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Preliminary communication

The π-orbital overlap requirement in 1,2-anionic rearrangements

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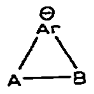
Our continuing interest in the mechanism of 1,2-anionic rearrangements★,★★ of aryl groups[1] has now focused on the geometrical requirements of the migrating group. Our migratory studies with the β,β-diphenyl-β-(2- and 4-pyridyl) ethyl systems and our preparation of model spiro intermediate (I, A = CH_2, B = CMe_2, Ar = *N*-Me-4-pyridyl)[1] supported the view that bridging structures, such as I, are intermediates, rather than transition states, in these rearrangements. We hoped to strengthen and generalize the force of this conclusion by attempting to distinguish between a bridging intermediate I and a cleavage-recombination pathway[2g] for the rearrangement itself (II)★★★.



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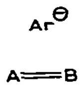

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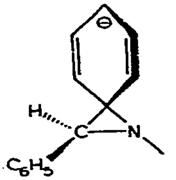

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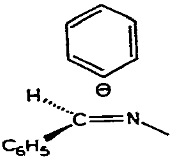


(VI)

In order to achieve this mechanistic distinction, we have examined the rearrangement tendencies of the benzylic anions obtained from benzyldiphenylamine (III) and *N*-benzylcarbazole (IV), respectively. We reasoned that if the rearrangement occurs via a cyclic intermediate I or V, then the plane of the phenyl group in the anion of III would have to be perpendicular with respect to the C–N bond axis, in order to enjoy maximum overlap between the anion orbital and the aromatic π*-orbitals. The inability of the aryl group in the anion of IV to attain such perpendicularity should therefore retard, or prevent altogether, the rearrangement. If, on the other hand, the reaction can occur via a cleavage-recombination pathway (II or VI), no such geometrical requirement could be involved and the anions of both III and IV should rearrange.

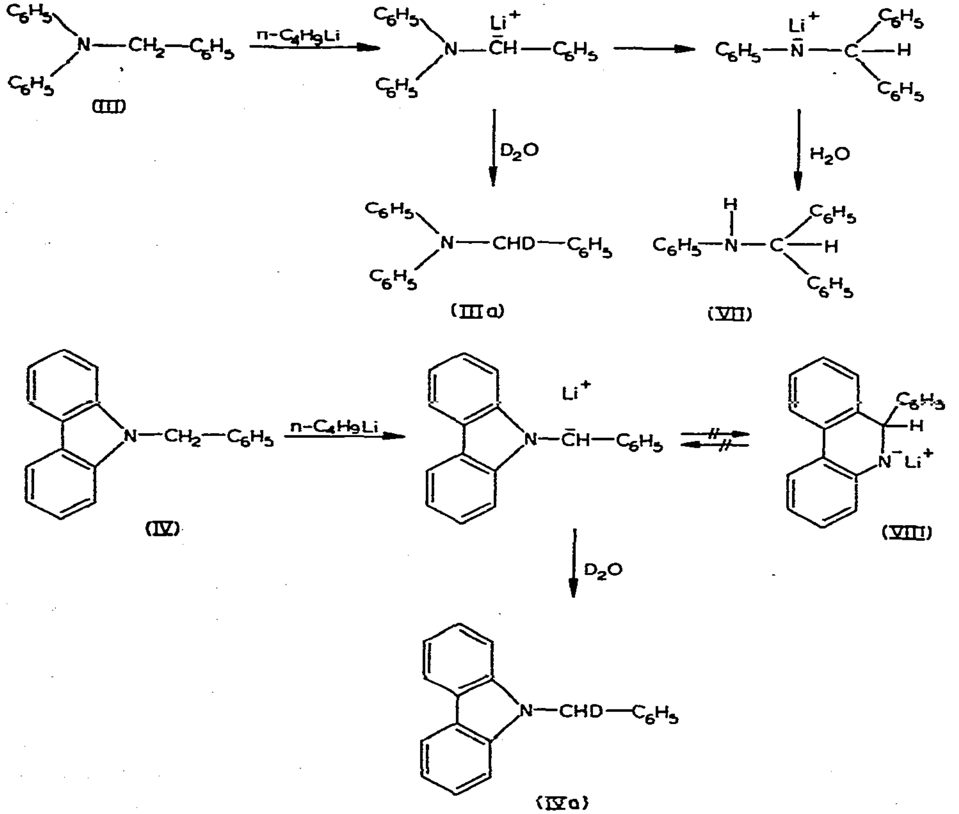
★ By an anionic rearrangement we mean one in which both the starting reagent and the final product are anions; our use of this term does not intend a judgment on the mechanism of the process, which may be anionic, radical-anionic or radical (*cf.* ref. 2f and 2g).

★★ For previous work on the intramolecularity of 1,2-aryl shifts in anionic rearrangements, *cf.* the studies of Zimmerman[2j] and of Grovenstein[2k].

★★★ Even in the Wittig rearrangement of aryl ethers, $RCH_2OC_6H_5$, nothing definite is known about the nature of aryl migration[2g].

Rather surprisingly, this nitrogen analog of the Wittig ether rearrangement has been little explored[2]. It differs from the Stevens rearrangement, in that it occurs with aryl migration as well and does not require a quaternary nitrogen. Stevens has heated benzylic tertiary amines with alkali metal amides or organometallic reagents in the temperature range, 140–200°, and obtained hydrocarbons assumed to be formed via such a rearrangement[3b] ★. Also, the rearrangement of two tertiary amine derivatives of 9-aminofluorene by agency of $LiAlH_4$ in tetrahydrofuran has been reported[4] ★.

We were gratified to find that treating III or IV with n-butyllithium in tetrahydrofuran solution caused the immediate formation of a dark red color. After stirring for one h at 25° the solution was quenched with D_2O (99.8%) and then worked up to yield recovered IIIa or IVa. By individual mass spectral analyses both IIIa and IVa were found to be ca. 90% monodeuterated and by NMR analysis principally deuterated on the methylene group★★ (Scheme 1). When a solution of anion IV was permitted to stand at 25° for up to 72 h before



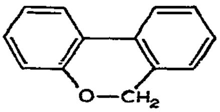
[★] The yields reported in ref. 3b are generally poor and the possible generation of carbenoids, via α-elimination rather than an actual amine rearrangement, was not ruled out, The structures of the rearranged secondary amines reported in ref. 4 were not definitely established nor was the yield stated. The present report appears, therefore, to be the first well-authenticated case of the nitrogen Wittig rearrangement.

[★★] Hauser and coworkers[5] reported that n-butyllithium metallates dialkylbenzylamines in the *ortho*-position; Gilman and coworkers[6] similarly found that *N*-ethylcarbazole undergoes metallation *ortho* to the nitrogen.

hydrolytic quenching, work-up showed that no rearrengement to the lithium salt of 6-phenyl-5,6-dihydrophenanthridine (VIII) had occurred. To rule out the possibility that the thermodynamic instability of VIII with respect to the anion of IV prevented the observation of a rearrangement, VIII was produced in an independent manner and examined. Thus, when VIII was generated quantitatively by the addition of phenyllithium to phenanthridine[7] in tetrahydrofuran solution and then allowed to stand for 60 h, only 6-phenyl-5,6-dihydrophenanthridine, free of IV, was obtained upon hydrolysis.

However, after the anion of III was allowed to stand at 25°, hydrolytic work-up revealed that benzyldiphenylamine had been almost completely converted into benzhydrylaniline (VII, $>$ 75% by NMR analysis). Isolated and purified, VII was identified by comparison with an authentic sample. In order to test for the reversibility of the rearrangement, pure VII was treated with n-butyllithium and then hydrolyzed after 24 h. Since no III was detected upon hydrolysis, the rearrangement appears to be irreversible (Scheme 1).

These findings offer strong support for a cyclic intermediate pathway (I and V) for aryl migration in this nitrogen Wittig rearrangement, over the cleavage-recombination alternative (II and VI). Furthermore, it provides a valuable experimental model for assessing the π-orbital overlap requirements for many allied 1,2-anionic, cationic and radical rearrangements. Specifically, we are pursuing the overlap requirements of the Wittig ether rearrangement itself by examining the behavior of IX and we aspire to assess the minimum overlap necessary by studying the rearrangement tendencies of X, where n = 1,2,3, etc.



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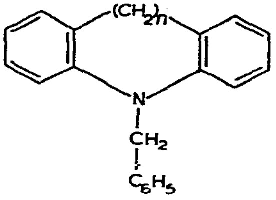

(X)

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