ORGANOSODIUM COMPOUNDS OF N-SUBSTITUTED IMIDAZOLES

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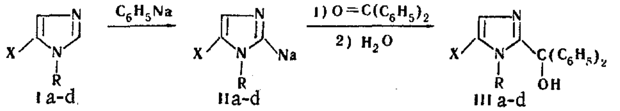
The corresponding 2-sodioimidazoles were obtained from N-substituted imidazoles and phenylsodium. If the 2 position of imidazole is occupied, the 5-sodio derivative is formed.

Metallation leading to 2-lithioimidazoles [1,2] occurs during the reaction of N-substituted imidazoles with butyllithium [1,2].

We used phenylsodium as the metallating agent to obtain organosodium compounds of 1-alkyl-, 1-arylalkyl-, and 1-arylimidazoles. The 2-sodioimidazoles are formed in good yields and are quite stable compounds.

The yields of the organosodium compounds (II) were determined from the yields of the diphenylimidazolylcarbinols (III):



I a-d   IIa-d   III a-d

I, II, III a X = H, R = CH_3; b X = H, R = $CH_2C_6H_5$; c X = H, R = C_6H_5; d X = Cl, R = CH_3

The results of the metallation of N-substituted imidazoles are presented in Table 1.

The sodioimidazoles readily enter into the diverse reactions of active organometallic compounds. Thus, for example, they give arylimidazolylcarbinols and formylimidazoles with aromatic aldehydes and dimethylformamide, respectively.

Under the influence of phenylsodium, 1,2-dimethylimidazole is metallated at the 5 position to form 5-sodio-1,2-dimethylimidazole (IV), the structure of which was proved by conversion into the previously described diphenyl(1,2-dimethyl-5-imidazolyl)- (V) and phenyl(1,2-dimethyl-5-imidazolyl)carbinols [3].

EXPERIMENTAL

Metallation of N-Substituted Imidazoles. Powdered sodium [2 g (0.087 g-atom)] in 30 ml of toluene was activated with isoamyl alcohol, and 4.8 g (0.043 mole) of chlorobenzene was added in the course of 1 h to the stirred suspension under nitrogen. The temperature of the mixture was held at 30-40°. After addi-

TABLE 1. Data from the Metallation of N-Substituted Imidazoles

Compound	Mp, °C	Empirical formula	Found %			Calc. %			Yield, %
			C	H	N	C	H	N	
IIIa	188—189	$C_{17}H_{16}N_2O$	77,3	6,0	10.5	77,2	6,1	10,6	85
IIIb	182—183	$C_{23}H_{20}N_2O$	81,0	6,2	7,9	81,1	5,9	8,2	66
IIIc	197—198	$C_{22}H_{18}N_2O$	80,7	5,3	8,5	81,0	5,6	8,6	72
IIId	190—191	$C_{17}H_{15}ClN_2O$	68,0	5,0	9,4	68,3	5,1	9,4	80
V	186—187[3]	$C_{18}H_{18}N_2O$	—	—	—	—	—	—	70

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tion of chlorobenzene, the reaction was allowed to proceed for another hour at room temperature. The resulting phenylsodium was cooled to −15°, and 0.03 mole of the N-substituted imidazole (I) in 15-20 ml of toluene was added to it in the course of 30 min. The reaction was complete 1 h after introduction of the imidazole. A solution of 7.3 g (0.04 mole) of benzophenone in 40 ml of toluene was allowed to react with it in order to determine the yield of 2-sodioimidazole. After 1.5 h the unchanged sodium was removed with 10 ml of alcohol, the mixture was heated with 50 ml of 10% hydrochloric acid, and the diphenylimidazolylcarbinol (III) was precipitated from the hydrochloric acid solution with NaOH. Compounds III were recrystallized from chloroform with petroleum ether.

Arylimidazolylcarbinols. These were obtained from the 2-sodioimidazoles and aromatic aldehydes in the same way that was used for the diphenylimidazolylcarbinols.

Phenyl(1-methyl-2-imidazolyl)carbinol. This was obtained in 80% yield and had mp 114-115° (from benzene with petroleum ether). Found %: C 70.0; H 6.8; N 14.5. $C_{11}H_{12}N_2O$. Calculated %: C 70.2; H 6.4; N 14.9.

3,4-Dimethoxyphenyl(1-methyl-2-imidazolyl)carbinol. This was obtained in 77% yield and had mp 129-130° (from benzene). Found %: C 62.6; H 6.7; N 11.1. $C_{13}H_{16}N_2O$. Calculated %: C 62.9; H 6.5; N 11.3.

Phenyl(1-phenyl-2-imidazolyl)carbinol. This was obtained in 61% yield and had mp 121-122° (from octane). Found %: C 76.5; H 5.5; N 11.0. $C_{16}H_{14}N_2O$. Calculated %: C 76.8; H 5.6; N 11.2.

1-Methyl-2-formylimidazole. Dimethylformamide [6 g (0.082 mole)] was added rapidly to 2-sodio-1-methylimidazole [from 3 g (0.037 mole) of 1-methylimidazole] at −15°. After 1 h the mixture was treated with 20 ml of 25% acetic acid. The layers were separated, and the base was extracted from the organic layer with 20 ml of 10% hydrochloric acid. The combined acid extracts were neutralized with sodium carbonate, and the aldehyde was extracted repeatedly with ether. The ether layer was dried with magnesium sulfate, the ether was removed, and 1.4 g (35%) of 1-methyl-2-formylimidazole with mp 39-40° was isolated from the residue using the method in [3]. According to [4], the product has mp 41-42°. Found %: C 54.8; H 5.0; N 25.4; $C_5H_6N_2O$. Calculated %: C 54.5; H 5.4; N 25.7.

Phenyl(1,2-dimethyl-5-imidazolyl)carbinol. This was obtained in 63% yield (based on 1,2-dimethylimidazole) from IV and benzaldehyde and had mp 177-178° (from benzene with petroleum ether), which is in agreement with the melting point reported in [3].

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