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Novel photorearrangement of a 4-chloromethylazulene

Carlos A. A. Ruiz, Vicente G. Toscano, Daisy de Brito Rezende and Wilhelm J. Baader*

Instituto de Química, Universidade de São Paulo, Cx. Postal 26077, 05599-970 Sao Paulo, SP, Brazil

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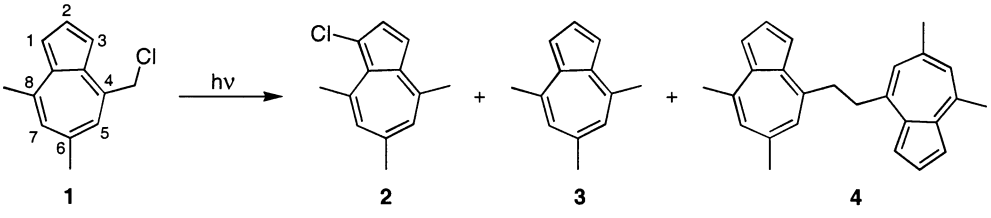
Abstract—1-Chloro-4,6,8-trimethylazulene is formed almost exclusively upon UV irradiation of a deaereted benzene solution of 4-chloromethyl-6,8-dimethylazulene. This photoproduct was identified by ^{1}H and ^{13}C NMR spectroscopy of both the isolated photoproduct and the one prepared by a thermal route. The mechanism proposed involves the recombination of the intimate radical pair initially formed by the photohomolysis of the C–Cl bond, followed by a sigmatropic [1,9] hydrogen shift. © 2001 Published by Elsevier Science Ltd.

Although various studies on the photocleavage of substituted arylmethyl compounds have been reported since the 1960s,[1] there is a continued interest in the subject[2] because the mechanisms operative in this process remain not entirely understood.

In the course of our investigation on the photolysis of halomethylazulenes in apolar solvents, we have observed for the first time, a rearrangement of 4-chloromethyl-6,8-dimethylazulene (**1**) to 1-chloro-4,6,8-trimethylazulene (**2**), which is interesting from both preparative and mechanistic points-of-view, because the only low-molecular-weight by-products formed occur in trace amounts (Scheme 1). This is an unexpected result, as the products coming from biradicalar recombination are present only in negligible amounts, as opposed to what we have observed in a previous study concerning the related α-bromomethylxylenes.[3]

Photolysis of an oxygen-free benzene solution of **1** yields **2** and the minor products 4,6,8-trimethylazulene (**3**) and 1,2-bis(4,6-dimethylazulen-8-yl)ethane (**4**), which were characterized by GC/MS and GC (coinjection of authentic standards, prepared by thermal routes). When photolysis of **1** was performed in the presence of the well established hydrogen donor 1,4-cyclohexadiene (**CHD**), the rate for the consumption of **1** decreased ca. 25% (see Figs. 1 and 2) and the relative amount of **3** was greater than that formed when the irradiations were performed in pure benzene (see Table 1, where the yields reported for product formation have been calculated as percentages of the total amount of **1**, in moles, consumed after irradiating for 1 h). The quantum yields determined[3] for the consumption of **1** are greater in benzene than in benzene/**CHD** due to the competitive absorption by **CHD** at 254 nm.

The ^{1}H and ^{13}C NMR spectra of **2** prepared either by thermal or by photochemical pathways are identical, indicating that the only possible structure for **2** is the 1-chloro-isomer. They contain three signals due to the methyl substituents, two doublets for the five-membered ring protons and two (slightly broadened) singlets for the remaining aromatic protons. These features indicate that product **2** does not present a C_2 symmetry axis and so it cannot be the 2-chloro isomer. Furthermore, if **2** were the 5-chloro-isomer, then the H-2



Scheme 1.

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* Corresponding author. Fax: +55-11 3815-5579; e-mail: wjbaader@iq.usp.br

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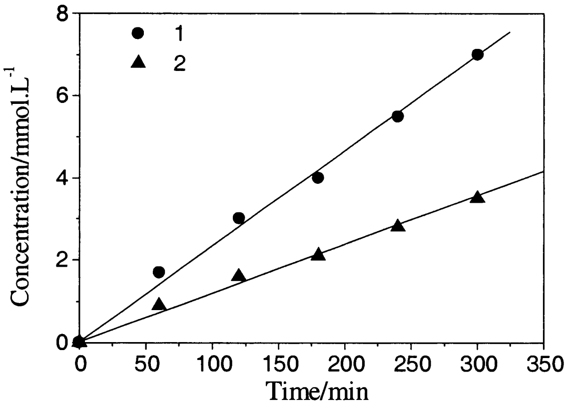


Figure 1. Photolysis kinetic profile ($\lambda_{exc}=254$ nm) for **1**, in benzene. **1**: in moles consumed, at time t; $C_0=1.1\times10^{-2}$ mol L^{-1}; $b=(2.60\pm0.07)\times10^{-5}$ mol L^{-1} min^{-1}; $r=0.995$. **2**: $b=(1.19\pm0.03)\times10^{-5}$ mol L^{-1} min^{-1}; $r=0.997$.

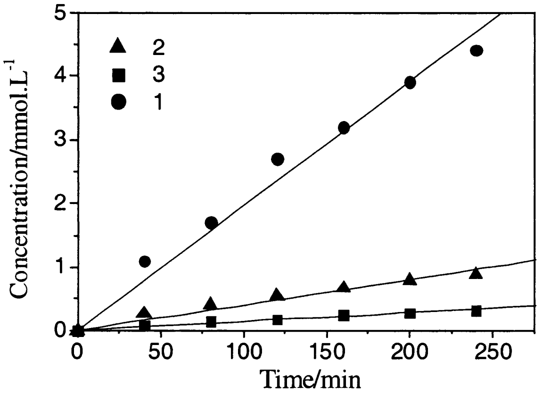


Figure 2. Photolysis kinetic profile ($\lambda_{exc}=254$ nm) for **1**, in benzene/CHD 1.0 mol L^{-1}. **1**: in moles consumed, at time t; $C_0=1.0\times10^{-2}$ mol L^{-1}; $b=(1.96\pm0.06)\times10^{-5}$ mol L^{-1} min^{-1}; $r=0.993$. **2**: $b=(4.0\pm0.2)\times10^{-6}$ mol L^{-1} min^{-1}; $r=0.987$. **3**: $b=(1.42\pm0.06)\times10^{-6}$ mol L^{-1} min^{-1}; $r=0.990$.

should be present as a triplet (due to coupling with both H-1 and H-3), which is not the case. The presence of a chloro substituent in the molecule is confirmed by the consistence between the observed and the calculated relative intensities of the molecular-ion peak ($M^{\bullet+}$, which is also the base peak) and those due to the natural isotopic abundance ratios of C, H and Cl (see Experimental).

Our results can be explained by assuming the initial photoevent to be the homolytic cleavage of the carbon–halogen bond, forming an intimate radical pair that deactivates preferably by the formation of the isomer **2**, a process that can be rationalized by the mechanism outlined in Scheme 2: initial chlorine atom attachment to the five-membered ring in position 3 leads to compound **5**, which should rearomatize rapidly through a thermally allowed, suprafacial, sigmatropic [1,9] hydrogen shift. In the presence of **CHD**, those radicals that diffuse away from the initial intimate radical-pair are able to abstract hydrogen from it, forming **3** in appreciable amounts. The occurrence of trace amounts of **3** in neat benzene can be assigned to H-abstraction from another molecule of **1** in the ground state.

Experimental. *Instruments and methods*—All qualitative and quantitative chromatographic analyses were performed on a Shimadzu CG-14-A gas chromatograph using a 50 m×0.25 mm×0.25 μm Quadrex methylsilicone column. Quantitative determinations were performed after correcting for the experimentally determined FID response factors for each compound. GC–MS analyses were done on a Finnigan-MAT ITD-800 ion trap mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 20°C on a Varian unity Inova 300 spectrometer, at 300 and 75 MHz, respectively. The acquisition and processing parameters employed were analogous to those already described.[4] *Irradiations*—A solution of 2.04 g (10.00 mmol) of compound **1** in 25.00 cm^3 of spectroscopic grade benzene was irradiated inside the cavity of an Ultraviolet Products PCQ-X1 Irradiation System, consisting of four 18 W doughnut-type low-pressure mercury-vapor lamps contained in a cylindrical mirror. The solution was flushed with benzene-saturated argon for 30 minutes before irradiation, the argon flux being maintained throughout the irradiation. *Quantum yields*[3]—Calculated from the angular coefficients (b) of the linear regression fits presented in Figs. 1 and 2, using the equation $\Phi=b\cdot V/I_0$, where $V=3.0\times10^{-3}$ L and the photon flux, $I_0=1.2\times10^{-8}$ einstein min^{-1}, determined with a potassium ferrioxalate actinometer.[5] *Materials*—4-Chloromethyl-6,8-dimethyl-

Table 1. Photolysis of **1** in benzene at 254 nm

	Yield[a] (%)				Φ (10^{-2})				Recovered[a,b] (%)
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	
Neat	19[c]	53[d]	Traces	Traces	6.6[e]	3.0[f]	–	–	53
CHD (1.0 mol L^{-1})	40[c]	23[d]	11[d]	Traces	4.9[e]	1.1[f]	0.4[f]	–	34

[a] After 1 h of UV-exposition.

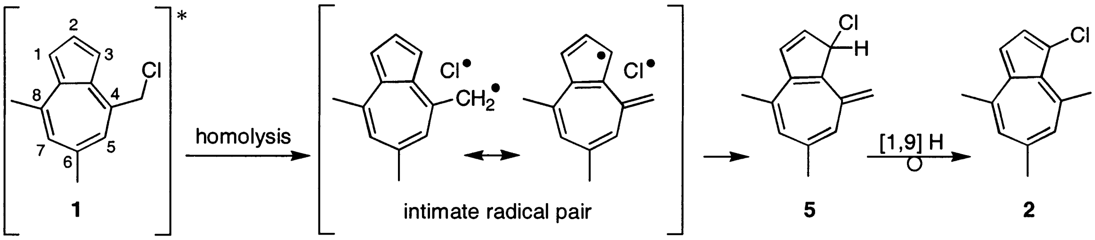
[b] Recovered refers to the total amount of photoproducts detected and quantified by GC analysis relative to the moles of **1** consumed, as a percentage; the remainder are non-volatile high-molecular-weight materials for which characterization was not pursued.

[c] Moles of **1** consumed, as a percentage.

[d] Relative to the moles of **1** consumed, as a percentage.

[e] Quantum yield (Φ) for the consumption of **1**.

[f] Quantum yield (Φ) for product formation calculated from b, in Figs. 1 and 2 (see Experimental).



Scheme 2.

azulene (**1**) was prepared from 4,6,8-trimethylazulene as previously described.[6] 1,2-Bis(4,6-dimethylazulen-8-yl)ethane (**4**) was prepared as reported by Hafner et al.[7] 1-Chloro-4,6,8-trimethylazulene (**2**): (i) *by preparative photolysis*—50.0 cm^3 solution of **1**, irradiated as described above, the product being purified by elution with hexane/ether (20:1) through a column of basic alumina (100–230 mesh) of activity II–III (80 g of alumina+2 g of H_2O). The product, a deep-blue oily liquid, was isolated in 56% yield. (ii) *By thermal route*—a solution of *N*-chlorosuccinimide (0.3 g; 2.2 mmol) in anhydrous ether was added to 2 mmol of sodium 4,6-dimethyl-8-methylene-azuleneate,[7] dissolved in the same solvent. The reaction mixture was stirred for 2 h at room temperature, while being filtered; the filtrate was washed until neutrality with 2 mol L^{-1} hydrochloric acid and water and dried over anhydrous magnesium sulphate. After total removal of the solvent, the product was redissolved in hexane and purified by column chromatography on neutral alumina (activity II) eluted with hexane/ether 95:5. The product was isolated in 35% yield. ^1H NMR (δ, $CDCl_3$, TMS = 0): 2.47 (3H, s); 2.71 (3H, s); 3.07 (3H, s); 6.83 (1H, s); 6.85 (1H, s); 7.15 (1H, d, J = 4.25); 7.39 (1H, d, J = 4.25). ^{13}C NMR (δ, $CDCl_3$, TMS = 0): 25.04 (CH_3); 27.51 (CH_3); 28.56 (CH_3); 114.14 (CH); 116.58 (C); 127.05 (CH); 128.78 (C); 129.44 (CH); 133.50 (CH); 135.20 (C); 146.53 (C); 147.70 (C) 147.80 (C). Mass spectra (70 eV): 153 (79.1%, m/z = 169-CH_4); 169 (71.1%; $M^{\bullet+}$–Cl); 189 (24.4%; $^{35}M^{\bullet+}$–CH_3); 191 (22.73%; $^{37}M^{\bullet+}$–CH_3); 204 (100%; $^{35}M^{\bullet+}$); 205 (17.8%; $^{35}M^{\bullet+}$ +1); 206 (33.3%; [$^{35}M^{\bullet+}$ +2 and $^{37}M^{\bullet+}$]; 207 (4.44%; $^{37}M^{\bullet+}$ +1); requires: $^{35}M^{\bullet+}$ = 100%; $^{35}M^{\bullet+}$ +1 = 14.26%; $^{35}M^{\bullet+}$ +2 and $^{37}M^{\bullet+}$ = 33.54%; $^{37}M^{\bullet+}$ +1 = 4.65.

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