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THE REACTIONS OF BENZYLIDENEMALONONITRILES AND β-NITROSTYRENES WITH O-PHENYLENEDIAMINE INCLUDING THE NEW ORGANIC REDOX REACTIONS BETWEEN THE OLEFINS AND 2-PHENYLBENZIMIDAZOLINES

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The reactions of benzylidenemalononitriles and β-nitrostyrenes with o-phenylenediamine in ethanol at boiling temperature gave the reduced products of the olefins. The reactions were rationalized on the basis of the role of 2-phenylbenzimidazolines as a hydrogen donor.

In heterocyclic chemistry, it has been accepted that benzimidazoline (**4a**) is an unstable intermediate and rapidly oxidized to form benzimidazole (**5a**).[1] Although 1,3-dimethylbenzimidazoline is known to act as a hydride donor in some particular reaction systems,[1] there has been no study concerning the reactivity of 1,3-unsubstituted benzimidazolines. Now we found the selective reductions of carbon-carbon double bonds in benzylidenemalononitriles (**2a**-**e**) and β-nitrostyrenes (**2f**-**i**) to take place when these olefins were allowed to react with diamine (**1**) in ethanol at boiling temperature and this fact was ascribed to be due to the action of benzimidazolines (**4**) as a hydrogen donor. In this paper, we describe the reactions of olefins (**2**) with diamine (**1**) including the new organic reductions of the olefins (**2**) with benzimidazolines (**4**).

When **2a** was heated with half molar amount of diamine (**1**) in ethanol, the mixture of benzylmalononitrile (**6a**) and benzimidazole (**5a**) was given in high yields. The other p-substituted benzylidenemalononitriles (**2b**-**e**) also afforded the corresponding reduced products (**6b**-**e**) and benzimidazoles (**5b**-**e**). similarly, the reactions of olefins (**2f**-**i**) with diamine (**1**) under the same reaction conditions afforded 2-nitroethylbenzenes (**6f**-**i**) and benzimidazoles (**5f**-**i**) in high yields. These reactions could be also performed in benzene to give the same products but yields were low. In above cases, the formation of malononitrile or nitromethane was observed. The reduced products were purified by short column chromatography on silica gel after the separation of benzimidazoles from the reaction mixture and their structures were confirmed by ^{1}H-NMR, IR and Mass spectra.

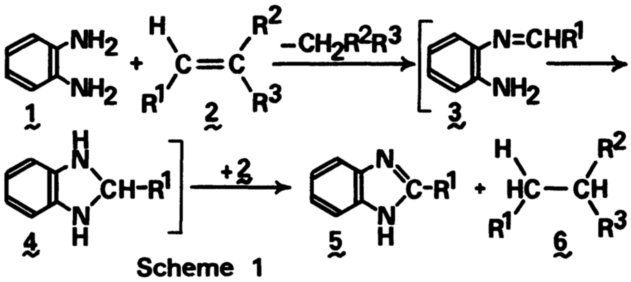
Hammad et al.[2] reported the synthesis of **5a** by the reaction of **2a** with diamine (**1**) (180°C, without solvent). In this reaction, the product comes from the route through the autoxidation of **4a**. Particularly remarkable point in our cases is the observation that the equimolar mixture of benzimidazoles (**5**) and the reduced products (**6**) was constantly given as shown in Table 1. Although the structures of the intermediates (**3** and **4**) can't be confirmed,[1] this shows the quantitative reductions

Table 1. Products obtained by the reactions of 1 with 2.[a)]

Olefin (2)	R^1	R^2	R^3	Solvent	Yield of product/%	
					5[b)]	6[c)]
a	C_6H_5	CN	CN	EtOH	91	100
a	C_6H_5	CN	CN	Benzene	82	79
b	$p\text{-}CH_3C_6H_4$	CN	CN	EtOH	89	94
c	$p\text{-}CH_3OC_6H_4$	CN	CN	EtOH	97	99
d	$p\text{-}NO_2C_6H_4$	CN	CN	EtOH	94	98
e	$p\text{-}ClC_6H_4$	CN	CN	EtOH	95	99
f	C_6H_5	NO_2	H	EtOH	85	72
f	C_6H_5	NO_2	H	Benzene	61	4
g	$p\text{-}CH_3C_6H_4$	NO_2	H	EtOH	76	64
h	$p\text{-}CH_3OC_6H_4$	NO_2	H	EtOH	97	69
i	$p\text{-}ClC_6H_4$	NO_2	H	EtOH	95	81

a) The reactions were carried out in ethanol (3 ml) by the use of 1 mmol of 1 and 2 mmol of 2. b) Isolated yield. c) Determined by GLC.

of olefins (2) with benzimidazolines (4) formed from N-benzylidene-o-phenylenediamine (3) and it sugests that the compensating oxidations are those of benzimidazolines (4) to benzimidazoles (5). Scheme 1 shows the reaction process for these redox reactions.



Scheme 1

The role of 4 in the present cases resembles that of 1,3-dimethylbenzimidazoline[3)] and the mechanism including hydride transfer seems to be reasonable.

The development of methods applicable to the selective reductions of carbon-carbon double bonds conjugated with cyano, nitro and ester group has been a synthetic subject. Although several reports[4)] have appeared describing such selective reductions, virtually no sufficient methods are known. From present results, 2-phenylbenzimidazoline as a reducing agent is expected to be useful for these purpose and methodical applications of it are now in progress.

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