.15 (dd, J = 9, 2 Hz, 2 H), 5.36–6.15 (m, 2 H), 7.10 (br s, 1 H), 7.20–7.70 (br m, 3 H), 8.24 (br s, 1 H)	for $C_{19}H_{21}N_3$ 78.38 (78.32)	7.25 (7.26)	14.42 (14.42)
5c	179–180	2225	1.40–2.30 (m, 6 H), 2.52 (d, J = 13 Hz, 1 H), 3.00 (d, J = 13 Hz, 1 H), 4.28 (br s, 1 H), 7.05–8.00 (m, 10 H)	for $C_{20}H_{19}N_3$ 79.70 (79.70)	6.38 (6.35)	13.88 (13.94)
5d	104–105	2220	1.35–2.70 (m, 6 H), 2.27 (d, J = 7 Hz, 2 H), 4.22 (br s, 1 H), 5.01 (dd, J = 18, 2 Hz, 1 H), 5.10 (dd, J = 8, 2 Hz, 1 H), 5.35–6.0 (m, 1 H), 7.20–7.75 (m, 5 H)	for $C_{16}H_{17}N_3$ 76.49 (76.46)	6.84 (6.82)	16.53 (16.72)

acetate (0.646 g, 3.3 mmol) dissolved in a solution of 20 mL each of dioxane and water was warmed to 50 °C for 2.5 h. After the mixture was filtered, the solution layer was extracted with diethyl ether (3 × 20 mL). The ether layer was dried with anhydrous sodium sulfate. After the ether was distilled off, the residue was purified by means of column chromatography. Thus, 6,10-pentadecanedione (**3a**) was obtained in 94% yield (0.268 g): mp 68.0–68.5 °C; IR (KBr) ν_{CO} 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_3Si, 60 MHz) δ 0.90 (t, J = 5 Hz, 6 H), 1.1–1.6 (br m, 12 H), 1.6–2.1 (m, 2 H), 2.39 (t, J = 6 Hz, 4 H), 2.43 (t, J = 6 Hz, 4 H). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.80; H, 11.54.

2,6-Heptanedione (3b). By the same procedure, the hydrolysis of **2b** (0.241 g, 1.0 mmol) using ethanol (20 mL) and cupric sulfate (0.749 g, 3.0 mmol) instead of dioxane and cupric acetate, respectively, was carried out to give **3b** (0.095 g, 74% yield): colorless oil (lit.[9] mp 29–32 °C). The ^{1}H NMR spectrum agreed with that reported in the literature.[9]

1,7-Diphenyl-2,6-heptanedione (3c). By the same procedure, the hydrolysis of **2c** (0.791 g, 2.0 mmol) using 20 mL each of dioxane and ethanol, and cupric sulfate (0.999 g, 4 mmol) was carried out to give **3c** (0.520 g, 93% yield): mp 41.5–42.5 °C; IR (KBr) ν_{CO} 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 1.72 (pent, J = 6 Hz, 2 H), 2.37 (t, J = 6 Hz, 4 H), 3.57 (s, 4 H), 7.20 (br s, 10 H). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.50; H, 7.17.

(IV) Preparation of α,β-Unsaturated Cyclohexenones 4 by Hydrolysis. The typical procedure is as follows: A mixture of **2a** (0.342 g, 1.0 mmol) dissolved in a solution of 10 mL of THF and 5 mL of 15% aqueous hydrochloric acid was gently refluxed for 26 h and then extracted with diethyl ether (3 × 20 mL). The ether layer was washed with brine and dried with anhydrous sodium sulfate. After the solvent was distilled off, the residue was purified by means of column chromatography. Thus, **4a** was obtained in 100% yield (0.215 g): colorless oil; IR (neat) ν_{CO} 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 0.92 (t, J = 5 Hz, 6 H), 1.11–1.68 (m, 10 H), 1.70–2.58 (m, 10 H). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.90; H, 11.58.

3-Methyl-2-cyclohexenone (4b). By the same procedure, the hydrolysis of **2b** (0.566 g, 2.4 mmol) was carried out. However, **4b** is volatile and is isolated as its 2,4-dinitrophenyl hydrazone: After the hydrolysis was done, the reaction solution was neutralized with sodium hydrogen carbonate, and then to the reaction solution was added a mixture of 2,4-dinitrophenylhydrazine (0.961 g, 4.85 mmol) dissolved in a mixture of sulfuric acid (4 mL), water (6 mL), and 95% ethanol (6 mL). The solution was stirred for 24 h at room temperature. The hydrazone was extracted with benzene (100 mL) and purified by means of column chromatography. Thus, the 2,4-dinitrophenyl hydrazone of **4b** was obtained in 62% yield (0.426 g): mp 179–180 °C (lit.[10] mp 175 °C).

3-Benzyl-2-phenyl-2-cyclohexenone (4c). By the same procedure with the case of **4a**, the hydrolysis of **2c** (0.743 g, 1.9 mmol) was carried out to give **4c** (0.498 g, 100% yield): mp 117–118 °C; IR (KBr) ν_{CO} 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 1.54–2.20 (m, 2 H), 2.29 (t, J = 6 Hz, 2 H), 2.47 (t, J = 6 Hz, 2 H), 3.42 (s, 2 H), 6.90–7.50 (m, 10 H). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.69; H, 6.90.

Registry No. *cis*-**1a**, 98217-26-6; *trans*-**1a**, 98217-27-7; *cis*-**1b**, 98217-28-8; *trans*-**1b**, 98217-29-9; *cis*-**1c**, 98195-08-5; *trans*-**1c**, 98217-30-2; **2a**, 98217-31-3; **2b**, 98217-32-4; **2c**, 98217-33-5; **2d**, 98217-34-6; **3a**, 22633-24-5; **3b**, 13505-34-5; **3c**, 97388-62-0; **4a**, 98217-35-7; **4b**, 1193-18-6; **4b** (2,4-dinitrophenylhydrazone), 3234-76-2; **4c**, 98217-36-8; **5c**, 98217-37-9; **5d**, 98217-38-0; glutaraldehyde, 111-30-8; aniline, 62-53-3; *p*-anisidine, 104-94-9; benzylamine, 100-46-9; *n*-amyl bromide, 110-53-2; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; *trans*-stilbene, 103-30-0.

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The Electronic Structure of Triazolinediones. Photoelectron Spectroscopic Investigations[†]

Rolf Gleiter* and Wolfgang Schäfer

Institut für Organische Chemie der Universität Heidelberg,
Im Neuenheimer Feld 270, D-6900 Heidelberg,
West Germany

Heinrich Wamhoff

Institut für Organische Chemie und Biochemie der
Universität Bonn, D-5300 Bonn 1, West Germany

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The *N*-alkyl-or *N*-aryltriazolinediones are probably the most reactive dienophiles available today.[1a] Besides this high dienophilicity they also react with various olefins,[1b] acetylenes,[1c] and electron-rich π-systems.[1d] Furthermore a strong selectivity in proper model systems like propellanes has been observed.[2] The sequence of the frontier orbitals as well as the ionization energies of triazolinediones are useful in judging their reactivity and selectivity. To

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[†] Dedicated to Professor David Ginsburg on the occasion of his 65th birthday.

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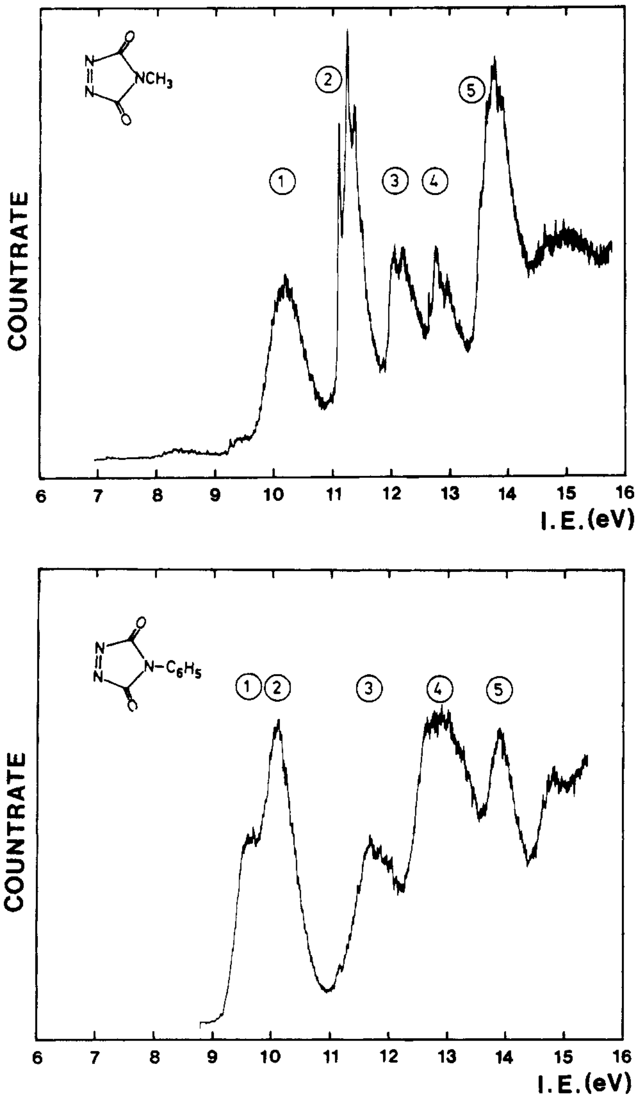


Figure 1. He I PE spectra of 1 and 2.

Table I. Vertical Ionization Energies ($I_{v,j}$) of *N*-Methyltriazolinedione 1 and *N*-Phenyltriazolinedione 2 with Assignments

compd	band	$I_{v,j}$ eV	assignment
1	1	10.19	n^-_{NN}
	2	11.23	π
	3	12.1	n^+_O
	4	12.8	n^-_O
	5	13.5–14.2	π_{NN} n^+_{NN}
2	1	9.63 (sh)	n^-_{NN}
	2	9.8–10.3	π,π,π
	3	11.6–12.1	
	4	12.5–13.2	
	5	13.8	

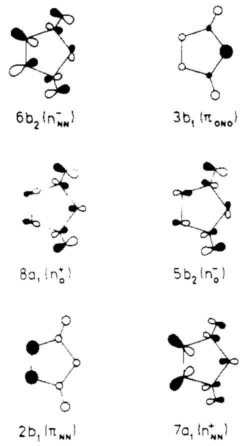


Figure 2. Schematic drawing of the highest occupied MO's of 1.

Table II. Calculated Orbital Energies of 1 (in eV)

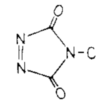
$\Gamma^{a,c}$	$\Gamma^{b,c}$	$-\epsilon$ (MNDO)	$-\epsilon$ (INDO)	$-\epsilon$ (STO-3G)	6 31G
$6b_2$	8a″ (n^-_{NN})	11.22	10.93	8.56	11.72
$3b_1$	13a′ (π_{ONO})	11.67	11.47	9.14	12.27
$8a_1$	12a′ (n^+_O)	13.28	12.67	11.82	14.86
$5b_2$	7a″ (n_O^-)	14.65	13.33	16.11	14.95
$7a_1$	11a′ (n^+_{NN})	15.07	14.99	14.07	16.88
$2b_1$	10a′ (π_{NN})	14.23	14.28	12.51	17.06

[a] The irreducible representation for the parent compound, triazolinedioine. [b] The irreducible representation for *N*-methyltriazolinedione 1. [c] Only the valence electrons are considered.

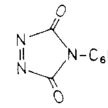
Table III. Geometrical Parameters Adopted for the Triazolinedione Ring in 1 and 2 (in Å)

bond	1	2
N(1)-N(2)	1.19	1.22
N(2)-C(3)	1.45	1.49
C(3)-N(4)	1.40	1.42
C(3)-O	1.20	1.21
N(4)-C	1.43	1.43

provide the sequence of the highest occupied molecular orbitals together with the corresponding energy values, we have recorded the He I photoelectron (PE) spectra of 4-methyl- and 4-phenyltriazolinedione 1 and 2 and assigned their first bands.



1



2

PE Spectra. In Figure 1 the PE spectra of both compounds are shown and in Table I the first vertical ionization energies are listed. In the spectrum of 1 we can recognize five bands nicely separated from each other. The first one shows a Gaussian shape and the second one a steep onset with vibrational fine structure. Bands 3 and 4 are less intense than band 2 but also show finer structure. From intensity arguments we assign one transition to bands 1–4 but two to band 5. The PE spectrum of 2 is less structured; we find a shoulder at the low energy side of a relatively broad intense band around 10 eV well separated from two further broad bands around 11.6 and 12.5 eV. To assign the first bands of the spectra we proceed in two ways: We either correlate the bands with calculated orbital energies or compare them with the spectra of related species.

MO Calculations. To assign the spectra we assume that we can describe the various ionic states observed by ground-state wave functions. This allows us to set equal the measured vertical ionization energy ($I_{v,j}$) of the state

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Table IV. Calculated Orbital Energies of 2 (in eV)

$-\epsilon$ (MNDO)[a]	Γ[b]	$-\epsilon$ (STO-3G)[a]	Γ[b]
9.90	$8b_1$ (π_{Ar})	7.42	$16b$ (n^-_{NN})
10.00	$2a_2$ (π_{Ar})	8.16	$16a$ (π_{Ar})
11.28	$7b_1$ (n^-_{NN})	8.68	$15b$ (π_{ONO})
11.57	$8b_2$ (π_{ONO})	9.86	$14b$ (π_{Ar}–n^-_O)
13.10	$11a_1$ (n^+_O)	11.59	$15a$ (n^+_O)
13.23	$6b_1$ (π_{Ar})	12.28	$13b$ (π_{NN})

[a] For the MNDO calculations a twist angle between the triazoline and the phenyl rings of $\theta = 90°$ has been adopted. For the HF STO-3G calculations θ was 45°. [b] Only the valence orbitals are considered

j with the calculated negative value of the orbital energy (ϵ_j) (Koopmans' theorem[3]). In Table II we have listed the results of two semiempirical calculations (MNDO,[4] INDO[5]) and Hartree–Fock ab initio calculations using the STO-3G and 6-31G basis set[6] on 1. The ab initio results on 1 are based on geometrical parameters derived by the MNDO method by minimizing all geometrical parameters with respect to its heat of formation ($\Delta H_f° = -29.56$ kcal/mol). The bond lengths obtained for 1 are listed in Table III. All three methods used agree in so far as they predict the same orbital sequence for the three highest MO's. The HOMO is predicted to be the antibonding linear combination of the nitrogen lone pairs (see Figure 2). The following MO is of π-type strongly localized on the imide nitrogen as shown in Figure 2. The third MO from top is predicted to be the in phase (n_+) linear combination of the 2p orbitals of the carbonyl oxygen atoms.

The assignment for the first three bands seems also reasonable if we use qualitative band shape criteria. The Gaussian shape of the first band is typical for the n_- linear combination in cyclic azo compounds.[7,8] The steep onset of the second band favors a weakly bonding π-orbital.

For 2 the assignment of the peaks to individual transitions is not only hampered by a strong overlap of bands but also due to the uncertainty of the dihedral angle between the phenyl ring and the triazolinedione moiety. To estimate the bond lengths we have used the MNDO method[4] and minimized all geometrical parameters with respect to its heat of formation. This procedure predicts a dihedral angle θ of 90° between the two ring moieties ($\Delta H_f° = 2.79$ kJ/mol). Using the MNDO parameters (see Table III), we have carried out Hartree–Fock (HF) ab initio calculations on 2 using the STO-3G basis set.[6] By variation of the dihedral angle between the two ring moieties a minimum at 45° is predicted. In Table IV we have listed the MO sequence obtained for 2 with the MNDO method adopting $\theta = 90°$ and with the STO-3G basis set adopting $\theta = 45°$. As anticipated from the previous section the orbital sequences differ considerably: The MNDO method predicts two π-MO's of the aromatic ring on top of three MO's mainly localized on the triazoline moiety. In contrast, the HF ab initio calculations predict the lone-pair combination at the N atoms on top of three π-MO's, two of which are localized on the aromatic ring. We favor the latter sequence n_- on top of π-MO's (see Table I), arguing that the phenyl ring shifts the HOMO of 1 toward higher orbital energies (lower ionization energies) as experienced in many examples. A comparison between the differences in calculated orbital energies for 1 (Table II) and measured ionization energies reveals that the split between n^-_{NN} and π_{ONO} (1.0 eV) is strongly underestimated by MNDO (0.4 eV) and the other methods used; thus the predicted orbital sequence for 2 by the MNDO method has to be taken with care.

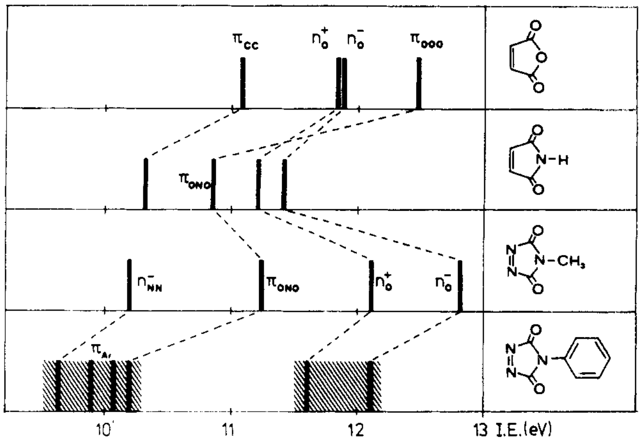
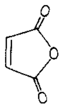


Figure 3. Correlation between the first bands of the PE spectra of 1–4.

Correlation with Related Species. To assign the sequence of the higher bands in the PE spectra of 1 and 2 empirically we compare their bands with those of the PE spectra of maleic anhydride (3), maleic imide (4), and five-membered azo compounds as shown in Figure 3. The comparison with 3 and 4 should give us an estimate of those MO's arising from the lone-pair combinations on the carbonyl oxygens.



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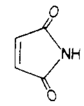

4

Adopting the assignment of Kimura et al. for the PE spectrum of 3,[9] we are able to correlate the PE spectrum of 4 with that of 3. The smaller electronegativity of N (3.0) compared to that of O (3.5)[10] together with an electron-donating effect of the N–H bond[11] allows us to rationalize the strong lowering of the π-MO localized at the anhydride or imide group, respectively. Replacing the CC double bond by the NN double bond will cause a lowering of all MO's (rising of all ionization energies). Thus bands 3 and 4 should be correlated with the two lone-pair combinations n^+_O and n^-_O as shown in Figure 3.

What remains is the assignment of the in-phase linear combination of the nitrogen lone pairs and the π-MO localized at the azo bridge. To assign the corresponding MO's we make use of the investigations of a number of five-membered rings containing the azo group.[8] It is reported that the split $I_v(n_+) - I_v(n_-)$ is about 3 eV and that the π band is relatively close to the n_+ band. If we adopt

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these findings to our problem we estimate $I_v(n_+) \simeq I_v(\pi_{NN}) = 13.2$ eV. This calculation favors the assignment of band 5 in the PE spectrum of **1** to ionizations from n^+_{NN} and π_{NN} as indicated in Table I. The correlation given in Figure 3 confirms the assignment of the first ionic states of **1** and **2** given in Table I. It furthermore strengthens the impression that the orbital sequence predicted by the MNDO calculations on those heterocycles with a large number of heteroatoms has to be taken with great care.

Experimental Section

The PE spectra of **1** and **2** have been recorded with a PS 18 instrument of Perkin-Elmer Ltd. (Beaconsfield, England) and were calibrated with Ar. A resolution of about 20 meV of the $^2P_{3/2}$ Ar line was obtained. The samples had to be heated to the following temperatures: **1**, 45 °C; **2**, 95 °C.

Both compounds were prepared according to the literature.[12]

Acknowledgment. We are grateful to A. Flatow for recording the PE spectra. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen, for financial support.

Registry No. **1**, 13274-43-6; **2**, 4233-33-4.

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Diels–Alder and Ene Reactions of 4-Substituted 1,2,4-Triazoline-3,5-diones and Some Substituted Styrenes

Yu-Chin Lai, Shadpour E. Mallakpour, and
George B. Butler*

Center for Macromolecular Science and Engineering and Department of Chemistry, University of Florida, Gainesville, Florida 32611

Gus J. Palenik

Center for Molecular Structure and Department of Chemistry, University of Florida, Gainesville, Florida 32611

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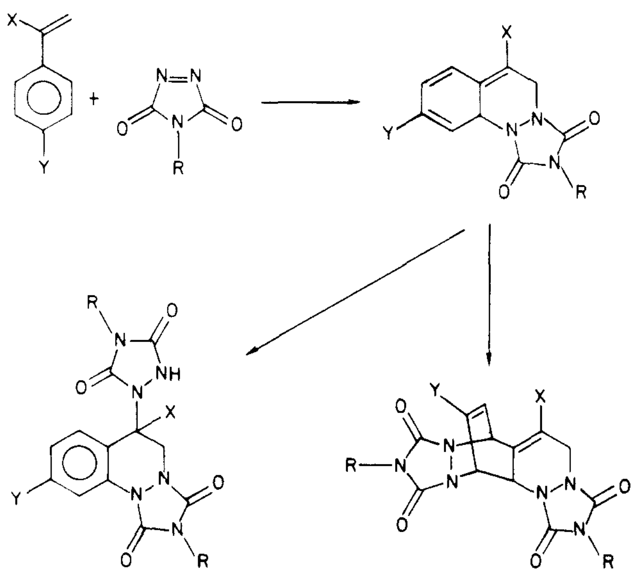
Introduction

Although PhTD (4-phenyl-substituted 1,2,4-triazoline-3,5hdione) has been reported to be one of the most reactive dienophiles[1] and enophiles,[2] only the DA (Diels–Alder) reactions have been extensively investigated. However, in a study of the ene reactions of PhTD with a series of substituted alkenes, bicycloalkanes as well as bicycloalkenes have been reported recently.[3]

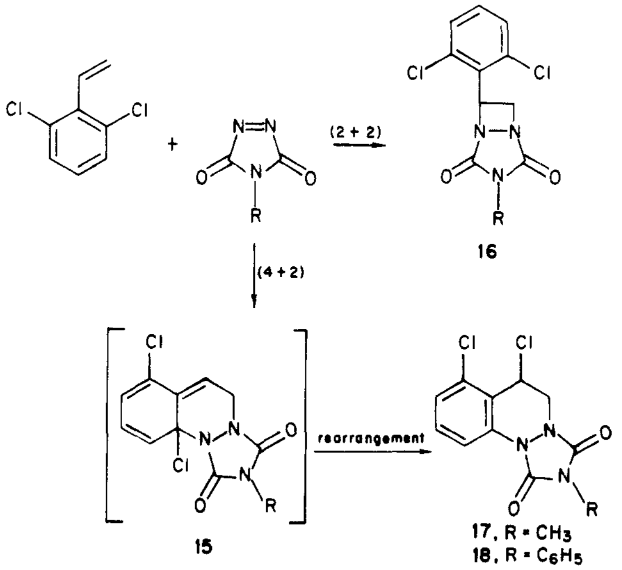
The reaction of PhTD and styrene at room temperature was reported to give a dDA adduct,[4] **1** (Scheme I).

Scheme I



R = C_6H_5	R = CH_3		R = C_6H_5	R = CH_3
2	**4**	X = H; Y = H	**1**	**3**
6	**8**	X = H; Y = Cl	**5**	**7**
9	**10**	X = H; Y = *t*-Bu		
11	**12**	X = CH_3; Y = H		
13	**14**	X = H; Y = NO_2		

Scheme II



However, a reinvestigation of this reaction demonstrated that the DAe (Diels–Alder ene) adduct, **2**, was the predominate product in a 2:1 ratio.[5] The reaction of MeTD (4-methyl-substituted 1,2,4-triazoline-3,5-dione) with styrene also gives a 1:2 ratio of the dDA (double Diels–Alder) adduct, **3**, and the DAe adduct, **4**. Although an initial DA adduct is a reasonable intermediate, no such product has been isolated. This investigation was undertaken to isolate an initial DA adduct.

In addition, a systematic study of the reactions of PhTD and MeTD with some α- and para-substituted and 2,6-disubstituted styrenes was undertaken. In the case of 2,6-dichlorostyrene we have demonstrated by an X-ray crystal structure study that the product is not the reported

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