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MECHANISM AND KINETICS OF PHOTOREACTIONS OF SUBSTITUTED DIAZA-(2,2)-SPIRENS

SPECTROSCOPIC INVESTIGATIONS

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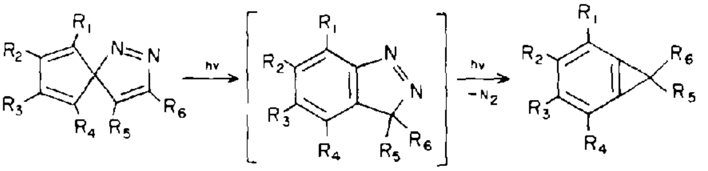
Abstract—Spectral properties and photoreactions of substituted diaza-(2,2)-spirenes are reported. The photoreactions are analysed by using Mauser-diagrams and identification of photoproducts. Quantum yields of the individual steps are determined. Energy transfer between the two perpendicular parts of the molecules cannot be ascertained.

A considerable amount of evidence concerning the reactions of cyclopentadiene-spiropyrazoles which are strongly controlled by substitution has been accumulated mainly by Dürr *et al.*[1-3] According to these investigations the molecules **1a** to **1d** form benzocyclopropenes (**3a** to **3d**) if they are irradiated by UV light. An intermediate of indazole structure (**2**) is assumed.



1 2 3

	R_1	R_2	R_3	R_4	$R_5 = R_6$
a	Ph	H	H	Ph	$-(CH_2)_6-$
b	Ph	H	H	Ph	$-COOCH_3$
c	Ph	Ph	Ph	Ph	$-COOCH_3$
d	Ph	Ph	Benzo-		$-COOCH_3$

This paper will report the photoreaction mechanism and the quantum yields of the individual photochemical steps. The reaction is monitored by UV spectroscopy in dilute ethanolic solution (*ca.* 10^{-4} M). The photoreaction is induced by monochromatic light.

The photoreaction mechanism of **1a.** There are two questions to this reaction sequence: (1) is it possible to detect the postulated intermediate **2** and (2) is the sequence complete? The "Extinktions (E)"- and "Extinktions-Differenzen-Quotienten (EDQ2)"-diagrams which were developed by Mauser,[4] are the adequate means to answer these questions as they provide evidence for the number of the linearly independent reaction steps of a complex reaction system.[5]

Two sets of experiments at different irradiation wavelengths were performed. Figure 1 shows the reaction spectrum of **1a** under 366 nm-irradiation. This reaction exhibits isosbestic points and linear E-diagrams (Fig. 2) and can be classified as uniform (s = 1) under these specific reaction conditions.

If, however, the reaction product of this first photoreaction is subjected to further irradiation at 313 nm a new photoreaction takes place (Fig. 3). This reaction is no longer uniform: The curved E- and linear EDQ2-diagrams (Figs. 2 and 4) suggest now a consecutive photoreaction. When the irradiation is interrupted, no dark reaction can be observed.

In the other set of experiments the starting material **1a** was subjected to 313 nm irradiation. This photoreaction gave an E-diagram which is nearly linear and connects the points A and D in Fig. 2 missing the point C only slightly. This virtual uniform reaction is a peculiarity of the system, as A, C and D lie nearly on a straight line. The final UV spectrum of the photoreaction induced by 313 nm is identical to that of the 366/313 nm irradiation (Fig. 5). According to these results we formulate the mechanism for irradiation of **1a**:

$$A \xrightarrow[366/313]{h\nu} B \xrightarrow[313]{h\nu} C \xrightarrow[313]{h\nu} D.$$

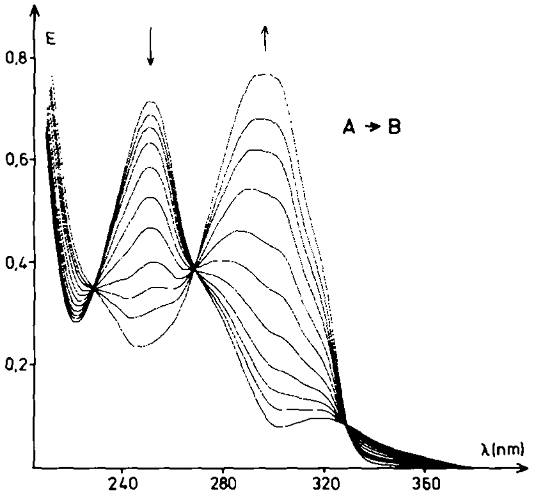


Fig. 1. Photoreaction of **1a**; irradiation wavelength: 366 nm.

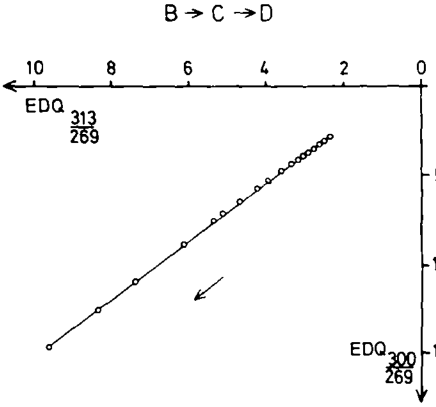


Fig. 4. "Extinktions-Differenzen-Quotienten-"diagram of the photoreaction of **3a** (Irradiation at 313 nm).

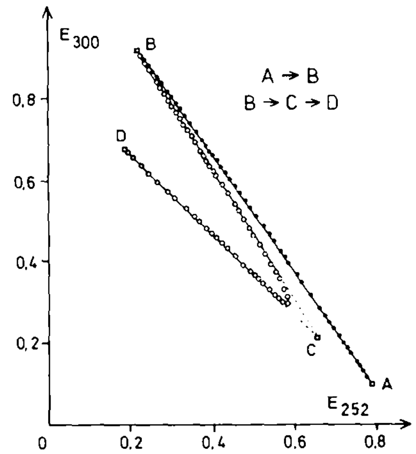


Fig. 2. "Extinktions-"diagram of the photoreaction of **1a** and **3a** ··· $\overline{AB}$: Irradiation of **1a** at 366 nm, ○○○ $\overline{BD}$: Irradiation at 313 nm of the **3a** formed by 366 nm-photolysis, C: Extrapolated E_{300} and E_{252} values of the intermediate product **4**.

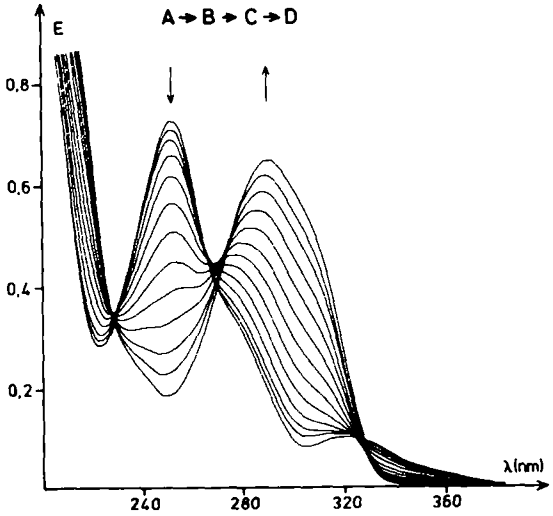


Fig. 5. Reactionspectrum of the photoreaction of **1a** when irradiating the starting material only at 313 nm.

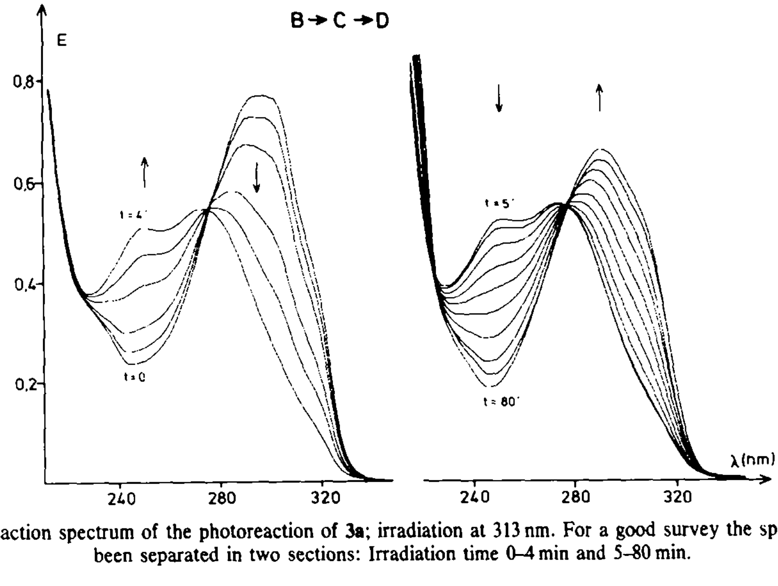


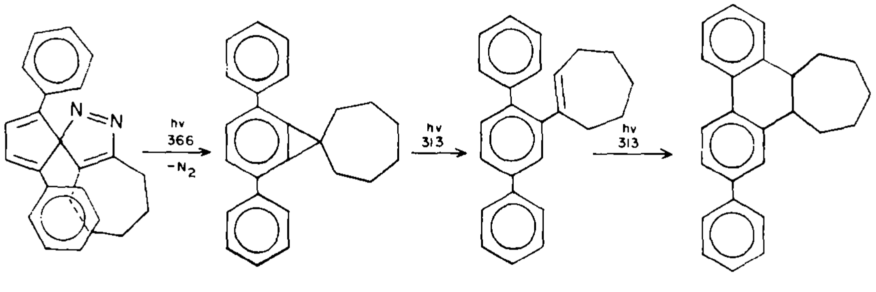
Fig. 3. Reaction spectrum of the photoreaction of **3a**; irradiation at 313 nm. For a good survey the spectrum has been separated in two sections: Irradiation time 0–4 min and 5–80 min.

Identification of the reaction products of **1a**. In order to prove the mechanism and to identify the compounds B, C and D, the reaction products were isolated (Experimental). Elementary analysis and mass spectrum proved that the product B formed by 366 nm irradiation does no longer contain nitrogen. The ^{13}C-NMR spectrum of B has formerly been assigned to **3a**.[6] The intermediate **2a** therefore can exist under these reaction conditions only in concentrations according to the demands of the hypothesis of the quasi stationary state (Bodenstein-hypothesis).[7]

Product C is 2-cycloheptenyl-p-terphenyl (**4**), formed by opening of the cyclopropene ring. This molecule has recently been identified as the product of the thermolysis of **3a**.[2] The identity of the analytical and spectroscopic data (F.p., ^{1}H-NMR, MS and IR) supports the assignment of the photoproduct.

Product D has the same mass spectrum as B and C *m*/*e* = 324 (M^+), 267 (M^+–C_4H_9). This fact and the other spectroscopic data (fluorescence,[8] ^{1}H-NMR, ^{13}C-NMR) support the structure of a dihydrophenanthrene derivative **5** which is formed from **4** by a conrotatory ring closure and 1,3-hydrogen shift.

The kinetic analysis[9] of the photoreaction of **1a** in ethanol at a long wavelength (366 nm) and a short wavelength (313 nm) irradiation is thus in agreement with the following mechanism:



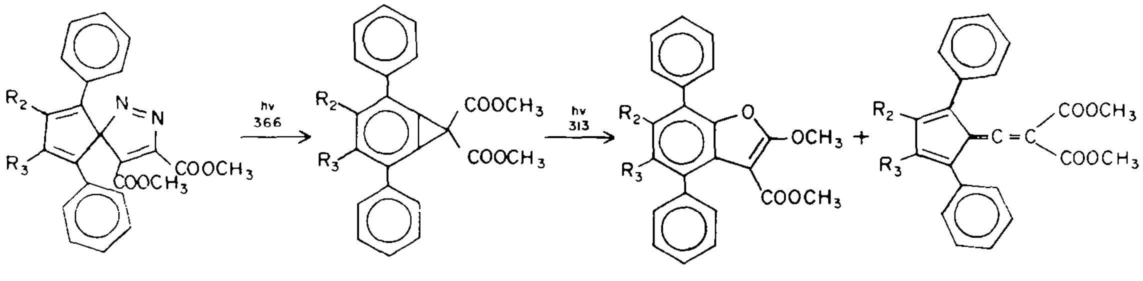
1a 3a 4 5

Photoreactions of the molecules **1b**, **1c** *and* **1d**. The photoreaction of the molecules **1b**, **1c** and **1d** may also be led in two separate sections according to the suitable choice of the irradiation wavelength. Excitation with 366 nm leads to the benzocyclopropenes **3b**, **3c** and **3d**. This may be concluded from the very similar reaction spectra (absorption maximum of the benzocyclopropenes: ~300 nm) and fluorescence spectra (emission at 390 nm). Compounds **3b** and **3c**—in the same way as **3a**—are formed at this excitation wavelength in a uniform reaction from the spiropyrazole. The corresponding molecule **3d** exhibits minor side reactions as indicated by slight deviation from linearity of the E-diagram. This can be attributed to the fact that this molecule has a small absorbance at the irradiation-wavelength 366 nm contrary to **3a**, **3b** and **3c**.

A second photoreaction can be observed when the molecules **3b**, **3c** and **3d** are subject to another irradiation period with 313 nm-radiation. Although the cyclopropane ring can also be opened in this case, a structure analogous to **4** cannot be formed as there is no possibility of hydrogen abstraction from the methoxycarbonyl moieties. In this case photolytical ring opening is followed by cyclization and leads to a benzofuran-derivative **6** and to a fulvene allene **7**. The formation of **6** is in agreement with the thermolysis of this type of benzocyclopropenes.[1] The detailed preparative study of this photoreaction is published elsewhere.[10]

The E-diagrams of the photoreaction of **3b** and **3c** (irradiation: 313 nm) are linear for a considerable part of the reaction; the small deviation from linearity toward the end of the reaction may be explained by a very slow consecutive photoreaction of the benzofurane. The kinetic analysis shows, that the amount of this side reaction could be neglected. Therefore we may formulate the following mechanism for the compounds **3b** and **3c**.

As we observed byproducts in the photoreaction of **1d** even with a long wavelength excitation we did not investigate kinetics of the photoreaction of **3d** with a short wavelength excitation.



1 b,c 3 b,c 6 b,c 7 b,c

Quantum yields. By the method of "formal integration"[11] a quantity $\varphi^A \cdot \epsilon'_A$ can be determined for the reaction $A \xrightarrow{h\nu} B$. The differential quantum yield[12] φ^A can be calculated, when the extinction coefficient of A at the irradiation wavelength ϵ'_A is known. For the consecutive photoreaction $B \xrightarrow{h\nu} C \xrightarrow{h\nu} D$ in an analogous procedure two values are calculated which have to be correlated to $\varphi^B \cdot \epsilon'_B$ and $\varphi^C \cdot \epsilon'_C$.

If one can decide whether $\kappa = (\varphi^C \cdot \epsilon'_C / \varphi^B \cdot \epsilon'_B)$ is greater or less than unity, an unequivocal correlation is possible. For example we have estimated φ^i and ϵ'_i and got $\kappa \approx 0.1$. In case of $\kappa < 1$ the position of the pure intermediate C in the E-diagram may be found by constructing the tangents at the beginning and end of the curve (Fig. 2). Thus it is possible to determine the extinction coefficient, and hence the absorption spectrum, of the intermediate C.[13]

A computer program simulation[9] showed good agreement of the postulated mechanisms with the experimental results in all cases of the reactions of Table 1.

Table 1. Quantum yields

	$\mathbf{1} \xrightarrow{366} \mathbf{3}$	$\mathbf{3} \xrightarrow{313} \mathbf{4} \xrightarrow{313} \mathbf{5}$		$\mathbf{3} \xrightarrow{313} \mathbf{6} + \mathbf{7}$
a	0.03	0.16	0.2	—
b	0.005	—	—	0.04
c	0.007	—	—	0.04
d	0.004	—	—	

The quantum yield of the reaction step $\mathbf{1} \rightarrow \mathbf{3}$ of **1a** is considerably higher than the corresponding quantum yields of molecules **1b**, **1c** and **1d**. This difference is in agreement with the fact that molecule **1a** is the only investigated diazaspirene that does not fluoresce (Table 2).

Similar values for the quantum yields have been obtained by a completely different technique.[3]

Spectroscopic properties. Energy transfer of varying efficiency between the orthogonal electronic systems of spiro compounds has been reported.[14,15] Part of this study was done to investigate if dual emission could be detected or if the separate excitation of the cyclopentadiene or the pyrazole parts would lead to different photoreactions. The spectral properties of compounds **1a** to **1d** and of their photoproducts are listed in Table 2.

No dual fluorescence could be found and as the absorption spectra of the constitutive parts of the spiro molecules are superimposed, selective excitation is impossible. 313- and 366 nm-irradiation gave the same reaction $\mathbf{1} \rightarrow \mathbf{3}$. The very strong shift of the fluorescence of the molecules **1** to short wavelength by lowering temperature is attributed to the viscosity dependent increase of rotational relaxation time for the phenyl units.[16]

EXPERIMENTAL

(a) *Instrumentation*. Absorption measurements: Single beam spectrophotometer ZEISS PMQ II with double monochromator,[16] double beam spectrophotometer ZEISS DMR 21[17] and DMR 10. NMR measurements: Bruker WH 90 and Varian EM 360; Mass spectra: VARIAN-MAT 311 A; IR-spectra: IR-spectrograph LEITZ with micro-attachment; fluorescence measurements: AMINCO-Bowman SPF and FARRAND MK I.

(b) *Isolation of the photoproducts*. Compound **3a**: 250 ml of a 10^{-3} M ethanolic soln of **1a** was irradiated with 366 nm (Schott UV-PIL-filter) from a HPK 125 (Philips) mercury lamp ($I_0 = 2 \times 10^{-9}$ Einstein s^{-1} cm^{-2}).[18] The progress of the photoreaction was monitored by taking samples. By careful evaporation of the solvent the reaction product **3a** can be precipitated. Purification by recrystallization from EtOH. Fp 133° (uncorr). Elementary analysis: C, 92.41 (92.55%); H, 7.49 (7.45%).

Compound **4a**: 200 ml of a 10^{-3} M EtOH-soln of **3a** was irradiated with the same lamp and 313 nm Schott UV PIL-filter in

Table 2. Spectral properties of **1a** to **1d** and photoproducts

	1a	**1b**	**1c**	**1d**	
Absorbance	320,252	365, 335,262	315,255	355,265	Starting Spiro-pyrazoles
298K Flu-Em.	-	480	490	480	
298K Flu.Ex.	-	345,285	325	370,285	
77K Flu-Em	-	425	435	420	
77K Flu.Ex.	-	350,295	320,280	360,275	
	3a	**3b**	**3c**	**3d**	
Absorbance	300	305	290	305	Photo-products hv 366nm
298K Flu-Em.		390	385	390	
298K Flu.Ex.		295(260)	285	305	
77K Flu-Em.		385,370,352	355	390	
77K Flu.Ex.		325	305(260)	320	
77K Phos-Em.		(550)520	(520)495		
77K Phos.Ex.		325	305(260)		
	4				
Absorbance	(275)250	(270)248	(270)249		Photo-products hv 313nm
	5				
Absorbance	290				
298K Flu-Em.	352				
298K Flu.Ex.	310				
77K Flu-Em.	345				
77K Flu.Ex.	315				

Peak maxima of uncorrected spectra in wavelength (nm)

(values in paranthesis are shoulders)

Flu-Em. : Fluorescence - Emission
Flu.Ex. : Fluorescence - Excitation
Phos-Em.: Phosphoresc. - Emission
Phos-Ex.: Phosphoresc. - Excitation

a quartz flask until the maximum concentration of **4a** (as indicated by absorbance at 255 nm) was reached. After concentration **4a** is precipitated at −5°. F.p. 93–96° (uncorr). Ea. C, 92.35 (92.55%); H, 7.61 (7.45%).

Compound **5a**: **4a** (or **1a** or **3a**) was irradiated with 313 nm until no further reaction was observed (UV control). Precipitation after concentration at −10°. Recrystallization from EtOH with very small amount of H_2O. F.p. 88–90° (uncorr.); E.a.: C, 92.39 [92.55%); H, 7.38 (7.45%); ϵ_{290}: 30.500; $\phi_{Fl} = 1.0$; ^{13}C: 143.3, 142.9, 141.6, 140.3, 135.0, 134.4, 128.8, 127.5, 127.2, 126.5, 125.2, 124.7, 124.4, 123.1, 122.0, 45.0, 29.1, 27.0, 25.6 (ppm to TMS); ^1H: 7.9–7.2, 2.8–1.2 ppm; IR: 695, 730, 760, 845, 885, 895, 915, 945, 965, 1030, 1050, 1080, 1180, 1260, 1410, 1460, 1490, 1610, 2900, 2950, 3100, 3400 cm^{-1}. Column chromatography was not used, as all products easily rearrange.[1]

(c) *Computing program*. To calculate the EDQ2-diagram, a program KINAL (author: G. Gauglitz), for the kinetic analysis and simulation a program KINALYSE (author: H. J. Niemann[9]) has been used. These programs are concepted in FORTRAN IV for a CDC 3300.

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