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Photolysis of 11-Methylenepentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-*spiro*-3'-diazirine. Medium Dependent Reaction

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11-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-*spiro*-3'-diazirine (**1**) has been synthesized and its photochemical decomposition in different media has been investigated. Irradiation of N_2-purged benzene solution of diazirine **1** produced a mixture of four azine-isomers **7a-d**. However, photolysis of **1** in pentane gave a mixture of hydrocarbons **6** as the main insertion products and traces of 1,3-bishomopentaprismane (**5**). The photolytic decomposition of **1** in N_2-matrix at –196 °C proved the formation of diazo-compound **8**, which upon warm-up gave traces of 1,3-bishomopentaprismane (**5**).

Key words: cage compounds, diazirine, azines, carbenes

INTRODUCTION

The chemistry of carbene intermediates has been of considerable interest to organic chemists over the past decades.[1] Although some aspects of the chemistry of carbene generated in different media appear to be relatively well understood, it is generally not possible to predict with certainty the reaction of cage-annulated carbenes.[2–4]

In our previous study,[2] concerned with generation of 11-methylene-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-ylidene (**9**), we found that thermolysis of 11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one tosylhydrazone sodium salt afforded 1,3-bishomopentaprismane (**5**). However, generation of carbene **9** by pyrolysis of the corresponding diazirine (*i.e.* **1**, Scheme 2) gave

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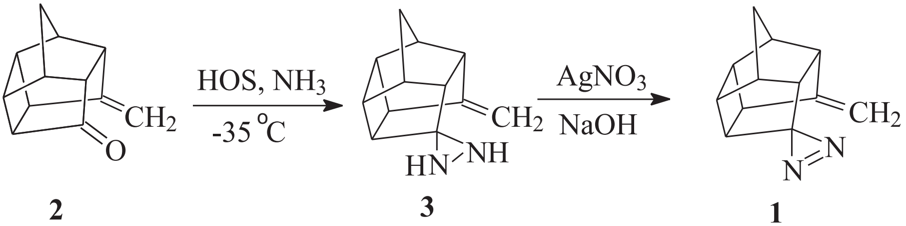
tricyclic tetraene **4** as the major product. Also, we recently reported[3] on the carbene reactions of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan- -8-ylidene and showed that the fate of this carbene depends upon reaction conditions under which it is generated.

It has been shown that carbene may be produced by the thermal or photolytic decomposition of diazirines, which have become increasingly popular and widely used carbene precursors.[5] Upon thermolysis or photolysis, they usually eliminate molecular nitrogen to form highly reactive divalent carbon species.

We now wish to report our results on the photolysis of 11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-*spiro*-3'-diazirine (**1**) in different media.

RESULTS AND DISCUSSION

The synthesis of diazirine **1** started from pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8,11-dione.[6] Monoketalization of dione, followed by modified Wittig methylenation[7] and formic acid catalyzed deketalization, afforded methylene ketone **2** in a 55% overall yield.[8] Treatment of methylene ketone **2** with freshly prepared hydroxylamin-*O*-sulfonic acid[9] (HOS) in methanolic ammonia at –35 °C afforded diaziridine **3** which was oxidized with silver oxide[4a] to give diazirine **1** in 72% yield (Scheme 1).

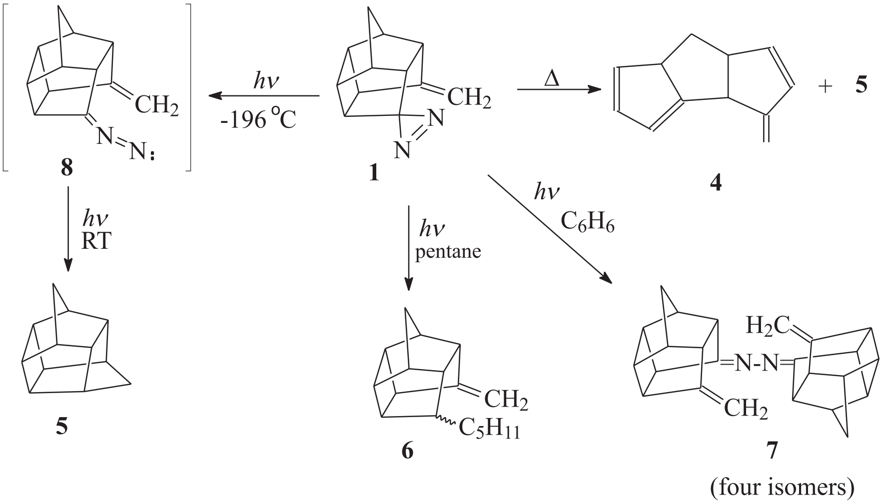


Scheme 1

Flash vacuum pyrolysis of diazirine **1** at 320 °C and 0.75 mm Hg gave a mixture of two products, tetraolefin **4**[2] and hydrocarbon **5**[10] in a 9:1 ratio, respectively.[11] The ratio of products was obtained from the quantitative ^{13}C NMR spectrum of crude reaction mixture. By way of contrast, generation of carbene **9** *via* photolysis of diazirine **1** resulted in the formation of different products (*i.e.*, **5**, **6** or **7**, Scheme 2).

Irradiation of N_2-purged benzene solution of diazirine **1** in a Pyrex vessel by 350 nm radiation[12a] produced merely a mixture of four azines **7a-d**[12b]

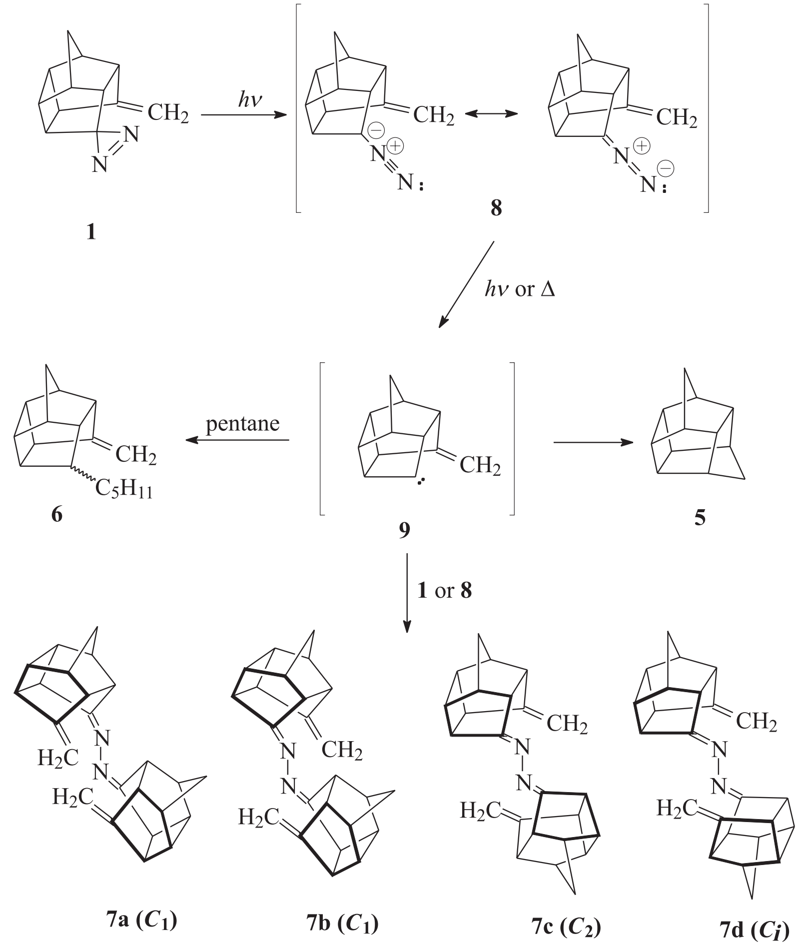
(Sheme 3). ^{13}C NMR spectrum of the mixture showed six signals of the corresponding different carbon atoms at 175.1, 174.6, 174.2, 172.4, 172.3, and 172.2 ppm, which could be assigned to the six different C=N groups and eleven signals at 153.7, 153.6, 153.5, 153.3, 153.2, 153.1, 104.7, 104.6, 104.5, 104.3, and 104.2 (2C) ppm, which belong to the $C=CH_2$ carbon atoms. This is in accord with the structures of four azine-isomers, two of which with C_1 symmetry (**7a** and **7b**) and the other two with C_2 (**7c**) and C_i (**7d**) symmetry.[13]



Scheme 2

The result obtained from the photolysis of **1** in pentane is in contrast to that in benzene. Here, the main product (56%) is composed of the mixture of three isomeric hydrocarbons **6,** which are obtained by insertion of carben to pentane CH-bond in a 1:2:8 ratio,[14] and a small amount of 1,3-bishomopentaprizmane (**5**).

The formation of all products could be explained by formation of carbene **9**, which reacts further, depending on reaction conditions, to give **5**, **6** or **7** as shown in Scheme 3. The formation of linear diazo-intermediate has been proposed in the photodecomposition of adamantane-2-*spiro*-3'-diazirine.[15] Also, Stevens and coworkers[16] have provided evidence of the formation of diazocycloalkane in the initial phase of liquid-phase photolysis of cycloalkane-s*piro*-diazirines. However, it has also been proposed that azine may arise from the reaction of carbene with diazirine. The mechanism of nitrogen loss from diazirines and diazo-compounds has been the subject of many reports.[5b]



Scheme 3

To gain more information about the intermediates, diazirine **1** was photolyzed in N_2-matrix at –196 °C and the product was analyzed by IR spectroscopy (Figure 1).[17] After irradiation of **1** with high pressure mercury lamp for 30 min, the band at 1580 cm^{-1}, characteristic of the diazirine-group, disappeared and two new bands appeared at 2340 and 2050 cm^{-1} (Figure 1 c). The same IR spectrum was obtained when diazo compound **8** was deposited on cold CsI window (–196 °C) by pyrolizing its tosylhydrazone sodium salt under reduced pressure (0.75×10^{-3} mm Hg, Figure 1f), and then photolyzing the product for 30 min (Figure 1e). Upon warm-up to room temperature, in both photolyses (Figure 1c and e), identical IR spectra (d) were obtained. According to ^1H NMR spectra, traces of 1,3-bishomopentaprismane (**5**) were obtained. (See Experimental).

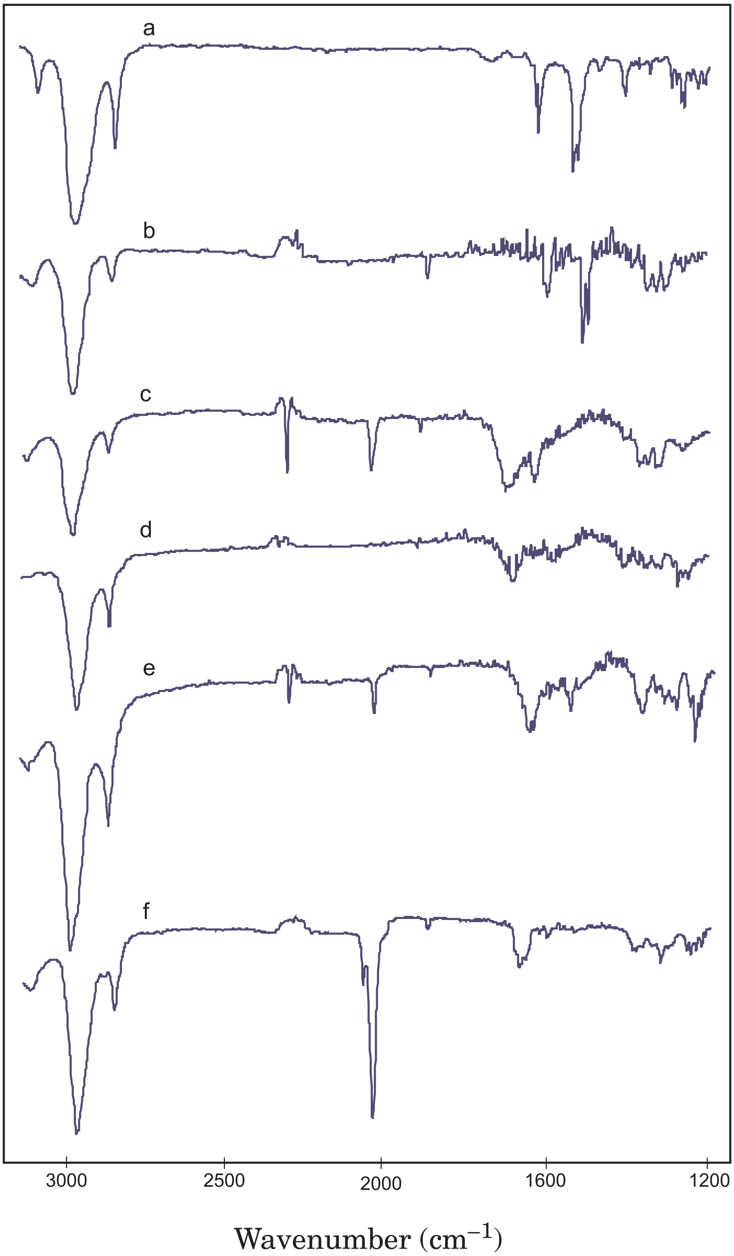


Figure 1. (a) IR spectrum of **1** in KBr at room temperature; (b) IR spectrum of **1** on CsI window at –196 °C; (c) IR spectrum after photolysis of **1** at –196 °C; (d) IR spectrum after photolysis of **1** and warm-up to room temperature; (e) IR spectrum after photolysis of **8** at –196 °C; (f) IR spectrum of **8** deposited on CsI window at –196 °C.

CONCLUSIONS

11-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-*spiro*-3'-diazirine (**1**) has been synthesized *via* the method shown in Scheme 1 and photochemical decomposition of **1** in different media was studied. Photolysis of diazirine **1** in benzene solution afforded a mixture of four azine-isomers **7a-d**, while irradiation of **1** in pentane solution gave a mixture of hydrocarbons **6** as main products with a small amount of 1,3-bishomopentaprismane (**5**). Also, photolysis of **1** in N_2-matrix at –196 °C gave evidence that the photodecomposition of diazirine **1** takes place through the formation of diazocompound **8**, which then gives the carbene **9** by elimination of nitrogen.

EXPERIMENTAL

Purity of all compounds was determined by GLC and/or ^{13}C NMR. GLC analyses were carried out on a Varian 3300 gas chromatograph on capillary columns DB-210 and DB-1. ^{1}H and ^{13}C NMR spectra were taken on a Varian Gemini 300 (300/75 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer M-297 spectrophotometer. UV spectra were recorded on a Philips PU 8730 UV/VIS spectrophotometer. Melting points (uncorrected) were determined on the Kofler hot-stage apparatus and elemental analyses were performed in the Central Analytical Laboratory, Rudjer Bošković Institute.

*11-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (**2**).*

A mixture of 11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one ethylene ketal (4.2 g, 19 mmol) and formic acid (16.4 mL) was stirred for 10 minutes at 65 °C, then poured into cold water (50 mL) and extracted with 4:1 mixture of pentane/ether (3 × 30 mL). Combined extracts were washed with saturated aqueous $NaHCO_3$ solution and dried over $MgSO_4$. Evaporation of solvent yielded crude product **2,** which was purified by column chromatography on Al_2O_3 (activity II/III) with pentane/ether (4:1) as eluent and 3.0 g (90%) of pure methylene ketone **2** was obtained. IR and ^{1}H NMR spectra of **2** are in accord with the literature data.[8]
^{13}C NMR ($CDCl_3$) δ/ppm: 217.1 (s), 149.9 (s), 105.3 (t), 54.8 (d), 53.7 (d), 48.5 (d), 46.1 (d), 44.0 (d), 43.6 (d, 2C), 38.8 (d), 36.9 (t).

*11-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-*spiro*-3'-diazirine (**1**).*

A solution of methylene ketone **2** (0.3 g, 1.7 mmol) in abs. methanol (4.5 mL) was cooled to –70 °C and liquid ammonia (*ca.* 15 mL) was added dropwise. Stirring was continued for 45 min and freshly prepared HOS (hydroxylamine-*O*-sulfonic acid,[9] 0.4 g, 3.5 mmol) dissolved in methanol (2 mL) was added. The reaction mixture was stirred for 3 hours at –35 °C and then overnight at room temperature. Reaction mixture was poured into water (20 mL). Crude compound **3** was extracted with CH_2Cl_2 (3 × 20 mL). Combined extracts were dried over $MgSO_4$. Evaporation of the solvent yielded crude diaziridine **3**. The purity of **3** was checked with IR and the crude material was submitted to the next reaction.

3: IR (KBr) ν_{max}/cm^{-1} 3190, 2960, 2860, 1670, 1450, 1420, 1380, 1350, 1280, 1190, 1170, 1040, 880.

To a solution of crude diaziridine **3** in methanol (15 mL), a 1 N solution of $AgNO_3$ (2.8 mL) was added and then slowly a 2.5 N solution of NaOH (1 mL). The mixture was stirred 15 min at room temperature and filtered. Filtrate was diluted with (50 mL) water and extracted with CH_2Cl_2 (3 × 20 mL). The extracts were dried over $MgSO_4$. Solvent was evaporated to afford **1**, which was purified by column chromatography on Al_2O_3 (activity II/III) with pentane as eluent and 0.170 g (54%) of pure 11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-*spiro*-3'-diazirine (**1**) was obtained as a waxy solid.

UV (EtOH) λ_{max}/nm(log ε): 350.2 (2.22), 367.2 (2.24); IR (KBr) ν_{max}/cm^{-1}: 3060, 2960, 2860, 1680, 1580, 1570, 1450, 1280, 1270, 1140; ^{1}H NMR ($CDCl_3$) δ/ppm: 4.96 (d, J = 1.28 Hz, 1H), 4.89 (d, J = 1.28 Hz, 1H), 3.12–3.04 (m, 1H), 3.00–2.70 (m, 4H), 2.49 (br.s, 1H), 1.80–1.60 (m, with clear doublet at 1.72, J = 10.5 Hz, 2H), 1.50–1.35 (m, with clear doublet at 1.43, J = 10.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ/ppm: 152.7 (s), 104.8 (t), 50.4 (d), 48.6 (d), 47.7 (d), 44.8 (d), 42.7 (d), 42.6 (d), 41.3(d), 41.2 (d), 38.1 (s), 36.5 (t); HRMS for $C_{12}H_{12}N_2$ [M+1] calculated:185.107873, found: 185.107327.

Pyrolysis of diazirine 1

A two-neck flask containing diazirine **1** (0.250 g, 1.35 mmol) was connected to a horizontal glass tube (22 cm long, 8 mm i.d.), heated to 320 °C by an external ribbon, followed by a »U« trap cooled by liquid nitrogen and attached to the vacuum. A gentle stream of nitrogen was introduced through the flask to maintain moderate vacuum (0.75 mm Hg) in the system. The product (0.088 g, 0.56 mmol, 41%) collected in the trap was dissolved in $CDCl_3$ and analyzed by GLC to be a mixture of two products in a 9:1 ratio.[11] On the basis, of its spectra the major product was identified as tetraolefin **4**[2] and the minor product as the 1,3-bishomopentaprismane (**5**).[2,10]

Photolysis of diazirine 1

Photolysis in benzene: A solution of **1** (0.111 g, 0.6 mmol) in benzene (1 mL) was placed in a Pyrex tube, purged for 30 min. with a stream of nitrogen and then irradiated in a Rayonet reactor equipped with sixteen 350 nm lamps for 0.5 h. After evaporation of solvent, the crude reaction mixture was chromatographed on a silica gel column with 0 → 30% ethylacetate in CH_2Cl_2 as eluent to give 62 mg (56%) of a mixture of four azines **7**.[18]

IR (KBr) ν_{max}/cm^{-1}: 3080, 2960, 2860, 1670, 1450, 880; ^{1}H NMR (C_6D_6) δ/ppm: 4.80–4.55 (m, 4H), 4.20–3.73 (m, 2H), 3.20–2.15 (m, 14H), 1.60–1.40 (m, 2H), 1.25–1.08 (m, 2H); ^{13}C NMR (C_6D_6) δ/ppm: 175.1 (s), 174.6 (s), 174.2 (s), 172.4 (s), 172.3 (s), 172.2 (s), 153.7 (s), 153.6 (s), 153.5 (s), 153.3 (s), 153.2 (s), 153.1 (s), 104.7 (t), 104.6 (t), 104.5 (t), 104.3 (t), 104.2 (t, 2C), 53.5 (d), 53.4 (d), 53.2 (d), 52.8 (d), 52.6 (d), 51.5 (d), 51.4 (d), 51.3 (d), 48.2 (d), 48.1 (d), 48.0 (d), 47.9 (d), 46.2 (d), 46.1 (d), 46.0 (d), 45.8 (d), 45.4 (d), 45.2 (d), 44.7 (d), 44.6 (d), 44.5 (d), 44.3 (d), 43.8 (d), 43.7 (d), 43.5 (d), 43.4 (d), 43.3 (d), 40.6 (d), 40.5 (d), 40.1 (d), 40.0 (d), 39.9 (d), 39.8 (d), 38.5 (d, 2C), 37.99 (t), 37.93 (t, 2C), 37.87 (t, 2C), 37.84 (t).

Anal. Calcd. for $C_{24}H_{24}N_2$ ($Mr = 340.42$): C 84.67, H 7.10, N 8.23%; found: C 84.48, H 7.24, N 8.24%.

Photolysis in pentane: A solution of **1** (0.173 g, 0.94 mmol) in pentane (450 mL) was placed into a Pyrex vessel, purged for 30 min with a stream of nitrogen, then cooled to 10 °C and irradiated in a Rayonet reactor equipped with sixteen 350 nm lamps for 1.5 h. Pentane was evaporated end the crude product was analyzed on GLC (capillary column DB-1, 30 m, 130–200 °C and DB-210, 15 m, 95 °C) to be a mixture of three products in a 1:2:8 ratio.[14] We were not able to separate this mixture. After chromatography on a silica gel column with pentane as eluent, 120 mg (56%) of the mixture of hydrocarbons **6** was obtained as a viscous oil.
IR (KBr-film) ν_{max}/cm^{-1}: 3080, 2960, 2860, 1670, 1460, 1380, 880; ^1H NMR ($CDCl_3$) δ/ppm: 4.65 (br.s, 1H), 4.57 (br.s, 1H), 2.83–2.25 (m, 8H), 1.66 (d, $J = 10.5$ Hz, 1H), 1.37–0.70 (m, 13H); ^{13}C NMR ($CDCl_3$) δ/ppm: 155.3, 103.6, 102.9, 50.1, 47.4, 47.3, 47.0, 46.4, 44.1, 43.9, 42.1, 42.0, 41.8, 40.9, 38.9, 37.6, 35.8, 34.9, 32.4, 32.1, 29.5, 25.9, 22.1, 20.5, 20.0, 19.5, 17.7, 16.4, 14.3; MS m/z: 228 (25), 199 (21), 149 (43), 148 (100), 119 (24), 107 (52), 93 (51), 91 (48), 79 (32), 77 (28), 65 (15), 51 (11), 43 (33), 41 (39).

Photolysis in nitrogen-matrix: Diazirine **1** was codeposited with N_2 on a cold CsI window[17] at –196 °C for 1 hour and its IR spectrum was recorded. Then, the matrix was irradiated with a 400 W high-pressure mercury lamp for 30 min and the IR spectra were taken at 10 min intervals. After 30 min of irradiation, the signal at 1580 cm^{-1} (frequency characteristic of the diazirine group) completely disapeared and two new signals appeared at 2340 and 2050 cm^{-1}. Then, the matrix was irradiated with a UVP R-52G lamp (max. 254 nm) for additional 30 minutes and the IR spectra were taken. However, no significant change in the IR spectra was observed. The matrix was allowed to warm-up slowly to room temperature and the product was washed off from the CsI-finger in the NMR-tube with $CDCl_3$ and the ^1H NMR spectrum was recorded. Besides the polymeric material, the signals of 1,3-homopentaprismane (**5**) were observed.

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11. The ratio of products varied with the applied temperature. At 300 °C, the ratio of **4** : **5** was 8 : 1. For the mechanism of the formation of **4** and **5,** see reference 2.
12. (a) The excitation wavelength of 350.0 nm was chosen in accord with the absorption spectrum of **1** ($\lambda_{\text{max1}} = 350.2$ and $\lambda_{\text{max2}} = 367.2$). (b) According to the ^{13}C NMR spectra, the mixture of azines is composed of the four isomers **7a-d** in a similar ratio.
13. The structures of azines **7a-d** were optimized by semiempirical PM3 calculations using the HyperChem 5.0 program. Geometries were optimized until the root mean square value of the energy gradient was less than 0.001 kcal mol^{-1} Å^{-1} using the Restricted Hartree Fock method (RHF) and convergence limit of 10^{-5} kcal mol^{-1} with optimization of all geometrical variables (bond length, bond angles, and dihedral angles).
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18. When the reaction was carried out in 10 mL of benzene, a small amount of 1,3-bishomopentaprismane (**5**) was obtained.

SAŽETAK

Fotoliza 11-metilenpentaciklo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undekan-8-*spiro*-3'-diazirina. Reakcija ovisna o mediju.

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Sintetiziran je 11-metilenpentaciklo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undekan-8-*spiro*-3'-diazirin (**1**) i proučavana je njegova fotoliza u različitim reakcijskim uvjetima. Osvjetljavanjem benzenske otopine diazirina **1** nastaje smjesa izomernih azina **7a-d**. Međutim, fotolizom pentanske otopine diazirina **1** kao glavni produkt nastaje smjesa ugljikovodika **6** i mala količina 1,3-bishomopentaprizmana (**5**). Fotolitičkom dekompozicijom diazirina **1** u N_2-matrici pri –196 °C potvrđeno je nastajanje diazo-spoja **8** koji zagrijavanjem daje 1,3-bishomopentaprizman (**5**).