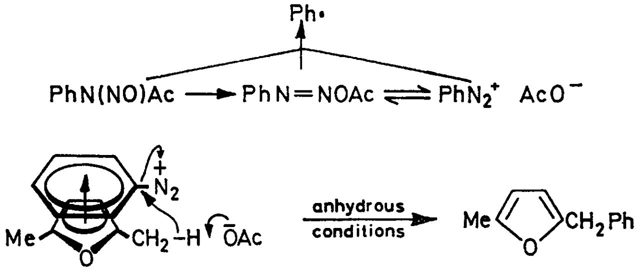
Conversion of 2,5-Dimethylfuran into 2-Benzyl-5-methylfuran by *N*-Nitrosoacetanilide: An Unprecedented Aromatic Side-chain Phenylation

By J. I. G. CADOGAN,*† M. J. P. HARGER, J. R. MITCHELL,† and J. T. SHARP †

(*Departments of Chemistry, University of Edinburgh, West Mains Road, Edinburgh,*† *and University of St. Andrews, St. Andrews, Fife, Scotland*)

Summary Decomposition of *N*-nitrosoacetanilide in a mixture of 2,5-dimethylfuran and benzene at room temperature gave biphenyl, formed *via* phenyl radicals, and 2-benzyl-5-methylfuran formed, it is suggested *via* a novel deprotonation by acetate ion of a dimethylfuran-benzenediazonium cation complex, the expected radical-derived products from 2,5-dimethylfuran being absent.

IT is known that decomposition of *N*-nitrosoacetanilide (NNA) in furan at room temperature gives 2-phenylfuran *via* radical phenylation,[1] while the corresponding reaction in toluene proceeds *via* radical nuclear phenylation and side-chain abstraction to give methylbiphenyls and bibenzyl.[2] It might be expected, therefore, that decomposition of NNA in 2,5-dimethylfuran would give a mixture of 2,5-dimethyl-3-phenylfuran and possibly 5,5′-dimethylbifurfuryl. We now report that this is not the case and that the reaction proceeds *via* an unprecedented side-chain phenylation to give 2-benzyl-5-methylfuran. We also present evidence that a novel ionic reaction occurs *via* a complex of the furan with the benzenediazonium cation. Thus, decomposition at room temperature of NNA (1 mol) in a mixture of 2,5-dimethylfuran (2 mol) and benzene (20 mol) gave 2-benzyl-5-methylfuran (0·27 mol) and biphenyl (0·06 mol), the low yield of the latter being remarkable in view of the large excess of benzene used. 2,5-Dimethyl-3-phenylfuran and 5,5′-dimethylbifuryl were absent (0·2% would have been detected by g.l.c.). The corresponding reaction of NNA in 2,5-dimethylfuran and t-butylbenzene again gave 2-benzyl-5-methylfuran (0·17 mol) rather than 2-(t-butylbenzyl)-5-methylfuran, thus ruling out the possible reaction of 5-methylfurfuryl radicals or carbonium ions with the solvent. Additionally, in t-butylbenzene, an isomeric mixture of t-butylbiphenyls (0·06 mol) was produced by radical phenylation (by comparison with an authentic radical-produced mixture). Decomposition of *m*-methoxy-*N*-nitrosoacetanilide in 2,5-dimethylfuran (2 mol) in benzene (20 mol) gave isomerically pure 2-methyl-5-(*m*-methoxybenzyl)furan (0·19 mol) and 3-methoxybiphenyl (0·06 mol). Decomposition of authentic sources of phenyl radicals (phenylazotriphenylmethane or pentyl nitrite–aniline[3]) in 2,5-dimethylfuran gave no 2-benzyl-5-methylfuran. Thus the side chain phenylation by NNA does not involve phenyl radicals but it does involve the phenyl moiety of NNA.



SCHEME

These results can be explained on the basis of the Scheme, whereby NNA is converted in the normal way into benzenediazonium acetate which in part decomposes normally to give phenyl radicals,[4] which phenylate benzene (present in excess). The remainder of the benzenediazonium cation is then assumed to be π-complexed with the strongly electron rich dimethylfuran, there being evidence that π-complexing is better developed in 2,5-dimethylfuran than in furan.[5] Formation of the π-complex (I) would lead to increased acidity of the furan-methyl protons which could then be removed by the acetate counter ion, the resulting, more strongly complexed, 5-methylfurfuryl carbanion then reacting by nucleophilic displacement of the diazonium group to give the observed product. In further accord with this proposal, addition of water suppressed the formation of 2-benzyl-5-methylfuran by solvation of, and hence lowering the basicity of, the acetate ion in agreement with our previous demonstration of the suppressing effect of water on ease of aryne formation *via* reaction of acetate ion with protons *ortho* to the diazonium function.[4,6]

The course of the corresponding reaction with tetramethylfuran also supports the Scheme. Thus, the resulting mixture (0·28 mol) of 2-benzyl-3,4,5-trimethylfuran (8·6 parts) and 3-benzyl-2,4,5-trimethylfuran (1 part) reflects the relative acidities of the 2- and 3-methyl groups.

An alternative route *via* induced decomposition of NNA by 5-methylfurfuryl radicals does not accommodate the effect of water on the reaction nor the observed substituent effects in substituted NNA to be described in the full paper.

(*Received September 17th*, 1971; *Com.* 1633.)

[1] D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, **1967**, **727**.

[2] C. S. Rondestvedt and H. S. Blanchard, *J. Amer. Chem. Soc.*, 1955, **77**, 1769.

[3] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

[4] J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186.

[5] Z. Yoshida and E. Osawa, *J. Amer. Chem. Soc.*, 1966, **88**, 4019.

[6] J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.*, 1971, 1; J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *J. Chem. Soc. (C)*, in the press.