

4. É. D. Chekurovskaya, A. N. Akimov, T. G. Vaistub, and T. A. Bol'shinskova, in: Abstracts of Papers of the Fourth All-Union Symposium on the Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds, Riga (1987), p. 67.
5. Yu. N. Usov, É. D. Chekurovskaya, T. G. Vaistub, and A. N. Akimov, *Neftekhimiya*, No. 6, 810 (1985).
6. O. A. Bozhenova, V.G. Kharchenko, and A. D. Shebaldova, *Koord. Khim.*, No. 6, 4499 (1983).
7. V. I. Bystrenina, A.D. Shebaldova, and G. V. Bespalova, in: Abstracts of Papers of the 16th All-Union Chernyaevskii Conference on the Chemistry, Analysis, and Technology of Platinum Metals, Novosibirsk (1989), p. 107.
8. Yu. N. Kukushkin, R. I. Vlasova, and Yu. Kh. Pazukhina, *Zh. Prikl. Khim.*, No. 11, 2381 (1969).

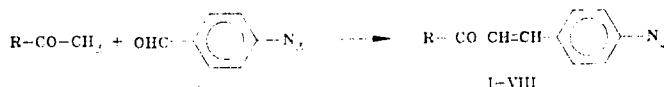
SYNTHESIS AND PROPERTIES OF HETEROCYCLIC ANALOGS OF 4-AZIDOCHALCONE

M. F. Budyka, M. M. Kantor, and M. V. Alfimov

UDC 543.51:547.8:547.572.6

A study has been made of the spectral and photochemical properties of a series of heterocyclic analogs of 4-azidochalcone, specifically the pyridine, quinoline, isoquinoline, and quinoxaline derivatives. It has been shown that the absorption spectra of most of the 4-azidocinnamoyl-arenes are shifted bathochromically in comparison with 4-azidochalcone. The quantum yields of photodissociation of the compounds that were investigated were found to vary within the limits 0.70 ± 0.15 . With steric hindrance for the planar conformation of the molecule, a hypsochromic shift of the absorption spectra is observed, along with a slight decrease of the quantum yield.

Aromatic azides including a propenone grouping $-\text{CO}-\text{CH}=\text{CH}-$ in the overall conjugation chain are finding extensive applications as initiators of photocrosslinking of polymeric molecules [1, 2]. The most active compounds often prove to be those with a p-azidocinnamoyl group [3]. With the aim of determining the influence of the nature of a heterocyclic moiety and the extent of the conjugated system on the spectral and photochemical properties of the aromatic azide, we have synthesized and studied a series of analogs of 4-azidobenzaldehyde with various aromatic and heterocyclic methyl ketones:



R = 2-pyridyl (I), 3-pyridyl (II), 4-pyridyl (III), 2-quinolyl (IV), 4-quinolyl (V),
1-isoquinolyl (VI), 2-quinoxalyl (VII), 3-methyl-2-quinoxalyl (VIII)

In the traditional procedure [4], an aqueous solution of NaOH is added to a methanol solution of the mixed aldehyde and ketone. We found that the use of this sequence in mixing the reactants often leads to self-condensation of the ketone (compare [5]) and to much lower yields of the desired azidochalcone. To avoid this effect, we adopted a procedure in which a solution of the ketone was added slowly to a stirred solution of the aldehyde with caustic; in this manner we obtained a series of 4-azidocinnamoylarenes I-VIII (Table 1).

In the PMR spectra of the azides, signals of olefinic protons are observed in the form of two doublets at 7.0/8.0 (α) and 7.3/8.5 (β) with $J = 15/16$ Hz, indicating the *trans* configuration of the substituents at the double bond. It is interesting to note the considerable downfield shift of the signal of the β -olefinic proton in the case of the 2-pyridine, 2-quinoline, and 2-quinoxaline derivatives. In these compounds, quite possibly, the β -olefinic proton, as a consequence of the *trans* configuration, may fall into the region of deshielding of the aromatic ring because of the planar conformation of the molecule.

Institute of Chemical Physics, Chernogolovka Branch, Russian Academy of Sciences. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 10, pp. 1340-1343, October, 1991. Original article submitted July 4, 1990.

TABLE 1. Azidocinnamoylarenes $R-CO-\overset{\alpha}{CH}=\overset{\beta}{CH}-\text{C}_6\text{H}_4-N_3$

Com- pound	T_m , °C	M*	PMR spectrum (in $CDCl_3$), δ , ppm				IR spectrum, ν , ppm		Yield, %
			α -H	β -H	<i>c</i> -H	<i>d</i> -H	N_3	CO	
I	90	250	7.86	8.24	7.68	7.02	2140	1680	68
II	105	250	7.40	7.76	7.59	7.02	2110	1670	35
III	116	250	7.80*	7.84	7.94	7.21	2130	1670	7
IV	133	300	7.96; 7.94*	8.51; 8.58	7.78; 7.94	7.10, 7.25	2130	1680	95
V	135	300	7.42*	7.65	7.85	7.19	2130	1670	54
VI	120	300	7.83*	8.08	7.88	7.21	2140	1680	31
VII	143	301	7.98	8.34	7.76	7.09	2130	1670	64
VIII	138	315	7.79	7.98	7.66	7.04	2140	1680	71

*In deuterioacetone.

TABLE 2. Absorption Spectra and Quantum Yields of Dissociation of Azidocinnamoylarenes upon Irradiation at 365 nm in Toluene Solution ($c = 10^{-4}$ M)

Com- pound	Long-wave band		Φ^*	Com- pound	Long-wave band		Φ	Com- pound	Long-wave band		Φ^*
	λ_{max} , nm	\log ϵ			λ_{max} , nm	\log ϵ			λ_{max} , nm	\log ϵ	
I	347	4.25	0.80	IV	350	4.41	0.85	VII	359	4.39	0.77
II	343	4.37		V	338	4.35	0.58	VIII	350	4.32	
III	345	4.38		VI	355	4.42	0.74				

*No values of Φ were measured for compounds I, III, or VII.

If there is steric hindrance for such a conformation, for example if a methyl group is introduced into position 3 of the quinoxaline ring, the signal of the β -olefinic proton undergoes a sharp upfield shift.

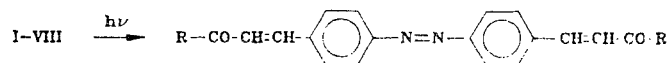
Signals of the aromatic protons of the *para*-substituted phenylazide fragment are manifested in the form of two doublets with values of the constant $J = 8$ and 9 Hz at 6.6 and 8.0 ppm.

In the IR spectra, stretching vibrations of the carbonyl group are observed in the 1630 - 1680 cm^{-1} interval, corresponding to conjugation of the carbonyl with the π -bond system; also, an intense band is observed at 2110 - 2150 cm^{-1} , due to stretching vibrations of the azido group. The band at 965 - 990 cm^{-1} is additional evidence of the *trans* configuration of these compounds [5].

In the electronic absorption spectra of most of the azidocinnamoylarenes (Table 2), a bathochromic shift of the long-wave band is observed in comparison with 4-azidochalcone, for which the absorption maximum occurs at 340 nm. Depending on electronic and steric factors of the substituent in the azidocinnamoylarenes, this maximum may vary from 340 to 360 nm. It is interesting to note that in the case of the 4-quinoline substituent (compound V), we observe a rather strong short-wave shift of the band in comparison with the 2-quinoline substituent (compound IV). This is probably related to steric hindrance for the planar conformation of the molecule in compound V, created by the *peri* hydrogen in position 5 of the quinoline ring; this steric hindrance disrupts the conjugation.

We have measured the quantum yields of photodissociation for a number of these azides upon excitation by light at 365 nm. In all cases, rather high values of Φ were obtained (Table 2). The disruption of the coplanar position of the carbonyl group as a result of steric hindrance in the 4-quinoline derivative V is responsible for a slight decrease in quantum yield.

In the absence of oxygen, the main product from photolysis of solutions of *p*-azidocinnamoylarenes is the corresponding azo compound:



Thus, in the photolysis of the azide IV, a 70% yield of the azo compound was obtained. A distinctive feature of the azides is their tendency to split out a molecule of nitrogen when subjected to the action of photons, a tendency that is also manifested when they are subjected to electron impact: In the mass spectra of compounds I-VIII, the maximum-intensity peak is that of the ion $[M - 28]^+$. Under the ionization conditions that were selected (12 eV), the molecular ion peaks are also higher in intensity (26-90%). A more detailed comparative analysis of mass spectra of the azides and the corresponding amines is given in [6].

EXPERIMENTAL

Electronic absorption spectra were measured in Specord UV-Vis and Specord M-40 spectrophotometers. The IR spectra were measured in a UR-20 spectrophotometer. NMR spectra were obtained in a Bruker WH-360 instrument with TMS as an internal standard. The mass spectra were taken in a Hitachi M80A instrument with an M003 data processing system, ionizing electronenergy 12 eV, emission current 100 μ A, and ionization chamber temperature 200°C.

The photolysis of the azides was performed by irradiation with a DRSh-1000 mercury lamp, with a combination of glass filters to segregate the lines of the mercury spectrum.

Column chromatography was performed in glass columns with Silpearl silica gel.

The following compounds were synthesized by methods that had been described previously in the literature: 2-acetylquinoline [7], 4-acetylquinoline [8], 2-acetylpyridine [9], 3-acetylpyridine [10], and 4-acetylpyridine [11].

2-Acetylquinoxaline. To 2 g (15 mmoles) of quinoxaline, 7 ml of 40% H_2SO_4 was added. The mixture was cooled to 5°C, 5.6 ml (100 mmoles) of acetaldehyde was added; then, 9 ml of *tert*-butylhydroperoxide and a solution of 28 g of $FeSO_4 \cdot 7H_2O$ in 70 ml of water were added simultaneously and dropwise while stirring. The reaction mixture was allowed to stand for 2 h, after which it was neutralized with sodium carbonate to pH 6 and extracted with ether in an extractor. The ether extract was dried over $MgSO_4$, and the ether was driven off. By column chromatography, 82 mg (31%) of acetylquinoxaline was recovered, mp 76°C, in comparison with mp 77°C reported in [12].

1-Acetylisquinoline was obtained analogously, with a 21% yield, mp 14°C, in comparison with mp 14-15°C reported in [13].

2-Acetyl-3-methylquinoxaline. A mixture of 2 g (18 mmoles) of *o*-phenylenediamine, 4.8 g (37 mmoles) of isonitrosoacetylacetone, and 6 ml of acetic acid was heated ($\sim 100^\circ C$) for 4 h. The mixture was cooled to room temperature and filtered, and the filtrate was neutralized with sodium carbonate and extracted with ether. The ether extract was dried over $MgSO_4$, the ether was removed under vacuum, and the residue was chromatographed in a column, obtaining 300 mg of 2-acetyl-3-methylquinoxaline (9%), mp 84°C, in comparison with mp 86.5°C reported in [14].

General Method for Synthesis of 4-Azidocinnamoylarenes. To a solution of 1 mmole of 4-azidobenzaldehyde in 1 ml of methanol, 0.3 ml of a 10% NaOH solution was added; then, a solution of 1 mmole of the appropriate acetylarene in 1 ml of methanol was added dropwise while stirring. The mixture was stirred for 2-10 h; the residue was filtered off, washed with 70% methanol, and recrystallized from benzene or ethanol. The substances are light-yellow crystals that decompose when exposed to light.

LITERATURE CITED

1. *Prospects and Possibilities in Nonsilver Photography* [in Russian], Khimiya, Leningrad (1988), p. 90.
2. A. V. El'tsov (ed.), *Light-Sensitive Polymeric Materials* [in Russian], Khimiya, Leningrad (1985).
3. T. A. Zueva, V. M. Treushnikov, and A. V. Oleinik, *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, **30**, 44 (1985).
4. S. A. Tsukerman, Ch. K. Shon, and V. F. Lavrushin, *Zh. Obshch. Khim.*, **34**, 2881 (1964).
5. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, 2nd edn., Methuen, London (1958).
6. M. F. Budyka, M. M. Kantor, and A. P. Pleshkova, *Khim. Geterotsikl. Soedin.*, No. 5, 660 (1991).
7. B. R. Brown, *J. Am. Chem. Soc.*, **71**, 2577 (1949).
8. A. Kaufmann, H. Peyer, and V. Kunkler, *Ber. Dtsch. Chem. Ges.*, **45**, 3093 (1912).
9. T. C. Bruice, *J. Am. Chem. Soc.*, **79**, 702 (1957).
10. G. S. Kolesnikov, *Synthesis of Vinyl Derivatives of Aromatic and Heterocyclic Compounds* [in Russian], Moscow (1960), p. 251.

11. *Sint. Geterotsikl. Soedin.*, No. 7, 17 (1966).
12. G. Henscke and K. J. Bahner, *Chem. Ber.*, **91**, 1605 (1958).
13. J. J. Padbury and H. G. Lindwall, *J. Am. Chem. Soc.*, **67**, 1268 (1945).
14. F. Sachs and H. Barschall, *Ber. Dtsch. Chem. Ges.*, **34**, 3047 (1901).

SPECTRAL AND LUMINESCENT PROPERTIES OF 9-ARYLAMINOACRIDINES

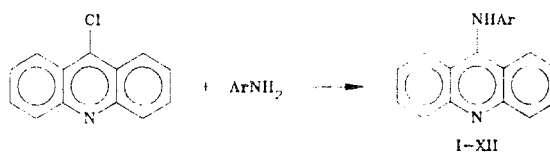
M. F. Budyka and R. M. Fatkulbayanov

UDC 547.835.3+535.37

A study has been made of the influence of electronic and steric factors of the aromatic substituent in 9-arylaminoacridines on the behavior of these compounds when subjected to light quanta or electron impact. It has been shown that the introduction of donor substituents shifts the absorption and luminescence spectra toward longer wavelengths, with a simultaneous increase of the Stokes shift and a decrease of the quantum yield of luminescence; it has been established that the introduction of sterically hindered substituents has a similar effect. In the mass spectra, the introduction of substituents with stronger donor properties tends to increase the stability of the molecular ions.

Because of the spectral properties of aminoacridines, they are being investigated actively as generation media of lasers [1] and as luminescent labels in biology [2]. Among the isomeric compounds, 9-arylaminoacridines are distinguished by ready availability and the possibility of varying their properties over a broad range by changing the structure of the aromatic radical Ar. However, data that have been reported in the literature on the spectral and luminescent properties of these compounds are very limited, and often are only qualitative in nature.

We have synthesized a series of derivatives of 9-aminoacridine by a nucleophilic substitution reaction from 9-chloroacridine and the appropriate aromatic amine, and we have also investigated their spectral characteristics.



We found that acceptor substituents in the aromatic amine retard the reaction, whereas donor substituents accelerate the reaction significantly (see Table 1). With excess amine, the 9-chloroacridine is converted almost quantitatively to the aminoacridine; variations in the preparative yield most likely reflect differences in the behavior of compounds I-XII in the course of purification by crystallization.

Spectral and luminescence characteristics of the arylaminoacridines have been determined (Table 2). For comparison, the quantum yields of luminescence of the compounds are referred to the quantum yield of the simplest representative of the series, 9-phenylaminoacridine (I). In the electronic spectrum of this compound we observe a broad absorption band at λ_{\max} 397 nm; in the short-wave part, bands that are characteristic for absorption by the acridine ring are preserved (345 and 361 nm) [3]. In the long-wave part we observe a weak inflection that becomes more and more distinct when donor substituents are introduced into the *para* position of the phenyl ring; this absorption increases to give an additional maximum with λ_{\max} 436 nm for the dimethylamino derivative V. At the same time, the intensity of the principal maximum drops off.

The luminescence spectra are affected to an even greater degree by the introduction of donor substituents into compound I. For the methoxy derivative III, the luminescence maximum is shifted "bathofluorically" by 105 nm, and the Stokes shift ($\Delta\nu$) increases to 9000 cm^{-1} . Because of the insolubility of the hydroxy derivative IV in toluene, we were unable to determine its spectral characteristics.

Institute of Chemical Physics, Chernogolovka Branch, Russian Academy of Sciences. Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 10, pp. 1344-1349, October, 1991. Original article submitted July 4, 1990.