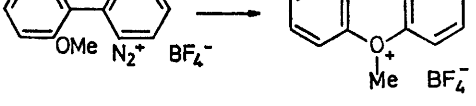
O-Methyldibenzofuranium Fluoroborate. A New Meerwein Reagent

By A. J. Copson, H. Heaney,* A. A. Logun, and R. P. Sharma
(*Department of Chemistry, The University of Technology, Loughborough, Leicestershire* LE11 3TU)

Summary 2′-Methoxybiphenyl-2-yldiazonium fluoroborate loses nitrogen when heated in benzene to afford a solid which acts as a powerful methylating agent; better yields of alkylated derivatives are obtained when the reagent is generated *in situ* in methylene dichloride.

Although triethyloxonium fluoroborate is readily available,[1] and is well known as a powerful alkylating agent,[2] trimethyloxonium fluoroborate is less conveniently prepared.[3] We now report the use of 2′-methoxybiphenyl-2-yldiazonium fluoroborate (**1**) as a precursor to a methylating agent which is potentially more powerful than trimethyloxonium fluoroborate and which may be compared with methyl fluorosulphonate.[4]

The conversion of 2′-halogenobiphenyl-2-yldiazonium fluoroborates into halonium salts under mild conditions,[5] suggested that the compound (**1**) should cyclise readily to afford *O*-methyldibenzofuranium fluoroborate (**2**) which, because of the low basicity of dibenzofuran, should be a more powerful methylating agent than trimethyloxonium fluoroborate. Precedent for the cyclisation exists.[6]



(1) (2)

2-Methoxy-2′-nitrobiphenyl is readily prepared in good yield either by a mixed Ullmann reaction[7] or by the decarboxylation of *o*-nitrobenzoic acid with Cu_2O in the presence of *o*-iodoanisole.[8] Reduction of the nitro-compound with hydrazine hydrate in the presence of palladium[9] gave 2-amino-2′-methoxybiphenyl in almost quantitative yield. Conversion into the diazonium salt (**1**) with sodium nitrite in the presence of aqueous fluoroboric acid was achieved in 85% yield. The yellow diazonium salt could be stored *in vacuo* for several days over phosphoric anhydride.

When the dry diazonium salt (**1**) was heated in anhydrous benzene the colour was rapidly discharged and an unstable off-white solid was obtained which was presumed to be the fluoroborate (**2**). The addition of excess of pyridine resulted in the formation of *N*-methylpyridinium fluoroborate (33%)† which was characterised as the double picrate.[10] The diazonium salt was virtually insoluble in chloroform but after 14 h at 35° a solution was obtained which showed an n.m.r. singlet at τ 5·4. The diazonium salt decomposes more readily when heated in CH_2Cl_2 and gave a quantitative yield of *N*-methylpyridinium fluoroborate when the decomposition was carried out in the presence of pyridine. Similarly *NN*-dimethyl-1-naphthylamine gave *NNN*-trimethyl-1-naphthylammonium fluoroborate[4a] in quantitative yield; benzo[*b*]thiophen gave *S*-methylbenzo[*b*]thiophenium fluoroborate[11] (55%); dimethyl sulphoxide gave the *O*-methylated salt[12] (75%); tetrahydrofuran gave methyltetrahydrofuranium fluoroborate[13] (75%); and benzonitrile gave the nitrilium salt[14] which was characterised as *N*-methylbenzamide (70%).

Pentachloropyridine might be expected to be methylated only with difficulty. However, *N*-methylpentachloropyridinium fluoroborate was isolated in 32% yield. The

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† The yields reported are based on the amount of the diazonium salt taken and not, as is more usual, using an excess of the alkylating agent. Dibenzofuran was also isolated in almost quantitative yield in each reaction.

alkylation of anisole has not been achieved using methyl fluorosulphonate.[15] We have found that when the diazonium salt (**1**) was decomposed in the presence of phenetole evidence for *O*-alkylation was obtained by the detection of anisole after quenching the reaction mixture with water.

(*Received*, 14*th January* 1972; *Com.* 058.)

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