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RUTHENIUM-CATALYSED REARRANGEMENTS OF AZOBENZENES

III *. PREPARATION OF *N*-PHENYL-1,2-PHENYLENEDIAMINE AND N^1-PHENYL-N^2-(sec-ALKYL)-1,2-PHENYLENEDIAMINE AND DERIVATIVES THEREOF BY THE RUTHENIUM-CATALYSED REACTION OF AZOBENZENES WITH SECONDARY ALCOHOLS

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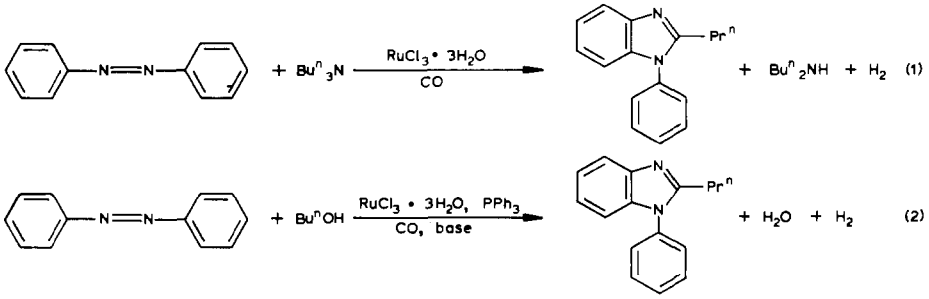
Summary

$RuCl_3 \cdot 3H_2O$ in presence of PPh_3 and a mild base and under an atmosphere or carbon monoxide catalyses the reaction of azobenzene and 2-propanol to give *N*-phenyl-1,2-phenylenediamine and N^1-phenyl-N^2-(2-propyl)-1,2-phenylenediamine. The selectivity towards the two products can be controlled by varying the amount of base (NaOAc or LiOAc) and 2-propanol used. Secondary alcohols which are less effective for *N*-alkylation than 2-propanol favour the former product. Substituents in the azobenzene derivative have a marked effect on the yield. Where the azobenzene derivative used permits isomer formation within the *N*-phenylphenylenediamine unit, all possible isomers usually occur.

Introduction

We have already described the synthesis of 2-substituted 1-phenylbenzimidazole derivatives [1] by the ruthenium-catalysed reaction of azobenzenes with tertiary amines [2] (eq. 1) or primary alcohols [3] (eq. 2).



* For part II see ref. 3.

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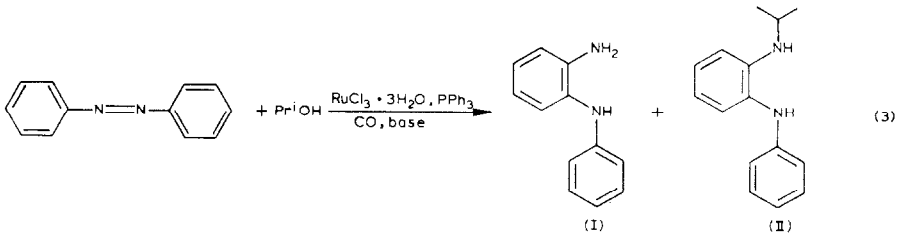
In view of equation 2 we have studied the behaviour of secondary alcohols in this reaction [4], since formation of an analogous product would then be impossible without the most improbable elimination of the elements of an alkane. In fact, the products formed are *N*-phenyl-1,2-phenylenediamine and N^1-phenyl-N^2-(sec-alkyl)-1,2-phenylenediamine derivatives. The former are intermediates in the conventional synthesis of benzimidazoles [5] and the latter are of interest as oxidation inhibitors for petrol [6]. We report here our findings.

Results

The ruthenium-catalysed reaction of azobenzene with 2-propanol occurs under similar conditions to those for equation 2 above [1,3] and gives as products *N*-phenyl-1,2-phenylenediamine (I) and N^1-phenyl-N^2-(2-propyl)-1,2-phenylenediamine (II) (eq. 3).



(3)

The selectivity between I and II can be controlled by varying the amount of base and 2-propanol used, and the two products can be readily separated by chromatography. The general conditions were similar to those used for the reaction of equation 2, $RuCl_3 \cdot 3H_2O$ in presence of triphenylphosphine being used as catalyst precursor under an atmosphere of carbon monoxide. A base (NaOAc or LiOAc) is also needed and tetramethylurea was again used as solvent.

Table 1 shows the effect of varying the quantities of LiOAc and 2-propanol on the formation of I and II. Compound II could be obtained in a yield of 79% and free from compound I by employing a five-fold excess of 2-propanol and only 4 mol% of

TABLE 1

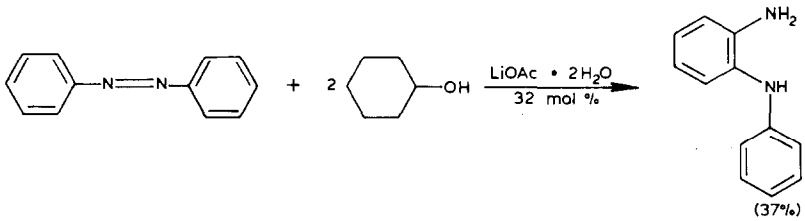
EFFECT OF VARYING THE QUANTITY OF BASE AND ALCOHOL ON THE RUTHENIUM-CATALYSED REACTION OF 2-PROPANOL WITH AZOBENZENE

(Azobenzene 25 mmol, 2-propanol and anhydrous lithium acetate see table, $RuCl_3 \cdot 3H_2O$ 0.25 mmol, PPh_3 1 mmol, tetramethylurea 12.5 ml, 180°C, 8 h, CO at normal pressure.)

Mol % [a]	100	140	160	200	300	500	2-propanol
0						30/27	
4	19/5 [b]	35/15			14/61	0/79	
40	17/5		31/17		32/31		
60				28/17			
100	21/6		24/8	33/25		27/30	
120			28/19	32/22			
LiOAc							

[a] relative to azobenzene. [b] Yields in %, compound I/compound II, by gas chromatography.

LiOAc relative to azobenzene, but compound I became the major product only under conditions where the total yield was low, and the best selectivity towards I was only ca. 80%. Formation of compound I is favoured principally by use of a smaller excess of 2-propanol. Alternatively, if a secondary alcohol is used which shows a lesser tendency towards *N*-alkylation, than 2-propanol, the formation of I is favoured. Cyclohexanol is useful in this respect (eq. 4). The conditions for this reaction were not optimised. The N^2-cyclohexyl product forms in very low yield, but is easily removed by chromatography on a short column.



(4)

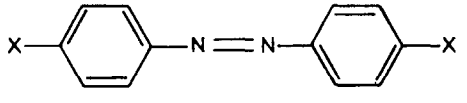
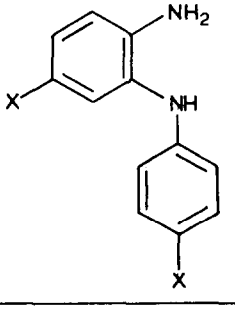
In Tables 2 and 3, 4,4′-disubstituted azobenzenes were caused to react with 2-propanol under conditions which favour the formation of analogues of compounds I and II respectively. In order better to study the effect of substituents on the selectivity towards I and II, these reactions were repeated under conditions where with azobenzene I and II were formed in roughly equal amounts (Table 4).

When the azobenzene derivative used permits isomer formation, all isomers are generally found as observed previously in the synthesis of *N*-phenylbenzimidazole

TABLE 2

THE RUTHENIUM-CATALYSED SYNTHESIS OF *N*-PHENYL-1,2-PHENYLENEDIAMINE DERIVATIVES FROM 4,4′-DISUBSTITUTED AZOBENZENES AND 2-PROPANOL

(Azobenzene derivative 50 mmol, 2-propanol 80 mmol, anhydrous lithium acetate 50 mmol, $RuCl_3 \cdot 3H_2O$ 0.5 mmol, PPh_3 2 mmol, tetramethylurea 25 ml, 180°, 8 h, CO at normal pressure.)

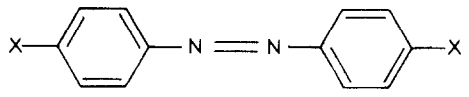
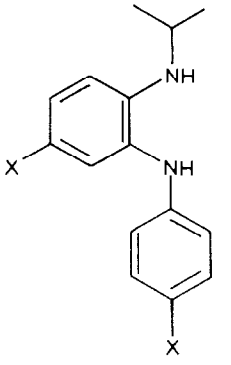
Substituent X in 	Yield[a] (%) of 
Me	28
Cl	23
F	33

[a] Isolated yield.

TABLE 3

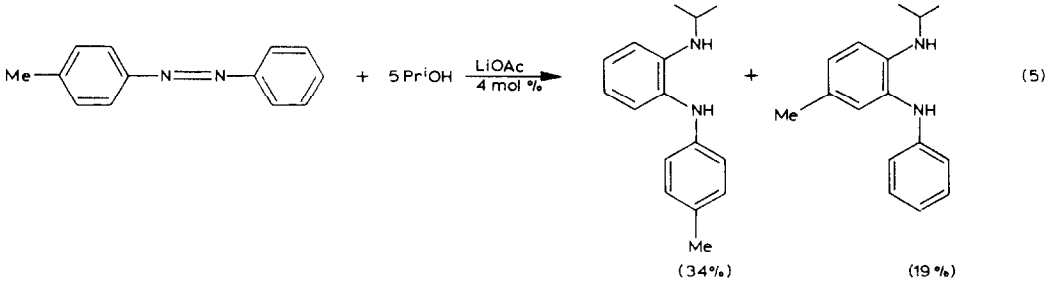
THE RUTHENIUM-CATALYSTED SYNTHESIS OF N^1-PHENYL-N^2-(2-PROPYL)-1,2-PHENYL-ENEDIAMINE DERIVATIVES FROM 4,4′-DISUBSTITUTED AZOBENZENES AND 2-PROPANOL

(Azobenzene derivative 50 mmol, 2-propanol 250 mmol, anhydrous lithium acetate 2 mmol, $RuCl_3 \cdot 3H_2O$ 0.5 mmol, PPh_3 2 mmol, tetramethylurea 25 ml, 180°C, 8 h, CO at normal pressure).

Substituent X in 	Yield[a] (%) of 
Me	54
Cl	45
F	56

[a] Isolated yield.

derivatives [2,3]. An example is given in equation 5 where conditions were chosen which favour the N^2-alkyl product (as Table 3).



(5)

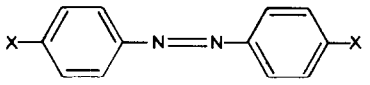
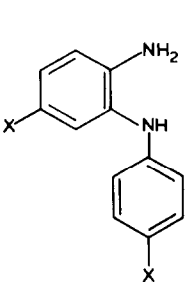
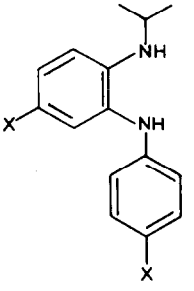
When 3,3′-dimethylazobenzene was caused to react under the same conditions, both isomers of the analogues of compounds I and II were formed in comparable amounts, the total yield being 70%.

The ruthenium-catalysed 1-phenyl benzimidazole synthesis previously reported involves the reaction of azobenzene derivatives with tertiary amines [2] or primary alcohols [3]. In view of the reactions described here an attempt was made to find a tertiary amine version of this reaction. Since tri-2-propylamine does not appear to exist, ethyldi-2-propylamine was used (eq. 6). The reaction was carried out as for the 1-phenylbenzimidazole synthesis with tertiary amines [2]. The product was 1-phenyl-

TABLE 4

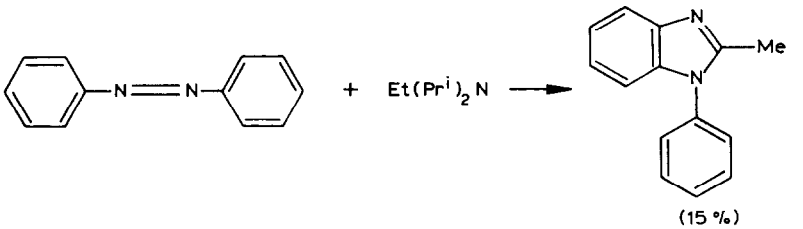
PRODUCT SELECTIVITY IN THE RUTHENIUM-CATALYSED REACTION OF 4,4'-DISUBSTITUTED AZOBENZENES WITH 2-PROPANOL

(Azobenzene derivative 25 mmol, 2-propanol 50 mmol, anhydrous lithium acetate 25 mmol, $RuCl_3 \cdot 3H_2O$ 0.25 mmol, PPh_3 1 mmol, tetramethylurea 12.5 ml, 180°C, 8 h, CO at normal pressure.)

Substituents X in 	Yield[a] (%) of 	
Me	35	24
Cl	30	14
F	32	15

[a] Isolated as product mixture; composition from 250 MHz ^1H NMR spectra.

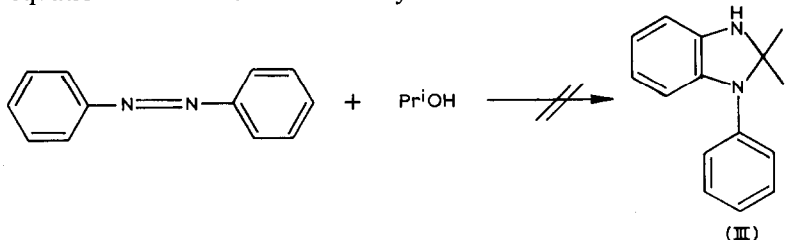
2-methylbenzimidazole, indicating that only the ethyl group of the amine had reacted.



(6)

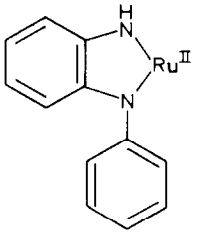
Discussion

General aspects of these reactions and factors affecting the activation of the azobenzene derivative, its rearrangement and the subsequent incorporation of the alkyl group have already been discussed [2,3]. Of interest here is that the product of equation 7 was not observed in any case.

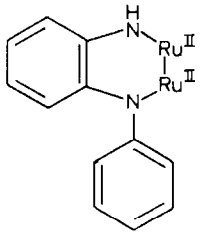


(7)

Small traces of unidentified products were sometimes present, but significant amounts of III were not formed. The rearrangement of the azobenzene is expected to lead to intermediates such as IV or V [2,3], in which a deprotonated *o*-semidine

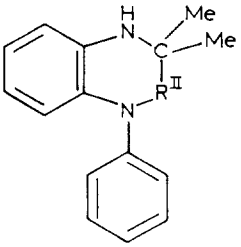


(IV)



(V)

(*N*-phenyl-1,2-phenylenediamine) ligand is present. Since 2-propanol is an efficient hydrogen donor for homogeneously catalysed transfer hydrogenations [7,8], the formation of compound I is readily explained. The occurence of compound II as the other major product, rather than compound III, is presumed to be due to steric difficulties with the ring-closure step when a secondary alcohol is involved. Conceivably, an intermediate such as VI or its analogue derived from V forms, which then undergoes cleavage of the Ru–N and Ru–C bonds to give II.



(VI)

The use of larger excesses of 2-propanol favours the formation of the N^2-alkyl product (Table 1) as would be expected. The amount of base used has a significant effect on the product selectivity only when a large excess of 2-propanol is used. The reason for this is not clear at present. The effect of substituents in the para-position of the azobenzene derivative on the product selectivity is more readily explained (Table 4). Whereas roughly comparable amounts of the three *o*-semidine derivatives are formed, the yields of the N^2-alkyl products decrease with the basicity of the nitrogen atom to be alkylated, as may be expected.

Experimental

Chemicals, instruments and apparatus were as previously [2,3] described. Anhydrous lithium acetate was obtained by drying the dihydrate at 150°C/0.3 mmHg. All products were fully characterised and gave satisfactory elemental analyses.

The following preparations are representative. More examples will be found in ref. 4.

Preparation of N-(4-Methylphenyl)-5-methyl-1,2-phenylenediamine

In a 110 ml glass pressure tube [3] were placed 4,4'-dimethylazobenzene (10.5 g, 50 mmol), anhydrous lithium acetate (3.3 g, 50 mmol), 2-propanol (6.14 ml, 80 mmol) and tetramethylurea (25 ml). The mixture was stirred magnetically and carbon monoxide was passed for 5 min. Ruthenium trichloride hydrate (0.1308 g, 0.5 mmol) and triphenylphosphine (0.524 g, 2 mmol) were added and the tube was cappped under normal pressure of carbon monoxide and stirred in an oil-bath at 180°C for 8 h. After removal of the solvents, the crude product was separated by distillation in vacuo and recrystallised from n-hexane (50 ml) with cooling in ice. Yield 3.0 g (28%). Colourless crystals, m.p. 108°C. Anal. Found: C, 79.29; H, 7.59; N, 13.10. $C_{14}H_{16}N_2$ calcd.: C, 79.21; H, 7.60; N, 13.20%.

Preparation of N^1-(4-Fluorophenyl)-N^2-(2-propyl)-5-fluoro-1,2-phenylene diamine

In a 110 ml glass pressure tube [3] were placed 4,4'-difluoroazobenzene (10.9 g, 50 mmol), anhydrous lithium acetate (0.132 g, 2 mmol), 2-propanol (19.2 ml, 250 mmol) and tetramethylurea (25 ml). The mixture was stirred magnetically and carbon monoxide was passed for 5 min. Ruthenium trichloride hydrate (0.1308 g, 0.5 mmol) and triphenylphosphine (0.524 g, 2 mmol) were added and the tube was capped under carbon monoxide at normal pressure and stirred in an oil-bath at 180°C for 8 h. The reaction mixture was then diluted with diethyl ether (50 ml) and extracted three times with water (50 ml). After drying over magnesium sulphate (5 g) and removal of the solvents, the crude product was separated by distillation in vacuo. This was chromatographed in dichloromethane on Kieselgel (100 g) and recrystallised from n-pentane (50 ml) with cooling to ca. −25°C. Yield 7.3 g (56%). Colourless crystals, m.p. 81°. Anal. Found: C, 68.88; H, 6.20; N, 10.79; F, 14.46. $C_{15}H_{16}N_2F_2$ calcd.: C, 68.68; H, 6.14; N, 10.68; F, 14.50%.

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