SYNTHESIS OF 1-AMINO-2-ARYLETHYLENEIMINE ARYLHYDRAZONES

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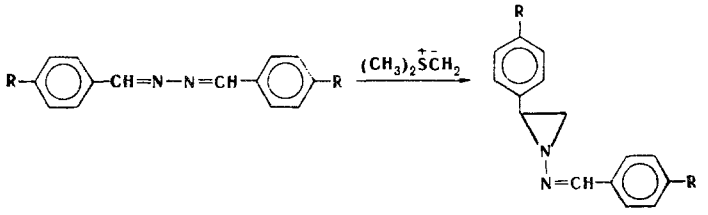
UDC 547.717'525.2:543.51

In a continuation of our research [1] on the inversion of nitrogen in 1-aminoethyleneimine derivatives we synthesized 1-amino-2-arylethyleneimine arylhydrazones (Ia-d) via the reaction of dimethylsulfoniummethylide with symmetrical azines in order to accumulate data to ascertain the principles of the change in the energy barrier to inversion of nitrogen in aziridine derivatives.



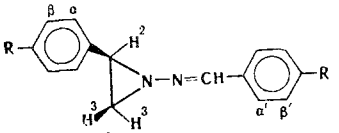
I a R = F; b R = Cl; c R = Br; d R = OCH_3 I a-d

TABLE 1. Physicochemical Characteristics of Arylhydrazones Ia-d

Compound	mp, °C	Empirical formula	Found, %			Calc., %			UV spectra*		Yield, %
			C	H	N	C	H	N	λ_{max}, nm	$\varepsilon 10^{-4}$	
Ia	49—51	$C_{15}H_{12}F_2N_2$	69.7	4.8	10.7	69.7	4.6	10.8	253	0.74	58
Ib	72—73	$C_{15}H_{12}Cl_2N_2$	60.8	4.5	9.4	61.1	4.1	9.5	262	0.66	54
Ic	115—116	$C_{15}H_{12}Br_2N_2$	47.2	3.1	7.2	47.4	3.1	7.3	265	0.60	61
Id	82—83	$C_{17}H_{18}O_2N_2$	72.3	6.4	10.0	72.3	6.4	9.9	272	0.68	64

*The electronic spectra of Ia-d were obtained from n-hexane solutions.

TABLE 2. Parameters of the PMR Spectra of Hydrazones of the Ia-d Type



cis trans

Compound	Chemical shifts, τ, ppm, relative to tetramethylsilane									SSCC*, Hz	
	H^2	H^3 cis	H^3 trans	—CH=	α	β	α′	β′	R	H^2H^3 trans ^3J	H^2H^3 cis ^3J
Ia	7.00	7.77	7.57	1.57	2.80	3.05	2.41	3.00	—	4.7	7.6
Ib	7.02	7.78	7.57	1.67	2.89	2.89	2.53	2.77	—	4.7	7.8
Ic	7.02	7.77	7.57	1.67	2.97	2.67	2.70	2.70	—	4.8	7.7
Id	7.06	7.81	7.62	1.62	2.90	3.29	2.51	3.24	6.36 (R′) 6.39 (R)	4.9	7.7

*The abbreviation SSCC represents spin-spin coupling constant; $^2J = 0$.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 426-427, March, 1975. Original article submitted September 9, 1974.

The physicochemical characteristics of the synthesized compounds (Ia-d) are presented in Table 1, and the parameters of the PMR spectra are given in Table 2.

LITERATURE CITED

1. S. A. Giller, A. V. Eremeev, M. Yu. Lidak, V. A. Pestunovich, É. É. Liepin'sh, and I. Ya. Kalvin'sh, Khim. Geterotsikl. Soedin., 45 (1971).