

Calculated: C 60.6; H 5.5; N 9.2%. PMR spectrum: 1.17 and 1.37 [each 3H, s, 3,3-(CH₃)₂], 2.83 (3H, s, 1-CH₃), 5.52 (1H, d, 3'-H), 7.18 (1H, d, 4'-H, J_{3',4'} = 10.5 Hz), 4.09 (4H, q, J = 7.0 Hz, 5'-, 7'-OCH₂), 1.49 and 1.39 [each 3H, t, 5'- and 7'-OCH₂CH₂], 6.47-8.15 (3H, m, Ar-H).

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NITROGENOUS HETEROCYCLES.

6.* REACTIONS OF ORGANOMAGNESIUM DERIVATIVES OF 7-AZA- AND BENZOINDOLES WITH DIETHYL OXALATE AND THE REACTIVITY OF ETHOXALYLINDOLES

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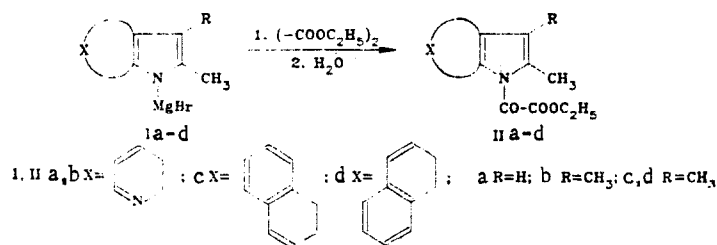
UDC 547.484'754'759:543.422

The reactions of organomagnesium derivatives of 2-methyl- or 2,3-dimethyl-7-azaindoles and 2,3-dimethylbenz[4,5]- or -[6,7]indoles with diethyl oxalate, and the reactivity of the resulting ethoxalyloindoles towards phenylmagnesium bromide, have been examined. It has been shown that the course of the reaction is dependent on the solvent and the structures of the starting materials.

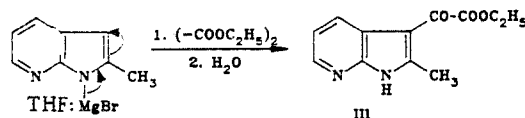
Previous studies of the reactions of 2-substituted N-indolylmagnesium bromides with dialkyl oxalates have shown [1-3] that when the reaction is carried out in ether, depending on the nature of the substituent in the heteronucleus either 3- or 1-derivatives of indole are obtained. The 1-alkoxalyloindoles have been used [4, 5] for the synthesis of substituted benzopyrrolizines [6, 7]. Continuing these studies, we have examined the reactions of the organomagnesium derivatives of 2-methyl- and 2,3-dimethyl-7-azaindoles (Ia, b) and of 2,3-dimethylbenzo[4,5]- or -[6,7]indoles (Ic, d) with diethyl oxalate, and have shown that when the reaction is carried out in ether substituted 1-ethoxalyloindoles are invariably obtained, i.e., no transfer of the reaction center takes place in (Ia).

*No footnote given in Russian original - Publisher.

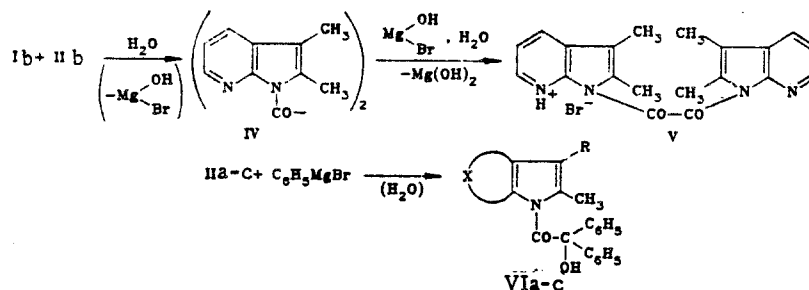
A. M. Gor'kii Perm State University, Perm 614600. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 9, pp. 1206-1209, September, 1987. Original article submitted February 5, 1986.



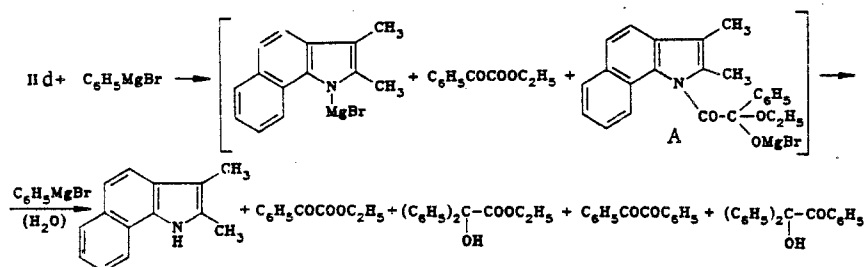
Transfer of the reaction center to the 3-position has been observed when the reaction is carried out in THF, which has a greater dipole moment ($\mu = 1.87$ D) than ether ($\mu = 1.27$ D) [8]. In this case, ethyl 2-methyl-7-azaindolyl-3-glyoxylate (III) was obtained.



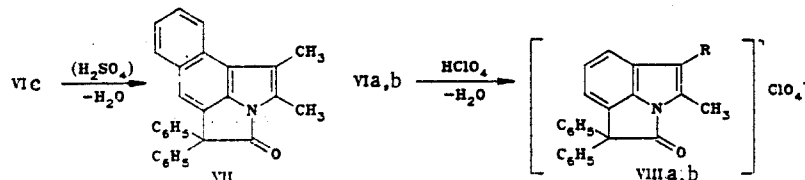
Only in a single case, on reaction of compounds (Ib) and (IIb), were the oxalyldiamide (IV) and its monohydrobromide (V) isolated. The formation of the latter may be due to the reaction of (IV) with hydroxymagnesium bromide when the reaction mixture was hydrolyzed with water.



The reaction of compounds (IIa-d) with phenylmagnesium bromide gave essentially diphenylglycollic acid derivatives (VIa-c). However, when (II d) was reacted with phenylmagnesium bromide there were obtained 2,3-dimethylbenzo[6,7]indole, ethyl phenylglyoxylate, ethyl diphenylglycollate, dibenzoyl, and diphenylbenzoyl carbinol. This reaction appears to follow the course:



This mode of reaction is due to steric overloading, both in the starting material (II d), and perhaps in the resulting ethoxymagnesium ethoxycarbinolate A.



Compound (VIc), on treatment with concentrated sulfuric acid, was converted into the substituted 9,10,11H-naphtho[1,2,3-g,h]pyrrolizine-10-one (VII).

Compounds (VIa, b) cyclize only in the presence of perchloric acid, to give 6-methyl- or 5,6-dimethyl-1-azabeno[g,h]pyrrolizin-8-one perchlorates (VIIIa, b).

The structures of the products were confirmed by their elemental analyses and their IR and PMR spectra.

TABLE 1. Products of the Reaction of 7-Aza- and Benzoindolyl-magnesium Bromides with Diethyl Oxalate

Com- pound	T _{mp.} °C (alcohol)	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N (Hal)		C	H	N (Hal)	
IIa	106—107	61.9	5.1	12.1	C ₁₂ H ₁₂ N ₂ O ₃	62.1	5.2	12.1	73
IIb	120—121	63.3	5.7	11.3	C ₁₃ H ₁₄ N ₂ O ₃	63.4	5.7	11.4	21
IIc	95—96	73.1	5.7	4.7	C ₁₈ H ₁₇ NO ₃	73.2	5.8	4.8	72
IId	99—100	73.1	5.9	4.8	C ₁₈ H ₁₇ NO ₃	73.2	5.8	4.6	77
III	175—176	62.0	5.2	12.0	C ₁₂ H ₁₂ N ₂ O ₃	62.1	5.2	12.1	64
IV	135—136	69.4	5.3	16.2	C ₂₀ H ₁₈ N ₄ O ₂	69.3	5.2	16.2	14
V	212—214*	56.4	4.4	13.2 (18,8)	C ₂₀ H ₁₈ N ₄ O ₂ ·HBr	56.2	4.5	13.1 (18,7)	12
VIa	121—122	77.1	5.3	8.1	C ₂₂ H ₁₈ N ₂ O ₂	77.2	5.3	8.2	78
VIb	128—129	77.3	5.5	7.8	C ₂₃ H ₂₀ N ₂ O ₂	77.5	5.6	7.9	72
VIc	116—117	83.1	5.6	3.5	C ₂₈ H ₂₃ NO ₂	82.9	5.7	3.4	68
VII	138—140	87.0	5.4	3.5	C ₂₈ H ₂₁ NO	86.8	5.5	3.6	92
VIIIa	228—230	62.3	3.9	6.5 (8,4)	C ₂₂ H ₁₇ ClN ₂ O ₅	62.2	4.0	6.6 (8,3)	88
VIIIb	222—224	62.3	4.4	6.4 (7,9)	C ₂₃ H ₁₉ ClN ₂ O ₅	62.4	4.3	6.3 (8,0)	85

*From DMF.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrophotometer as pastes in perfluorovaseline oil. The PMR spectra of (V) and (VIIIa, b) were obtained in solution in DMF-D₇, and the remainder in CCl₄, on a Tesla BS-487C spectrometer (80 MHz), internal standard HMDS.

Compounds (IIa-d). An ether solution of (Ia-d), prepared from 0.1 mole of the appropriate indole and 0.11 mole of ethylmagnesium bromide, was added dropwise to an ether solution of 16.1 g (0.1 mole) of diethyl oxalate. After heating for 2 h, the mixture was hydrolyzed with water [for (Ia, b)] or 10% hydrochloric acid [for (Ic, d)]. The ether layer was separated from the aqueous, dried over sodium sulfate, and the solvent removed. The residue was treated repeatedly with hexane, and the crystals which separated on cooling were purified by recrystallization from alcohol.

Following extraction of (IIb) with hexane, the residual solid was treated with alcohol, from which was isolated the bis-compound (IV). Recrystallization of the residue from DMF gave the monohydrobromide (V), also obtained by direct synthesis by the reaction of an alcoholic solution of (IV) with 10% HBr. A mixed sample with (V) obtained from the reaction mixture gave no depression of melting point.

Ester (III) was obtained by the reaction between (Ia) and diethyl oxalate on heating for 2 h in THF. Following heating, the reaction mixture was treated with 100 ml of ether, hydrolyzed with water, and worked up as for (IIa-d).

Compounds (VIa-c) were obtained by adding 0.062 mole of an ether solution of phenylmagnesium bromide to 0.03 mole of the 1-ethoxalylindole (IIa-c), followed by hydrolysis and workup as described above. In the case of the reaction with (IId), the following products were isolated (yields as % of theory): 2,3-dimethylbenzo[6,7]indole (78), ethyl phenylglyoxylate (16), ethyl diphenylglycollate (14), dibenzoyl (11), and diphenylbenzoyl carbinol (6), separated by crystallization from hexane and described in [9].

Compounds (VII) and (VIIIa, b). Compounds (VIa-c) (0.01 mole) in 10 ml of glacial acetic acid were treated with 2 ml of sulfuric or perchloric acid, heated to the boil, cooled, and the crystals which separated were filtered off.

The IR spectra of (IIa-d) showed absorption for ester carbonyl at 1730-1740 and amide-I at 1710 (IIa, d), 1685 (IIa) and 1660 cm⁻¹ (IIb); (III) -1740 (C=O_{est}), 1710 (C=O_{ket}), 3300 (NH); (IV) - 1655 (amide-I); (V) - 1650 and 1675 cm⁻¹ (C=O bonded to nonprotonated and protonated rings); (VIa-c) - 1650 (amide-I) and 3350 (OH); (VII) - 1690 (amide-I); (VIIIa, b) - 1700 cm⁻¹ (amide-I). PMR spectra, δ, ppm: (IIa) - 1.28 (3H, t, OCH₂CH₃); 2.44 (3H, s, CH₃); 4.12 (2H, q, OCH₂); 6.92 (1H, s, β-H); 7.10-7.80 (3H, br. m, arom.); (IIb) - 1.35 (3H, t, OCH₂CH₃); 2.20 (3H, s, β-CH₃); 2.42 (3H, s, α-CH₃); 4.28 (2H, q, OCH₂); 7.13 (1H, d.d, 5-H); 7.95 (1H, d, 4-H); 8.08 (1H, d, 6-H); (IIc) - 1.30 (3H, t, OCH₂CH₃); 2.18 (3H, s, β-CH₃); 2.22 (3H, s, α-CH₃); 4.32 (2H, q, OCH₂); 6.90-7.60 (6H, br. m. arom.); (IId) - 1.04 (3H, t,

OCH₂CH₃); 2.10 (3H, s, β-CH₃); 2.32 (3H, s, α-CH₃); 4.04 (2H, q, OCH₂); 6.85-7.50 (6H, br. m, arom.); (III) - 1.26 (3H, t, OCH₂CH₃); 2.38 (3H, s, CH₃); 4.18 (2H, q, OCH₂); 7.34 (1H, d.d, 5-H); 7.98 (1H, d, 4-H); 8.13 (1H, d, 6-H); (IV) - 2.18 (6H, s, β-CH₃); 2.42 (6H, s, α-CH₃); 7.10-8.00 (6H, br. m, arom.); (V) - nonprotonated ring: 2.07 (3H, s, β-CH₃); 2.27 (3H, s, α-CH₃); 7.60-8.00 (br. m, arom.); protonated ring: 2.61 (3H, s, β-CH₃); 2.81 (3H, s, α-CH₃); 7.60-8.00 (2H, br. m, 4- and 5-H); 8.10 (1H, d, 6-H); (VIa) - 2.38 (3H, s, CH₃); 6.80 (1H, s, β-H); 7.00-7.50 (13H, br. m, arom.); (VIb) - 2.14 (3H, s, β-CH₃); 2.32 (3H, s, α-CH₃); 7.00-7.45 (3H, br. m, arom.); (VIc) - 2.12 (3H, s, β-CH₃); 2.18 (3H, s, α-CH₃); 6.80-7.50 (16H, br. m, arom.); (VII) - 2.15 (3H, s, β-CH₃); 2.20 (3H, s, α-CH₃); 6.80-7.50 (15H, br. m, arom.); (VIIIa) - 2.48 (3H, s, CH₃); 7.00-7.55 (11H, br. m, β-H + 2-C₆H₅); 7.68 (1H, d.d, 5-H); 8.05 (1H, d, 4-H); 8.42 (1H, d, 6-H); (VIIIb) - 2.33 (3H, s, β-CH₃); 2.44 (3H, s, α-CH₃); 7.00-7.50 (10H, br. m, arom.); 7.62 (1H, d.d, 5-H); 8.00 (1H, d, 4-H); 8.36 (1H, d, 6-H).

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5-HYDRAZINO-2-PYRAZOLINES

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542.953:543.422'51

1-Acyl-5-hydrazino-2-pyrazolines have been obtained by reaction of the appropriate hydrazines with aliphatic 1,3-diketones, 1-acyl-5-hydroxy-2-pyrazolines, and 1-acyl-5-methylene-2-pyrazolines. The latter were synthesized by acylating 3,4,4,5-tetramethyl-4H-pyrazole with carboxylic anhydrides. The structures of the products were established by ¹H and ¹³C NMR spectroscopy and mass spectrometry.

We have recently shown in a few instances [1, 2] that the condensation products of hydrazines with 1,3-diketones in a ratio of 2:1 are the 1-acyl-5-hydrazino-2-pyrazolines (I) rather than the bisacylhydrazones, as previously believed [3, 4]. It was then found that (I) can be synthesized also by reacting hydrazines with 1-acyl-5-hydroxy-2-pyrazolines (IV).

We here report the results of a study of the synthesis of this new group of compounds. Their possible preparation from the hydrazines (III) and 2,4-pentanedione and its 3-methylated homologs (II), or the corresponding compounds (IV), has been examined. In addition,

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