Acknowledgment. We are grateful to the Swedish Board of Technical Development and the Swedish Natural Science Research Council for financial support and to Thomas Antonsson for performing the syntheses of **18** and **19** during his undergraduate work. We also thank Dr. B. Nilsson (Chemical Center, Lund, Sweden) for a gift of ethyl (*E*)-4,6-heptadienoate.

Registry No. (*E*)-**1**, 34414-28-3; (*Z*)-**1**, 55613-61-1; **1′**, 96039-67-7; (*E*)-**2**, 24529-80-4; (*Z*)-**2**, 24529-81-5; **2′**, 38872-51-4; (*E*)-**3**, 53060-20-1; (*Z*)-**3**, 95177-48-3; **3′**, 96039-68-8; (*E*)-**4**, 76355-81-2; (*Z*)-**4**, 96039-69-9; **5a**, 82736-36-5; **5b**, 82736-37-6; **6a**, 96039-70-2; **6b**, 96039-71-3; **6′**, 96039-72-4; **7a**, 96039-73-5; **7b**, 96039-74-6; **7′**, 96039-75-7; (*R*,R**)-**10**, 95177-49-4; (*R*,S**)-**10**, 95177-50-7; *cis*-**11**, 82736-39-8; *trans*-**11**, 96039-76-8; *cis*-**12**, 96039-77-9; *trans*-**12**, 96039-78-0; **13**, 96039-79-1; α-CH_3-**13**, 96039-80-4; α-CH_3-**14**, 96039-81-5; β-CH_3-**14**, 96039-82-6; **15**, 82736-40-1; **16**, 96039-83-7; **17**, 96039-84-8; **17′**, 96039-85-9; **18**, 96039-86-0; **19**, 96094-31-4; **20**, 58511-44-7; **20′**, 96039-87-1; (*R*,R**)-**21a**, 96039-88-2; (*R*,S**)-**21a**, 96039-89-3; (*R*,R**)-**21c**, 96039-90-6; (*R*,S**)-**21c**, 96039-91-7; (*R*,R**)-**21d**, 95177-61-0; (*R*,S**)-**21d**, 95177-63-2; **22** (R^1 = CH_3; R^2 = H), 53588-14-0; (*E*)-**22a**, 95177-57-4; (*Z*)-**22a**, 95177-58-5; (*E*)-**22b**, 59830-31-8; (*Z*)-**22b**, 89345-64-2; (*E*)-**22c**, 95177-59-6; (*Z*)-**22c**, 95177-60-9; (*E*)-**34**, 3780-51-6; (*Z*)-**34**, 96039-92-8; **35**, 96039-93-9; **36** (R^1 = CH_3; R^2 = H), 96055-48-0; **36a**, 95199-57-8; **36b**, 95199-58-9; **36c**, 95199-59-0; $Pd(PPh_3)_4$, 14221-01-3; $Pd(PhCN)_2Cl_2$, 14220-64-5; CH_2=CHCH=CH_2, 106-99-0; PPh_3, 603-35-0; $Pd(OAc)_2$, 3375-31-3; LiCl, 7447-41-8; LiOAc, 546-89-4; CH_2=$C(CH_3)C(CH_3)$=CH_2, 513-81-5; (*E*)-CH_2=$C(CH_3)CH$=$CHCH_3$, 926-54-5; (*E*)-CH_2=CHCH=$CH(CH_2)_2$Ph, 77605-16-4; (*E*)-CH_2=CHCH=$CH(CH_2)_2$COOEt, 71779-51-6; (*E,Z*)-CH_3CH=CHCH=$CHCH_3$, 5194-50-3; (*E,E*)-CH_3CH=CHCH=$CHCH_3$, 5194-51-4; CH_2=$C(CH_3)CH$=CH_2, 78-79-5; (*Z*)-CH_2=CHCH=$CHCH_3$, 1574-41-0; (*E*)-CH_2=CHCH=$CHCH_3$, 2004-70-8; $Pd(acac)_2$, 14024-61-4; Me_2NH, 124-40-3; Et_2NH, 109-89-7; $CH_2(COOMe)_2$, 108-59-8; $PhSO_2Na$, 873-55-2; 6-acetoxy-1,3-cycloheptadiene, 29207-42-9; 6-hydroxy-1,3-cycloheptadiene, 1121-63-7; 1,3-cyclohexadiene, 592-57-4; 2-methyl-1,3-cyclohexadiene, 1489-57-2; 6-methyl-4a,5,8,8a-tetrahydro-5,8-ethano-1,4-naphthoquinone, 96039-94-0; 5-methyl-1,3-cyclohexadiene, 19656-98-5; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; dimethyl (*cis*-4-acetoxy-2-cyclohexenyl)malonate, 82736-52-5; dimethyl (*trans*-4-acetoxy-2-cyclohexenyl)malonate, 82736-53-6.

Supplementary Material Available: Experimental data on compounds **22** and **36** (2 pages). Ordering information given on any current masthead page.

Synthesis, Thermolysis, and Photolysis of the Azoalkane 4,5-Diazatricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene: Denitrogenation vs. Azirane Formation

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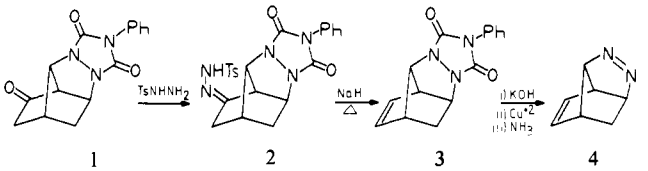
Contribution from the Institute of Organic Chemistry, University of Würzburg, D-8700 Würzburg, West Germany. *Received August 6, 1984*

Abstract: The azoalkane 4,5-diazatricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene (**4**) was prepared by reaction of the keto urazole **1** with *p*-toluenesulfonohydrazide, treatment of the hydrazone with sodium hydride, which lead to the corresponding urazole **3**, and subsequent oxidative hydrolysis. Thermolysis of the azoalkane **4** gave mainly (ca. 95%) the retro-Diels–Alder product (*Z*)-pyrazole **7**, which isomerized to the (*E*)-pyrazole **7** and the dihydroindazole **8**. To a small extent (5%) the 1- and 2-vinylcyclopentadienes were produced, presumably via thermolysis of the tricyclo[3.2.0.$0^{2,7}$]hept-3-ene (**5**). In the direct photolysis the tricycloalkene **5** and the azirane **6** were formed in the ratio of ca. 1:1, together with traces of quadricyclane, whereas in the benzophenone-sensitized photolysis the azirane **6** was obtained exclusively. In terms of a Salem diagram it is proposed that in the $^{1,3}n,\pi^*$-excited azoalkane C–C bond cleavage occurs leading to a doubly allyl-stabilized $D_{\pi,\pi}$ diradical, which subsequently cyclizes into the azirane **6**. In the direct photolysis competitive C–N bond cleavage is observed, leading almost exclusively to the tricycloalkene **5** and a little quadricyclane, but no norbornadiene. The 1,3-diradical **12** serves as immediate precursor to the tricycle **5**.

A recent paper[1] on the unusual valence isomerization of perfluoronorbornadiene, involving a thermal di-π-methane rearrangement of quadricyclane into tricyclo[3.2.0.$0^{2,7}$]hept-3-ene presumably via the 1,3-diradical bicyclo[2.2.1]hept-5-ene-2,7-diyl, prompts us to report our results on the latter parent species, generated in the thermolysis and photolysis of 4,5-diazatricyclo-[4.3.0.$0^{3,7}$]nona-4,8-diene (**4**). The synthesis of this new azoalkane commenced with the known keto urazole **1**[2] (eq 1); its details and spectral data are given in the Experimental Section.



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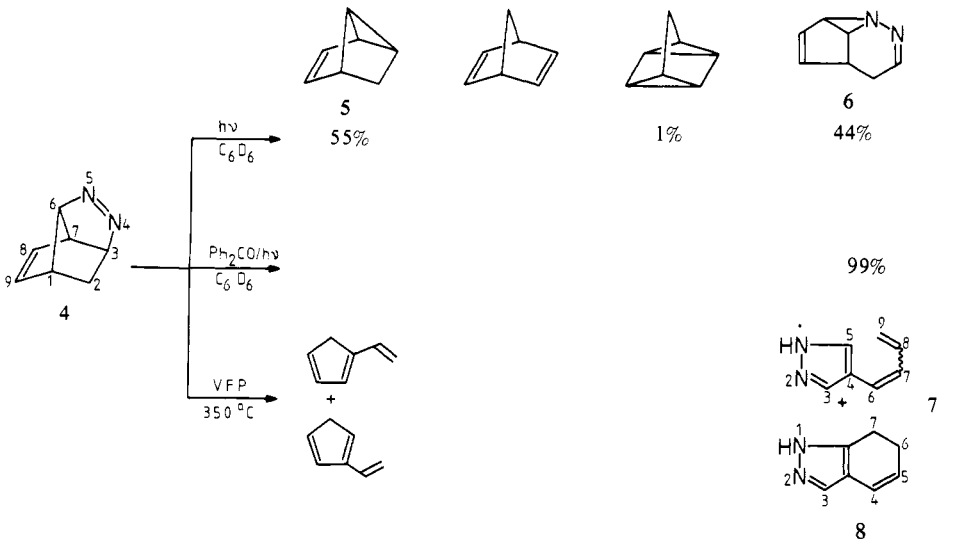
† Doctoral Dissertation, University of Würzburg, West Germany, July 1984.

The products of the thermal (vacuum flash pyrolysis or VFP at 350 °C and 20 torr) and direct photochemical (irradiation with the 334-, 351-, and 364-nm lines of an argon ion laser in C_6D_6 or CD_3CN) and triplet sensitized reactions (0.45 M benzophenone in C_6D_6, irradiating only with the 364-nm line of an argon ion laser) are given in Scheme I. The product yields were determined by quantitative ^1H NMR (400 MHz) and/or capillary GC (50-m Carbowax 20 M; injector, column, and detector temperatures of 80, 60 and 120 °C; nitrogen carrier gas pressure 0.25–0.30 kg/cm^2). Product balance was better than 75%, remainder being intractable high-molecular-weight material. The retention times and spectral data of the known volatile products tricycloalkene **5**,[3] norbornadiene, quadricyclane, and mixture of vinylcyclopentadienes[4] were identical with authentic compounds. The

(1) Dailey, W. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1169.
(2) Adam, W.; De Lucchi, O.; Hill, K. *J. Am. Chem. Soc.* **1982**, *104*, 2934.
(3) (a) Story, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 3347. (b) Brown, H. C.; Bell, H. M. *J. Am. Chem. Soc.* **1963**, *85*, 2324. (c) Franzus, B.; Snyder, E. I. *J. Am. Chem. Soc.* **1963**, *85*, 3902.

0002-7863/85/1507-3686$01.50/0

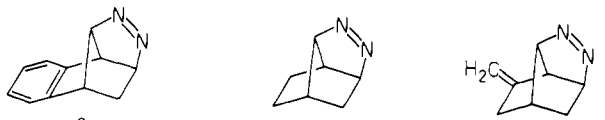
Scheme I



hitherto unknown azirane **6**, the pyrazole **7** (*Z*,*E* mixture), and the dihydroindazole **8** were fully characterized (cf. Experimental Section). Catalytic hydrogenation (Pd/C) afforded the known 3-*n*-butylpyrazole[5] and tetrahydroindazole.[6]

Control experiments on authentic materials showed that the tricycloalkene **5**, norbornadiene, and quadricyclane were stable toward the laser photolysis conditions. Not even traces of diazoalkanes could be detected by IR or UV–vis under the photolysis conditions.[7] Nor did the direct photolysis in the presence of 1,3-pentadiene (triplet quencher) lead to alteration of the production composition. Apparently intersystem crossing ($^1n,\pi^* \rightarrow {}^3n,\pi^*$) is inefficient for the azoalkane **4**. Under the VFP conditions the tricycloalkene **5** was quantitatively converted into the mixture of vinylcyclopentadienes. When the pyrolysis temperature was raised from 350 to 400 °C, the ratio of pyrazole to dihydroindazole changed from ca. 2:1 to 1:2. This latter finding implicates that the initially formed (*Z*)-pyrazole **7** cyclizes into the dihydroindazole **8** in competition with its isomerization into the (*E*)-pyrazole **7**.

The present product picture is quite similar to the benzo derivative **9** of the azoalkane **4**,[8] except that in the thermolysis some



(ca. 5%) denitrogenation into tricycloalkane **5** (detected as mixture of vinylcyclopentadienes under the VFP conditions) and in the direct photolysis nearly equal amounts of denitrogenation into tricycloalkene **5** and rearrangement into azirane **6** occurred. Mechanistically more significant, the saturated analogue **10** gave on thermolysis essentially exclusively the corresponding pyrazole, but the direct and triplet-sensitized photolyses gave only denitrogenated products with no traces of the respective azirane **6**.[5] Consequently, the double bond in the azoalkane **4** is essential in this case for azirane **6** formation. A concerted photochemical 1,3-sigmatropic shift is presumably unlikely,[9] especially since the

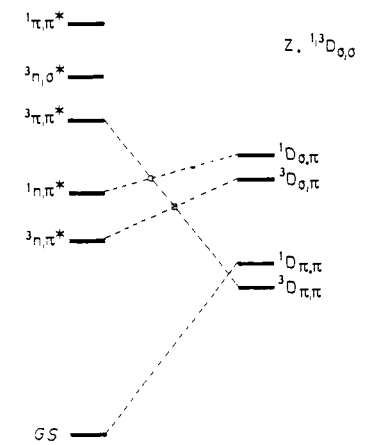
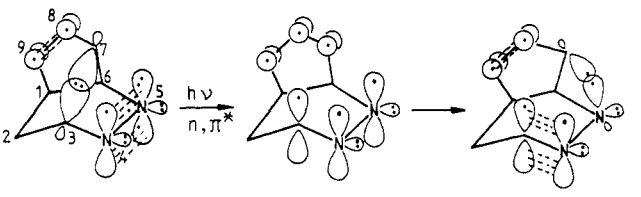


Figure 1. Salem diagram for the formation of the $D_{\pi,\pi}$ diradical in the photorearrangement of azoalkane **4** into azirane **6**.

4 → **6** rearrangement is triplet-state derived. We postulate that the triplet $^3D_{\pi,\pi}$ diradical is the precursor to the azirane **6** product (eq 2), in which both radical sites are allyl stabilized.



(2)

Inspection of molecular models shows that the $C_9{=}C_8C_7C_3{-}N_4{=}N_5$ fragment (hetero-Cope system) is optimally aligned to give on C_3–C_7 cleavage the allyl-stabilized $D_{\pi,\pi}$ diradical. With minor conformational adjustments, the latter is predestined for N_5–C_7 bonding to give azirane **6** (eq 2). In fact, besides the helpful polarization factor of the nitrogen center, rotation of the 2p lobes at N_5 and C_7 should promote efficient spin–orbital coupling during N_5–C_7 bond formation, converting the triplet $^3D_{\pi,\pi}$ diradical into azirane **6**.[10]

A problem with this hypothesis is that n,π* excitation, the most likely accessible excited state in the long-wavelength ($\lambda > 300$ nm) photochemistry of azoalkanes,[11] will lead either to an excited

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(5) Adam, W.; Carballeira, N.; De Lucchi, O. *J. Am. Chem. Soc.* **1981**, *103*, 6406.
(6) (a) von Auwers, K.; Buschmann, W.; Heidenreich, R. *Liebigs Ann. Chem.* **1923**, *435*, 277. (b) Wallach, O. *Liebigs Ann. Chem.* **1903**, *329*, 109.
(7) (a) Adam, W.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473. (b) Adam, W.; Carballeira, N.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473.
(8) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133.
(9) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333.
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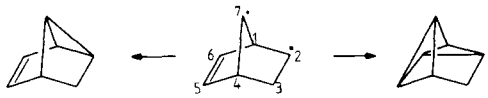
(11) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

state of the $^{1,3}D_{\pi,\pi}$ diradical (four electrons in the π-system and three in the lone pairs of the $C_3N_4{=}N_5$ moiety) or to a conformationally prohibited $^{1,3}D_{\sigma,\pi}$ diradical. However, a Salem diagram[12] (Fig. 1) provides some insight into this problem. As can be seen, the triplet as well as singlet $^{1,3}n,\pi^*$ states of the azoalkane **4** intersect with the energy surface which connects the $^3\pi,\pi^*$ triplet state of the azoalkane **4** with the $^3D_{\pi,\pi}$ diradical state. Forbidden surface crossing for these triplet states obliges the $^3n,\pi^*$ triplet excited state to become the $^3D_{\pi,\pi}$ diradical state, which under spin inversion leads to the azirane product. The $^1n,\pi^*$ singlet excited state, on the other hand, must first intersystem cross near the intersection with the $^3\pi,\pi^*$–$^3D_{\pi,\pi}$ energy surface. This additional energy barrier for spin inversion and the fact that apparently the $^1n,\pi^*$ into $^1D_{\sigma,\pi}$ transformation is energywise uphill are responsible either for decay to its ground state or selecting a different chemical channel.[13]

Denitrogenation is presumably this photochemical alternative in the direct photolysis of azoalkane **4** (Scheme I), leading to the tricycloalkene **5** (55%) and quadricyclane (1%). Although the exomethylenic azoalkane derivative **11** entails a far more efficient example for this mode of reaction,[14] suffice it to say at this point for the azoalkane **4** that the di-π-methane-type 1,3-diradical **12** is the likely immediate precursor to these denitrogenation products (eq 3). Thus, bonding between C_2 and C_7 in the 1,3-diradical



(3)

5 12

12 gives tricycloalkene **5**, while simultaneous bonding between C_2 and C_6 and between C_7 and C_5 leads to quadricyclane. Although this novel quadricyclane route is indistinguishable in its skeletal connectivity with quadricyclane resulting from photochemical (2 + 2) cycloaddition of norbornadiene, this hitherto unrecognized di-π-methane mode involving the 1,3-diradical **12** cannot be important in the norbornadiene–quadricyclane transformation. Were it so, then significant amounts of tricycloalkene **5** should be formed in the latter process.[15] In actual fact (Scheme I), the 1,3-diradical **12**, which is formed via denitrogenation of azoalkane **4**, preferentially cyclizes into the tricycloalkene **5** (55%) than rearranging into quadricyclane (1%). Consequently, the interesting perfluoronorbornadiene valence isomerization[1] is unusual and not related to the parent system.

Experimental Section

Methods: UV spectra, Varian Cary 17; IR spectra, Beckman Acculab 4; ^1H NMR, Hitachi–Perkin-Elmer R-24B (60 MHz), Varian EM-390 (90 MHz), Bruker WM-400 (400 MHz); ^{13}C NMR, Bruker WM-400 (100 MHz); chemical shifts in δ, relative to tetramethylsilane (Me_4Si) or chloroform for protons and deuterochloroform for carbons; mass spectra (MS), Varian CH-7; melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected; combustion analysis for elemental composition were run in-house or by Professor G. Maier's staff at the Institute of Organic Chemistry, University of Giessen; thin-layer chromatography (TLC), Polygram SIL/G/UV (40 × 80 mm), Machery & Nagel; column chromatography, silica gel 70–230 mesh ASTM (activity III); preparative layer chromatography, Chromatotron Model 7924, Harrison Research, equipped with a glass disc with a 1-mm layer of silica gel 60 PF 254 from Merck; analytical gas chromatography, Carlo Erba Strumentazione Model 2900 Fractovap Series or Model 4100, equipped with capillary columns and FI detector; preparative gas chromatography, Varian Aerograph 920 or Carlo Erba Model 4200; the photolyses were run in a Rayonet Photochemical Reactor (75 W, 250 V), Southern New England Ultraviolet Co., equipped with 350- and 300-nm lamps, respectively, or in a Coherent CR-18 Supergraphite Argon Ion Laser, using the 334-, 351-, and 364-nm lines.

Materials. Commercial reagents and solvents were purchased from standard chemical suppliers and used as such, if not mentioned otherwise. Benzene as solvent in the photolysis experiments was purified by azeotropic destillation, refluxing over sodium wire, and final destillation. Known compounds were prepared according to literature procedures. Volatile liquids were purified by preparative gas chromatography before combustion and MS analysis. Reaction mixtures after aqueous workup were dried over $MgSO_4$ or Na_2SO_4.

***N*-Phenyl-8-[(*p*-tolylsulfonyl)hydrazono]-4,5-diazatricyclo[4.3.0.0^{3,7}]-nonan-4,5-dicarboximide (2).** To a hot solution of 2.70 g (14.5 mmol) of *p*-toluenesulfonohydrazide in 450 mL of ethanol was added 3.50 g (12.4 mmol) of the urazole **1**.[2] The reaction mixture was refluxed for 5 h. After cooling to ca. 20 °C, the white precipitate was collected on a Büchner funnel, washed with ethanol, and dried to yield 4.80 g (86%) of a white solid, mp 259 °C dec. The hydrazone is insoluble in chlorinated solvents and only a little soluble in pyridine or Me_2SO. IR (KBr) 3200, 1785, 1725, 1600, 1500, 1400, 1335, 1170, 710, 680 cm^{-1}; ^1H NMR (Me_2SO-d_6, 90 MHz) δ 1.2–2.0 (m, 2 H, 2-H), 2.4 (s, 3 H, CH_3) 4.6 (m, 2 H, 3-H, 6-H), pseudo-AB (δ_A 7.40, δ_B 7.77, J = 7.8 Hz, 4 H), 7.50 (br s, 5 H), the bridgehead protons 1-H and 7-H and the 9-H's are covered by the solvent signals; MS (70 eV), *m/e* 423 (1%, $M^+ - N_2$), 296 (6), 267 (31), 246 (4), 148 (16), 119 (54), 105 (19), 91 (100), 78 (50), 65 (44). Anal. Calcd for $C_{22}H_{21}N_5O_4S$ (451.5): C, 58.58; H, 4.69; N, 15.51. Found: C, 58.76; H, 4.62; N, 15.43.

***N*-Phenyl-4,5-diazatricyclo[4.3.0.0^{3,7}]non-8-en-4,5-dicarboximide (3).** A suspension of 4.80 g (10.6 mmol) of the hydrazone **2** in 550 mL of dry toluene was heated to reflux under nitrogen atmosphere and 12.0 g (400 mmol) of sodium hydride (80% dispersion in mineral oil) was added. After 7 h of reflux the mixture was cooled to ca. 20 °C and 200 mL of water was carefully added. The organic layer was separated and washed with water (2 × 100 mL). The combined aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were dried and concentrated by rotoevaporation at 80 °C and 25 torr. Column chromatography (ca. 15:1 ratio of adsorbant to substrate) with a 20:1 ratio of CH_2Cl_2/EtOAc as eluent yielded 1.08 g (39%) of a white solid, which was recrystallized in ethanol, mp 179–181 °C, colorless prisms: IR (KBr) 3050, 2980, 2950, 1780, 1720, 1505, 1420, 1260, 1140, 1080, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.38 (ddd, $J_{2n,2x}$ = 12.5, $J_{2n,3}$ = 5.0, $J_{2n,6}$ = 1.6 Hz, 1 H, 2-*endo*-H), 1.91 (dd, $J_{2x,1}$ = 5.2 Hz, 1 H, 2-exo-H), 3.24 (m, 2 H, 1-H, 7-H), 4.44 (m, 2 H, 3-H, 6-H), 5.93 (ddd, $J_{8,9}$ = 6.2, $J_{8,7}$ = 4.3, $J_{8,1}$ = 1.4 Hz, 1 H, 8-H), 6.36 (ddd, $J_{9,1}$ = 4.2, $J_{9,7}$ = 1.0 Hz, 1 H, 9-H), 7.35–7.51 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.30 (t), 44.71 (d), 52.30 (d), 56.99 (d), 77.46 (d), 125.42 (d), 126.97 (d), 128.30 (d), 129.18 (d), 131.70 (s), 139.66 (d), 156.17 (s), 156.24 (s); MS (70 eV), *m/e* 267 (78%, M^+), 148 (38), 119 (79), 105 (47), 91 (100), 78 (89), 65 (33), 51 (15), 39 (28). Anal. Calcd for $C_{15}H_{13}N_3O_2$ (267.3): C, 67.42; H, 4.90; N, 15.72. Found: C, 67.56; H, 4.68; N, 15.64.

4,5-Diazatricyclo[4.3.0.0^{3,7}]nona-4,8-diene (4). A sample of 1.08 g (4.04 mmol) of the urazole **3** was added to a solution of 2.14 g (38.1 mmol) of potassium hydroxide in 30 mL of isopropyl alcohol and refluxed under nitrogen for 14 h. The reaction mixture was diluted with ca. 20 mL of ice water and concentrated HCl was added to adjust the pH ~1–2. After warming up to 50 °C for ca. 4 min, the mixture was cooled to ca 5 °C with an ice bath and neutralized with 6 M NH_3 to pH ~7–8, and 10 mL of a saturated copper(II) chloride solution was added. The color of the reaction mixture turned dark red and within ca. 20 min a red-brown solid precipitated. Precipitation was complete when the supernatent solution was green. The solid was collected on a Büchner funnel, washed with ca. 30 mL of water, and dissolved in 130 mL of aqueous 2 N NH_3. The blue solution was extracted with CH_2Cl_2 (4 × 50 mL); the combined organic layers were washed with 2 N HCl (3 × 40 mL) and water (2 × 30 mL), dried, and concentrated by rotoevaporation at 0 °C and 22 torr. The crude product was purified by bulb-to-bulb destillation (140 °C at 25 torr) to yield 375 mg (77%) of a colorless oil: IR (GC–FTIR)[16] 3078, 3013, 1493, 1330, 1269, 1211, 914, 845 cm^{-1}; UV (benzene) λ_{max} (log ϵ) 356 (2.77); ^1H NMR ($CDCl_3$, 400 MHz)[17] δ 1.01 (dd, $J_{2x,2n}$ = 12.2, $J_{2x,1}$ = 5.5 Hz, 1 H, 2-exo-H), 1.23 (dd, $J_{2n,3}$ = 4.7 Hz, 1 H, 2-endo-H), 2.39 (mc, $J_{1,9}$ = 3.0, $J_{1,6}$ = 2.6, $J_{1,7}$ = 1.2, $J_{1,8}$ = 1.1 Hz, 1 H, 1-H), 2.98 (m, $J_{7,8}$ = 3.1, $J_{7,6}$ = 2.4, $J_{7,3}$ = 2.2, $J_{7,9}$ = 0.8 Hz, 1 H, 7-H), 4.70 (ddd, $J_{3,6}$ = 0.7 Hz, 1 H, 3-H), 5.15

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(13) If the $^3\pi,\pi^*$ state is of sufficiently low energy so that it mixes into the $^3n,\pi^*$ state, the alternative is likely that the $^3D_{\pi,\pi}$ diradical is produced directly by excitation of the azoalkane **4** above $\lambda > 300$ nm.
(14) Adam, W.; Hill, K., unpublished results.
(15) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388.
(16) We thank Dr. H. A. Witek and his staff, Bio-Rad Laboratories, Section Digilab, München, for running the IT-IR spectrum.
(17) (a) Chemical shifts and coupling constants were determined by computer simulation with the LAOCOON III program;[17b] although a *Z,E* mixture was in hand, it was possible to assign the distinct proton resonances to the individual isomers. (b) Bothner-By, A. A.; Castellano, S. In "Computer Programs for Chemistry"; DeTar, D. F., Ed. A. W. Benjamin: New York, 1968; Vol. 1.

(pseudo-t, 1 H, 6-H), 5.57 (ddd, $J_{8,9}$ = 5.8 Hz, 1 H, 8-H), 6.11 (ddd, 1 H, 9-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.10 (t, C-2), 35.55 (d, C-1), 60.84 (d, C-7), 72.90 (d, C-3), 98.46 (d, C-6), 126.18 (d, C-9), 134.21 (d, C-8); MS (70 eV), *m/e* 120 (21%, M^+), 119 (38), 92 (41), 91 (100), 66 (45), 65 (38), 51 (14), 39 (56). Anal. Calcd for $C_7H_8N_2$ (120.1): C, 69.97; H, 6.71; N, 23.31. Found: C, 69.84; H, 6.58; N, 23.29.

Vacuum Flash Thermolysis of Azoalkane 4. A sample of 75.0 mg (0.624 mmol) of the azoalkane **4** was pyrolyzed by subliming it at ca. 120 °C and 28 torr through a hot tube, consisting of Pyrex glass (35 cm long, ϕ = 1.3 cm), which was externally heated at 350 or 400 °C by means of a resistance wire. The volatile products were condensed onto a cold finger, kept at liquid nitrogen temperature, although most of the pyrolysate collected already at the exit of the hot tube. After flushing the apparatus with nitrogen and warmup to ca. 15 °C, the products were recovered from the pyrolysis apparatus by dissolving them in $CDCl_3$. On solvent removal 70.0 mg (93%) of material was obtained, consisting of at least two products in a ca. 2:1 ratio (at a pyrolysis temperature of 400 °C the ratio was ca. 1:2), as was shown by ^{1}H NMR and TLC analysis. On dissolution of the product mixture, a white solid precipitated within a few minutes, indicating fast formation of high-molecular-weight material. Separation of the pyrolysate was performed on the Chromatotron, eluting with a 20:1 mixture of CH_2Cl_2/EtOAc. Fraction 1 consisted of 25 mg (33%) of the pyrazoles **7**, which were recrystallized from *n*-hexane, mp 86–88 °C, colorless plates. The second fraction, ca. 16 mg (22%), consisted of a mixture of the two pyrazoles **7** and the dihydroindazole **8**. The third fraction, ca. 8 mg (11%), was pure dihydroindazole **8**, obtained as colorless oil that did not crystallize.

(*Z*,*E*)-4-(1,3-Butadienyl)-1*H*-pyrazole (7) IR (KBr) 3200, 3100, 3040, 2980, 1640, 1630, 1390, 995, 895, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) (*Z* isomer)[17] δ 5.43 (d of m, $J_{9t,8}$ = M, $J_{9t,9c}$ = 2.0, $J_{9t,6}$ = 1.4, $J_{9t,7}$ = 0.8 Hz; 1 H, 9-*trans*-H), 5.36 (d of m, $J_{9c,8}$ = 16.8, $J_{9c,6}$ = 1.0, $J_{9c,7}$ = 0.8 Hz, 1 H, 9-*cis*-H), 6.15 (pseudo-t, $J_{7,6}$ = 1.5, $J_{7,8}$ = 10.9 Hz, 1 H, 7-H), 6.26 (br d, $J_{6,8}$ = 1.0, 1 H, 6-H), 6.90 (mc, 1 H, 8-H), 7.67 (s, 2 H, 3-H, 5-H), 11.41 (br s, 1 H, 1-H); ^{1}H NMR ($CDCl_3$, 400 MHz) (*E* isomer)[17] δ 5.10 (d of m, $J_{9t,8}$ = 10.2, $J_{9t,9c}$ = 1.6, $J_{9t,6}$ = 0.6, $J_{9t,7}$ = 0.5 Hz, 1 H, 9-trans-H), 5.25 (d, of m, $J_{9c,8}$ = 17.1, $J_{9c,6}$ = 1.1, $J_{9c,7}$ = 0.5 Hz, 1 H, 9-cis-H), 6.45 (d of psuedo-*t*, $J_{8,7}$ = 10.4 Hz, 1 H, 8-H), 6.46 (d, $J_{6,7}$ = 15.9 Hz, 1 H, 6-H), 6.57 (dd, 1 H, 7-H), 7.67 (s, 2 H, 3-H, 5-H), 11.41 (br s, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 116.01 (t), 118.51 (s), 118.68 (t), 119.77 (d), 120.16 (s), 122.47 (d), 128.80 (d), 131.80 (br.d), 133.37 (d), 133.57 (br d), 137.17 (d); MS (70 eV), *m/e* 120 (48%, M^+), 119 (100), 92 (41), 65 (30), 39 (36). Anal. Calcd for $C_7H_8N_2$ (120.1): C, 69.97; H, 6.71; N, 23.31. Found: C, 69.86; H, 6.43; N, 23.66.

6,7-Dihydro-1*H*-indazole (8): ^{1}H NMR ($CDCl_3$, 400 MHz)[17] δ 2.46 (mc, $J_{6,7}$ = 8.5, $J'_{6,7}$ = 8.5, $J_{6,5}$ = 4.4, $J_{6,4}$ = 1.8 Hz, 2 H, 6-H), 2.84 (pseudo-t, 2 H, 7-H), 5.75 (dt, $J_{5,4}$ = 9.5 Hz, 1 H, 5-H), 6.43 (dt, 1 H, 4-H), 7.30 (s, 1 H, 3-H), 1-H could not be detected.

Reduction of the Pyrolysate from the Thermolysis of Azoalkane 4. To a solution of 15.0 mg (0.124 mmol) of a ca. 1:2 mixture of the pyrazoles **7** and the indazole **8** in 5 mL of EtOAc was added ca. 1 mg of 20% palladium on charcoal and the mixture was stirred for 2 h under a hydrogen atmosphere. Filtration to remove catalyst and solvent rotoevaporation (50 °C at 25 torr) yielded a colorless oil, which contained two products of a ca. 1:2 ratio, as shown by GC. Separation was performed by preparative GC, using a 1.5-m glass column, packed with 10% Carbowax M on Chromosorb WHP, operated at injector, detector, and column temperatures of 200 °C and a carrier gas pressure (N_2) of 2.0 kg/cm^2. Fraction 1 (t_R 1740 s) contained the 4-(*n*-butyl)-1*H*-pyrazole as the minor product, as confirmed by comparison with the literature data.[6] Fraction 2 (t_R 3300 s) contained the 4,5,6,7-tetrahydro-1*H*-indazole as main product, which was identical (t_R and ^{1}H NMR) with an authentic sample prepared below.

4,5,6,7-Tetrahydro-1*H*-indazole, 298 mg (89%), colorless solid, mp 83–84 °C from *n*-hexane (lit.[6] 57–59 °C from methanol), was prepared following the reported procedure[6] starting from 500 mg (2.73 mmol) 2-formylcyclohexane semicarbazone: IR (KBr) 3210, 3160, 3100, 3080, 3000, 2930, 2850, 1450, 1355, 1340, 975 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.78 (mc, 4 H, 5-H, 6-H), 2.60 (mc, 4 H, 4-H, 7-H), 7.32 (s, 1 H, 3-H), 11.61 (br s, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.53 (t), 22.13 (t), 23.25 (t), 23.70 (t, C-4, C-5, C-6, C-7), 114.97 (s, C-3a), 131.84 (d, C-3), 143.23 (s, C-7a); MS (70 eV), *m/e* 122 (42%, M^+), 94 (100), 81 (5), 67 (9), 52 (6), 41 (10), 39 (14).

Direct Laser Photolysis of the Azoalkane 4. A solution of 40.0 mg (0.333 mmol) of the azoalkane **4** in ca. 0.5 mL of C_6D_6 was deaerated by three freeze–pump–thaw cycles and irradiated in a sealed NMR tube with the 334-, 351-, and 364-nm lines of the argon ion laser at ca. 5 °C. The reaction progress was monitored by ^{1}H NMR and after ca. 20 min the azoalkane was consumed. A 400-MHz ^{1}H NMR spectrum of the crude photolysis mixture indicated the formation of the two tricyclic compounds **5** and **6** and quadricyclane. The mass balance was determined by 90-MHz ^{1}H NMR, using benzene as an internal standard. The product distribution is given in Scheme I. A solution of the tricycloheptene **5** in C_6D_6 was obtained by distilling the photolysate at ca. 30 °C and 17 torr. The 60-MHz ^{1}H NMR spectrum was in accord with literature data.[3] Bulb-to-bulb destillation at 70 °C and 0.1 torr of the residue yielded the azirane **6** as a colorless oil, which on standing in air quickly deteriorated. It was, therefore, not possible to obtain a satisfactory elemental analysis by combustion.

Tricyclo[3.2.0.0^{2,7}]hept-3-ene (5): ^{1}H NMR (C_6D_6, 400 MHz) δ 0.56 (dd, $J_{6n,6x}$ = 8.3, $J_{6n,1}$ = 2.4, $J_{6n,3} \simeq$ 0.5 Hz, 1 H, 6-endo-H), 1.58 (mc, $J_{7,2}$ = 5.0, $J_{7,1}$ = 4.0, $J_{7,6x}$ = 2.8, $J_{7,5} \simeq$ 2.5 Hz, 1 H, 7-H), 1.93 (mc, $J_{2,1}$ = 5.2, $J_{2,3}$ = 2.1, $J_{2,4}$ = 1.1 Hz, 1 H, 2-H), 2.41 (ddd, $J_{6x,5}$ = 6.9 Hz, 1 H, 6-exo-H), 2.59–2.65 (m, $J_{1,5} \simeq$ 2.7 Hz, 2 H, 1-H, 5-H), 5.78 (ddd, $J_{4,3}$ = 5.3, $J_{4,5}$ = 2.8 Hz, 1 H, 4-H), 5.96 (d of m, $J_{3,5}$ = 1.1 Hz, 1 H, 3-H); ^{13}C NMR (C_6D_6, 100 MHz) δ 17.59 (C-7), 28.57 (C-6), 29.45 (C-2), 43.25 (C-5), 43.41 (C-1), 124.78 (C-3), 133.64 (C-4).

2,3-Diazatricyclo[4.3.0.0^{2,9}]nona-3,7-diene (6): ^{1}H NMR (C_6D_6, 400 MHz) δ 1.10 (ddd, $J_{5n,5x}$ = 16.8, $J_{5n,4}$ = 5.6, $J_{5n,6}$ = 2.5 Hz, 1 H, 5-endo-H), 1.77 (ddd, $J_{5x,6}$ = 4.0, $J_{5x,4}$ = 1.7 Hz, 1 H, 5-exo-H), 2.23 (mc, $J_{6,1}$ = 6.3, $J_{6,7}$ = 1.9, $J_{6,8} \simeq J_{6,4} \simeq$ 1.0 Hz, 1 H, 6-H), 2.95 (ddd, $J_{1,9}$ = 3.9, $J_{1,7}$ = 1.6 Hz, 1 H, 1-H), 3.32 (m, $J_{9,8}$ = 1.8, $J_{9,7}$ = 1.7 Hz, 1 H, 9-H), 5.36 (dm, $J_{8,7}$ = 5.6 Hz, 1 H, 8-H), 5.41 (m, 1 H, 7-H), 7.65 (br d, 1 H, 4-H); ^{13}C NMR (C_6D_6, 100 MHz) δ 25.11 (t, *J* = 132.2 Hz, C-5), 34.72 (d, *J* = 142.4 Hz, C-6), 45.30 (d, *J* = 183.0 Hz, C-9), 52.84 (d, *J* = 185.0 Hz, C-1), 126.41 (d, *J* = 168.0 Hz, C-8), 137.31 (d, *J* = 165.4 Hz, C-7), 154.67 (d, *J* = 180.0 Hz, C-4); MS (70 eV), *m/e* 120 (2%, M^+), 119 (3), 118 (6), 92 (41), 91 (100), 79 (6), 77 (6), 65 (23), 63 (11), 51 (11), 39 (29).

Direct Laser Photolysis of Azoalkane 4 in the Presence of 1,3-Pentadiene. A solution of the azoalkane **4** in CD_3CN (0.25 M) was irradiated in the laser as described above in the presence or absence of 1,3-pentadiene (1.4 M). No change in the product ratio could be detected by ^{1}H NMR.

Direct Laser Photolysis of Azoalkane 4 at λ = 334 nm. A solution of azoalkane **4** (0.12 M) in benzene was irradiated in the laser at λ = 334 nm and ca. 40 °C. The reaction progress was monitored by UV and all azoalkane had been consumed after ca. 25 min. The photolysate was concentrated by rotoevaporation at 5 °C and 25 torr. The residual yellow oil showed not diazoalkane by UV or IR.

Benzophenone-Sensitized Photolysis of Azoalkane 4. A solution of azoalkane (0.12 M) and benzophenone (ca. 0.50 M) in C_6D_6 was irradiated with the 364-nm laser line at ca. 15 °C. After 30 min no azoalkane could be detected by ^{1}H NMR. The 90-MHz ^{1}H NMR showed as single product the tricyclic azirane **6**. Only traces of norbornadiene were detected by capillary GC.

Vacuum Flash Thermolysis of Tricyclo[3.2.0.0^{2,7}]hept-3-ene (5). A solution of ca. 10 mg (0.109 mmol) of the tricycle **5** in 0.5 mL of C_6D_6 was pyrolyzed by subliming it at ca. 50 °C and 28 torr through a hot tube, consisting of Pyrex glass (35 cm long, ϕ = 1.3 cm), which was externally heated at ca. 250 °C by means of a resistance wire. The pyrolysate was collected in a liquid nitrogen cold trap and analyzed by ^{1}H NMR. The chemical shifts of the proton signals of the pyrolysis products were in accord with those reported[4] for a mixture of 1- and 2-vinylcyclopentadienes.

Acknowledgments are made to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financing.

Registry No. 1, 96227-96-2; **2**, 96227-97-3; **3**, 96227-98-4; **4**, 96227-99-5; **5**, 6006-21-9; **6**, 96228-03-4; (*E*)-**7**, 96228-00-1; (*Z*)-**7**, 96228-01-2; **8**, 96228-02-3; $TsNHNH_2$, 1576-35-8; 4-(*n*-butyl)-1*H*-pyrazole, 17061-19-7; 4,5,6,7-tetrahydro-1*H*-indazole, 2305-79-5; quadricyclane, 278-06-8; 1,3-pentadiene, 504-60-9; benzophenone, 119-61-9; 1-vinylcyclopentadiene, 24460-02-4; 2-vinylcyclopentadiene, 32379-33-2.