

REACTION OF 1-PHENYLDIAZOETHANE WITH TETRACHLORO-*p*- AND *o*-BENZOQUINONES

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Summary: Reaction of 1-phenyldiazoethane(1) with tetrachloro-*p*-benzoquinone(2) gave 1-alkoxy-4-ethenyloxy-tetrachlorobenzene(4). With tetrachloro-*o*-benzoquinone(5), 1 provided 1-alkoxy-2-ethenyloxy-tetrachlorobenzene(7) and tetrachlorobenzo-1,3-dioxolane(8). The mechanism and the effect of added methanol were discussed.

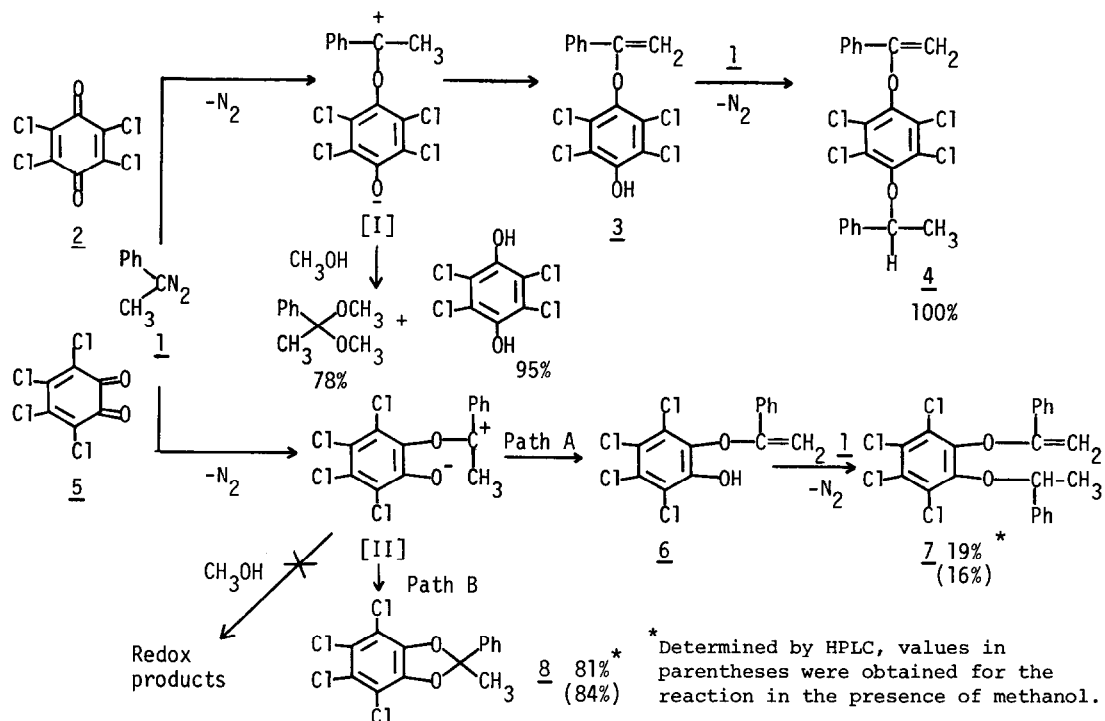
As one area of chemistry of diazoalkanes, much attention is paid for the reactions with quinones from the synthetic and mechanistic point of view.¹ A number of reports are concerned with the reaction of diazomethane because of its high reactivity. Diazomethane adds to the conjugated C=C bonds of 1,4-benzoquinone² and its di-,³ and trihalogenated derivatives⁴ to yield pyrazolines. While, the C=O bonds become active when the inherently reactive C=C bonds are completely blocked with the bulky halogens as exemplified in the formation of oxirane in the reaction with tetrachloro-*p*-benzoquinone(2).⁵

Recently, we have found that the higher diazomethane derivatives such as phenyl- and diphenyldiazomethanes react to the C=O bond of 2 but give stilbenes and spirooxetanes,⁶ and poly(tetrachlorohydroquinone benzhydrylether)s,⁷ respectively. The marked product changes depending on the structures of diazoalkanes prompted us to investigate the reactivity of 1-phenyldiazoethane(1) because this diazoalkane is sterically located between the above diazomethane derivatives.

Reaction of 3 eq. excess 1 with 2 in benzene at 25°C for 6h yielded quantitatively 1-alkoxy-4-ethenyloxy-tetrachlorobenzene(4). Whereas, equimolar 1 gave 4-ethenyloxy-tetrachlorophenol(3, 69%), which was transformed into 4 by treatment with 1 (Scheme). These chemical findings confirm the reaction sequence as the formation of 1:1 betaine intermediate(I), the following proton migration, and the etherification of the resulting 3 with 1. In harmony with this mechanism, added CH₃OH(10 eq) collapsed the betaine intermediate to afford acetophenone dimethyl acetal and tetrachlorohydroquinone as the redox products.

On the other hand, tetrachloro-*o*-benzoquinone(5) is known to provide only

one type of products, tetrachlorobenzo-1,3-dioxolanes, in the reactions with diazomethane,⁸ phenyl-⁴ and diphenyldiazomethanes.⁹ However, reaction of 3 eq excess 1 with 5 in benzene at 25°C for 6h gave 1-alkoxy-2-ethenyloxy-tetrachlorobenzene(7) and the usual benzo-1,3-dioxolane(8) in the ratio of 1:4 (Scheme). Isolation of 7 supports that a key intermediate is also 1:1 betaine (II) which leads to 6 via proton migration(Path A) and 8 via intramolecular cyclization(Path B), respectively. Contrary to the case of 2, added CH₃OH(10 eq) did not participate in the reaction because of the preferential intramolecular processes.



References

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