EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C instrument at 80 MHz in deuterochloroform with HMDS as internal standard. The IR spectra were recorded on a Specord 75-IR instrument in tablets with potassium bromide. The tertiary cyanoacetylene alcohols (IIa, b) were obtained by the method in [5].

2-Imino-4-(1-hydroxy-1-methylethyl)benzimidazo[2,3-c]-1,3-thiazine (IVa). A mixture of 0.3 g (0.002 mole) of the thione (I), 0.2 g (0.002 mole) of the alcohol (IIa), and 0.05 g of potassium hydroxide in 15 ml of dioxane was stirred at ~ 20°C for 10 h. After removal of the solvent the residue was crystallized from benzene. We isolated 0.2 g (38%) of (IVa); mp 140-143°C. Found: C 60.29; H 5.01; S 12.02; N 16.25%. $C_{13}H_{13}SN_3O$. Calculated: C 60.21; H 5.05; S 12.36; N 16.20%. IR spectrum (ν, cm^{-1}): 3596 (OH), 3313 (=NH), 2980, 2940, 2870 (CH_3), 1630 (N−C=CH). PMR spectrum (δ, ppm): 1.53 s (CH_3), 6.41 s (3H), 7.23 m (aromatic protons).

2-Imino-4-(1-hydroxy-1-methylpropyl)benzimidazo[2,3-c]-1,3-thiazine (IVb). was obtained similarly from the thione (I) and the alcohol (IIb); mp 131-133°C (from benzene). The yield was 55%. Found: C 61.54; H 5.63; S 11.92; N 15.50%. $C_{15}H_{15}SN_3O$. Calculated: C 61.51; H 5.53; S 11.73; N 15.37%. IR spectrum (ν, cm^{-1}): 3597 (OH), 3313 (=NH), 2970, 2930, 2880, (CH_2, CH_3), 1640 (NC = CH). PMR spectrum (δ, ppm): 0.8 t and 1.76 t (CH_2CH_3), 1.48 s (CH_3), 6.43 s (3H), 7.25 m (aromatic protons).

CONCLUSIONS

2-Iminobenzimidazo-1,3-thiazines containing a hydroxyl group were obtained by the reaction of benzimidazole-2-thione with tertiary cyanoacetylene alcohols. It was observed that they have enhanced stability toward alkalis.

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CATALYZED SYNTHESIS OF DIHYDROSILAAZAANTHRACENES – SILICON- AND NITROGEN-CONTAINING HETEROCYCLES

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Catalytic dehydrocyclization of substituted silylpyridines is the only method for the synthesis of dihydrosilaazaanthracenes, heterocycles containing silicon and nitrogen. Derivatives of these compounds could be of interest as pesticides, antimicrobials, and antiviral drugs [1].

Using the industrial dehydrogenation catalyst K-16 [3], 3-methyl-4-dimethylphenyl- (Ia) and 3-methyl-4-diphenylsilylpyridine (Ib) have afforded 10,10-dimethyl- (IIa) and 10-methyl-10-phenyl-9,10-dihydro-10-sila-2-azaanthracene (IIb) [2] in yields of 17-25%, only in a few instances reaching 35%.

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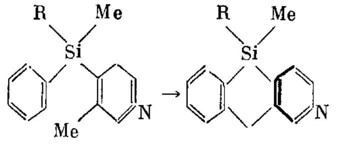
TABLE 1. Conversions of γ-Triorganosilylpyridines over Chromium Catalysts

Starting material	Reaction conditions			Catalyzator*			
	T., °C	v_{mass} h^{-1}	Time, min	A	B	A	B
				amounts of (II) in catalyzate, %		yield of (II) on starting material, %	
3-Methyl-4-dimethylphenylsilylpyridine	540–560	0,7	60	35	20	24,5	17
	540–560	1,5	90	25	12	20	8,4
	570–580	0,5	120	44	25	35	17
	570–580	1,0	120	36	23	30	20
	570–580	1,5	120	21	15	17	13
3-Methyl-4-diphenylsilylpyridine	570–580	1,0	120	34	25	25	17

* A) 5% Cr_2O_3, Polirite 5%, K_2O 1%, γ-Al_2O_3 89%; B) Cr_2O_3 51.3%, Fe_2O_3 25.2%, ZnO 23%, SiO_2 0.5%.



(I) (II)

R = Me(a), Ph(b).

We have found conditions for the catalytic synthesis of (IIa, b) over a chromium-containing oxide catalyst, developed for the preparation of alkylthiophenes by heterocyclization, viz., reaction of C_5-C_6 hydrocarbons with H_2S [4].

EXPERIMENTAL

The experiments were carried out in a through-flow quartz reactor (d 30 mm, *l* 250 mm). The reactor was charged with 6.6-20 g of catalyst 119R (Institute of General Chemistry, Academy of Sciences of the USSR) of composition 5% Cr_2O_3, 1% K_2O, 5% Polirite (Cr_2O_3 2.7, La_2O_3 1.3, Nd_2O_3 0.75, and Pr_2O_3 0.25%), and 89% grade A-1 alumina. To compare catalytic activity, experiments were also carried out in the presence of catalyst K-16. Pyridines (Ia, b) were added in benzene solution (1:2) at 540-580°C, $v_{mass} = 0.5$-$1.5\ h^{-1}$ over 1-2 h. When the experiment was complete, benzene was passed through the catalyst. The yields of liquid catalyzate were 70-75%. In the preparation of (IIa), the residue after the benzene had been distilled off was fractionated, bp 156-160°C (2 mm). Crystallization from heptane gave (IIa), mp 86-86.5°C. In the preparation of (IIb), the residue after removal of the benzene was converted into the picrate. Fractional crystallization from acetone gave the picrate of dihydrosilaazaanthracene (IIb), which was decomposed on alumina (eluent, chloroform) to give (IIb) as colorless crystals, mp 132-133°C (from heptane). The purity of (IIa) and (IIb) was checked by TLC (grade II alumina, eluent 3:1 by volume mixture of heptane and ethyl acetate), and by the melting point of a sample admixed with standard samples [2].

DISCUSSION OF RESULTS

As will be seen from Table 1, the yields of dehydrocyclization products are dependent on the reaction temperature and the rate of charging of the pyridine starting material. The K-16 industrial dehydrogenation catalyst (composition 51.3% Cr_2O_3, 25.2% Fe_2O_3, 23% ZnO, and 0.5% SiO_2 [3]) was much less active under the conditions chosen than 119R catalyst (composition 5% Cr_2O_3, 5% Polirite, 1% K_2O, and 89% of γ-Al_2O_3) over the latter catalyst, at 570-580°C (v_{mass} 1.0 h^{-1}), the dehydrocyclization products (IIa) and (IIb) were obtained in yields of 25-35% based on the pyridine taken.

The results show that the dehydrocyclization of γ-triorganosilylpyridines is preferably catalyzed by the γ-Al_2O_3 based catalyst. In comparison with the K-16 catalyst, in this case the concentration of Cr_2O_3 may be reduced by a factor of ten, and the total of Fe and Zn oxides (48.2%) can be replaced by a mixture of rare earth oxides (5%) and K (1%). The catalytic properties of the aluminum–lanthanum–chromium–potassium catalyst 119R have been studied extensively [5] in heterocyclization, as exemplified by the reaction of C_4 hydrocarbons with H_2S, and the roles of the individual constituents in this reaction have been demonstrated. In particular, Cr_2O_3 promotes dehydrogenation and heterocyclization, and the potassium and rare earth oxides enhance heterocyclization and dehydrogenation, and inhibit the cracking and carbonization properties of the aluminum–chromium catalyst. In the presence of catalyst 119R in an acid medium (H_2S), p-cymene has also been obtained from myrcene [6].

CONCLUSIONS

3-Methyl-4-dimethylphenyl- and 3-methyl-4-diphenylsilylpyridine have been dehydrocyclized over a chromium catalyst (composition 5% chromium(III) oxide, 5% Polirite, 1% potassium oxide, and 89% γ-Al_2O_3) to give 10,10-dimethyl- and 10-methyl-10-phenyl-9,10-dihydro-10-sila-2-azaanthracene.

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ALKYLATION OF PHENOLS BY OLEFINS USING GRAPHITE LAYER COMPOUNDS AS CATALYSTS

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The catalytic activity of graphite layer compounds (GLC) containing metal and nonmetal halides ($AlCl_3$, $FeCl_3$, SbF_5, etc.) in the Friedel–Crafts reaction have been studied [1-3]. The possibility of using these GLC as catalysts in electrophilic substitutions is related both to the acidic properties of the halides themselves, and to the formation of positive charges in the graphite lattice following the introduction of salts. GLC can react with metal halides by a heterogeneous mechanism, without the salt passing into solution. In those cases in which the inserted halide passes from the GLC into solution, the reaction is a homogeneous one, and the GLC functions as an 'internal dispenser' of the catalytically active metal halide. This latter mechanism is the more likely when using reactants containing H atoms with considerable proton mobility, such as phenols.

We have studied the alkylation of phenol and o-, m-, and p-cresols with branched-chain olefins such as 2-methyl-1-pentene, 2,3-dimethylbutenes, and 2,4,4-trimethylpentenes (molar ratio phenol:olefin = 1:1.5) in the presence of GLC–SbF_5, GLC–$AlCl_3$, GLC–$ZnCl_2$, and GLC–$FeCl_3$ (10% of the weight of phenol), at 70°C. Reaction of phenol with $CH_2{=}CMe(CH_2)_2Me$ in the presence of GLC–SbF_5 gives 4-($PrCMe_2$)C_6H_4OH in 70% yield (Table 1), perhaps as a result of steric control of the reaction as well as of isomerization of the o- to the p-isomer. That this isomerization takes place under the reaction conditions was shown in separate experiments. Apparently for the same reason, the reaction of phenol with 2,4,4-trimethylpentene (a mixture of ~ 80% of the

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