Registry No. **3a**, 95667-41-7; **3b**, 81827-59-0; **3c**, 95667-43-9; **3d**, 96150-02-6; **3e**, 92817-04-4; **3f**, 122948-47-4; **3h**, 696-62-8; **3i**, 99-90-1; **3j**, 619-44-3; **3k**, 622-50-4; **3l**, 591-50-4; **4**, 6089-09-4; **5** (R_2 = Me), 136041-11-7; **5** (R_2 = $(CH_2)_2COEt$), 136041-10-6; **5** (R_2 = CH_2cyclohexane), 136041-09-3; **5** (R_2 = $CH_2C_4H_3O$), 136041-07-1; **5** (R_2 = CH_2CH:CHPh), 137742-20-2; **6a**, 137742-21-3; **6b**, 137742-22-4; **6c**, 137768-00-4; **6d**, 137742-23-5; **6e**, 137742-24-6; **6f**, 137742-25-7; **6g**, 137742-26-8; **6h**, 137742-27-9; **6i**, 137742-28-0; **6j**, 137742-29-1; **6k**, 137742-30-4; **6l**, 69063-22-5; **7a** (isomer 1), 137742-31-5; **7a** (isomer 2), 137820-53-2; **7b** (isomer 1), 137742-32-6; **7b** (isomer 2), 137820-54-3; **7d** (isomer 1), 137742-33-7; **7d** (isomer 2), 137820-55-4; **7f** (isomer 1), 137742-34-8; **7f** (isomer 2), 137742-35-9; **7g** (isomer 1), 137742-36-0; **7g** (isomer 2), 137742-37-1; **7h** (isomer 1), 137742-38-2; **7h** (isomer 2), 137742-39-3; **7i** (isomer 1), 137742-40-6; **7i** (isomer 2), 137742-41-7; **7j** (isomer 1), 137742-42-8; **7j** (isomer 2), 137742-43-9; **8a**, 137742-44-0; **8b**, 135129-15-6; **9a**, 137742-45-1; **9b**, 137742-46-2; **15**, 126378-11-8; **16**, 137742-47-3; **20**, 137742-48-4; **21**, 137742-49-5; $Pd(OAc)_2(PPh_3)_2$, 14588-08-0; $Pd(PPh_3)_4$, 14221-01-3; n-Bu_4NCl, 1112-67-0; PhI, 591-50-4; p-$MeOC_6H_4I$, 696-62-8; 4-phenylcyclohexanone, 4894-75-1; trifluoromethanesulfonic anhydride, 358-23-6.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **6d**, **9a**, and **16** (6 pages). Ordering information is given on any current masthead page.

Trapping of Cyclopentanediyl and Trimethylenemethane Triplet Diradicals with the Nitroxide 1,1,3,3-Tetramethyl-1,3-dihydroisoindolin-2-yloxyl

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Nitroxide trapping constitutes a convenient and effective alternative to dioxygen for the detection of triplet diradical intermediates. Thus, photolysis of the azoalkanes **1a–c** in the presence of the nitroxide 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl produced the bisalkoxyamines **3a–c** by trapping of the transient triplet diradicals **5a–c**. The resulting bis-adducts **3a–c** were fully characterized, and their regio- and stereochemistry were established on the basis of spectral and X-ray data for *trans*-**3a** and *trans*-**3b**. The novel bis-azoalkane **1d** was prepared and its photochemical loss of nitrogen studied in the presence of the above nitroxide or dioxygen as scavengers. In the case of the nitroxide, the tetrakis-adduct **3d** was obtained, tentatively assigned in view of its thermal instability, while with dioxygen the stable bis-peroxide **4d** was isolated and rigorously characterized. Instead of concurrent double denitrogenation to afford the high-spin non-Kekule species **5d** or its low-spin quinoid diradical **5d′**, stepwise loss of dinitrogen and trapping is proposed to be the pathway to these products.

The importance of diradicals in chemical reactions is reflected in the large number of recent studies on these short-lived intermediates, especially in photochemical transformations.[1] While most investigations of reactive diyl intermediates have utilized time-resolved laser flash techniques[2] and oxygen trapping, the latter technique has proven particularly useful both for lifetime determinations[3] and even for some synthetic purpose.[4] Oxygen trapping of diradicals has the advantage that no chromophores are needed and also that subtle features such as conformational effects on the ISC process[5] may be investigated. However, there exist some limitations with this trapping method in that the paramagnetic dioxygen molecule may enhance triplet to singlet ISC and that the peroxide trapping products are often unstable. Nonetheless, to date the use of other intermolecular trapping agents is quite limited, e.g. SO_2[6] and alkenes[7] have been employed to scavenge transient diradical species, which have been generated by laser flash photolysis (LFP).

Besides the well-established trapping by dioxygen, nitroxide radicals represent potentially useful scavenging agents for detecting diradicals. It is known that nitroxides bind to carbon-centered radicals at close to diffusion-controlled rates[8] and that the resultant alkoxyamine adducts can be readily isolated and characterized.[9] The nitroxide 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl appears to be ideal for this purpose as it contains a UV chromophore, which facilitates detection and structural elucidation of the resulting alkoxyamines. Despite these apparent advantages, the use of nitroxides has received much less attention in the detection of triplet diradicals, presumably due to enhanced ISC,[10] which has been claimed responsible for the lack of incorporation of nitroxides in the final diradical product. For photomechanistic purposes, nitroxides have been employed in LFP quenching studies of triplet diradicals.[10,11]

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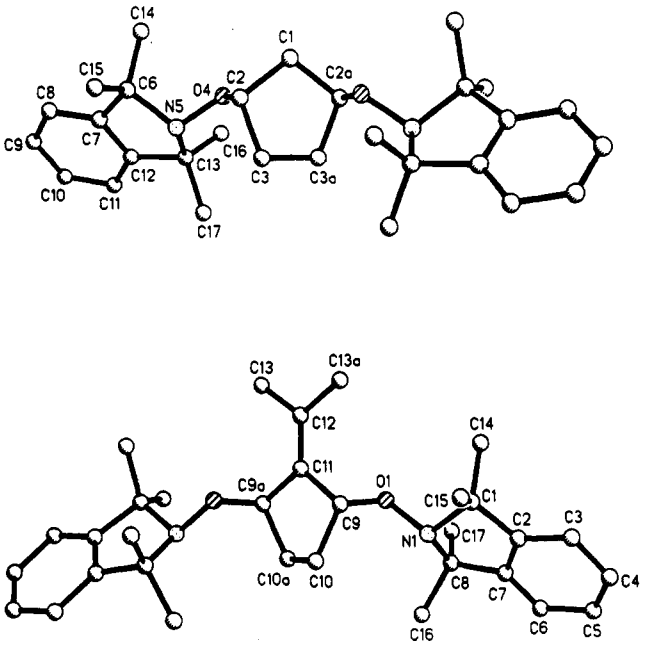


Figure 1. X-ray structure of *trans*-**3a** and *trans*-**3b**.

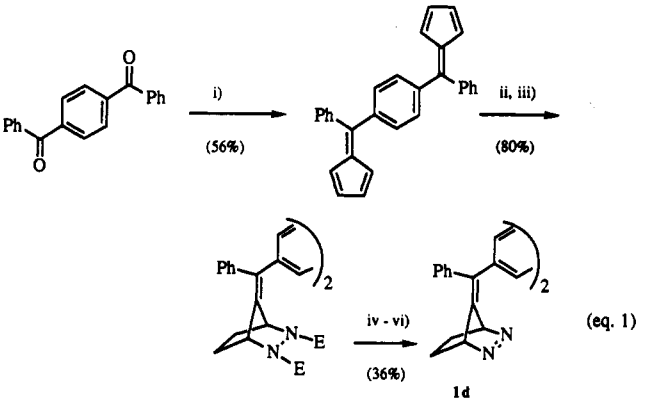
Here we present the full details[12] of the nitroxide trapping of the cyclopentanediyl and trimethylenemethane triplet diradicals derived from the azoalkanes **1a–c** and also of the novel bis-azoalkane **1d**. The extent of trapping by the nitroxide was high, as evidenced in the good yields of isolated adducts that were observed. The bis-azoalkane **1d** was prepared in an attempt to explore potential two-photon versus one-photon effects on its denitrogenation.[13] Simultaneous double denitrogenation would afford the high-spin double non-Kekule species **5d** or its low-spin quinoid diradical **5d'**. Trapping by nitroxide should be advantageous compared to molecular oxygen because in its quinoid diradical form **5d'** the two radical sites are too far apart to be bridged by a peroxide linkage.

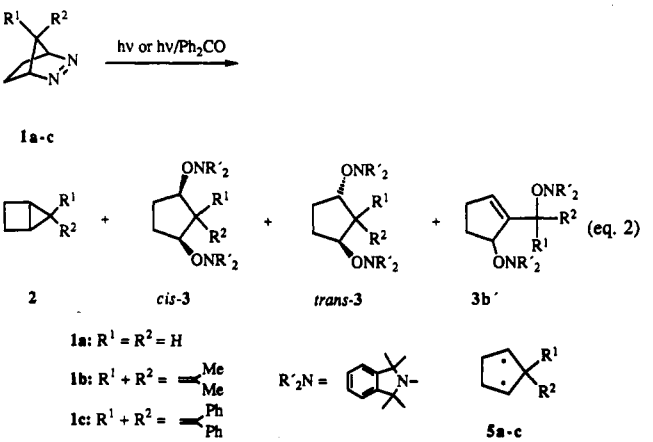
5d **5d'**

Results

Synthesis of the Azoalkanes 1. The azoalkanes **1a–c** were prepared according to literature procedures.[14] The bis-azoalkane **1d** was obtained from the bis-fulvene by a double Diels–Alder addition of diethyl azodicarboxylate (eq 1). The stereochemistry of the unsaturated bis-carbamate could not be assessed from the ^1H and ^{13}C data, and good-quality crystals for X-ray analysis could not be obtained. Catalytic hydrogenation of the unsaturated bis-carbamate led to the saturated bis-carbamate, which by subsequent hydrolysis and oxidation afforded the bis-azoalkane **1d** in a 15% overall yield. The azoalkane **1d** is labile and decomposes at temperatures above 20 °C.

Trapping of the Diradicals by Nitroxide and Dioxygen. The nitroxide trapping products of the azoalkanes **1a–c** are given in eq 2. For example the azoalkane





1a, when photolyzed ($300 < \lambda < 350$ nm) in a Rayonet photoreactor under benzophenone sensitization in the presence of the nitroxide, afforded the bisalkoxyamine adducts *cis*- and *trans*-**3a** in 21% and 39% yields in a mass balance of >90% for 60% conversion. In addition to the stereoisomeric adduct **3a**, the housane **2a** (40%) was also produced. This experiment was conducted in *n*-heptane rather than the usually employed acetonitrile in order to separate the azoalkane from the solvent to permit GC analysis. The nitroxide concentration in nearly saturated *n*-heptane was only 0.035 M, but more concentrated solutions (ca. 0.076 M) may be attained in the more polar acetonitrile, and thereby the amount of trapping product **3** increased. The proton coupling patterns for the two stereoisomeric **3a** are characteristic and closely correspond to the known ^1H NMR spectra for similar 1,3-disubstituted cyclopentanes.[15] As an unequivocable proof, an X-ray crystallographic analysis on the bis-nitroxide adduct *trans*-**3a** (Figure 1) confirmed the proposed structure.

When the azoalkane **1b** was directly irradiated ($300 < \lambda < 350$ nm) in a Rayonet photoreactor in the presence of the nitroxide, the two adducts *trans*-**3b** and **3b'** were obtained in a mass balance of 88% for >95% conversion. By preparative HPLC either on reversed-phase or SiO_2 columns the two regioisomeric adducts could not be separated, but they could be resolved by analytical reversed-phase HPLC. By means of HPLC and ^1H NMR analysis the regioisomeric adducts *trans*-**3b** and **3b'** were shown to be formed in a ratio of 34:66. The adduct mixture gave a satisfactory elemental analysis, which confirms the isomeric nature of these products. Slow crystallization of

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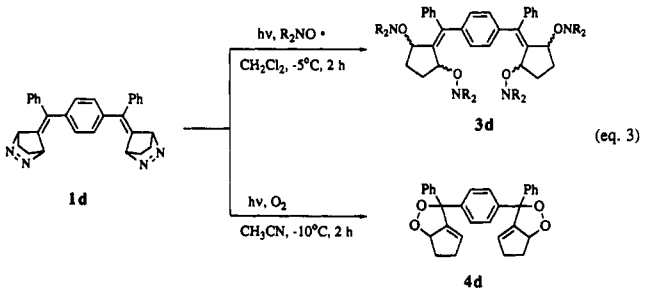
the mixture from 1:14 acetone/petroleum ether gave a few suitable crystals for X-ray analysis, which established the *trans*-**3b** structure (Figure 1). Of key importance for the determination of the product distribution and the spectral assignment were the characteristic proton resonances at δ 5.15 and 5.93 for the vinylic system of **3b'** as compared to the signal at δ 4.90 for the α-hydrogen of the alkoxyamine moiety (*trans*-**3b**).

The azoalkane **1c** gave on direct photolysis at $300 < \lambda < 350$ nm (Rayonet photochemical reactor) in the presence of the nitroxide and subsequent isolation by reversed-phase HPLC the two adducts *trans*- and *cis*-**3c** in 90% and 10% yields in a mass balance of 93% for >95% conversion. Once isolated, the compounds are quite stable in the solid state; however, in solution at room temperature the adducts decomposed into complex colored mixtures. These features made it difficult to obtain satisfactory crystals for X-ray analysis. Nonetheless, by comparison of the spectra of these adducts with those of *cis*-**3b** and by means of low-temperature 400-MHz decoupling experiments, the structures of the *cis*- and *trans*-**3c** products could be convincingly assigned.

A mixture of the bis-azoalkane **1d** and the nitroxide gave on irradiation by the UV lines (333, 352, and 364 nm) of a CW argon ion laser a complex mixture of four adducts **3d**, isolated by column chromatography, which could not be separated by reversed-phase HPLC. These adducts were shown to contain four nitroxide units from the integration of the alkoxyamine aromatic signals against the cyclopentane ring CH protons which bear the alkoxyamine groups. Unfortunately, the tetrakis-adduct **3d** was too labile to permit chromatographic separation and rigorous spectral characterization. There were no spectral hints for bis-adducts with a quinoid structure in the crude product mixture.

Photolysis under oxygen gas pressure (5 bar) produced the novel bis-endoperoxide **4d**, which was readily isolated in 70% yield by column chromatography and was fully characterized (eq 3). On monitoring the photolysis of



(eq. 3)

reaction by means of TLC, a transient product was detected, which displayed positive azo[16a] and peroxide tests;[16b] however, attempted isolation of this labile compound by column chromatography afforded only the bis-peroxide **4d**.

Control Experiments. A mixture of azoalkane **1a** and nitroxide gave, after standing for 4 days at room temperature and under protection from light, no adduct **3a**, as determined by TLC and reversed-phase HPLC. In another experiment, the azoalkane **1a** was converted to the housane **2a** on prolonged irradiation in a Rayonet photoreactor (64 h) or by a CW argon ion laser (4 h), nitroxide was added and the photolysis continued, but no adduct **3a** could be detected by TLC and reversed-phase HPLC. When the azoalkane **1a** was photolyzed in the presence of the nitroxide but in the absence of the triplet sensitizer benzophenone, the adduct **3a** was produced only to the extent of <20% of the amount observed in the triplet-sensitized reaction.

The photoreluctant azoalkane 2,3-diazabicyclo[2.2.2]-oct-2-ene (Φ [$-N_2$] = 0.01)[17] and the nitroxide were photolyzed at $300 < \lambda < 350$ nm in a Rayonet photochemical reactor for 16 h, but no adducts were detected by reversed-phase HPLC. This result indicates that under the photolysis conditions of the trapping experiment the nitroxide does not attack the azo linkage of this photoreluctant azoalkane.

Photolysis of the azoalkane **1b** in $CFCl_3$ at −78 °C produced the housane **2b**, as confirmed by low-temperature ^{1}H NMR.[18] When the nitroxide was added to this photolysate and the reaction mixture allowed to warm up to room temperature, the same adducts *trans*-**3b** and **3b'** as in the direct photolysis of **1b** were produced exclusively; no dimers of the intervening diradicals were detected. In fact, no dimer products[1e] of the non-Kekule diradicals investigated were observed even when only a stoichiometric amount of the nitroxide was employed.

Discussion

The nitroxide scavenging technique represents a powerful and convenient method of detecting triplet diradicals **5**. The adducts are generally easily separated and can be characterized by NMR and quantified by HPLC.

Control experiments on azoalkane **1a** confirm that the nitroxide does indeed scavenge the triplet diyl species **5a**. Firstly, it was ascertained that the nitroxide and the bicyclo[2.1.0]pentane (**2a**), the denitrogenation product of azoalkane **1a**, do not react since no adducts were formed when **2a** was treated with the nitroxide under the reaction conditions. Secondly, the azoalkane does not react with the nitroxide in the absence of light. Finally, no adducts were formed when the photoreluctant azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene was irradiated in the presence of benzophenone and the nitroxide, which indicates that the nitroxide does not induce cleavage of the C–N bond in these azoalkanes to produce the trapping-type adducts **3**. Therefore, we conclude on the basis of these results that the nitrogen-free triplet diyl **5a** is being trapped by the nitroxide.

In this context it is relevant to rationalize the appreciable amount (ca. 20% of that observed on triplet sensitization) of trapping product **3a** formed in the direct photolysis of the azoalkane **1a**. Also in this direct photolysis experiment the nitroxide must be trapped by the triplet diradical **5a**, because the corresponding singlet diradical is much too short-lived for diffusion-controlled trapping to compete. For example, since the resonance-stabilized 1,3-diphenyl-1,3-cyclopentanediyl possesses a singlet lifetime of only ca. 22 ps,[19] the parent singlet 1,3-diyl **5a** should be at least 1 order of magnitude shorter lived (the relative triplet lifetimes of ca. 20 μs for 1,3-diphenyl-1,3-cyclopantanediyl versus ca. 100 ns for **5a** may serve as a guide for comparison). Thus, bimolecular trapping by nitroxide, which at best can operate at diffusion-controlled rates, cannot compete with unimolecular cyclization of the singlet 1,3-diyl **5a** into the housane product **2a**. This implies that in the direct photolysis

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experiment of azoalkane **1a** singlet to triplet ISC must be fast enough for the diradical **5a** to compete effectively with cyclization and produce appreciable amounts of its triplet state, which then is subsequently scavenged by the nitroxide.

Indeed, when the direct photolysis was performed under O_2 pressure, the azoalkane **1a** afforded detectable quantities of endoperoxide (positive peroxide test[16b]). Again, this result implies that on direct photodenitrogenation of **1a** a scavengeable quantity of triplet **5a** is generated by singlet to triplet ISC. Whether such ISC is an inherent phenomenon of the 1,3-diyl **5a** or is catalyzed by the paramagnetic trapping agents $^3O_2$ and $R_2NO^\bullet$ cannot be answered with certainty. However, it has recently been reported[20] that the direct photolysis of **1a** in the gas phase generates the triplet diradical **5a**, as detected by time-resolved CARS studies. Moreover, direct photolysis of azoalkane **1a** under matrix isolation (5.5 K) enables measurement of the ESR spectrum of the triplet 1,3-diyl **5a**.[21] Since in these two experiments spin catalysis by paramagnetic agents and collisional activation are at best minimal, inherent singlet to triplet ISC for **5a** is feasible for the direct photolysis in solution.

Of mechanistic interest from the point of view of diradical dimerizations were azoalkanes **1b,c**, the precursors to the corresponding triplet non-Kekule species **5b,c** produced on direct photolysis. For example, it is known[18] that the thermally labile isopropylidenebicyclo[2.1.0]pentane (**2b**) reacts on warming (>53 °C) to afford denitrogenated dimers through coupling of triplet diradicals **5b** as intermediates. When housane **2b** was generated independently by photodenitrogenation of the corresponding azoalkane **1b** at low temperature (−78 °C), addition of nitroxide and warming to room temperature produced the same adducts *trans*-**3b**/**3b'** as were observed in the direct photodenitrogenation of the azoalkane **1b** in the presence of nitroxide. Mechanistically more significant, no dimers of the triplet diradical **5b** were detected in both experiments. Consequently, the scavengeable intermediate is the relatively long-lived triplet non-Kekule species **5b**, obtained after nitrogen loss from azoalkane **1b**. For reasonable rates of dimer formation to be observed at diffusion control, at least a micromolar stationary state concentration of such triplet trimethylenemethane diradicals **5b** must build up. However, at the much higher concentration of the nitroxide scavenger (ca. 0.076 M), dimer formation is completely suppressed and nitroxide adducts **3b** exclusively produced. Of course, we suppose that the rate constants for dimerization and for nitroxide trapping of the triplet diyls **5b** are nearly the same, a reasonable assumption since diffusion-controlled kinetics should apply. Similar arguments pertain to the diphenyl-substituted trimethylenemethane species **5c**, accessible from azoalkane **1c** and its housane **2c**.

In regard to the nitroxide trapping experiments with the bis-azoalkane **1d**, which on double denitrogenation may furnish the high-spin double non-Kekule species **5d** or its low-spin quinoid diradical **5d'**, our results are unfortunately inconclusive. In view of the thermal instability of the nitroxide trapping product, presumably the tetrakis-adduct **3d** on the basis of ^1H NMR (400 MHz), rigorous characterization was not possible. However, dioxygen trapping experiments suggest that successive denitrogenation of the bis-azoalkane **1d** takes place. Although the final trapping product was the bis-endoperoxide **4d** (identical in structure to the mono-endoperoxide **4b** obtained by dioxygen trapping of the non-Kekule species **5b** derived from azoalkane **1b**,[22] i.e. fused-ring rather than bridged-ring bicyclization), an intermediary product was detected besides the bis-endoperoxide **4d** by TLC monitoring of the photodenitrogenation in the presence of $^3O_2$. This product displayed positive peroxide and azo tests, but to our regret, it was too labile for isolation and insufficient amounts accumulated for spectral characterization. Single denitrogenation and subsequent scavenging by dioxygen, followed by repetition of these events to produce finally the stable bis-endoperoxide **4d**, seem to operate. It is, therefore, unlikely that the high-spin double non-Kekule species **5d** or its quinoid diradical **5d'** intervened, and concurrent double loss of N_2 from the bis-azoalkane **1d** under our conditions is an improbable event.

Similar arguments apply to the nitroxide trapping results of the bis-azoalkane **1d** to afford the tetrakis-adduct **3d**. We postulate that successive photo-denitrogenation and nitroxide trapping leads to **3d**, with the bis-adduct/mono-azoalkane as intermediate product. Of course, for the nitroxide as scavenger the possibility must be entertained that a bis-adduct of the low-spin quinoid diradical **5d'** may have been formed, which on thermal activation[23] populates a new diradical state and further trapping by nitroxide generates the tetrakis-adduct **3d**; however, this possibility is improbable in view of the above discussion for dioxygen.

Despite the fact that the structure of the nitroxide tetrakis-adduct **3d** could not be rigorously established in view of its thermal lability, the bis-adducts **3a–c** were sufficiently persistent to permit unequivocal elucidation on the basis of the spectral and X-ray data (Figure 1). Several stereo- and regiochemical features are of interest in regard to the mechanism of trapping, which merit brief discussion. Thus, the trans isomer of the bis-adduct **3** prevails in all cases, i.e. the trans/cis ratios are ca. 60:40 (**3a**), 100:0 (**3b**), and 90:10 (**3c**). Steric effects must be responsible, in that once one bulky nitroxide unit has become attached at the planar triplet diradical intermediate, the second one enters more readily from the opposite side to afford preferentially the trans diastereomer. This steric control is more pronounced for the rigid non-Kekule species, since for the mono-adduct of the 1,3-diyl **5a** conformational equilibration may place the alkoxyamine moiety into the less obstructing equatorial position, so that appreciable amounts of cis bis-adduct result.

Steric effects are also presumably responsible for why exclusively endocyclic trapping of **5c** by the nitroxide to give the regioisomer **3c** has taken place, while for **5b** exocyclic trapping to afford the regioisomer **3b'** dominates (**3b'**/**3b** ratio ca. 66:34). Molecular models reveal that the bulky exocyclic benzhydryl group in diradical **5c** encumbers sufficient close approach of the large nitroxide scavenger for effective bonding at the exocyclic site, so that endocyclic trapping is preferred. Nevertheless, the exocyclic isopropyl substituent in diradical **5b** is sterically much less obstructing, and trapping at the exocyclic site dominates.

In summary, we have herein demonstrated that stable nitroxides serve as convenient and efficient scavengers for triplet diradicals of the 1,3-cyclopentanediyl and trimethylenemethane type. The bisalkoxyamine trapping products are sufficiently stable for isolation, purification, and rigorous characterization by spectral and X-ray analysis. In view of the bulky nitroxide scavenger used

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in the present study, appreciable steric effects are exhibited in the trapping process, as revealed by the observed regio- and stereochemistry of the bis-adducts. Nonetheless, the scavenging must take place at nearly diffusion-controlled rates because for the non-Kekule triplet species **5b,c**, dimer formation is completely suppressed. Triplet to singlet ISC catalyzed by the nitroxide appears to be ineffective for the planar triplet diradicals investigated herein.

Experimental Section

General Aspects. Melting points were measured in glass capillaries on a Büchi 535 melting point apparatus. GC determinations were done on a 60-m OV-1 capillary column at an injection temperature of 150 °C and a detector temperature of 200 °C with N_2 as the carrier gas by employing a Carlo Erba 4100 gas chromatograph fitted with a flame ionization detector. For quantitative GC analyses isoprene was used as an internal standard.

Analytical HPLC was performed on a KONTRON twin T414 LC pump computer-managed gradient HPLC system. Detections were made by means of a UVIKON 720 LC micro-variable wavelength UV detector set at 270 nm. Integrations were achieved by using the Anacomp 220 computer. For analytical work mostly a 250 × 4-mm Polygosil 5-mm C_{18}-column was utilized. Eluents for reversed-phase separations were all mixtures of methanol and H_2O. In addition, some analyses were performed on a LiChrosorb Si60 5-mm silica column with mixtures of distilled petroleum ether (bp 60–70 °C) and ethyl acetate as eluent. Preparative separations were done isocratically on a KONTRON T-414 LC pump fitted with a larger displacement head. Detections were achieved by means of a UVIKON 720 LC micro-variable detector set at 270 nm. For preparative work either a 250 × 20 mm Polygosil 5-mm C_{18}-column with mixtures of methanol, ethanol, and H_2O or a 250 × 20 mm LiChrosorb 5-mm silica column with mixtures of petroleum ether (bp 60–70 °C) and ethyl acetate as eluent were employed.

Photolyses were conducted in Pyrex vessels by irradiating with $300 < \lambda < 350$ nm lamps in a Rayonet photoreactor (RPR-100) or with the 333-, 352-, and 364-nm lines (MLUV) of a Coherent Innova 100 CW argon ion laser at powers between 2 and 3 W. The NMR spectra were run on Bruker WM 400, AC 250 or AC 200 spectrometers with either TMS or $CHCl_3$ as internal standards. For low-temperature spectra either a Bruker WM 400 or AC 200 instrument was used.

Benzophenone, commercially available material, was recrystallized twice from ethanol (mp 49–51 °C). 1,1,3,3-Tetramethyl-1,3-dihydroisoindolin-2-yloxyl, mp 127–128 °C, was prepared in 56% overall yield according to the procedure of Rizzardo and Solomon et al.[24] 2,3-Diazabicyclo[2.2.1]hept-2-ene (**1a**),[14] 2,3-diazabicyclo[2.2.2]oct-2-ene,[14] 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (**1b**),[14] and 7-(diphenylmethylidene)-2,3-diazabicyclo[2.2.1]hept-2-ene (**1c**)[14] were prepared according to known procedures.

1,4-Bis(6-phenylfulven-6-yl)benzene. To a solution of 560 mg (24.5 mmol) of sodium in 40 mL of absolute EtOH and 3.50 g (12.3 mmol) of 1,4-dibenzoylbenzene in 40 mL of EtOH at 30 °C under nitrogen gas was added dropwise 2.33 g (35.0 mmol) of freshly distilled cyclopentadiene over a 10-min period. The mixture was refluxed for 2 h and then stirred for 4 h under nitrogen gas. The red crystalline product was collected by filtration. The crude product was chromatographed on silica gel with dichloromethane as eluant to yield the bis-fulvene (5.25 g, 56%) as red pellets, mp 156–157 °C (R_f 0.93). IR (CCl_4): ν 3070, 2920, 2850, 1660, 1585, 1465, 1440, 1360, 1195, 1080, 915 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.25–6.35 (m, 4 H), 6.56–6.64 (m, 4 H), 7.23–7.56 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 124.2 (d, C-1 and C-4), 124.5 (d, C-2 and C-3), 127.8 (d), 128.8 (d), 131.5 (d), 132.1 (d), 132.5 (d), 132.7 (d), 141.1 (s), 141.6 (s), 144.4 (s, C-5), 151.1 (s, C-6). UV (CH_3CN): λ_{max} (lg ϵ) 217 (4.244), 2.45 (4.264), 278 (4.044), 322 (4.126), 345 nm (4.188). MS (70 eV): m/z (%) 383 (4) [$M^+ + 1$], 382 (11) [M^+], 334 (6), 322 (4), 280 (4), 229 (8), 220 (4), 111 (35), 97 (58), 95 (41), 85 (34), 83 (55), 81 (44), 71 (57), 57 (100), 55 (77), 49 (30), 43 (77), 41 (45), 28 (28), 18 (67). Anal. Calcd for $C_{30}H_{22}$ (382.2): C, 94.20; H, 5.80. Found: C, 94.12; H, 6.01.

1,4-Bis[2,3-bis(ethoxycarbonyl)-7-(phenylmethylidene)-2,3-diazabicyclo[2.2.1]hept-5-en-7-yl]benzene. To a solution of 1.14 g (2.99 mmol) of the above bis-fulvene in 50 mL of dry CH_2Cl_2 was added at 0 °C a solution of diethyl azodicarboxylate (1.04 g, 5.98 mmol) in 50 mL of dry CH_2Cl_2. The resulting mixture was stirred for 2 h at 20 °C, and the solvent was removed by evaporation (20 °C/17 Torr). The crude product was chromatographed on silica gel by eluting with a 9:1 mixture of CH_2Cl_2 and EtOAc to yield the unsaturated bis-carbamate (1.62 g, 90%) as a colorless powder, mp 154–156 °C dec (R_f 0.46). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.21–1.40 (m, 12 H, CH_3), 4.16–4.24 (q, J = 7.0 Hz, 8 H, CH_2), 5.10–5.40 (br s, 4 H, 1-H and 4-H), 6.70–6.80 (br s, 4 H, 5-H and 6-H), 7.09–7.35 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0 (q, CH_3), 62.5 (s, C-1 and C-4), 64.5 (t, CH_2), 121.8, 126.4, 127.6, 128.2, 129.2, 129.3, 129.7 (d, Ar-C), 131.9, 136.5 (s), 137.3, 138.6, 139.1, 158.5 (s, C=O).

1,4-Bis[2,3-bis(ethoxycarbonyl)-7-(phenylmethylidene)-2,3-diazabicyclo[2.2.1]heptan-7-yl]benzene. The above unsaturated bis-carbamate (1.50 g, 2.49 mmol) and 100 mg of 10% Pd/C in 250 mL of EtOAc were vigorously stirred at 20 °C for 120 h under a H_2 gas atmosphere. Removal of the catalyst by filtration and the solvent by distillation (30 °C/20 Torr) gave 1.28 g (85%) of the saturated carbamate, which after recrystallization from EtOAc was obtained as a colorless powder, mp 164–165 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.21–1.40 (m, 12 H, CH_3), 1.80–2.20 (m, 8 H, 5-H and 6-H), 4.16–4.24 (q, J = 7.0 Hz, 8 H, CH_2), 4.80 (br s, 4 H, 1-H and 4-H), 7.09–7.35 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 13.4 (q, CH_3), 27.4 (t), 29.9 (t), 32.6 (t), 59.3 (s, C-1 and C-4), 59.4 (s, C-1 and C-4), 61.1 (t, CH_2), 61.4 (t, CH_2), 125.6 (d), 125.7 (d), 125.8 (d), 126.2 (d), 126.6 (d), 126.8 (d), 126.9 (d), 127.0 (d), 127.2 (d), 127.3 (d), 127.6 (d), 127.7 (d), 128.0 (d), 128.4 (d), 136.3 (s), 136.7 (d), 137.4 (d), 138.7 (d), 139.2 (d), 141.8 (d), 153.7 (s), 156.4 (s). In view of its poor solubility and thermal lability, no satisfactory CHN analysis could be obtained.

1,4-Bis(7-phenylmethylidene)-2,3-diazabicyclo[2.2.1]-hept-2-en-7-yl)benzene (1d). A sample of 1.23 g (2.36 mmol) of the above bis-carbamate was added to a solution of 730 mg (13.1 mmol) of KOH in 100 mL of i-PrOH and refluxed under nitrogen gas for 15 h. The reaction mixture was diluted with 100 mL of ice water, and concd HCl was added to adjust the pH to ca. 1–2. The pH was brought to 5–6 with 12% NH_3 solution, and 10 mL of a saturated $CuCl_2$ solution was added dropwise to precipitate the brown complex. The solid was collected by filtration and dissolved in 50 mL of 12% aqueous NH_3 solution. After 15 min, the aqueous solution was extracted with CH_2Cl_2 (5 × 60 mL) and the combined organic layers were washed with 2 × 50 mL of H_2O, dried over $MgSO_4$, and concentrated by evaporation (0 °C/20 Torr). The crude product was purified by column chromatography (silica gel, 9:1 CH_2Cl_2/EtOAc, R_f 0.47) to afford 320 mg (36%) of yellow pellets, mp 102–103 °C dec. IR (CCl_4): ν 3065, 3035, 2980, 2950, 1660, 1595, 1490, 1445, 1305, 1275, 1200, 1185, 1110 cm^{-1}. UV (CH_3CN): λ_{max} (lg ϵ) 236 (3.944), 2.17 nm (4.003). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.18 (br d, J = 7.6 Hz, 4 H, 5-H_{endo} and 6-H_{endo}), 1.84 (br d, J = 7.6 Hz, 4 H, 5-H_{exo} and 6-H_{exo}), 5.37 (br s, 2 H, 1-H and/or 4-H), 5.43 (br s, 2 H, 1-H and/or 4-H), 6.95–7.28 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.3 (t, C-5 and C-6), 75.3 (s, C-1 and/or C-4), 75.5 (s, C-1 and/or C-4), 127.8 (d), 128.2 (d), 129.2 (d), 129.5 (d), 131.0 (s, C-7), 139.0 (s), 139.2 (s), 143.9 (s, C-8). The material was thermally labile already at room temperature which precluded to acquire a satisfactory elemental analysis.

General Procedure for Nitroxide Trapping. A sample of the azoalkane **1** and the nitroxide were dissolved in acetonitrile or CH_2Cl_2, placed into a Pyrex vessel, degassed by applying four freeze–pump–thaw cycles, and irradiated in a Rayonet photoreactor (300 nm < λ < 370 nm) or with the argon ion laser (λ = 364 nm) at −5 °C or 20 °C. After total conversion (negative azo test[16a]), the product mixture was analyzed and separated by HPLC.

Azoalkane 1a. An acetonitrile (10 mL) solution of **1a** (0.107 g, 1.10 mmol), nitroxide (1.46 g, 7.60 mmol), and benzophenone (0.98 g, 5.40 mmol) gave after 24 h irradiation (60% consumption

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of **1a**) in the Rayonet the housane **2a** (40%), the bis-nitroxide adduct *cis*-**3a** (60.0 mg, 21%) as a viscous oil and *trans*-**3a** (117 mg, 39%) as white prisms, mp 124.5–125.5 °C from MeOH. The two adducts were readily separated by reversed-phase HPLC.

***cis*-1,3-Bis(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)cyclopentane (*cis*-3a).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.34 (br s, 12 H, CH_3), 1.51 (br s, 12 H, CH_3), 1.78–2.04 (m, 5 H, 4-H, 5-H and 2-H_{eq}), 2.39 (pseudo quint, J = 7.1 Hz, 1 H, 2-H_{ax}), 4.34 (m, 2 H, 1-H and 3-H), 7.08 (m, 4 H, Ar-H), 7.21 (m, 4 H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 12.1 (q, 4 CH_3), 21.1 (q, 4 CH_3), 24.2 (t, C-4 and C-5), 37.7 (t, C-2), 66.2 (s, 2 C-1′), 67.4 (s, 2 C-3′), 83.6 (d, C-1 and C-3), 120.4 (d, 2 C-4′ and 2 C-7′), 126.0 (d, 2 C-5′ and 2 C-6′), 144.3 (s, 2 C-3a′ and 2 C-7a′). Anal. Calcd for $C_{29}H_{40}N_2O_2$ (448.6): C, 77.63; H, 8.99; N, 6.24. Found: C, 77.39; H, 9.00; N, 6.33. ***trans*-1,3-Bis(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)cyclopentane (*trans*-3a).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.32 (br s, 12 H, CH_3), 1.51 (br s, 12 H, CH_3), 1.81–2.16 (m, 4 H, 4-H and 5-H), 2.16 (t, J = 5.5 Hz, 2 H, 2-H), 4.54 (m, 2 H, 1-H and 3-H), 7.08 (m, 4 H, Ar-H), 7.21 (m, 4 H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.2 (q, 4 CH_3), 30.0 (t, C-4 and C-5), 30.3 (q, 4 CH_3), 38.9 (t, C-2), 67.2 (s, 2 C-1′ and 2 C-3′), 84.8 (d, C-1 and C-3), 121.5 (d, 2 C-4′ and 2 C-7′), 127.0 (d, 2 C-5′ and 2 C-6′), 145.2 (s, 2 C-3a′ and 2 C-7a′). Anal. Calcd for $C_{29}H_{40}N_2O_2$ (448.6): C, 77.63; H, 8.99; N, 6.24. Found: C, 77.87; H, 9.36; N, 6.27.

Azoalkane 1b. An acetonitrile solution (3 mL) of **1b** (100 mg, 0.735 mmol) and nitroxide (300 mg, 1.58 mmol) gave after 20 h irradiation (>95% consumption of **1b**) in the Rayonet 316 mg (88%) of *cis*-**3b** and **3b′** in relative ratio of 34:66 (^{1}H NMR, HPLC). By means of silica gel and reversed-phase HPLC, the adducts could not be separated. Slow crystallization of the mixture from 1:14 acetone/petroleum ether gave a small amount of crystalline *trans*-**3b**, mp 164–166 °C, as colorless rhombic crystals. ***trans*-1,3-Bis(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)-2-isopropylidenecyclopentane (*trans*-3b).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.28 (s, 6 H, 2 CH_3), 1.44 (s, 6 H, 2 CH_3), 1.50 (s, 6 H, 2 CH_3), 1.55 (s, 6 H, 2 CH_3), 1.79 (br d, J = 4.5 Hz, 2 H, 4-H and/or 5-H), 2.03 (s, 6 H, 2 CH_3), 2.48 (br d, J = 7.0 Hz, 2 H, 4-H and/or 5-H), 4.90 (br d, J = 2.4 Hz, 2 H, 1-H and 3-H), 7.00–7.10 (m, 4 H, Ar-H), 7.18–7.24 (m, 4 H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 24.1 (q, 2 CH_3), 25.1 (q, 2 CH_3), 25.4 (q, 2 CH_3), 29.2 (t, CH_2), 30.0 (q, 2 CH_3), 31.0 (q, 2 CH_3), 67.3 (s, C-1a or C-3a), 68.0 (s, C-1a or C-3a), 83.2 (s, C-1 and C-3), 122.0 (br d, C-4a and C-7a), 127.5 (d, C-5a or C-6a), 137.0 (s, C-2 or C-2′), 139.1 (s, C-2 or C-2′), 145.4 (s, 3a′ and 7a′). **1-(1′,1′,3′,3′-Tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)-2-[1-(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)ethyl]cyclopent-2-ene (3b).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.25 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.30 (s, 6 H, 2 CH_3), 1.42 (s, 6 H, 2 CH_3), 1.46 (s, 6 H, 2 CH_3), 1.50 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.85 (m, 1 H, 4-H), 2.20 (m, 1 H, 4-H), 2.45 (m, 1 H, 5-H), 2.61 (m, 1 H, 5-H), 5.15 (br d, J = 6.0 Hz, 1 H, 3-H), 5.93 (s, 1 H, 1-H), 7.0–7.10 (m, 4 H, Ar-H), 7.15–7.25 (m, 4 H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 24.2 (q, CH_3), 26.0 (q, CH_3), 26.5 (q, CH_3), 28.2 (q, CH_3), 28.9 (q, CH_3), 29.3 (q, CH_3), 30.1 (t, CH_2), 30.5 (q, CH_3), 30.6 (q, CH_3), 68.0 (s, C-1a and C-3a or C-2′), 68.1 (s, C-1a and C-3a or C-2′), 87.1 (d, C-3), 121.9 (d, C-1), 122.1 (2 d, C-4a and C-7a), 127.5 (d, C-5a or C-6a), 127.6 (d, C-5a or C-6a), 146.1 (s, 3a′ and 7a′), 160.9 (s, C-2). Anal. for the *trans*-**3b** and **3b′** mixture. Calcd for $C_{32}H_{44}N_2O_2$ (488.7): C, 78.65; H, 9.07; N, 5.73. Found: C, 78.40; H, 9.34; N, 5.63.

Bis-azoalkane 1c. An acetonitrile solution (5 mL) of **1c** (125 mg, 0.460 mmol) and nitroxide (220 mg, 1.10 mmol) gave after 25 h irradiation (>95% consumption of **1c**) in the Rayonet 262 mg (93%) of a mixture of *trans*-**3c** and *cis*-**3c** in a ratio of 90:10 (by HPLC). The two adducts were separated from the reaction mixture by reversed-phase HPLC (85:15 MeOH/H_2O, 8 mL/min). ***trans*-1,3-Bis(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)-2-(diphenylmethylidene)cyclopentane (*trans*-3c).** ^{1}H NMR ($CDCl_3$, −30 °C, 250 MHz): δ 1.05 (s, 6 H, 2 CH_3), 1.20 (s, 6 H, 2 CH_3), 1.41 (s, 6 H, 2 CH_3), 1.44 (s, 6 H, 2 CH_3), 1.84 (br d, J = 5.5 Hz, 2 H, 4-H and/or 5-H), 2.49 (br d, J = 7.4 Hz, 2 H, 4-H and/or 5-H), 5.21 (d, J = 2.5 Hz, 2 H, 1-H and 3-H), 6.85–6.96 (m, 2 H, Ar-H), 7.00–7.07 (m, 2 H, Ar-H), 7.10–7.30 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, −30 °C, 63 MHz): δ 23.7 (q, 2 CH_3), 24.8 (q, 2 CH_3), 27.8 (t, CH_2), 29.1 (q, 2 CH_3), 29.7 (q, 2 CH_3), 66.4 (s, C-1a or 3a), 67.1 (s, C-1a or C-3a), 81.1 (s, C-1 and C-3), 120.9 (d, C-4a or C-7a), 121.3 (d, C-4a or C-7a), 126.7 (d, C-5a or C-6a), 126.8 (d, Ar-C), 127.9 (d, Ar-C), 129.3 (d, Ar-C), 140.0 (s, C-2 or C-2′), 143.3 (s, 3a′ or 7a′ or Ar-C), 144.6 (s, 3a′ or 7a′ or Ar-C), 145.6 (s, 3a′ or 7a′ or Ar-C), 146.8 (s, C-2 or C-2′). Anal. Calcd for $C_{42}H_{48}N_2O_2$ (612.9): C, 82.31; H, 7.89; N, 4.57. Found: C, 82.46; H, 8.14; N, 4.62. ***cis*-1,3-Bis(1′,1′,3′,3′-tetramethyl-1′,3′-dihydroisoindolin-2′-yloxyl)-2-(diphenylmethylidene)cyclopentane (*cis*-3c).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.05 (s, 6 H, 2 CH_3), 1.22 (s, 6 H, 2 CH_3), 1.35 (s, 6 H, 2 CH_3), 1.40 (s, 6 H, 2 CH_3), 2.42 (br s, 2 H, 4-H and/or 5-H), 2.88 (br q, J = 7.8 Hz, 2 H, 4-H and/or 5-H), 4.90 (br s, 2 H, 1-H and 3-H), 6.98–7.10 (m, 4 H, Ar-H), 7.16–7.38 (m, 14 H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 26.0 (br q, CH_3), 30.0 (br q, CH_3), 30.7 (t, CH_2), 68.1 (s, C-1a or 3a), 68.4 (s, C-1a or C-3a), 83.7 (s, C-1 and C-3), 122.4 (d, C-4a or C-7a), 127.9 (d, C-5a or C-6a), 128.2 (d, Ar-C), 128.9 (d, Ar-C), 130.0 (d, Ar-C), 140.9 (s, C-2 or C-2′ or Ar-C), 144.0 (s, C-2 or C-2′ or Ar-C), 146.4 (s, 3a′ or 7a′), 146.8 (s, 3a′ or 7a′), 147.2 (s, C-2 or C-2′). Anal. Calcd for $C_{42}H_{48}N_2O_2$ (612.9): C, 82.31; H, 7.89; N, 4.57. Found: C, 82.50; H, 8.01; N, 4.62.

Bis-azoalkane 1d. A CH_2Cl_2 solution (3 mL) of **1d** (150 mg, 0.340 mmol) and the nitroxide (640 mg, 3.40 mmol) was irradiated for 2 h (100% consumption of **1d**) with the argon ion laser at −5 °C and subsequently evaporated (20 °C/15 Torr) to dryness. Flash chromatography on silica gel and elution with a 1:14 acetone/petroleum ether mixture gave a complex, labile mixture of tetrakis-adducts (by ^{1}H NMR), which could not be separated by HPLC.

1,4-Bis(1′-phenyl-2′,3′-dioxabicyclo[3.3.0]oct-7′-enyl)-benzene (4d). The bis-azoalkane **1d** (80.4 mg, 0.182 mmol) was dissolved in 5 mL of acetonitrile and irradiated under an O_2 atomsphere (5 bar) with the 333-, 352-, and 364-nm lines of the argon ion laser at −10 °C. After 2 h irradiation, the bis-azoalkane **1d** was completely consumed (negative azo test[16a]). Preparative column chromatography on silica gel by eluting with CH_2Cl_2 gave 57.3 mg (70%) of the bis-peroxide **4d**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.79–2.01 (m, 2 H), 2.06–2.30 (m, 2 H), 2.63–2.95 (m, 4 H), 5.32–5.44 (m, 2 H), 5.54–5.62 (m, 2 H), 7.15–7.34 (m, 14 H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 30.7 (t), 30.8 (t), 37.0 (t), 37.1 (t), 87.3 (s), 90.9 (s), 91.1 (d), 91.2 (d), 125.2 (d), 125.3 (d), 125.9 (d), 126.0 (d), 126.2 (d), 126.3 (d), 126.5 (d), 127.1 (d), 127.3 (d), 127.4 (d), 139.1 (s), 139.4 (s), 140.4 (s), 141.1 (s), 156.8 (s), 157.0 (s). Anal. Calcd for $C_{30}H_{28}O_4$ (450.5): C, 79.98; H, 5.82. Found: C, 80.21; H, 5.74.

Treatment of Azoalkane 1a with the Nitroxide in the Dark. A mixture of the azoalkane **1a** (25.0 mg, 0.260 mmol) and the nitroxide (100 mg, 0.526 mmol) in 2 mL of acetonitrile was degassed by three freeze–pump–thaw cycles and stirred at room temperature under protection from light for 4 d. There was no production of adduct **3a**, as determined by TLC and reversed-phase HPLC.

Photolysis of the Bicyclo[2.1.0]pentane 2a in the Presence of the Nitroxide. The azoalkane **1a** (20.0 mg, 0.208 mmol) in 2 mL of acetonitrile was converted to bicyclopentane **2a** by photolysis in a Rayonet photoreactor for 64 h. TLC indicated 100% consumption of the azoalkane **1a** (negative azo test[16a]). Addition of the nitroxide (50.0 mg, 0.263 mmol) and continued photolysis for 20 h gave no adduct **3a**, as determined by TLC and reversed-phase HPLC.

Direct Photolysis of Azoalkane 1a in the Presence of the Nitroxide. The azoalkane **1a** (9.83 mg, 0.102 mmol) and the nitroxide (148 mg, 0.779 mmol) in 1 mL acetonitrile was photolyzed in the absence of benzophenone. The adducts *cis*, *trans*-**3a** were produced only to the extent of 20% of that obtained in the benzophenone-sensitized reaction, as determined by analytical reversed-phase HPLC.

Photolysis of 2,3-Diazabicyclo[2.2.2]oct-2-ene in the Presence of the Nitroxide. A solution of the azoalkane (20.0 mg, 0.182 mmol), benzophenone (50.0 mg, 0.275 mmol), and the nitroxide (50.0 mg, 0.263 mmol) in 3 mL of acetonitrile were photolyzed in a Rayonet photoreactor (300 < λ < 350 nm) at 20 °C, and even after 16 h no adducts were detected by reversed-phase HPLC.

Reaction of 5-Isopropylidenebicyclo[2.1.0]pentane (2b) with the Nitroxide. Photolysis of the azoalkane **1b** (30.0 mg,

0.221 mmol) in 3 mL of $CFCl_3$ at -78 °C in a Rayonet photoreactor produced the bicyclopentane **2b** as shown by its low temperature NMR.[18] When nitroxide (50.0 mg, 0.263 mmol) was added to this solution and the reaction allowed to warm up to room temperature, the same amounts of the adducts *trans*-**3b** and **3b'** were produced as in the direct photolysis of azoalkane **1b**.

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Registry No. **1a**, 2721-32-6; **1b**, 31689-32-4; **1c**, 66322-90-5; **1d**, 138062-33-6; **2a**, 185-94-4; **2b**, 72447-89-3; *cis*-**3a**, 134278-19-6; *trans*-**3a**, 134278-20-9; *cis*-**3b**, 138062-37-0; *trans*-**3b**, 138062-39-2; **3b'**, 138062-38-1; *cis*-**3c**, 138062-41-6; *trans*-**3c**, 138062-40-5; **4d**, 138062-42-7; 1,4-dibenzoylbenzene, 3016-97-5; cyclopentadiene, 542-92-7; 1,4-bis[(2,4-cyclopentadien-1-ylidenephenyl)methyl]-benzene, 138062-34-7; 1,4-bis[2,3-bis(ethoxycarbonyl)-7-(phenylmethylidene)-2,3-diazabicyclo[2.2.1]hept-5-en-7-yl]benzene, 138062-35-8; 1,4-bis[2,3-bis(ethoxycarbonyl)-7-(phenylmethylidene)-2,3-diazabicyclo[2.2.1]heptan-7-yl]benzene, 138062-36-9; diethyl azodicarboxylate, 1972-28-7; 2,3-diazabicyclo[2.2.2]oct-2-ene, 3310-62-1; 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl, 80037-90-7.

Supplementary Material Available: X-ray crystallographic data for *trans*-**3a** and *trans*-**3b**, including atomic coordinates, equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, H atom coordinates, and isotropic displacement parameters, and ^{13}C and ^{1}H NMR spectra for **1d** and its precursors, namely the diethyl azodicarboxylate adduct and its hydrogenated derivative (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reaction Retrieval from Databases for Organic Chemists

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A general rationalization of organic reactions is described, based on the net structural change at the skeletal atoms in the reacting center. We define four generalized kinds of attachments any skeletal atom may have and how they change in any reaction. Unit reactions are defined as unit exchanges of these attachments. With this logical basis a simple organization of all organic reactions is developed to provide a logical overview of all organic reactions. A program, RETRIEVE, is described to index all the entries in two common reaction databases and to retrieve all precedents for a given reaction. A statistical breakdown of the reaction types in these databases is presented. Most entries are just single or double unit reactions and can be quickly accessed and closely matched to the reactive center of any input query.

In organic chemistry there is a long history of searching catalogs for structures, but very little organized indexing for reactions. Indexing name reactions is common but these are haphazard, gratuituous, and not systematic. Now that computer databases of reactions have made an appearance there is a need for a logical basis for indexing organic reactions. This requires a general system to describe the net structural change in any reaction in terms of what bonds are made and broken. Such a system should proceed from the general to the particular to allow for nesting of categories, and it must provide that every possible reaction change have a place in the indexing format, regardless of whether there are known examples. This idea reflects the successful Beilstein system for indexing structures in that any structure, known or not, has a place in the system. This assures that if any compound is included it will be found and, if not included, one is assured that it is unknown.

In this paper we present such an indexing system for reactions and describe a program, called RETRIEVE, which uses it for the retrieval of reactions for computer databases. We will show that most reactions in two large popular databases can be efficiently indexed and reliably retrieved by the use of this simple system, which also provides a useful understanding of their contents. In turn, the successful application of the system confirms the validity of the system itself for organizing and cataloguing organic reactions.

To describe all organic reactions we need to define a general, abstract definition of the nature of bond changes to accommodate all possible instances, independent of mechanism. It is important to focus only on the *net structural change* at the reacting centers themselves. The remaining atoms, which do not change, are not relevant to the search. Hence, a search procedure organized by structural similarities at *all* the atoms is likely to miss good precedents in which the reacting centers are the same but the remainder of the molecule may be quite different.

System of Reaction Description. The system we apply is based on a structural premise of a backbone skeleton of linked carbons which bear functionality in the form of π-bonds and attached heteroatoms.[1] Two kinds of heteroatom attachments are distinguished initially, electropositive and electronegative, to afford recognition of the oxidation state of the carbon to which they are attached. Isohypsic attachments[2,3] to another carbon are distinguished between the σ-bond, the skeletal attachment, and the π-bond, a functional group. This creates a fundamental and generalized definition of four synthetically important kinds of attachments at any carbon in a structure: H for a bond to hydrogen or electropositive atom (B, Al, Si, Sn, metals); R for a σ-bond to carbon (skeletal); Π for a π-bond to carbon (functional); Z for any bond (π- or σ-) to an electronegative heteroatom (N, O, S, Hal, etc.)

(1) This backbone skeleton may incorporate atoms other than carbon (cf., N, O, S), but it is simpler first to define in terms of a carbon skeleton, leaving the others for discussion later; they will be seen to follow the same procedure exactly.

(2) The term *isohypsic*, from the Greek for "equal level", was introduced to mean neither oxidative nor reductive.[3]

(3) Hendrickson, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 6847.

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