

Furan derivatives. LXXV.
**Reaction of diazoaminobenzene derivatives with Lewis acids
and isopentyl nitrite in furan and thiophene**

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A new method for arylation of furan and thiophene by reaction of diazoaminobenzene with Lewis acids ($4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, POCl_3 , HClO_4 , SOCl_2 , H_3PO_4 , PCl_5 , Ac_2O) is presented. The reaction mechanism of triazene derivatives with isopentyl nitrite is discussed.

В работе приводится новый способ арилирования фурана и тиофена при помощи реакции диазоаминобензола с кислотами Льюиса ($4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, POCl_3 , HClO_4 , SOCl_2 , H_3PO_4 , PCl_5 , Ac_2O). Обсуждается также механизм реакции производных триазена с изопентилнитритом.

The generation of an aryl radical from derivatives of diazoaminobenzene by a homolytic cleavage at $150\text{--}160^\circ\text{C}$ [1], or from 1-aryl-3,3-dialkyltriazene by gaseous hydrogen chloride [2] has already been reported. Both methods, however, are not suitable for arylation of furan and thiophene for their low boiling points and ability to polymerize in the presence of HCl . Considering both the formation of an aryl radical by an aprotic diazotization of derivatives of diazoaminobenzene with isopentyl nitrite, as presented in our previous paper [3], and also the Elks—Hey method of acid catalyzed arylation, we presumed that the quaternization of nitrogen bound to the azo group (excepting thermal decomposition) is necessary when derivatives of diazoaminobenzene are the arylation agents.

In this paper we wish to describe the reaction of diazoaminobenzene with furan (thiophene) with some Lewis acids where the quaternization was supposed to occur. We ascertained that diazoaminobenzene reacts with Lewis acids ($4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, POCl_3 , HClO_4 , SOCl_2 , H_3PO_4 , PCl_5 , Ac_2O) in an aromatic solvent to form the arylated solvent and gaseous nitrogen. Yields of the reaction in furan or thiophene are given in Table 1; as seen, they are — with the exception of tosyl chloride — lower than with isopentyl nitrite [3], where two more moles of 2-phenylfuran or 2-phenylthiophene were formed from 1 mole of diazoaminoben-

Table 1

Yields^a of the reaction of diazoaminobenzene and Lewis acids in furan (thiophene)

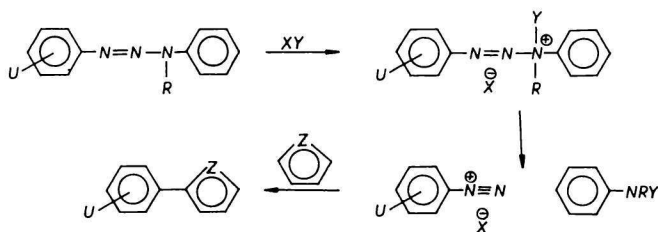
Compound	C ₅ H ₁₁ ONO ^b	TsCl	POCl ₃	HClO ₄	SOCl ₂	H ₃ PO ₄	PCl ₅	Ac ₂ O
2-Phenylfuran	40.8	38.0	24.2	24.0	32.1	10.8	10.4	10.4
2-Phenylthiophene	35.8	45.0	26.8	28.4	24.5	12.0	10.0	12.1

a) Yields of the pure isolated product.

b) The yield of one mole of diazoaminobenzene with two moles of 2-phenylfuran and 2-phenylthiophene, respectively.

zene. The method of arylation with diazoaminobenzene derivatives and the above-mentioned Lewis acids is of rather theoretical than practical importance.

The mechanism of the reaction of diazoaminobenzene with Lewis acids in furan or thiophene can be postulated as shown in Scheme 1.



	I	II	III	IV	V	VI	VII	VIII
R	H	H	H	H	H	H	H	CH ₃
U	H	H	H	H	H	H	H	4-Br
YX	H(ClO ₄)	H(H ₃ PO ₄)	CH ₃ CO(OCOCH ₃)	(PCl ₄)Cl	POCl ₂ Cl	(SOCl ₂)Cl	TsCl	(C ₅ H ₁₁ O)NO

Scheme 1

The first step of this reaction is the quaternization of diazoaminobenzene; the *N*-quaternary substance undergoes decomposition to furnish the corresponding diazonium salts, which give in turn the phenyl radical [4, 5]. A radical aromatic substitution in furan or thiophene affords 2-phenylfuran or 2-phenylthiophene. The support for the suggested mechanism was the presence of aniline and acetanilide [1] in the reaction mixture when HClO₄, H₃PO₄, and Ac₂O, respectively, were the Lewis acids. In addition, biphenyl was identified in all cases in an amount not exceeding 1%.

The first step of the reaction of diazoaminobenzene derivatives with isopentyl nitrite in an aromatic solvent is supposed to be *N*-nitrosodiazoaminobenzene [3]. We were unable to prove its generation under the given reaction conditions (temperature 30°C) since its spontaneous decomposition is reported [6] to occur at 0°C.

We tried, therefore, to evidence indirectly its formation by means of a model arylation of 1,3-diphenyl-3-methyltriazene with isopentyl nitrite. This starting material is convenient because it does not exist in another tautomeric form, as is the case of diazoaminobenzene, neither forms a phenyl radical from *N*-nitroso-*N*-methylaniline. The latter when reacted with isopentyl nitrite in furan or thiophene does not form 2-phenylfuran or 2-phenylthiophene at all (see Experimental, mixture VIII). The formed diazonium salt should decompose in furan or thiophene to give aryl derivatives of furan or thiophene and the generation of *N*-nitroso-*N*-methylaniline should prove the *N*-nitrosation as the first step of this reaction.

The mixture VIII obtained from 3-(4-bromophenyl)-1-phenyl-1-methyltriazene and isopentyl nitrite in thiophene was analyzed by means of g.l.c. (UCW-98 at 160°C): 2-(4-bromophenyl)thiophene ($t_r = 19.14$ min) and *N*-nitroso-*N*-methylaniline ($t_r = 3.20$ min) were identified, but no 2-phenylthiophene was found. Thereby it has been proved that *N*-nitroso derivative is the intermediate through which the reaction of triazenes with isopentyl nitrite in an aromatic solvent proceeds.

Experimental

The reactions were monitored by g.l.c. using a 18×0.2 cm column coated with 10% of methylvinylsilane at 162°C. The temperature of the flame-ionization detector was set at 223°C. Quantitative and qualitative determinations were performed according to Part 85 of this series [7] using an internal standard program.

1-(X-Phenyl)-3-phenyl-3-methyltriazene derivatives were prepared from the corresponding diazonium salts and *N*-methylaniline. *N*-Nitroso-*N*-methylaniline synthesized by diazotization of *N*-methylaniline according to [8] had b.p. 135–137/1.7 kPa, $t_r = 3.16$ min (UCW-98, 160°C) and also by reacting *N*-methylaniline with isopentyl nitrite in furan.

Reaction of diazoaminobenzene with Lewis acids in furan and thiophene

The mixture consisting of diazoaminobenzene (8×10^{-3} M), Lewis acid (8×10^{-3} M), and furan (thiophene) kept at 30°C for 24 hrs, was gradually washed with water and sodium hydrocarbonate solution to neutral reaction. The solvent was removed under diminished pressure and the residue chromatographed over alumina with light petroleum (b.p. 40–60°C) or light petroleum—chloroform 1:1 when Ac₂O was used.

Arylation of furan in the presence of HClO₄ or H₃PO₄ afforded aniline ($t_r = 1.07$ min) in 28 and 26.8% yield, respectively; in the presence of Ac₂O acetanilide ($t_r = 3.55$ min) was obtained in a 72.8% yield.

Reaction of N-methylaniline with isopentyl nitrite in furan

N-Methylaniline (1.07 g; 0.01 mole), isopentyl nitrite (2 ml; 0.017 mole), and furan (30 ml) were kept at 30°C for 24 hrs. Furan was distilled off and the residue chromatographed over SiO₂ with benzene. The yield of *N*-nitroso-*N*-methylaniline was 1.2 g (88.4%). No 2-phenylfuran could be found by g.l.c.

Reaction of N-nitroso-N-methylaniline with furan

N-Nitroso-*N*-methylaniline (1.36 g; 0.01 mole) in furan (30 ml) was heated at 30°C for 24 hrs and worked up as described with *N*-methylaniline. The unreacted starting material was recovered in virtually quantitative yield. No 2-phenylfuran could be detected by g.l.c.

Reaction of 1,3-diphenyl-3-methyltriazene with isopentyl nitrite

1,3-Diphenyl-3-methyltriazene (2.1 g; 0.01 mole), isopentyl nitrite (2 ml; 0.017 mole), and furan (30 ml) were reacted and worked up under the standard reaction conditions. Elution with benzene yielded 2-phenylfuran (*III*) (0.58 g; 41.2%) and *N*-nitroso-*N*-methylaniline, b.p. = 130—135°C/1.6 kPa, $n_D^{20} = 1.5768$.

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