Photoaddition of Aliphatic Ethers to 4-Methyl-1,2,4-triazoline-3,5-dione: Application to the Synthesis of Functionalized Crown Ethers and Mechanism

Florence Risi,[a] Ana-Maria Alstanei,[b] Elena Volanschi,[b] Micheline Carles,[a] Louis Pizzala,[a] Jean-Pierre Aycard*[a]

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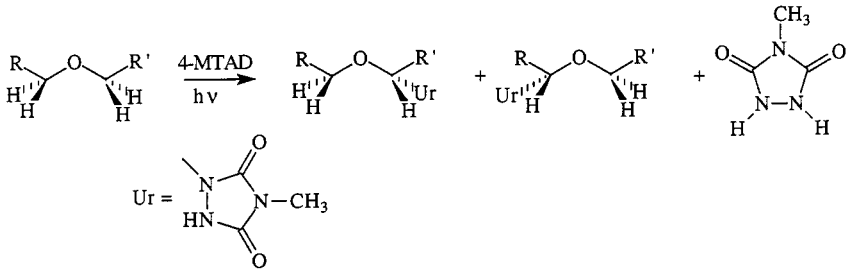
The photoaddition of 4-methyl-1,2,4-triazoline-3,5-dione (4-MTAD) with a wide variety of acyclic, cyclic and crown aliphatic ethers has been investigated. Monochromatic (λ = 514.5 nm) or polychromatic ($\lambda \geq 310$ nm) irradiations give identical mono-urazolyl ethers as reaction products. Unsymmetrical acyclic ethers afford a mixture of the two α and α′ mono-urazolyl ethers. In the case of 12-crown-4, mono and di-substituted products are obtained. ESR experiments and quantum calculations at the AM1 and 6–31G* levels were performed and a possible reaction mechanism is proposed in which the most probable photochemical process is the H-abstraction leading to a urazolyl radical.

Introduction

4-Substituted-1,2,4-triazoline-3,5-diones (4-RTAD) are cyclic electron deficient azo compounds that readily react thermally with olefinic[1–6] and dienic[7–9] sites. As such they have been employed as intermediates in the synthesis of a wide variety of heterocyclic systems. Furthermore, they exhibit rather unique and fascinating photochemical properties. However, the photochemical reactivity of 4-RTAD has been less investigated than their thermal processes.[10–12] These compounds undergo self-reaction to yield triazolo-[1,2a]-s-triazole,[10] deaza dimers[11] and polymers.[13] They decompose photochemically to yield carbon monoxide, nitrogen and isocyanate.[10–12] Photolysis performed in argon matrices has led to the formation of aziridine-2,3-dione transients.[14] Reactions with benzene,[15] naphthalene[16] and phenanthrene[17] give ($4\pi + 2\pi$) photoadducts. Hall[18] found that polyalkoxybenzenes react with 4-RTAD to give aromatic substitution products. However, the rate constant was found to be dependent on the exposure time of 4-RTAD solution to normal laboratory light. Photoreaction with simple aliphatic ether compounds has been reported only briefly in the literature. Wamhoff and Wald[10] previously reported that 4-RTAD (R = Ph) compounds add aliphatic ethers photochemically and thermally to give substituted urazoles. In the latter case, THF and dioxane give even better yields of the addition products. Moreover, the search for ligands that exhibit selectivity for specific metal ions is a major field of research[19] and therefore much effort has been focused on the development of macrocyclic ethers that are able to complex selectively the alkali and alkaline earth cations.[20–22]

The aims of the present work were to study the photochemical addition reaction of aliphatic ethers to 4-methyl-1,2,4-triazoline-3,5-dione (4-MTAD) (see Scheme 1), to examine its generality and to use it in the synthesis of functionalized crown ethers. Quantum calculations and ESR experiments were performed to furnish theoretical and experimental support for the proposed reaction mechanisms.



Scheme 1. Photochemical reaction of aliphatic ethers with 4-MTAD

Results

The formulas of the compounds are represented in Scheme 2. Irradiation of the red 4-MTAD solutions leads

[a] UMR CNRS 6633 – Physique des Interactions Ioniques et Moléculaires, Equipe de Spectrométries et Dynamique Moléculaire, Université de Provence,
Case 542, F-13397 Marseille Cedex 20, France
[b] Department of Physical Chemistry, University of Bucharest, Bdul Republicii, Bucharest, RO-7034, Romania

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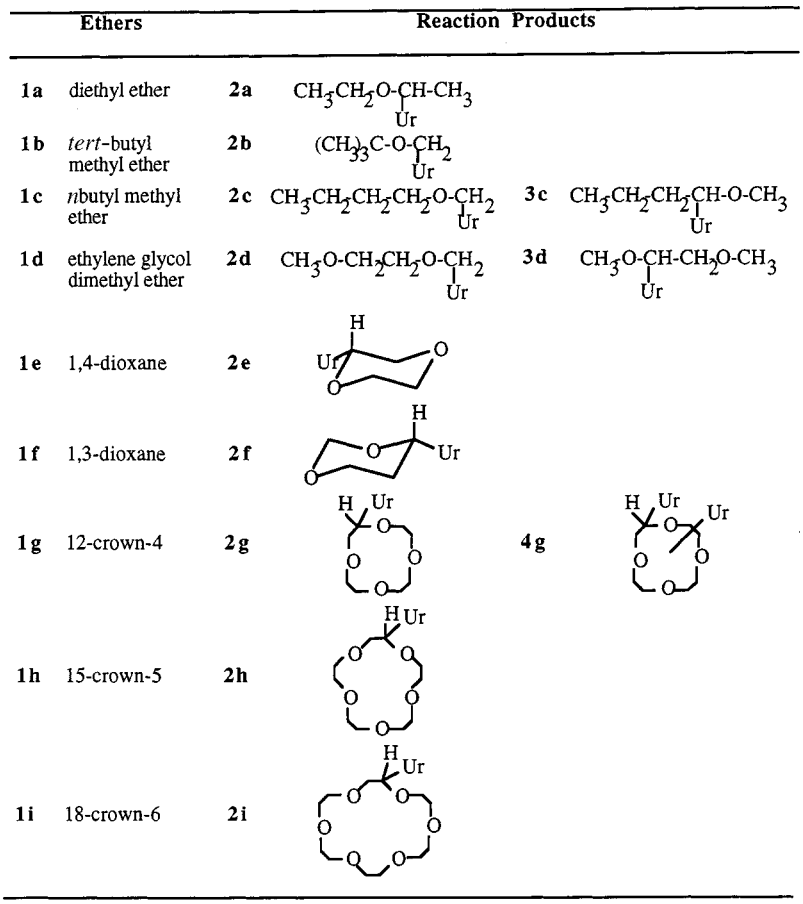


Scheme 2. Formula of ethers and reaction products

to a faster decolorization in pure ethers than in corresponding solutions in CCl_4. The colorless reaction mixtures were purified by column or thin layer chromatography (see Experimental Section) after solvent evaporation. In all cases, with the exception of the reaction with 12-crown-4 (**1g**), the major and frequently the only product isolated from the reactions of simple aliphatic ethers are the α-urazolyl ethers. These compounds are obtained by the replacement of a hydrogen atom on the functionalized carbon. Small amounts of methyl urazole were also obtained as an alternative reaction product (less than 10%). Experimental conditions and reaction results are summarized in Table 1. It is significant to note that unsymmetrical acyclic ethers such **1c** and **1d** give a mixture of the two α and α' urazolyl ethers in a ratio showing that 4-MTAD abstracts a hydrogen atom more readily from methylene than from methyl groups (see Table 1).

In the case of 1,3-dioxane (**1f**) the 2-position is unaffected by the reaction as is the case for the methylene groups of trioxane, which do not react with 4-MTAD under monochromatic or long wavelength irradiations. Most of the reaction products are solid and readily characterizable materials. Identifications of these compounds was established by ^1H, ^{13}C and IR spectroscopies and also by comparison with data found in the literature.[10] Assignments of ^1H and ^{13}C chemical shifts (see Table 2) are based on conventional

Table 1. Addition of 4-methyl-1,2,4-triazoline-3,5-dione to aliphatic ether compounds: reaction conditions, products, and yields

Ethers	Reaction conditions	Products (mp, ratio)	Yield, % reaction
1a	40 min[a]	**2a** (93–94)	68
1b	1 h[a]	**2b** (78–80)	82
1c	16 h[a]	**2c** (20%) + **3c** (80%)	59
1d	3 h[a]	**2d** (40%) + **3d** (60%)	–
1e	3 h[b]	**2e** (170)	97
1f	17.5 h[b]	**2f** (158–160)	–
1g	2 d[b]	**2g** (104–106, 99%) + **4g** (210–215, 1%)	96
1h	3 d[b]	**2h** (72)	25
1i	3 d[b]	**2i** (oil)	87

[a] With lamp, $\lambda \geq 310$ nm. – [b] With laser, $\lambda = 514.5$ nm.

NMR experiments (see Experimental Section). In the ^1H-NMR spectra, two sets of signals are generally observed for the protons in the α and β positions of the urazolyl substituent. The α protons are identified in the range $\delta = 4.90$–5.71. The signals of the β protons are observed in the ranges $\delta = 1.40$–1.60 and $\delta = 3.40$–4.04 for the CCHβ CUr and OCHβCUr moieties respectively. The characteristic singlet of the *N*-methyl group is always observed at around $\delta = 2.90$–3.00 as in *N*-methyl urazole ($\delta = 3.05$). In the ^{13}C-NMR spectra, the appearance of two carbonyl carbon res-

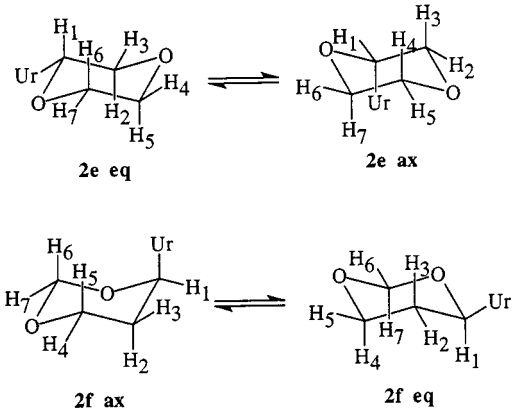
Table 2. Chemical shifts of the characteristic ^{1}H- and ^{13}C-NMR signals of the addition compounds

$\delta^{[a]}$		Compounds **2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**3c**	**3d**	**4g**
N–CH_3	^{1}H	3.05	2.88	3.02	3.05	2.89	2.90	3.05	3.00	2.98	3.03	3.05	2.90
	^{13}C	25.2	24.6	25.1	24.4	24.7	24.7	25.1	24.9	24.7	25.0	25.1	24.8
–CHα-Ur	^{1}H	5.38	4.79	4.90	4.97	5.09	5.37	5.71	5.42	5.30	5.10	5.27	5.34
	^{13}C	82.4	69.2	75.8	71.2	79.3	80.9	83.8	82.8	83.4	86.5	84.5	84.1
–CHβ	^{1}H	1.41	–	–	–	3.63	1.60	3.80	3.71	3.78	1.50	3.63	3.48
								3.89	3.75	4.04			3.70
C=O	^{13}C	153.4	153.3	153.5	153.4	154.5	154.4	153.5	153.1	153.6	153.2	154.2	153.9
		155.2	153.8	155.8	154.6	154.6	–	154.2	153.2	153.8	154.8	154.8	154.2

[a] δ values in ppm, referred to TMS. The other chemical shifts are given in the Experimental Section.

onances suggested the unsymmetrical structure of the urazolyl moiety.

The ^{1}H coupling constant values of derivatives **2e** and **2f** (see Scheme 3) are obtained from LAOCOON[23] analysis (see Table 3). The data agree with a chair structure in which the urazolyl group lies in an equatorial position.



Scheme 3. Conformational equilibrium of **2e** and **2f**

Table 3. Coupling constants (Hz) of **2e** and **2f**

	J_{12}	J_{13}	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{46}	J_{47}	J_{56}	J_{57}	J_{67}
2e	9.3	2.8	11.4	–	–	–	–	–11.6	2.7	1.0	11.0	2.5	–11.9
2f	2.6	11.6	–12.2	2.0	1.4	12.2	4.9	–11.5	–	–	–	–	6.5

Compound **4g** is the only disubstituted product obtained in our experiments. The small number of observed resonances in its ^{1}H- and ^{13}C-NMR spectra (only seven signals) is consistent with a symmetrical 1,3- or 1,7-disubstitution pattern even though we could not determine its *cis*- or *trans*-stereochemistry.

Analysis of the major reaction products indicates that the investigated photoaddition reaction is in fact a reductive addition to the –N=N double bond, i.e. a photoreduction similar to the photoreductive reactions of carbonyl compounds.[24] This reaction supposes the urazolyl radicals to be reactive intermediates and would explain the formation of α-substituted ethers as major reaction products. This mechanism is also similar to the previously observed H-atom abstraction by *tert*-butoxyl from a variety of cyclic and acyclic ethers.[25,26]

ESR and MO calculations were performed to identify the reaction intermediates and to confirm the mechanism.

ESR Experiments

Two kinds of ESR experiments were performed: (1) irradiation of MTAD in the solid state (powder) or in solution in different solvents, at both room and low temperatures, and (2) the use of spin-trapping, in order to provide evidence for transient radical species in solution, at room temperature.

(1) Examination of the powder spectra indicates a weak ESR signal centered at g = 2.0052 even before irradiation, i.e. laboratory light exposure is sufficient to obtain a small amount of radicals. This signal increases with the irradiation time in the first 90 minutes at room temperature, this increase being less marked at low temperatures. If the irradiation is performed on diethyl ether solutions at 77 K, the increase of the intensity of the ESR signal with the irradiation time is much more rapid, as shown in Figure 1. These statements are compatible with the formation of urazolyl radicals, as already pointed out by Wamhoff and Wald.[10] However, an ESR signal could not be detected at room temperature in solutions, not only in diethyl ether but also in a wide variety of solvents (dichloromethane, acetonitrile, tetrahydrofuran, diisopropyl ether), as reported for PTAD by different authors.[1,10,27] It was therefore concluded that the methyl urazolyl radical is much too reactive in solution at room temperature to be studied directly by ESR.

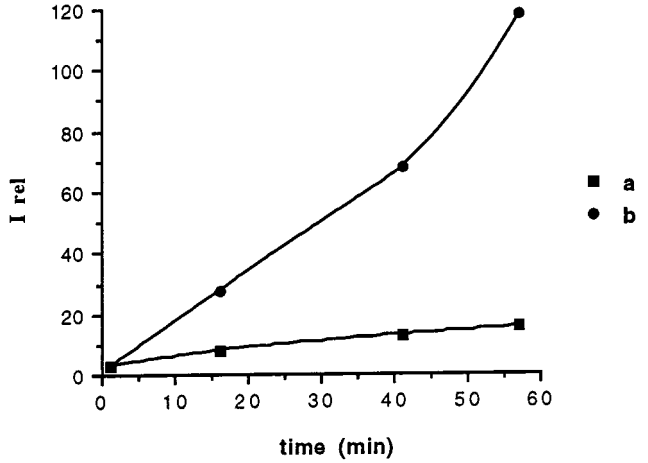


Figure 1. Relative intensity of the ESR signal vs the irradiation time (min): (a) MTAD powder, room temperature; (b) MTAD diethyl ether, 77 K. The experimental conditions used were: 100 kHz modulation frequency microwave power 0.4 mW, modulation amplitude 0.05–0.5 mT; irradiations were performed outside the ESR cavity at room temperature or 77 K and inside the cavity at 15 K, using a 100-W high-pressure Hg lamp.

The single radical species that is stable enough to be investigated by ESR spectroscopy in solution, at room temperature, is the anion-radical, which is proposed as the intermediate in the thermal reaction of MTAD leading to the deazadimer by Borhani and Greene.[11] In the conditions described in this paper the anion-radical was obtained by reduction with *tert*-butoxide in DMSO and identified by comparison with the literature data.[28] It is worth noting that the same spectrum was obtained with KOH in DMSO, i.e. the anion-radical of MTAD may be obtained by electron transfer in the presence of a nucleophile and is stabilised in highly polar solvents such as DMSO.

(2) As no urazolyl radicals were evidenced from MTAD at room temperature in solvents, spin-trapping experiments were performed using 5,5-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (DMPO) as a spin trap.

Mixing a solution of MTAD in different solvents (CH_2Cl_2, diethyl ether, THF) with DMPO led to a rapid disappearance of the color and to an intense ESR spectrum (see Figure 2) characterized by the parameters reported in Table 4. This spectrum is compatible with a spin adduct with an N-centered radical, the hyperfine splitting constants (hfs) of which vary little with the solvent. No other adduct or radical species was detected. The structure of the spin adduct, i.e. the fact that urazolyl radicals are trapped rather than any other N-centered radical species resulting from a cleavage of the MTAD molecules, was verified by the spectral analysis of the reaction product. The IR and NMR spectra agree with the formation of a single reaction product, corresponding to the structure **5**, and so **6** is the structure assigned to the spin adduct (see Scheme 4), which confirms the existence of urazolyl radicals in the MTAD solutions at room temperature. The reaction between 4-*R*-1,2,4-triazoline-3,5-diones with DMPO was investigated[29] and the results were rationalised in terms of a reaction sequence in which the spin adduct is formed by a modified version of the Forrester–Hepburn mechanism.[30]

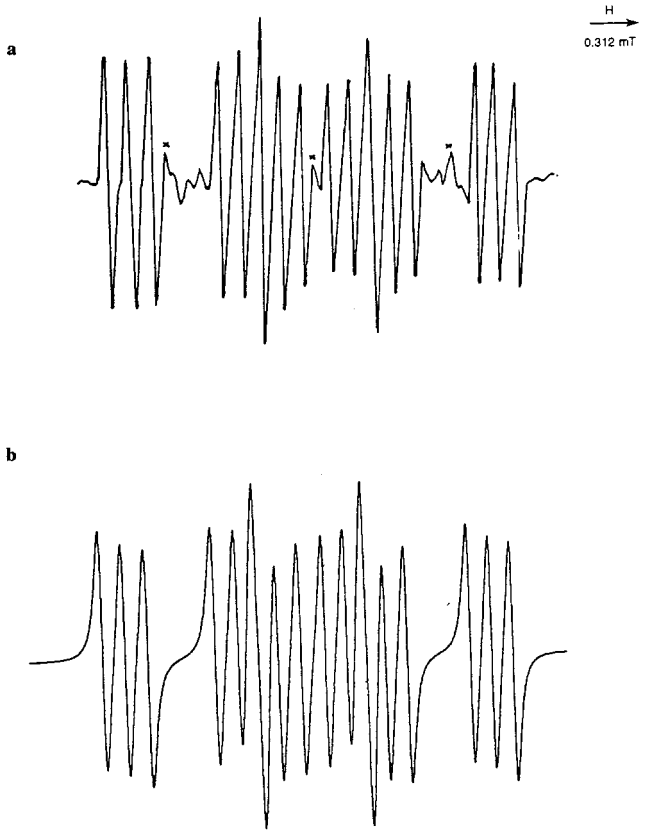
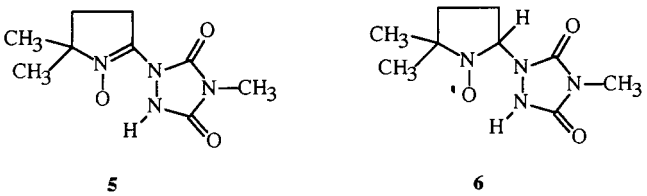


Figure 2. ESR spectrum of the spin adduct of MTAD with DMPO in diethyl ether recorded on a spectrometer in the X-band frequency, using potassium peroxylamine disulfonate as a marker (aN = 1.3 mT, g = 2.0055): (a) experimental (the marked lines belong to an unidentified nitroxide radical); (b) simulated with the hfs constants in Table 4

Table 4. ESR parameters of the spin adducts with DMPO in different solvents

	ESR parameters				
Solvents	g factor	a_N^{NO} (mT)	a_H (mT)	a_N (mT)	δ (mT)
CH_2Cl_2	2.0057	1.380	1.89	0.284	0.094
$(C_2H_5)_2O$	2.0059	1.342	1.86	0.281	0.078
THF	2.0059	1.345	1.84	0,278	0.077



5 **6**

Scheme 4. Structure of spin adduct **5** and the reaction product **6**

MO Calculations

AM1 Results

The AM1-optimised geometries in the fundamental and excited S_1 and T_1 states of MTAD (Table 5) indicate that

both excited states are practically planar, while in the ground state a dihedral angle of about 23° is obtained for the N atom in site 1. The similarity in geometry of both

Table 5. AM1-optimised geometries for MTAD in the ground (S_0) and excited (S_1 and T_1) states with and without solvent

	MTAD				
Parameters	S_0	$S_0(\varepsilon = 35)$	S_1	T_1	T_1 ($\varepsilon = 35$)
Bonds (Å)					
N_1–C_2	1.429	1.424	1.439	1.439	1.430
C_2–N_3	1.534	1.535	1.479	1.478	1.487
N_3–N_4	1.214	1.214	1.235	1.235	1.237
C_2–O_7	1.225	1.231	1.225	1.224	1.227
Angles (degrees)					
$N_1C_2N_3$	106.16	106.62	104.18	103.93	104.47
$N_4N_3C_2$	110.52	110.24	111.74	111.83	111.35
$C_8N_1C_2$	124.41	124.32	125.77	125.61	125.53
$O_7C_2N_3$	126.13	124.95	127.29	127.24	125.63
$C_8N_1C_2C_5$	–156.44	–155.22	–173.88	–173.97	–174.15

excited states has to be noted as well as the fact that the excitation does not alter the carbonyl regions, but rather the N–N and C–N bonds. Both excited states are almost pure single configurational states and correspond to an n-π* excitation, i.e. to the transition from an n-type sp^2 orbital, localised on the azo and the carbonyl groups, to a π* antibonding orbital as pointed out by Pocius and Yardley[31,32] on basis of Huckel MO calculations. The calculated excitation energy is slightly higher than the experimentally obtained value (18400–18700 cm^{-1}, 53–54 kcal·mol^{-1}) and smaller than most carbonyl-centered n-π* transitions, which are usually in the range 70–75 kcal·mol^{-1} (greater than 24000 cm^{-1}), with ΔE (S_1-T_1) of about 7–8 kcal·mol^{-1} (3000 cm^{-1}). The character of the n-π* excitation is best outlined by examination of the last occupied MO's in both S_1 and T_1 states (see Figure 3), and results in a decrease of the electronic density in the plane of the ring. If the reaction is an H-atom abstraction, which is supposed to proceed via free radical intermediates, these excited n-π* states will act as hydrogen abstractors due to the in-plane decrease of electron density. The charge distributions in both excited states are also similar. The evolution of bond orders (Table 6) evidences a weakening of the N=N and C=O bonds with a simultaneous strengthening of the C=N bonds, i.e. a higher weight of an –N=C–O^- type structure in the excited state. However, the variation of the calculated dipole moment in the excited in comparison with the ground state (Δμ = 0.80 D) suggests that no significant internal charge transfer occurs in the excited state. The effect of the aprotic polar solvents in the frame of the continuum dielectric model, with a dielectric constant of 35–46 (ACN-DMSO), indicates the stabilisation of both ground and excited states, the difference in energy remaining nearly the same (i.e. ΔE_{S0-S1} = 67 and ΔE_{S0-T1} = 59 kcal·mol^{-1}). The influence on the geometry is also insignificant. However, the charge distribution in both S_0 ad T_1 states is modified, implying a stronger polarisation of the C=O groups. The spin density charts were calculated for the radical species of MTAD. It may be

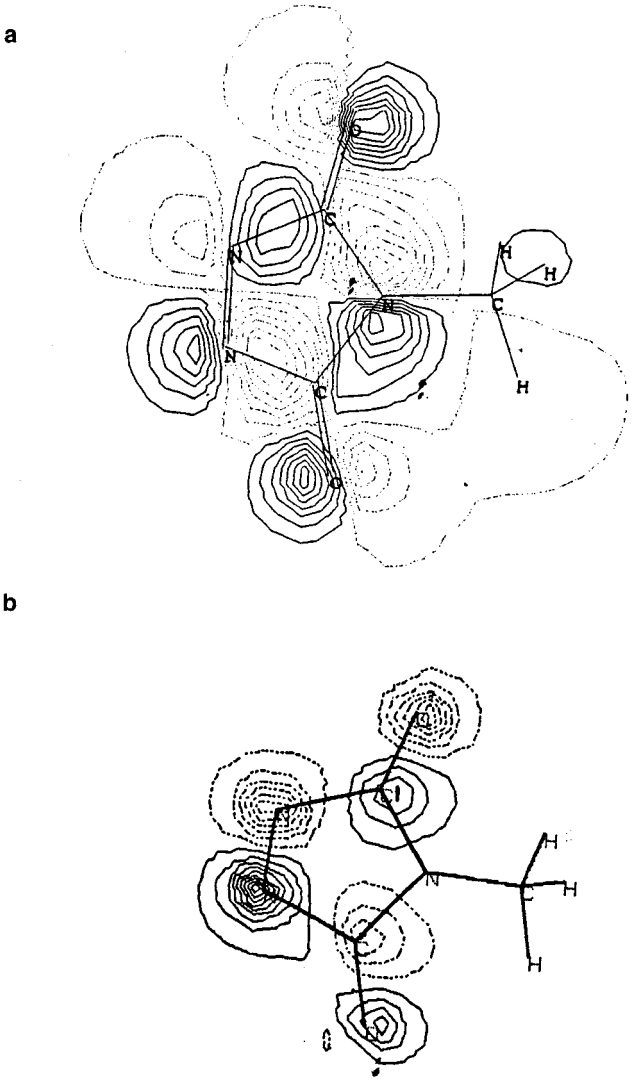


Figure 3. AM1-calculated last two occupied MO's of MTAD in the S_1 excited state: (a) $\varepsilon_{MO(21)}$ = –8.01 eV, (b) $\varepsilon_{MO(22)}$ = –5.21 eV. The distribution for the T_1 state is similar

Table 6. AM1-calculated bond orders, net atomic charges and dipole moments in the ground (S_0) and excited (S_1 and T_1) states for MTAD

	MTAD		
Parameters	S_0	S_1	T_1
Bond orders			
N_1–C_2	0.968	0.928	0.928
C_2–N_3	0.823	0.863	0.862
N_3–N_4	2.038	1.658	1.658
C_2–O_7	1.895	1.765	1.768
Net atomic charges			
N_1	–0.3520	–0.2933	–0.2952
C_2	0.2542	0.2623	0.2642
N_3	0.0051	–0.0601	–0.0614
O_6	–0.2116	–0.1881	–0.1872
μ (D)	2.42	3.22	3.22

observed that both species have a π-radical character; for the anion-radical a higher spin-density is predicted for the two equivalent nitrogen atoms, the unpaired electron being

Table 7. Ab initio-calculated parameters for the radical species: anion radical and urazolyl radical

	Anion radical			Urazolyl radical		
Energies (a. u.)	–389.4127565			–389.9680328		
Parameters	net total atomic charges	total atomic spin densities	Hfs (mT)	total atomic charges	total atomic spin densities	Hfs (mT)[a]
N_1	–0.8891	–0.0544	0.187	–0.8943	–0.0332	0.144
C_2	0.8907	–	–	1.0154	–	–
N_3	–0.4562	0.3785	0.487	–0.6263	0.1120	0.473
N_4	–0.4562	0.3785	0.487	–0.2231	0.8272	0.806
C_5	0.8907	–	–	0.9258	–	–
O_6	–0.6753	0.1856	–	–0.5044	0.3117	–
O_7	–0.6753	0.1856	–	–0.5659	0.0930	–
H_8	0.3707	–	–	0.4363	–	–
H_9	–	–	–	0.4365	–0.0148	0.659

[a] A. Alberti, G. F. Pedulli, *J. Org. Chem.* **1983**, *48*, 2544.

delocalised on the whole TAD ring, in agreement with the experimental hf splittings. For the urazolyl radical the highest spin-density is on the N(4)-atom, again in agreement with literature[27] hyperfine splitting constants (hfs) and attesting to the smaller degree of delocalisation of the single electron. This spin distribution accounts well for the higher reactivity of the urazolyl radical as compared to the anion-radical, in agreement with the ESR experiments performed.

Ab initio Results

The optimised geometries for both compounds are nearly planar (for urazole the ring is only slightly deformed) and maintain the C_{2v} symmetry, although not imposed, and are generally similar to those obtained with the AM1 results. However, shorter C–O and C–N bonds in both compounds, in comparison with the corresponding AM1 values, suggest a more conjugated structure in the ground state. Although not so reliable as the IP, as compared to the experimental data, the L.E.M.O. energy for the HTAD (S_0) state is 0.33 ev, a value in good agreement with that from the reduction potential determined experimentally by Bausch et al.[33] (+0.31V/NHE by cyclic voltammetry in DMSO) and suggesting the high reducibility of this molecule. The result of the first photochemical process is either the urazolyl radical, in the case of a hydrogen atom abstraction (case A), or the anion-radical of RTAD, in the case of an electron transfer from the ether (case B). Therefore the electronic structure of these intermediates is presented comparatively in Table 7. Correlation of the charge with the spin density distribution in the case of the anion-radical indicates a high contribution of a resonance formula with the unpaired electron on the nitrogen atoms, the negative charge being mainly located on the carbonyl oxygen atom. This is in agreement with the experimental hyperfine splittings and with the AM1 results. In the case of the urazolyl radical the unpaired electron is mainly delocalised on the nitrogen atom in site 4 and on the oxygen atom of the adjacent carbonyl group, which is in agreement with the literature experimental data.[27]

Discussion

The experimental results suggest a photoreduction/addition process with urazolyl radical intermediates (Scheme 5).

As MTAD was found to be a good spin trap for carbon- and metal-centered radicals,[27] the reaction of MTAD with the alkyloxy radicals to give substituted urazolyl radicals, which can further act as H-atom abstractors from the ether to give the reaction product, is also possible. Reaction (5) and the disproportionation reaction (6), which was found to be almost thermoneutral from analysis of bond energies,[33] would also account for the formation of methyl urazole as a secondary product. Although reaction (2), which leads to the major reaction product, seems to be of low probability, it must be inferred that the ether is also the solvent and so the reaction takes place in the solvent cage surrounding the urazolyl radical. If the electron transfer is the primary photochemical process (see Scheme 5, case B) this would lead to the formation of the anion-radical of MTAD and the cation-radical of the ether. We think that this process is less probable in our case for the following reasons:

(i) if the anion-radical of MTAD were the reactive intermediate then a radical anion chain mechanism would be operative, leading to deazadimer as a major reaction product, as pointed out by Borhani and Greene[11] for the thermal reactions of RTADs. In ethereal solvents (THF and dioxane) the deazadimer is formed in a proportion of 90–95% if the reaction is initiated by metallic sodium or sodium naphthalenide, but the reactivity of MTAD is found to be much lower than that of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). In acidic media (acetic acid) the main reaction product is the corresponding urazole, which is readily understood by the rapid protonation of the anion radical to the urazolyl radical, followed by further reduction. In none of these thermal reactions was the monosubstituted urazole the major reaction product, in contrast to the results obtained under our conditions;

(ii) if the electron transfer were the first step, it would be expected that PTAD would be more reactive in view of its

stronger electron-acceptor character (reduction potential +0.38V/NHE vs +0.31V/NHE for MTAD). However, in the reaction of PTAD with diethyl ether only 2% substituted urazole is obtained, the main reaction product being phenylurazole and the deazadimer, as is the case in the thermal reactions.[34]

From quantum calculations the decisive factors for the nature of the primary photochemical process are:

(i) the nature and charge distribution of the excited state of the reacting molecule;

(ii) the bond dissociation energy of the X–H bond to be cleaved;

(iii) the ionisation potential of the substrate.

If the first photochemical process is an H-atom abstraction (case A), the reactivity of a given spin multiplicity excited state varies in the order $k(\text{n-}\pi^*) > k(\pi\text{-}\pi^*) >> k(\text{CT})$.[24]

The MO calculations performed indicate the predominant (n-π*) character and the small contribution of the intramolecular charge transfer in both excited states of MTAD, as reflected by the charge distribution and the small increase of the calculated dipole moment in the excited state. It was also shown[24] that there is a rough correlation between the ionisation potential of the H-donor and the quenching rate of the n-π* excited state of a carbonyl compound, with the H-atom abstraction being predominant for saturated hydrocarbons and alcohols (high IP and moderate bond strengths) and the transfer charge interaction or the electron transfer being predominant for substrates with low IP and high H-bond strengths. Saturated ethers have high ionisation potentials and possess a fairly labile H-atom on the carbon atom α to the ether function, like alcohols, and it is known that abstraction of an H-atom from an alcohol is generally exothermic if the excitation energy is around 70 kcal·mol^{-1}. AM1 calculations for diethyl ether as a simple model compound give 10.39 ev for IP and a bond order of 0.953 for the α C–H bond as opposed to 0.974 for the other C–H bonds, and therefore H-atom abstraction seems more probable in this case. The AM1-calculated heats of formation have already been used to investigate the reactivity of different compounds (i.e. quinones) in electron and proton transfer reactions.[32] Generally, AM1-calculated heats of formation are reasonably close to the experimental values and therefore may be used to evaluate the energetics of the H-atom abstraction by excited MTAD from diethyl ether as a model compound. As both closed shell and open shell structures are implied, RHF values were employed for the former and both ROHF and UHF values were used for the radical species formed. It should be noted that UHF and ROHF calculated heats of formation are close, the UHF values being lower by 3–5 kcal·mol^{-1}. With the ROHF, the calculated values are: 12.11 kcal·mol^{-1} for Ur·, –35.66 kcal·mol^{-1} for the ether radical and –64.35 kcal·mol^{-1} for diethyl ether, and the calculated heats of formation for the excited states of MTAD (75.86 kcal·mol^{-1} for T_1 and 83.56 kcal·mol^{-1} for S_1), ΔH of –35 kcal·mol^{-1} and –43 kcal·mol^{-1} are obtained for the T_1 and S_1 states, respectively. Using the UHF calculated values (7.23 kcal·mol^{-1} for Ur·, –37.94 kcal·mol^{-1} for the ether radical) gives energy values of –42 and –50 kcal·mol^{-1} for the T_1 and S_1 states, respectively, proving that the H-atom abstraction reaction from diethyl ether by excited MTAD is exothermic. If the first photochemical step is an electron transfer (case B) decisive factors for this mechanism are the enhanced reducibility of MTAD in the excited state and the oxidation potential of the ether. Considering a Rehm–Weller formula,[35] ΔG^0 for the electron transfer (ET) from an electron donor to excited MTAD was calculated:

$$\Delta G^0 = E^0(D^+/D) - E^0(A/A^-) - \Delta E_{0,0} - C$$

where $E^0(D^+/D)$ is the oxidation potential of the donor (the ether), $E^0(A/A^-)$ is the ground state reduction potential of MTAD (0.31 V/NHE determined by cyclic voltammetry in DMSO) and $\Delta E_{0,0}$ is the energy of the first excited S_1 or T_1 states from which the reaction is supposed to take place. $\Delta E_{0,0}$ for the S_1 state was determined from the experimental n-π* transition (2.29 eV) for the T_1 state and a value of about 8 kcal·mol^{-1} lower was considered, as indicated by AM1 calculations and in agreement with data for other carbonyl compounds. Oxidation potential values for saturated ethers were taken from the literature (linear sweep voltammetry, ACN, vs an Ag/Ag^+ reference electrode[36] and corrected vs NHE by considering the potential of an $Ag/AgNO_3$ 0.1 M = 0.337 V/SCE, i.e. 0.578 V/NHE).[37] Thus, a value of 3.578 V/NHE was obtained. With these values in mind, and taking into account the electrostatic correction term for an average dielectric constant of 10 and a distance of 6 Å in the formed ion-pair (about –5.5 kcal·mol^{-1}), a ΔG^0 of 17 kcal·mol^{-1} was found for the S_1 and 24.6 kcal·mol^{-1} for the T_1 states of MTAD. A rough estimate of the state in the frame of this model shows that the electron transfer is too slow to compete with the other deactivation pathways of the excited states. As aliphatic ethers are very poor electron donors[38] this is very unlikely, and therefore we consider that in our case this mechanism is less probable than the H-atom abstraction reaction, in spite of the pronounced acceptor character of MTAD.

Conclusion

In summary, at $\lambda \geq 310$ nm and $\lambda = 514.5$ nm, 4-MTAD undergoes a photochemical addition reaction with a variety of aliphatic ethers to yield mono α-urazolyl derivatives, except with 12-crown-4. Analysis of the reaction products, as well as ESR experiments and quantum calculations, agree better with the radical mechanism initiated by an H-atom abstraction process than by electron transfer.

Experimental Section

Melting points are uncorrected. The identification of products was carried out by IR and NMR spectroscopy. The IR spectra were measured using KBr pellets. The ^{1}H- and ^{13}C-NMR spectra were

recorded with Bruker 400 MHz and 100 MHz instruments (FT mode), respectively, on $CDCl_3$ or [D_6]DMSO solutions at 25 °C. Chemical shifts were indirectly referenced to TMS using the solvent signals ($CDCl_3$, δ = 7.26 for ^1H and δ = 77.00 for ^{13}C; [D_6]DMSO, δ = 2.50 for ^1H and δ = 39.51 for ^{13}C). The coupling constants were obtained by first order analysis or by second order analysis with the LAOCOON program. The different types of carbon in the structures were identified by DEPT techniques.

The experimental conditions used for ESR spectroscopy were: 100 kHz modulation frequency microwave power 0.4 mW, modulation amplitude 0.05–0.5 mT. Irradiations were performed outside the cavity at room temperature and at 77 K, or inside the cavity at 15 K using a 100 W high-pressure Hg lamp.

ESR spectra of the spin-trapping experiments were recorded on a spectrometer in the X-band frequency, using potassium peroxylamine disulfonate as a marker (a_N = 1.3 mT, g = 2.0055).

The anion radical was obtained by reduction with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) and its ESR spectrum was simulated with two values of a_N (0.487 mT and 0.187 mT), a_{CH3} = 0.075 mT and a g factor of 2.0045.

MO Calculations: MTAD, methyl urazole, MTAD anion-radical, methyl urazolide anion and MTAD dianion ground (S_0) and excited (S_1 and T_1) states were calculated using the AM1 Hamiltonian in the AMPAC 2–19 program package.[39] The influence of the solvent on the electronic structure was considered in the frame of the COSMO model[40] implemented into AMPAC (option COSMO = ε, the dielectric constant of the solvent) based on the dielectric continuum model. The ab initio calculations were performed on model compounds containing H instead of a methyl group, with the GAUSSIAN-92 program package[41] using the Hartree–Fock model with the standard split valence 6–31G* basis set.[42]_[44]

Irradiation Techniques: Polychromatic irradiations were carried out using an Osram 200 W high-pressure mercury lamp equipped with a quartz envelope. The broad band was filtered at λ 310 nm. Monochromatic irradiations were performed using an ionized argon laser working at 514.5 nm, the maximum power being 500 mW.

Solvents were dried over 3-Å molecular sieves; dichloromethane and ethers were eluted through a 20 cm alumina (neutral) column to eliminate small quantities of hydrogen chloride or peroxides; commercial crown ethers were used without further purification.

The synthesis of 4-methyl-1,2,4-triazoline-3,5-dione (4-MTAD) by oxidation of 4-methyl urazole was described previously.[14,45] 4-MTAD was purified before use by two sublimations under high vacuum.

4-Methyl-1,2,4-triazoline-3,5-dione: Pink solid. m.p. 112±2 °C. – ^1H NMR ($CDCl_3$): δ = 3.05 (s, 3 H, N–CH_3). – ^{13}C NMR ($CDCl_3$): δ = 24 (1C, N–CH_3), 157 (2C, C=O). – IR (KBr): ṽ = 2966 (vw), 1782 (s, br), 1745 (s), 1540 (w), 1445 (m, br), 1392 (m), 1273 (m), 1101 (w), 1025 (vw), 952 (m), 739 (m), 673 (s, br), 626 (w), 554 (w) cm^{-1}. – UV (CH_2Cl_2) n π* λ_{max} = 535 nm (ε_{max} = 184 $mol^{-1}\cdot L\cdot cm^{-1}$), π p* λ_{max} = 290 nm (ε_{max} = 2000 $mol^{-1}\cdot L\cdot cm^{-1}$).

General Procedure: 4-MTAD was dissolved in the smallest amount of ether and the pink solution was exposed to either the UV light or the laser beam. The solution was decolorised and the solvent was evaporated under vacuum. In the case of expensive liquid ethers (**1c**, **1f**, **1g**, **1h**), 4-MTAD was added in 50 mg portions to the solvent until decolorization occurred. For solid ethers (**1i**) carbon tetrachloride was used as the solvent.

2-Urazolyl-3-oxapentane (2a): A pink solution of 300 mg (2.65 mmol) of 4-MTAD in 100 mL of diethyl ether (**1a**) was colorless after a 40 min irradiation period with the UV lamp. After vacuum evaporation of the solvent, the crude material was washed with chloroform to yield 339 mg (1.81 mmol, 68% yield) of white crystals: m.p. 93–94 °C. – ^1H NMR ($CDCl_3$): δ = 1.19 (t, 3 H, CH_3, J = 7 Hz), 1.41 (d, 3 H, CH_3, J = 6 Hz), 3.05 (s, 3 H, N–CH_3), 3.57 (m, 2 H, OCH_2, J = 9.8, 7 Hz), 5.38 (q, 1 H, OCHUr, J = 6 Hz), 8.50 (br s, 1 H, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.9 (CH_3), 18.7 (CH_3), 25.2 (N–CH_3), 64.4 (OCH_3), 82.4 (OCHUr), 153.4 (C=O), 155.2 (C=O). – IR: ṽ = 3172, 3054, 2968, 1760, 1685, 1496, 1113 cm^{-1}. – MS; *m/z:* 187 , 168, 142, 128, 115, 97, 85, 73, 58, 45, 31.

3,3-Dimethyl-1-urazolyl-2-oxabutane (2b): After a 1 h exposure period (UV-lamp) the pink solution of 500 mg of 4-MTAD (4.42 mmol) in 100 mL of *tert*-butylmethyl ether was colorless. Vacuum evaporation of excess ether yielded 727 mg (3.62 mmol, 82%) of crude product, whose spectral data are consistent with structure **2b**: m.p. 78–80 °C. – ^1H NMR ([D_6]DMSO): δ = 1.17 (s, 9 H, 3 CH_3), 2.88 (s, 3 H, N–CH_3), 4.79 (s, 2 H, OCH_2Ur), 9.00 (br s, 1 H, NH). – ^{13}C NMR ([D_6]DMSO): δ = 24.6 (N–CH_3), 27.6 (CH_3), 69.2 (OCH_2Ur), 73.9 [$C(CH_3)_3$], 153.3 (C=O), 153.8 (C=O). – IR: ṽ = 2975, 1766, 1695, 1485, 1093 cm^{-1}. – $C_8H_{15}N_3O_2$ (185): calcd. C 47.76, H 7.46, N 20.90; found C 47.91, H 7.87, N 21.06.

1-Urazolyl-2-oxahexane (2c) and 3-Urazolyl-2-oxahexane (3c): To a flask containing 5.58 g (63.4 mmol) of *n*-butylmethyl ether (**1c**) was added, with continuous magnetic stirring and under UV irradiation, 1.11 g (9.8 mmol) of 4-MTAD in 50 mg portions (each portion was added after the pink coloration of the preceding portion had disappeared). Complete addition required a 16 h irradiation. After the usual treatment, 1.158 g (5.76 mmol, 59%) of a crude oil was obtained and the ^1H-NMR spectrum shows evidence for a 1:4.5 mixture of **2c** and **3c**. – **2c:** ^1H NMR ($CDCl_3$): δ = 0.86 (t, 3 H, CH_3, J = 7.4 Hz), 1.50 (m, 4 H, CH_2–CH_2), 3.02 (s, 3 H, N–CH_3), 3.55 (t, 2 H, OCH_2), 4.90 (s, 2 H, OCH_2Ur), 10.10 (br s, 1 H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3), 19.0 (CH_2), 25.1 (N–CH_3), 31.2 (CH_2), 69.3 (OCH_2), 75.8 (OCH_2Ur), 153.5 (C=O), 155.8 (C=O). – **3c:** ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3, J = 7.4 Hz), 1.50 (m, 4 H, CH_2–CH_2), 3.05 (s, 3 H, N–CH_3), 3.30 (s, 3 H, OCH_3), 5.10 (t, 1 H, OCHUr, J = 6.7 Hz), 10.10 (br s, 1 H, NH). – ^{13}C NMR ([D_6]DMSO): δ = 13.4 (CH_3), 17.8 (CH_2), 25.0 (N–CH_3), 34.4 (CH_2), 56.2 (OCH_3), 86.5 (OCHUr), 153.2 (C=O), 154.8 (C=O). – IR (**2c** + **3c**): ṽ = 3082, 2940, 2825, 1772, 1697, 1485, 1110 cm^{-1}.

1-Urazolyl-2,5-dioxahexane (2d) and 3-Urazolyl-2,5-dioxahexane (3d): A solution of 500 mg (4.42 mmol) of 4-MTAD in 100 mL of ethylene glycol dimethyl ether was decolorized after a 3 h exposure period to the UV radiation. Evaporation of the solvent under vacuum gave a mixture whose ^1H-NMR spectrum shows a 2:3 ratio of the substitution products **2d** and **3d**. – **2d:** ^1H NMR ($CDCl_3$): δ = 3.05 (s, 3 H, N–CH_3), 3.33 (s, 3 H, OCH_3), 3.54 (m, 2 H, OCH_2, J = 2.5 Hz), 3.76 (m, 2 H, OCH_2, J = 6.3 Hz), 4.97 (s, 2 H, OCH_2Ur). – ^{13}C NMR ($CDCl_3$): δ = 24.4 (N–CH_3), 58.5 (OCH_3), 63.3 (OCH_2), 67.9 (OCH_2), 71.2 (OCH_2Ur), 153.4 (C=O), 154.6 (C=O). – **3d:** ^1H NMR ($CDCl_3$): δ = 3.05 (s, 3 H, N–CH_3), 3.33 (s, 3 H, OCH_3), 3.36 (s, 3 H, OCH_3), 3.54 (m, 1 H, OCH_2, J_{AB} = 10.3, J_{AX} = 4.2 Hz), 3.63 (m, 1 H, OCH_2, J_{BX} = 6.1 Hz), 5.27 (dxd, 1 H, OCHUr). – ^{13}C NMR ($CDCl_3$): δ = 25.1 (N–CH_3), 56.6 (OCH_3), 59.4 (OCH_3), 71.5 (OCH_2), 84.5 (OCHUr), 154.2 (C=O), 154.8 (C=O). – IR: ṽ (C=O) = 1773 and 1701 cm^{-1}. – IR (**2d** + **3d**): ṽ = 3099, 2951, 2875, 1770, 1703, 1481, 1090 cm^{-1}.

– $C_7H_{13}N_3O_4$ (203): calcd. C 41.38, H 6.40, N 20.69; found C 41.20, H 6.00, N 20.41.

2-Urazolyl-1,4-dioxane (2e): A 3 h exposure period to the laser beam (P = 500 mW) of a solution of 650 mg (5.75 mmol) of 4-MTAD in 180 mL of 1,4-dioxane (**1e**) led to a colorless mixture, which after vacuum evaporation afforded 1.121 g (5.58 mmol, 97% yield) of a solid product. After washing with a small volume of methanol, the solid (mp = 170 °C) had spectral properties in agreement with structure **2e**. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.89 (s, 3 H, N–CH$_3$), 3.63 (m, H$_3$), 3.77 (m, H$_2$), 3.43 (m, H$_5$), 3.63 (m, H$_4$), 3.70 (m, H$_6$), 3.85 (m, H$_7$), 5.09 (dxd, H$_1$), 10.45 (br s, 1 H, NH); J_{12} = 9.3, J_{13} = 2.8, J_{23} = 11.4, J_{45} = –11.6, J_{46} = 2.7, J_{47} = 1.0, J_{56} = 11.0, J_{57} = 2.5, J_{67} = –11.9 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 24.7 (N–CH$_3$), 65.0, 65.7, 66.3 (OCH$_2$), 79.3 (OCHUr), 154.5 (C=O), 154.6 (C=O). – IR: $\tilde{\nu}$ = 3181, 3070, 2923, 2870, 1779, 1718, 1496, 1125 cm^{-1}.

4-Urazolyl-1,3-dioxane (2f): By a procedure similar to that used for **2c** and **3c**, 579 mg (5.12 mmol) of 4-MTAD was added portionwise to 1.066 g (12.11 mmol) of 1,3-dioxane with magnetic stirring and under UV irradiation. After 17.5 h all the 4-MTAD had been added and consumed. The oily crude product was diluted with a small volume of dichloromethane and then pentane was added: the white crystals that precipitated after vigorous shaking were isolated by filtration. This procedure was repeated 5 times to give pure **2f**: m.p. 158–160 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.60 (m, H$_2$), 2.09 (m, H$_3$), 2.90 (s, 3 H, N–CH$_3$), 3.77 (m, H$_4$), 4.07 (m, H$_5$), 4.76 (m, H$_6$), 4.96 (m, H$_7$), 5.37 (dxd, H$_1$), 10.55 (br s, 1 H, NH); J_{12} = 2.6, J_{13} = 11.6, J$_{23}$ = –12.2, J_{24} = 2.0, J_{25} = 1.4, J_{34} = 12.2, J_{35} = 4.9, J_{45} = –11.5, J_{67} = 6.5 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 24.7 (N–CH$_3$), 28.4 (CH$_2$), 65.0 (OCH$_2$), 80.9 (OCHUr), 91.9 (OCH$_2$O), 154.4 (C=O). – IR: $\tilde{\nu}$ = 3192, 3062, 2963, 2876, 1766, 1693, 1493, 1016 cm^{-1}. – $C_7H_{11}O_4N_3$ (201): calcd. C 41.79, H 5.47, N 20.90; found: C 41.76, H 5.62, N 20.81.

α-Urazolyl-12-crown-4 (2g) and α,α′-Diurazolyl-12-crown-4 (4g): A 2 d irradiation with the laser beam (P = 500 mW) was necessary for the complete reaction of 1.5 g of 4-MTAD (13.27 mmol) added portionwise to 6 g (34 mmol) of 12-crown-4 (**1g**). The crude product (7.167 g, 96% yield) was dissolved in the minimum amount of dichloromethane and pentane was added to afford, after shaking, white crystals; after repeating this process 5 times the residue contained only unchanged 12-crown-4. Compound **2g** (2.041 g, 7.06 mmol, 54% yield) was obtained in this way. Compound **4g** (40 mg, 0.1 mmol, 1%) was obtained by filtration during the first dissolution of the crude product in CH_2Cl_2. – **2g:** m.p. 104–106 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.05 (s, 3 H, N–CH$_3$), 3.50–3.90 (m, 12 H, OCH$_2$), 3.80 (m, 1 H, J_{AB} = 12.35, J_{AX} = 3.96 Hz), 3.89 (m, 1 H, J_{BX} = 4.20 Hz), 5.71 (dd, 1 H, OCHUr). – ^{13}C NMR ($CDCl_3$): δ = 25.1 (N–CH$_3$), 67.6, 69.4, 70.2, 70.3, 70.5, 70.8, 71.5 (OCH$_2$), 83.8 (OCHUr), 153.5 (C=O), 154.2 (C=O). – IR: $\tilde{\nu}$ = 3162, 3059, 2944, 2863, 1765, 1687, 1497, 1100 cm^{-1}. – $C_{11}H_{19}N_3O_6$ (289): calcd. C 45.67, H 6.57, N 14.53; found: C 45.27, H 6.46, N 14.56. – **4g:** m.p. 210–215 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.90 (s, 6 H, 2 N–CH$_3$), 3.40–3.90 (m, 8 H, 4 OCH$_2$), 3.48 (m, 2 H, J_{AB} = 12.4, J_{AX} = 2.3 Hz), 3.70 (m, 2 H, J_{BX} = 8.9 Hz), 5.34 (dd, 2 H, 2 OCHUr), 10.1 (br s, 2 H, 2 NH). – ^{13}C NMR ([D$_6$]DMSO): δ = 24.78 (N–CH$_3$), 68.1, 69.9, 70.3 (OCH$_2$), 84.1 (OCHUr), 153.9 (C=O), 154.2 (C=O). – IR: $\tilde{\nu}$ = 3162, 3096, 2922, 2824, 1757, 1694, 1499, 1109 cm^{-1}.

α-Urazolyl-15-cronw-5 (2h): A 3 d irradiation period using the laser beam (500 mW) was necessary to achieve complete reaction of 2.573 g (22.8 mmol) of 4-MTAD added portionwise to 9.3 g (42.3 mmol) of 15-crown-5 (**1h**). In order to separate the components of the mixture obtained, 1.994 g of the crude product was eluted through a silica gel column with an 8:3:1 mixture of CH_2Cl_2/pentane/ethanol. A pure sample of compound **2h** (562 mg, 1.30 mmol, 25%) was obtained: m.p. 72 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.0 (s, 3 H, N–CH$_3$), 3.71 (m, 1 H, J_{AB} = 11.2, J_{AX} = 4.07 Hz), 3.75 (m, 1 H, J_{BX} = 5.68 Hz), 3.40–3.80 (m, 16 H, OCH$_2$), 5.42 (dd, 1 H, OCHUr). – ^{13}C NMR ($CDCl_3$): δ = 24.9 (N–CH$_3$), 67.0, 69.7, 69.8, 70.0, 70.1, 70.3, 70.7, 70.9, 71.1 (OCH$_3$), 82.8 (OCHUr), 153.1 (C=O), 153.2 (C=O). – IR: $\tilde{\nu}$ = 3113, 2873, 1769, 1708, 1477, 1119 cm^{-1}.

α-Urazolyl-18-cronw-5 (2i): A 3 d irradiation period with the laser beam (P = 200 mW) was necessary to achieve the complete decoloration of 103 mg (0.91 mmol) of 4-MTAD added portionwise to a solution of 269 mg (1 mmol) 18-crown-6 in 15 mL of carbon tetrachloride. After removal of the solvent, the crude product (323 mg, 87%) was dissolved in the minimum volume of CH_2Cl_2 and then pentane was added. This procedure, after being repeated 5 times, gave almost pure **2i**. – ^{1}H NMR ($CDCl_3$): δ = 2.98 (s, 3 H, N–CH$_3$), 3.40–3.90 (m, 18 H, OCH$_2$), 3.78 (m, 1 H, J_{AB} = 10.10, J_{AX} = 4.02 Hz), 4.04 (m, 1 H, J_{BX} = 6.68 Hz), 5.3 (dd, 1 H, OCHUr). – ^{1}H NMR ($CDCl_3$): δ = 24.7 (N–CH$_3$), 66.3, 69.1, 69.5, 69.7, 69.8, 69.85, 69.9, 70.0, 70.2, 70.4, 71.8 (OCH$_2$), 83.4 (OCHUr), 153.6 (C=O), 153.8 (C=O). – IR: $\tilde{\nu}$ = 2906, 1772, 1705, 1476, 1106 cm^{-1}.

Supporting Information Available: ^{1}H-, ^{13}C-NMR and IR spectra of the mixture of **2b**, **2c** and **3c**, **2f**, **2g**, **4g**, **2h**, **2i**, ^{1}H- and ^{13}C-NMR spectra of **3d**, IR and ^{1}H-NMR spectra of the mixture of **2d** and **3d**, observed and simulated ESR spectra of anion radical of MTAD (K*t*BuO in DMSO), AM1-UHF-calculated total spin density chart for the radical species of MTAD, ab initio optimised geometries, energies and total atomic charges for HTAD and urazole in the ground state S$_0$, ^{1}H- and ^{13}C-NMR spectra of product (MTAD + DMPO).

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