SYNTHESIS OF 4,5-DIARYL-2-(N-METHYL-3-CARBAZOLYL)- AND 4,5-DIARYL-2-(N-METHYL-1,2,3,4-TETRAHYDRO-7-CARBAZOLYL)IMIDAZOYL RADICALS

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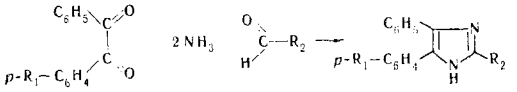
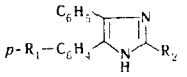
A number of imidazoles were obtained by the reaction of substituted benzils with aldehydes of the carbazole series. Chlorobenzene solutions of the imidazoles take on a green coloration on oxidation with lead dioxide. The presence of free radicals in these solutions is confirmed by the ESR spectra and by the reaction with hydroquinone, diphenylamine, carbazole, and α,α-diphenyl-β-picrylhydrazine.

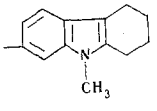
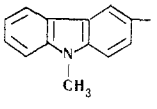
Free radicals of the triarylimidazolyl series have a high dehydrogenating capacity and, on reaction with α,α-diphenyl-β-picrylhydrazine, convert it to α,α-diphenyl-β-picrylhydrazyl, during which they are reduced to the starting imidazoles [1]. Furyl(or thienyl) diphenylimidazoles reduce α,α-diphenyl-β-picrylhydrazyl and are converted to polymeric products [2]. In this paper, we have studied the effect of replacement of one of the phenyl rings by a carbazole ring on the dehydrogenating capacity of diarylcarbazolylimidazolyls.

In this connection, we undertook the synthesis of 4,5-diaryl-2-(N-methyl-1,2,3,4-tetrahydro-7-carbazolyl)imidazole, which was accomplished by heating substituted benzils with aldehydes of the carbazole series in glacial acetic acid in the presence of ammonium acetate [3]:



Chlorobenzene solutions of the diarylcarbazolylimidazoles become green on oxidation with lead dioxide due to the presence of radicals, which was confirmed by the ESR spectra. The first derivative of the ESR spectrum is a singlet (Fig. 1).

TABLE 1. 

R_1	R_2	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
H		358—360	$C_{28}H_{25}N_3$	82,7	6,7	10,3	83,1	6,2	10,4	61
Br		372—373	$C_{28}H_{24}BrN_3$	69,8	5,1	8,2	69,7	5,0	8,7	50
CH_3O		360—361	$C_{29}H_{27}N_3O$	80,1	6,6	9,3	80,4	6,2	9,7	55
C_2H_5O		350—351	$C_{30}H_{29}N_3O$	80,1	6,4	9,1	80,5	6,5	9,4	59
CH_3		362—363	$C_{29}H_{27}N_3$	83,0	6,5	9,9	83,4	6,5	10,1	64
H		337—338	$C_{28}H_{21}N_3$	84,3	5,4	10,8	84,2	5,3	10,5	70
CH_3O		346—347	$C_{29}H_{23}N_3O$	81,0	5,7	10,1	81,1	5,4	9,8	67
C_2H_5O		320—321	$C_{30}H_{25}N_3O$	81,7	6,1	9,6	81,3	5,7	9,5	61

N. P. Ogarev Mordovo State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1550-1551, November, 1971. Original article submitted July 7, 1970.

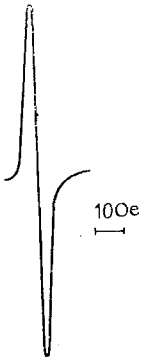


Fig. 1. First derivative of the ESR spectrum of the 4,5-diphenyl-2-(N-methyl-3-carbazolyl)imidazolyl radical.

Solutions of the radicals are decolorized by the addition of hydroquinone, diphenylamine and carbazole. When α,α-diphenyl-β-picrylhydrazine is added, the green color caused by the presence of the diarylcarbazolylimidazolyl radical vanishes, and the violet color of α,α-diphenyl-β-picrylhydrazyl appears. Thus, as in the case of triarylimidazolyl, the dehydrogenating capacity of diarylcarbazolylimidazolyl is higher then that of diphenylpicrylhydrazyl.

EXPERIMENTAL

The aldehydes of the carbazole series were obtained by known methods [4, 5].

4,5-Diphenyl-2-(N-methyl-1,2,3,4-tetrahydro-7-carbazolyl)imidazole. A mixture of 1.065 g (0.005 mole) of N-methyl-1,2,3,4-tetrahydro-7-formylcarbazole, 1.05 g (0.005 mole) of benzil, 25 ml of glacial acetic acid, and 3 g of ammonium acetate was refluxed for 1 h, cooled, and poured into 250 ml of water. The gray-green, pasty precipitate was recrystallized from chlorobenzene to give a colorless, high-melting substance.

All of the remaining imidazoles, which, in contrast to triphenylimidazole, are only very slightly soluble in alcohol, benzene, and the other usual solvents, were similarly obtained. The characteristics of the imidazoles obtained are presented in Table 1.

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