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단 신

HMPT 용매에서 몇가지 클로로- 및 니트로-벤젠과 메톡시화 이온의 반응

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Reaction of Some Chloro- and Nitro-benzenes with Methoxide Ion in Hexamethylphosphoramide

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Unactivated aryl halides are generally known to be unreactive with nucleophiles under ordinary conditions[1]. However the reactivity of nucleophiles are so enhanced in dipolar aprotic solvents [2,3] such as hexamethylphosphotriamide (HMPT) that despite lack of activating group, SnAr mechanism operates for the reaction of aryl halides with anionic nucleophiles.[4]

Shaw and his coworkers reported that unactivated aryl chloride reacted solely by SnAr mechanism with sodium methoxide in HMPT to give in most cases good yields of methyl aryl ethers.[4] It occured to us that Shaw's reaction system might be useful in organic syntheses, and we examined the substituent effect on the SnAr reaction of chlorobenzenes with NaOMe in HMPT. Since some interesting observations were made during this study, we wish to report the experimental results.

The results of experiments are summarized in *Table* 1. The reaction of chlorobenzene, *o*- or *m*-dichlorobenzene, or *p*-chlorotoluene gave the results comparable with those of Shaw's experiments.[4] It is intersting to note that among three dichlorobenzenes *p*-dichlorobenzene gave the lowest yield of the corresponding anisole. Whereas *p*-chloronitrobenzene and *o*-chlorobenzonitrile reacted with NaOMe smoothly (100% substitution at lower reaction temperature), the reaction of *o*- or *p*-chlorotoluene was proceeded poorly as expected.

It is interesting that *o*-chloronitrobenzene gave a mixture of *o*-nitroanisole and *o*-chloroanisole, indicating that methoxide anion attacked arene carbons bearing chloro and nitro group competitively. Nitrobenzene itself reacted with sodium methoxide to give anisole in a moderate yield under the reaction conditions. Replacement of nitro group by a nucleophile in SnAr reaction is not common, but a few cases are known.[5] For example, the reaction of piperidine with 1,2,4-trinitrobenzene or with *o*-dinitrobenzene in benzene afforded 2,4-dinitro-1-piperidinobenzene or 2-nitro-1-piperidinobenzene, respectively in quantitative yield.[6] Substitution of a nitro group by the methoxy

Table 1. Reaction of chloro- and nitro-benzenes with sodium methoxide in HMPT.

Reactant	Reaction condition			Product	Yield, %
	Temp, °C	Time, hr	Molar equiv MeONa		
Chlorobenzene	120	20	2.0	Anisole	56
o-Dichlorobenzene	100	20	1.2	*o*-Chloroanisole	82
m-Dichlorobenzene	100	20	1.2	*m*-Chloroanisole	86
p-Dichlorobenzene	100	20	1.2	*p*-Chloroanisole	47
o-Chlorotoluene	120	20	1.5	*o*-Methylanisole	11
m-Chlorotoluene	120	20	1.5	*m*-Methylanisole	4
p-Chlorotoluene	120	20	1.5	*p*-Methylanisole	7
Nitrobenzene	27	20	2.5	Anisole	18
Nitrobenzene	80	20	2.5	Anisole	37
o-Chloronitrobenzene	27	20	2.5	*o*-Nitroanisole	75
				o-Chloroanisole	15
o-Chloronitrobenzene	80	20	2.5	*o*-Nitroanisole	78
				o-Chloroanisole	13
p-Chloronitrobenzene	27	20	2.5	*p*-Nitroanisole	100
o-Chlorobenzonitrile	27	20	2.0	*o*-Cyanoanisole	94
o-Chlorobenzonitrile	80	20	1.5	*o*-Cyanoanisole	100
o-Nitrotoluene	20	20	1.5	Methyl anthranilate*	—

*Spectral evidences only.

group[7] or by a thiophenoxide nucleophile[8] has also been reported.

Most intersting result was obtained from the reaction of *o*-nitrotoluene with sodium methoxide: the main product seemed to be methyl anthranilate, a compound formed likely *via* intramolecular redox reaction. We have some spectral evidences for the formation of this ester, and further investigation on the reaction is under way. It should be noted that this type of reaction is not unprecedented: when heated with aqueous alkali, *o*-nitrotoluene yielded anthranilic acid.[9]

EXPERIMENTAL SECTION

Representative Reation Procedure. In a side armed 100 m*l* flask equipped with a reflux condenser 1.296 g (24 mmole) of sodium methoxide is placed. Then 30m*l* of HMPT is injected under dry nitrogen with stirring. A solution of chlorobenzene (2.28 g, 20 mmole) in 10 m*l* of HMPT is injected into the mixture and heated to 120 °C.

After heating 20 hours, the reaction mixture is cooled, poured into 80 m*l* of water, and extracted twice with 80 m*l* portions of diethylether. The combined ethereal solution is washed three times with 20 m*l* portions of water, dried over anhydrous sodium sulfate, and filtered. The filtrate is concentrated under reduced pressure by Rotavapor-R to give 3 g of liquid product for analysis.

Identification of Products. All products are identified by their retention time in comparison with their authentic samples by GC (Yanaco G8-TCD; 12′×1/8″, 20% Carbowax 20M, 60/80 Chromosorb W), and isolated by GC (R&M Model 720; 6′×1/4″, 20% Carbowax 20M), Their IR (Beckman IR 8) and NMR (Varian Model A60) spectra are good agree-

ment with the spectra published.[10]

REFERECENS

1. J. F. Bunnett, *Acc. Chem. Res.*, **5**, 139 (1972).
2. H. Normant, *Angew. Chem. Intern. Edit.*, **6**, 1064 (1967).
3. A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).
4. J. E. Shaw, D. C. Kunerth, and S. B. Swanson, *J. Org. Chem.*, **41**, 732 (1976).
5. J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).
6. F. Pietra and Vitali, *J. Chem. Soc., Perkin* II, 385 (1972).
7. V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1962 (1964).
8. J. J. D'Amico, C. C. Tung, W. E. Dahl, and D. J. Dahm, *J. Org. Chem.*, **42**, 2896 (1977).
9. J. D. Loudon and G. Tennant, *Quart. Rev.*, **18**, 389 (1964).
10. (a) C. J. Pouchert, "The Aldrich Library of Infrared Spectra", 2nd Ed., Aldrich, 1975; (b) "NMR Spectra", Sadtler Research Lab. Inc.