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Synthesis, Thermolysis, and Photolysis of the Azoalkanes Spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-ene-8,2′-[1,3]dioxolane] and 4,5-Diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-one: On the Mechanism of the Oxadi-π-methane Rearrangement of 5-Norbornen-2-one

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4,5-Diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-one (**4**) and spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-ene-8,2′-[1,3]dioxolane] (**5**) were prepared starting from bicyclo[2.2.1]hept-5-en-2-one (**1**) by cycloaddition with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to the corresponding urazole **7**, followed with acetalization to the urazole **9** and subsequent hydrolysis and oxidation. The regioselectivity of the PTAD-cycloaddition leading to urazole **7** was confirmed by an *X*-ray analysis. Direct and benzophenone-sensitized photolyses of azoalkane **5** gave the tricycloalkane **13**, while in the thermolysis also the pyrazole **12** was formed. Direct and benzophenone-sensitized photolyses of azoalkane **4** yielded bicyclo[2.2.1]hept-5-en-2-one (**1**), tricyclo[3.2.0.0^{2,7}]heptan-3-one (**2**), and bicyclo[3.2.0]hept-3-en-6-one (**3**). Thermolysis gave only the bicyclic ketones **1** and **3**. It is postulated that the photolysis and thermolysis of azoalkane **4** first lead to diazenyl diradicals **19a, b**, which are differentiated in their chemical behavior on account of spin state multiplicities (singlet *versus* triplet) and electronic configurations ($D_{\sigma,\sigma}$ *versus* $D_{\sigma,\pi}$). Formation of the oxadi-π-methane-type 1,3-diradical **20** by denitrogenation involving double C–N cleavage represents a minor product channel.

Synthese, Thermolyse und Photolyse der Azoalkane Spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-en-8,2′-[1,3]dioxolan] und 4,5-Diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-on. Über den Mechanismus der Oxadi-π-methan-Umlagerung von 5-Norbornen-2-on

4,5-Diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-on (**4**) und Spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-en-8,2′-[1,3]dioxolan] (**5**) wurden ausgehend von Bicyclo[2.2.1]hept-5-en-2-on (**1**) synthetisiert, indem das entsprechende Urazol **7** durch Cycloaddition von 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion (PTAD) erhalten wurde. Acetalisierung zum Urazol **9** und anschließende Hydrolyse und Oxidation führten zu den Azoalkanen **4** und **5**. Die Regioselektivität der PTAD-Cycloaddition zum Urazol **7** wurde röntgenographisch bewiesen. Direkte und benzophenonsensibilisierte Photolysen des Azoalkans **5** führten zum Tricycloalkan **13**, während Thermolyse auch das Pyrazol **12** ergab. Bei der direkten und benzophenonsensibilisierten Pho-

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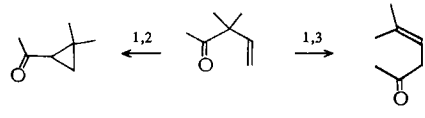
tolyse des Azoalkans **4** entstanden Bicyclo[2.2.1]hept-5-en-2-on (**1**), Tricyclo-[3.2.0.0^{2,7}]heptan-3-on (**2**) und Bicyclo[3.2.0]hept-3-en-6-on (**3**). Bei der Thermolyse wurden nur die bicyclischen Ketone **1** und **3** erhalten. Es wird postuliert, daß die Photolyse und Thermolyse des Azoalkans **4** primär zu den Diazenyl-Diradikalen **19a, b** führt, deren unterschiedliches chemisches Verhalten auf Spinmultiplizität (Singulett- bzw. Triplettzustände) und Elektronenkonfiguration ($D_{\sigma,\sigma}$- bzw. $D_{\sigma,\pi}$-Konfiguration) zurückzuführen ist. Die Bildung des Oxadi-π-methan-Diradikals **20** während der Stickstoffabspaltung durch Doppelbruch der C—N-Bindungen entspricht einem untergeordneten Reaktionsweg.

One of the mechanistically still perplexing photochemical rearrangements[1] concerns the β,γ-enones [Eq. (1)]. The major products are either cyclopropyl ketones (oxadi-π-methane or ODPM-type products), produced formally via 1,2-acyl shifts, or isomeric β,γ-enones, thought to arise via 1,3-acyl shifts. At least in principle one could consider one common diradical manifold [Eq. (2)], in which the isomeric β,γ-enones are interconverted via successive 1,2-shifts involving the isomeric ODPM-type 1,4- and 1,3-diradicals. The latter would serve also as immediate precursor to the cyclopropyl ketone (ODPM-type product), thereby providing a convenient mechanistic construct for rationalizing such complex photochemical transformations.



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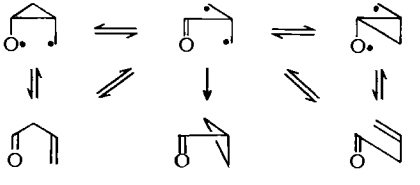
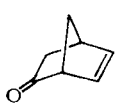


(2)

An interesting case represents 5-norbornen-2-one (**1**), which has been shown[2] to afford on irradiation the tricyclic ketone **2** (ODPM-type product) as well as the isomeric bicyclic ketone **3** (1,3-acyl shift product). More significant for our purposes, the isomeric bicyclic ketone **3** also leads to the tricyclic ketone **2** on photolysis. Whether the 5-norbornen-2-one (**1**) is as well formed in the latter process, could not be ascertained in view of the fact that the photoreactivity of **1** is appreciable greater than that of its bicyclic isomer and **1** would therefore not accumulate[2d]. Nevertheless, this system represents an interconnected set of ODPM-type and 1,3-acyl shift products[1], amenable for testing the mechanistic hypothesis in Eq. (2). For this purpose it was essential to generate the corresponding 1,3-diradical [Eq. (2)] by an independent and authentic route and establish whether it affords the three isomeric ketones **1**—**3**. Consequently, 4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-one (**4**) and for comparison spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-ene-8,2′-[1,3]dioxolane] (**5**) were prepared and their thermal

and photochemical denitrogenation investigated. Besides serving as mechanistic probe for the postulated generalized ODPM-scheme in Eq. (2), these azoalkanes would permit testing the effect of carbonyl and acetal substitution on the competitive diazoalkane versus denitrogenation modes of decomposition of the parent azoalkane 4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-ene[3] (**6a**) and its spirocyclopropane derivatives[4] **6b**–**d**. Preliminary results of this investigation have been reported[5]; herein we present the full experimental details and their mechanistic rationalization.



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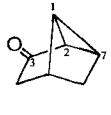

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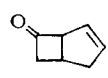

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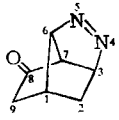

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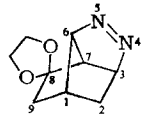

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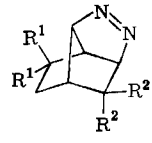


6a: $R^1 = R^2 = H$
b: $R^1 + R^1 = -[CH_2]_2-$; $R^2 = H$
c: $R^1 = H$; $R^2 + R^2 = -[CH_2]_2-$
d: $R^1 + R^1 = R^2 + R^2 = -[CH_2]_2-$

Results

Preparation and Characterization of Azoalkanes

The azoalkanes **4** and **5** were prepared from 5-norbornen-2-one (**1**) according to Eq. (3). Thus, **1**[6] was treated with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) at 80°C in $Cl_2CHCHCl_2$ affording the rearranged urazole **7** only in 9% yield, the remainder of the product mixture being undefined high-molecular-weight material containing largely decomposed PTAD. Efforts to optimize the yield failed. Although the NMR spectral data (cf. Experimental Part) was consistent with the proposed regiochemistry of the urazole **7**, an *X*-ray crystal structure determination of its *N*-methyl derivative (Fig. 1), prepared from **1** and 4-methyl-4*H*-1,2,4-triazole-3,5-dione (MTAD), provided rigorous proof. The unusual directing effect of the carbonyl group towards electrophilic attack by PTAD[7] on 5-norbornen-2-one (**1**) has been previously recognized[8]. Attempts to hydrolyze the urazole **7** led to its total destruction without even traces of the desired azoalkane **4**. However, on acetalization with ethylene glycol in toluene under *p*-toluenesulfonic acid catalysis gave the dioxolane-substituted urazole **9** in 93% yield. Subsequent saponification of **9** with KOH in isopropyl alcohol and cupric chloride oxidation[9] led to azoalkane **5** in 67% yield. Hydrolysis of azoalkane **5** with concentrated HCl gave the desired ketoazoalkane **4** in 78% yield. The spectral data and elemental analyses of the urazoles **7** and **9** and the azoalkanes **4** and **5** are given in the Experimental Part. An attempt to short-cut the synthetic sequence [Eq. (3)] by preparing the urazole **9** directly from the norbornenone acetal **8**[10] failed in that the latter was completely inert toward PTAD. Furthermore, the thioacetal **10** gave with PTAD the unusual insertion product **11** [Eq. (4)] and none of the expected rearranged urazole. A few examples of this type of triazoledione chemistry exist[11].

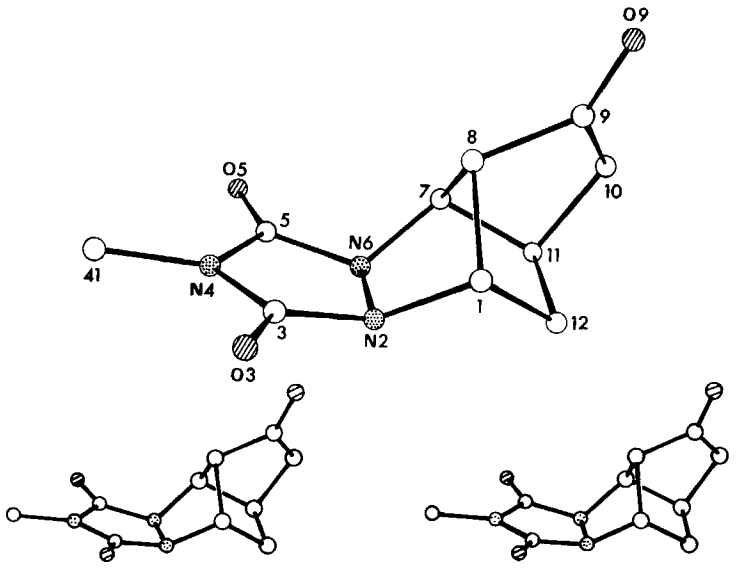
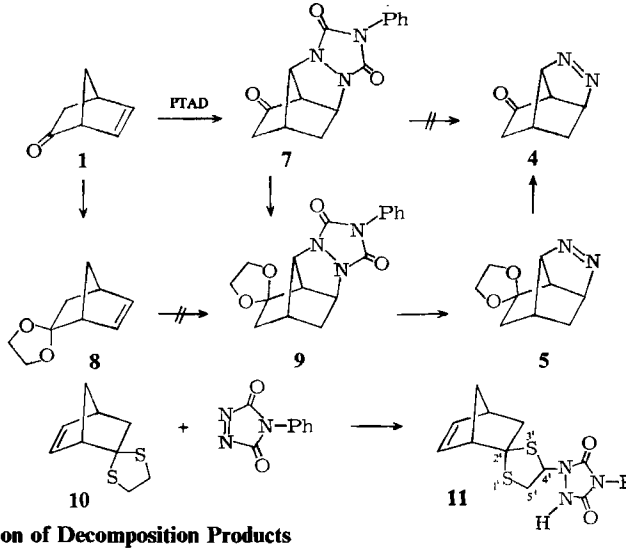


Figure 1. Perspective drawing and stereopair of the crystal structure of the *N*-methyl derivative of urazole **7**; the numbering of the atoms corresponds to Tables 2 and 3



(3)

(4)

Characterization of Decomposition Products

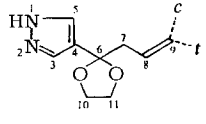
The thermal and photochemical decompositions of azoalkane **4** led to the three isomeric ketones **1**–**3**, the proportions depending on the reaction conditions (Table 1). The identity of these denitrogenation products was established by comparison of the capillary GC retention times and spectral data of the GC collected products with the authentic ketones **1**–**3**. The authentic samples of the tricyclic ketone **2** and the bicyclic ketone **3** were prepared by photolysis of 5-norbornen-2-one (**1**) in acetone and GC collection[2].

Table 1. Product compositions of the denitrogenation of the azoalkanes **4** and **5**

Conditions	Conversion (%)	Rel. yields (%)[a] 1	2	3	12	13	Absol. yields (%)[b]
1. **5**; VT, 400°C/0.1 Torr	100				33	67	95
2. **5**; $h\nu$[c,d,e]	100				–	100	96
3. **5**; $h\nu$, Ph_2CO[c,f]	100				–	100	87
4. **4**; VT, 300°C/22 Torr	100	87	–[g]	13			98
5. **4**; $h\nu$[c,d,h]	40	50	7	43			84
6. **4**; $h\nu$, 1,3-cyclohexadiene[c,d,i]	40	43	4	53			–
7. **4**; $h\nu$, Ph_2CO[c,f]	30	68	28	4			67
8. **4**; TMD, 85°C[j]	10	59	30	5			–
9. **1**; $h\nu$, Ph_2CO, 366 nm[k]	45		0.042	0.006			–

[a] Determined by capillary-GC on a 50-m OV-101-capillary column, operated at injector, column, and detector temperatures of 200, 90, and 200°C, respectively, and a carrier gas pressure (N_2) of 0.8 kg/cm^2; the relative yields are within 10% of the stated values and normalized to 100% conversion; several unidentified volatile products (< 3%) were detected in each run. – [b] The absolute yields were determined by ^{1}H NMR at 100% conversion. – [c] The photolyses were run in the Rayonet at 350 nm and 30°C; the benzene solutions were either saturated with nitrogen or degassed by three "freeze-pump-thaw" cycles. – [d] [**4**] = [**5**] = 0.01 M in benzene. – [e] The photolyses were run on preparative scale with the laser. – [f] [Ph_2CO] = 0.09 M in benzene. – [g] **2** is stable under the thermolysis conditions. – [h] Corrected for ca. 7% conversion of **1** into **3**. – [i] [1,3-Cyclohexadiene] = 0.102 M in benzene. – [j] [**4**] = [tetramethyl-1,2-dioxetane (TMD)] = 0.0102 M in benzene; T = 85°C; corrected for ca. 5% conversion of **1** into **2** under these conditions. – [k] Quantum yields from Ref.[2d].

The decomposition products of the dioxolane-substituted azoalkane **5** differed substantially from those of the ketoazoalkane **4**. For example, on gas phase thermolysis at 400°C and 0.1 Torr a mixture of the pyrazole **12** and the spirotricycloalkane **13** was obtained in 33% and 67%, respectively. These products are akin to those observed in the thermolysis of azoalkanes **6**[3,4]. The pyrazole ring in the retrocyclic product **12** exhibited the NH moiety in the IR at 3160 cm^{-1} and in the ^{1}H NMR as broad signal at δ = 11.12, while the aromatic protons occurred as a sharp singlet at δ = 7.57[12]. The complex ^{1}H NMR signals of the dioxolane protons and the allyl protons were simulated with the help of the LAOCOON III computer program[13]. Also the ^{13}C NMR signals corresponded as expected (cf. Experimental Part). It is significant in this context to mention that the vacuum flash thermolysis of the ketoazoalkane **4** did not produce even traces of the corresponding pyrazole via retrocleavage.



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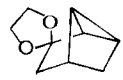

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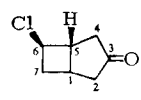

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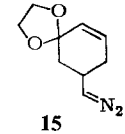

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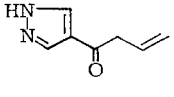
While the proposed structure of the tricycloalkane **13** was consistent with the ^1H and ^{13}C NMR data (cf. Experimental Part), definitive structure proof came from hydrolysis of the acetal functionality to produce the known tricyclic ketone **2**. All spectral and physical data matched well with that of an authentic sample. However, it should be pointed out that the success of the latter hydrolysis depended critically on the acid used. Thus, with *p*-toluenesulfonic acid no problems were encountered and the tricyclic ketone **2** was obtained in ca. 70% yield. However, when concentrated HCl was used, the bicyclic ketone **14** was obtained. Extensive double resonance experiments were necessary to elucidate this ring-opened product[14]. The benzophenone-sensitized photolysis of azoalkane **5** in C_6D_6 gave the tricycloalkane **13** exclusively and the direct photolysis at 350 nm in C_6D_6 additionally ca. 2% of several unidentified volatile products, as detected by capillary GC. The latter were presumably formed from the intermediary diazoalkane **15**[3,4]. Indeed, a weak band at 2060 cm^{-1} in the IR, that was observed in the laser photolysis (334 nm) of azoalkane **5** at 40°C, implicated the formation of a diazoalkane, presumably structure **15**. The small amount (<2%) of diazoalkane **15** that was formed did not permit a rigorous characterization. It is significant to mention in this context that even the laser photolysis (334 nm) of the ketoazoalkane **4** gave only traces, if any, of the corresponding diazoalkane as retrocleavage product.

Quantitative Product Studies and Control Experiments

The products of the vacuum flash pyrolysis, the tetramethyl-1,2-dioxetane (TMD) chemienergized thermolysis, and the direct and benzophenone-sensitized photolyses were determined by means of capillary GC and ^1H NMR (90 or 400 MHz). The relative yields were obtained by electronic integration with the help of capillary GC. The absolute yields were acquired by running the decompositions to 100% conversion and assessing the amount (mol-%) of each individual product with 1H NMR (90 MHz) by means of integration of characteristic proton signals against trioxane or benzophenone as internal standards. The product balance in most cases was high (greater than 95%); the small deficit being due to formation of undefined high-molecular-weight material.

It was essential to establish that the isomeric ketones **1**–**3** were primary products of the denitrogenation of the ketoazoalkane **4**. For this purpose control experiments were conducted. It was shown that the ketones **1**–**3** were stable towards the vacuum flash pyrolysis conditions used for the ketoazoalkane **4**. A deliberate search for retrocleavage products[4,12] such as pyrazole **16** showed that these were not formed in the pyrolysis of **4**. To test whether the 8-keto group in **4** assists the thermal denitrogenation, the azoalkanes **4** and **5** in benzene solution were thermolyzed simultaneously in the GC-injector and the decrease relative to



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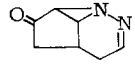

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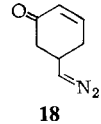

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naphthalene as internal standard determined. At a thermolysis temperature of 300°C the 8-keto group accelerated the denitrogenation by ca. 8-fold.

All three ketones **1**–**3** were also stable toward the benzophenone-sensitized photolysis conditions during the period of ca. 30% consumption of ketoazoalkane **4**. No evidence for the azirane-type[12,15] product **17** could be provided even by careful ^{1}H NMR (400 MHz) examination of the product mixture immediately after triplet-sensitized photolysis.

In the direct photolysis at 350 nm in the Rayonet photoreactor the ketones **2** and **3** were photostable during the period of ca. 40% ketoazoalkane **4** consumption. However, 5-norbornen-2-one (**1**) was converted into the isomeric bicyclic ketone **3** to the extent of ca. 7%. The results in Table 1 were corrected for this secondary photolysis. Only traces, if any, of the expected[3,4] diazoalkane **18** could be detected by IR (characteristic 2060 cm^{-1} band of the diazo group) in the laser photolysis (334 nm) of the ketoazoalkane **4**.

A triplet quenching experiment with 1,3-cyclohexadiene showed that in the direct photolysis of the ketoazoalkane **4** the tricyclic ketone **2** was substantially reduced, i.e. from 7% to ca. 3.5%. Thus, the tricyclic ketone **2** derived from a triplet process. The most convincing evidence for this supposition was the fact that the TMD-chemienergized thermolysis of ketoazoalkane **4** gave as much as 30% tricyclic ketone **2**, while the vacuum flash thermolysis gave none (Table 1).

Discussion

Before entering into the mechanistic details on the thermal and photochemical decompositions of the azoalkanes **4** and **5** and link these to the photochemistry of the isomeric ketones **1**–**3**, it merits to summarize the results accumulated here on the azoalkanes **4** and **5** (Table 1), together with the already known results[2] on the isomeric ketones **1**–**3**. These are:

a) The ketoazoalkane **4** gives only denitrogenation products, i.e. the ketones **1**–**3**,

b) the thermolysis of ketoazoalkane **4** gives only ketones **1** and **3**, the former in ca. 7-fold predominance (Table 1, Entry 4); no ketone **2** is formed, although the latter is stable under the thermolysis conditions,

c) no pyrazole **16** is formed in the thermolysis of ketoazoalkane **4**, but substantial amounts (ca. 33%) of pyrazole **12** are produced in the thermolysis of the acetalazoalkane **5**,

d) the relative rate for thermal denitrogenation of ketoazoalkane **4** in the gas phase is ca. 8-fold larger than for the acetalazoalkane **5**,

e) the benzophenone-sensitized photolysis (Table 1, Entry 7) of ketoazoalkane **4** gives substantial amounts (28%) of ketone **2**, but predominantly the ketones **1** and **3**, the former in ca. 17-fold preference,

f) the TMD-chemienergized thermolysis (Table 1, Entry 8) of ketoazoalkane **4** gives essentially the same results as the benzophenone-sensitized photolysis (Table 1, Entry 7),

g) the triplet-sensitized processes (benzophenone and TMD) of the ketoazoalkane **4** did not afford the azirane **17**, nor did the acetalazoalkane **5** give the corresponding azirane-type product,

h) the direct photolysis (Table 1, Entry 5) of the ketoazoalkane **4** gives in ca. 13-fold preference the ketones **1** and **3**, essentially in equal amounts, compared to the ketone **2**,

i) in the presence of the triplet quencher 1,3-cyclohexadiene (Table 1, Entry 6) the ketone **2** is substantially reduced (ca. 50%) in the direct photolysis of the ketoazoalkane **4**,

j) while small amounts of diazoalkane, presumably **15**, are detected in the direct photolysis of the acetalazoalkane **5**, only traces if any of the corresponding diazoalkane **18** were formed in the case of the ketoazoalkane **4**,

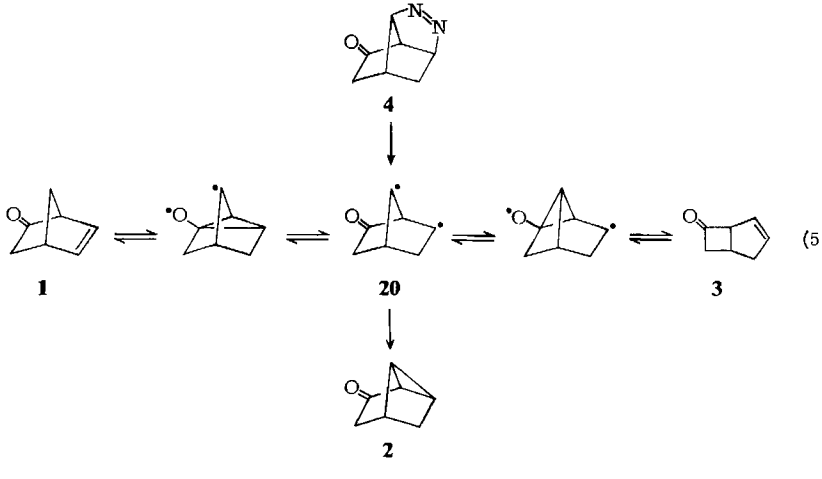
k) the benzophenone-sensitized and direct photolyses of the acetalazoalkane **5** give essentially quantitatively the cyclization product **13** and no rearrangement products,

l) the bicyclic ketones **1** and **3** are converted[2] into one another during triplet-sensitized photolysis and both lead to ketone **2**,

m) generally the 1,2-acyl shift (ODPM rearrangement) leading to cyclization ketone is with few exceptions a triplet state process, involving preferentially the $^3\pi,\pi^*$ state of the bicyclic β,γ-enone[1],

n) generally the 1,3-acyl shift leading to rearrangement ketones can be singlet and/or triplet state derived, involving $^{1,3}n,\pi^*$ states of the bicyclic β,γ-enone[1],

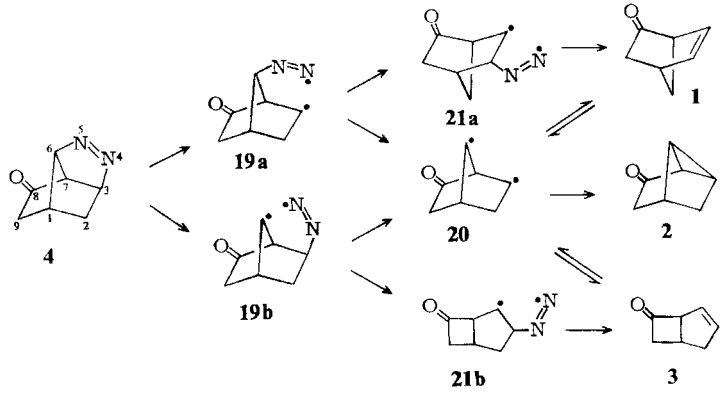
o) the postulated 1,3-diradical [Eq. (2)] of the ODPM process may be formed via direct 1,2-acyl shift or via prior generation of a 1,4-diradical of the cyclopropyldicarbinyl type [Eq. (2)], mechanistic alternatives which are difficult to distinguish[1].



These experimental facts are difficult to accommodate in terms of the simplistic mechanism [Eq. (5)] of interconverting 1,4- and 1,3-diradicals given in our preliminary reports[5]. The problem is more complex! For example, the rate of deni-

trogenation of the ketoazoalkane **4** is considerably faster (8-fold) than that of the acetalazoalkane **5** and the parent system **6a** (fact d)). This unquestionably signals that the carbonyl group participates in the C–N bond breaking of the thermal process. We suggest that in the thermolysis an unsymmetrical transition state is involved, leading first to a diazenyl diradical via one-bond cleavage rather than directly to the 1,3-diradical via two-bond cleavage [Eq. (5)]. Stepwise denitrogenation via diazenyl diradicals appears to become the prevailing opinion in the thermolysis of azoalkanes[16].

For the photochemical process the question of diazenyl diradicals as initial intermediates is more debatable[17]. However, in this context it urges to recall the theoretical analysis concerning the photochemical decomposition of the parent *cis*-diazene[18]. Thus, all low lying excited states of the azo chromophore, namely $^{1,3}n_-,\pi^*$ and $^3\pi,\pi^*$ states, exhibit significantly larger (almost double) activation energies for concerted than for stepwise loss of nitrogen. That photochemical denitrogenations display activation energies (ca. 6–11 kcal/mol) is an established fact, especially in the case of "reluctant" azoalkanes[19]. We, therefore, propose that also in the photochemical denitrogenation the excited azoalkane suffers initially one-bond cleavage to yield a diazenyl diradical. The subsequent chemical fate of the diazenyl diradical depends on its spin state, i.e. singlet versus triplet, and its electronic configuration, i.e. $D_{\sigma,\sigma}$ versus $D_{\sigma,\pi}$ (Fig. 2)[18].



(6)

The mechanistic scheme for the thermal and photochemical denitrogenation of the ketoazoalkane **4** is given in Eq. (6). It should be noticed that this modified scheme [Eq. (6)] incorporates the previous [Eq. (5)], i.e. the branching point **20**→**1** + **2** + **3**; however, we have dispensed with the 1,4-diradicals of the cyclopropyldicarbinyl type [Eq. (5)]. Thermochemical estimates[20] suggest that conversion of a homoallylic radical into a cyclopropylcarbinyl one is considerably more endothermic for the oxyl case. In terms of the proposed mechanism [Eq. (6)] and the Salem diagram (Fig. 2) we shall now attempt to rationalize the experimental facts enumerated at the beginning of our discussion. For convenience we take up each activation mode separately.

The absence of ketone **2** in the *thermolysis* of azoalkane **4** (point b)) implies that no 1,3-diradical **20** intervenes. Therefore, the diazenyl 1,5-diradicals **19a, b**, presumably in the $^1D_{\sigma,\sigma}$ configuration (Fig. 2)[18], rearrange first into the diazenyl 1,4-diradicals **21a, b** and subsequently denitrogenate into the bicyclic rearrangement ketones **1** and **3**, respectively. If the rearrangement step **19a, b**→**21a, b** and the denitrogenation steps of **21a, b** to **1** and **3** are concerted events, then the 1,2-acyl shifts in the diazenyl 1,5-diradicals **19a, b** can outwin over denitrogenation into the 1,3-diradical **20**. For that matter, the sequences **4** → **19a** → **21a** → **1** and **4** → **19b** → **21b** → **3** might be completely concerted in the thermolysis.

Our present data cannot differentiate between these alternatives; all we can say with certainty is that the 1,3-diradical **20** does not intervene in the thermolysis (point b)) and that the carbonyl group participates (point d)). That ketone **1** is formed with 7-fold predominance (point b)) can be explained by the greater stability of the diazenyl diradical **19a** versus **19b** since in **19a** the carbon radical centre is located in the less strained ethano bridge.

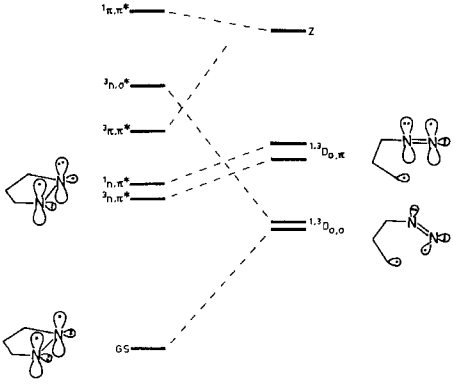


Figure 2. Salem diagram for stepwise cleavage of azoalkanes into diazenyl diradicals

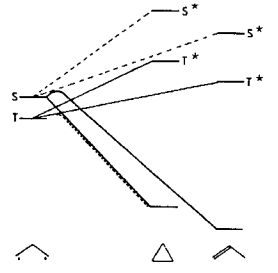


Figure 3. Energy profile for the formation of cyclopropane and propene from trimethylene

Also the results of the *triplet-sensitized process* with benzophenone (point e)) and with TMD (point f)) nicely fit into the proposed mechanistic scheme [Eq. (6)]. Clearly, ketone **2** is a triplet state product, requiring the triplet 1,3-diradical **20** as precursor. The fact that ketones **1** and **3** give both ketone **2** on triplet-sensitized photolysis (point l)) requires also that the triplet 1,3-diradical **20** is involved, formed via the 1,2-acyl shifts **1** → **20** and **3** → **20**. At least in principle the possibility exists that these 1,2-shifts operate also in the reverse sense, so that the ketones **1** and **3** could be formed from the triplet 1,3-diradical **20**. The photochemical interconversions of ketones **1** and **3**, traditionally considered as 1,3-shifts (point n)), could be alternatively rationalized as successive 1,2-shifts via the 1,3-diradical **20**, i.e. **1** ⇄ **20** ⇄ **3**. Thus, the ODPM rearrangements and the 1,3-acyl shifts may be mechanistically connected via the 1,3-diradical **20**. It seems essential and important to scrutinize this mechanistic possibility.

That the ketones **1** and **3** are not formed exclusively via appropriate 1,2-shifts from the triplet 1,3-diradical **20** can be supported on the following grounds. Numerous examples have accumulated which show that triplet 1,3-diradicals such as **20** almost exclusively cyclize to cyclopropane-type products[3,4,5b]. In fact, recently a revealing theoretical justification has been proposed to account for this astounding fact[21] (Fig. 3). For the parent 1,3-diradical (trimethylene) it was concluded that its singlet state possesses an activation barrier (ca. 5 kcal/mol) towards rearrangement via 1,2-shift to give propene, but none for cyclization into cyclopropane. Its slightly more stable (ca. 1 kcal/mol) triplet state intersects with the energy surface connecting the singlet trimethylene with ground state cyclopropane prior to that connecting with the ground state propene product. Efficient intersystem crossing[22] leads to preferential cyclization versus 1,2-shift. Consequently, the predominant fate of triplet 1,3-diradicals derived from triplet-sensitized denitrogenation of azoalkanes[3,4,5b] is cyclization to cyclopropane-type products.

In the particular case of the triplet 1,3-diradical **20** also the predominant pathway should be cyclization into the tricyclic ketone **2**. However, the triplet-sensitized reactions of the azoalkane give mainly the ketones **1** and **3** (points e) and f)), the former in 17-fold preference. Consequently, an alternative route to the 1,2-shifts of the triplet 1,3-diradical **20** into the ketones **1** and **3** must be pursued in this denitrogenation. Indeed, the triplet diazenyl 1,5-diradicals **19a, b** serve well for this purpose. Formed from the ^{3}n,π* excited azoalkane **4** as $^3D_{\sigma,\pi}$ and/or $^3D_{\sigma,\sigma}$ electronic configurations (Fig. 2)[18], the diazenyl 1,5-diradicals **19a, b** rearrange predominantly to the corresponding diazenyl 1,4-diradicals **21a, b** via 1,2-shifts, which subsequently denitrogenate to the ketones **1** and **3** with spin inversion. Presumably, the diazenyl 1,5-diradicals **19a, b** do also denitrogenate to some extent into the triplet 1,3-diradical **20**; but our data do not enable us to estimate how much of the 1,5-diradicals **19a, b** are partitioned into the 1,3-diradical **20** versus the 1,4-diradicals **21a, b**. If none of the triplet 1,3-diradical **20** transposes into the bicyclic ketones **1** and **3**, then the lower limit of denitrogenation of the triplet 1,5-diradicals **19a, b** into the triplet 1,3-diradical **20** would be ca. 30%, i.e. the amount of tricyclic ketone **2** (points e) and f)). Therefore, like in the thermolysis, so also in the triplet-sensitized photolysis the diazenyl 1,5-diradical **19a** is produced preferentially compared to **19b**.

In the *direct photolysis* some ketone **2** is produced, but by far the major products are the ketones **1** and **3** (point h)). Since ketone **2** is substantially (ca. 50%) reduced in the direct photolysis by quenching with 1,3-cyclohexadiene (point i)), most of the ketone **2** appears to be derived via a triplet route, e.g. intersystem crossing[19] of the singlet excited (^{1}n,π*) azoalkane **4**.

The major pathway (ca. 13-fold) is formation of the ketones **1** and **3**. If also here the singlet diazenyl diradicals **19a, b** intervene, they behave differently from those involved in the thermolysis. For example, in the photolysis (point h)) the ketones **1** and **3** are obtained in essentially equal amounts, while in the thermolysis (point b)) ketone **1** is formed in ca. 7-fold preference over ketone **3**. Either the thermolysis, as stated before, entails a concerted process and the direct photolysis a stepwise one, with the singlet diazenyl diradicals **19a, b** as *bona fide* interme-

diates, or different electronic configurations of the **19a, b** species are involved. As shown in Figure 2[18], n,π*-excitation leads to a $^1D_{\sigma,\pi}$ diradical, while thermal activation affords a $^1D_{\sigma,\sigma}$ diradical. These electronically distinct species are expected to portray different chemical fates. For example, the $D_{\sigma,\pi}$ species would be reluctant to denitrogenate into the 1,3-diradical **20** because an n,π*-excited nitrogen molecule would result. The less energetic $D_{\sigma,\sigma}$ species should behave more selectively.

In summary, the mechanistic hypothesis that thermal and photochemical denitrogenation of azoalkanes proceed via stepwise one-bond cleavage leading to diazenyl diradicals [Eq. (6) and Fig. 2] explains most consistently the experimental data described here. The oxadi-π-methane 1,3-diradical **20** plays a minor role in the formation of denitrogenated products.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous support of our work. Dr. *G. Lange* (mass spectra) and Dr. *D. Scheutzow* (NMR spectra) we thank for their kind assistance.

Experimental Part

UV spectra: Varian Cary 17. – IR spectra: Beckman Acculab 4. – ^{1}H NMR spectra: Hitachi Perkin-Elmer R-24 B (60 MHz), Varian EM-390 (90 MHz), Bruker WM-400 (400 MHz). – ^{13}C NMR spectra: Bruker WM-400 (100 MHz); chemical shifts in δ relative to TMS or $CHCl_3$ for protons and $CDCl_3$ for carbons. – Mass spectra: Varian CH-7. – Melting points: Reichert Thermovar Kofler apparatus, uncorrected. – Combustion analyses: Run in house or by Prof. Dr. *G. Maier's* staff at the Institute of Organic Chemistry, University of Gießen. – Thin-layer chromatography (TLC): Polygram SIL/G/UV (40 × 80 mm), Macherey und Nagel. – Column chromatography: Silica gel 70–230 mesh ASTM (activity III). – Analytical gas chromatography: Carlo Erba Model 2900 Fractovap Series or Model 4100, equipped with capillary columns and F. I. detector. – Preparative gas chromatography: Varian Aerograph 920 or Carlo Erba Model 4200. – Photolyses: Rayonet Photochemical Reactor (75 W, 250 V), Southern New England Ultraviolet Company, equipped with 350-nm or 300-nm lamps; Coherent CR-18 Supergraphite Argon Ion laser, utilizing the 334-, 351-, and 364-nm lines. – Commercial reagents and solvents were purchased from standard chemical suppliers and used as such, if not mentioned otherwise. Benzene as solvent in the photolysis experiments was purified by azeotropic distillation, refluxing over sodium wire and final distillation. Known compounds were prepared according to literature procedures. Volatile, liquid compounds were purified by preparative gas chromatography before combustion and MS analysis. After aqueous work-up, organic layers were dried over $MgSO_4$ or Na_2SO_4.

Tricyclo[3.2.0.0^{2,7}]heptan-3-one (**2**) *via Hydrolysis of Dioxolane* **13**: A suspension of ca. 30 mg (0.20 mmol) of **13** and ca. 25 mg of *p*-toluenesulfonic acid in ca. 4 ml of $CDCl_3$ was stirred at 25°C for 16 h. Water (2 ml) was added, the organic layer separated, washed with water (2 × 1 ml), dried and concentrated by roto-evaporation (0°C at 25 Torr). From the residue the tricyclic ketone **2** was isolated by means of preparative GC, using the same conditions as for the isolation of the dioxolane **13**; ca. 15 mg (70%) colourless oil, which was identical by IR, ^{1}H NMR (400 MHz) and t_R (capillary GC) with the authentic material. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (ddd, $J_{6n,6x}$ = 9.9, $J_{6n,1}$ = 2.9, $J_{6n,5}$ = 0.8 Hz; 1H, 6-*endo*-H), 1.89 (d, $J_{4n,4x}$ = 16.9 Hz; 1H, 4-*endo*-H), 1.97 (dd, $J_{2,7}$ = 6.4, $J_{2,1}$ = 4.0 Hz; 1H,

2-H), 2.10 (m; 1H, 7-H), 2.33 (d of m, $J_{4x,5}$ = 5.4 Hz; 1H, 4-*exo*-H), 2.65 (m; 1H, 6-*exo*-H), 2.82 (m; 1H, 5-H), 2.96 (m; 1H, 1-H).

4,5-Diazatricyclo[4.3.0.0^{3,7}]non-4-en-8-one (**4**): A mixture of 350 mg (1.94 mmol) of **5** in 30 ml of dichloromethane and 3 ml of conc. HCl was stirred in the dark for 2 h at ca. 25°C. The reaction mixture was washed with water (5 × 15 ml), dried, and concentrated by roto-evaporation (5°C at 22 Torr). The crude product was recrystallized from CCl_4/*n*-pentane to yield 205 mg (78%) of colourless prisms, m.p. 121–124°C. – IR (CCl_4): 3000, 2955, 2884, 1760, 1505, 1420, 1276, 1247, 1135, 1102 cm^{-1}. – UV (*n*-pentane): λ_{max} (lg ε) = 342 (2.33), 281 (1.75), 273 nm (1.80). – ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 0.96 (dddd, $J_{2x,2n}$ = 12.8, $J_{2x,1}$ = 6.3, $J_{2x,9x}$ = 2.5, $J_{2x,7} \simeq$ 0.8 Hz; 1H, 2-*exo*-H), 1.29 (dd, $J_{2n,3}$ = 4.0 Hz; 1H, 2-*endo*-H), 2.33 (m; 1H, 1-H), 2.42 (dd, $J_{9n,9x}$ = 17.1, $J_{9n,1} \simeq$ 0.8 Hz; 1H, 9-*endo*-H), 2.50 (d of m, $J_{9x,1}$ = 3.9 Hz; 1H, 9-*exo*-H), 2.63 (m; 1H, 7-H), 5.10 (mc, $J_{3,7}$ = 2.7, $J_{3,6}$ = 1.1 Hz; 1H, 3-H), 5.50 (br. s, $J_{6,1} \simeq J_{6,7} \simeq$ 2.0 Hz; 1H, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.45 (t; C-2), 29.63 (d; C-1), 48.26 (t; C-9), 65.73 (d; C-7), 76.25 (d; C-3), 86.32 (d; C-6), 208.14 (s; C-8). – MS (70 eV): *m/e* = 108 (1%, $M^+ - N_2$), 79 (13), 66 (100), 51 (5), 39 (18).

$C_7H_8N_2O$ (136.1) Calcd. C 61.73 H 5.93 N 20.59 Found C 61.71 H 5.89 N 20.42

Spiro[4,5-diazatricyclo[4.3.0.0^{3,7}]non-4-ene-8,2'-[1,3]dioxolane] (**5**): A sample of 1.00 g (3.06 mmol) of **9** was added to a solution of 1.30 g (23.2 mmol) of potassium hydroxide in ca. 30 ml of isopropyl alcohol and refluxed under nitrogen for 16 h. The reaction mixture was diluted with ca. 20 ml of ice water and concentrated HCl added to adjust the pH ≈ 1–2. After warming up to 50°C for ca. 4 min, the mixture was cooled to ca. 5°C with an ice bath, neutralized with 6 M NH_3 to pH ≈ 7–8, and 7 ml of an aqu. 3 M copper(II) chloride solution was added. The color of the reaction mixture turned dark red and after ca. 10 min a red-brown solid precipitated. Precipitation was complete when the supernatant solution was green coloured. The solid was collected on a Büchner funnel, washed with ca. 30 ml of water and then dissolved in 100 ml of 2 N aqu. ammonia. The blue solution was extracted with dichloromethane (4 × 40 ml), the combined organic layers were washed with 2 N HCl (3 × 30 ml) and water (2 × 30 ml), dried, and concentrated by roto-evaporation at 10°C and 22 Torr. The crude product was purified by sublimation (112°C at ca. 0.1 Torr), collecting the product on a cold finger kept at −78°C. A colourless solid, m.p. 48–50°C, 369 mg (67%), was obtained. – IR (KBr): 2990, 2940, 2880, 1500, 1352, 1340, 1226, 1150, 1100, 1070 cm^{-1}. – UV (*n*-pentane): λ_{max} (lg ε) = 340 nm (2.37). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.71 (dddd, $J_{2x,2n}$ = 12.5, $J_{2x,1}$ = 6.4, $J_{2x,9x}$ = 2.4, $J_{2x,7} \simeq$ 0.9 Hz; 1H, 2-*exo*-H), 1.49 (dd, $J_{2n,3}$ = 4.1 Hz; 1H, 2-*endo*-H), 1.98 (m; 1H, 1-H), 2.03 (dd, $J_{9n,9x}$ = 12.9, $J_{9n,1} \simeq$ 0.9 Hz; 1H, 9-*endo*-H), 2.16 (d of pseudo-t, $J_{9x,1}$ = 3.5 Hz; 1H, 9-*exo*-H), 2.25 (br. s; 1H, 7-H), 3.69–3.97 (m; 4H, 4'-H, 5'-H), 4.96 (mc, $J_{3,7}$ = 2.6, $J_{3,6} \simeq$ 0.8 Hz; 1H, 3-H), 5.18 (br. s, $J_{6,1} \simeq J_{6,7} \simeq$ 2.0 Hz; 1H, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.39 (t; C-2), 30.62 (d; C-1), 45.27 (t; C-9), 62.02 (d; C-7), 64.07 and 64.75 (two t; C-4', C-5'), 76.36 (d; C-3), 85.37 (d; C-6), 111.06 (s; C-8). – MS (70 eV): *m/e* = 180 (0.2%, M^+), 93 (10), 86 (100), 79 (7), 66 (15), 42 (31).

$C_9H_{12}N_2O_2$ (180.2) Calcd. C 60.00 H 6.67 N 15.56 Found C 60.03 H 6.57 N 15.46

8-Oxo-N-phenyl-4,5-diazatricyclo[4.3.0.0^{3,7}]nonane-4,5-dicarboximide (**7**): A sample of 5.00 g (46.3 mmol) of **1**[6] and 16.0 g (91.4 mmol) of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) were dissolved in 150 ml of 1,1,2,2-tetrachloroethane and magnetically stirred at 75–80°C for 2 d in a stoppered flask. The precipitate of the brown reaction mixture was removed by filtration and the filtrate concentrated by roto-evaporation (80°C/20 Torr). The residue was chromatographed on silica gel (ca. 15:1 ratio of adsorbant to substrate), eluting

with 10:1 CH_2Cl_2/EtOAc. The urazole **7** was purified by recrystallization from ethyl acetate and obtained in a 1.15 g (9%) yield, m.p. 210–214°C. – IR (KBr): 3080, 3060, 3000, 1800, 1790, 1750, 1730, 1505, 1420, 1146, 1080 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.68 (dd, $J_{2n,2x}$ = 13.5, $J_{2n,3}$ = 4.7 Hz; 1H, 2-*endo*-H), 2.18 (m; 1H, 2-*exo*-H), 2.21 (d, $J_{9n,9x}$ = 17.2 Hz; 1H, 9-*endo*-H), 2.34 (d of pseudo-t, $J_{9x,1} \simeq J_{9x,2x} \simeq$ 3.2 Hz; 1H, 9-*exo*-H), 2.90 (br. s; 1H, 7-H), 3.10 (br. s; 1H, 1-H), 4.72 (dd, $J_{3,7}$ = 2.2 Hz; 1H, 3-H), 4.82 (br. s; 1H, 6-H), 7.3–7.6 (m; 5H, phenyl). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 33.40 (t), 37.97 (d), 46.94 (t), 58.14 (d), 59.18 (d), 69.76 (d), 125.36 (d), 128.63 (d), 129.30 (d), 131.33 (s), 156.51 (s), 157.72 (s), 206.52 (s). – MS (70 eV): *m/e* = 283 (30%, M^+), 119 (100), 107 (12), 95 (12), 91 (13), 79 (18), 66 (22), 53 (6).

$C_{15}H_{13}N_3O_3$ (283.3) Calcd. C 63.60 H 4.63 N 14.83 Found C 63.55 H 4.53 N 14.73

N-Phenylspiro[4,5-diazatricyclo[4.3.0.0^{3,7}]nonane-8,2′-[1,3]dioxolane]-4,5-dicarboximide (**9**): A mixture of 1.10 g (3.88 mmol) of **7**, 320 mg (5.16 mmol) of ethylene glycol and ca. 5 mg of *p*-toluenesulfonic acid in 60 ml of dry toluene was placed into a 100 ml, round-bottomed flask, provided with water separator and reflux condenser, and refluxed for 5 h. After cooling to ca. 25°C, the reaction mixture was added to 70 ml of CH_2Cl_2, washed with water (1 × 50 ml), 2 N NaOH (1 × 50 ml), and again water (1 × 50 ml), dried and concentrated by roto-evaporation (50°C/22 Torr). The residue was recrystallized from 2:1 ethanol/ethyl acetate to yield 1.18 g (93%) of colourless prisms, m.p. 188–190°C. – IR (KBr): 3060, 2980, 2950, 2900, 1785, 1715, 1515, 1405, 1130, 1090 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.5–2.3 (m; 4H, 2-H, 9-H), 2.62 (br. s; 1H, 7-H), 2.73 (br. s; 1H, 1-H), 3.92 (m; 4H, 4′-H, 5′-H), 4.53 (br. s; 2H, 3-H, 6-H), 7.2–7.6 (m; 5H, phenyl). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.97 (t), 38.50 (d), 43.60 (t), 54.87 (d), 58.35 (d), 64.58 (t), 65.10 (t), 67.99 (d), 110.58 (s), 125.43 (d), 128.29 (d), 129.16 (d), 131.90 (s), 156.39 (s), 156.94 (s). – MS (70 eV): *m/e* = 327 (60%, M^+), 283 (13), 150 (100), 119 (73), 113 (59), 86 (56), 79 (16), 66 (13).

$C_{17}H_{17}N_3O_4$ (327.3) Calcd. C 62.38 H 5.24 N 12.84 Found C 62.40 H 5.08 N 12.83

Spiro[bicyclo[2.2.1]hept-5-ene-2,2′-[1,3]dithiolane] (**10**): A mixture of 3.00 g (27.8 mmol) of **1**[6], 3.20 g (34.0 mmol) of dithioethylene glycol and 12 ml of BF_3-etherate in 40 ml of acetic acid was stirred at 20°C for 4.5 h. Water was added (50 ml) and the reaction mixture extracted with CH_2Cl_2 (3 × 40 ml). The combined organic layers were washed with water (3 × 30 ml) and saturated brine (3 × 30 ml), dried, and concentrated by roto-evaporation at 40°C and 25 Torr. Distillation of the residue yielded 2.50 g (50%) of **10**, b.p. 65–69°C/0.2 Torr. – IR (neat): 3070, 2980, 2930, 2880, 1465, 1450, 1425, 1335, 1280, 1015 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.70 (m; 2H, 7-H), 1.92 (br. d, $J_{3n,3x}$ = 12.7 Hz; 1H, 3-*endo*-H), 2.40 (dd, $J_{3x,4}$ = 3.6 Hz; 1H, 3-*exo*-H), 2.84–3.05 (m; 2H, 1-H, 4-H), 3.30 (mc; 4H, 4′-H, 5′-H), 6.27 (m; 2H, 5-H, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 39.95 (t), 40.64 (t), 42.34 (d), 47.40 (t), 50.32 (t), 57.08 (d), 70.13 (s), 135.49 (d), 139.07 (d). – MS (70 eV): *m/e* = 184 (10%, M^+), 156 (4), 118 (100), 90 (13), 66 (11).

$C_9H_{12}S_2$ (184.3) Calcd. C 58.64 H 6.56 Found C 58.43 H 6.51

4-Phenyl-1-[spiro[bicyclo[2.2.1]hept-5-ene-2,2′-[1,3]dithiolane]-4′-yl]-1,2,4-triazolidine-3,5-dione (**11**): A mixture of 500 mg (2.72 mmol) of **10** and 1.00 g (5.70 mmol) of PTAD in 40 ml of 1,1,2,2-tetrachloroethane was stirred at 75°C for 24 h. Suspended matter was removed by filtration, the filtrate concentrated by roto-evaporation at 80°C and 25 Torr, and the residue submitted to column chromatography (ca. 50:1 adsorbant to substrate ratio) eluting with 4:1 CH_2Cl_2/EtOAc. Final recrystallization from ethanol yielded the pure product, 280 mg (29%) colourless prisms, m.p. 205°C. – IR (KBr): 3200, 3070, 2970, 1770, 1700, 1510, 1435, 1235, 1205, 770 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.69 (m; 2H, 7-H), 2.16 (br. d, $J_{3n,3x}$ = 13.5 Hz; 1H, 3-*endo*-H), 2.34 (dd, $J_{3x,4}$ = 3.6 Hz; 1H, 3-*exo*-H),

2.83–3.13 (m; 2H, 1-H, 4-H), 3.56 (m; 2H, 5′-H), 6.20 (m; 1H, 4′-H), 6.34 (m; 2H, 5-H, 6-H), 7.3–7.6 (m; 5H, phenyl), 8.1 (m; 1H, NH). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 41.93 (d), 42.20 (d), 44.67 (t), 45.23 (t), 45.41 (t), 46.13 (t), 49.32 (t), 50.38 (t), 56.05 (d), 56.43 (d), 70.36 (d), 71.05 (d), 71.16 (s), 71.28 (s), 125.65 (d), 128.31 (d), 129.15 (d), 131.29 (s), 134.73 (d), 135.89 (d), 138.98 (d), 139.89 (d), 151.66 (s), 151.90 (s) (mixture of isomers). – MS (70 eV): *m/e* = 360 (0.1%, $M^+ + 1$), 183 (7), 157 (79), 119 (21), 118 (12), 117 (100), 116 (62), 91 (14), 84 (11), 79 (12), 66 (26), 56 (5).

$C_{17}H_{17}N_3O_2S_2$ (359.5) Calcd. C 56.80 H 4.77 N 11.69 Found C 56.78 H 4.65 N 11.61

4-[2-(2-Propenyl)-1,3-dioxolan-2-yl]-1H-pyrazole (**12**): A sample of 91.8 mg (0.509 mmol) of **5** was pyrolyzed by subliming it at ca. 120°C and 0.1 Torr through a hot tube, consisting of Pyrex glass (35-cm long, ∅ = 1.3 cm), which was externally heated at ca. 400°C by means of a resistance wire. The pyrolysate was condensed into a cold trap, kept at liquid nitrogen temperature. After flushing the apparatus with nitrogen and warm-up to ca. 15°C, the product mixture (90 mg) was dissolved in $CDCl_3$. Its composition was determined by ^{1}H NMR and capillary GC, consisting of a ca. 2:1 mixture of the dioxolane **13** and the pyrazole **12**. The solution was concentrated by roto-evaporation at 60°C and 22 Torr and the residue recrystallized from *n*-hexane, affording 30 mg (33%) of **12** as colourless needles, m.p. 71°C. – IR (KBr): 3160, 3042, 2960, 2880, 2835, 1387, 1190, 1048, 1023, 990, 955 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.71 (d of pseudo-t, $J_{7,8}$ = 7.0, $J_{7,9c}$ = 1.5, $J_{7,9t}$ = 1.1 Hz; 2H, 7-H), AA′KK′ ($\delta_{AA'}$ = 3.91, $\delta_{KK'}$ = 4.03, J_A = 7.0, J_K = 7.0, J = 7.6, J' = 6.2 Hz; 4H, 10-H, 11-H), 5.10 (d of m, $J_{9c,8}$ = 17.1, $J_{9c,9t}$ = 2.1 Hz; 1H, 9-*cis*-H), 5.10 (d of m, $J_{9t,8}$ = 10.3 Hz; 1H, 9-*trans*-H), 5.80 (mc; 1H, 8-H), 7.57 (s; 2H, 3-H, 5-H), 11.12 (br. s; 1H, 1-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 45.10 (t; C-7), 64.85 (t; C-10, C-11), 106.78 (s; C-6), 118.41 (t; C-9), 124.16 (s; C-4), 132.14 (d; C-3, C-5), 132.36 (d; C-8). – MS (70 eV): *m/e* = 139 (87%, $M^+ - C_3H_5$), 119 (1), 95 (100), 92 (1), 81 (1), 68 (5), 65 (2), 53 (2), 41 (7), 39 (11).

$C_9H_{12}N_2O_2$ (180.2) Calcd. C 60.00 H 6.67 N 15.56 Found C 59.63 H 6.64 N 15.43

Spiro[1,3-dioxolane-2,3′-tricyclo[3.2.0.0^{2,7}]heptane] (**13**): A solution of 42.4 mg (0.235 mmol) of **5** in ca. 0.5 ml of C_6D_6 was deaerated by purging with a slow stream of nitrogen gas for ca. 20 min and irradiated with an argon ion laser at 334 nm and ca. 50°C. The reaction progress was monitored by ^{1}H NMR and all azoalkane **5** was consumed within ca. 20 min. An UV spectrum of the reaction mixture showed no absorption higher than 320 nm. The photolysate was concentrated by roto-evaporation at 0°C and 25 Torr. The residue exhibited a very small signal in the IR at 2060 cm^{-1}, indicating the presence of traces of a diazoalkane. Capillary GC analysis showed two minor products (each ca. 0.8%) and one main product, which could be isolated by preparative GC, using a 1.5-m glass column, packed with 10% Carbowax M on Chromosorb WHP, operated at injector, detector, and column temperatures of 200, 200, and 148°C, respectively, and a carrier gas pressure (N_2) of 0.6 kg/cm^2. The dioxolane **13** was obtained as a colourless oil, ca. 25 mg (70%). – IR (neat): 3060, 2980, 2890, 1375, 1340, 1295, 1185, 1130, 1095, 1030, 960, 800, 778 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (ddd, $J_{6'n,6'x}$ = 9.1, $J_{6'n,1'}$ = 2.6, $J_{6'n,5'}$ = 1.0 Hz; 1H, 6′-*endo*-H), 1.56–1.61 (m; 2H, 2′-H, 7′-H), 1.68 (d, $J_{4'n,4'x}$ = 12.7 Hz; 1H, 4′-*endo*-H), 2.02 (br. dd, $J_{4'x,5'}$ = 4.3 Hz; 1H, 4′-*exo*-H), 2.32–2.38 (m; 1H, 6′-*exo*-H), 2.46–2.51 (br. s; 2H, 1′-H, 5′-H), 3.90–4.14 (m; 4H, 4-H, 5-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.07 (d; C-7′), 27.26 (t; C-6′), 28.62 (d; C-1′), 29.74 (d; C-2′), 35.59 (d; C-5′), 46.93 (t; C-4′), 64.30 and 64.94 (two t; C-4, C-5), 118.02 (s; C-3′). – MS (70 eV): *m/e* = 152 (0.5%, M^+), 91 (7), 86 (100), 79 (12), 77 (7), 66 (11), 53 (6), 42 (36).

$C_9H_{12}O_2$ (152.2) Calcd. C 71.03 H 7.95 Found C 70.90 H 7.85

6-exo-Chlorobicyclo[3.2.0]heptan-3-one (**14**): A solution of ca. 20 mg of **13** in 0.5 ml of $CDCl_3$ was mixed with ca. 0.1 ml of conc. HCl and stirred at 25°C for 2 h. To the mixture was added 1 ml of water, the organic layer separated, dried and the product isolated by preparative GC, using the same conditions as in the isolation of **13**. Of the chloroketone **14** were obtained ca. 15 mg (79%) as a colourless oil.

In another run, in which only half the amount of conc. HCl was used, the ^1H NMR of the crude reaction mixture in $CDCl_3$ showed two products, namely the chloroketone **14** and the tricyclic ketone **2**, in a ca. 1:2 ratio. When this reaction mixture was treated with ca. 0.1 ml of conc. HCl for 5 d, **2** was converted completely to **14**, as confirmed by ^1H NMR. – IR ($CDCl_3$): 2980, 2940, 2900, 1745, 1410, 1275, 1250, 1150, 1135, 870 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (dd, $J_{2n,2x}$ = 19.4, $J_{2n,1}$ = 3.9 Hz; 1H, 2-*endo*-H), 2.37 (br. d, $J_{4n,4x}$ = 19.5, $J_{4n,5} \simeq$ 2.0 Hz; 1H, 4-*endo*-H), 2.40 (dddd, $J_{7n,7x}$ = 13.3, $J_{7n,6}$ = 7.5, $J_{7n,1}$ = 3.7, $J_{7n,5}$ = 1.1 Hz; 1H, 7-*endo*-H), 2.49 (ddd, $J_{4x,5}$ = 8.8, $J_{4x,2x}$ = 2.0 Hz; 1H, 4-*exo*-H), 2.58 (ddd, $J_{2x,1}$ = 10.0, $J_{2x,4x}$ = 2.0 Hz; 1H, 2-*exo*-H), 2.62 (dddd, $J_{7x,1}$ = 9.0, $J_{7x,6}$ = 7.5, $J_{7x,5}$ = 1.0 Hz; 1H, 7-*exo*-H), 3.17 (mc, $J_{1,5} \simeq$ 9.5 Hz; 1H, 1-H), 3.25 (mc; 1H, 5-H), 4.20 (d of pseudo-t, $J_{6,5}$ = 5.5 Hz; 1H, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.33 (d; C-1), 38.91 (t; C-2), 43.40 and 43.79 (two t; C-4, C-7), 47.58 (d; C-5), 56.89 (d; C-6), 218.73 (s; C-3). – MS (70 eV): *m/e* = 146 (7%, $M^+ + 2$), 144 (21, M^+), 102 (30), 81 (100), 67 (79), 54 (96), 41 (81).

Quantitative Product Analyses

Direct Photolysis: A 1 ml aliquot of a 0.01 M solution of the corresponding azoalkane in benzene was transferred into a Pyrex tube and degassed by means of three "freeze-pump-thaw" cycles. The reaction vessel was placed into the Rayonet photoreactor and irradiated at 350 nm and ca. 30°C. The reaction progress was monitored via capillary GC. The results and GC-conditions are given in Table 1. Minor products were detected, but were not identified.

Benzophenone-sensitized Photolysis: The photolysis was carried out as described above, except in the presence of 0.15 M benzophenone. The results are given in Table 1.

Direct Photolysis in the Presence of 1,3-Cyclohexadiene: The photolysis was carried out as described above, except in the presence of 0.10 M 1,3-cyclohexadiene as triplet quencher. The results are given in Table 1.

Tetramethyl-1,2-dioxetane (TMD) Chemienergized Decomposition of Azoalkane **4**: A sample of 1.67 mg (0.012 mmol) of **4** and 0.135 ml (0.012 mmol) of 0.089 M TMD in benzene were heated in a sealed ampoule for 1.5 h at 85°C. The product mixture was analyzed by capillary GC. The results are given in Table 1.

Vacuum Flash Thermolysis: A sample of 26.4 mg (0.194 mmol) of azoalkane **4** was pyrolyzed by subliming it at 150°C and 28 Torr through a hot Pyrex tube (35 cm long, ∅ 1.3 cm), which was externally heated at ca. 300°C by means of a resistance wire. The products were collected in a cold trap, kept at liquid nitrogen temperature. After flushing the apparatus with nitrogen and warm-up to ca. 15°C, the products were dissolved in $CDCl_3$. The relative product composition (%) was determined by capillary GC, the absolute yields (%) by 90 MHz ^1H NMR, using trioxane as an internal standard. The results are given in Table 1.

Mass Balance: A solution of ca. 0.3 mmol of the corresponding azoalkane in 0.5 ml of C_6D_6 (in the sensitized photolysis ca. 1.5 mmol of benzophenone was added) was placed into a NMR-tube, deaerated by purging with a slow stream of nitrogen gas for ca. 20 min, and irradiated at ca. 5°C with the argon ion laser with the 334, 351, and 364 nm lines. ^1H

NMR monitoring revealed complete consumption of the azoalkane after ca. 20 min of irradiation. To the photolysate was added the required amount of trioxane (internal standard) and the quantitative analysis of the products carried out by means of 90 MHz ^{1}H NMR. The absolute yields (%) were determined by integration of the product resonances versus the internal standard. The results are listed in Table 1.

Preparation of the Ketones **2** *and* **3**: A solution of 500 mg (4.63 mmol) of **1**[6] in 85 ml of acetone (distilled from $KMnO_4$) was deaerated by purging with a slow stream of nitrogen gas for 30 min and irradiated under a nitrogen atmosphere at ca. 40°C in the Rayonet photoreactor, equipped with 300 nm lamps. The reaction progress was monitored by capillary GC and the photolysis was discontinued after 4 h, when ca. 30% of the starting ketone were consumed. The reaction mixture was concentrated by roto-evaporation at 0°C and 22 Torr. The residual yellow oil was separated by means of preparative GC using a 6-m SE 30 stainless steel column, operated at injector, detector and column temperatures of 140, 140, and 100°C, respectively, and a carrier gas flow of ca. 90 ml/min. The first fraction yielded 150 mg starting ketone **1**, the second fraction ca. 20 mg bicyclo[3.2.0]hept-3-en-6-one (**3**)[2a,b] together with ca. 8% starting ketone **1** and the third fraction ca. 25 mg tricyclo[3.2.0.0^{2,7}]heptan-3-one (**2**)[2c]. The spectral data of the ketones **2** and **3** matched those reported[2].

X-Ray Analysis of the N-Methyl Derivative of Urazole **7***)

The orientation matrix and the cell parameters were determined from a clear colourless crystal of dimensions 0.15 × 0.75 × 0.1 mm on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, Mo-K_α, 2Θ maximum = 55°. The intensities

Table 2. Positional (× 10^4) and thermal (× 10^3) parameters in Å^2 of the *N*-methyl derivative of urazole **7**[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	3140(2)	4229(2)	-2309(7)	68(2)	57(2)	62(2)	4(2)	-7(2)	5(2)
N(2)	2577(2)	4258(2)	-552(6)	67(2)	52(2)	71(2)	9(2)	1(2)	12(2)
C(3)	1899(2)	3956(2)	-845(8)	59(2)	64(3)	78(3)	14(2)	4(2)	15(2)
O(3)	1483(2)	4067(2)	-2378(6)	66(2)	135(3)	111(3)	57(2)	-13(2)	13(2)
N(4)	1774(2)	3530(2)	1049(5)	56(2)	63(2)	58(2)	-1(2)	2(2)	8(2)
C(5)	2390(2)	3422(2)	2263(7)	67(3)	60(2)	48(2)	-16(2)	4(2)	10(2)
O(5)	2469(2)	3000(2)	3832(4)	86(2)	93(2)	47(1)	7(2)	1(2)	8(2)
N(6)	2896(2)	3910(2)	1397(5)	64(2)	58(2)	55(2)	-14(2)	-1(2)	4(2)
C(7)	3599(2)	3632(2)	582(6)	62(2)	52(2)	53(2)	-2(2)	-8(2)	2(2)
C(8)	3469(2)	3461(2)	-1903(6)	60(2)	50(2)	50(2)	-8(2)	-5(2)	-6(2)
C(9)	4219(2)	3426(2)	-2927(7)	65(2)	73(3)	69(3)	-14(2)	-4(2)	-2(2)
O(9)	4418(2)	3063(2)	-4489(5)	75(2)	93(2)	83(2)	-26(2)	15(2)	2(2)
C(10)	4700(3)	3828(3)	-1266(9)	79(3)	112(4)	108(4)	-3(3)	-8(3)	-11(3)
C(11)	4144(2)	4262(2)	225(8)	66(3)	67(3)	90(3)	-14(3)	-11(2)	-9(2)
C(12)	3758(2)	4733(2)	-1527(7)	89(3)	60(2)	69(3)	-2(2)	4(2)	-12(2)
C(41)	1103(2)	3164(3)	1550(7)	71(3)	107(4)	74(3)	4(3)	11(2)	-4(3)

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

*) Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany) by specifying registry number CSD 51077, author, and the reference to this publication.

of 2305 reflections were measured, 1522 of them with $F \geqq 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 199 strong reflections were determined and from the resulting *E*-map approximate positions of all non-hydrogen atoms could be refined by anisotropic least squares cycles to $R = 0.081$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

Urazole **7** (*N* methyl derivative) crystallizes orthorhombically in the space group *Pbca* (No. 61) with $a = 1860.9$ (9), $b = 1818.2$ (9), $c = 594.4$ (3) pm. The unit cell contains $Z = 8$ formula units, the density was calculated to be 1.461 g · cm^{-3}. All atomic coordinates are listed in Table 2. The labeling of the atoms is given in Figure 1. Bond distances and angles are summarized in Table 3.

Table 3. Bond lengths (pm) and angles (deg) of the *N*-methyl derivative of urazole **7** [a]

C(1) - N(2)	148.1(5)	C(3) - O(3)	121.2(6)	C(5) - O(5)	121.6(5)	C(8) - C(9)	152.3(6)
C(1) - C(8)	154.4(5)	C(3) - N(4)	138.6(5)	C(5) - N(6)	139.3(5)	C(9) - O(9)	119.9(5)
C(1) - C(12)	154.2(6)	N(4) - C(5)	136.9(5)	N(6) - C(7)	148.4(5)	C(9) - C(10)	152.0(7)
N(2) - C(3)	138.7(5)	N(4) - C(41)	144.6(5)	C(7) - C(8)	152.9(5)	C(10) - C(11)	157.7(7)
N(2) - N(6)	144.7(5)			C(7) - C(11)	154.4(6)	C(11) - C(12)	152.7(6)

N(2) - C(1) - C(8)	101.6(3)	N(4) - C(5) - O(5)	126.6(4)	C(8) - C(9) - O(9)	128.1(4)
N(2) - C(1) - C(12)	107.1(3)	N(4) - C(5) - N(6)	106.3(3)	C(8) - C(9) - C(10)	105.1(3)
C(8) - C(1) - C(12)	101.3(3)	O(5) - C(5) - N(6)	127.0(4)	O(9) - C(9) - C(10)	125.8(4)
C(1) - N(2) - C(3)	122.8(3)	N(2) - N(6) - C(5)	107.2(3)	C(9) - C(10) - C(11)	102.7(4)
C(1) - N(2) - N(6)	105.0(3)	N(2) - N(6) - C(7)	104.5(3)	C(7) - C(11) - C(10)	97.9(3)
C(3) - N(2) - N(6)	107.5(3)	C(5) - N(6) - C(7)	120.1(3)	C(7) - C(11) - C(12)	101.6(3)
N(2) - C(3) - N(4)	105.8(4)	N(6) - C(7) - C(8)	104.2(3)	C(10) - C(11) - C(12)	101.9(4)
N(2) - C(3) - O(3)	127.5(4)	N(6) - C(7) - C(11)	111.8(3)	C(1) - C(12) - C(11)	102.8(3)
N(4) - C(3) - O(3)	126.6(4)	C(8) - C(7) - C(11)	97.0(3)		
C(3) - N(4) - C(5)	111.6(3)	C(1) - C(8) - C(7)	91.7(3)		
C(3) - N(4) - C(41)	124.7(3)	C(1) - C(8) - C(9)	109.7(3)		
C(5) - N(4) - C(41)	123.3(3)	C(7) - C(8) - C(9)	104.4(3)		

[a] The standard deviations are given in parentheses.

[1] *D. I. Schuster*, in Rearrangement in Ground and Excited States, Vol. 3, pp. 232–279, *P. de Mayo*, Ed., Academic Press, New Vork 1980.

[2] [2a] *G. O. Schenck* and *R. Steinmetz*, Chem. Ber. **96**, 520 (1963). – [2b] *D. I. Schuster, M. Axelrod*, and *J. Auerbach*, Tetrahedron Lett. **1963**, 1911. – [2c] *J. Ipaktschi*, Chem. Ber. **105**, 1840 (1972). – [2d] *M. A. Schexnayder* and *P. S. Engel*, Tetrahedron Lett. **1975**, 1153.

[3] *W. Adam, N. Carballeira*, and *W. D. Gillaspey*, Tetrahedron Lett. **24**, 5473 (1983).

[4] *W. Adam, M. Dörr, K. Hill, E.-M. Peters, K. Peters*, and *H. G. von Schnering*, J. Org. Chem. **50**, 587 (1985).

[5] [5a] *W. Adam, O. De Lucchi*, and *K. Hill*, J. Am. Chem. Soc. **104**, 2934 (1982). – [5b] *W. Adam, N. Carballeira, O. De Lucchi*, and *K. Hill*, in Stereochemistry and Reactivity of Systems Containing π-Electrons, pp. 241–278, *W. H. Watson*, Ed., Verlag Chemie International, Deerfield Beach, Florida 1983.

[6] *S. Ranganathan, D. Ranganathan*, and *A. K. Mehrotra*, Synthesis **1977**, 289.

[7] *F. D. Greene*, in Lit.[5b], pp. 197–240.

[8] *P. Vogel*, in Lit.[5b], pp. 147–195.

[9] *L. A. Paquette, M. J. Wyvratt, H. C. Berk*, and *R. E. Moerck*, J. Am. Chem. Soc. **100**, 5845 (1978).

[10] *J. Meinwald* and *B. C. Cadoff*, J. Org. Chem. **27**, 1539 (1962).
[11] [11a] *R. B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan*, and *H. Vorbrüggen*, J. Am. Chem. Soc. **88**, 852 (1966). – [11b] *W. Ando, K. Ito*, and *T. Takata*, Tetrahedron Lett. **23**, 3909 (1982).
[12] *W. Adam* and *O. De Lucchi*, J. Org. Chem. **46**, 4133 (1981).
[13] *A. A. Bothner-By* and *S. Castellano*, in Computer Programs for Chemistry, 1st Ed., Vol. 1, *D. F. De Tar*, Ed., A. W. Benjamin, New York 1968.
[14] *A. S. Kende* and *J. Y. C. Chu*, J. Org. Chem. **38**, 2252 (1973).
[15] *M. H. Chang* and *D. A. Dougherty*, J. Am. Chem. Soc. **104**, 2333 (1982).
[16] [16a] *P. S. Engel, C. J. Nalepa, D. W. Horsey, D. E. Keys*, and *R. T. Grow*, J. Am. Chem. Soc. **105**, 7102 (1983). – [16b] *P. S. Engel* and *D. B. Gerth*, J. Am. Chem. Soc. **105**, 6849 (1983). – [16c] *J. J. Dannenberg* and *D. Rocklin*, J. Org. Chem. **47**, 4529 (1982). – [16d] *P. C. Hiberty* and *Y. Jean*, J. Am. Chem. Soc. **101**, 2538 (1979).
[17] *P. S. Engel*, Chem. Rev. **80**, 99 (1980).
[18] *B. Bigot, A. Sevin*, and *A. Devaquet*, J. Am. Chem. Soc. **100**, 2639 (1978).
[19] *P. S. Engel, D. W. Horsey, D. E. Keys, C. J. Nalepa*, and *L. R. Soltero*, J. Am. Chem. Soc. **105**, 7108 (1983).
[20] *S. W. Benson*, Thermochemical Kinetics, 2nd Edition, John Wiley and Sons, New York 1972.
[21] *C. Doubleday jr.*, *J. W. McIver jr.*, and *M. Page*, J. Am. Chem. Soc. **104**, 6533 (1982).
[22] *A. H. Goldberg* and *D. A. Dougherty*, J. Am. Chem. Soc. **105**, 284 (1983).

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