

REACTION OF ARYNE WITH N,N-DIETHYL-1,3-BUTADIENYLAMINE

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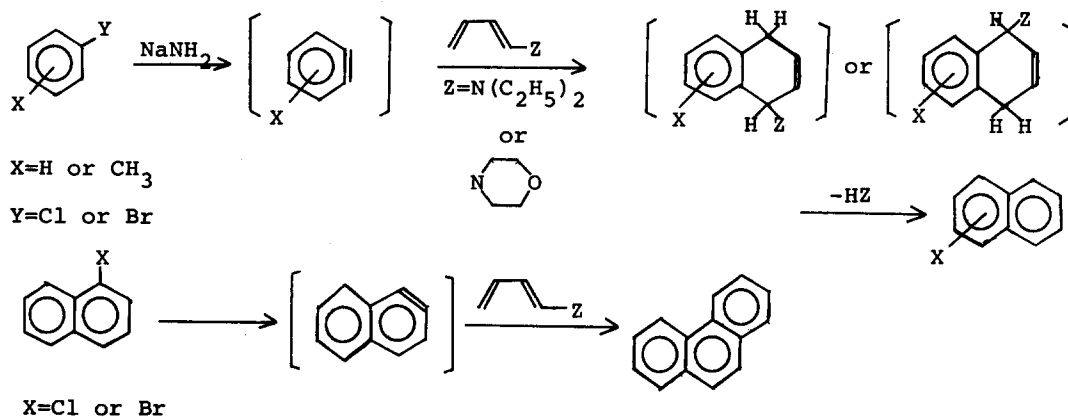
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It has been well documented that aryne acts as a 2π addend in the Diels-Alder reaction with cyclic 1,3-dienes.¹ Several examples of this type of reaction with benzyne have been presented by Wittig²⁻¹⁰, Stiles¹¹ and other workers. On the other hand, relatively little work has been directed toward the same type reaction with acyclic 1,3-dienes. A previous report¹² has described the Diels-Alder reaction of benzyne with buta-1,3-diene, a parent member of acyclic 1,3-dienes, but the yield was very poor. Even with the nascent buta-1,3-diene generated from 2,5-dihydrothiophene 1,1-dioxide, the yield of 1,4-dihydronaphthalene was only 9%.¹³ In the case of the reaction with isoprene or 2,5-dimethyl-2,4-hexadiene, a hydrogen abstraction reaction takes place and none of the expected Diels-Alder adduct was detected.¹⁴ Very recently, we have found that this cycloaddition can take place readily with use of the amino derivative of 1,3-butadiene, further followed by the deamination to give an aromatic system. 2,3-Benzo-1,6-methano[10]annulene was prepared from N,N-diethyl-1,3-butadienylamine (DBA) and the aryne generated by the action of a strong base on 2-bromo-1,6-methano[10]annulene.¹⁵ The present communication describes that this reaction can serve as a general method to prepare naphthalene or phenanthrene from halo-benzene or halonaphthalene in both an one-step manner and a desirable yield.

The reactions between DBA or 4-(1,3-butadienyl)morpholine (BDM) and halo-benzenes or halonaphthalenes were carried out under the condition of a 1:3 mole ratio of haloaromatics- NaNH_2 at 90-100° for 7 hr. The products were obtained in

15-41% yield (Table). A reaction temperature of 90-100° is necessary to permit a desirable yield of product.



The best result was obtained when DBA or BDM was used as both reagent and solvent. In the reaction between bromobenzene and DBA, attempts to find a base-solvent combination that gives a more excellent yield of naphthalene than in the NaNH_2/DBA system have been almost unsuccessful. The base/solvent systems such as KO-t-Bu/toluene , $\text{NaNH}_2/\text{toluene}$, $\text{NaNH}_2/\text{HMPA}$ plus THF^{16} , KO-t-Bu/DMF resulted in decreased yields of naphthalene in all cases. Also no synthetic advantage was obtained by employing a mixture of NaNH_2 and KO-t-Bu or a large excess of NaNH_2 such as sixfold.

A general procedure is as follows: To a stirred mixture containing 16 g of DBA (or 18 g of BDM) and 25 mmol of haloaromatics was added 75 mmol of NaNH_2 in a nitrogen atmosphere, and then stirred for 7 hr at 90-100°. The dark-brown solution was cooled and poured into a mixture of ice water and ether. The aqueous layer was removed, and the organic layer was washed with three portions of 80 ml of 7% HCl , and once with 100 ml of water. After drying over anhydrous magnesium sulfate and evaporation of the solvent, the residue was recrystallized or fractionally distilled at reduced pressure. Also, the combined 7% HCl washings were made basic with sodium hydroxide aqueous solution and extracted with ether. Drying of the ether solution by anhydrous magnesium sulfate followed by vacuum distillation yield the basic by-products.

Table

Run no.	Starting haloaromatics	Solvent	Base Mole ratio of haloaromatics:base	Products ^a (Yield, ^b %)	
				Objective	Other
1	Bromobenzene	DBA	NaNH ₂ (1:3)	Naphthalene ^c (24)	N,N-Diethylaniline ^d (13)
2	Bromobenzene	DBA	NaNH ₂ (1:6)	Naphthalene ^c (20)	N,N-Diethylaniline ^d (15)
3	Bromobenzene	DBA	NaNH ₂ (1:3) plus KO-t-Bu (1:1)	Naphthalene ^c (22)	N,N-Diethylaniline ^d (14)
4	Chlorobenzene	DBA	NaNH ₂ (1:3)	Naphthalene ^c (24)	e
5	<i>o</i> -Bromotoluene	DBA	NaNH ₂ (1:3)	1-Methylnaphthalene ^f (27)	e
6	<i>p</i> -Bromotoluene	DBA	NaNH ₂ (1:3)	2-Methylnaphthalene ^f (15)	e
7	<i>o</i> -Chlorotoluene	DBA	NaNH ₂ (1:3)	1-Methylnaphthalene ^f (24)	e
8	1-Bromonaphthalene	DBA	NaNH ₂ (1:3)	Phenanthrene ^c (40)	{ N,N-Diethyl-1-naphthyl-amine (5-6) N,N-Diethyl-2-naphthyl-amine (9-8)
9	1-Chloronaphthalene	DBA	NaNH ₂ (1:3)	Phenanthrene ^c (41)	e
10	Bromobenzene	BDM	NaNH ₂ (1:3)	Naphthalene ^c (19)	e
11	1-Bromonaphthalene	BDM	NaNH ₂ (1:3)	Phenanthrene ^c (30)	e

^a Identification of these products were based on the identity of nuclear magnetic resonance and infrared spectra for the authentic compound.

^b All yields represent pure compound isolated by distillation or recrystallization and are based on haloaromatics.

^c Recrystallized from ethanol.

^d N,N-Diethylaniline is apparently formed by the reaction of benzyne with diethylamine generated in the requisite reaction. It is well established that N,N-dialkylanilines are obtained in good yield if bromobenzene and the appropriate dialkylamine are allowed to react in the presence of NaNH₂: E. R. Biehl, S. M. Smith, R. Patrizi and P. C. Reeves, J. Org. Chem., 37, 137 (1972).

^e Because of its minor importance the isolation of the basic products was not put in practice.

^f Distilled at reduced pressure.

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