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REARRANGEMENTS OF 1,5,8-TRIMETHOXYBENZOBARRELENE IN ACIDIC MEDIA - A RETRO FRIEDEL-CRAFTS ALKYLATION AND AROMATISATION

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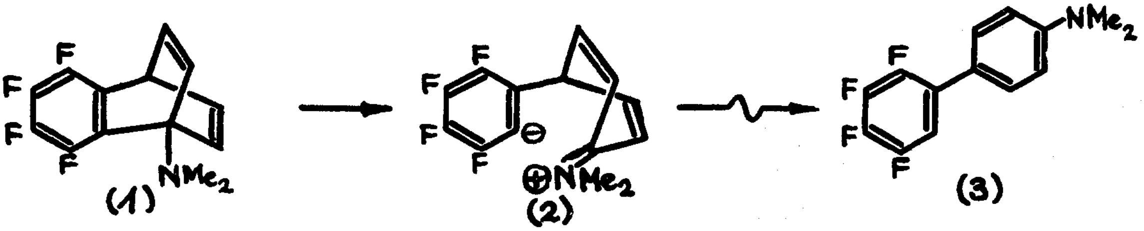
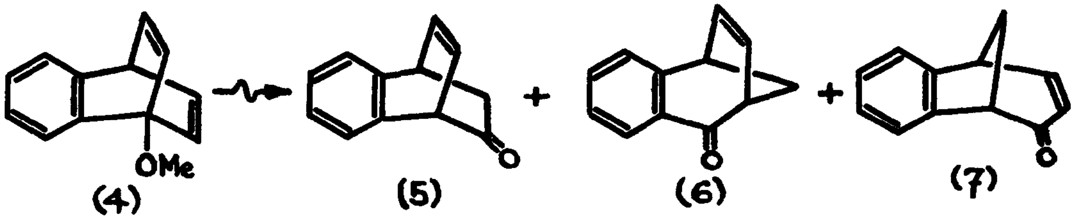
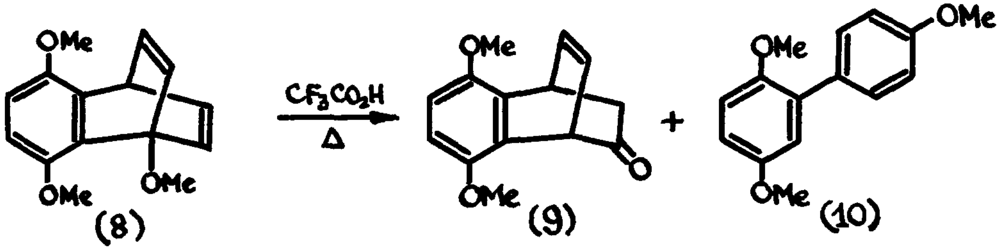
Previous investigations of rearrangements of 1-substituted-benzobarrelene derivatives have shown that control of the various pathways operating depended on precise structural features. Thus the rearrangement of 1-N,N-dimethylamino-tetrafluorobenzobarrelene (1) afforded 2,3,4,5-tetrafluoro-4'-N,N-dimethylaminobiphenyl (3) following protonation of the betaine (2).[1] On the other hand the rearrangement of 1-methoxybenzobarrelene (4) only proceeds in strongly acidic media to afford products (5), (6), and (7) which are derived by initial protonation of an olefinic residue.[2] In our search for the opposite end of the mechanistic spectrum we argued that the presence of correctly positioned electron releasing substituents would lead to ipso protonation and so to the possibility of a retro-Friedel-Crafts alkylation followed by aromatisation.



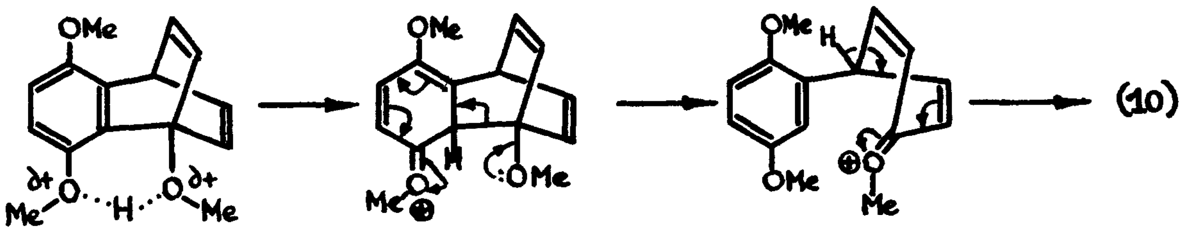


The availability of 3,6-dimethoxyanthranilic acid[3] and hence the title compound[4] from the reaction of 3,6-dimethoxybenzyne with anisole allowed us to investigate this possibility. Although ipso protonation of a polyalkyl benzene (except hexamethylbenzene) has not been established,[5] even in superacid media, the transalkylation of alkylbenzenes in the presence of Friedel-Crafts catalysts is well known[6] and requires electrophilic attack at an ipso position.

A solution of the title compound (8), when heated under reflux in trifluoro-acetic acid for 2 h. was converted cleanly into a mixture of two major products. These were shown to be the ketone (9), the analogue of (5), and 2,4',5-trimethoxybiphenyl (10) which were isolated in 36 and 34% yields respectively. The structure of the biphenyl (10) was confirmed by a Gomberg-Bachman-Hey synthesis (5.5%) using 1,4-dimethoxybenzene and 4-amino-anisole. The very low yield in this reaction was undoubtedly due to our inability to use 1,4-dimethoxybenzene as a solvent in this reaction.



The isolation of the compound (9) is unexceptional except for the fact that the compound (4) only undergoes rearrangement under more forcing conditions. A mechanism which accounts for the formation of the biphenyl (10) is shown in the Scheme.



SCHEME

Thus the two possible extremes of fragmentation pathways are observed in the reactions of 1-substituted-benzobarrelene derivatives.

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References and footnotes

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