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THE DEDIAZOTIZATION OF 2-ETHYLBIPHENYL-2'-YL DIAZONIUM CHLORIDE: AN UNEXPECTED CONTRIBUTION TO THE MECHANISM OF THE MASCARELLI REACTION.[1)]

Rainer W. Stumpe

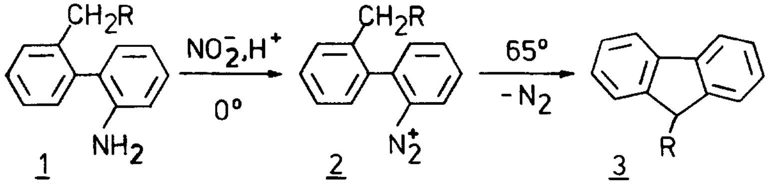
University of Siegen, Organic Chemistry, D-5900 Siegen 21, West Germany[2)]

Summary: A product was isolated after dediazotization of the title compound, implying the formation of a benzylic cation from the initially formed 2-alkylbiphenyl-2'-yl enium ion.

Over 40 years ago, Mascarelli and co-workers[3)] discovered the formation of fluorene derivatives from dediazotization of 2-alkylbiphenyl-2'-yl diazonium salts (Scheme 1). While the involvement of arene carbonium ions during the dediazotization of aromatic diazonium salts is well established,[4)] several different explanations of its course in the Mascarelli reaction were published: The first proposition was a [1,5]-hydride shift from the α-position followed by an electrophilic attack by the benzylic cation to the neighboring phenyl ring,[5)] the second involved a dipolar structure,[6)] and finally a penta-co-ordinate carbo-cation was envisaged.[7)] Here an observation is reported, which is only explained by the formation of a benzylic cation species during the Mascarelli reaction.

Scheme 1:

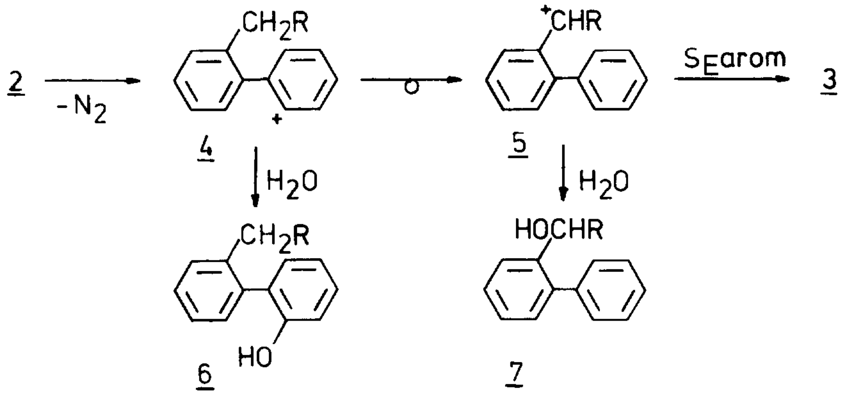
a: R = H
b: R = CH_3



To prepare 2-ethyl-2'-hydroxybiphenyl (6b), the reaction sequence given by Mascarelli[8)] was carried out and that compound, which Mascarelli believed to be the phenol 6b, was isolated (8% yield[9)]). While the physical properties matched those originally[8)] given, the spectra (mass, NMR) proved it to be 1-(biphenyl-2-yl)ethanol (7b). The desired phenol 6b was extracted from the reaction mixture with Claisen's alkali[10)] (30% yield[9)]); Mascarelli obviously discarded that compound. 9-Methylfluorene (3b) was obtained in 23% yield.[9)]

The formation of a benzyl alcohol derivative 7 from the Mascarelli reaction has never been described, and can not be rationalized by one of the other[6,7)] mechanistic propositions. It can, however, easily be interpreted as the hydration product of a benzylic cation 5, which also forms fluorene 3 via electrophilic substitution of the neighboring phenyl ring (Scheme 2). Obviously the route from arene carbonium ion 4 to benzyl cation 5 involves a [1,5]-hydride shift.[5)]

Scheme 2:



a: R = H
b: R = CH_3

It is also well established that cation 5b is more stable than cation 5a, involved in all previous studies.[6,7] Thus one might argue, there are different mechanisms operative in the Mascarelli reaction, depending on the stability of the intermediate cation 5. To disprove this assumption, the dediazotization of 1a[11] was also reexamined. The benzyl alcohol 7a was formed, but only in trace quantities, as was expected because of the lower stability of the cation 5a. The structure was confirmed by co-chromatography with an authentic sample and by comparison of GC-MS- and ^{1}H-NMR-spectra.

More experiments with labelled compounds and further stabilized cations are under investigation.

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2) Temporary address: The Ohio State Univ., Chem. Dept., Columbus, Ohio 43210

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