Photochemical Generation of Iminoquinone Methides by 1,4-Hydrogen Migration in Derivatives of *o*-Tolylnitrene

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Dedicated to Prof. Henning Hopf on the occasion of his 60th birthday

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The photochemistry of a series of derivatives of *o*-tolyl azide, bearing a variety of substituents in the benzylic positions, has been investigated using matrix isolation spectroscopy and density functional calculations. It has been found that introduction of any substituent possessing a lone pair (i.e., R = Br, Cl, MeO, Me_2N) allows a 1,4-hydrogen shift to take place, yielding iminoquinone methides. Additional methyl groups in the benzylic position, however, do not promote a photochemical conversion into iminoquinone methides. If the benzylic substituent itself is part of a ring system, the size of this ring plays an important role. Thus, 2-methyl-8-nitrenotetrahydroisoquinoline rearranges very easily, whereas 4-nitrenophthalan does not give the reaction. Density functional calculations [B3LYP/6-31G(d)] have been used to gain an understanding of the reaction. It has been found that the activation energies depend strongly on the nature of the substituent, being lowest if R = NMe_2. Incorporation of the benzylic substituent into a ring reduces the flexibility of the system and results in significantly raised barriers.

Introduction

The mechanisms governing the complex photochemistry of aryl azides have only recently been elucidated in detail.[1−12] The primary product formed is a singlet arylnitrene, which, depending on factors such as substitution and temperature, either undergoes intersystem crossing (ISC) to the ground state triplet nitrene or adds to a neighboring C=C bond in the arene system to yield didehydroazepines via intermediary azirines.[13−15] This ring-enlargement reaction prevails at ambient temperature, while low-temperature conditions generally favor ISC. Thus, the synthetic potential of reactions involving arylnitrenes is essentially restricted to the preparation of azepine derivatives.[16,17] A possible means of circumventing this limitation lies in the use of *o*-alkyl-substituted arylnitrenes, as a 1,4-hydrogen shift would yield *o*-iminoquinone methides, which are valuable reaction intermediates for trapping in Diels−Alder reactions.[18−22] Unfortunately, the 1,4-hydrogen shift in *o*-tolylnitrene has a barrier high enough to require flash vacuum pyrolysis conditions.[23−25] Photochemical formation of *o*-iminoquinone methide from *o*-tolylnitrene is possible under matrix isolation spectroscopy conditions. It requires UV irradiation and has a very low quantum yield.[24] Hence, for practical application of this reaction, there is a requirement for substituents that may weaken the benzylic C−H bond needing to be broken in the process and/or stabilize the product iminoquinone methide.

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The aim of this study is to investigate the influence on the photochemical behavior of triplet phenyl nitrene of a variety of substituents in *o*-benzylic positions, ranging from simple alkyl groups to halogens, methoxy groups, and dialkylamino substituents. In particular, dialkylamino substituents seemed promising candidates, as it is well known that hydrogen atoms in positions α to a tertiary amine are particularly prone to abstraction.[26] Thus, a number of *o*-substituted derivatives of phenyl azide were synthesized and their photochemistry investigated by means of matrix isolation spectroscopy, density functional theory, and ab initio theory. For comparative purposes, the substituent was in one case (2-azidophenethyl system) placed further away from the nitrene center.

Results and Discussion

1. Alkyl Substituents in Benzylic Positions

Alkyl substituents in benzylic positions might activate the benzylic C−H bond. For this reason, the photochemistry of 1-azido-2-ethylbenzene and 1-azido-2-isopropylbenzene was investigated with the aid of matrix isolation spectroscopy.

Photolysis (λ = 254 nm) of 1-azido-2-ethylbenzene (**1**) resulted in depletion of the starting material. Prominent new IR bands appearing at $\tilde{\nu}$ = 1890.0 and 1559.7 cm^{-1} indicated formation both of a didehydroazepine (1890 cm^{-1})[7] and of a triplet nitrene (1559.7 cm^{-1}).[27] Extended photolysis did not result in formation of further products. Experiments performed using UV/Vis detection were consistent with this scheme. The UV/Vis spectrum recorded after very brief photolysis (λ = 320 nm) shows a weak,

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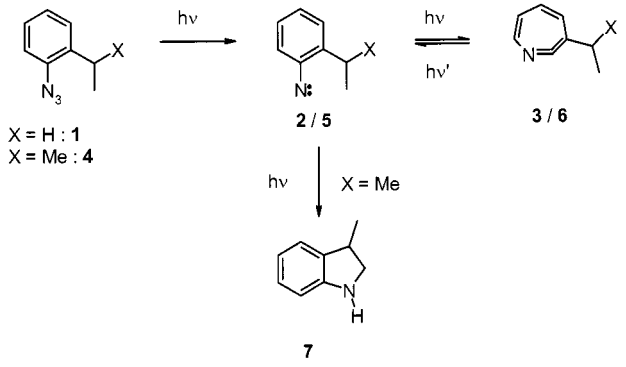
broad, structured band tailing out to ca. 520 nm, with maxima at λ = 496 and 486 nm, which is typical of a triplet nitrene.[3] A further weak band (λ_{max} = 382 nm) is also found. Broad-band photolysis resulted in the formation of new UV bands with λ_{max} = 418 nm (medium intensity) and 330/308 nm (strong), which is indicative of didehydroazepine formation (probably **3**).[3] If the matrix was again irradiated with λ = 320 nm, the bands attributed to triplet 2-ethylphenylnitrene (**2**) were partially restored.

Photolysis (λ = 254 nm) of 1-azido-2-isopropylbenzene (**4**) initially also resulted in the formation of a didehydroazepine ($\tilde{\nu}$ = 1893.7 cm^{-1}) and a triplet nitrene ($\tilde{\nu}$ = 1550.1 cm^{-1}).[27] Extended photolysis with broad-band UV radiation, however, resulted in the disappearance of these primary products and in the formation of a secondary product, which, by comparison with the infrared spectrum of matrix-isolated authentic material,[28] could be identified as 3-methylindoline (**7**).[29] The UV/Vis spectrum recorded after brief photolysis (λ = 320 nm) of **4** (structured weak band tailing out to ca. 520 nm, λ_{max} = 494 and 484 nm, weak band with λ_{max} = 384 nm) is consistent with a triplet nitrene being formed as primary product. Thus, photolysis of 2-isopropylphenylnitrene had reversibly produced triplet 2-isopropylphenylnitrene (**5**) and a didehydroazepine, most probably[17] **6**, and − less efficiently − had irreversibly produced 3-methylindoline (**7**).



In conclusion, alkyl substituents do not activate the benzylic C−H bonds of *o*-tolylnitrene enough to make the photochemical formation of iminoquinone methides a preferred pathway. The reactions observed are typical of singlet nitrenes, which undergo facile ring-expansion reactions, and of excited triplet nitrenes, which have previously been reported to undergo C−H abstraction reactions from nearby alkyl groups.[30] Substituents bearing lone pairs, which might help to weaken the benzylic C−H bonds and stabilize the iminoquinone methides, might offer better chances of achieving the desired reaction.

2. Halogen and Simple Alkoxy and Dialkylamino Substituents in Benzylic Positions

Photolysis of 1-azido-2-bromomethylbenzene (**8**), matrix-isolated in Ar at 10 K, with λ = 320 nm resulted in depletion of the starting material. After brief photolysis, a set of new bands had appeared. The infrared spectrum of the initially formed products displays bands typical of a didehydroazepine[7] at $\tilde{\nu}$ = 1889.3 cm^{-1} (broad), but also bands (1558.9, 745.2 cm^{-1}) indicative of triplet nitrene formation.[27] Upon extended photolysis, these bands disappeared again, being replaced by a new set. Long-wavelength (λ > 475 nm) irradiation produced an increase in intensity of one part of the new set of bands, while the intensity of the other part was reduced. This observation indicates that a mixture of two compounds in photostationary equilibrium had been formed. The shift in photostationary equilibrium was reversible; broad-band visible (λ > 420 nm) irradiation resulted in reversion to the initial concentrations. In order to identify the final products formed, the infrared spectra of a number of possible structures were calculated at the B3LYP/6-31G(d,p) level of theory. The experimental difference spectrum (of the long-wavelength interconversion) can be convincingly correlated with a calculated difference spectrum of two stereoisomers **11** and **12** of a bromoiminoquinone methide (Figure 1; Supporting Information, Tables S1, S2).

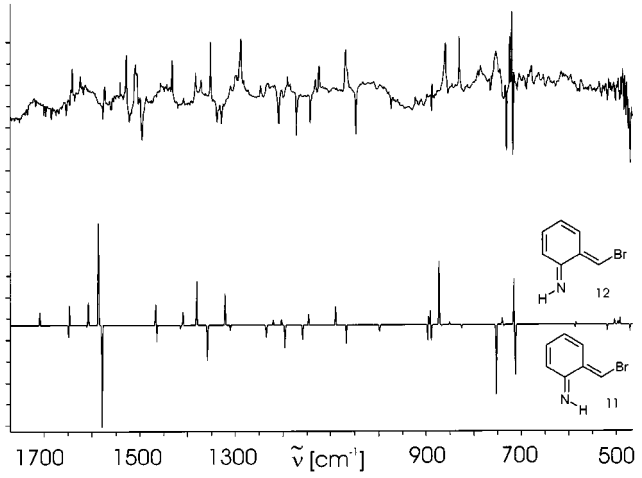
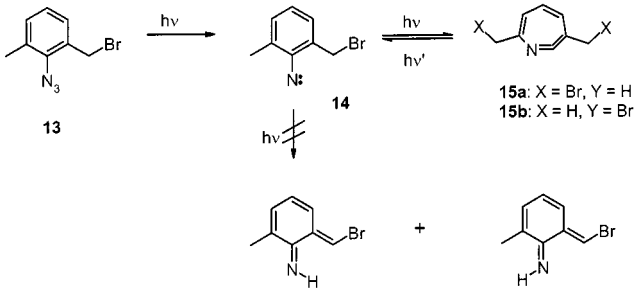


Figure 1. Top: IR difference spectrum, obtained after photolysis (λ = 305−320 nm, 24 h, then λ > 475 nm, 16 h, then λ > 435 nm, 1 h; Ar, 10 K) of azide **8**; the intensity of bands pointing up increases during photolysis with λ > 435 nm, while the intensity of bands pointing down decreases; bottom: calculated (B3LYP/6-31G**) IR difference spectrum of the iminoquinone methides **12** and **11**

The intermediates formed upon photolysis of matrix-isolated **8** were also characterized by UV/Vis spectroscopy. Photolysis (λ = 320 nm) of **8** primarily resulted in the formation of a product displaying a UV/Vis spectrum typical of a triplet nitrene, with a weak, broad, structured band (λ_{max} = 486, 496, 506 nm) extending up to ca. 520 nm, a further weak band (λ_{max} = 384 nm), and a sharp band with λ_{max} = 316 nm. Extended photolysis under identical conditions resulted in the disappearance of the triplet nitrene spectrum and in the formation of a broad band with λ_{max} = 340 nm. Long-wavelength photolysis (λ > 475 nm) shifted the absorption maximum slightly; this shift was reversible by broad band (λ > 420 nm) irradiation. In conclusion, matrix experiments indicated that photolysis of **8**, matrix-isolated in Ar, results in initial formation of a triplet nitrene

9 in photostationary equilibrium with a didehydroazepine (such as **10**). Extended photolysis converted the primary product mixture into a mixture of two stereoisomeric iminoquinone methides **11** and **12**, which again was in photostationary equilibrium. In these iminoquinone methides, the bromo substituent points away from the imino functionality.

Photolysis (λ = 320 nm) of 1-azido-2-bromomethyl-6-methylbenzene (**13**) (Scheme 1), matrix-isolated in argon at 10 K, resulted in formation of triplet 2-bromomethyl-6-methylphenylnitrene (**14**), as evidenced by comparing the experimental difference spectrum with an IR spectrum calculated at the B3LYP/6-31G(d,p) level of theory (Figure 2; Supporting Information, Table S3). Small quantities of didehydroazepine **15a/b**, in photostationary equilibrium with triplet nitrene **14**, were also formed ($\tilde{\nu}$ = 1890.9 cm^{-1}).[31] The triplet nitrene **14** was also characterized by a typical UV/Vis spectrum (broad, weak, structured band extending to λ = 540 nm with maxima at λ = 526, 518, 506, 490, 476, and 462 nm, broad band with λ_{max} = 364 nm, medium-intensity band with λ_{max} = 324 nm). In this system, however, no evidence for formation of an iminoquinone methide could be found. Prolonged photolysis under various photolytic conditions did not give rise to formation of IR bands that might, on the basis of DFT calculations, be attributable to any of the possible iminoquinone methide products.



Scheme 1

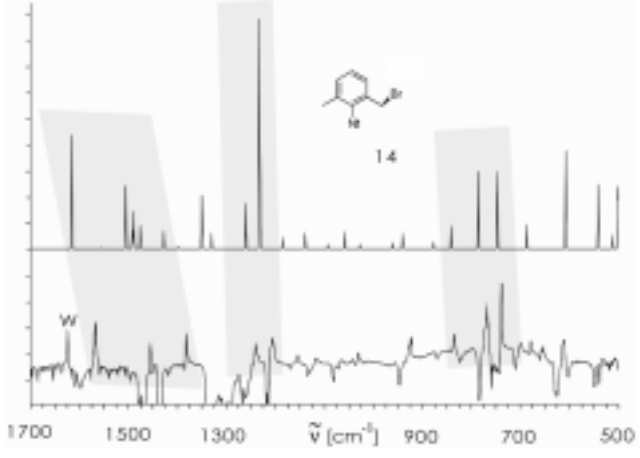
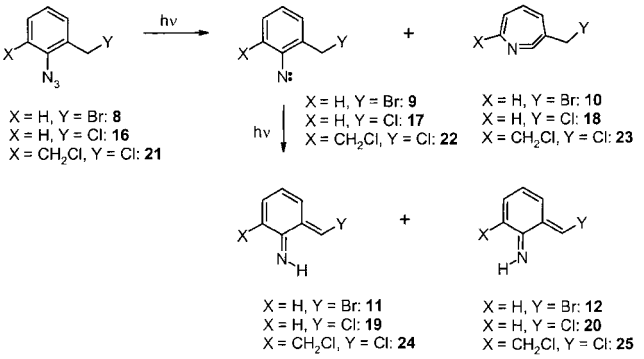


Figure 2. Bottom: IR difference spectrum, obtained after photolysis (λ = 320 nm, 20 min; Ar, 10 K) of azide **13**; bands pointing up grow upon photolysis, bands pointing down disappear (azide **13**); the band labeled "W" belongs to matrix-isolated water; top: calculated (B3LYP/6-31G**) IR spectrum of triplet nitrene **14**



Photolysis (λ = 295−480 nm) of 1-azido-2-chloromethylbenzene (**16**) (Scheme 1), matrix-isolated in argon at 10 K, resulted in initial formation of a didehydroazepine (probably **18**) and triplet nitrene **17**, as shown by IR bands at $\tilde{\nu}$ = 1895.7 cm^{-1} (**18**) and $\tilde{\nu}$ = 1561.7 cm^{-1} (**17**). The UV/Vis spectrum recorded after brief photolysis (λ = 320 nm, Xe arc lamp with monochromator) of **14** is consistent with this assignment, displaying features typical of a triplet nitrene (broad, weak band with λ_{max} = 496, 486, and 464 nm, λ_{max} = 384, 372 nm). Brief long-wavelength photolysis (λ = 475 nm) reduced the intensity of the bands attributable to nitrene **17** and produced a strengthening of a broad band with $\lambda_{max} \approx$ 370 nm. This absorption can be attributed to a didehydroazepine (probably **18**), which has to be in photostationary equilibrium with nitrene **17**, since brief UV photolysis (λ = 320 nm) restored the initial concentration of **17**. Extended photolysis ($\lambda > 455$ nm, Hg arc lamp) resulted in the disappearance of the bands attributed to both **17** and **18**. New infrared bands appeared at $\tilde{\nu} \approx$ 1576, 1515, and 730 (vs) cm^{-1}. Again, the new set of bands were attributable to a mixture of two stereoisomers (**19** and **20**) of an iminoquinone methide: Broad-band photolysis (λ = 420−680 nm) of the new products gave rise to a slight shift in band intensities, reversible by long-wavelength photolysis ($\lambda > 475$ nm). The experimental difference spectra thus obtained correlated with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory (Supporting Information, Tables S4, S5). The chlorine atom must thus point away from the imine functionality in both stereoisomers formed.

The formation of the iminoquinone methides **19** and **20** could also be monitored by UV/Vis spectroscopy. Extended photolysis (λ = 400 nm, several hours) resulted in the disappearance of the bands attributable to **17** and **18** and to the build up of a broad band with $\lambda_{max} \approx$ 350 nm. Using long-wavelength irradiation (λ = 475 nm), the intensity of the band was reduced for $\lambda > 390$ nm, while the intensity at λ_{max} increased. This shift was reversible by irradiation with λ = 350 nm. These findings are consistent with two iminoquinone methides (displaying slightly different ab-

sorption maxima) being formed in photostationary equilibrium. Figure 3 shows the relevant UV/Vis spectra.

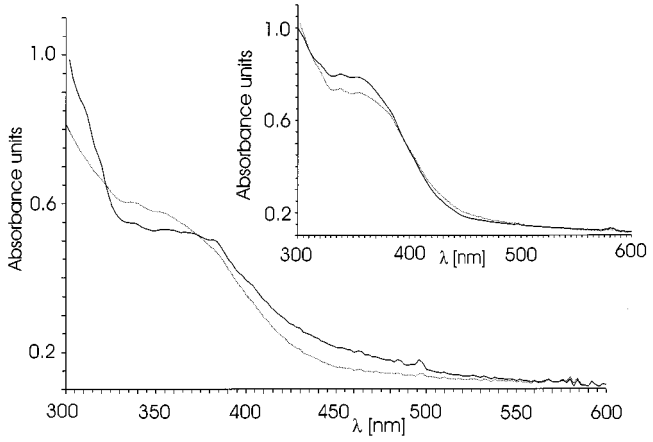


Figure 3. Main part: dashed line: UV/Vis spectrum, obtained after photolysis (λ = 320 nm, 3 h, then $\lambda > 475$ nm, 5 h; Ar, 10 K) of azide **16**; solid line: UV/Vis spectrum, obtained after photolysis (λ = 320 nm, 3 h, then $\lambda > 475$ nm, 5 h, then λ = 340 nm, 30 min; Ar, 10 K) of azide **16**; inset: UV/Vis spectra illustrating the interconversion of iminoquinone methides obtained by irradiation (λ = 270 nm, 20 h, then λ = 470 nm, 1 h, then λ = 340 nm, 1 h) of the sample characterized in the main part of Figure 3; solid line: before irradiation with λ = 340 nm; dashed line: after irradiation with λ = 340 nm

Photolysis (λ = 320 nm, Ar, 10 K) of 2,6-bis(chloromethyl)azidobenzene (**21**) (Scheme 1) provided observations very similar to those made with azide **16**. Again, a triplet nitrene **22** was observed [$\tilde{\nu}$ = 1569.9 cm^{-1} (vs)], while only a trace of a didehydroazepine **23** ($\tilde{\nu}$ = 1890.5 cm^{-1}) was detected. Long-wavelength photolysis ($\lambda > 475$ nm, several hours) of nitrene **22** resulted in its disappearance and in the formation of new bands, which, by comparison with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory, were assigned to the chloroiminoquinone methides **24** and **25** (Supporting Information, Tables S6, S7). The vinylic chlorine atom points away from the imino moiety in these products.

Brief photolysis (λ = 320 nm, 2 min) of matrix-isolated 1-azido-2-(methoxymethyl)benzene (**26**) resulted in the formation of a prominent new band at $\tilde{\nu}$ = 1843.6 cm^{-1}, indicative of a didehydroazepine (probably **28**). When the photolysis was prolonged, a set of new bands appeared at the expense of the primary products. Long-wavelength irradiation ($\lambda > 475$ nm) of the secondary mixture again resulted in an increase in intensity of some IR bands, while others became weaker. As in the case of the halogen-substituted systems, this shift in a photostationary equilibrium was reversible by broad-band visible irradiation (λ = 420−680 nm). Identification of the final products was again achieved by comparison of experimental IR spectra with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory. This comparison clearly showed that two stereoisomers (**29** and **30**) of a methoxy-substituted iminoquinone methide had been formed (Figure 4; Supporting Information, Tables S8, S9). The methoxy group points away from the imino functionality in these products.

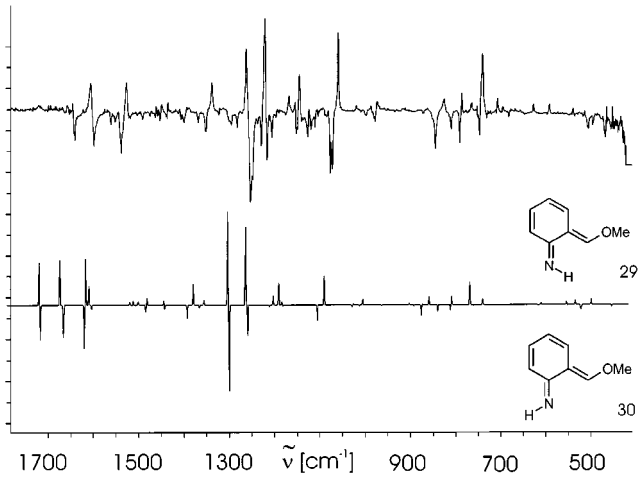
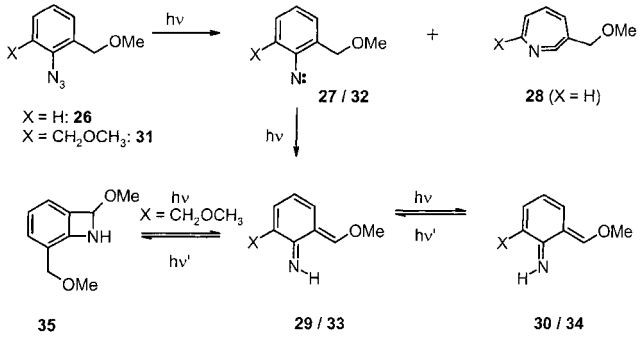


Figure 4. Top: IR difference spectrum, obtained by photolysis (λ = 320 nm, 11 h, then $\lambda > 475$ nm, 2 min; Ar, 10 K) of azide **26**; bands pointing up grow in upon irradiation with $\lambda > 475$ nm, bands pointing down are depleted; bottom: calculated (B3LYP/6-31G**) IR difference spectrum of the iminoquinone methides **29** and **30**



Observations made using UV/Vis detection were consistent with the conclusions derived from the IR spectra. The UV/Vis spectrum recorded after very brief photolysis (1 min, λ = 320 nm) of azide **26** shows features typical of a triplet nitrene [λ_{max} = 500, 488, 476, 466 nm (w), 384 and 372 nm (m), 298 nm (sh, s)]. Upon continuation of photolysis, a broad band with λ_{max} = 390 nm grows in; this can be attributed to a didehydroazepine. Both this band and the features assigned to triplet nitrene **27** disappeared upon prolonged photolysis, while newly appearing bands, with λ_{max} = 400 nm (weaker than the band assigned to **28**) and 320 nm, had to be attributable to two compounds, as they could be interconverted photochemically, with an isosbestic point at λ = 344 nm. The observation of two final products in photostationary equilibrium is consistent with the conclusions derived from analysis of the IR spectra.

Similar observations were made with 2,6-bis(methoxymethyl)azidobenzene (**31**). Photolysis of **31** in argon matrix resulted in the initial formation of triplet 2,6-bis(methoxymethyl)phenylnitrene (**32**) (Supporting Information, Table

S10). In the infrared spectrum (Ar, 10 K), the formation of **32** is evident from an IR band at $\tilde{\nu}$ = 1569.7 cm^{-1}, which is only detectable after brief irradiation (λ = 320 nm, ca. 2 min). After prolonged photolysis of azide **31**, IR bands indicative of iminoquinone methide formation were detected.[32] Again, a shift in the photostationary equilibrium of two stereoisomers was achieved by irradiation with λ = 475−680 nm, while being reversible by broad-band visible (λ = 420−680 nm) photolysis. By comparison with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory, it was possible to identify the two stereoisomers found as **33** and **34** (Supporting Information, Tables S11, S12). As in the case of the monomethoxy-substituted derivatives **29** and **30**, the vinylic methoxy substituent points away from the imino nitrogen atom in these systems. Extensive irradiation using λ_{exc} = 420−680 nm produced a decrease in intensity of the bands attributed to **33** and **34**, and resulted in the formation of a new set of bands, with a prominent ν_{C-O} = 1126.9 cm^{-1}. This photochemical conversion could be reversed by using UV irradiation (λ = 260−320 nm). The experimental difference spectrum correlates reasonably well with a calculated IR spectrum for the benzazetine **35** [B3LYP/6-31G(d,p)] (Figure 5; Supporting Information, Table S13).

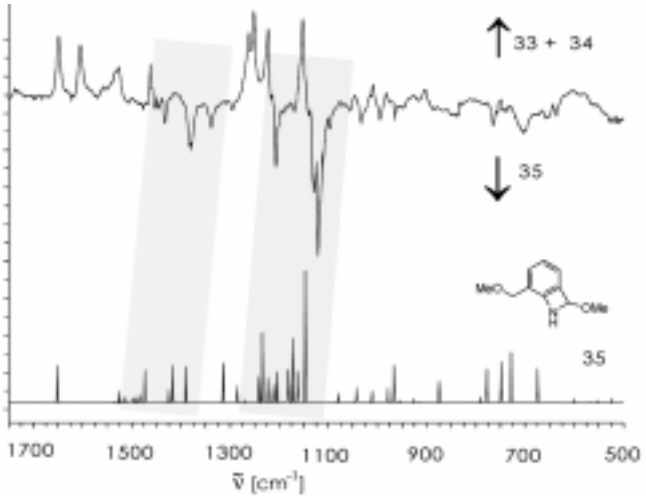


Figure 5. Top: IR difference spectrum, obtained by photolysis (λ = 305−320 nm, 2 h, then λ > 435 nm, 20 h, then λ = 260−320 nm, 20 min, then λ = 350−450 nm, 25 min, then λ = 260−320 nm, 35 min; Ar, 10 K) of azide **31**; bands pointing up grow upon irradiation with λ = 260 −320 nm (mixture of iminoquinone methides **33** and **34**), bands pointing down are depleted upon irradiation with λ = 260−320 nm; bottom: calculated (B3LYP/6-31G**) IR spectrum of benzazetine **35**; the areas shaded gray highlight some band assignments; correlations are shown between bands pointing down, assigned to **35**, and the calculated IR spectrum of **35**

Further evidence for a hydrogen shift from the benzylic position in nitrene **32** (and *not* from the terminal methyl groups) was obtained by examination of the photochemistry of the azide [D_6]-**31**, in which the methyl groups of the methoxymethyl functionalities were substituted by trideuteriomethyl groups. In accordance with the predictions of DFT calculations, the ν_{N-H} of the imino groups of the iminoquinone methides were always exceedingly weak IR bands at the limit of detectability. Upon extended photolysis of [D_6]-**31** (Ar, 10 K), a very weak band was formed at $\tilde{\nu}$ = 3276.4 cm^{-1}, while no such band was detected at $\tilde{\nu} \approx$ 2340 cm^{-1}, where a ν_{N-D} would have been expected to appear.

Matrix experiments performed using UV/Vis-spectroscopic detection agree with the picture derived from infrared spectroscopy. Nitrene **32**, which was detected after brief photolysis of **31**, displayed a characteristic UV/Vis spectrum, including the typical broad, weak, structured band with maxima at λ = 524, 510, 504, 496, and 490 nm, a weak λ_{max} = 388 nm, and strong bands at λ_{max} = 300 and 289 nm. Upon extended photolysis, these bands assigned to **32** disappeared again, being replaced by a broad, intense band with λ_{max} = 390 nm, attributable to the mixture of iminoquinone methides **33** and **34**. Broad-band irradiation in the visible part of the spectrum (420−680 nm) then produced a decrease in intensity of the 390 nm band, which could be restored by UV irradiation of the matrix (λ = 260−320 nm). This behavior confirmed that formation of a benzazetine (**35**) was also possible in this system.

If 2-azido-*N*,*N*-dimethylbenzylamine (**36**), matrix-isolated in Ar at 10 K, was irradiated with the output of a 75-W Xe arc lamp coupled to a monochromator set at λ = 320 nm, the IR bands of the starting material were soon replaced by a new set of bands. At the same time, the matrix took on a reddish brown color. Further irradiation (Hg arc lamp with Schott GG 475 cut-off filter) resulted in an increase in the intensity of some bands, while others become less intense. This apparent shift in a photostationary equilibrium was confirmed by UV/Vis detection. The absorption maximum found upon initial irradiation with λ = 320 nm is λ_{max} = 462 nm; it was shifted to λ_{max} = 454 nm upon irradiation with λ > 475 nm. Subsequent irradiation with λ = 320 nm brought λ_{max} back to 462 nm. Irradiation of 2-azido-*N*,*N*-diethylbenzylamine (**37**) under identical conditions resulted in very similar observations. Here, λ_{max} = 468 nm after initial irradiation with λ = 320 nm; it

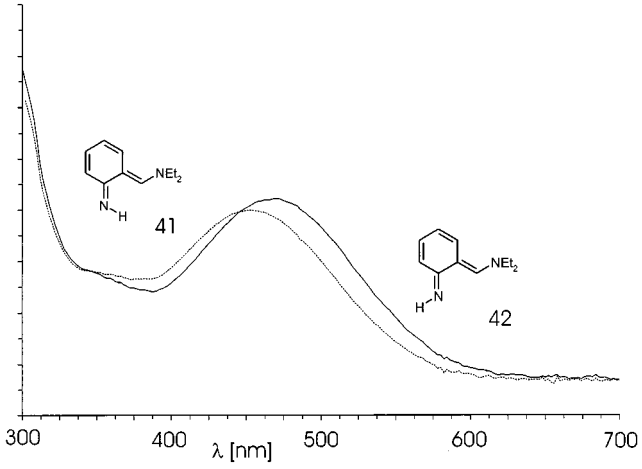
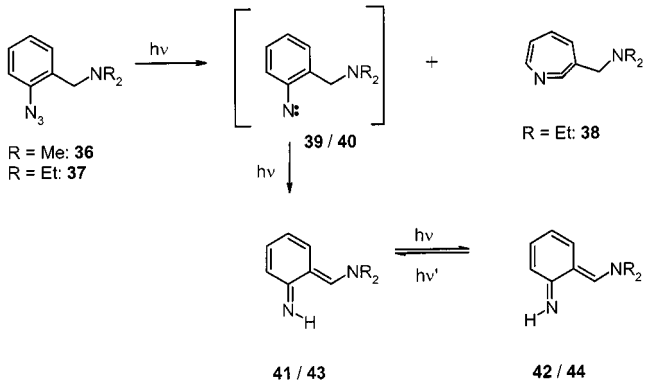


Figure 6. UV/Vis spectra obtained after photolysis (λ = 380 nm, 1 h, then λ = 365 nm, 17 h, then λ = 400 nm, 10 min, then λ = 575 nm, 30 min; Ar, 10 K) of azide **37**; solid line: before irradiation with λ = 575 nm; dashed line: after irradiation with λ = 575 nm



was shifted to λ_{max} = 452 nm upon irradiation with λ > 475 nm (Figure 6). The IR spectrum of the products formed is very similar to the spectrum measured upon irradiation of **36**. Again, the shift in photostationary equilibrium was reversible. If **37** was irradiated with λ = 350−450 nm, another photoproduct was observed in very small amounts during the initial stage of photolysis. This product featured an infrared band at $\tilde{\nu}$ = 1843 cm^{-1}, slightly below the range typical of didehydroazepines.[7] Prolonged photolysis with λ = 350−450 nm resulted in the disappearance of this new band. In the UV/Vis spectrum, under identical photolytic conditions, a band with λ_{max} = 346 nm was observed, showing the same behavior as the IR band at $\tilde{\nu}$ = 1843 cm^{-1}.

In order to identify the products formed, the infrared spectra of some possible photoproducts of **36** were calculated using density functional theory [B3LYP/6-31G(d,p)]. The calculations clearly showed that the iminoquinone methides **41** and **42** had been formed (Table 1). In their case, the experimental difference spectrum obtained by subtraction of the IR spectrum before long-wavelength irradiation from that measured after irradiation with λ > 475 nm is very accurately matched by its calculated counterpart (Figure 7, see also Table 1). Thus, the *syn-anti* isomer **41** shows a λ_{max} = 454 nm, while the *anti-anti* isomer **42** absorbs at a slightly lower frequency (λ_{max} = 462 nm). Correspondingly, the iminoquinone methides formed upon photolysis of **37** show λ_{max} of 468 nm (**44**) and 452 nm (**43**).

Azide **37** was also photolyzed in 2-methylpentane glass at 77 K. Brief photolysis (< 20 min) with 350 nm < λ < 450 nm resulted in the disappearance of bands attributable to the starting material, while a new band appeared at λ_{max} = 346 nm. Prolonged photolysis resulted in the disappearance of this new band, while a broad band of a secondary product (λ_{max} = 490 nm) emerged. At the same time, the glassy matrix took on a reddish brown color. Warming the glass resulted in the decay of both species. The product

Table 1. Experimental and calculated infrared data for iminoquinone methides **41**−**44**

ν_{exp}(**41**) (int.)[a]	$\tilde{\nu}_{calc}$(**41**) (int.)[b]	$\tilde{\nu}_{exp}$(**43**) (int.)[c][d]	$\tilde{\nu}_{exp}$(**42**) (int.)[a]	$\tilde{\nu}_{calc}$(**42**) (int.)[b]	$\tilde{\nu}_{exp}$(**44**) (int.)[c][e]
1632.3 (s)	1697.0 (47)	1634.1 (s)	1626.4 (s)	1695.1 (60)	1629.0 (s)
1601.7 (vs)	1651.1 (100)	1591.5 (vs)	1591.5 (vs)	1647.9 (100)	1585.2 (vs)
1535.4 (w)	1595.9 (37)	−	1523.9 (vs)	1594.5 (62)	1525.2 (s)
1517.8 (m)	1581.4 (71)	1511.4 (m)	[f]	1580.4 (81)	1517.1 (s)
1460.2 (w)	1503.5 (8)	−	1467.1 (vw)	1510.5 (2)	1467.8 (m)
1452.9 (vw)	1495.5 (2)	−	1445.4 (vw)	1492.9 (2)	−
1432.0 (s)	1477.7 (36)	1429.6 (s)	1427.6 (s)	1473.9 (54)	1421.3 (s)
1421.3 (s)	1463.2 (9)	−	1416.6 (s)	1462.5 (4)	−
1411.6 (m)	1449.5 (17)	−	1407.7 (s)	1443.4 (9)	−
1397.6 (s)	1433.3 (44)	1402.4 (w)	1392.3 (s)	1432.1 (42)	−
1337.6 (w)	1368.3 (5)	1357.8 (w)	1344.6 (s)	1377.7 (22)	1354.0 (m)
1321.6 (w)	1351.2 (9)	−	1332.6 (m)	1366.8 (13)	1332.1 (s)
1210.7 (w)	1237.2 (5)	1234.0 (w)	1267.8 (s)	1297.0 (17)	1265.2 (w)
1171.2 (m)	1198.6 (12)	1168.5 (m)	1204.9 (w)	1233.9 (2)	1228.6 (s)
1147.6 (w)	1167.1 (9)	1149.0 (w)	1152.4 (w)	1172.9 (10)	−
1113.6 (s)	1140.1 (21)	1125.1 (m)	1142.7 (w)	1166.9 (5)	−
1099.3 (w)	1122.9 (17)	1097.6 (vw)	1123.0 (s)	1145.7 (25)	1132.3 (s)
1053.0 (s)	1076.7 (21)	1054.2 (s)	1063.4 (s)	1085.9 (23)	1065.8 (s)
988.6 (m)	1014.4 (4)	988.7 (vw)	939.0 (vw)	977.7 (18)	948.0 (w)
908.7 (s)	932.5 (17)	911.7 (w)	895.4 (vw)	909.8 (1)	−
850.1 (vw)	871.0 (4)	−	833.7 (s)	856.8 (16)	832.7 (s)
806.7 (m)	822.5 (9)	822.8 (w)	−	812.8 (7)	813.8 (m)
794.0 (m)	810.5 (5)	803.1 (w)	783.6 (s)	803.3 (13)	782.6 (m)
733.8 (vs)	752.9 (14)	730.9 (s)	729.6 (vw)	750.5 (2)	−
709.2 (s)	732.1 (9)	708.4 (m)	617.8 (m)	627.9 (3)	616.9 (w)
611.8 (m)	621.7 (4)	611.5 (w)	544.7 (w)	554.6 (2)	−
548.5 (w)	557.7 (3)	−	518.7 (w)	529.2 (3)	−
530.7 (vw)	535.5 (4)	−	−	−	−

[a] Experimental band positions for **41/42** in cm^{-1}, approx. rel. intensity. − [b] B3LYP/6-31G**, unscaled (relative intensity is given in brackets). − [c] Experimental data for the corresponding bands of **43/44** (in cm^{-1}, obtained by comparing band patterns.) − [d] **43** shows further weak bands at $\tilde{\nu}$ = 1298.5, 1073.7, 933.7, 875.4, 752.7, 682.9, and 667.8 cm^{-1}. − [e] **44** shows further strong bands at $\tilde{\nu}$ = 660.0 and 655.0 cm^{-1} and weak bands at $\tilde{\nu}$ = 1306.8, 1143.6, and 769.5 cm^{-1}. − [f] The very intense band at 1523.9 cm^{-1} probably includes this vibration.

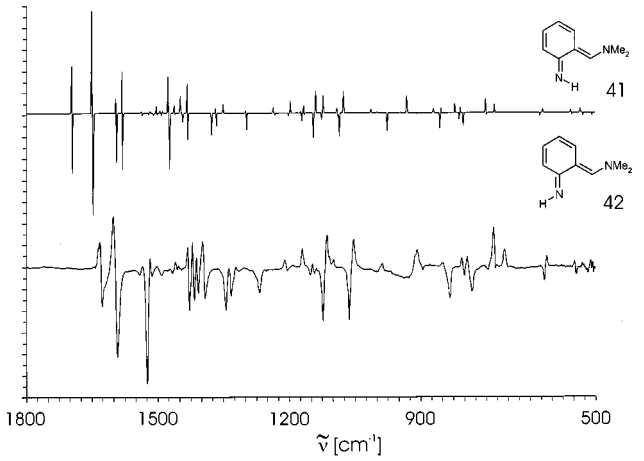


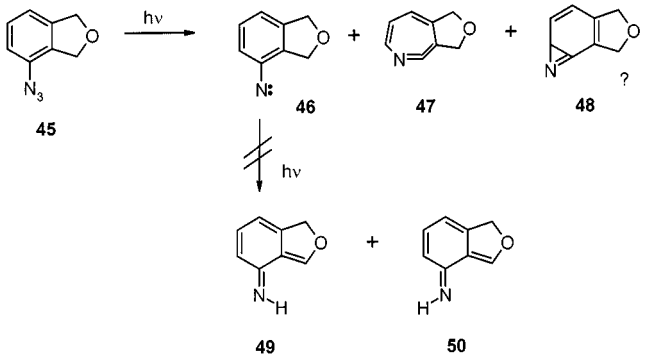
Figure 7. Bottom: IR difference spectrum obtained after photolysis (λ = 305−320 nm, 25 h, then λ > 530 nm, 25 min; Ar, 10 K) of azide **36**; bands pointing up grow upon irradiation with λ > 530 nm, bands pointing down are depleted; top: calculated (B3LYP/6-31G**) IR difference spectrum of iminoquinone methides **41** and **42**

with λ_{max} = 490 nm disappeared first, at T = 120 K ($\tau \approx$ 5 min). The residual product with λ_{max} = 346 nm was somewhat less reactive, decaying within 20 min at T = 140 K.

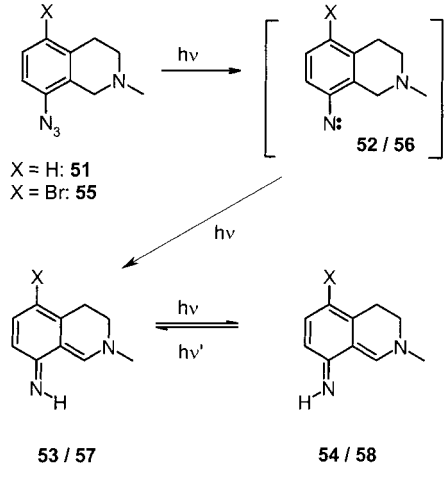
The results obtained in 2-methylpentane matrix are consistent with a didehydroazepine (probably **38**) being the primary product upon long-wavelength photolysis of **37**, while the secondary product can most probably be assigned to a highly reactive iminoquinone methide of unknown stereochemistry. The didehydroazepine is also formed in Ar matrix. In this environment, however, only very small quantities of this intermediate were detected.

3. Alkoxy and Dialkylamino Substituents as Part of a Ring System

In order to investigate the influence of the spatial orientation of the benzylic substituents, some *o*-tolyl azide derivatives in which the substituent was forced to point away from the nitrene center, by making it part of a ring system, were synthesized and investigated by matrix isolation spectroscopy.



Photolysis (λ = 320 nm) of 4-azidophthalan (**45**), matrix-isolated in argon, resulted in depletion of the starting material and the formation of new bands at $\tilde{\nu}$ = 1867.9 (s), 1726.6 (m), and 1556.6 (m) cm^{-1}. Irradiation of the primary mixture with λ = 260−320 nm resulted in an increase in intensity of the bands at $\tilde{\nu}$ = 1867.9 and 1556.6, at the expense of the band at $\tilde{\nu}$ = 1726.6 cm^{-1}. Long-wavelength irradiation (λ > 435 nm) reversed this change in concentrations in a photostationary equilibrium. While the band at $\tilde{\nu}$ = 1867.9 cm^{-1} is characteristic of a didehydroazepine [**47**: B3LYP/6-31G(d,p): $\tilde{\nu}$ = 1948.3 cm^{-1}], and the band at $\tilde{\nu}$ = 1556.6 cm^{-1} can be assigned to triplet 4-nitrenophthalan (**46**) [UB3LYP/6-31G(d,p): $\tilde{\nu}$ = 1598.5 cm^{-1}], the identity of the band at $\tilde{\nu}$ = 1726.6 cm^{-1} is less clear. One possible structure might be the azirine **48**, as compounds of this type have previously been reported to exhibit a $\nu_{C=N}$ at slightly lower wavenumbers.[33] Formation of iminoquinone methides in this system, however, can be ruled out. Under no conditions were IR bands attributable to either one of the iminoquinone methides **49** and **50** [by comparison with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory] detected. Using UV/Vis detection, a typical triplet nitrene spectrum was found, with a weak, broad, structured band extending to ca. 540 nm (λ_{max} = 526, 514, 486 nm), a weak band with λ_{max} = 388 nm, and two medium-intensity bands with λ_{max} = 314/306 nm and 280/272 nm. Long-wavelength photolysis (λ > 435 nm) produced an increase of broad absorptions around 330 and 250 nm at the expense of the bands assigned to nitrene **46**. This effect was reversible by UV (λ = 260−320 nm) irradiation. In conclusion, no evidence for formation of iminoquinone methides upon photolysis of the azidophthalan **45** could be found. This result could in principle indicate a necessity for direct interaction between nitrene and substituent. In order to verify this hypothesis, an azidotetrahydroisoquinoline with a dialkylamino substituent incorporated in a six-membered ring (**51**) was synthesized.



Photolysis (λ = 320 nm) of 8-azido-2-methyl-1,2,3,4-tetrahydroisoquinoline (**51**) under matrix isolation spectroscopy conditions produced results very similar to those obtained with azides **36** and **37**. Even after very brief irradiation, the matrix immediately took on a deep reddish-brown color, and the precursor was consumed in a very

short time. The products formed could be identified as the isomeric iminoquinone methides **53** and **54**, by comparison with calculated IR spectra (Figure 8; Supporting Information, Tables S14, S15). Upon long-wavelength irradiation ($\lambda > 595$ nm), isomer **53** increased at the expense of **54**. Broad-band visible photolysis ($\lambda > 420$ nm) restored the initial concentrations. Isomer **54** was the predominant constituent of the mixture under all conditions, however.

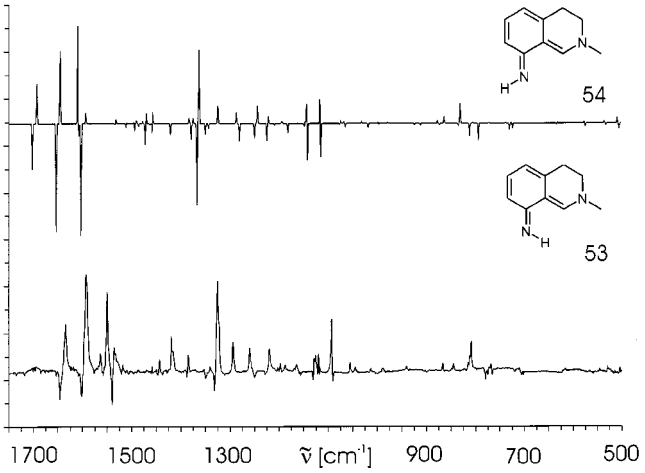


Figure 8. Bottom: IR difference spectrum obtained after photolysis ($\lambda = 320$ nm, 50 min, then $\lambda > 590$ nm, 30 min, then $\lambda > 455$ nm, 10 min, then $\lambda > 420$ nm, 5 min; Ar, 10 K) of azide **51**; bands pointing up grow upon irradiation with $\lambda > 420$ nm, bands pointing down are depleted; top: calculated (B3LYP/6-31G**) IR difference spectrum of iminoquinone methides **53** and **54**

The iminoquinone methides **53** and **54** were also characterized by UV/Vis spectroscopy. The mixture obtained upon photolysis ($\lambda = 320$ nm) of **51** showed a broad band with $\lambda_{max} = 472$ nm. Long-wavelength photolysis ($\lambda > 595$ nm) gave rise to a very small blue-shift of λ_{max} ($\Delta\lambda \approx 2$ nm), which was reversible by broad-band irradiation.

In summary, photolysis of the matrix-isolated azidotetrahydroisoquinoline **51** resulted in highly efficient formation of two isomeric iminoquinone methides. This example demonstrates that direct interaction between nitrene and substituent is not a general prerequisite for the hydrogen shift to occur.

Photolysis of the bromotetrahydroquinolyl azide **55**, matrix-isolated in Ar, gave rise to observations practically identical with those obtained with azide **51**. For this reason, the spectra will not be discussed in detail. IR frequencies and comparison with DFT data are given as Supporting Information (Tables S16, S17).

4. Dimethylamino Substituent in Phenethyl Position

Photolysis ($\lambda = 320$ nm) of matrix-isolated 2-(2-azidophenyl)-*N*,*N*-dimethylethylamine (**59**) primarily resulted in formation of a triplet nitrene **60**, as evidenced by typical UV/Vis absorptions ($\lambda_{max} = 500$, 486 nm, the matrix has a brownish color) and an IR band at $\tilde{\nu} = 1558.1$ cm^{-1}. Upon extended photolysis, however, the matrix became colorless again, and a single product was formed. This product showed prominent IR bands at $\tilde{\nu} = 1614.2$, 1501.6, and 748.9 cm^{-1}, indicative of an arene. Comparison with the calculated IR spectra [B3LYP/6-31G(d,p)] of several possible product molecules allowed the product to be identified as the tetrahydrobenzodiazepine **62** (Figure 9; Supporting Information, Table S18). The formation of iminoquinone methides can be ruled out in this system.

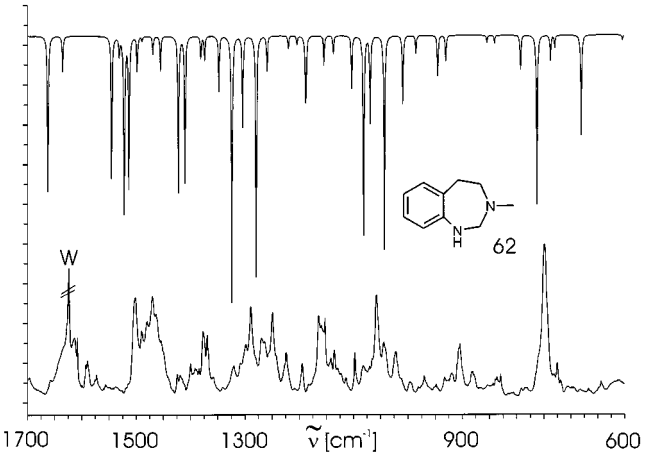
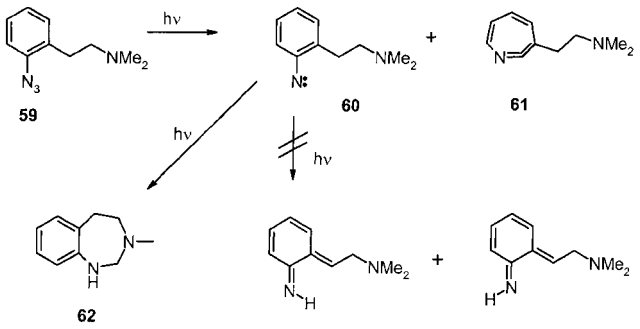


Figure 9. Bottom: IR spectrum obtained after photolysis ($\lambda = 305-320$ nm, 16 h; Ar, 10 K) of azide **59**; the band labeled "W" belongs to matrix-isolated water; top: calculated (B3LYP/6-31G**, inverted) IR spectrum of tetrahydrobenzodiazepine **62**



At this point, the experimental findings presented so far are summarized in brief.

– The primary products of the photolysis of the azides presented in this work are triplet nitrenes, which in some cases may be reversibly converted into didehydroazepines.

– With only a few exceptions, the photochemical formation of iminoquinone methides from arylnitrenes substituted with π-donors in *o*-benzylic positions seems to be a general phenomenon.

– Simple alkyl groups in benzylic positions or π-donors further away from the nitrene center do not promote the reaction. While a photochemical 1,4-hydrogen shift for *o*-tolylnitrene has been reported,[24] no evidence for such a reaction was obtained in this study of 2-ethyl- and 2-isopropylphenylnitrene.

– The reaction is not observed in the cases of 2-bromomethyl-6-methylphenylnitrene and 4-nitrenophthalan.

– The quantum yield of iminoquinone methide formation strongly depends on the nature of the benzylic substituent. A very high quantum yield is observed in the case of

R = NR_2, while the reaction requires prolonged irradiation if R = halogen.

– The stereochemical outcome of the reaction is generally such that the substituent points away from the imino functionality (the *anti* isomers are formed). On the basis of the IR patterns, the formation of *syn* isomers can definitely be ruled out.

– Generally, two stereoisomers with different imino hydrogen atom orientations are formed, and may be interconverted photochemically.

– In one instance, reversible photochemical conversion of an iminoquinone methide to the benzazetine **35** was observed.

Calculation of Reaction Enthalpies and TS Energies

The stabilization of iminoquinone methides and rearrangement transition states was studied by optimization of the triplet nitrene product and TS geometries using density functional theory [(U)B3LYP/6-31G(d) {or 6-31G(d,p)}]. The activation energies given are corrected for zero-point vibrational energy.

Because of the electrophilic nature of the *exo*-methylene carbon atom in iminoquinone methides, these compounds should probably be stabilized by donor substituents at this site. Hence, a comparison of the reaction enthalpies for the reaction triplet nitrene → singlet iminoquinone methide was performed, calculated for different substituents X. While the absolute reaction enthalpies thus determined would not be accurate, the differences between the reaction enthalpies calculated for different substituents should probably be significant. The calculated reaction enthalpies are shown in Table 2. This table also gives energies for a selection of triplet nitrenes, as well as transition states for formation of iminoquinone methides on both the triplet and singlet surfaces. The barriers to rearrangement on the singlet surface shown in Table 2 correspond to the difference in energy between singlet TS and triplet nitrene minus singlet–triplet splitting of the nitrene. The electronic configuration of the singlet nitrenes was expected to be of open-shell $\sigma_1\pi_1$ character.[13,15] The singlet-triplet splitting was assumed not to be dependent on the substitution and taken as a constant 18.3 kcal/mol.[34,35]

The following conclusions can be drawn from Table 2.

– Thermodynamically, iminoquinone methides are stabilized by π-donor substituents, and also, to a lesser degree, by alkyl substituents. The degree of stabilization correlates with the π-donor ability of the substituent ($O^- >> NR_2 >$ OR > F > Cl > Br). The π-accepting cyano group is also predicted to facilitate the reaction slightly.

– This stabilization in most cases is reflected by a decrease in activation energy.

– The only exceptions to this rule are the nitrenophthalan and nitrenotetrahydroisoquinoline systems, in which, despite significant stabilization of the product, the barriers for 1,4-hydrogen shift are calculated to be high.

Table 2. Energies (in Hartrees) for triplet nitrenes and triplet and singlet transition states for 1,4-H shift in derivatives of *o*-tolylnitrene; calculated barriers (corrected for ZPE) and overall reaction enthalpies (all in kcal/mol)

X	Y	Azide[a]	*E*(nitrene, T)[b]	*E*(TS, T)[c]	*E*(TS, S)[d]	Barrier (T)[e]	Barrier (S)[f]	ΔH[g]
H	H		−325.627573	−325.575185	−325.601346	29.5	20.3	−17.0
Me	H	**1**	−364.939564	−364.893358	−364.879766	25.4	16.5	−20.1
Me_2	H	**4**	−404.252820	−404.211503	−404.192527	22.2	16.7	−20.0
Br	H	**8**	−2896.728556	−2896.681663	−2896.669269	26.1	16.4	−18.0
Br	CH_3	**13**	−2936.048397	−2936.002306[h]	−2935.990847[h]	25.6[h]	15.4[h]	−18.4
Br	CH_3	**13**	−2936.048397	−2935.997243[i]	−2935.985687[i]	28.7[i]	18.9[i]	−17.4
Cl	H	**16**	−785.218256	−785.172285	−785.159966	25.5	15.8	−19.7
Cl	CH_2Cl	**21**	−1284.126692	−1284.085053	−1284.072640	24.3	13.4	−21.6
F	H		−424.847442	−424.801594	−424.791468	25.4	14.3	−23.7
CN	H		−417.861920	−417.820012	−417.805199	23.2	15.1	−21.1[j]
OPht[k]	H	**45**	−438.934157	−438.857287	−438.849426	45.0	32.2	−29.9
OMe	H	**26**	−440.135865	−440.096604	−440.083998	21.5	11.9	−25.5
O^-	H		−400.226867	−400.216092	−400.188507	3.7	4.2	−71.1[j]
NH_2	H		−380.965078	−380.930859	−380.917445	18.8	9.9	−29.5[j]
NMe_2	H	**36**	−459.583473	−459.551100	−459.536411	17.4	9.3	−29.3
NMe_2	CH_3		−498.902904	−498.871291[l]	−498.856930[l]	16.9[l]	8.4[l]	−28.1[j]
NMe_2	CH_3		−498.902904	−498.853584[i]	−498.842866[i]	27.7[i]	17.4[i]	−14.3[j]
NIq[m]	H	**51**	−497.698176	−497.638996	−497.631675	33.5	20.7	−33.6
CH_2NMe_2	H	**59**	−498.895082	−498.849896	−498.837403	24.8	15.4	−20.1[j]

[a] Number assigned to precursor azide, see text and schemes. – [b] Energy of triplet nitrene in Hartrees, as calculated by UB3LYP/6-31G*. – [c] Energy of transition state for hydrogen shift on the triplet surface (in Hartrees, UB3LYP/6-31G*). – [d] Energy of transition state for hydrogen shift on the singlet surface (in Hartrees, B3LYP/6-31G*). – [e] Barrier to hydrogen shift on the triplet surface (from UB3LYP/6-31G*, in kcal/mol, corrected for ZPE). – [f] Barrier to hydrogen shift on the singlet surface. This value corresponds to [*E*(TS, S) − *E*(nitrene, T)] − 18.3 kcal/mol, corrected for ZPE. It is based on the assumption of a triplet-singlet splitting of 18.3 kcal/mol for derivatives of phenyl nitrene. – [g] Overall reaction enthalpy for hydrogen shift. This value corresponds to *E*(triplet nitrene {UB3LYP/6-31G**}) − *E*(singlet IQM {B3LYP/6-31G**}). IQM stereochemistry was selected as *syn-anti*. – [h] H shift from bromomethyl group. – [i] H-shift from methyl group. – [j] Calculated as described in footnote[g], using (U)B3LYP/6-31G* instead of (U)B3LYP/6-31G**. – [k] 4-Nitrenophthalan **46**. – [l] H shift from (dimethylamino)methyl group. – [m] Nitrenotetrahydroisoquinoline **52**.

– If the assumption of a constant Δ(S – T) of 18.3 kcal/mol holds for the nitrenes under discussion, the barriers are generally lower on the singlet surface than on the triplet surface.

– The introduction of further substituents, not directly involved in the 1,4-hydrogen shift, lowers the barrier to this reaction. For example, the 1,4-H shift from the methyl group of 2-(dimethylaminomethyl)-6-methylphenylnitrene is predicted to have a barrier lower than that for the 1,4-H shift in *o*-tolylnitrene by 2.9 kcal/mol.

– The π-donor substituents have to be situated in benzylic positions. Otherwise, the activation energy for the 1,4-hydrogen shift is not reduced.

– The reason of the exclusive *anti* stereochemistry (as regards the exocyclic methylene functionality) can be found by analysis of the vibrational spectra calculated for the transition states of the 1,4-H shift. This shows that the vibrational modes with negative frequencies represent one hydrogen atom moving from the benzylic methylene group to the nitrene nitrogen atom. At the same time, the second benzylic hydrogen atom also moves towards the nitrene nitrogen atom, thus determining product stereochemistry. This statement holds for all systems studied, irrespective of spin multiplicity.

– Stereoisomers with exocyclic *syn*-methylene stereochemistry are found to be minima. For the reason described above, they are not formed.

Transition State Geometries

At this point, it is worthwhile to examine some of the geometries calculated for the stationary points relevant to this study. Figure 10 displays the geometry of the transition state (singlet surface) of the rearrangement of *o*-tolylnitrene, calculated at the B3LYP/6-31G(d) level of theory. Table 3 lists a number of parameters.

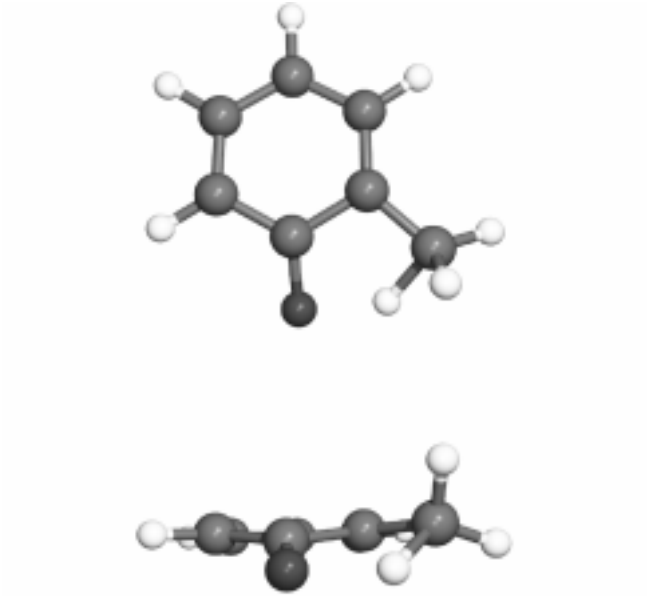
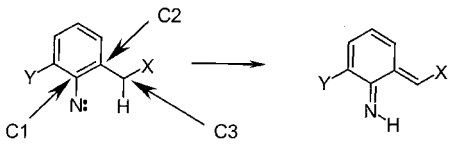


Figure 10. Calculated [B3LYP/6-31G(d)] geometry of the transition state for the rearrangement of singlet *o*-tolylnitrene to *syn o*-iminoquinone methide; top: top view; bottom: front view



Some features are common to nearly all the singlet transition states studied: (i) The dihedral angle described by the migrating hydrogen atom H, the methylene carbon atom C3, and the two ring carbon atoms (C2 and C1) connecting the nitrene nitrogen atom and the methylene moiety is generally 23±2°. (ii) The angle described by H, N, and C1, and also that described by H, C3, and C2, are consistently in the range of 91±3°. (iii) The C1–N bond length is 130±1 pm. (iv) The C2–C3 bond length is 145±1 pm. (v) The angle described by N, C1, and C2, and also that described by C3, C2, and C1, are both significantly smaller than 120° (A_{NC1C2} = 117±1°, A_{C3C2C1} = 107±3°), which means that the exocyclic nitrogen and carbon atoms are bent towards each other.

In the TS for rearrangement of singlet *o*-tolylnitrene, the $N-H_{migr}$ and $C-H_{migr}$ distances are 150 and 131 pm, respectively. Introduction of alkyl or halogen substituents does not significantly change these figures, while introduction of a methoxy substituent or – particularly – a dimethylamino substituent results in a significant lengthening of the $N-H_{migr}$ distance (r = 168 pm for R = NMe_2) and a pronounced shortening of the $C-H_{migr}$ distance (r = 121 pm for R = NMe_2). This indicates that, in accordance with the more favorable thermodynamics of the reaction, the TS for rearrangement of singlet 2-(dimethylaminomethyl)phenylnitrene (**39**) has a more nitrene-like structure and occurs early on the reaction coordinate. However, if the dialkylamino substituent is part of a ring, as it is the case of R = NIq (**52**), then $r(N-H_{migr})$ and $r(C-H_{migr})$ are calculated to be 153 pm and 133 pm, similar to the parameters found for the TS of the rearrangement of singlet *o*-tolylnitrene. If R is part of a dihydrofuran ring – as in the phthalan system **46** – the sum of the two distances grows significantly: $r(N-H_{migr})$ = 168 pm and $r(C-H_{migr})$ = 133 pm. In this system, the methylene carbon atom is unable to approach the nitrene nitrogen atom (A_{C3C2C1} = 116.43°) sufficiently closely. This may be the reason why the activation energy calculated for the rearrangement of **46** is significantly higher than in any other system studied. In the case of the tetrahydroisoquinoline derivative **52**, the geometric constraints imposed upon the system are not as severe as in **46**, yet the calculated barrier is relatively high. The discrepancy between the TS geometries calculated for **39** and **52** indicates that the constraints imposed by the additional six-membered ring present in **52** prevent the system from adopting an ideal conformation for rearrangement.

Table 3. Geometric parameters describing the transition state geometries for 1,4-H shift of derivatives of *o*-tolylnitrene on the singlet surface, as calculated using B3LYP/6-31G*; R in pm, A and D in °

X	Y	Azide[a]	R_{NH}	R_{C3H}	R_{C1N}	R_{C2C3}	A_{HNC1}	A_{HC3C2}	A_{NC1C2}	A_{C3C2C1}	$D_{HC3C2C1}$	$D_{XC3C2C1}$
H	H		150	131	129	144	89.7	90.7	116.8	107.0	25.1	152.8
CH_3	H	**1**	152	130	130	145	89.2	90.8	117.2	107.0	24.9	152.4
$(CH_3)_2$[b]	H	**4**	151	130	130	146	89.0	89.7	117.1	107.3	24.2	145.6
Br	H	**8**	151	128	130	145	90.3	93.1	117.0	105.5	24.4	150.3
Cl	H	**16**	152	128	130	145	90.1	93.1	117.3	105.4	24.7	150.7
F	H		153	128	130	145	90.0	93.4	117.5	105.4	25.9	151.5
MeO	H	**26**	159	125	130	146	89.5	94.3	118.1	106.2	24.5	149.6
Me_2N	H	**36**	168	121	130	148	88.9	95.9	118.8	107.1	21.8	148.2
NIq[c]	H	**51**	153	133	130	144	89.9	89.7	116.3	109.8	23.3	153.6
OPht[d]	H	**45**	168	133	129	141	87.5	88.2	116.9	116.4	21.9	152.5
Br	CH_3	**13**	150	129	130	145	90.6	92.9	116.7	105.6	23.7	150.5
H	CH_2Br	**13**	149	131	129	144	90.1	90.7	116.6	106.9	24.6	152.7
H	CH_2NMe_2		149	132	129	144	90.0	90.5	116.5	107.1	24.4	152.9

[a] Numbering of the precursor azides, see text and schemes. – [b] 2-Isopropylphenylnitrene **5**. – [c] Nitrenotetrahydroisoquinoline **52**. – [d] Nitrenophthalan **46**.

As far as 2-bromomethyl-6-methylphenylnitrene (**14**) is concerned, the results of the calculations do not offer any clues as to why no 1,4-H shift is observed in this system, since the transition state geometries calculated for the rearrangement of **14** and 2-(bromomethyl)phenylnitrene (**9**) are very similar. Thus, this question, together with the paradoxical situation that the tetrahydroisoquinolylnitrene **52** rearranges very smoothly despite a significant barrier predicted for this reaction, remain unsolved. If the rearrangement occurs from a higher singlet excited state of the nitrene, the transition state geometries and energies presented are no longer relevant for an understanding of the reaction, as the structures and energies of conical intersections would have to be considered. Thus, for in-depth understanding of the reaction and of the substituent effects, more elaborate calculations are required.

Conclusion

Introduction of π-donor substituents into the benzylic positions of *o*-tolylnitrene affords access to a photochemical 1,4-hydrogen shift, which yields iminoquinone methides, highly reactive dienes of potential synthetic value. The reaction takes place most efficiently if R = NR_2, while the quantum yield is significantly lower if R = MeO or halogen. The reaction requires a certain degree of flexibility around the bonds involved, and incorporation of the benzylic substituent into an additional ring results in drastically increased calculated barriers. In spite of this, highly efficient hydrogen transfer was observed in the case of the tetrahydroisoquinoline system **52**, which possibly points towards the involvement of higher excited nitrene states or hot ground state chemistry. The involvement of higher excited nitrene singlet states would imply that structures and energies at conical intersections rather than transition states would be relevant for interpretation of the experimental data. The results presented give no indication that a direct nitrene–lone pair interaction may play a significant role. Neither experiments nor calculations give evidence for the involvement of ylide structures or products derived from them.

Experimental Section

General: The matrix isolation set-up used in this work has been described before.[36] As light sources, Hg high-pressure lamps (Osram, 500 W, Oriel housing) were used in combination with various Schott cut-off filters and dichroic mirrors for wavelength preselection. Argon was used as matrix material. Most of the azides used in this work were prepared by treatment of 1-azido-2-(bromomethyl)benzene, 1-azido-2,6-bis(bromomethyl)benzene, or 1-azido-2,3-bis(bromomethyl)benzene with nucleophiles. The benzyl bromides themselves were synthesized by NBS bromination of azidotoluene or azidoxylenes,[37] which were in turn prepared by diazotization of the corresponding aniline derivatives, followed by treatment with aq. NaN_3. The tetrahydroisoquinoline derivatives were synthesized from 8-amino-*N*-methyltetrahydroisoquinoline[38] by diazotization, followed by treatment with aq. NaN_3. NMR spectra were recorded using $CDCl_3$ as solvent.

1-Azido-2-bromomethylbenzene (8): This compound was synthesized as described by Mornet et al.[37] Yield 80%. – IR (Ar, 10 K): $\tilde{\nu}$ = 2136.9 (s), 2126.5 (vs), 2121.6 (vs), 2107.9 (m), 2085.5 (m), 1603.6 (w), 1585.8 (m), 1498.0 (s), 1485.8 (m), 1455.8 (m), 1438.0 (vw), 1324.4 (w), 1309.4 (s), 1298.3 (s), 1289.7 (m), 1280.6 (m), 1241.7 (vw), 1230.7 (w), 1222.3 (w), 1205.4 (vw), 1185.3 (vw), 1167.0 (vw), 1154.9 (vw), 1131.4 (vw), 1086.0 (w), 1052.0 (vw), 1040.6 (vw), 943.0 (vw), 877.1 (vw), 857.8 (vw), 836.6 (w), 791.5 (vw), 752.5 (m), 749.5 (m), 742.3 (w), 699.4 (vw), 680.9 (w), 663.8 (w), 652.9 (m), 613.8 (w), 570.0 (w), 536.6 (w), 513.0 (vw), 484.9 (vw), 469.5 (vw) cm^{-1}.

1-Azido-2-chloromethylbenzene (16): 1-Azido-2-(bromomethyl)benzene (630 mg, 3 mmol) and LiCl (460 mg, 11 mmol) in DMF (5 mL) were stirred at ambient temperature for 12 h. The mixture was then poured into 50 mL of *n*-hexane and 30 mL of water, the organic layer was separated, washed once with water, and dried with Na_2SO_4. Evaporation of the solvent yielded 376 mg (75%) of a yellow liquid, which crystallized upon standing. The substance could be recrystallized from *n*-pentane. – M.p. 56 °C. – IR (Ar, 10 K):

$\tilde{\nu}$ = 3086.7 (vw), 3035.0 (vw), 2974.0 (vw), 2965.5 (vw), 2127.3 (vs), 2093.7 (m), 1591.1 (m), 1501.2 (m), 1491.7 (m), 1487.9 (s), 1457.9 (s), 1432.5 (vw), 1335.0 (w), 1361.2 (w), 1308.7 (m), 1300.0 (vs), 1284.8 (s), 1297.5 (m), 1269.4 (w), 1192.9 (vw), 1182.7 (vw), 1167.0 (w), 1154.7 (w), 1149.1 (vw), 1093.5 (w), 1088.2 (w), 1062.0 (vw), 1052.9 (vw), 1041.3 (w), 949.9 (vw), 940.2 (vw), 908.4 (vw), 858.7 (vw), 839.7 (m), 833.4 (vw), 795.1 (vw), 761.4 (vw), 750.9 (s), 748.8 (vs), 702.3 (vw), 683.6 (m), 666.6 (m), 652.3 (w), 580.6 (w), 537.5 (w), 486.7 (vw) cm^{-1}. − ^1H NMR: δ = 4.56 (s, 2 H), 7.15 (d, 1 H), 7.16 (d, 1 H), 7.36 (dt, 1 H), 7.39 (d, 1 H). − ^{13}C NMR: δ = 41.4, 118.4, 125.0, 128.7, 130.0, 131.0, 138.5. − MS: *m*/*z* = 167/169 [M^+], 139, 138, 132, 112, 104 (100%), 77, 63, 51, 39. − $C_7H_6ClN_3$ (167.6): calcd. C 50.3, H 3.6, N 25.1; found C 49.8, H 3.5, N 25.2.

1-Azido-2-(methoxymethyl)benzene (26): 1-Azido-2-(bromomethyl)-benzene (1.0 g, 4.72 mmol) and NaOMe (270 mg, 5 mmol) were dissolved in dry methanol (30 mL) and stirred in the dark at ambient temperature for 72 h. The solvent was then evaporated and the residue was worked up by column chromatography [SiO_2; petroleum ether (PE) 60−80, gradient to PE 60−80/CH_2Cl_2 (1:1)]. Yield 450 mg (2.76 mmol, 58.5%), yellow oil. − IR (Ar, 10 K): $\tilde{\nu}$ = 3070.5 (vw), 3037.1 (vw), 2993.9 (w), 2933.3 (w), 2879.0 (w), 2828.8 (w), 2810.7 (vw), 2135.7 (vs), 2122.9 (vs), 2095.5 (s), 1596.7 (w), 1586.4 (m), 1502.0 (w), 1491.2 (m), 1474.4 (w), 1452.7 (m), 1385.3 (w), 1321.5 (w), 1297.2 (s), 1282.5 (s), 1239.4 (vw), 1210.7 (w), 1196.4 (m), 1160.9 (vw), 1122.5 (s), 1083.3 (s), 1040.9 (w), 980.7 (m), 936.3 (vw), 913.3 (vw), 863.3 (vw), 832.7 (vw), 804.0 (vw), 752.2 (s), 707.3 (w), 677.6 (m), 654.9 (vw), 607.2 (vw), 536.8 (w), 487.2 (vw) cm^{-1}. − ^1H NMR: δ = 3.40 (s, 3 H), 4.41 (s, 2 H), 7.13 (m, 2 H), 7.32 (dt, 1 H), 7.38 (d, 1 H). − ^{13}C NMR: δ = 58.3, 69.8, 117.9, 124.7, 128.9, 129.6, 135.3, 137.9. − MS: *m*/*z* = 163 [M^+], 134, 120, 104, 92, 77, 65, 51, 45, 39. − HRMS: calcd. 163.074562, found 163.074700. − $C_8H_9N_3O$ (163.2): calcd. C 58.9, H 5.52, N 25.7; found C 58.7, H 5.52, N 25.5.

1-Azido-2-(dimethylaminomethyl)benzene (36): 1-Azido-2-(bromomethyl)benzene (1.0 g, 4.74 mmol) was dissolved in THF (10 mL). A solution of dimethylamine in THF (2 M, 10 mL, 20 mmol) was added to this solution. The mixture was allowed to stand for 30 min. Dimethylamine hydrobromide was then filtered off, and the solvent was evaporated. The residue was extracted with *n*-pentane, and the extract was concentrated. Column chromatography (SiO_2; *tert*-butyl methyl ether) yielded 520 mg (63%) product, as a yellow liquid. − IR (Ar, 10 K): $\tilde{\nu}$ = 3083.3 (vw), 3036.2 (vw), 2985.4 (m), 2950.6 (m), 2857.7 (m), 2823.3 (m), 2779.4 (m), 2127.4 (vs), 2085.7 (s), 1587.1 (m), 1488.8 (s), 1453.5 (s), 1367.0 (m), 1324.4 (w), 1298.8 (s), 1291.8 (s), 1264.1 (w), 1177.8 (w), 1153.3 (w), 1037.5 (m), 1025.5 (w), 986.6 (vw), 973.0 (vw), 939.4 (vw), 866.5 (w), 836.4 (w), 826.9 (w), 799.8 (vw), 753.4 (s), 709.4 (vw), 675.8 (w), 655.6 (w), 615.8 (vw), 538.1 (vw), 441.9 (vw) cm^{-1}. − ^1H NMR: δ = 2.25 (s, 6 H), 3.38 (s, 2 H), 7.09 (dt, 1 H), 7.13 (d, 1 H), 7.29 (t, 1 H), 7.31 (d, 1 H). − ^{13}C NMR: δ = 45.3, 58.7, 118.2, 124.5, 128.6, 129.8, 131.5. − MS: *m*/*z* = 176 [M^+], 147 [$M^+ - H - N_2$], 133, 118, 104, 92, 77, 65, 58, 51, 42. − HRMS: found 176.106900; calcd. 176.106197.

1-Azido-2-(diethylaminomethyl)benzene (37): This compound was prepared similarly to 1-azido-2-(dimethylaminomethyl)benzene, using neat diethylamine as solvent. Yield: 60%, yellow liquid. − IR (Ar, 10 K): $\tilde{\nu}$ = 3081.4 (vw), 3034.5 (vw), 2983.8 (m), 2946.1 (w), 2803.9 (w), 2127.4 (vs), 2087.7 (s), 1587.9 (m), 1494.0 (m), 1487.4 (m), 1474.9 (w), 1453.7 (w), 1387.9 (w), 1374.2 (w), 1299.3 (s), 1206.5 (w), 1171.8 (w), 1122.5 (vw), 1092.4 (vw), 1071.7 (vw), 1060.5 (w), 993.2 (vw), 939.0 (vw), 884.7 (vw), 796.3 (vw), 779.6 (vw), 752.6 (s), 723.8 (vw), 706.2 (vw), 673.7 (w), 660.7 (vw), 538.1 (vw) cm^{-1}. − ^1H NMR: δ = 1.07 (t, 6 H), 2.57 (q, 4 H), 3.56 (s, 2 H), 7.10 (m, 2 H), 7.28 (t, 1 H), 7.50 (d, 1 H). − ^{13}C NMR: δ = 11.4, 46.9, 51.8, 118.0, 124.7, 128.3, 130.1, 131.2, 138.4. − MS: *m*/*z* = 204 [M^+], 189 [$M^+ - CH_3$], 175, 161 [$M^+ - CH_3 - N_2$], 147, 130, 119, 106, 92, 86, 77, 65, 51, 42. − HRMS: found 204.137200; calcd. 204.137497.

1-Azido-2,6-bis(bromomethyl)benzene: 1-Azido-2,6-dimethylbenzene (6.1 g, 41.5 mmol), NBS (16.3 g, 91.3 mmol), and AIBN (1.33 g) in dry benzene (125 mL) were heated under reflux for 12 h. The mixture was then poured into water and diethyl ether, and the ether layer was dried with sodium sulfate. The ether was then evaporated, and the residue worked up by column chromatography [SiO_2; hexane/CH_2Cl_2 (10:1)]. The yellow product (3rd fraction) crystallized upon standing. Yield 6.0 g (47.4%), m.p. 41 °C. − IR (Ar, 10 K): $\tilde{\nu}$ = 2146.3 (s), 2118.5 (vs), 1599.2 (s), 1541.2 (w), 1467.1 (m), 1450.7 (s), 1438.3 (w), 1369.1 (vw), 1341.4 (m), 1309.4 (m), 1293.2 (s), 1265.5 (m), 1241.9 (m), 1183.3 (vw), 1169.6 (vw), 1123.3 (vw), 1071.8 (vw), 1059.7 (vw), 979.6 (vw), 876.1 (w), 871.8 (w), 853.1 (vw), 833.7 (vw), 818.6 (vw), 759.9 (w), 768.6 (m), 765.0 (w), 749.2 (w), 718.6 (w), 681.5 (vw), 666.9 (vw), 662.5 (vw), 619.7 (w), 605.1 (m), 589.7 (w), 564.0 (m), 553.9 (w), 535.5 (m), 514.2 (w) cm^{-1}. − ^1H NMR: δ = 4.56 (s, 4 H), 7.16 (t, 1 H), 7.33 (d, 2 H). − ^{13}C NMR: δ = 28.6, 126.7, 131.9, 133.1, 137.3. − MS: *m*/*z* = 303/305/307 [M^+], 275/277/279, 224/226, 196/198, 116, 89, 63, 51, 39. − HRMS: found 302.900500; calcd. 302.900670. − $C_8H_7Br_2N_3$ (305.0): calcd. C 31.5, H 2.3, N 13.8; found C 30.9, H 2.25, N 13.4.

1-Azido-2,6-bis(chloromethyl)benzene (21): This compound was prepared from 1-azido-2,6-bis(bromomethyl)benzene by halogen exchange with LiCl in DMF, in analogy to 1-azido-2-(chloromethyl)-benzene. Purification was achieved by column chromatography (SiO_2; petroleum ether 60−80). Yield 80%, yellow liquid. − IR (Ar, 10 K): $\tilde{\nu}$ = 3075.5 (vw), 3032.0 (vw), 2933.7 (vw), 2146.4 (s), 2120.1 (vs), 1599.1 (m), 1462.8 (s), 1452.7 (s), 1443.6 (s), 1431.1 (w), 1340.8 (s), 1301.3 (s), 1294.4 (s), 1282.9 (s), 1268.8 (m), 1245.8 (w), 1230.0 (vw), 1217.9 (w), 1182.8 (vw), 1170.6 (vw), 1150.2 (vw), 1132.1 (vw), 1081.5 (vw), 1076.6 (vw), 1064.1 (vw), 990.5 (vw), 976.6 (vw), 904.6 (vw), 870.3 (vw), 821.9 (vw), 801.6 (vw), 772.5 (m), 767.0 (m), 753.1 (m), 731.3 (m), 690.7 (m), 645.9 (w), 594.9 (w), 575.9 (vw), 567.5 (vw), 536.5 (w), 518.2 (vw) cm^{-1}. − ^1H NMR: δ = 4.77 (s, 4 H), 7.29 (t, 1 H), 7.47 (d, 2 H). − ^{13}C NMR: δ = 42.2, 126.6, 131.6, 132.6, 137.4. − MS: *m*/*z* = 215/217 [M^+], 187/189, 152/154, 125, 116, 89, 77, 63, 51, 39. − $C_8H_7Cl_2N_3$ (216.1): calcd. C 44.4, H 3.2, N 19.4; found C 44.1, H 3.6, N 18.6.

1-Azido-2,6-bis(methoxymethyl)benzene (31): 1-Azido-2,6-bis(bromomethyl)benzene (1.5 g, 5 mmol) and NaOMe (0.8 g, 10.2 mmol) in dry methanol (30 mL) were stirred in the dark at ambient temperature for 72 h. The solvent was then evaporated and the residue was extracted with dichloromethane. The extract was concentrated and residual solvent removed in vacuo. − Yield 0.9 g (87%), yellow liquid. − IR (Ar, 10 K): $\tilde{\nu}$ = 3077.7 (vw), 3003.9 (w), 2932.3 (m), 2896.9 (m), 2832.6 (m), 2122.4 (vs), 2107.6 (vs), 1605.1 (w), 1459.4 (s), 1452.9 (s), 1440.2 (m), 1389.2 (m), 1375.9 (m), 1326.6 (s), 1312.6 (w), 1297.6 (m), 1274.8 (w), 1201.9 (vs), 1195.3 (m), 1129.6 (vs), 1111.7 (m), 1101.6 (s), 961.9 (w), 939.2 (w), 900.9 (vw), 781.9 (w), 758.5 (vw), 675.2 (w), 425.2 (w) cm^{-1}. − ^1H NMR: δ = 3.38 (s, 6 H), 4.52 (s, 4 H), 7.15 (t, 1 H), 7.31 (d, 2 H). − ^{13}C NMR: δ = 58.3, 71.1, 125.6, 129.5, 132.2, 136.6. − MS: *m*/*z* = 207 [M^+], 180, 164, 148, 134, 121, 104, 91, 77, 65, 51, 45, 39. − HRMS: found 207.100000; calcd. 207.100777.

1-Azido-2,6-bis(trideuteriomethoxymethyl)benzene ([D_6]-31): A suspension of NaH in mineral oil (55%, 0.54 g, 12.3 mmol) was added

to a solution of CD_3OH (0.5 mL, 12.3 mmol) in dry ether (20 mL). When the evolution of hydrogen had ceased, 1-azido-2,6-bis(bromomethyl)benzene (0.61 g) in dry acetonitrile (20 mL) was added. The solution was stirred in the dark at ambient temperature for 48 h; then water was added. The aq. phase was extracted twice with *tert*-butyl methyl ether, and the combined organic phases were then washed twice with water and dried with anhydrous sodium sulfate. The solvent was then removed and the residue purified by column chromatography [SiO_2; PE 60−80/EtOAc (8:2)]. The product eluted as the first fraction. Yield: 256 mg (60%), yellow liquid (room temp. > m.p. > 8 °C). − IR (Ar, 10 K): $\tilde{\nu}$ = 3077.5 (vw), 3046.8 (vw), 2924.0 (vw), 2869.6 (w), 2821.6 (vw), 2250.1 (w), 2197.7 (w), 2141.6 (s), 2120.7 (vs), 2105.4 (s), 2060.4 (m), 1602.9 (w), 1539.3 (w), 1491.0 (vw), 1452.7 (s), 1393.0 (w), 1386.6 (w), 1378.1 (m), 1236.3 (m), 1308.2 (w), 1295.9 (m), 1271.0 (w), 1169.9 (m), 1150.1 (vs), 1140.0 (m), 1131.0 (m), 1124.5 (s), 1096.6 (w), 1084.8 (w), 1058.1 (vw), 1004.8 (m), 968.4 (vw), 951.9 (w), 926.5 (vw), 901.4 (vw), 875.6 (vw), 860.1 (vw), 814.2 (vw), 780.0 (m), 754.3 (w), 676.2 (w), 670.9 (w), 610.0 (vw), 539.0 (vw), 523.1 (vw), 468.9 (vw) cm^{-1}. − ^1H NMR: δ = 4.52 (s, 4 H), 7.15 (t, 1 H), 7.31 (d, 2 H). − ^{13}C NMR: δ = 57.5 (m), 71.0, 125.6, 129.5, 132.2, 136.6. − MS: *m*/*z* (%) = 213 [M^+], 167, 151, 135, 121, 104, 77, 65, 48 (100).

1-Azido-2,3-dimethylbenzene: 2,3-Dimethylaniline (12.1 g, 0.1 mol) in HCl (6 N, 50 mL) was diazotized with a solution of sodium nitrite (7.0 g, 0.11 mol) in water (20 mL), such that the temperature of the solution containing the diazonium salt never exceeded 5 °C. After complete addition of the nitrite solution, the solution was stirred at 0 °C for another 30 min. A solution of sodium azide (6.6 g, 0.11 mol) in water (20 mL) was then added dropwise, keeping the temperature below 5 °C. The solution was then again stirred for 1 h, gradually warming up to ambient temperature. It was extracted twice with *tert*-butyl methyl ether. The organic extracts were combined, and washed with dilute NaOH (2 ×) and $NaHCO_3$ (2 ×). The extract was then dried with sodium sulfate, concentrated, and purified by column chromatography (SiO_2; PE 60−80). Yield 10.0 g (68%), yellow liquid. − IR (film): $\tilde{\nu}$ = 2928 (m), 2172 (m), 2114 (vs), 2038 (m), 1606 (m), 1579 (m), 1467 (s), 1385 (w), 1291 (s), 1207 (m), 1163 (w), 1094 (w), 1040 (w), 770 (s), 747 (m), 705 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 2.13 (s, 3 H), 2.26 (s, 3 H), 6.95 (m, 2 H), 7.12 (t, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 13.3, 20.1, 115.6, 126.2, 126.3, 128.2, 138.2, 138.5. − MS: *m*/*z* = 147 [M^+], 118, 104, 91, 77, 65, 51, 39. − HRMS: found 147.080100; calcd. 147.079647.

1-Azido-2,3-bis(bromomethyl)benzene: 1-Azido-2,3-dimethylbenzene (4.41 g, 30 mmol), NBS (11.78 g, 66 mmol), and AIBN (1.0 g) in dry benzene (100 mL) were refluxed for 18 h. After 15 h, another 200 mg of AIBN was added to the mixture. The mixture was then poured into water and diethyl ether, and the ether layer was dried with Na_2SO_4. The ether was then evaporated off and the residue purified by column chromatography (SiO_2; PE 60−80). The product solidified upon standing and could be recrystallized from pentane. Yield 6.7 g (74%), yellow crystals, m.p. 63 °C. − IR (KBr): $\tilde{\nu}$ = 3040 (w), 2957 (w), 2116 (vs), 1582 (s), 1466 (s), 1300 (s), 1220 (s), 1189 (m), 1167 (m), 952 (w), 848 (w), 826 (m), 798 (m), 757 (m), 743 (m), 624 (s) cm^{-1}. − ^1H NMR: δ = 4.58 (s, 2 H), 4.66 (s, 2 H), 7.13 (d, 2 H), 7.32 (t, 1 H). − ^{13}C NMR: δ = 23.5, 29.3, 118.9, 127.1, 127.9, 130.1, 138.7, 139.8. − MS: *m*/*z* = 303/305/307 [M^+], 275/277/279, 196/198, 169/171, 138, 116, 89, 63, 51, 39. − $C_8H_7Br_2N_3$ (305.0): calcd. C 31.5, H 2.3, N 13.8; found C 31.4, H 2.16, N 13.5.

4-Azidophthalan (45): This compound was prepared in analogy to the synthesis of phthalan from *o*-xylylene dibromide described by Kirmse and Kund.[39] Thus, 1-azido-2,3-bis(bromomethyl) benzene (610 mg, 2 mmol) was dissolved in 1,4-dioxane (1 mL) and a solution of NaOH in water (5 N, 10 mL) was added. The mixture was heated to 80 °C for 12 h. After cooling, the aqueous phase was repeatedly extracted with ether and the collected organic extracts were dried with Na_2SO_4. The solvent was then removed and the residue worked up by column chromatography (SiO_2; CH_2Cl_2). Light yellow solid, m.p. 54 °C. Yield 70 mg (22%). − IR (Ar, 10 K): $\tilde{\nu}$ = 3078.5 (vw), 3045.1 (vw), 2961.8 (w), 2930.3 (w), 2875.5 (m), 2859.4 (m), 2145.2 (m), 2129.6 (vs), 2116.1 (vs), 2096.7 (s), 1601.3 (m), 1477.8 (s), 1375.1 (w), 1324.0 (s), 1305.4 (s), 1300.8 (m), 1239.2 (vw), 1204.9 (vw), 1185.2 (vw), 1174.1 (vw), 1159.0 (vw), 1143.1 (vw), 1125.9 (vw), 1106.2 (vw), 1067.3 (m), 1062.6 (m), 961.5 (w), 907.6 (m), 845.4 (vw), 768.5 (m), 754.2 (vw), 732.3 (m), 698.6 (vw) cm^{-1}. − ^1H NMR: δ = 5.04 (s, 2 H), 5.08 (s, 2 H), 6.99 (d, 1 H), 7.00 (d, 1 H), 7.28 (t, 1 H). − ^{13}C NMR: δ = 71.9, 73.8, 108.4, 116.7, 117.2, 129.2, 134.3, 141.6. − MS: *m*/*z* = 161 [M^+], 133, 104, 78, 65, 51, 39. − HRMS: found 161.059600; calcd. 161.058912.

1-Azido-2-(bromomethyl)-6-methylbenzene (13): This compound was synthesized analogously to 1-azido-2-(bromomethyl)benzene,[37] using 1-azido-2,6-dimethylbenzene as starting material. Reflux time was 5 h, workup by column chromatography (SiO_2; PE 60−80). The product eluted as the 2nd fraction. Yield 8.5 g (76%) from 50 mmol of starting material. Yellow oil. − IR (Ar, 10 K): $\tilde{\nu}$ = 3077.0 (vw), 2995.3 (vw), 2968.2 (vw), 2931.3 (vw), 2136.2 (s), 2107.7 (vs), 1595.0 (w), 1479.1 (w), 1469.5 (s), 1450.7 (w), 1439.2 (m), 1384.3 (vw), 1335.5 (w), 1314.0 (w), 1300.7 (m), 1290.3 (m), 1267.7 (w), 1218.4 (w), 1169.5 (vw), 1133.6 (vw), 1081.5 (vw), 1071.5 (vw), 1037.2 (vw), 946.9 (w), 869.8 (vw), 824.6 (vw), 784.2 (w), 759.0 (m), 710.2 (vw), 629.8 (w), 606.5 (vw), 548.8 (vw), 538.6 (w), 497.0 (vw), 467.8 (vw) cm^{-1}. − ^1H NMR: δ = 2.43 (s, 3 H), 4.53 (s, 2 H), 7.06 (t, 1 H), 7.13 (d, 1 H), 7.20 (d, 1 H). − ^{13}C NMR: δ = 17.0, 29.7, 126.2, 128.8, 131.7, 132.1, 133.4, 137.1. − MS: *m*/*z* = 225/227 [M^+], 197/199, 146, 118, 102, 91, 77, 65, 51, 39. − $C_8H_8BrN_3$ (226.1): calcd. C 42.5, H 3.57, N 18.6; found C 42.7, H 3.7, N 18.6.

1-Azido-2-ethylbenzene (1): This compound was prepared as described by Sundberg et al.[40] − IR (Ar, 10 K): $\tilde{\nu}$ = 3083.1 (vw), 3033.4 (vw), 2979.9 (m), 2975.5 (m), 2942.0 (w), 2890.1 (w), 2132.2 (vs), 2108.4 (s), 2086.6 (m), 2062.4 (m), 1585.3 (m), 1492.7 (s), 1467.6 (w), 1455.8 (s), 1435.2 (vw), 1382.0 (vw), 1373.3 (vw), 1347.6 (w), 1321.3 (w), 1304.2 (m), 1297.9 (s), 1285.0 (s), 1275.0 (w), 1244.8 (vw), 1194.0 (vw), 1158.5 (w), 1108.1 (w), 1098.1 (w), 1055.7 (w), 1038.2 (vw), 980.5 (vw), 965.1 (vw), 932.8 (vw), 821.1 (vw), 786.4 (w), 776.2 (vw), 766.7 (w), 749.2 (vs), 698.9 (vw), 659.9 (w), 651.1 (w), 538.9 (w) cm^{-1}.

1-Azido-2-isopropylbenzene (4): This compound was prepared as described by Smolinsky.[41] − IR (Ar, 10 K): $\tilde{\nu}$ = 3082.9 (vw), 3032.8 (vw), 2980.5 (m), 2972.9 (m), 2937.5 (w), 2876.6 (w), 2127.6 (vs), 2099.8 (s), 2086.0 (s), 1584.7 (m), 1493.0 (s), 1467.3 (w), 1456.0 (m), 1447.1 (w), 1383.9 (vw), 1364.9 (vw), 1347.6 (vw), 1315.1 (w), 1295.9 (s), 1292.4 (s), 1285.1 (s), 1275.1 (w), 1158.7 (vw), 1143.7 (w), 1107.9 (vw), 1098.4 (vw), 1080.5 (w), 1069.1 (vw), 1039.9 (w), 935.5 (vw), 920.0 (vw), 815.3 (vw), 786.6 (vw), 751.6 (s), 657.0 (m), 582.1 (vw), 537.0 (w), 476.2 (vw) cm^{-1}.

For the synthesis of 2-(2-azidophenyl)-*N*,*N*-dimethylethylamine, 2-(2-azidophenyl)ethyl tosylate was required. Attempts to generate 2-(2-azidophenyl)ethanol from 2-(2-aminophenyl)ethanol by conventional diazotization, however, resulted in rearrangement of the phenylethanol moiety. For this reason, the alcohol functionality was protected by a TBDMS group, which was removed later in the synthesis.

1-(2-*tert*-Butyldimethylsilyloxy)ethyl-2-nitrobenzene: Pyridine (5 mL) was slowly added to an ice-cooled mixture of 2-(2-nitrophenyl)ethanol (3.0 g, 18 mmol) and *tert*-butylchlorodimethylsilane (2.71 g). The mixture was then hydrolyzed by adding some ice and poured into MeO*t*Bu. The aq. phase was extracted once with *t*BuOMe, and the combined organic layers were concentrated. The residue was distilled using a Kugelrohr apparatus. B.p. ca. 165 °C/0.03 Torr. Yield 4.28 g (84%), yellow oil. − IR (film): $\tilde{\nu}$ = 2958 (s), 2933 (s), 2861 (s), 1613 (w), 1580 (w), 1529 (vs), 1474 (m), 1440 (m), 1351 (s), 1257 (s), 1101 (s), 922 (w), 836 (s), 779 (s), 743 (m), 704 (m), 663 (m) cm^{-1}. − ^1H NMR: δ = −0.08 (s, 6 H), 0.80 (s, 9 H), 3.09 (t, 2 H), 3.87 (t, 2 H), 7.33 (t, 1 H), 7.37 (d, 1 H), 7.48 (t, 1 H), 7.86 (d, 1 H). − ^{13}C NMR: δ = −5.6, 18.2, 25.8, 36.3, 63.0, 124.5, 127.2, 132.4, 133.3, 134.2, 149.7. − MS: *m*/*z* (%) = 281 (< 1) [M^+], 266, 224 (100), 194, 179, 161, 147, 133, 120, 104, 89, 75, 57. − $C_{14}H_{23}NO_3Si$ (281.4): calcd. C 59.8, H 8.2, N 5.0; found C 59.5, H 7.9, N 5.3.

1-Amino-2-[2-(*tert*-butyldimethylsilyloxy)ethyl]benzene: 1-[2-(*tert*-Butyldimethylsilyloxy)ethyl]-2-nitrobenzene (4.28 g, 15.1 mmol) in methanol (50 mL) was reduced catalytically (1 atm H_2) in the presence of 10% Pd/C (50 mg). When 3 equiv. H_2 had been taken up, the solution was filtered and the solvent evaporated. Kugelrohr distillation yielded 3.0 g (79%) product, colorless liquid. − IR (film): $\tilde{\nu}$ = 3442 (m), 3361 (s), 3028 (w), 2933 (s), 2862 (s), 1626 (s), 1587 (m), 1501 (s), 1473 (s), 1462 (s), 1390 (w), 1363 (w), 1258 (s), 1094 (s), 1006 (w), 915 (m), 836 (s), 813 (m), 779 (m), 748 (m), 663 (w) cm^{-1}. − ^1H NMR: δ = −0.03 (s, 6 H), 0.85 (s, 9 H), 2.77 (t, 2 H), 3.85 (t, 2 H), 4.38 (s, br, 2 H), 6.74 (m, 2 H), 7.01 (m, 2 H). − ^{13}C NMR: δ = −5.6, 18.3, 25.9, 35.2, 64.5, 115.8, 118.7, 125.2, 127.3, 130.5, 144.5. − MS: *m*/*z* (%) = 251 [M^+], 194, 176, 118, 106, 75 (100), 69. − $C_{14}H_{25}NOSi$ (251.4): calcd. C 66.9, H 10.0, N 5.6; found C 66.6, H 10.0, N 6.0.

1-Azido-2-[2-(*tert*-butyldimethylsilyloxy)ethyl]benzene: 1-Amino-2-[2-(*tert*-butyldimethylsilyloxy)ethyl]benzene (3.0 g, 12 mmol) was dissolved in ethanol (50 mL). Conc. HCl (1.33 mL) was added, and the mixture was cooled in an ice bath. Isoamyl nitrite (2.15 mL, 16 mmol) was added dropwise at T < 5 °C. After diazotization, the mixture was stirred at T = 0 °C for another 30 min. A solution of NaN_3 (1.04 g, 16 mmol) in H_2O (25 mL) was then slowly added. When evolution of N_2 had ceased, the solution was allowed to warm up to ambient temperature, and 50 mL of *tert*-butyl methyl ether was added. The aq. phase was extracted once with *t*BuOMe, and the combined organic layers were washed twice with conc. $NaHCO_3$ and once with water and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue purified by column chromatography [SiO_2; PE 60−80/EtOAc (9:1)]. Yield 1.35 g (41%), yellow liquid. As a side product, 200 mg (10%) of 2-(2-azidophenyl)ethanol were isolated. − IR (film): $\tilde{\nu}$ = 3032 (vw), 2959 (s), 2933 (s), 2861 (s), 2125 (vs), 1585 (m), 1492 (s), 1474 (m), 1465 (m), 1454 (m), 1389 (w), 1362 (w), 1287 (s), 1257 (s), 1151 (w), 1107 (s), 1052 (w), 1006 (w), 939 (w), 916 (m), 869 (m), 835 (s), 776 (s), 751 (s), 652 (w) cm^{-1}. − ^1H NMR: δ = −0.02 (s, 6 H), 0.87 (s, 9 H), 2.81 (t, 2 H), 3.76 (t, 2 H), 7.06 (t, 1 H), 7.13 (d, 1 H), 7.19 (d, 1 H), 7.26 (t, 1 H). − ^{13}C NMR: δ = −5.5, 18.3, 25.9, 34.9, 63.0, 118.0, 124.5, 127.7, 130.5, 131.7, 138.2. − MS: *m*/*z* (%) = 249 (< 1) [$M^+ - N_2$], 234, 220, 192, 178, 162 (100), 147, 132, 117, 89, 75, 73, 57. − HRMS: found 277.157898; calcd. 277.157400.

2-(2-Azidophenyl)ethanol: 1-Azido-2-[2-(*tert*-butyldimethylsilyloxy)-ethyl]benzene (1.35 g, 4.9 mmol) was added to a 1 M solution of tetra-*n*-butylammonium fluoride in THF (10 mL). The mixture was stirred in the dark at ambient temperature for 12 h. The solvent was then evaporated and the residue worked up by column chromatography [SiO_2; PE 60−80/EtOAc (9:1)]. Quantitative yield, yellow solid, m.p. 43−46 °C. − IR (film): $\tilde{\nu}$ = 3357 (s, br), 2939 (w), 2124 (vs), 1584 (m), 1492 (s), 1453 (m), 1286 (s), 1150 (w), 1096 (w), 1049 (m), 751 (s) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.58 (s, 1 H), 2.93 (t, 2 H), 3.90 (t, 2 H), 7.24 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 34.7, 62.6, 118.2, 124.8, 128.0, 130.0, 131.3, 138.4. − MS: *m*/*z* = 163 [M^+], 134, 118, 106, 90, 77, 63, 51, 39. − $C_8H_9N_3O$ (163.2): calcd. C 58.9, H 5.52, N 25.8; found C 59.1, H 5.58, N 25.7.

2-(2-Azidophenyl)ethyl-*p*-toluenesulfonate: This compound was synthesized according to the procedure reported for the synthesis of 2-(2-nitrophenyl)ethyl-*p*-toluenesulfonate.[42] The compound could be recrystallized from PE 60−80 to yield colorless crystals, m.p. 53 °C. For use in further reactions, this procedure, however, should be avoided, as it significantly reduces the yield. − IR (KBr): $\tilde{\nu}$ = 2129 (vs), 1602 (m), 1588 (m), 1493 (s), 1453 (m), 1359 (s), 1283 (s), 1190 (s), 1177 (vs), 1152 (m), 1103 (m), 1063 (m), 1039 (w), 981 (s), 964 (s), 940 (w), 898 (s), 851 (w), 766 (s), 665 (s) cm^{-1}. − ^1H NMR: δ = 2.42 (s, 3 H), 2.88 (t, 2 H), 4.17 (t, 2 H), 7.0 (m, 2 H), 7.10 (d, 1 H), 7.2 (m, 3 H), 7.64 (d, 2 H). − ^{13}C NMR: δ = 21.6, 31.1, 69.1, 118.0, 124.8, 127.3, 127.8, 128.4, 129.7, 131.6, 138.1, 144.6. − MS: *m*/*z* (%) = 317 (3.5) [M^+], 289, 273, 261, 194, 155, 134, 117, 106, 91 (100), 77, 65, 51, 39. − $C_{15}H_{15}N_3O_3S$ (317.4): calcd. C 56.8, H 4.7, N 13.2, S 10.1; found C 56.8, H 4.8, N 13.2, S 10.2.

2-(2-Azidophenyl)-*N*,*N*-dimethylethylamine (59): 2-(2-Azidophenyl)-ethyl-*p*-toluenesulfonate (634 mg, 2 mmol) was dissolved in 10 mL of acetonitrile. A solution of dimethylamine in THF (2 M, 6 mL, 12 mmol) was added. The mixture was stirred in the dark at ambient temperature for 24 h. The solvent was then evaporated, and water and a solution of $NaHCO_3$ was added to liberate the free base of the product, which was then extracted with ether, and purified by column chromatography (SiO_2; *tert*-butyl methyl ether). Yield 210 mg (60%), yellow liquid. − IR (Ar, 10 K): $\tilde{\nu}$ = 3089.1 (vw), 3032.8 (vw), 2980.6 (m), 2948.9 (w), 2859.3 (w), 2820.6 (m), 2779.0 (w), 2123.5 (vs), 2077.1 (m), 1587.9 (m), 1494.2 (s), 1469.1 (m), 1462.8 (m), 1455.6 (m), 1444.0 (w), 1367.7 (w), 1308.6 (m), 1287.6 (s), 1267.8 (w), 1233.9 (vw), 1194.9 (vw), 1164.6 (m), 1154.8 (m), 1141.0 (w), 1097.3 (w), 1056.7 (m), 1040.9 (w), 1018.5 (w), 970.0 (vw), 936.2 (vw), 922.5 (vw), 904.5 (w), 875.7 (w), 850.0 (vw), 829.8 (vw), 779.3 (vw), 749.8 (s), 655.1 (m), 602.4 (vw), 535.6 (w) cm^{-1}. − ^1H NMR: δ = 2.35 (s, 6 H), 2.54 (t, 2 H), 2.78 (t, 2 H), 7.04 (dt, 1 H), 7.10 (d, 1 H), 7.18 (dd, 1 H), 7.23 (dt, 1 H). − ^{13}C NMR: δ = 29.2, 45.0, 59.7, 118.1, 124.8, 127.7, 130.8. − MS; EI: *m*/*z* = 58; FAB$^+$: *m*/*z* (%) = 191 [M^+ + 1], 176, 154, 136, 118, 107, 58 (100). − $C_{10}H_{14}N_4$ (190.2): calcd. C 63.2, H 7.4, N 29.5; found C 62.2, H 8.0, N 28.5.

8-Azido-2-methyl-1,2,3,4-tetrahydroisoquinoline (51): 5-Bromo-*N*-methyl-8-nitroisoquinolinium tosylate[38] (1.76 g, 4 mmol) in methanol (30 mL) was reduced catalytically (1 atm H_2) in the presence of 10% Pt/C (100 mg). After take-up of 6 equiv. (24 mmol) H_2, the solution was filtered, and the solvent was evaporated. The aniline derivative thus obtained was used in the next step without further purification. Thus, HCl (6 N, 1.6 mL) and water (3 mL) were added, and the solution was diazotized (T < 5 °C) using $NaNO_2$ (276 mg, 4 mmol) in water (2 mL). The solution of the diazonium salt was then stirred for furthe 30 min at 0 °C. A solution of NaN_3 (300 mg) in 3 mL of water was then added dropwise, and the mixture was allowed to warm gradually to ambient temperature. The solution was made alkaline with NaOH (400 mg, 10 mmol), and extracted three times with MeO*t*Bu. The combined organic layers were

washed with water, dried with Na_2SO_4, and concentrated to dryness. Column chromatography [SiO_2; *tert*-butyl methyl ether/PE 60−80 (1:1)] gave 390 mg of product (52%), as a yellow liquid. As a side product, **55** was obtained (see below). − **51**: IR (Ar, 10 K): $\tilde{\nu}$ = 2985.3 (vw), 2944.8 (w), 2923.6 (vw), 2847.5 (vw), 2807.6 (vw), 2782.7 (w), 2771.4 (vw), 2748.4 (vw), 2118.5 (vs), 1594.2 (m), 1481.3 (w), 1470.9 (m), 1464.1 (m), 1452.3 (vw), 1430.9 (vw), 1382.1 (w), 1349.0 (w), 1307.5 (m), 1291.6 (s), 1264.5 (vw), 1209.9 (w), 1163.1 (vw), 1134.9 (w), 1086.8 (vw), 1062.2 (vw), 1049.1 (w), 1003.2 (w), 970.4 (vw), 956.4 (vw), 887.6 (vw), 874.3 (vw), 840.7 (vw), 767.9 (m), 751.0 (w), 708.9 (w), 668.6 (w), 601.3 (vw) cm^{-1}. − ^1H NMR: δ = 2.47 (s, 3 H), 2.66 (t, 2 H), 2.90 (t, 2 H), 3.47 (s, 2 H), 6.88 (d, 1 H), 6.94 (d, 1 H), 7.15 (t, 1 H). − ^{13}C NMR: δ = 136.6, 135.8, 130.6, 126.9, 125.1, 115.1, 53.4, 52.1, 45.9, 29.1. − MS: *m*/*z* (%) = 188, 159, 144, 132, 117, 90, 57, 42 (100). − HRMS: found 188.106900; calcd. 188.106197.

8-Azido-5-bromo-2-methyl-1,2,3,4-tetrahydroisoquinoline (55): This compound was obtained as a side product in the synthesis of **51**. Yield ca. 10%, brown crystals, m.p. 55 °C. − IR (Ar, 10 K): $\tilde{\nu}$ = 2990.3 (vw), 2951.8 (w), 2849.4 (w), 2807.5 (vw), 2783.6 (w), 2742.4 (vw), 2121.5 (vs), 2052.9 (w), 1594.7 (w), 1579.2 (w), 1471.0 (m), 1458.8 (s), 1446.8 (w), 1437.1 (vw), 1423.3 (vw), 1383.1 (w), 1361.7 (vw), 1344.3 (m), 1310.4 (w), 1300.4 (m), 1296.3 (s), 1281.8 (m), 1264.2 (vw), 1216.5 (vw), 1207.7 (w), 1178.4 (w), 1148.2 (vw), 1131.2 (w), 1125.2 (w), 1091.6 (vw), 1070.2 (w), 1050.3 (w), 1004.5 (m), 990.6 (vw), 970.1 (w), 951.1 (vw), 894.4 (vw), 867.8 (w), 800.0 (m), 760.7 (w), 715.2 (vw), 670.7 (vw), 616.0 (vw), 569.2 (vw), 5388 (vw), 511.9 (vw) cm^{-1}. − ^1H NMR: δ = 2.45 (s, 3 H), 2.65 (t, 2 H), 2.83 (t, 2 H), 3.42 (s, 2 H), 6.84 (d, 1 H), 7.40 (d, 1 H). − ^{13}C NMR: δ = 30.6, 45.7, 52.2, 53.7, 116.5, 120.5, 128.7, 130.6, 135.7, 135.9. − MS: *m*/*z* (%) = 266/268 [M^+], 237/239, 224, 210, 159, 144, 131, 116, 102, 89, 63, 51, 42 (100). − $C_{10}H_{11}BrN_4$ (267.1): calcd. C 44.9, H 4.11, N 21.0; found C 44.9, H 4.3, N 20.6.

3-Methylindoline (7): This compound was prepared according to a published procedure.[28] − IR (Ar, 10 K): $\tilde{\nu}$ = 3430.9 (w), 3412.7 (vw), 3087.3 (vw), 3063.4 (w), 3037.8 (w), 2969.3 (s), 2936.1 (m), 2877.9 (m), 2847.4 (m), 1615.4 (vs), 1490.8 (vs), 1466.7 (vs), 1455.7 (s), 1407.1 (w), 1378.0 (w), 1347.5 (w), 1324.3 (m), 1308.4 (w), 1243.4 (s), 1198.7 (vw), 1165.6 (vw), 1154.1 (w), 1111.0 (w), 1097.5 (vw), 1090.5 (vw), 1042.7 (w), 1019.0 (m), 989.4 (vw), 919.2 (vw), 889.7 (vw), 858.5 (vw), 744.4 (vs), 730.1 (w), 685.8 (w), 607.4 (vw), 588.2 (vw), 564.0 (vw), 547.0 (m), 542.5 (m), 509.8 (s) cm^{-1}.

Supporting Information: Experimental vibrational frequencies and comparisons with calculated vibrational frequencies for the iminoquinone methides, some nitrenes, and other reactive intermediates characterized in this study (Tables S1−S18; see also the footnote on the first page of this article).

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[1] M. S. Platz, *Acc. Chem. Res.* **1995**, *28*, 487−492.
[2] A. Marcinek, M. S. Platz, *J. Phys. Chem.* **1993**, *97*, 12674−12677.
[3] G. B. Schuster, M. S. Platz, "Photochemistry of Phenyl Azide", in: *Advances in Photochemistry* (Eds.: D. H. Volman, G. Hammond, D. C. Neckers), John Wiley & Sons, Inc., **1992**, vol. 17, p. 69−143.
[4] E. Leyva, M. S. Platz, G. Persy, J. Wirz, *J. Am. Chem. Soc.* **1986**, *108*, 3783−3790.
[5] T. Kobayashi, H. Ohtani, K. Suzuki, T. Yamaoka, *J. Phys. Chem.* **1985**, *89*, 776−779.
[6] T-Y. Liang, G. B. Schuster, *J. Am. Chem. Soc.* **1987**, *109*, 7803−7810.
[7] Y-Z. Li, J. P. Kirby, M. W. George, M. Poliakoff, G. B. Schuster, *J. Am. Chem. Soc.* **1988**, *110*, 8092−8098.
[8] C. J. Shields, D. R. Chrisope, G. B. Schuster, A. J. Dixon, M. Poliakoff, J. J. Turner, *J. Am. Chem. Soc.* **1987**, *109*, 4723−4726.
[9] N. P. Gritsan, T. Yuzawa, M. S. Platz, *J. Am. Chem. Soc.* **1997**, *119*, 5059−5060.
[10] R. Born, C. Burda, P. Senn, J. Wirz, *J. Am. Chem. Soc.* **1997**, *119*, 5061−5062.
[11] N. P. Gritsan, Z. Zhu, C. M. Hadad, M. S. Platz, *J. Am. Chem. Soc.* **1999**, *121*, 1202−1207.
[12] N. P. Gritsan, D. Tigelaar, M. S. Platz, *J. Phys. Chem. A* **1999**, *103*, 4465−4469.
[13] W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* **1997**, *119*, 1378−1387.
[14] W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* **1997**, *119*, 3347−3350.
[15] C. R. Kemnitz, W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* **1998**, *120*, 3499−3503.
[16] I. R. Dunkin, A. El Ayeb, M. A. Lynch, *Chem. Commun.* **1994**, 1695−1696.
[17] B. A. DeGraff, D. W. Gillespie, R. J. Sundberg, *J. Am. Chem. Soc.* **1974**, *96*, 7491−7496.
[18] Y. Ito, E. Nakajo, T. Saegusa, *Synth. Commun.* **1986**, *16*, 1073−1080.
[19] H. Steinhagen, E. J. Corey, *Angew. Chem.* **1999**, *111*, 2054−2056; *Angew. Chem. Int. Ed.* **1999**, *38*, 1928−1931.
[20] K. Wojciechowski, *Tetrahedron* **1993**, *49*, 7277−7286.
[21] E. M. Burgess, L. McCullagh, *J. Am. Chem. Soc.* **1966**, *88*, 1580−1581.
[22] M. Lancaster, D. J. H. Smith, *Chem. Commun.* **1980**, 471−472.
[23] W. Sander, J. Morawietz, *Tetrahedron Lett.* **1993**, *34*, 1913−1916.
[24] J. Morawietz, W. Sander, M. Träubel, *J. Org. Chem.* **1995**, *60*, 6368−6378.
[25] J. Morawietz, W. Sander, *Liebigs Ann.* **1996**, 2029−2037.
[26] G. W. Dombrowski, J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, *J. Org. Chem.* **1999**, *64*, 427−431.
[27] J. C. Hayes, R. S. Sheridan, *J. Am. Chem. Soc.* **1990**, *112*, 5879−5881.
[28] D. E. Ames, H. R. Ansari, A. D. G. France, A. C. Lovesey, B. Novitt, R. Simpson, *J. Chem. Soc. C* **1971**, 3088−3097.
[29] 3-Methylindoline is also formed upon thermolysis of **4** in solution (ref.[41]).
[30] A. Albini, G. Bettinetti, G. Minoli, *J. Am. Chem. Soc.* **1997**, *119*, 7308−7315.
[31] The infrared spectra calculated for the two isomers are very similar and do not allow definite identification of the isomer being formed.
[32] In the course of this study, the presence of a set of three bands of medium to strong intensity at $\tilde{\nu}$ = 1650, 1600, and 1530 cm^{-1} has been found to serve as a "landmark" for formation of iminoquinone methides.
[33] J. Morawietz, W. Sander, *J. Org. Chem.* **1996**, *61*, 4351−4354.
[34] M. J. Travers, D. C. Cowles, E. P. Clifford, G. B. Ellison, *J. Am. Chem. Soc.* **1992**, *114*, 8699−8701.
[35] R. N. McDonald, S. J. Davidson, *J. Am. Chem. Soc.* **1993**, *115*, 10857−10862.
[36] W. W. Sander, *J. Org. Chem.* **1989**, *54*, 333−339.

[37] R. Mornet, N. J. Leonard, J. B. Theiler, M. Doree, *J. Chem. Soc., Perkin Trans. 1* **1984**, 879−886.
[38] M. Rey, T. Vegnani, A. S. Dreiding, *Helv. Chim. Acta* **1985**, *68*, 1828−1834.
[39] W. Kirmse, K. Kund, *J. Org. Chem.* **1990**, *55*, 2325−2332.
[40] R. J. Sundberg, S. R. Suter, M. Brenner, *J. Am. Chem. Soc.* **1972**, *94*, 513−520.
[41] G. Smolinsky, *J. Am. Chem. Soc.* **1961**, *83*, 2489−2493.
[42] U. Siemeling, T. Türk, U. Hammermeister, *Monatsh. Chem.* **1995**, *126*, 725−732.

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