The Decomposition of Azibenzil, PhC(N_2)COPh, by Catalytic Amounts of Carbanions or of Sodium Borohydride: Evidence for a Hydride-ion Transfer Chain Reaction

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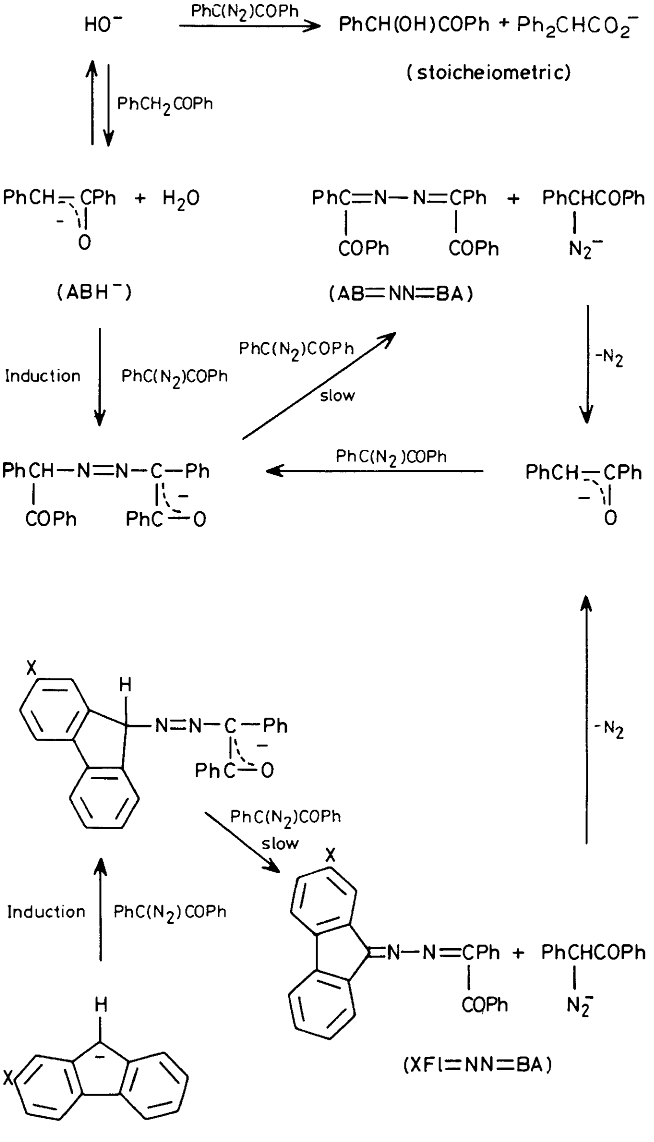
Evidence is presented that the conversion of azibenzil, PhC(N_2)COPh, into benzil azine induced by catalytic quantities of carbanions or of $NaBH_4$ in Me_2SO or MeCN involves a novel hydride-ion transfer chain mechanism.

Cyclic voltammetric studies of the cathodic reduction of azibenzil, PhC(N_2)COPh (ABN_2), in MeCN–Et_4NBF_4 have shown that the initially formed anion radical $ABN_2^{\cdot-}$ undergoes a rapid first order reaction not involving the solvent and gives rise to the carbanion $Ph\bar{C}HCOPh$ (ABH^-) as the only detectable product.[1] However, constant current electrolysis of ABN_2 (0.01—0.05 M) at a Pt cathode at low current densities yielded the carbanion (estimated as $PhCH_2COPh$) and benzil azine PhCOC(Ph)=NN=C(Ph)COPh (AB=NN=BA) in comparable yields in a process that showed the characteristics of an electrochemically induced chain process.[2] Addition of phenyl t-butyl nitrone had no effect on the chain process once initiated, suggesting a non-radical pathway, and indeed decomposition of ABN_2 can be induced by catalytic quantities of ABH^- or other carbanions generated by essentially complete conversion of the parent carbon acid using Et_4NOH in Me_2SO containing 2% (v/v) H_2O under an atmosphere of purified nitrogen. Thus, ABN_2 (0.05 M) in the presence of ABH_2 (5×10^{-3} M) and Et_4NOH (0.01 M) yielded the azine in 95% yield with total recovery of ABH_2. Under the same conditions a series of 2-substituted fluorenes $XFlH_2$ gave AB=NN=BA (74—81% yield), ABH_2 (8—10%) together with the mixed azine XFl=NN=BA (6—10%). Carbon acids having only one acidic hydrogen (*e.g.*, 9-phenylfluorene, phenylacetylene) also promoted the decomposition but reactions were in general much slower and incomplete. In the absence of a carbon acid, ABN_2 and Et_4NOH led to nitrogen evolution which was quite rapid initially but ceased when a roughly stoicheiometric amount had been liberated; reaction products were azine, benzoin, and diphenylacetate ion as previously reported.[3]

The kinetics of the reaction between ABH^- and ABN_2 were followed using a pressure transducer to monitor the evolution of nitrogen. With a small excess of Et_4NOH over ABH_2, the pressure–time curve was sigmoid, showing a short induction period followed by a rapid pressure increase, the rate decaying according to a first-order kinetic law. At higher hydroxide excesses the induction period was overlaid by the nitrogen evolution resulting from the stoicheiometric reaction. Based on the pressure–time curve after *ca.* 20% decomposition, it was established that the rate of nitrogen evolution was given by $v = k_{ABH_2}[ABN_2][ABH_2]$ independent of the excess (2- to 5-fold) of Et_4NOH over ABH_2. Using Et_4NOD with ABD_2 in D_2O–$(CD_3)_2SO$, nitrogen evolution was very much slower and reaction of the diazoketone was incomplete. Since the stoicheiometric reaction of DO^- with ABN_2 appears to be only slightly accelerated compared with that of HO^-, a substantial kinetic isotope effect on the carbanion induced reaction is indicated.

We believe that the mechanism in Scheme 1 is consistent with our observations. Hydride-ion transfer from the adduct of ABN_2 and the carbanion to a further ABN_2 molecule is the slow step in each cycle of the mechanism. In this mechanism hydride ion functions in an analogous fashion to the proton in acid-catalysed reactions. To the best of our knowledge this constitutes the first demonstration of such hydride-ion transfer catalysis in organic systems.



Scheme 1

Support for our interpretation comes from our observation that ABN_2 undergoes conversion into azine (plus a little hydrazone, $ABNNH_2$) by treatment with a catalytic amount of $NaBH_4$ in dry Me_2SO or 2% aqueous MeCN. Pressure–time curves for such reactions are again sigmoid and the rate of nitrogen evolution in the later stages of reaction fits the equation $v = k_{NaBH_4}[ABN_2][NaBH_4]$ with k_{NaBH_4} *ca.* = $0.6k_{ABH_2}$. We believe that we are observing the same chain-propagating reaction, $NaBH_4$ generating ABH^- by hydride transfer to the diazo-carbon of ABN_2 followed by loss of nitrogen. The rate discrepancy is attributable to different efficiencies of generating ABH^- in the two systems. By using $NaBD_4$ (98% D) in $(CD_3)_2SO$, the observed value of k_{NaBH_4}/k_{NaBD_4} was 2.1 at 30 °C indicating a value of about 2.3 after correction for isotopic purity.

Similar experiments on 9-diazofluorene (FlN_2) are underway, but the situation there seems more complex than for ABN_2. FlN_2 is converted by $NaBH_4$ into its azine (plus hydrazone) in high yield and the reaction shows a kinetic form similar to the ABN_2 reaction, but with an apparent isotope effect of only 1.3. However, Et_4NOH in $Me_2SO–H_2O$ or $MeCN–H_2O$ gives a more rapid reaction forming azine quantitatively and showing a similar small kinetic isotope effect in a perdeuteriated solvent. Added carbon acids have no detectable effect on the rate or products.[4] Since reaction mixtures exhibit strong (though unresolvable) e.s.r. signals, we incline to the view that, in the presence of HO^-, FlN_2 decomposes by an ion-radical chain mechanism (ETC catalysis)[5] analogous to that induced electrochemically[6] for which the apparent solvent isotope effect on the propagation step is 1.2.[2] The mechanism of initiation of this chain reaction is still under investigation.

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