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CATALYTIC CARBONYLATION OF NITROBENZYL- AND NITROARYLPYRIDINES

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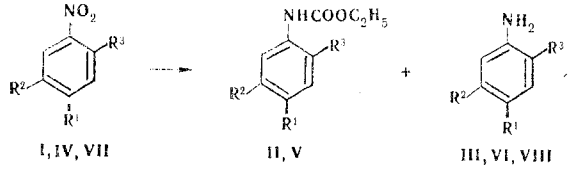
The corresponding carbamates were obtained by carbonylation in the presence of selenourea of benzyl- and aryl-substituted pyridines that contain a nitro group in the benzene ring and as a result of carbonylation of 7-nitro-1-azafluorene. The reaction is accompanied by simultaneous reduction of the nitro group to an amino group.

The catalytic carbonylation of nitro compounds is a convenient method for the synthesis of carbamic acid derivatives that are of interest as pesticides [1]. The search for new pesticides among carbamic acid derivatives with a pyridine ring is promising, since it is known that some active pesticides are pyridine derivatives [1]. Accessible nitrobenzyl- and nitrophenyl-substituted pyridines, the catalytic carbonylation of which has not been previously studied, can be the starting compounds for such studies.

We used 4-methyl-2-(4'-nitrobenzyl)-, 2,5-dimethyl-4-(4'-methyl-3'-nitrophenyl)-, and 2-methyl-3-(4'-nitrophenyl)pyridines (I, IV, and VII) as the starting pyridine bases for the preparation of carbamoylarylpyridines.

The carbonylation was carried out in ethanol at 170-180°C and a carbon monoxide pressure of 60-100 atm in the presence of selenourea. Since the initial step in the carbonylation of nitro compounds is evidently the formation of nitrenes [5], the corresponding amines may also be formed in addition to ethoxycarbamoyl derivatives as a result of the reaction. Complete conversion of the starting compounds occurs after 2 h under the indicated conditions. In the carbonylation of I and IV the principal reaction products are, respectively, 4-methyl-2-(4'-ethoxycarbamoylbenzyl)pyridine (II) and 2,5-dimethyl-4-(4'-methyl-3'-ethoxycarbamoylphenyl)-pyridine (V). 4-Methyl-2-(4'-aminobenzyl)- and 2,5-dimethyl-4-(4'-methyl-3'-aminophenyl)-pyridines (III, VI) were obtained in very low yields in these experiments:



I, IV, VII II, V III, VI, VIII

I–III, VII, VIII $R^2 = R^3 = H$; IV–VI $R^1 = H$, $R^3 = CH_3$; I–III R^1 = 4-methyl-2-picolyl; IV–VI R^2 = 2,5-dimethyl-4-pyridyl; VII, VIII R^1 = 2-methyl-3-pyridyl

A carbamic acid derivative was not detected in the carbonylation of nitrophenyl-substituted pyridine base VII, and only 2-methyl-3-(4'-aminophenyl)pyridine (VIII) was obtained.

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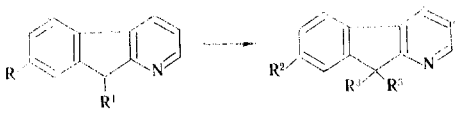
The cyclic analog of nitrophenylpyridine VII is 7-nitro-1-azafluorene (IX) [4], which was also subjected to the reaction with carbon monoxide under the same conditions. We were able to isolate only 7-ethoxycarbamoyl-1-azafluorene (X) from the complex and markedly resinified mixture of reaction products by chromatography.



IX, XI X, XII

IX $R=NO_2$, $R^1=H$; X $R^2=NHCOOC_2H_5$, $R^3=H$; XI R=H, $R^1=OH$; XII $R^2=H$, $R^3=I$

We made an attempt to realize the carbonylation of 1-aza-9-fluorenol (XI) [6] in order to obtain 1-azafluorene-9-carboxylic acid. The reaction was carried out in the presence of rhodium triiodide and hydriodic acid. The only compound that was isolated from the complex mixture of reaction products was 9,9-diiodo-1-azafluorene (XII). Replacement of the hydroxy group and the hydrogen atom attached to C_9 by iodine atoms evidently takes place considerably more rapidly than carbonylation.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ was recorded with a BSV 97 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets were obtained with a UR-10 spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer at an ionizing voltage of 70 V. The isolation and monitoring of the purity of the products were achieved by chromatography on activity II aluminum oxide. The characteristics of the compounds obtained are presented in Table 1.

4-Methyl-2-(4'-ethoxycarbamoylbenzyl)pyridine (II) and 4-Methyl-2-(4'-aminobenzyl)pyridine (III). An unsealed glass ampul containing a solution of 1.15 g (5 mmole) of nitrobenzylpyridine I, 0.23 g (2 mmole) of selenourea, and 0.28 ml of triethylamine in 20 ml of ethanol was placed in a 0.15-liter stainless steel autoclave, and carbon monoxide was blown through it twice at a pressure of 20 atm, after which the pressure was raised to 90 atm. The temperature was raised to 170°C in the course of an hour and maintained at that level for 2 h. The reaction was carried out with rotation of the autoclave at 90 rpm. The reaction mixture was cooled, the triethylamine and ethanol was removed by distillation, and the crystalline precipitate (0.9 g) was chromatographed (h = 37 cm, d = 2 cm, elution with ether). The first substance isolated was urethane II (0.38 g) in the form of light-yellow crystals. PMR spectrum: 1.18 (t, 3H, CH_2CH_3), 2.18 (s, 3H, 4-CH_3), 3.98 (s, 2H, CH_2), 4.10 (q, 2H, CH_2CH_3), 6.82 (broad s, 2H, 3-H and 5-H), 7.02 (broad s, 1H, NH), and 8.28 ppm (d, 1H, 6-H). The next substance eluted from the column was amino derivative III (0.06 g) in the form of slightly yellow crystals. PMR spectrum: 2.19 (s, 3H, 4-CH_3), 3.95 (s, 2H, CH_2), 3.18 (broad s, 2H, NH_2), 6.77 (d, 2H, $J_{3',2'}$ = 8 Hz, 3'-H and 5'-H), 7.05 (broad s, 2H, 3-H and 5-H), 7.22 (d, 2H, $J_{2',3'}$ = 8 Hz, 2'-H and 6'-H), and 8.55 ppm (d, 1H, $J_{6,5}$ = 5 Hz, 6-H).

2,5-Dimethyl-4-(4'-methyl-3'-ethoxycarbamoylphenyl)pyridine (V) and 2,5-Dimethyl-4-(4'-methyl-3'-aminophenyl)pyridine (VI). The carbonylation of 1.2 g (5 mmole) of nitrophenylpyridine IV was carried out similarly at the same molar ratios of the reagents with chromatographic separation of the reaction products [successive elution with ether and ether–ethanol (40:1)] to give 0.4 g (32%) of colorless crystals of urethane V. PMR spectrum: 2.17, 2.22, and 2.46 (singlets, 3H, each CH_3 group); 1.23 (t, 3H, CH_2CH_3); 4.18 (q, 2H, CH_2CH_3); 6.59 (broad s, 1H, NH); 6.98 (s, 1H, 3-H); 7.19 (d, 2H, $J_{2',3'}$ = 9 Hz, 2'-H and 3'-H); 7.82 (s, 1H, 6'-H); 8.34 ppm (s, 1H, 6-H). At the end of the chromatographic process, 0.08 g (8%) of aminophenylpyridine VI, with mp 79-80°C (from ether) [3], was isolated.

2-Methyl-3-(4'-aminophenyl)pyridine (VIII). The reaction of 1.1 g (5 mmole) of nitrophenylpyridine VII as in the preceding experiment gave 0.25 g of pale-yellow crystals of aminophenylpyridine VIII. PMR spectrum: 2.64 (s, 3H, 2-CH_3), 3.66 (broad, s, 2H, NH_2), 6.69 (d, 2H, $J_{3'2'}$ = 8.4 Hz, 3'-H and 5'-H), 7.07 (d, $J_{2',3'}$ = 8.4 Hz, 2'-H and 6'-H), 7.45 (dd, 1H, $J_{4,5}$ = 10 Hz, $J_{4,6}$ = 2 Hz, 4-H), and 8.43 ppm (dd, 1H, $J_{6,5}$ = 5 Hz, $J_{6,4}$ = 2 Hz, 6-H).

7-Ethoxycarbamoyl-1-azafluorene (X). The reaction of 2.8 g (13 mmole) of nitroazafluorene IX was carried out in the preceding experiment to give black crystals (0.9 g), which were insoluble in ordinary solvents and DMSO but soluble in hydrochloric acid with visually

TABLE 1. Carbamoylbenzyl(phenyl)- and Aminobenzyl(phenyl) pyridines

Compound	mp, °C (from ether)	R_f (in ether)	IR spectrum, cm^{-1}	Found				Empirical formula	Calc.				Yield, %
				C, %	H, %	N, %	M+		C, %	H, %	N, %	M+	
II	125—127	0,51	3230, 3180, 1725	71,5	6,9	10,3	270	$C_{16}H_{18}N_2O_2$	71,1	6,7	10,4	270	28
III	78—80	0,26	3380, 3200	78,6	7,4	13,9	198	$C_{13}H_{14}N_2$	78,8	7,1	14,1	198	6
V	131—132	0,68	3220, 1717	71,4	7,1	9,9	284	$C_{17}H_{20}N_2O_2$	71,8	7,0	9,9	284	32
VIII	98—99	0,36	3420, 3320, 3180	78,1	6,9	14,9	184	$C_{12}H_{12}N_2$	78,3	6,5	15,2	184	27
X	179—180	0,37	3230, 3185, 1725	71,0	6,0	10,7	254	$C_{15}H_{14}N_2O_2$	70,9	5,5	11,0	254	2

observable decomposition. The mother liquor after separation of these crystals was evaporated, and the residue (1 g) was chromatographed [elution with ether–ethanol (40:1)] to give 0.06 g of X. PMR spectrum: 1.26 (t, 3H, CH_2CH_3), 3.93 (s, 2H, 9-CH_2), 4.22 (q, 2H, CH_2CH_3), 6.79 (broad s, 1 H, NH), 7.10-7.75 (aromatic protons), 7.89 (dd, 1H, $J_{4,3}$ = 8 Hz, 4-H), and 8.43 ppm (dd, 1H, $J_{2,3}$ = 5 Hz, 2-H).

9,9-Diiodo-1-azafluorene (XII). A solution of 0.07 g of rhodium triiodide trihydrate in 10 g of 40% hydriodic acid was placed in an ampul, 5 ml of water and 22 g of acetic acid were poured into the solution, the ampul was placed in an autoclave, and carbon monoxide was blown into the autoclave at 6 atm, after which the pressure was raised to 7 atm. After 20 min, the temperature was raised to 110°C, and the reaction mixture was maintained at this temperature for 3 h. After cooling and reducing the pressure, a solution of 1.3 g (7 mmole) of azafluorenol XI in 10 g of acetic acid was added to the prepared catalyst, and carbonylation was carried out at 40 atm and 180°C. The resulting precipitate was separated, washed with acetic acid and water, and dried to give 0.98 g (33%) of red-brown crystal of XII with mp 174-175°C (from acetic acid) and R_f 0.75 [ether–benzene (50:1)]. Found, %: C 34.1; H 2.3; I 60.5; N 3.2. $C_{12}H_7I_2N$. Calculated, %: C 34.4; H 1.7; I 60.6; N 3.3.

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