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THE FORMATION OF DIAZOALKANES FROM
THE REACTION OF HYDRAZONE ANIONS
WITH p-TOLUENESULFONYL AZIDE

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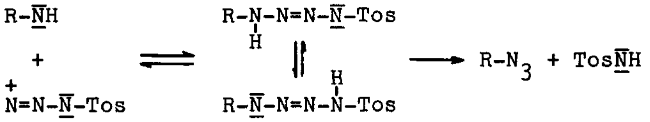
Recently, we reported the conversion of anions of primary amines to the corresponding azides *via* a *diazo* transfer reaction with p-toluenesulfonyl azide.[1] Our interest in the chemistry of N-azidamines prompted the application of this reaction to anions of hydrazones, which will be the subject of this communication.

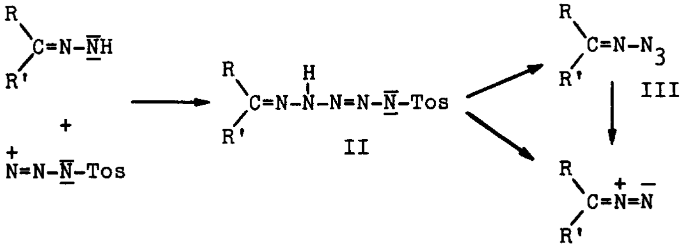


$$\begin{array}{c} R\text{-}\bar{N}H \\ + \\ \overset{+}{N}{=}N\text{-}\bar{N}\text{-}Tos \end{array} \rightleftharpoons \begin{array}{c} R\text{-}\underset{H}{N}\text{-}N{=}N\text{-}\bar{N}\text{-}Tos \\ \Updownarrow \\ R\text{-}\bar{N}\text{-}N{=}N\text{-}\overset{H}{N}\text{-}Tos \end{array} \longrightarrow R\text{-}N_3 + Tos\bar{N}H \qquad (1)$$

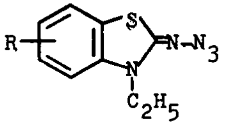
We had hoped that, under the present reaction conditions, the intermediate N-azidimines (III) would be stable enough to be detected.[2] However, the characteristic red color of diphenyldiazomethane appeared instantly upon the addition of a solution of tosyl azide to benzophenone hydrazone anion in tetrahydrofuran at room temperature. Copious evolution of gas was observed during the course of the reaction. Diphenyldiazomethane was characterized by comparison of its infrared spectrum with that of an authentic sample and by its conversion to benzhydryl 3,5-dinitrobenzoate, m.p. 141-142°, lit.[3] 142°. The yield of diphenyldiazomethane, determined from the weight of the ester formed, was 50%; p-toluenesulfonamide was isolated in 48% yield. Benzophenone hydrazone was recovered in 22% yield. Similarly, the corresponding diazoalkanes were formed from the anions of fluorenone, acetophenone and benzil hydrazones. All the reactions were performed in an atmosphere of nitrogen to exclude the oxidation of the hydrazone anions as a possible source of the diazoalkanes.[4]

$$\mathrm{RR'C{=}N{-}\overline{\underline{N}}{-}H + TosN_3 \longrightarrow RR'C{=}\overset{+}{N}{=}\overline{N}^{-} + N_2 + Tos\overline{\underline{N}}H} \quad (2)$$

The addition of tosyl azide to fluorenone hydrazone anion gave a precipitate, presumably the adduct (II). Diazofluorene was not generated until the mixture was poured into water. Although the formation of diazoalkanes seems to be instantaneous under the conditions used, it is not possible to rule out N-azidimines (III) as intermediates since, by operating at very low temperatures, Balli[2] was able to isolate compounds to type I. Thus, the reaction may proceed by either of the two paths shown (reaction 3). The loss of p-toluenesulfonamide anion would give III which could then lose nitrogen to give the diazo compounds. On the other hand, a concerted fragmentation of the adduct (II), perhaps via a cyclic mechanism,[1] would lead directly to the diazoalkanes.



(3)



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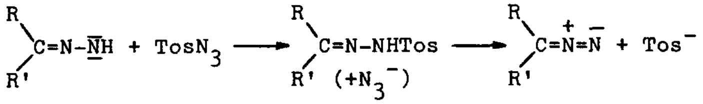
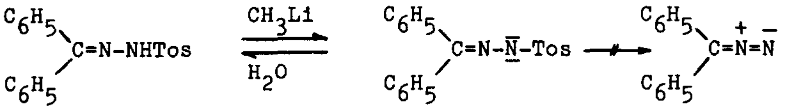
It could be argued that the formation of the diazoalkanes occurred via a Bamford-Stevens reaction[5] of the tosylhydrazones resulting from the tosylation of the hydrazone anions by tosyl azide (reaction 4). With methyllithium, benzophenone p-toluenesulfonylhydrazone in tetrahydrofuran gave a



(4)

yellow solution of the tosylhydrazone anion. However, upon addition of water, the color was discharged.



(5)

The reaction of hydrazone anions with p-toluenesulfonyl azide constitutes a novel entry into the formation of diazoalkanes. It may find use in cases where extremely mild and nonoxidizing conditions are required. Further investigations of this reaction are in progress in our laboratories.

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* To whom all correspondence should be sent.

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