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THE ACID CATALYZED STIEGLITZ-SCHMIDT REARRANGEMENT OF N-BENZHYDRILIDENE AZIDOBENZHYDRYLAMINE

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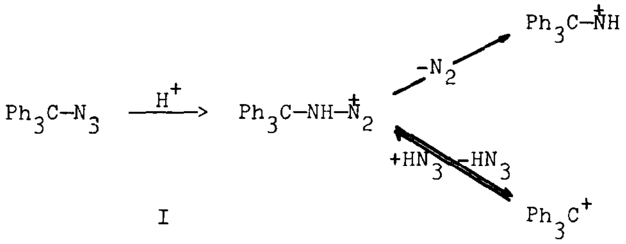
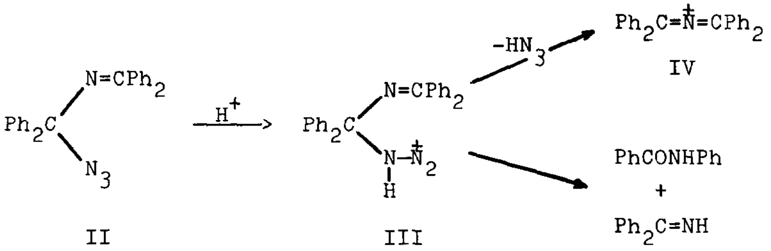
Triarylmethyl azides of type I are remarkably resistant to the acid-catalyzed Stieglitz rearrangement (Schmidt conditions).[1,2] The preferential cleavage of the C–N rather than the N–N bond has been ascribed[2e] to the stability of the resulting trityl carbonium ion. This, in fact, allows these azides to be prepared from the carbonium ions and hydrazoic acid.[2] However, the expected rearrangement does occur in related aryl substituted methylazides which incorporate structural and electronic features not present in I. For example, whereas 9-azido-9-phenylthiaxanthene failed to rearrange, 9-hydroxy-9-phenylthiaxanthene-10,10-dioxide reacted readily with hydrazoic acid in the presence of acid to give the expected rearranged product in high yields.[2e] Relief of strain and aromatization may also provide the driving force for the rearrangement as evidenced by the conversion of 9-hydroxy-9-phenylfluorene to 9-phenylphenanthridine.[3]



I

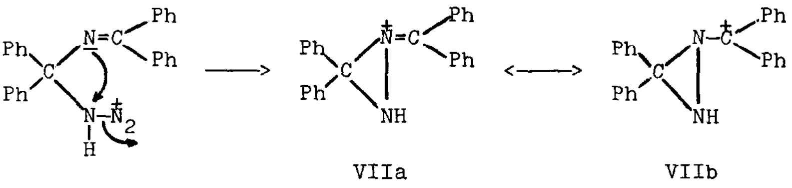
We have recently reported on the thermal and photolytic decomposition of N-benzhydrylidene azidobenzhydrylamine(II);[4] it was of interest to investigate its behavior under the conditions of the Stieglitz-Schmidt reaction. On the basis of the results described above and the rapid hydrolysis of II under extremely mild conditions,[5] it was anticipated that the C–N bond would cleave to give products of hydrolysis; the stability of the salts of the azaallylic ion (IV),[6,7] the presumed intermediate of the C–N cleavage process, further supported this expectation.

However, when II was treated with trifluoracetic acid at room temperature for two hrs, gas evolution was observed; benzanilide (79%) and benzophenone imine (65%) contaminated with traces of benzophenone, were isolated. Similar results were obtained with conc. sulfuric acid at room temperature. With aluminum chloride and gaseous hydrogen chloride, the reaction took place at -30°. Presumably, benzanilide was formed via the Stieglitz-Schmidt rearrangement.[8] As in the thermal and photolytic decomposition reported earlier,[4]

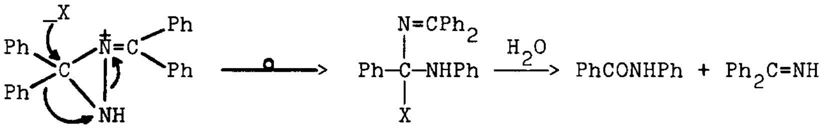


benzophenone azine (V) could not be detected as a reaction product; control experiments showed that both V and N-phenyl-N'-benzhydrylidene benzamidine (VI)[4,9] were stable to the conditions of the reaction.

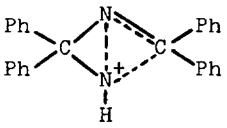
The explanation for the unexpected rearrangement of II, though of necessity involving the $Ph_2C=N$ group, is not readily apparent. We would like to suggest, however, that the imino nitrogen is close enough to the protonated nitrogen atom of the azide to provide anchimeric assistance for the expulsion of nitrogen; furthermore, the π electron system of the benzhydrylidene amino group may provide additional stabilization for the incipient nitrenium ion via the formation of the diaziridinium ion.



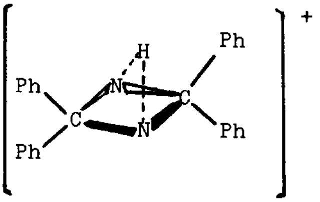
Since it was found that VI is stable to the reaction conditions (see above), it is likely that the migration of the phenyl group in VII is further assisted by concomitant attack of the gegen-ion at the carbon atom. Hydrolysis of this intermediate would then lead to the observed products. The



question as to the participation of non-classical ions such as VIII and IX must await further experimental work.



VIII



IX

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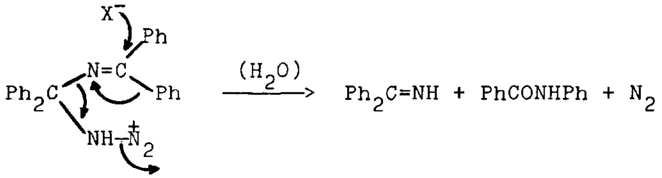
8. Although a Beckmann-like fragmentation shown below could also account for the formation of the observed products, we favor the mechanism involving anchimeric assistance of the imino group.



9. Compound VI is the product of the thermal and photo-induced Stieglitz rearrangement of II.