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CLEAVAGE OF THE N—N BOND IN 1-SUBSTITUTED INDAZOLES UNDER THE INFLUENCE OF ARYLLITHIUM COMPOUNDS

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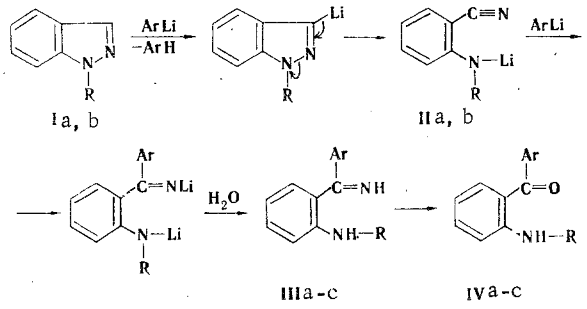
Upon reaction with aryllithium compounds (phenyllithium and m-tolyllithium) m-methyl- and 1-isopropylindazoles undergo cleavage at the N—N bond to give N-substituted 2-aminobenzophenones. The heterocyclic ring of 1-isopropyl-3-phenylindazole also undergoes cleavage at this bond under the influence of phenyllithium.

In [1] it was shown that 1-methylindazole upon metallation with butyllithium undergoes partial conversion to 1-lithiomethylindazole. Since the metallation of azoles may be accompanied by a side reaction involving the addition of the metallating agent to the C=N bond of the heterocyclic ring, it was of interest to study the reaction of 1-substituted indazoles with reagents that are less nucleophilic than butyllithium. In the reaction of 1-methyl- and 1-isopropylindazoles with aryllithium compounds we observed that a reaction does not occur under the conditions indicated in [1]; however, if the process is carried out at the boiling point of the mixture, the corresponding N-substituted 2-aminobenzophenones are formed. Our results and the data in [2, 3] make it possible to propose the following reaction scheme:



I, II a $R=CH_3$; b $R=CH(CH_3)_2$; III, IV a $R=CH_3$, $Ar=C_6H_5$; b $R=CH(CH_3)_2$, $Ar=C_6H_5$; c $R=CH(CH_3)_2$, $Ar=m\text{-}CH_3C_6H_4$

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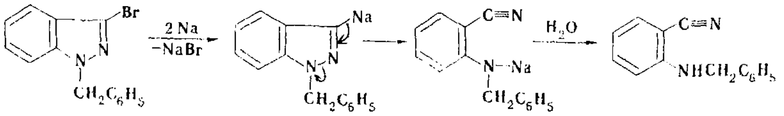
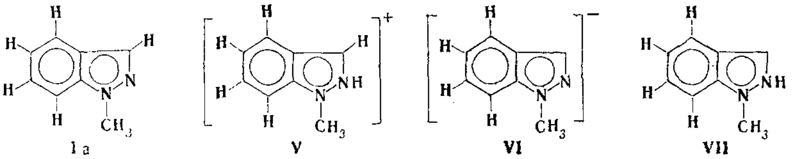
We were unable to establish the formation of the nitrile of N-substituted anthranilic acid; however, the nitrile of N-benzylanthranilic acid was detected in the products of the reaction of 1-benzyl-3-bromoindazole with sodium metal, which indirectly confirms the scheme for the conversion of I to IV.



Ketimine IIIb was isolated in the form of the dihydrochloride. In aqueous solution this compound is gradually converted to 2-isopropylaminobenzophenone hydrochloride.

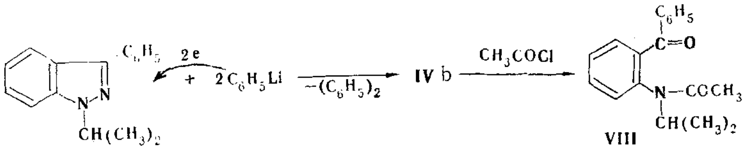
The IR spectra of IVa, b contain absorption bands of a C=O group at 1628 and 1630 cm^{-1} and of an NH group at 3310 and 3352 cm^{-1}, as well as bands at 706 and 755 and at 707 and 750 cm^{-1} (mono- and o-disubstituted benzene rings).

We have established that 1-methyl- and 1-isopropylindazole do not react with phenylsodium. This fact indicates the substantial role of prior coordination of the N_2 heteroatom with the organometallic compound or with the metal halide formed during its preparation in metallation reactions of 1-substituted indazoles. It is known that the ability to undergo coordination is less pronounced in the case of sodium compounds than in the case of lithium compounds. The conclusion regarding the effect of coordination on the CH acidity of 1-substituted indazoles is in agreement with the results of calculations by the CNDO/2 method [4] of the total charges in 1-methylindazole and in cation V. The calculations showed that $N_2 \rightarrow H$ coordination appreciably increases the positive charge on the C_3 atom. The charge on this atom was found to be +0.0288 in Ia, as compared with +0.1006 in cation V.

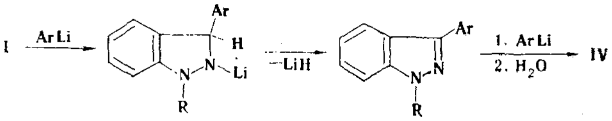


A comparison of the total energies (E_t) of 1-methylindazole Ia, cation V, and conjugate bases VI and VII is a more rigorous approach to the problem under consideration. The $-[E_t(\mathrm{Ia}) - E_t(\mathrm{VI})]$ and $-[E_t(\mathrm{V}) - E_t(\mathrm{VII})]$ differences calculated by this method are, respectively, 24.99 and 17.38 eV.* Thus the results of calculations of the total energies of Ia, V, VI, and VII and their differences also indicate that deprotonation of 1-substituted indazoles in the 3 position should be facilitated in the case of complexing with participation of the N_2 atom.

It should be noted that 1-isopropyl-3-phenylindazole also undergoes cleavage at the N–N bond under the influence of phenyllithium, as a result of which 2-isopropylaminobenzophenone IV, which was isolated in the form of N-acetyl derivative VIII, is formed. This reaction evidently has redox character.



In connection with this observation, the possibility of the conversion of indazoles I to ketones IV via the following pathway is not excluded:



However, if this pathway is realized in addition to that presented above, it may not be the principal pathway, because ketone IVb is formed in appreciably smaller amounts from 1-isopropyl-3-phenylindazole than from 1-isopropylindazole.

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*The calculations were carried out for the standard bond lengths without optimization of the geometry.

EXPERIMENTAL

The IR spectra of suspensions in mineral oil were recorded with a UR-20 spectrometer.

1-Methylindazole (Ia). This compound was obtained by the method in [5].

1-Isopropylindazole (Ib). A mixture of 8.8 h (0.039 mole) of the silver salt of indazole and 8 g (0.047 mole) of isopropyl iodide in 40 ml of toluene was refluxed for 6 h, after which the precipitate was removed by filtration, and the filtrate was washed with a 10% solution of sodium bisulfite and water and dried with sodium sulfate. The toluene was removed by distillation, and the 1-isopropylindazole distilled at 117-118°C (12 mm). The yield was 3.5 g (56%); Found: C 74.8; H 7.6; N 17.6%. $C_{10}H_{12}N_2$. Calculated: C 75.0; H 7.5; N 17.5%. The picrate had mp 120-121°C.

1-Isopropyl-3-phenylindazole. This compound was synthesized in 52% yield by a method similar to that used to prepare 1-isopropylindazole and had bp 184-185°C (5 mm). Found: C 81.7; H 6.7; N 11.7%. $C_{16}H_{16}N_2$. Calculated: C 81.3; H 6.8; N 11.9%. The compound forms a picrate, the color of which changes from yellow to red during recrystallization. It has been indicated [6] that the picrates of 1-alkyl-3-arylindazoles have similar behavior.

2-Methylaminobenzophenone (IVa). A solution of 3.5 g (0.026 mole) of 1-methylindazole in a mixture of 8 ml of toluene and 8 ml of ether was added to phenyllithium obtained from 1.2 g (0.17 mole) of lithium and 13 g (0.083 mole) of bromobenzene in 40 ml of ether, and the mixture was refluxed for 2 h. It was then cooled and washed with water, the organic layer was separated, and the base was extracted with 10 ml of 17% hydrochloric acid. The hydrochloric acid extract was diluted with 30 ml of water, and the mixture was refluxed for 15 min and neutralized with 10% ammonium hydroxide. The liberated oil was extracted with ether, the extract was dried with magnesium sulfate, the ether was removed by distillation, and the residue was distilled in vacuo to give 2.8 g (50%) of a product with bp 168-170°C (6 mm) and mp 68-69°C. Found: C 79.9; H 6.1; N 6.7%. $C_{14}H_{13}NO$. Calculated: C 79.6; H 6.2; N 6.6%.

2-Isopropylaminobenzophenone (IVb). A 4-g (0.025 mole) sample of 1-isopropylindazole in 15 ml of ether and phenyllithium [from 1.2 g (0.17 mole) of lithium and 13 g (0.083 mole) of bromobenzene] were subjected to reaction in 30 ml of ether. At the end of the reaction, 20 ml of water was added, and the ether layer was separated and treated with 5 ml of 17% hydrochloric acid. The hydrochloric acid extract was cooled to −8°C and treated with 0.5 ml of concentrated hydrochloric acid. The liberated crystals were removed by filtration, and the compound was identified as 2-isopropylaminobenzophenone imine dihydrochloride. Found: Cl 22.7; N 9.1%. $C_{16}H_{18}N_2 \cdot 2HCl$. Calculated: Cl 22.8; N 9.0%. The crystalline product was dissolved in 30 ml of 5% hydrochloric acid, the solution was refluxed for 15 min, and 2-isopropylaminobenzophenone was isolated by the method described above. The yield of product with bp 185-190°C (8 mm) was 2.5 g (42%). Found: C 80.4; H 7.3; N 5.7%. $C_{16}H_{17}NO$. Calculated: C 80.3; H 7.2; N 5.9%.

2-Isopropylamino-3'-methylbenzophenone (IVc). This compound was obtained by the reaction of 3.5 g (0.022 mole) of 1-isopropylindazole and m-tolyllithium [from 1.05 g (0.15 mole) of lithium and 13.5 g (0.079 mole) of m-bromotoluene] in 45 ml of ether. The yield of product with bp 202-204°C (7 mm) was 3.5 g (63%). Found: C 80.3; H 7.5; N 5.7%. $C_{17}H_{19}NO$. Calculated: C 80.6; H 7.6; N 5.5%.

N-Benzylanthranilic Acid Nitrile. A 3.7-g (0.013 mole) sample of 1-benzyl-3-bromoindazole was added to a suspension of 0.7 g (0.03 mole) of sodium in 40 ml of toluene, and the mixture was refluxed in a nitrogen atmosphere for 4 h. It was then cooled and treated with 10 ml of alcohol and 20 ml of water. The toluene layer was separated and washed with water, and the toluene was removed by distillation. The oily residue was distilled with alcohol, and the mixture was allowed to stand for 10-12 h. The precipitated N-benzylanthranilic acid nitrile was removed by filtration and recrystallized from alcohol to give 0.36 g (14%) of a product with mp 117-118°C (mp 118°C [2]). IR spectrum: 2215 (C≡N) and 3352 cm^{-1} (NH).

Reaction of 1-Isopropyl-3-phenylindazole with Phenyllithium. A 3.5-g (0.015 mole) sample of 1-isopropyl-3-phenylindazole in 25 ml of ether was added to phenyllithium [from 0.56 g (0.081 mole) of lithium and 6.3 g (0.04 mole) of bromobenzene] in 30 ml of ether, and the solution was refluxed for 3 h. It was then treated with 20 ml of water, and the organic layer was separated and treated with 25 ml of 10% hydrochloric acid. The liberated oil was extracted with ether, and the extract was dried with sodium sulfate and distilled to remove the ether. Benzene (10 ml), 1 g of pyridine, and 0.6 g of acetyl chloride were added to the residue, and the mixture was refluxed for 30 min. The usual workup gave 0.46 g (11%) of N-acetyl-2-isopropylaminobenzophenone with mp 138-139°C (from benzene with petroleum ether). Found: C 76.8; H 7.0; N 4.9%. $C_{18}H_{19}NO_2$. Calculated: C 76.8; H 6.8; N 5.0%. No melting point depression was observed for a mixture of this product with the substance obtained by acetylation of 2-isopropylaminobenzophenone. The IR spectra of the two samples were identical.

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2-N-IMIDAZOLYL- AND 2-N-PYRAZOLYL-1,3-INDANDIONES

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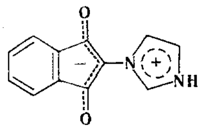
It was shown by spectroscopic methods that 2-N-imidazolyl-, 2-N-(N-methylimidazolyl)-, and 2-N-(N-methylpyrazolyl)-1,3-indandiones exist in the form of inner salts, whereas 2-N-pyrazolyl-1,3-indandione exists in the form of an enol with an intramolecular hydrogen bond.

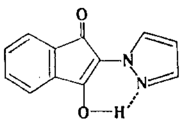
The reaction of 2-dicyanomethylene-1,3-indandione oxide with six-membered heteroaromatic compounds is a good method for the preparation of onium betaines of 1,3-indandione [1, 2], which are of interest as components for the preparation of charge-transfer complexes (CTC) [3] and as subjects for the study of the electrophysical properties of the solid state (the semiconductor properties and photosensitivities) [4].

2-N-Imidazolyl-1,3-indandione (I) and 2-N-pyrazolyl-1,3-indandione (II) are readily formed in the reaction of 2-dicyanomethylene-1,3-indandione oxide with imidazole and pyrazole.

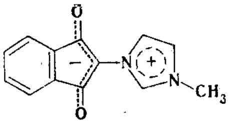
In order to establish their structures and to characterize their reactivities we studied the salt formation and alkylation, recorded the electronic, IR absorption, and PMR spectra, and determined the acidity constants (pK_a) and ionization potentials (IP).



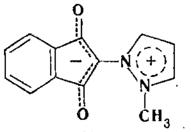
I



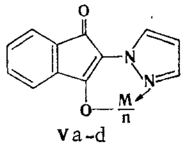
II



III



IV



Va-d

V a M=Cu, b Co, c Ni, d Mn

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