J. Org. Chem. **1981**, *46*, 4133–4138

Generation of 2,3-Benzobicyclo[2.2.1]hept-2-ene-5,7-diyl Diradicals via Denitrogenation of Appropriate Azoalkanes and Their Mechanistic Implications in the Di-π-methane Rearrangement of Benzonorbornadienes

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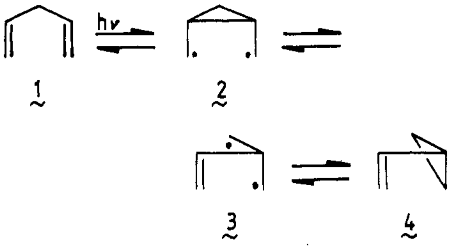
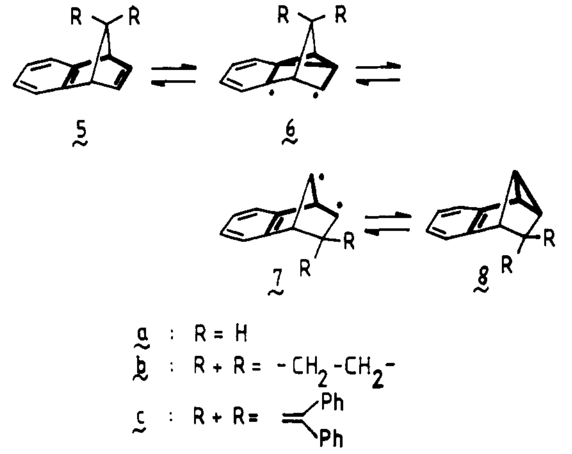
Received June 12, 1981

The azoalkanes **16a–c**, prepared from the bicycloalkadienes **5a–c** via dipolar cycloaddition with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) and subsequent oxidative hydrolysis, were submitted to thermal and direct and ketone-sensitized photochemical denitrogenation, with the intention of entering the diradical manifold postulated for the di-π-methane rearrangement. It is shown that in each case denitrogenation leads to the expected 2,3-benzobicyclo[2.2.1]hept-2-ene-5,7-diyl diradical **7**. Diradical **7** mostly cyclizes into the corresponding tricycloalkene **8**, and only a very small fraction (<5%) suffers retro-di-π-methane rearrangement into the bicycloalkadiene **5** via the cyclopropyl dicarbinyl radical **6**. Stabilizing substituents such as benzhydryl and spirocyclopropyl groups in a position α to the rearranging radical site in **7** discourage retro-di-π-methane reaction.

In the di-π-methane rearrangement, which constitutes one of the most ubiquitous photochemical transformations,[2] divinylmethane (**1**) is converted into a vinylcyclopropane (**4**), presumably via the initial cyclopropyl dicarbinyl diradical **2** and the ultimate 2-vinyl-1,3-trimethylene diradical **3** (eq. 1). A specific example of mechanistic significance is the photochemical rearrangement of 7-substituted benzonorbornadienes **5** into the corresponding tricycloalkenes **8**. The initial cyclopropyl dicarbinyl diradical **6** is formed by benzo-vinyl bonding and rearranges into the ultimate 2,3-benzobicyclo[2.2.1]hept-2-ene-5,7-diyl diradical **7** (eq. 2).



(1)



(2)

The parent benzonorbornadiene **5a** (R = H) was one of the first substrates to be investigated in this series. It was shown[3] that the **5a** → **8a** rearrangement was strictly a triplet process, since only the ketone-sensitized photolysis ($E_T \geq 70$ kcal) led to the tricyclic product. In fact, we could make good use of this spin-state-specific photorearrangment for the detection and quantitation of n–π^* triplet-state carbonyl products that are formed in the thermolysis of 1,2-dioxetanes and α-peroxy lactones.[4] A thorough investigation of benzo ring substituent effects on the regioselectivity of the benzo–vinyl bonding during the formation of the cyclopropyl dicarbinyl diradical **6a** was made by Paquette and colleagues.[5]

The di-π-methane reactions of the spiro derivative **5b** and the benzhydrylidene derivative **5c** have also been investigated.[6] It was shown that both the direct photolysis at $\lambda > 230$ nm in CH_3CN and the acetone-sensitized photolysis led to the respective di-π-methane products **8b** and **8c**. The spiro derivative **5b** was considerably more photoactive than the benzhydrylidene derivative **5c**. Furthermore, in both cases the direct photolysis was much less efficient than the acetone-sensitized photolysis. Although the triplet-state quencher piperylene did not influence the photorearrangement of the related 2,3-benzo-7-isopropylidenenorbornadiene, no definitive conclusion was reached concerning the spin state of the di-π-methane rearrangement of **5b,c**. However, it was suggested that the low efficiency of the direct photolysis might be rationalized in terms of competitive quadricyclane **9** formation from a singlet-state cyclopropyl dicarbinyl diradical **6**, while the di-π-methane product was derived from a triplet-state cyclopropyl dicarbinyl diradical **6** (eq 3). The singlet state sequence **5b,c** → ^{S}**[6b,c]** → **9b,c** would then constitute an energy dissipation route, competing with the triplet state sequence **5b,c** → ^{S}[**6b,c**] → ^{T}**[6b,c]** → **8b,c**, thereby explaining the low efficiency of the direct photolysis compared to the triplet-sensitized route **5b,c** → ^{T}**[6b,c]** → **8b,c**.

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(1) Direct correspondence to this author at the University of Würzburg.

(2) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 42, Part 3, Essay 16, pp 131–164.

(3) (a) Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 7103. (b) Hahn, R. C.; Johnson, P. R. *Ibid*, **1977**, *99*, 1508.

(4) Adam, W.; Cheng, C.-C.; Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1979**, *101*, 1324.

(5) (a) Paquette, L. A.; Yeh Ku, A.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972. (b) Yeh Ku, A.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5981. (c) Santiago, C.; McAlduff, E. J.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *Ibid.* **1978**. *100*, 6149. (d) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723. (e) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977**, *99*, 3734.

(6) (a) Eberbach, W.; Würsch, P.; Prinzbach, H. *Helv. Chim. Acta* **1970**, *53*, 1235. (b) Trost, B. M. *J. Org. Chem.* **1969**, *34*, 3644. (c) Hankinson, B.; Heaney, H.; Price, A. P.; Sharma, R. P. *J. Chem. Soc., Perkins Trans. 1* **1973**, 2569.

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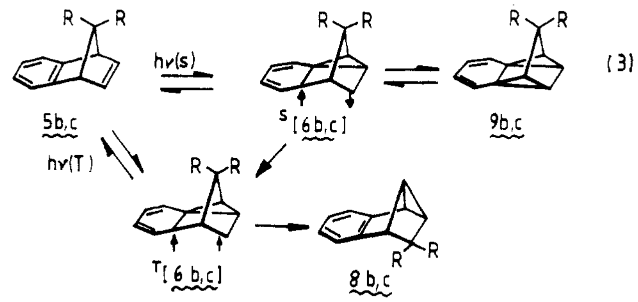
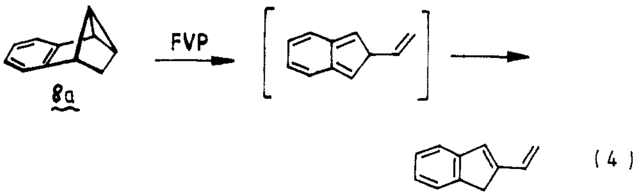


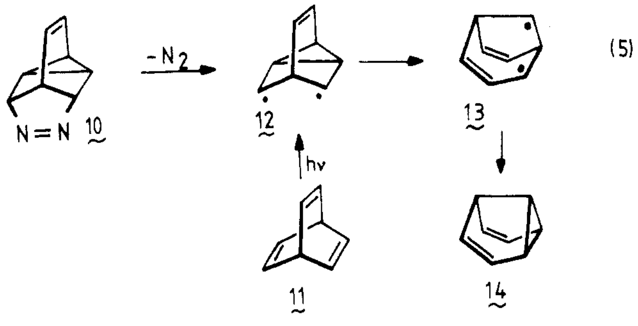
It appeared, therefore, of mechanistic interest and importance to understand the detailed behavior of the intermediary diradicals in the di-π-methane rearrangement of the benzonorbornadienes **5a–c**.

In view of the frequent difficulties and ambiguities involved in defining directly the spin states of diradical intermediates in photochemical rearrangements, it appeared to us more fruitful to generate the postulated diradical intermediates of the di-π-methane rearrangement via authentic spin-state-specific routes. Synthetic difficulties preclude use of the respective quadricyclanes **9** as precursors to the initial cyclopropyl dicarbinyl diradicals **6**. On the other hand, the readily available tricycloalkenes **8** do not photorevert in the di-π-methane sense, while thermally they undergo the cycloreversion shown in eq 4.[7]

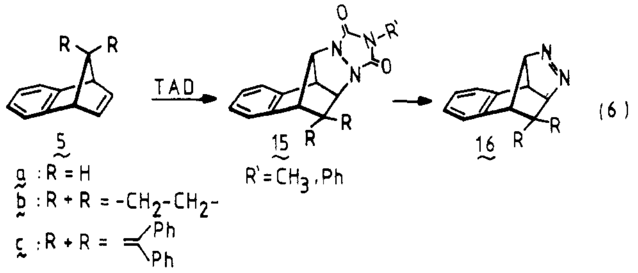


This complicates the possibility of generating the ultimate diradical **7** directly from the di-π-methane products **8**.[6] Consequently, indirect precursors must be employed in order to enter into the diradical manifold that is postulated for the di-π-methane rearrangement of benzonorbornadienes (eq 2).

The thermal and photochemical extrusion of nitrogen from appropriate azoalkanes[8] has served as a particularly convenient and effective method for the generation of authentic diradicals which have been postulated in photorearrangements.[9] For example, Zimmerman et al. elegantly employed the azoalkane **10** as precursor to the cyclopropyl dicarbinyl diradical **12** to explore the mechanistic details of the di-π-methane rearrangement of barrelene (**11**) to semibullvalene (**14**) via the diradical **13** (eq 5).[9a]



Recently we showed[10] that the benzonorbornadienes **5** undergo dipolar cycloaddition with *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to afford the urazoles **15**. These in turn could be converted into the azoalkanes **16** (eq 6).



Consequently, these hitherto synthetically inaccessible azoalkanes have the appropriate structural features and substitution patterns to serve as precursors to the ultimate di-π-methane 1,3-diradicals **7** (eq 2).

Presently we report the full details of this mechanistic study.[11] We addressed ourselves to the following questions concerning this di-π-methane rearrangement: (i) Does the singlet diradical **7**, generated by thermal denitrogenation of the azoalkane **16**, revert into benzonorbornadiene **5** via the sequence **16** → **7** → **6** → **5**, i.e., the retro-di-π-methane rearrangement? (ii) Does the triplet diradical **7**, generated by ketone-sensitized denitrogenation of azoalkane **16**, undergo such di-π-methane reversion? (iii) What are the spin states of these diradical intermediates in the direct photolysis of azoalkane **16**? (iv) Will the diradicals show wavelength dependence if the denitrogenation of azoalkane **16** is performed by excitation of the azo chromophore ($n_{-} \rightarrow \pi^*$) at 350 nm vs. excitation of the benzene chromophore ($\pi \rightarrow \pi^*$) at 254 nm? (v) What are the effects of substituents at the methylene bridge of **5** on the di-π-methane behavior of the diradical intermediates?

Results and Discussion

The conditions of denitrogenation and the product composition of the azoalkanes **16a–c** are summarized in Table I. Unfortunately, the di-π-methane product **8c** of the benzhydrylidene system was too involatile and thermally labile to allow GLC quantitation. Neither was it possible to separate the hydrocarbon products **8c** and **5c** by HPLC, obliging us to employ the less accurate (ca. 1% lower detection limit) ^{1}H NMR technique to assess the product yields. Furthermore, in the photochemical denitrogenations of **16**, control experiments revealed that the di-π-methane reaction **5** → **8** was negligible under the photodenitrogenation conditions. Thus, the low yield of the retro-di-π-methane product **5** from azoalkanes **16** is not due to concurrent di-π-methane cyclization. Even then, some interesting and valuable conclusions can be drawn from our results concerning the mechanism of the di-π-

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[7] Adam, W.; De Lucchi, O. *J. Org. Chem.* **1980**, *45*, 4167.

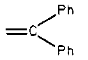
[8] (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

[9] (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680. (b) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *Ibid.* **1976**, *98*, 4320. (c) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *Ibid.* **1977**, *99*, 7388. (d) Cichra, D. A.; Duncan, C. D.; Berson, J. A. *ibid.* **1980**, *102*, 6527.

[10] Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806. Further spectroscopic data on **15a** (R' = CH_3): ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.70 (q, N-CH_3), 34.43 (t, CH_2), 46.14 (d, CH), 53.24 (d, CH), 58.38 (d, CHN), 76.76 (d, CHN), 120.39 (d, arom), 124.00 (d, arom), 127.02 (d, arom), 127.96 (d, arom), 135.86 (s, arom), 146.19 (s, arom), 157.98 (s, CO), 158.18 (s, CO). **16a**: ^{13}C NMR ($CDCl_3$, Me_4Si) δ 32.89 (t, CH_2), 37.50 (d, CH), 60.90 (d, CH), 75.11 (d, CHN), 97.78 (d, CHN), 120.69 (d, arom), 123.88 (d, arom), 126.52 (d, arom), 127.89 (d, arom) 136.41 (s, arom), 145.44 (s, arom).

[11] (a) Adam, W.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2109. (b) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762. (c) Erden, I.; Balci, M. *Tetrahedron Lett.* **1980**, 1825. The latter work was initially conceived and in part executed in our laboratory while both authors were present as postdoctoral associates. Such duplication is unfortunate, especially since it had been agreed to publish a full paper on this work jointly (cf. footnote 8 in ref 11).

Table I. Denitrogenation Conditions and Product Composition of Azoalkanes 16

			denitrogenation conditions			product composition, %			
azoalkane	R	R	mode	temp or λ (pressure)	solvent	8	5	others	note
16a	H	H	VFP[a]	ca. 400 °C (0.2–0.3 torr)	gas phase			100[d]	*g*
			hν	350 nm	pentane	99 ± 0.3	1 ± 0.3		*g*
			hν	254 nm	pentane	96 ± 0.3	4 ± 0.3		*g*
			hν	300 nm [$Ph_2C{=}O$][b]	benzene-d_6			100[e]	*h*
			hν	300 nm [$Me_2C{=}O$][b]	acetone	30 ± 1		70 ± 1[e]	*h*
16b	$-CH_2CH_2-$		VFP[a]	ca. 400 °C (0.2–0.3 torr)	gas phase	100			*g*
			hν	350 nm	pentane	99.5 ± 0.3	0.3 ± 0.2		*g*
			hν	254 nm	pentane	99.5 ± 0.3	0.3 ± 0.2		*g*
			hν	300 nm [$Ph_2C{=}O$][b]	benzene-d_6			100[f]	*h*
			hν	300 nm [$Me_2C{=}O$][b]	acetone	37 ± 1		63 ± 1[f]	*h*
16c			Δ[c]	175 °C	neat	⩾99	⩽1		*h*
			hν	350 nm	$CDCl_3$	⩾99	⩽1		*h*
			hν	300 nm [$Ph_2C{=}O$][b]	$CDCl_3$	⩾99	⩽1		*h*

[a] Vacuum flash pyrolysis. [b] Sensitizer. [c] Heated at its melting point. [d] Pyrazole **17a**. [e] Aziridine **18a**. [f] Aziridine **18b**. [g] Lower detection limit ca. 0.1%. [h] NMR detection (see Experimental Section), lower detection limit ca. 1%.

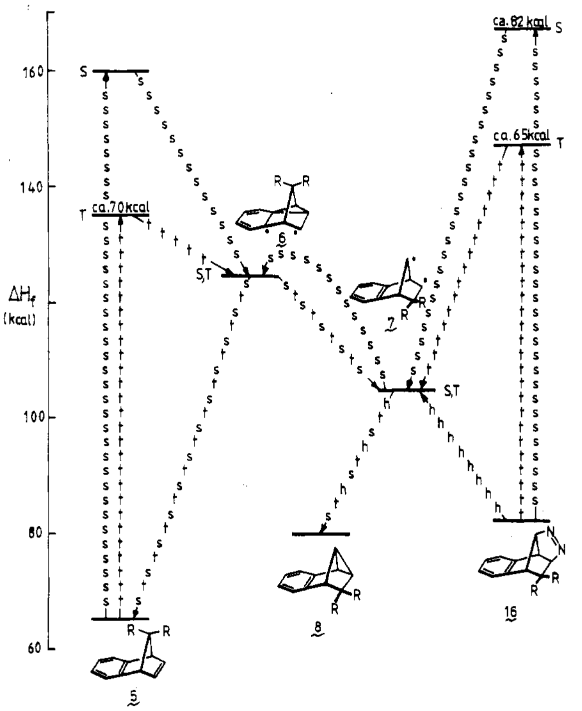
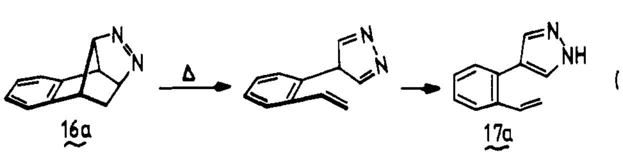


Figure 1. Qualitative energy diagram of the di-π-methane rearrangement of benzonorbornadienes (**5**) and the denitrogenation of their azoalkanes (**16**): s, direct photolysis; t, triplet-sensitized photolysis; h, thermolysis.

methane reaction. We shall conduct our discussion in terms of the qualitative energy scheme shown in Figure 1. The excited state energies (E_S, E_T) of **5** and **8** and the relative energies of the diradicals **6** and **7** refer to the parent system.[12]

Although the parent azoalkane **16a** has been the least cooperative to reveal its retro-di-π-methane properties, we shall commence our mechanistic analysis with this system and compare the others (**16b,c**) with it. Unfortunately, little could be learned from the thermolysis of azoalkane **16a** because instead of denitrogenating, it led to the pyrazole **17a** (eq 7).[11a]. Consequently, the retro-Diels–Alder



(7)

process, disengaging the C_1–C_6 and C_4–C_5 bonds, is the lower energy thermal route of **16a**. Precedents for this unusual retrocyclic process instead of denitrogenation have been reported.[13]

With respect to the spin-state specificity of the di-π-methane rearrangement, the failure of azoalkane **16a** to denitrogenate thermally is most unfortunate, because such thermal activation is the most unequivocal and direct means of generating thermally equilibrated singlet-state 1,3-diradicals **7**. For this reason we cannot say anything about the fate of the singlet-state 1,3-diradical **7a** because the thermolysis of **16a** did not allow us to enter the di-π-methane diradical manifold. However, the spiroazoalkane **16b** and the benzhydrylideneazoalkane **16c** denitrogenate quantitatively into the respective tricycloalkenes **8b,c** (Table I). Within the limits of GLC (≤0.1%) and ^1H NMR (≤1.0%) detection, no retro-di-π-methane products **5b,c** were formed in the thermal denitrogenation of **16b,c**, respectively. Clearly, the activation barrier for the diradical rearrangement $^S(\mathbf{7b,c}) \rightarrow \mathbf{6b,c}$ is too high ($E_a \geq 30$ kcal)[12] for the thermally equilibrated 1,3-diradicals **7b,c**, so that cyclization into the tricycloalkenes **8b,c** is prefered. We conclude, therefore, that the already strained and rigid thermally generated singlet-state 1,3-diradical **7** does not suffer di-π-methane reversion to bicycloalkadiene **5** via diradical **6**. In the cases of the spiro and benzhydrylidene derivatives, cyclopropyl carbinyl (**7b**) and allylic (**7c**) stabilization, respectively worth ca. 2 and 10 kcal/mol, constitute additional deterrents against di-π-methane reversion.

The ketone-sensitized denitrogenation of azoalkanes **16a** was equally problematic with respect to providing us with detailed mechanistic information concerning the fate of the triplet-state 1,3-diradical **7a**. Thus, the benzophenone-sensitized[9a] photolysis of **16a** gave exclusively the unusual aziridine **18a** (eq 8); denitrogenation did not take

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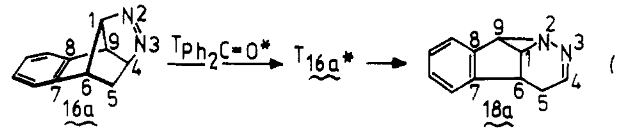
(12) The heats of formation of the diradicals **6** and **7** were determined with the help of group additivities. Cf.: Benson, S. w. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. For internal consistency their approximate energies were calculated relative to their hydrocarbons, **5** and **8**. The singlet-state energy of bicycloalkadiene **5a** is not known, while its triplet state energy ($E_T \approx 70$ kcal/mol) was taken from ref 3a. The singlet-state energy ($E_S \approx 82$ kcal/mol) of azoalkane **16a** was estimated from its fluorescence and absorption spectra, and its triplet state energy ($E_T \approx 65$ kcal/mol) was bracketed by ketone sensitization (K. Hannemann, unpublished results).

(13) (a) Tsuruta, H.; Kurabayashi, K.; Mukai, T. *J. Am. Chem. Soc.* **1968**, *90*, 7167. (b) Allred, E. L. *Chem. Commun.* **1969**, 72. (c) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5845.



(8)

place. Again, precedents for this menacing photorearrangement of azoalkanes have been documented.[14]

The structure assignment of **18a** rests mainly on its ^{1}H NMR (60 MHz) spectrum. In $CDCl_3$ it shows a broad doublet at 7.53 ppm attributed to the N=CH proton (H_4), a broad multiplet at 6.95–7.43 ppm ascribed to the aromatic protons (C_6H_4), a doublet at 3.93 ppm attributed to the bridgehead proton H_9, multiplets at 3.50 and 3.60 ppm due to the bridgehead protons H_1 and H_6, and a complex AB pattern at 2.63 and 2.17 ppm assigned to the geminal H_5 protons (exo and endo) of the methylene group. In C_6D_6 the bridgehead protons are better resolved, leading to a doublet for H_9 at 3.68 ppm, a doublet of doublets for H_1 at 3.12 ppm, and a multiplet for H_6 at 2.80 ppm. The complex AB pattern of the geminal H_5 protons (exo and endo) shows that each line is composed of four sublines. The coupling constants and decoupling experiments are given in the Experimental Section, but it is important to point out that the large geminal coupling of the H_5 protons ($J_{5\text{-endo},5\text{-exo}}$ = 16.8 Hz) is consistent with a methylene group in a six-membered ring. Inspection of Dreiding models reveals that the observed dihedral angles match reasonably well those estimated from the coupling constants by using the Karplus–Conroy equation. Finally, the ^{13}C NMR (cf. Experimental Section) spectrum shows that the ^{13}C–H coupling constant of H_4 is 174 Hz, which is consistent with the HC=N assignment. Similarly, the ^{13}C–H coupling constants of 187 Hz for the H_1 and H_9 protons is expected for an aziridine ring.

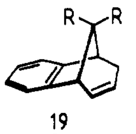
Although acetone-sensitization of azoalkane **16a** did lead to the tricycloalkene **8a** as minor product (Table I), control experiments confirmed that denitrogenation was an artifact arising either from singlet-state sensitization by acetone or from light leakage. In the latter case it was difficult to find a filter that allowed exclusive irradiation of the carbonyl n,π* chromophore without excitation of the azo n_-,π* chromophore. This could be convincingly demonstrated by employing tetramethyl-1,2-dioxetane (TMD)[15] as a thermal source of authentic acetone triplets. Thus, TMD chemienergization led exclusively to the aziridine **18a**.[16]

Similarly, the spiroazoalkane **16b** led exclusively to the aziridine **18b** on benzophenone sensitization (Table I). The acetone-sensitized photolysis afforded tricycloalkene **8b** as minor product, but again due to either singlet-state sensitization by acetone or to light leakage.[16] However, the benzhydrylidene system **16c** gave essentially quantitatively the desired di-π-methane product **8c**, but no bicycloalkadiene **5c**. Thus, while the benzhydrylidene system **16c** allowed us to enter into the di-π-methane diradical manifold via the triplet 1,3-diradical **7c**, the latter refused to revert via diradical **6c** to the bicyclo alkadiene **5c**. We are obliged to conclude that the presumably thermally equilibrated triplet diradical **7c** does not suffer retro-di-π-methane reaction. Apparently the energy barrier for the ^{T}(**7c**) → **6c** transformation must also be too high ($E_a \geq 30$ kcal/mol).[12] Again, allylic stabilization could be a major reason for this lack of retro-di-π-methane reactivity of the benzhydrylidene system.

This brings us now to the direct photolysis results (Table I). The greatest retro-di-π-methane reactivity is exhibited, not surprisingly, by the parent system **16a**. Approximately 1% retro-di-π-methane reaction and 99% cyclization are observed for the 1,3-diradical **7a** on excitation of the (n_-,π*)-azo chromophore. Excitation of the (π,π*)-benzene chromophore is more effective because 4% di-π-methane reversion results. Also the spiro system **16b** shows some retro-di-π-methane reactivity since ca. 0.5% bicycloalkadiene **5b** is formed for both the 350- and 254-nm irradiations. In contrast, the benzhydrylidene system does not revert, although the error limit of the quantitiative analysis (by ^{1}H NMR) is ca. 1%. Clearly, allylic stabilization (ca. 10 kcal/mol) is more effective than cyclopropylcarbinyl stabilization (ca. 2 kcal/mol) in preventing the diradical rearrangement **7** → **6**. The latter process is essential for retro-di-π-methane reaction. Since thermally equilibrated singlet-state 1,3-diradicals ^{S}(**7**) (generated via thermal denitrogenation of azoalkanes **16**) and the presumably thermally equilibrated triplet-state 1,3-diradicals ^{T}(**7**) do not rearrange to the initial di-π-methane diradical **6**, we speculate that the small degree of retro-di-π-methane reaction in the direct photolysis of azoalkanes **16** is derived from a vibrationally excited ("hot") singlet-state 1,3-diradical ^{S}(**7**)*. The fact that for the parent system **16a** more di-π-methane reversion is observed on 254-nm than on 350-nm irradiation is consistent with this mechanistic speculation.

Although the azoalkanes **16** have provided us with limited mechanistic information concerning the behavior of the diradicals postulated in the di-π-methane rearrangment of bicycloalkadienes **5**, some of the initially posed questions can be answered tentatively: (i) Thermally equilibrated singlet-state (thermolysis) and triplet-state (ketone-sensitized photolysis) 1,3-diradicals **7** do not show retro-di-π-methane reactivity. (ii) Vibrationally excited (hot) singlet-state 1,3-diradicals **7**, generated in the direct photolysis of azoalkanes **16**, do undergo di-π-methane reversion to a small extent, the relative efficiencies being **7a** > **7b** > **7c**. (iii) Excitation of the (π,π*)-benzene chromophore is more effective for retro-di-π-methane reaction than excitation of the (n_-,π*)-azo chromophore. (iv) The more stabilized the 1,3-diradical **7**, i.e., allylic stabilization (**7c**) more efficient than cyclopropylcarbinyl stabilization (**7b**), the more difficult the di-π-methane reversion is.

It is unfortunate that the strained and rigid bicyclo[2.2.1]alkadienes **5**, even the parent system **5a**, are so reluctant to undergo retro-di-π-methane reaction, thereby hiding the mechanistic details of this fascinating photorearrangement. The azoalkanes **20a–c** derived from the more flexible and less strained bicyclo[3.2.1]alkadienes, for which the parent system **19a** shows an appreciable



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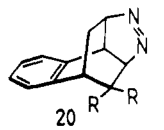
a : R= H
b : R + R = $-CH_2-CH_2-$
c : R + R = $=\!<^{Ph}_{Ph}$



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degree of retro-di-π-methane reactivity,[10] should be more suitable substrates to explore substituent and spin-state effects in the di-π-methane rearrangement. Moreover, since this system undergoes denitrogenation on thermolysis

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[14] (a) Closs, G. L.; Böll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173. (b) Franck-Neumann, M.; Martina, D.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1975**, 1763. (c) Miyashi, T.; Nishizawa, Y.; Sugiyama, T.; Mukai, T. *J. Am. Chem. Soc.* **1977**, *99*, 6109. (d) Nishizawa, Y.; Miyashi, T.; Mukai, T. *Ibid.* **1980**, *100*, 1176. (e) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, 1009. (f) Padwa, A.; Rodriguez, A. *Ibid.* **1981**, 187.

[15] Adam, W.; Cheng, C.-C.; Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1979**, *101*, 1324.

[16] Unfortunately the aziridines **18** are thermally labile at the temperatures (ca. 80 °C) for the thermal generation of acetone triplets from TMD. For this reason it was not possible to perform quantitative product studies.

as well as direct and ketone-sensitized photolysis, entry into the diradical manifold of the di-π-methane reaction is secured via all modes of activation.

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 4 or on a Perkin-Elmer 157G spectrophotometer and ^{1}H NMR spectra on a Hitachi Perkin-Elmer R-24B or on a Varian EM-390 spectrometer. Gas chromatography was carried out on a Perkin-Elmer 990 equipped with flame-ionization detection and using a 6 ft × $^1/_8$ in. stainless-steel column packed with 10% SE-30 on Chromosorb P (detection limit below 0.1%). The elemental analysis were performed by Atlantic Analytical Laboratories or carried out in-house. The solvent and starting materials, the latter either purchased from standard chemical suppliers or prepared according to known literature procedures, were purified to match the reported constants and spectral data, except the acetone and pentane used in the photolysis, which were purchased from Fisher as spectroscopic grade and used without any further purification. A Rayonet photoreactor (Southern New England Ultraviolet Co.) equipped either with 254-, 300-, or 350-nm lamps was used for the photolysis experiments.

Preparation of the Azoalkanes. Azoalkanes **16a–c** were prepared from the corresponding urazoles **15a–c** by following the reported procedure.[10] In our experience, the methyl (R^1 = Me) urazoles **15a–c** gave better yields of the corresponding azoalkanes than the phenyl (R^1 = Ph) derivatives in the oxidative hydrolysis. Urazole **15c** did not give the expected azoalkane **16c** according to the reported procedure (KOH; *i*-ProOH, reflux),[10] and a milder method was developed, which is described below.

2,3-Diaza-5-benzhydrylidene-7,8-benzotricyclo[4.3.0.0^{4,9}]-nona-2,7-diene 16c. A 50-mL, round-bottomed, two-necked flask, equipped with gas inlet and outlet tubes and a magnetic spinbar, was charged with 500 mg (1.19 mmol) of urazole **15c** in ca. 15 mL of Me_2SO, containing a few drops of H_2O, and 4 g of potassium *tert*-butoxide, taken from a freshly opened bottle. Under a slow stream of nitrogen, the reaction mixture was stirred at room temperature (ca. 25 °C) for 24 h, resulting in a thick precipitate. The light brown reaction mixture was poured into 100 mL of ice–water and acidified to pH 1–2 with concentrated HCl. A white precipitate appeared that persisted on neutralization with 2 N NH_4OH and was extracted with ether (2 × 50 mL) and with CH_2Cl_2 (1 × 50 mL). The separate ether and CH_2Cl_2 extracts were washed with brine (2 × 75 mL) and distilled water (1 × 100 mL), combined, and dried over anhydrous Na_2SO_4. After removal of the drying agent and the solvent, the reaction product was dissolved in ca. 20 mL of CH_2Cl_2 and stirred for 1.5 h with a large excess of freshly prepared MnO_2. The solids were removed after filtration, and after rotoevaporation (20 °C, 15 torr) of the solvent, 380 mg (95% yield) of the colorless azoalkane **16c** was obtained: mp 184 °C (with elimination of N_2) on recrystallization from ether; correct elemental composition by combustion analysis; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.42 (1 H, m), 3.57 (1 H, m), 5.43 (1 H, m), 5.62 (1 H, m), 7.03–7.50 (14 H, m); IR (KBr) ν 3030, 3010, 2970, 1590, 1565, 1475, 1450, 1432, 1290, 1205, 1173, 1090, 1070, 1020, 940, 920, 910, 800, 760, 745, 700, 695 cm^{-1}; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 146.76, 142.07, 141.53, 140.40, 139.08, 136.84, 134.96, 129.16, 128.03, 127.87, 127.70, 127.35, 126.84, 123.82, 122.10, 100.93, 81.90, 61.92, 45.59.

Direct Irradiation of 2,3-Diaza-7,8-benzotricyclo-[4.3.0.0^{4,9}]nona-2,7-diene (16a) and 2,3-Diaza-5,5-dimethylene-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (16b). A 10^{-4} M solution of **16a** or **16b** in spectrograde pentane was deoxygenated with nitrogen and placed into a Pyrex (for 350-nm irradiations) or quartz (for 254-nm irradiations) reaction vessel. It was transfered into the Rayonet photoreactor with appropriate lamps and irradiated continuously by maintaining the photolysis temperature below 40 °C by cooling with a fan. The progress of the reaction was monitored by periodic VPC analysis of small aliquots. The photolyses were completed usually within 1 h, when reasonably new lamps were employed. The product compositions (Table I) refer to ca. 5–10% conversion in order to minimize formation of secondary products. While the photoreaction is quite clean on 350-nm irradiation, some secondary products (ca. 5% yield) are formed during the 254-nm irradiation. No efforts were made in identifying these secondary products. In the case of the spiroazoalkane **16b** it was particularly critical to conduct the photodenitrogenations to low conversion (<5%), since the bicycloalkadiene **5b** is particularly prone to di-π-methane rearrangment to the tricycloalkene **8b**. A control experiment showed that during the photolysis conditions no tricycloalkene **8b** had been formed. The identity of the products was confirmed by VPC coinjection and spectral comparison with authentic samples.

Direct Irradiation of 2,3-Diaza-5-benzhydrylidene-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (16c) at 350 nm. An NMR tube was charged with a solution of 54 mg (0.16 mmol) of **16c** in 0.5 mL of $CDCl_3$, deairated with a slow stream of nitrogen gas, and placed into the Rayonet photoreactor, keeping the photolysis temperature between 20 and 40 °C. The progress of the reaction was monitored periodically by ^{1}H NMR. After ca. 1 h of irradiation ca. 90% of the azoalkane **16c** had been consumed, affording a product mixture consisting of ≥99% of cycloalkene **8c** and 1% of bicycloalkadiene **5c**. Control experiments show that the lower limit of detection of **5c** is ≤1%, since a solution of 0.5 mg of **5c** in 0.5 mL of $CDCl_3$ just barely exhibited the characteristic bridgehead protons of **5c** at δ 4.38. Furthermore, **5c** is not converted into the tricycloalkene **8c** under the photolysis conditions.

Direct Irradiation of 2,3-Diaza-5-benzhydrylidene-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (16c) at 254 nm. A sample of 53 mg (0.16 mmol) of **16c** was placed together with 35 mL of purified benzene (not all of the azoalkane **16c** had dissolved, but it solubilized readily during the irradiation) into a quartz vessel and deairated with a slow stream of nitrogen gas. The reaction vessel was transfered into the Rayonet photoreactor and irradiated at 254 nm, while a slow stream of nitrogen gas was passed through. The progress of the reaction was monitored periodically via ^{1}H NMR by rotoevaporation of 10-mL aliquots. After 1.2 h, ca. 90% of the azoalkane **16c** had been consumed. The sample was rotoevaporated (20 °C, 15 torr) and the yellow residue dissolved in 0.5 mL of $CDCl_3$. ^{1}H NMR spectroscopy showed that ca. 80% of tricycloalkene **8c** and other unidentified minor products had been formed. The detection limit of bicycloalkadiene **5c** was established to be ≤1%, but unfortunately **5c** rearranges into the tricycloalkene **8c** under these photolysis conditions.

Benzophenone-Sensitized Irradiation of the Azoalkanes 16a–c. An NMR tube was charged with a solution of 0.4 mmol of azo compound **16a–c** and 4.0 mmol of benzophenone, in 0.5 mL of deuterochloroform in the case of **16c** (this azoalkane is not soluble in hexadeuteriobenzene), and placed into a 12-mm-i.d. Pyrex test tube, containing a filter solution which transmits 300–330-nm radiation and consists of 0.42 g of potassium dichromate and 4.2 g of potassium carbonate in 200 mL of distilled water.[9a] Irradiation was carried out in a Rayonet photoreactor equipped with 300-nm lamps. ^{1}H NMR monitoring showed that after 5 h of irradiation azoalkanes **16a,b** had been converted to the aziridines **18a,b** and **16c** to the tricycloalkenes **8c**. Control experiments showed ≤1% of the tricycloalkenes **8a,b** and bicycloalkadienes **5a–c** should have been detected, had they been formed.

Preparation of 2,3-Diazo-7,8-benzotricyclo[4.3.0.0^{2,9}]-nona-3,7-diene (18a). A Pyrex tube was charged with ca. 15 mL of spectrograde acetone and 70 mg (0.41 mmol) of 2,3-diaza-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (**16a**). The sample was irradiated in a Rayonet photoreactor equipped with 300-nm lamps, while a stream of nitrogen gas was passed through. After 1 h of irradiation at ca. 30 °C, the solvent was rotoevaporated (20 °C, 14 torr), affording a transparent oil which on ^{1}H NMR analysis revealed a product composition consisting of 8% azoalkane **16a**, 28% tricycloalkene **8a**, and 64% of the aziridine **18a**. Two recrystallizations from acetone afforded 40 mg (57% yield) of analytically pure aziridine **18a**: mp over °C dec; correct elemental composition by combustion analysis; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.17 (1 H, $H_{5\text{-endo}}$, A part of AB system split into dd), 2.63 (1 H, $H_{5\text{-exo}}$, B part of AB system split into dd), 3.50 (1 H, H_6, m), 3.60 (1 H, H_1, dd), 3.93 (1 H, H_9, d), 6.95–7.43 (4 H, C_6H_4, m), 7.53 (1 H, H_4, d), $J_{1,6}$ = 6.0 Hz, $J_{1,9}$ = 3.6 Hz, $J_{4,5\text{-endo}}$ = 5.7, $J_{4,5\text{-exo}}$ = 3.6 Hz, $J_{5\text{-endo},5\text{-exo}}$ = 16.8 Hz (geminal coupling), $J_{5\text{-endo},6}$ = 2.4 Hz, $J_{5\text{-exo},6}$ = 1.8 Hz; ^{1}H NMR (C_6H_6–$CDCl_3$, Me_4Si) δ 1.53 (1 H, $H_{5\text{-endo}}$, A part of AB system split into dd), 1.98 (1 H, $H_{5\text{-exo}}$, B part of

AB system split into dd), 2.80 (1 H, H_6, m), 3.12 (1 H, H_1, dd), 3.68 (1 H, H_9, d), 6.52–7.13 (4 H, C_6H_4, m), H_4 is presumably covered by C_6H_6 impurity in the C_6D_6 solvent; coupling constants the same; in the double resonance experiments, irradiation of H_1 turns H_9 into a singlet, but H_6 is too perturbed to observe the expected doublet of doublets from $H_{5\text{-endo}}$ and $H_{5\text{-exo}}$ coupling, irradiation of H_9 turns H_1 into a doublet (H_6 coupling), while irradiation of H_6 simplifies the AB pattern of $H_{5\text{-endo}}$ and $H_{5\text{-exo}}$, and irradiation of H_5 turns H_4 into a singlet and H_6 into a complex doublet; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 156.99 (d), 147.02 (s), 137.27 (s), 127.87 (d), 127.30 (d), 125.84 (d), 123.01 (d), 51.47 (d), 46.96 (d), 33.24 (d), 27.24 (t); IR (KBr) ν 3050, 3035, 3030, 2955, 2921, 1600, 1480, 1460, 1442, 1345, 1330, 1310, 1230, 1200, 1160, 1070, 1005, 935, 920, 790, 780, 712, 670 cm^{-1}.

Preparation of 2,3-Diazo-5,5-dimethylene-7,8-benzotricyclo[4.3.0.0^{2,9}]nona-3,7-diene (18b). A sample of 100 mg (0.51 mmol) of 2,3-diaza-5,5-dimethylene-7,8-benzotricyclo-[4.3.0.0^{4,9}]nona-2,7-diene (**16b**) was dissolved in 12 mL of spectrograde acetone and placed into a Pyrex tube. The reaction vessel was transfered to the Rayonet photoreactor equipped with 300-nm lamps and, while a slow stream of nitrogen gas was passed through, was irradiated at 30 ± 5 °C for 1 h. Rotoevaporation (20 °C, 15 mmHg) of the solvent afforded a colorless oil, which according to ^1H NMR analysis showed a product composition consisting of 10% of azoalkane **16b**, 56% of aziridine **18b**, and 35% of tricycloalkene **8b**. Two recrystallization from acetone/pentane afforded product: 41 mg (41% yield); colorless prisms; mp 133–135 °C; satisfactory elemental composition by combustion analysis for the $C_{13}H_{12}N_2 \cdot H_2O$ empirical formula; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.6–1.3 (4 H, CH_2CH_2, m), 2.65 (1 H, H_6, d, $J_{1,6} = 5.8$ Hz), 3.62 (1 H, H_1, dd), 3.88 (1 H, H_9, d, $J_{1,9} = 3.7$ Hz), 6.90 (1 H, H_4, s), 6.90–7.40 (4 H, C_6H_4, m); IR (KBr) ν 3075, 3060, 3005, 1630, 1600, 1475, 1322, 1310, 1230, 1163, 1040, 990, 962, 770, 760, 700 cm^{-1}.

Vacuum Flash Pyrolyses of Azoalkanes 16a,b. A home-built, simplified model of the Bonnett–Brown–Smith[17] apparatus was used for the vacuum flash pyrolysis (VFP) of the azoalkane **16a,b**. A small sample of the azoalkane **16** was deposited on the walls of the sublimation vessel by slow rotoevaporation (0 °C, 15 torr) from a CH_2Cl_2 solution. The sublimation vessel was connected to the pyrolysis vessel consisting of a 25-cm long and heavy-walled Pyrex tube (12 mm o.d.) which was heated by means of a Nichrome resistance wire to the desired temperature. The outlet of the pyrolysis vessel was connected to a liquid nitrogen cooled trap, which in turn was connected via a three-way stopcock to a vacuum pump. At a vacuum of 0.3 torr, the sublimation vessel was heated at ca. 60 °C to volatilize the azoalkanes **16** into the pyrolysis vessel, which was maintained at ca. 400 °C. After completion of the sublimation, the condensed pyrolysate was recovered from the liquid nitrogen cold trap by dissolving it in CH_2Cl_2. Rotoevaporation (20 °C, 15 torr) of the solvent afforded the product.

Preparation of 2-(4-Pyrazolyl)styrene (17a). A sample of 50 mg (0.29 mmol) of 2,3-diaza-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (**16a**) was processed through the previously described vacuum flash pyrolysis procedure, affording quantitatively the 2-(4-pyrazolyl)styrene product. Recrystallization from CH_2Cl_2/pentane (1:2) gave colorless needles: mp 114 °C; satisfactory elemental composition on combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ 5.10–7.15 (3 H, $CHCH_2$, ABC pattern, $J_{AB} = 1.5$ Hz, $J_{BC} = 10.0$ Hz, $J_{AC} = 16.1$ Hz), 7.65 (2 H, pyrazole, s), 7.1–7.7 (4 H, C_6H_4, m), 10.4 (1 H, NH, br s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 115.34, 120.80, 126.38, 127.08, 127.81, 129.52, 131.23, 133.56, 136.22; IR (KBr) ν 3150, 3080, 2980, 1480, 1380, 1150, 1040, 1000, 960, 920, 875 cm^{-1}. Catalytic hydrogenation of pyrazole **17a** over Pd/C (10%) in ethyl acetate afforded quantitatively the expected ethylbenzene derivative: mp 102.5 °C; colorless needles from CH_2Cl_2/pentane; satisfactory elemental composition on combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ 1.15 (3 H, CH_3, t, $J = 6.7$ Hz), 2.68 (2 H, CH_2, q), 7.15 (4 H, C_6H_4, br s), 7.65 (2 H, pyrazole, br s), 10.00 (1 H, NH, br s); IR (KBr) ν 3140, 2950, 1465, 1455, 1380, 1150, 1040, 960, 875 cm^{-1}.

Thermolysis of 2,3-Diaza-5-benzhydrylidene-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene 16c. A sample of 50 mg (0.15 mmol) of **16c** was heated to its melting point in a Kofler melting point apparatus (Reichert Thermovar). Gas evolution was evident when the temperature approached 175 °C, and denitrogenation was completed within 10 min at 175–180 °C. The product was taken up into sufficient $CDCl_3$, and the ^1H NMR showed that tricyclicoalkene **8c** was formed essentially quantitatively with traces of unreacted azoalkane. No bicycloalkadiene **5c** could be detected (≤1% detection limit).

Acknowledgment is made to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the National Institutes of Health, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support of this work. We thank Dr. M. Balci for measuring and interpreting some of the ^{13}C NMR spectra and Professor Sandros from Gothenburg (Sweden) for determining the fluorescence spectrum of azoalkane **16a**.

Registry No. 5a, 4453-90-1; **5b**, 22003-58-3; **5c**, 28591-78-8; **8a**, 7213-64-1; **8b**, 22003-59-4; **8c**, 28591-80-2; **15a**, 78609-98-0; **15b**, 78609-99-1; **15c**, 78610-00-1; **16a**, 70332-88-6; **16b**, 74045-84-4; **16c**, 78610-01-2; **17a**, 73841-20-0; **18a**, 73834-11-4; **18b**, 78610-02-3.

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(17) Bonnett, R.; Brown, R. F. C.; Smith, R. G. *J. Chem. Soc., Perkin Trans. 1*, 1973, 1432.