SYNTHESIS OF VINYL DERIVATIVES OF ACRIDINE AND PHENANTHRIDINE*

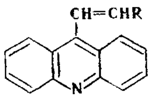
A. P. Kucherenko, S. G. Potashnikova,
S. S. Radkova, S. N. Baranov,
A. K. Sheinkman, and N. V. Volbushko

UDC 547.835'836.3.07

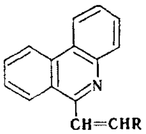
Vinyl derivatives of the acridine and phenanthridine series were obtained by reaction of 9-methylacridine and 6-methylphenanthridine with aromatic aldehydes in the presence of acyl halides.

One of us [2] has developed a method for the preparation of styrylpyridines by condensation of picolines with aromatic aldehydes in the presence of acyl halides. N-Acyl salts of picolines, which react with aldehydes in situ, are formed during the reaction; an N-acyl residue is split out, and styryl bases are formed.

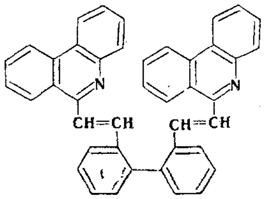
In the present study we were able to use this method to obtain styrylacridines (I), styryl phenthridines (II, III), and chalcones of the acridine series (IV) (Table 1).



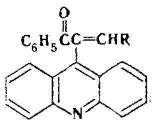
I



II



III



IV

Anhydrous dimethylformamide (DMFA) proved to be the most convenient medium for condensation of 9-methyl- and 9-phenacylacridines and 6-methylphenthridine with aromatic aldehydes in the presence of benzoyl chloride [2]. The reaction can be carried out in acetic anhydride without the addition of acyl halides via the method in [3], but the yields of I-IV are lower in this case.

The strong absorption bands in the IR spectra of styryls I-III at 970-980 and 1620-1635 cm^{-1} attest to the presence of a conjugated double bond. The intense absorption bands at 1620 and 1708 cm^{-1} in the spectra of chalcones IV are characteristic for C=O stretching vibrations. The absorption bands at 245-250 and 330-350 nm that are characteristic for such compounds [3] are present in their UV spectra (Table 2). As in styrylpyridines [2], the longwave band is due to a $\pi \rightarrow \pi^*$ transition. In some cases (Table 2) we observed two longwave absorption bands and, correspondingly, two luminescence bands, which are apparently related to the cis and trans isomers. trans-Styrylpyridines are formed from N-acyl salts of picolines [4]. However, the formation of admixtures of cis isomers was observed in the preparation of sterically hindered structures [5]. The cis isomers are probably formed partially in this case also: absorption bands at 314 (If), 307 (Ib), and 330 nm (IIj) and luminescence bands at 520-530 nm.

---

*Communication XXX from the series "Reactions of Cycloammonium cations." See [1] for communication XXIX.

Donetsk State University. Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1257-1260, September, 1974. Original article submitted July 2, 1973.

TABLE 1. 9-Styrylacridines (I,IV) and 6-Styrylphenanthridines (II,III)

Compound	R	mp, °C (crystallization solvent)	R_f*	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
Ia	C_6H_5	185—186 (ethanol)	0,59	$C_{21}H_{15}N$	89,3	5,8	5,1	89,6	5,4	5,0	44
Ib	p-$N(CH_3)_2C_6H_4$	241—242 (pentanol)	0,46	$C_{23}H_{20}N_2$	85.5	6,4	8,6	85,2	6,3	8,6	55
Ic	p-$N(C_2H_5)_2C_6H_4$	188—189 (ethanol)	0,16	$C_{25}H_{24}N_2$	85,5	6,4	7,9	85,2	6,9	7,9	43
Id	p-BrC_6H_4	254—255 (ethanol)	0,68	$C_{21}H_{14}BrN$	69,9	3,5	3,5	70,0	3,9	3,9	48
Ie	m-$NO_2C_6H_4$	229—230 (pentanol)	0,83	$C_{21}H_{14}N_2O_2$	78.2	4,7	8,9	77,3	4,3	8,6	50
If	p-$NO_2C_6H_6$	295—296 (chlorobenzene)	0,58	$C_{21}H_{14}N_2O_2$	76,9	4,1	8,8	77,3	4,3	8,6	49
Ig	o-$NO_2C_6H_4$	170—172 (pentanol)	0,62	$C_{21}H_{14}N_2O_2$	77,4	5,0	8,0	77,3	4,3	8,6	45
Ih	p-$CH_3OC_6H_4$	204—205 (butanol)	0,58	$C_{22}H_{17}NO$	84,0	5,2	4,7	84,7	5,5	4,5	47
Ii	3,5-(t-C_4H_9)$_2$-4-HOC_6H_2	163—165 (petroleum ether)	0,59	$C_{29}H_{31}NO$	85,3	7,4	2,9	85,0	7,6	3,4	40
IIa	p-$N(CH_3)_2C_6H_4$	146—147 (heptane)	0,69	$C_{23}H_{20}N_2$	85,3	6,2	8,6	85,2	6,2	8,6	60
IIb	p-$N(C_2H_5)_2C_6H_4$	138—139 (heptane)	0,81	$C_{25}H_{24}N_2$	85,2	6,9	8,0	85,2	6,9	7,9	55
IIc	p-$NO_2C_6H_4$	238—239 (hexanol)	0,66	$C_{21}H_{14}N_2O_2$	76,8	4,5	8,4	77,3	4,3	8,6	37
IId	m-$NO_2C_6H_4$	192—193†	0,64	$C_{21}H_{14}N_2O_2$	77,0	4,3	8,6	77,3	4,3	8,6	23
IIe	p-BrC_6H_4	212—213†	0,88	$C_{21}H_{14}BrN$‡	69,1	4,1	3,7	70,0	3,9	3,9	17
IIf	p-$CH_3C_6H_4$	159—160 (heptane)	0,82	$C_{22}H_{17}N$	88,8	6,0	5,3	89,0	6,0	4,9	20
IIg	p-$CH_3OC_6H_4$	142—143 (propanol)	0,75	$C_{22}H_{17}NO$	83,9	5,5	4,6	84,8	5,5	4,5	42
IIh	$C_6H_5CH{=}CH$	130—132 (heptane)	0,88	$C_{23}H_{17}N$	89,1	5,7	4,1	89,8	5,6	4,5	15
IIi	2-Methyl-6-pyridyl	225—224 (DMFA)	0,19	$C_{21}H_{16}N_2$	84,8	5,5	9,5	85,1	5,4	9,4	30
IIj	2-Furyl	128—130 (heptane)	0.55	$C_{19}H_{13}NO$	83,9	4,9	5,5	84,1	4,8	5,6	31
IIk	p-ClC_6H_4	214—215 (propanol—DMFA 1:1)	0.82	$C_{21}H_{14}ClN$‡	79,6	4,7	4,4	79,8	4,5	4,4	20
IIm	3,5-(t-C_4H_9)$_2$-4-HOC_6H_2	154—156	0,86	$C_{29}H_{31}NO$	84,8	7,1	3,6	85,0	7,6	3,4	21
III	—	379—380 (chlorobenzene)	0,32	$C_{42}H_{28}N_2$	89,1	5,1	5,1	89,9	5,1	5,0	15
IVa	p-$N(CH_3)_2C_6H_4$	253—254 (ethanol)	0,71	$C_{30}H_{24}N_2O$	83,7	6,1	6,6	84,1	5,6	6,5	72
IVb	p-$N(C_2H_5)_2C_6H_4$	172—173 (ethanol)	0,23	$C_{32}H_{28}N_2O$	84,5	6,0	6,5	84,2	6,2	6,1	54
IVc	o-$NO_2C_6H_4$	183—184 (methanol)	0,60	$C_{28}H_{18}N_2O_3$	78,6	4,3	6,8	78,1	4,2	6.5	69
IVd	o-$NO_2C_6H_4$	203—204 (ethanol)	0,63	$C_{28}H_{18}N_2O_3$	77,9	4,1	6,1	78,1	4,2	6,5	56
IVe	o-$C_6H_4OCH_3$	138—140 (ethanol)	0,34	$C_{29}H_{21}NO_2$	82,5	5,5	3,4	82,8	5,3	3,4	72

---

* In a thin layer of Al_2O_3 [benzene—hexane—chloroform (6:1:30].

† Preparative chromatographic separation on aluminum oxide [benzene—hexane—chloroform (6:1:30)].

‡ For IIe, found: Br 11.8%; calculated: Br 12.1%. For IIk, found: Cl 11.3%; calculated: Cl 11.2%.

TABLE 2. UV Spectra and Luminescence Spectra of Some Styrylacridines and Styrylphenathridines

Compound	λ_{max}, nm (lg ε)	Luminescence	
		λ_{max}, nm	φ
Ia	255, 302, 365, 425 (4,98; 4,60; 3,98; 4,56)	520, 558	0,31
Ib	245, 307, 365, 425 (4,98; 4,60; 3,96; 4,56)	525, 578	0,05
Ic	255, 313, 367, 427 (4,64; 3,99; 3,66; 3,88)	526, 579	0,03
If	252, 314, 370 (5,15; 4,38; 4,30)	524, 570	0,42
IIg	365 (4.14)	Does not fluoresce	
IIi	330, 349 (3,3; 3,2)	" "	
IIj	250, 370 (4,78; 4,67)	" "	

The vinyl derivatives of acridine and phenanthridine proved to be effective stabilizers for polyolefins. Their introduction into shock-resistant polystyrene increases the time that elapses prior to the onset of oxidative destruction of the polymer at 200° by a factor of 2-2.5 as compared with unstabilized polystyrene.

EXPERIMENTAL

The IR spectra of KBr pellets and mineral-oil pastes of the compounds were recorded with a UR-10 spectrometer. The UV spectra of dioxane solutions were recorded with a Specord UV spectrometer, while the luminescence spectra of dioxane solutions were recorded with an ISP-51 spectrograph with an FÉP-1 photoelectric adapter. Thin-layer chromatography (TLC) on Al_2O_3 was carried out by elution with benzene—hexane—chloroform (6 : 1 : 30); the chromatograms were developed with iodine vapors.

9-Styrylacridine. A 1.45-g (0.01 mole) sample of benzoyl chloride was added to a solution of 1.93 g (0.01 mole) of 9-methylacridine in 22 ml of anhydrous DMFA, and the mixture was stirred at room temperature for 20 min, after which 1.06 g (0.01 mole) of benzaldehyde was added, and the mixture was heated at 150-160° for 5 h. It was then cooled, acidified with concentrated hydrochloric acid, and steam distilled. Ammonium hydroxide was added to the residue until it was alkaline, and the resulting resinous precipitate was removed by filtration, washed to neutrality with water, dried, and recrystallized from ethanol to give 1.25 g (44%) of 9-styrylacridine with mp 185-186°.

The compounds obtained by this method are presented in Table 1.

LITERATURE CITED

1. A. K. Sheinkman, M. N. Mestechkin, A. P. Kucherenko, N. A. Klyuev, G. A. Mal'tseva, and L. A. Palagushkin, Khim. Geterotsikl. Soedin., 1096 (1974).
2. A. N. Kost, A. K. Sheinkman, and A. N. Rozenberg, Zh. Obshch. Khim., 34, 4046 (1964).
3. B. Shaw and E. Wagstaff, J. Chem. Soc., 77 (1933).
4. A. K. Sheinkman, A. N. Kost, V. I. Sheichenko, and A. N. Rozenberg, Ukr. Khim. Zh., 33, 941 (1967).
5. N. R. Kal'nitskii, A. K. Sheinkman, A. N. Rozenberg, and G. M. Bogdanov, Khim. Geterotsikl. Soedin., 1528 (1973).