Photoinduced Nitrene, Carbene, and Atomic Oxygen Transfer Reactions Starting from the Corresponding Pyridinium N-, C-, and O-Ylides

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Ultraviolet irradiation of the pyridinium ylides **1**, **2**, and **3** led to fragmentation of the exocyclic polar bonds, as well as to skeletal rearrangements. The photoinduced fragmentation processes gave the corresponding pyridines and highly reactive intermediates, i.e. ethoxycarbonylnitrene, dicyanocarbene and atomic oxygen (oxene), respectively. Trapping of the reactive intermediates by alkanes and alkenes permitted the determination of their spin multiplicity. Ethoxycarbonylnitrene was in its triplet ground state at the moment of its formation. Dicyanocarbene occurred as a mixture of singlet and triplet, as determined by dilution experiments with variable amounts of alkenes. As to atomic oxygen, all collected data point to its formation in solution in its triplet ground state.

Photoinduzierte Transfer-Reaktionen von Nitrenen, Carbenen und atomarem Sauerstoff aus den entsprechenden N-, C- und O-Pyridinium-Yliden

UV-Bestrahlung der Pyridinium-Ylide **1**, **2** und **3** führte sowohl zur Spaltung der polaren exocyclischen Bindungen, als auch zu Umlagerungen. Die Photolysen ergaben die entsprechenden Pyridine sowie die hochreaktiven Zwischenprodukte Ethoxycarbonylnitren, Dicyanocarben und atomaren Sauerstoff (Oxen). Durch Abfangreaktionen und Analyse der Produkte, konnte die Spinmultiplizität der Zwischenstufen ermittelt werden. So entsteht zum Beispiel Ethoxycarbonylnitren, sofort nach der N−N-Spaltung, im Triplett-Grundzustand. Dicyancarben dagegen entsteht als ein Gemisch der Triplett- und Singulett-Spezies; dies konnte durch Verdünnungsexperimente mit Olefinen ermittelt werden. Schließlich deuten alle Experimente darauf hin, daß der atomare Sauerstoff im Triplett-Grundzustand auftritt.

Fragmentation patterns which were observed during ultraviolet irradiation of the following pyridinium N-ylides will be described and discussed: *N*-(ethoxycarbonylimino)pyridinium ylide (**1**), pyridinium dicyanomethylide (**2**), and 2-cyanopyridine *N*-oxide (**3**). As a rule, these mesoionic compounds undergo two competing photoreactions:

– photolytic cleavage which leads to the corresponding pyridines and to nitrenes, to carbenes, and formally to "oxene", respectively;

– photoinduced rearrangement which gives either ring contraction or ring enlargement depending on the starting material[1].

In Scheme 1 are reproduced a few well-documented results which had been obtained during ultraviolet irradiation, in *benzene* solution, of the pyridinium ylides **1** and **2** and of the ring-unsubstituted pyridine *N*-oxide. The photoproducts of **1** were obtained in excellent overall yield, the ones of **2** and of pyridine *N*-oxide in poor yields[1]. In these three photochemical experiments the benzene molecules reacted:

– with ethoxycarbonylnitrene to give *N*-(ethoxycarbonyl)azepine[2],

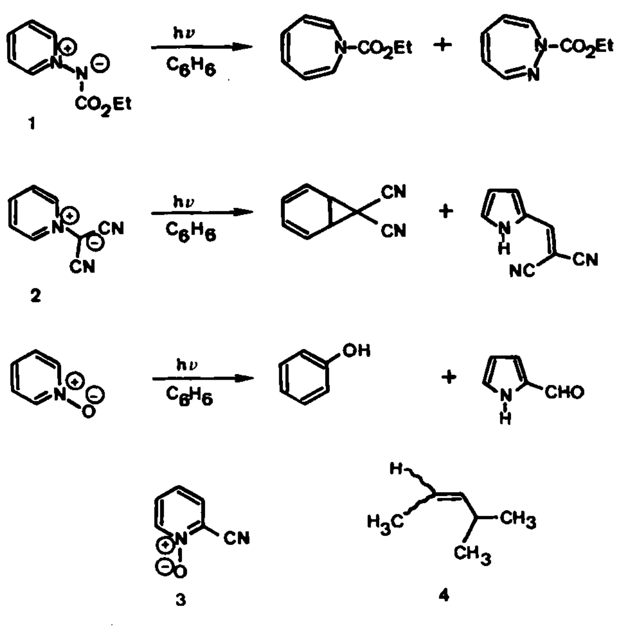
– with dicyanocarbene to give 7,7-norcaradienedicarbonitrile[3],

– with what can be considered formally as atomic oxygen to give phenol[4]. To our knowledge this latter result represented the first case of a photoinduced abiotic atomic oxygen transfer reaction.

In this publication we would like to discuss some mechanistic aspects and to give the full experimental results about the above-cited photoinduced transfer reactions. These latter ones had already been discussed in some preliminary short communications, with the exception of atomic oxygen transfer, for which some new results are presented herein.

Initially it was thought that the photoinduced rearrangement reactions (Scheme 1) proceeded from an excited singlet state, and the fragmentation patterns from an excited triplet state[1]. Such a clearcut dualistic behaviour is true indeed for the N-ylides of type **1** as will be demonstrated in the following chapter. Excited-state reactions of the other two pyridinium ylides proved to be more complex though.

Scheme 1



Photoinduced Ethoxycarbonylnitrene Transfer Reactions, Starting from Pyridinium N-Ylide 1

Direct ultraviolet irradiation of the pyridinium N-ylide **1** in methylene chloride in the presence of *trans*-4-methyl-2-pentene (**4**) led to a mixture of *cis*- and *trans*-aziridines **5**

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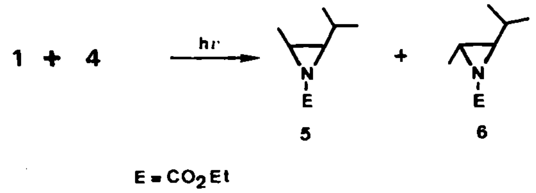
and **6** in poor yields (Scheme 2). The **5**/**6** aziridine ratio proved to be constant, whatever the relative concentrations of the ylide **1** and of the olefin **4** were (Table 1). When *cis*-4-methyl-2-pentene was used instead of the *trans* isomer, and when the same sequence of experiments was repeated, similar results were obtained: the **5**/**6** aziridine ratio again was constant, irrespective of the relative ylide/olefin concentration (Table 1 and Figure 1). This latter ratio though was different from the one obtained with the *trans* olefin **4**[5].

Ethoxycarbonylnitrene, which seems to be the most-studied nitrene, had been trapped in various ways[6-11]. It was found in particular that the distribution of the products — obtained by trapping this nitrene with various substrates — depends strongly on the spin multiplicity of the nitrene. The method we used above — addition of ethoxycarbonylnitrene to dissymmetric *cis* or *trans* olefins — had been worked out by Lwowski and his co-workers[8,12,13] and used ever since, in particular by Hayashi and Swern[14].

Scheme 2



The mechanistic interpretation of the data we have collected above seems to be straightforward. If the photochemically produced nitrene were in its excited singlet state, one would observe that the **5**/**6** aziridine ratio changes as a function of olefin concentration[6]: the lifetime of this excited singlet state is a short one indeed; so that by means of an intersystem crossing it would lead to the corresponding nitrene triplet, which happens to be the ground state[6,15]. Since it is known that singlet nitrenes add stereospecifically and in a concerted fashion to olefinic double bonds (whereas triplet nitrenes add in a nonconcerted and nonstereospecific manner), it follows that the **5**/**6** ratio would be expected to change as a function of olefin concentration[6]. Clearly, Table 1 and Figure 1 [(2)-curve] indicate with a good approximation that there is no change in the **5**/**6** ratio. One concludes therefore that the incipient ethoxycarbonylnitrene occurs photochemically in close to 100% yield in its triplet ground state.

Table 1. Relative amounts of *cis*-aziridine **5**[a] obtained during photolysis of (ethoxycarbonylimino)pyridinium ylide **1** in the presence of various amounts of *cis*- and *trans*-4-methyl-2-pentene **4**[b]

Concentration of *cis*- and of *trans*-**4** (mol-%)	33	15	10	5	1
cis-**5** (mol-%) formed during photolysis of **1** in the presence of *cis*-**4**	39.0	38.5	38.5	38.0	35.0
cis-**5** (mol-%) formed during photolysis of **1** in the presence of *trans*-**4**	19.4	21.0	19.0	19.6	19.1

[a] mol-% of *cis*-**5** + mol-% of *trans*-**6** = 100%. — [b] Concentration of **1**: 0.15 molar.

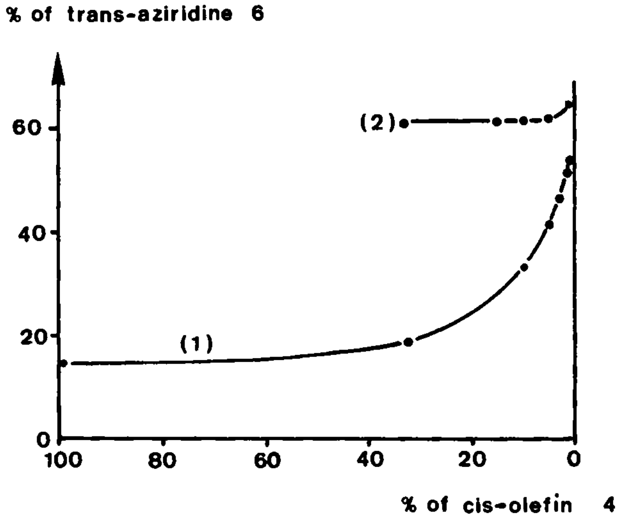


Fig. 1. Percentage of aziridine **6** obtained during photolysis of **1** as a function of olefin **4** concentration

One concludes furthermore that the precursor of this triplet nitrene is the ylide **1** in its excited triplet state, for the following two reasons:

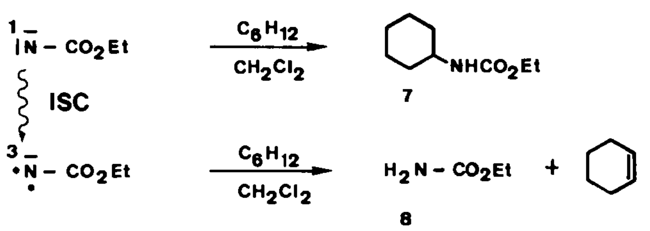
— The first excited triplet state of pyridine has an energy of 82 kcal/mol (100 kcal/mol for the first excited singlet state)[16], a value which cannot be attained with the photochemical conditions employed in these experiments (see Experimental).

— Photoexcitation of triplet sensitizers in the presence of the ylide **1** led *only* to N — N fragmentation[17], whereas direct irradiation gave mostly the corresponding diazepine (Scheme 1) and only small amounts of fragmentation products, i.e. pyridine and ethoxycarbonylnitrene[1].

The mechanistic interpretation we arrived at, for the formation of the nitrene in its triplet state, was corroborated by some complementary experiments. In one, we repeated Lwowski's thermolytic experiments starting from ethyl azidoformate, which led to nitrogen and to the ethoxycarbonylnitrene. In the presence of various amounts of *cis*-4-methyl-2-pentene, thermolysis of ethyl azidoformate led to a mixture of the two aziridines **5** and **6** in ratios which *changed dramatically* as a function of olefin concentration (Figure 1). The (1)-curve, which proved to be identical with the one published by Lwowski[13], clearly indicates that the incipient nitrene occurs in a singlet state which spin-relaxes to give the corresponding triplet ground state; the more so the less olefin is present. Furthermore, Lwowski had shown that ethoxycarbonylnitrene in its singlet state gave insertion reactions into the C — H bonds of cyclohexane, leading to cyclohexylurethane **7**; whereas the same nitrene in its triplet state reacted by hydrogen abstraction with cyclohexane, leading thereby to the urethane **8** and to cyclohexene (Scheme 3)[7,10,13]. Such a finely differentiated chemical behaviour of singlet and triplet ethoxycarbonylnitrene was used by Hayashi and Swern in order to determine the spin multiplicity of this nitrene when it was produced by photolysis of *N*-(ethoxycarbonylimino)sulfuranes[14]. When the ultraviolet irradiation of the ylide **1** was performed in a cyclohexane/methylene chloride mixture – and using experimental conditions similar to the ones described by Lwowski[7,10,13] – the urethane **8** was the only photoproduct (25% yield). Not even trace amounts of the cyclohexylurethane **7** were detected by GLC.

Similar results were obtained by Abramovitch and Takaya[18] and by Bird et al.[19]. Both groups irradiated some iminopyridinium N-ylides in a variety of solvents and observed homolytic fragmentation of the N–N bonds. In all these cases the incipient nitrenes led to hydrogen abstraction only, which demonstrates that they occurred in their triplet ground state.

Scheme 3



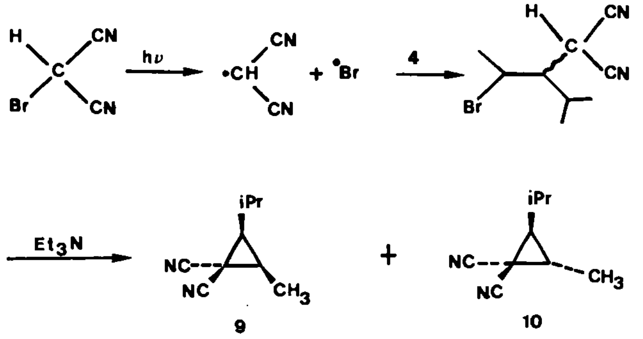
Lwowski has shown that α-methylstyrene traps triplet nitrenes selectively and at a fast rate[12]. UV irradiation of **1** in the presence of 4-methyl-2-pentene and of α-methylstyrene led to fragmentation of the N–N bond and to the formation of pyridine; nevertheless, aziridines **5** and **6** could not be detected in this experiment. These results are in good agreement with the conclusion that the incipient ethoxycarbonylnitrene is in its triplet state.

Photoinduced Dicyanocarbene Transfer Reactions, Starting from Pyridinium Dicyanomethylide (2)

Pyridinium dicyanomethylide (**2**) behaves as a 1,3-dipole in the ground state, since it undergoes cycloadditions with dipolarophiles[20]. When the lowest energy absorption band of **2** was excited with UV light, pyridine and dicyanocarbene were formed in low yields, among other photoproducts[3]; the photogenerated dicyanocarbene was trapped in benzene solution[3], leading thereby to 7,7-norcaradienedicarbonitrile (Scheme 1), a compound whose synthesis had already been described by Ciganek[21]. This author thermolyzed the highly unstable dicyanodiazomethane, and trapped it in benzene solution, whereby 7,7-norcaradienedicarbonitrile was isolated[21]. Ciganek demonstrated furthermore that, during thermolytic cleavage of dicyanodiazomethane, the incipient dicyanocarbene appeared in its singlet state which underwent an intersystem crossing to the corresponding triplet ground state. Both, singlet and triplet dicyanocarbenes, were trapped with *cis*- and *trans*-2-butene, leading to concerted–stereospecific, and to nonconcerted–nonstereospecific cycloadditions respectively, whereby the corresponding *cis*- and *trans*-cyclopropane derivatives were formed[22]. Ciganek's conclusions, pertaining to the spin multiplicity–reactivity relationship, corroborated Skell's rules[23,24].

Using the methodology described by Boldt et al.[25], we synthesized the two cyclopropane derivatives **9** and **10** (Scheme 4) as reference material. These two stereoisomers were separated by preparative GLC and identified by ^{13}C-NMR, ^{1}H-NMR spectra having been of no help. Close examination of the ^{13}C-NMR spectrum of the stereoisomer **9** shows a severe steric interaction between isopropyl and methyl groups, which leads to an important γ-gauche effect between C-6 and C-9. These two carbon atoms are shielded by 5.7 and 5.9 ppm respectively, when compared to the chemical shifts of the corresponding isopropyl and methyl substituents of the *trans* stereoisomer **10** (Table 2, Figure 2).

Scheme 4



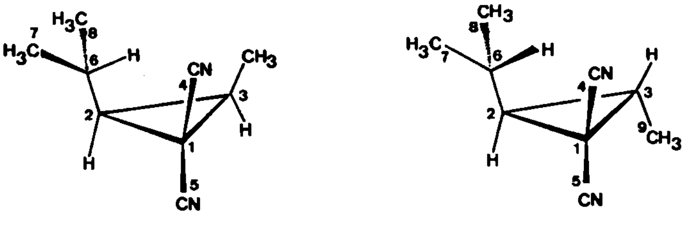


Fig. 2. *cis* and *trans* stereoisomers **9** and **10**

Table 2. ^{13}C-NMR data (δ values) of cyclopropane derivatives **9** and **10**

	δ(*trans*-10)	δ(*cis*-9)	δ(*trans*)–δ(*cis*)
C-1	9.7	8.3	1.4
C-2	45.8	42.4	3.4
C-3	32.2	30.3	1.9
C-4	114.1	112.6	1.5
C-5	114.2	116.1	–1.9
C-6	30.9	25.2	5.7
C-7	21.1	21.2	–0.1
C-8	20.9	20.8	0.1
C-9	15.0	9.1	5.9

Next we turned our attention to the thermolytic generation at 30°C of dicyanocarbene, starting from dicyanodiazomethane and using Ciganek's methodology[22]. This highly reactive carbene was then trapped with *cis*-4-methyl-2-pentene. As expected we isolated a mixture of both *trans*-**10** and *cis*-**9** cyclopropane derivatives. That these two adducts formed by direct reaction of dicyanocarbene and the olefinic double bond – and not via 1-pyrazoline formation followed by an ensuing nitrogen expulsion – was demonstrated as follows:

– Ciganek, using identical reaction conditions, had already shown that neither norbornene, nor dimethyl acetylenedicarboxylate led to the expected 1-pyrazoline adducts when treated with dicyanodiazomethane[26]. Thermal fragmentation of dicyanodiazomethane proved to be the first reaction step, followed by addition of the incipient dicyanocarbene to the olefins, leading thereby to the corresponding cyclopropane derivatives[26].

– Nitrogen evolution was monitored as a function of time for the following two experiments. Two vials containing the same amount of dicyanodiazomethane were placed in a thermostated bath (+30°C). In addition, vial 1 contained a 1/1 mixture of methylene chloride and of *n*-hexane, vial 2 a 1/1 mixture of methylene chloride and of *cis*-4-methyl-2-pentene. In both instances exactly the same volumes of nitrogen evolved as a function of time. This clearly indicates that no 1-pyrazoline adduct was formed in vial 2 and that in both vials dicyanocarbene and nitrogen are the primary reaction products to be formed.

After these preliminary experiments we proceeded with the thermolysis at +30°C of dicyanodiazomethane in methylene chloride, in the presence of various amounts of *cis*-4-methyl-2-pentene (**4**) and obtained the adducts **9** and **10** in ratios which changed as a function of olefin **4** concentration (Table 3 and Figure 3, lower curve). According to Ciganek the incipient dicyanocarbene – in this type of thermolytic experiment – is in its singlet state which can be trapped stereospecifically at high *cis*-**4** concentration, giving the cyclopropane **9**[22]. At lower olefin concentrations, the singlet dicyanocarbene undergoes partial intersystem crossing to its ground state triplet which adds in a nonstereospecific way to *cis*-**4** leading thereby to **9**/**10** mixtures whose ratios are olefin concentration-dependent[22].

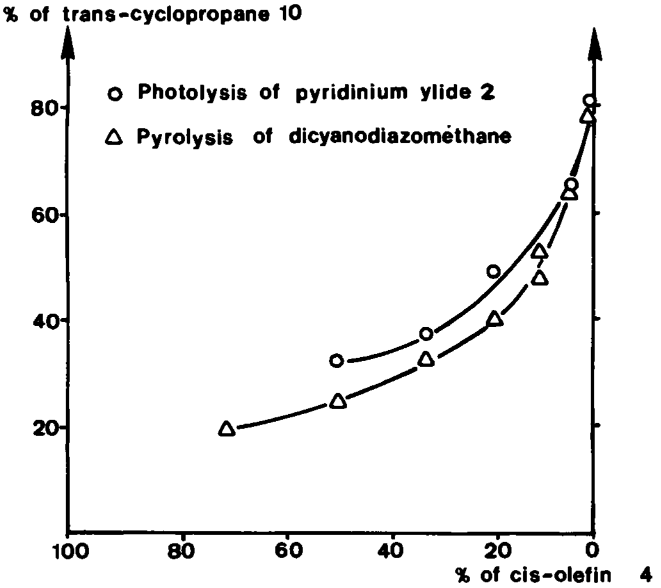


Fig. 3. Percentage of cyclopropane **10** obtained a) during photolysis of **2**, b) during pyrolysis of dicyanodiazomethane, as a function of olefin **4** concentration

Photolyses of pyridinium dicyanomethylide (**2**) were performed, using identical reaction media (methylene chloride and *cis*-**4** in various concentrations). Once again cyclopropane adducts **9** and **10** were formed in ratios which changed as a function of *cis*-**4** concentrations (Table 3 and Figure 3, upper curve). The overall shape of this curve is similar to the one obtained from the thermolytic experiments, but showed slightly higher concentrations of the *trans*-cyclopropane **10** for any given concentration of *cis*-**4**.

Comparison of the two curves of Figure 3 suggests that during photolysis of pyridinium dicyanomethylide (**2**) the incipient dicyanocarbene appears as a *mixture* of excited *singlet* state and of triplet ground state. This is in sharp contrast to the results we have described in the previous chapter, for the photolytic formation of ethoxycarbonylnitrene (this latter one formed as a triplet entity in quantitative yields).

Table 3. Relative amounts of cyclopropane derivative **10** obtained during thermolysis of dicyanodiazomethane and during photolysis of pyridinium dicyanomethylide (**2**), in the presence of various amounts of *cis*-4-methyl-2-pentene (**4**)

Concentration of *cis*-**4** (mol-%)	71	50	33	20	11	5	1
trans-**10** (mol-%) formed during pyrolysis of dicyanodiazomethane	19	24	32	40	51	64	78
trans-**10** (mol-%) formed during photolysis of **2**	–[a]	32	37	49	56	65	81

[a] At such a high olefin concentration the ylide **2** is not soluble.

Photoinduced Atomic Oxygen Transfer Reactions, Starting from 2-Cyanopyridine *N*-Oxide (3)

Pyridine *N*-oxides are known to undergo 1,3-dipolar cycloaddition reactions with "activated" olefins[27] in the ground state. When excited with UV light in organic solvents, they lead to fragmentation and to the formation of the parent pyridines and to some oxygenated products. These latter ones formally stem from atomic oxygen addition or insertion into solvent molecules[28].

The mechanism of these photoinduced oxygen transfer reactions is still heavily debated. Some authors favour oxygen transfer by a collision mechanism between a photoexcited pyridine *N*-oxide (or its oxaziridine isomer) and a substrate which can be either an aromatic or an olefinic hydrocarbon[29]. Currently a majority of authors tend to believe that atomic oxygen is formed right after photoexcitation of pyridine *N*-oxide, and that it is this atomic species which reacts in a second step with a substrate, usually the solvent molecules[30].

We favour this latter two-step mechanism which we believe operates when 2-cyanopyridine *N*-oxide (**3**) is irradiated by UV light in the presence of various substrates like i) benzene; ii) 4-methyl-2-pentene; iii) 2,3-dimethylbutane or cyclohexane.

We found that the rate of pyridine *N*-oxide disappearance stayed constant, *whatever the nature* of the cosolvent (benzene, 4-methyl-2-pentene, or 2,3-dimethylbutane) was during UV irradiation of **3** in methylene chloride solution, the solute to solvent ratio being constant (v/v = 1/2) in all cases. Iwasaki and his co-workers observed a similar kinetic be-

Table 4. Irradiation of *N*-oxide **3** in 2,3-dimethylbutane/methylene chloride mixtures: experimental conditions and monitoring of educt and reaction products by HPLC and GLC

Vial	2,3-Dimethylbutane	CH_2Cl_2	*N*-Oxide **3**	Irradiation time [h]	Conversion of **3**	2-Cyanopyridine formed [µmol]	Epoxide **12** formed[c] [µmol]	Alcohol **11** formed[c] [µmol]
1[a]	3 ml	–	40.9 mg (0.341 mmol)	24	46.9% (0.161 mmol)	16	7.75 48.4%[d]	0.21 1.3%[d]
2[b]	1.5 ml	1.5 ml	40.3 mg (0.336 mmol)	1.5	48.5% (0.163 mmol)	44	0.94 2.16[d]	6.95 15.8%[d]
3[b]	1.0 ml	2.0 ml	40.6 mg (0.339 mmol)	1.5	42.8% (0.146 mmol)	38	1.35 3.5%[d]	7.14 18.8%[d]
4[b]	0.5 ml	2.5 ml	39.8 mg (0.332 mmol)	1.5	43.4% (0.144 mmol)	46	2.19 4.8%[d]	6.27 13.6%[d]
5[b]	0.25 ml	2.75 ml	40.0 mg (0.333 mmol)	1.5	44.7% (0.149 mmol)	37	3.02 8.2%[d]	5.00 13.5%[d]
6[b]	0.125 ml	2.875 ml	40.1 mg (0.335 mmol)	1.5	39.4% (0.132 mmol)	42	3.90 9.3%[d]	4.57 10.9%[d]

[a] Stirred suspension. — [b] Stirred solution. — [c] The primary alcohol, 2,3-dimethyl-1-butanol, could not be detected below 0.05 µmol. — [d] Yield based on the 2-cyanopyridine production.

Table 5. Irradiation of *N*-oxide **3** in *cis*-4-methyl-2-pentene/methylene chloride mixtures: experimental conditions and monitoring of educt and reaction products by HPLC and GLC

Vial	*N*-Oxide **3**	*cis*-**4**	CH_2Cl_2	Irradiation time and conditions	Conversion of **3**	2-Cyanopyridine formed [mmol]	Epoxide **14** formed [mmol]	Epoxide **13** formed [mmol]	**13**/**14** Ratio	Epoxides **13** + **14** formed [mmol]
1	40 mg (0.333 mmol)	1.5 ml	1.5 ml	degassed under argon; 1.5 h	27.2% (0.085 mmol)	0.0185	0.0039 26%[a]	0.0109 72.7%[a]	2.79	0.0148 98.7%[a]
2	40 mg (0.333 mmol)	1.5 ml	1.5 ml	not degassed 1.5 h	27.0% (0.084 mmol)	0.0197	0.0066 35.3%[a]	0.0121 64.7%[a]	1.83	0.0187 100%[a]
3	40 mg (0.333 mmol)	0.25 ml	2.75 ml	degassed under argon; 1.5 h	18.8% (0.056 mmol)	0.0159	0.0036 23.7%[a]	0.0116 76.3%[a]	3.22	0.0152 100%[a]
4	40 mg (0.333 mmol)	0.25 ml	2.75 ml	not degassed; 1.5 h	29.3% (0.092 mmol)	0.0272	0.0105 36.8%[a]	0.0180 61.1%[a]	1.71	0.0285 97.9%[a]

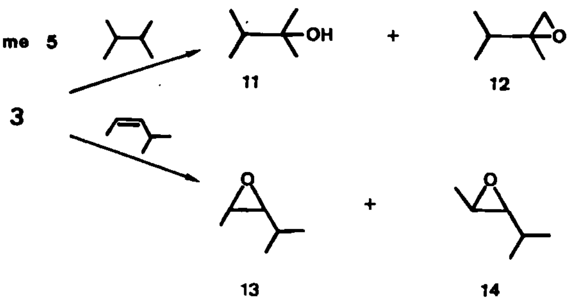
[a] Yield based on the 2-cyanopyridine production.

haviour when various aromatic *N*-oxides were irradiated in the presence *or in the absence* of "oxygen-acceptor" molecules, i.e. cyclohexene and anisole[30]. These results clearly indicate that the "oxygen-acceptor" substrate is not involved in the rate-determining step!

Furthermore, the following experimental results represent in our opinion a major argument in favour of the two-step mechanism: when **3** was photolyzed in the presence of cyclohexane or of 2,3-dimethylbutane, atomic oxygen insertion products formed, i.e. cyclohexanol, tertiary alcohol **11** (the primary alcohol could not be detected) and epoxide **12**, respectively (Table 4). The photolysis of **3** in the presence of 2,3-dimethylbutane was performed in homogenous CH_2Cl_2 solutions, with the exception of vial no. 1 which was devoid of any CH_2Cl_2. This vial contained a suspension of **3** in dimethylbutane, which explains why its rate of conversion was smaller than in the other vials. It also accounts for the fact that the **12**/**11** ratio is much bigger than in the homogenous solutions (Table 4). The product distribution in this vial after photolysis is reminiscent of very similar results which Mazur has observed when letting react atomic oxygen with dimethylbutane in a condensed phase (interface phenomena)[31,32], whereby **11** and **12** were obtained.

We also observe that the photoinduced atomic oxygen transfer reaction from **3** to *cis*-4-methyl-2-pentene is almost quantitative and leads to a mixture of both *cis*- and *trans*-epoxides **13** and **14** (Table 5).

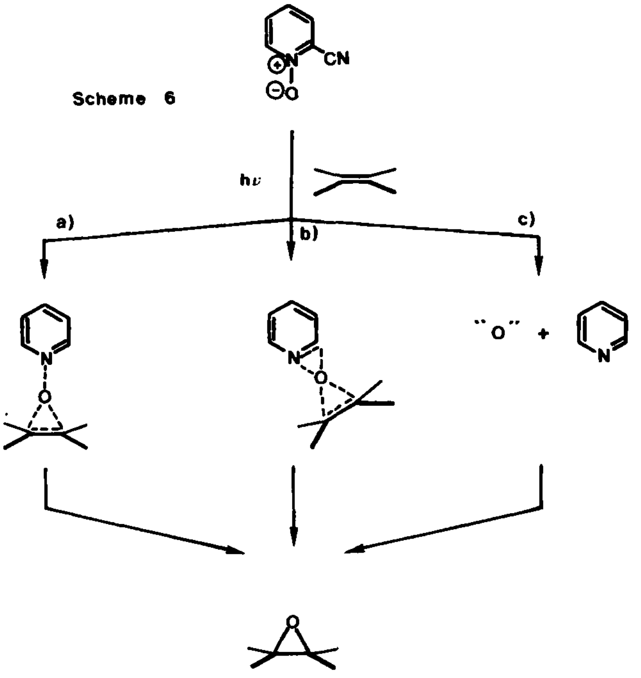
Scheme 5



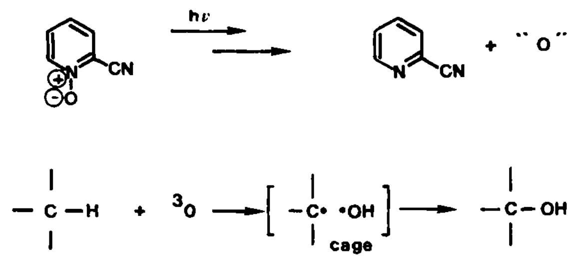
It appears from these latter experiments that olefins are far more efficient than saturated hydrocarbons for the trapping of the photogenerated "oxene". As a matter of fact only about 20% of the photogenerated oxene is trapped by saturated hydrocarbons. Nevertheless, in both types of experiments the rate of pyridine *N*-oxide disappearance is the same.

The above-cited experimental data seem to indicate that out of the three mechanistic pathways a), b), and c) which could in principle be proposed for the photoinduced epoxidation of olefins, only pathway c) does operate (Scheme 6). As to the atomic oxygen insertion into C – H bonds, we believe that it is best explained by the mechanistic pathway as represented in Scheme 7. The H-abstraction by an oxene [most likely in the (^{3}P) state] would lead to two radicals which are entrapped in a cage. These radicals should combine in a very fast process to yield an alcohol (or an epoxide) according to mechanisms which had already been postulated by Mazur[31,32].

Scheme 6



Scheme 7



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Experimental

Microanalyses were carried out by the *Service Central de Microanalyses* of the *Centre National de la Recherche Scientifique*. – Melting points were taken with a Büchi SMP-2 apparatus and are corrected. – UV spectra ⟨λ_{max} [nm] (ε)⟩ were recorded with a Varian Techtron 635 spectrophotometer. – IR spectra [cm^{-1}] were determined with a Perkin-Elmer 157 G spectrophotometer. – ^{1}H- and ^{13}C-NMR spectra were obtained with Varian T-60 (60 MHz) and with Brucker WH 80 DS (80 MHz) instruments, Me_4Si being the internal reference (δ values; *J*[Hz]). – Normal MS and high-resolution MS were measured with LKB 100 and with Thomson-Houston THN 208 mass spectrometers, respectively.

All photolytic experiments were performed in 10-ml Pyrex vials which were flushed with argon and tightly sealed with Teflon caps. These vials were placed in a merry-go-round irradiation apparatus, permitting thereby equal exposure to UV light of a Philips HPK-125 lamp which was placed along the rotation axis. Each vial was equipped with a small Teflon-coated magnetic bar which permitted a steady stirring, due to permanent magnets which were placed underneath the merry-go-round apparatus.

Quantitative determinations of educts and of reaction products were performed by HPLC for the aromatic compounds [Spectra-Physics 3500-B apparatus equipped with a UV-Schoeffel spectrophotometer and a Spectra-Physics 4100 calculator-integrator] and by GLC for all the other compounds [Girdel-75 apparatus for compounds **4**, **5**, **6**, **9**, **10**, **13**, and **14**, Delsi IGC 121 C apparatus for compounds **11** and **12**, both apparatus being equipped with flame-ionization detectors]. Preparative GLC separations were performed with a Girdel-3000 apparatus equipped with a catharometer detector. Various columns were used for the HPLC and GLC separations; their nature is indicated below in the experimental paragraphs.

Synthesis of the N-(Ethoxycarbonylimino)pyridinium Ylide **1**: Preparation according to the method described by Snieckus[33]; mp 109°C, IR, UV, and ^{1}H-NMR spectra were identical with those described in ref.[33].

Synthesis of the Aziridines **5** *and* **6**: A solution of *cis*-4-methyl-2-pentene (8.4 g, 0.1 mol) and of ethyl azidoformate[7] (11.5 g, 0.1 mol) in 100 ml of CH_2Cl_2 was irradiated at room temp. by a mercury vapour medium-pressure Philips HPK-125 lamp in a Hanovia internal cooling finger type reactor under nitrogen for 4.5 h. After evaporation of the solvent in vacuo the oily residue was distilled under reduced pressure (0.7 Torr) whereby a fraction was obtained (at 41°C) which contained both aziridines **5** and **6**. Separation of these two isomers was performed by preparative GLC (6-m column, 10% Carbowax 1500 on Chromosorb W; diameter 3/8 of an inch; oven temperature 165°C; carrier gas N_2; flow rate 50 ml/min). ^{1}H-NMR spectra of **5** and **6** were identical with those described by Lwowski for these compounds[12]; one notices in particular that the ring protons of **5** and **6** show coupling constants of 6.5 and 3.7 Hz, respectively.

Synthesis of the Cyclohexylurethane **7**: Photochemical set-up and reaction conditions were as above, using a solution of ethyl azidoformate (15 g; 130 mmol). After 4 h the organic solvents were evaporated in vacuo and the oily residue was distilled under reduced pressure over a Vigreux column (without any water-cooling) whereby a pale-yellow paste was obtained (bp 95°C/1.7 Torr) which was recrystallized (petroleum ether) at –5°C to give colourless crystals, mp 56°C, IR and ^{1}H-NMR spectra were identical with those described by Lwowski for **7**[7].

UV Irradiation of the Ylide **1** *in the Presence of 4-Methyl-2-pentene*: 10-ml Pyrex vials having a diameter of 15 mm, were filled each with 5-ml solutions containing **1** (125 mg, 0.70 mmol) and various amounts of 4-methyl-2-pentene (*cis* or *trans*) in CH_2Cl_2 (Table 1). They were flushed with argon, sealed, and irradiated as described in the introduction. During UV irradiation the disappearance of the ylide **1** was monitored by UV spectroscopy [λ_{max} =

340 nm (ε = 12000)]; total consumption of educt **1** required an irradiation time of about 300 h. For our purposes irradiation was stopped after 20−30% photoconversion of **1**. Aziridines **5** and **6** proved to be stable whatever the duration of the irradiation was. Experimental results are collected in Table 1. Each experiment was repeated three times for any given olefin concentration. Each GLC analysis was performed twice (4-m column, 10% Carbowax 1500 on Chromosorb W; oven temperature 150°C; carrier gas N_2; flow-rate 20 ml/min). It was found that the amount of *trans*-aziridine **6** was obtained with an error of less than 5%. Overall yields: 1.5% of pyridine, 0.7 to 0.4% of aziridines **5** and **6**, respectively, when the relative mol-% concentration of olefin varied between 1 and 33%, yields being calculated with respect to the ylide **1** which was consumed.

UV Irradiation of the Ylide **1** *in the Presence of cis-4-Methyl-2-pentene and of α-Methylstyrene:* A 10-ml Pyrex vial containing **1** (125 mg, 0.70 mmol), *cis*-4-methyl-2-pentene (2 ml), α-methylstyrene (1 ml), and 2 ml of CH_2Cl_2 was flushed with argon and irradiated by UV light as described above for 300 h, i.e. until complete disappearance of **1**. The composition of the reaction mixture was analyzed by GLC (same column and conditions as above) after consumption of 10, 50, and 100% of **1**. Aziridines **5** and **6** could not be detected in this experiment[12].

UV Irradiation of the Ylide **1** *in the Presence of Cyclohexane:* A 10-ml Pyrex vial containing a solution of **1** (125 mg, 0.70 mmol) in cyclohexane (4 ml) and CH_2Cl_2 (2 ml) was flushed with argon and irradiated as above until complete disappearance of the starting material. The composition of the reaction mixture was analyzed by GLC (same column and conditions as above) after consumption of 10, 50, and 100% of **1**; only pyridine and the ethylurethane **8** could be detected. The last analysis (100% conversion of **1**) showed that 1.24 mg (16 μmol) of pyridine and 0.34 mg (4 μmol) of **8** were formed. Cyclohexylurethane **7** could not be detected.

Synthesis of Dicyanodiazomethane: According to the procedure described by Ciganek[26] dicyanodiazomethane was obtained as a deep-red crystalline substance which, being an unstable compound, was kept at −10°C in a CH_2Cl_2 solution and used within 24 h after its preparation.

*Synthesis of cis-***9** *and trans-***10** *(2-Isopropyl-3-methyl-1,1-cyclopropanedicarbonitriles):* We used a procedure which is described by Boldt et al. for the preparation of analogous cyclopropanes[25] (Scheme 4). Addition of bromine to a solution of malonodinitrile in water led to the monobromo derivative in 20% yield, mp 63−64°C, identical with the one indicated in the literature for this compound[34]. UV irradiation of a solution of *cis*-4-methyl-2-pentene (7.5 g, 0.09 mol) and bromomalonodinitrile (13 g, 0.09 mol) in CH_2Cl_2 (35 ml) led to the acyclic monobromo adduct which was not isolated. The reaction mixture, which was slightly yellow, was diluted by addition of CH_2Cl_2 (65 ml) and cooled to 0°C. To this solution which was stirred vigorously triethylamine (9.1 g, 0.09 mol) in CH_2Cl_2 (50 ml) was added dropwise whereby the triethylammonium bromide precipitated. After 30 min the reaction mixture was evaporated to dryness in vacuo and the residue taken up in diethyl ether. The solid material was filtered off, washed twice with diethyl ether, and the combined ether solutions were evaporated to dryness in vacuo, whereby a brown oil was obtained. Distillation of the latter under reduced pressure (0.6 Torr) led at 69°C to a colourless oil (9 g, 67%) which was composed of about equal amounts of *cis*-**9** and *trans*-**10**. − IR ($CHCl_3$): 2960 cm^{-1}, 2930, 2857, 2240.

$C_9H_{12}N_2$ (148.2)	Calcd.	C 72.94	H 8.16	N 18.90
	Found	C 72.8	H 8.0	N 19.0

Separation of the two isomers **9** and **10** was performed by preparative GLC [6-m column, 7% FFAP on Chromosorb W; diameter 0.5 inch; oven temperature 170°C; carrier gas N_2; flow-rate 60 ml/min; retention times 16 s for **10**, 23 s for **9**]. 20 to 30 mg of each isomer could be isolated after each injection.

Isomer **9**: ^1H NMR (60 MHz): δ = 1.07 (3H, d, *J* = 5.5 Hz, Me of iPr), 1.18 (3H, d, *J* = 5.5 Hz, Me of iPr), 1.37 (3H, d, *J* = 6 Hz, Me), between 1.44 and 2.33 three complex multiplets (3H, 2-H, 3-H, 6-H). Severe steric interaction (Figure 2) in this stereoisomer lead to inhibition of free rotation for the iPr substituent. − ^{13}C NMR: See Table 2.

Isomer **10**: ^1H NMR (60 MHz): Large band between δ = 1.04 and 1.25 (6H, iPr), 1.40 (3H, d, *J* = 5.5 Hz, Me), between 1.25 and 2.00 three complex multiplets (3H, 2-H, 3-H, 6-H). − ^{13}C NMR: See Table 2.

Thermolysis of Dicyanodiazomethane in the Presence of cis-4-Methyl-2-pentene: 10-ml Pyrex vials, containing dicyanodiazomethane (37 mg, 0.4 mmol) in a mixture (5 ml) of CH_2Cl_2 and of various amounts of *cis*-4-methyl-2-pentene were flushed with argon and tightly sealed with Teflon caps. The vials were heated at 30°C in the dark for 24 h after which period the diazoalkane had disappeared. The relative concentrations of *cis*-**9** and *trans*-**10** were determined by analytic GLC (3-m column, Carbowax 20 M on Chromosorb W; diameter 1/8 of an inch; oven temperature 170°C; carrier gas N_2; flow-rate 20 ml/min) and are reproduced in Table 3 and Figure 3.

Thermolysis of Dicyanodiazomethane in the Presence and in the Absence of an Olefin: A 25-ml round-bottomed flask containing a solution of dicyanodiazomethane (60 mg, 0.65 mmol) in CH_2Cl_2 (5 ml) and *cis*-4-methyl-2-pentene (5 ml) was flushed with nitrogen and connected to a graduated inverted burette filled with water. A second 25-ml round-bottomed flask was also filled and flushed as above, the olefin being replaced by *n*-hexane (5 ml). Both flasks were then heated at 30°C in a thermostated bath, their solutions being stirred with a magnetic bar. At any time of the thermolysis process the water level was the same in each burette. After 7 h gas evolution ceased, the total amount of gas being 13.3 and 13.5 ml, respectively (average yield of thermal decompositions: 90%).

Synthesis of Pyridinium Dicyanomethylide (**2**): Preparation according to Rieche and Dietrich[35] starting from pyridine and tetracyanoethylene oxide; mp 247°C (acetone).

Photolysis of Pyridinium Dicyanomethylide in the Presence of cis-4-methyl-2-pentene: Same experimental procedures as those described above for the photolysis of pyridinium N-ylide, using again identical vials and a merry-go-round set-up. Analyses of the reaction products were performed by GLC (3-m column, Carbowax 20 M on Chromosorb W; diameter 1/8 of an inch; oven temperature 170°C; carrier gas N_2; flow-rate 20 ml/min), see Table 3 and Figure 3.

Synthesis of 1,2-Epoxy-2,3-dimethylbutane (**12**): To a stirred solution of 2,3-dimethyl-1-butene (commercial product) (2 g, 24 mmol) and of sodium hydrogen carbonate (4 g, 48 mmol) in CH_2Cl_2 (40 ml), which was kept at 0°C, was added in portions 3-chloroperbenzoic acid (6 g, 36 mmol). The reaction mixture was left to warm up to room temp. and stirred for about 12 h whereby a precipitate formed which was filtered off and washed with CH_2Cl_2. The combined organic solutions were treated consecutively with $NaHCO_3$ (10 ml of a 10-% solution) and NaCl (10 ml of a saturated solution), then dried with $MgSO_4$, and evaporated to dryness in vacuo. The liquid residue was distilled (bp 123°C, ref.[36] 123°C) to yield **12** as a colourless oil (1.935 g, 81%). − ^1H NMR (60 MHz,

$CDCl_3$): δ = 0.94 (3H, d, J = 7 Hz, 3-Me), 0.99 (3H, d, J = 7 Hz, 3-Me), 1.18 (3H, s, 2-Me), 1.21 (1H, broad m, 3-H), 2.72 (2H, broad s, CH_2).

2,3-Dimethyl-2-butanol (**11**): Commercial product.

2,3-Dimethyl-1-butanol: To a stirred solution of sodium tetrahydroborate (1.14 g, 30 mmol) and 2,3-dimethyl-1-butene (8.34 g, 97 mmol) in freshly distilled THF (50 ml) under nitrogen was added dropwise at room temp. over 1 h a solution of Et_2O-BF_3 (5.67 g 40 mmol) which had been freshly distilled over CaH_2. After 2 h excess hydride was destroyed by addition of a few drops of H_2O, the resulting solution was heated to 30–40°C, and 3 M NaOH (11 ml) and 30-% H_2O_2 (11 ml) were added consecutively, the second reagent dropwise. The reaction medium was saturated with NaCl, and the organic layer was washed twice with brine, dried with $MgSO_4$, and evaporated to dryness in vacuo. The resulting oil was distilled at 80°C (70 Torr) whereby the 2,3-dimethyl-1-butanol was obtained as a colourless oil. – ^1H NMR (60 MHz, $CDCl_3$) identical with that published in the Sadtler Research Laboratories atlas (no. 23041).

Synthesis of trans-2,3-Epoxy-4-methylpentane (**14**): To a stirred solution of *trans*-4-methyl-2-pentene (commercial product) (2.02 g, 24 mmol) and sodium hydrogen carbonate (4.03 g, 48 mmol) in chloroform (20 ml), which was kept at 0°C, was added dropwise over 30 min a solution of 3-chloroperbenzoic acid (8.26 g, 48 mmol) in chloroform (120 ml). After 2 h the solution was left to warm up and stand at room temp. for 24 h. Solid material was filtered off, and the filtrate was treated successively with $NaHCO_3$ (10 ml of a 10-% solution), with saturated NaCl solution (10 ml), then dried with $MgSO_4$, and evaporated to dryness in vacuo (50 Torr, only in order to avoid the codistillation of **14**). The residue was distilled at 97°C (ref.[37]) 96–97°C) to yield **14** (1.5 g, 63%). – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.98 (3H, d, J = 7 Hz, 4-Me), 1.04 (3H, d, J = 7 Hz, 4-Me), 1.34 (3H, d, J = 7 Hz, 1-Me), ≈1.44 (1H, partly hidden m, 4-H), 2.52 (1H, dd, J = 8 and 2.5 Hz, 3-H), 2.87 (1H, dq, J = 7 and 2.5 Hz, 2-H).

Synthesis of cis-2,3-Epoxy-4-methylpentane (**13**): Preparation as described above for **14** starting from *cis*-4-methyl-2-pentene (commercial product) (2.0 g, 24 mmol). Purification of **13** by distillation, bp 101°C (ref.[38]) 102–103°C). – ^1H-NMR (60 MHz, $CDCl_3$): δ = 0.98 (3H, d, J = 7 Hz, 4-Me), 1.08 (3H, d, J = 7 Hz, 4-Me), 1.32 (3H, d, J = 7 Hz, 1-Me), ≈1.46 (1H, partly hidden m, 4-H), 2.60 (1H, dd, J = 10 and 6 Hz, 3-H), 3.12 (1H, quint, J = 6 Hz, 2-H).

UV Irradiation of the N-Oxide **3** *in the Presence of 2,3-Dimethylbutane:* Six identical Pyrex vials (see introduction of the Experimental) containing various amounts of 2,3-dimethylbutane, *N*-oxide **3**, and CH_2Cl_2 (Table 4) were irradiated in a merry-go-round apparatus with UV light under argon atmosphere for 1.5 h, with the exception of vial 1 which was irradiated over a 24-h period. The heterocyclic products were detected by HPLC equipped with a UV-VIS detector [Spherisorb C-18 column, length 10 cm, fitted with a short filtering precolumn, granulometry 5 μ, eluent made up of MeOH and of an ammoniacal buffer (NH_4Cl/NH_4OH, pH = 9), injected volume 10 μl, flow-rate 1.2 ml/min, start for 1 min: 14.5% MeOH and 85.5% buffer, gradient over 5 min: from 14.5 to 37% MeOH, UV detection at 254 nm] (Table 4). The aliphatic compounds were detected by GLC (SE 30 capillary column, length 25 m, diameter 0.32 mm, carrier gas nitrogen; flow-rate 3 ml/min; injector/column/detector temperatures 150/35/150°C, respectively, injected volume 1 μl) (Table 4). For the precise identification of the reaction products the GLC/MS technique was used (DELSI DI 700 GLC apparatus fitted with a CP SIL 5 capillary column, length 25 m, diameter 0.22 mm and NERMAC R 10-10 C mass spectrometer). The MS of compounds **11** and **12**, which have been synthesized separately (vide supra), proved to be identical with those obtained during the photochemical experiments.

A second set of experiments was performed using the same solutions and irradiation durations but with different vials. The results proved to be identical with those reported in Table 4, ±2%, i.e. within the range of experimental errors.

UV Irradiation of the N-Oxide **3** *in the Presence of cis-4-Methyl-2-pentene* (**4**): Four identical Pyrex vials (see above) containing various amounts of *cis*-4-methyl-2-pentene (**4**) *N*-oxide **3**, and CH_2Cl_2 (Table 5) were irradiated in a merry-go-round apparatus with UV light for 1.5 h under argon atmosphere. The aromatic compounds were detected by HPLC equipped with a spectrophotometer [Spherisorb ODS, column length 25 cm, diameter 4.6 mm, granulometry 10 μ, eluent made up of MeOH (20%) and of an ammoniacal buffer (NH_4Cl/NH_4OH, pH = 9.2) and used in the isocratic mode, injected volume 10 μl, flow-rate 1.0 ml/min, UV detection at 254 nm] (Table 5). The aliphatic compounds were detected by GLC [10% Squalane on Chromosorb W, column length 5 m, diameter 1/8 of an inch, carrier gas nitrogen, flow-rate 25 ml/min, injector/column/detector temperatures 180/90/180°C, respectively, injected volume 1 μl] (Table 5).

A second set of experiments was performed using the same solutions and irradiation durations but with different vials. The results proved to be identical with those reported in Table 5.

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