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SYNTHESIS OF 2-*o*-AZIDOPHENYLBENZOTHIAZOLES AND THE FUSED HETEROCYCLES DERIVED THEREFROM

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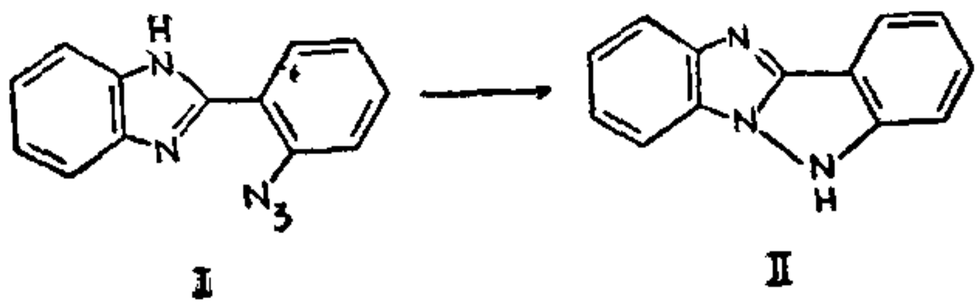
INTRAMOLECULAR insertion reactions of suitably substituted nitrenes have become the basis of a general method of synthesis of various heterocyclic systems[1]. In the majority of these instances, azides are involved as nitrene precursors. Relatively little is known about the intramolecular reactions of nitrene function with a $>C=N-$ component of a heterocyclic system. The only known example of such a heterocyclisation involving 2-*o*-azidoarylazoles is the formation of 6 H-indazolo (2, 3-*a*)-benzimidazole (II) on pyrolysis of 2-*o*-azidophenylbenzimidazole (I)[2].



I II

CHART-I

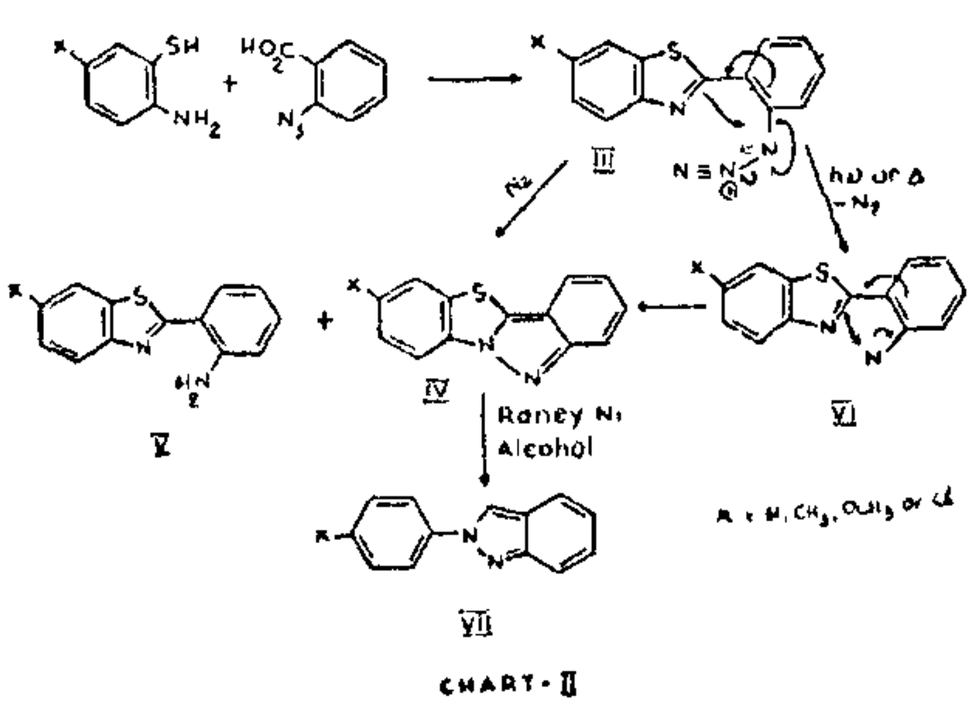
With a view to studying the formation of the new heterocyclic systems based on this approach, the synthesis of 2-*o*-azidophenylbenzothiazoles and their decomposition under thermal and photochemical conditions have now been undertaken.

A convenient method for the synthesis of 2-*o*-azidophenylbenzothiazole (III, X = H) has been developed in the present investigation, by the condensation of zinc salt of *o*-aminothiophenol with *o*-azidobenzoic acid in the presence of polyphosphate ester. This method has been extended to the synthesis of three other benzothiazoles (Table I). The I.R. spectra of all these compounds showed a strong absorption at 2120–2140 cm^{-1}, characteristic of the azido group[3].

TABLE I

Sl. No.	2-*o*-azidophenylbenzothiazoles (III)			Indazolo (2, 3-*b*) benzothiazoles (IV)		
	X	m.p.	% yield	X	m.p.	% yield
1.	H	133	50	H	143	75–80
2.	CH_3	108	55	CH_3	207	85
3.	CH_3O	158	60	CH_3O	163	90
4.	Cl	124	52	Cl	148	80–85

Cyclisation of 2-*o*-azidophenylbenzothiazole, as a representative case, has been studied in detail under thermal and photochemical conditions. The exposure of benzene solution of III (X = H) to sunlight or U.V. light for three hours resulted in the formation of a crystalline product (IV), m.p. 143°, in 60% yield. However, the decomposition of the azide, under these conditions, was found to be incomplete. The mass spectrum of the compound (IV) revealed the molecular ion at m/e 224 and showed a strong band at 1650 cm^{-1} in the I.R. spectrum. The absence of the azido function in the I.R. spectrum and the molecular weight of the compound strongly suggest indazolo (2, 3-*b*) benzothiazole structure for the compound (IV). It may be mentioned here that similar I.R. absorption has been reported in the case of pyrido (1, 2-*b*)-indazole[4] and has been attributed to the dipolar canonical form. Pyrolysis of III (X = H) with sand for 45 minutes at 160° yielded, in addition to IV (X = H ; 65% yield), 15% of 2-*o*-aminophenylbenzothiazole[5] (V, X = H). The formation of the latter can be explained through the nitrene (VI, X = H), in the triplet state, obtained by the loss of a molecule of nitrogen from III (X = H). In order to minimise the formation of by-products during the heterocyclisation, the azido compound was heated in toluene. Even after prolonged refluxing in this solvent no decomposition was observed. However, refluxing in xylene solution for four hours or heating a decalin solution at 150–55° for 45 minutes gave 75–80% yield of IV (X = H), exclusively. Thus, heating in neutral solvents around 150° appears to be the optimum condition for the heterocyclisation reaction. Adopting this procedure, three 2-*o*-azidophenylbenzothia-



V III IV VI VII

CHART-II

zoles with a substituent in 6-position have been cyclised to the corresponding indazolo (2, 3-*b*)-benzothiazoles.

The fact that none of these 2-*o*-azidophenyl benzothiazoles decompose below 140° favours a stepwise mechanism and not a concerted one. As a means of obtaining 2-arylindazoles (VII), all the indazolo (2, 3-*b*) benzothiazoles (IV) have been subjected to desulphurisation by refluxing with Raney Ni in alcohol for 6 hours. In all these cases the expected 2-arylindazoles have been obtained in excellent yields and in pure state.

After the completion of this work, the publication of Suschitzky *et al.*[6], which reported the conversion of 2-*o*-azidophenylbenzothiazole to III (X = H) came to our notice. Neither the method of preparation of III (X = H) nor the physical constants of III and IV (X = H) were mentioned in this report. They obtained 2-phenyltetrahydroindazole on desulphurisation of IV (X = H) in xylene. This result, in contrast to the one obtained in the present work, appears understandable in view of the drastic conditions employed.

Application of this method, for the synthesis of other fused heterocycles from 2-*o*-azidoarylazoles is in progress.

ACKNOWLEDGEMENT

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COPPER (II)-ETHYLENEDIAMINE-SULFADRUGS COMPLEXES

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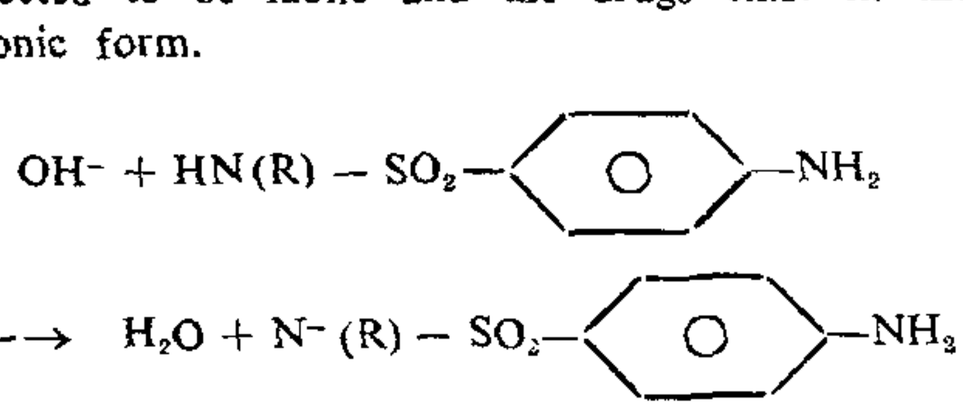
ABSTRACT

Cupper (II) complexes of the composition $Cu(en)_2D_2$ Where en = ethylenediamine and HD = sulfadrugs, *viz.*, sulfathiazole, sulfapyridine, sulfamerazine or sulfadiazine, have been prepared and characterized by analysis, infrared. electronic spectral and magnetic data. The complexes are planar and paramagnetic and the sulfadrug molecules act as anions.

INTRODUCTION

REACTIONS of the sulfadrugs with Zn (II), Cd (II), Hg (II)[1] and Cu (II)[2] have been successfully carried out using high concentrations of metal salts. In alkaline medium, however, the –NH– protons of the sulfadrug molecules are expected to be labile and the drugs exist in the anionic form.



In order to investigate such a behaviour of the sulfadrugs, the present study has been undertaken and some mixed Cu (II) compelxes of sulfadrugs and ethylenediamine are reported.

EXPERIMENTAL

The complexes were prepared by reacting solution of copper (II) chloride (10 m moles) or Copper (II) hydroxide (10 m moles) and ethylenediamine (2 ml) in the minimum amount of water (5 ml) with hot ethanolic solution (25 ml) of sulfadrug (20 m moles) and ethylenediamine (2 ml). The resulting solids were obtained on keeping the reactants for 1 hr., filtered and washed with 50% alcohol and dried at 110° C.

Metal part and sulphur in the complexes were estimated gravimetrically and nitrogen was analysed by micro-analytical technique using a coleman N-analyzer. Infrared and electronic spectra were recorded on Perkin–Elmer–257 and a Cary–14 model respectively. Magnetic measurements were made on Faraday Balance (Cahn, Magnetic susceptibility Apparatus) using Hg [$CO(NCS)_4$] as calibrant. Diamagnetic currections were applied using