direct SSCCs through one bond, $^1J(C_{4a}-H_{4a})$ = 137 and 145 Hz. The assignment of the signals of the C(4a) carbon atom was based on the fact that in the proton-coupled ^{13}C NMR spectra of compounds (IIa, b) the components of its doublets were broadened through its spin-spin coupling with the protons of the N-methyl group. The signals of the C(10a) carbon atom were shifted downfield (56.9 and 58.2 ppm) and had large values of the direct constants $^1J(C_{10a}-H_{10a})$ = 156 and 162 Hz for compounds (IIa) and (IIb), respectively.

Compound (IIa): ethyl 3,5-dimethyl-1-(4-nitrophenyl-1,4,4a,5,10,10a-hexahydropyridazino[3,4-b]quinoxaline-4-carboxylate: mp 191-192°C (from acetone), yield 40%; (IIb): ethyl 3,5-dimethyl-1-(2,4-dinitrophenyl)-1,4,4a,5,10,10a-hexahydropyridazino[3,4-b]quinoxaline-4-carboxylate; mp 160-161°C (from acetonitrile), yield 75%.

LITERATURE CITED

1. Y. C. Tong and H. O. Kerlinger, J. Heterocycl. Chem., 20, 365 (1983).
2. V. N. Charushin, O. N. Chapakhin, and A. I. Rezvukhin, Heterocycles, 16, 196 (1981).
3. V. N. Charushin, L. M. Naumova, G. G. Izmailova, and O. N. Chupakhin, Khim. Geterotsikl. Soedin., No. 8, 1120 (1983).

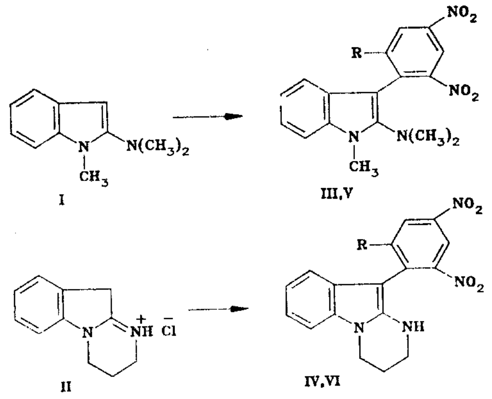
ARYLATION OF COMPOUNDS OF THE 2-AMINOINDOLE SERIES

E. S. Besidskii, G. A. Golubeva, and
L. A. Sviridova

UDC 547.754'759.2'583.42.07

It is known that indole and its alkyl derivatives are arylated by picryl chloride in position 3 only on prolonged heating in toluene or xylene [1].

We have found that the aminoindole (I) and the pyrimidoindole (II) react with picryl chloride in ethanol in the presence of pyridine (1:1:1) in a few minutes even at room temperature with the formation of β-aryl derivatives. In the case of the indole (II), the hydrochloride was used in the reaction and the ratio of the reagents became, accordingly, 1:1:2.



III, IV R=NO$_2$; V, VI R=H

The arylation of compounds (I) and (II) with 1-chloro-2,4-dinitrobenzene, not previously known in the indole series, took place under more severe conditions (ethanol, boiling for 12 h; or DMFA, 30 min) and likewise led to β-substituted compounds — (V) and (VI), respectively.

Compounds (III-VI) are difficultly fusible, sparingly soluble, strongly colored substances which permit the assumption of a considerable separation of the charges in the molecules.

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 708-709, May, 1985. Original article submitted October 8, 1984.

0009-3122/85/2105-0601$09.50

Details of their preparation are (substance, yield, %, mp, °C, λ_{max}, nm): (III) 80, 261, 540; (IV), 62, 241, (decomp.), 590; 1-methyl-3-picrylindole, —, 242, 433 [1]; (V) 55, 242, 376; (VI) 38, 222 (decomp.), 535. The PMR spectra and elementary analyses corresponded to the structures given for (III-VI).

Thus, the presence of a donor substituent — an amino group — in the α position greatly increases the nucleophilicity of the β position of the indole nucleus.

LITERATURE CITED

1. W. Treibs and M. Wahren, Chem. Ber., 94, 2142 (1961).

A NEW METHOD OF IDENTIFYING CONFIGURATIONAL ISOMERS OF HETEROCYCLIC OXIMES

L. B. Krivdin, G. A. Kalabin,
R. N. Nesterenko, and B. A. Trofimov

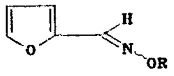
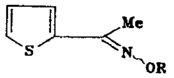
UDC 547.288.4'724'732:543.422.25

The assignment of the configuration of oximes is performed by various methods but not one of them is sufficiently universal, and their results are not always unambiguous [1-4]. We have found that in order to establish the configuration of oximes of heterocyclic ketones it is possible to use the direct $^{13}C—^{13}C$ SSCCs between the nuclei of the oxime carbon and the closest atom of the heterocyclic fragment.

The values of the $^{13}C—^{13}C$ SSCCs of the E isomers (unshared electron pairs on the nitrogen atom in the cis orientation with respect to the interacting ^{13}C nuclei) are 8-10 Hz greater than those of the Z isomers, which correspond to almost 15% of the actual value of the constant. The substitution of the oxime at the oxygen atom, which is used for protecting the hydroxy group, does not lead to an appreciable change (<1 Hz) in the constant under discussion, which is very convenient for establishing the configurations of various O-derivatives of oximes. It is also important to note that the $^{13}C—^{13}C$ SSCCs in the Z isomers coincide to within 1-3 Hz with the same constants in the corresponding aldehydes or ketones (68.9 or 59.2 Hz, respectively which presents additional possibilities for the configurational analysis of oximes.

The results given show the possibility of using the $^{13}C—^{13}C$ SSCCs as a new criterion for the unambiguous identification of the configurations of heterocyclic oximes and their O-derivatives.

TABLE 1. Values of the $^{13}C—^{13}C$ SSCCs (Hz) in Oximes of the Furan and Thiophene Series

					
R	Configuration	SSCC	R	Configuration	SSCC
H	E	80,5	H	E	70,2
H	Z	71,8	H	Z	60,4
CH(Me)OBu-*n*	E	79,5	$CH=CH_2$	E	70,0
CH(Me)OBu-*n*	Z	71,4	$CH=CH_2$	Z	59,8

A. A. Zhdanov Irkutsk State University. Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, p. 709, May, 1985. Original article submitted October 16, 1984.

0009-3122/85/2105-0602$09.50