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ALLYLIC SUCCINIMIDATION
OF
N-BENZHYDRYL DIPHENYLKETIMINE

K. Sakai, N. Koga and J.-P. Anselme*

Department of Chemistry
University of Massachusetts
Boston, Massachusetts 02116

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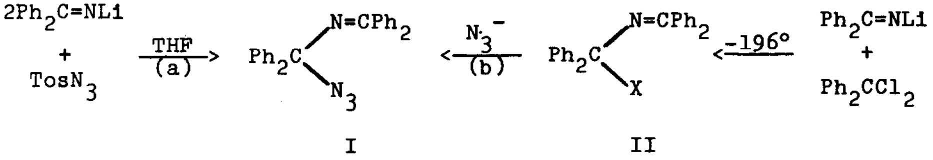
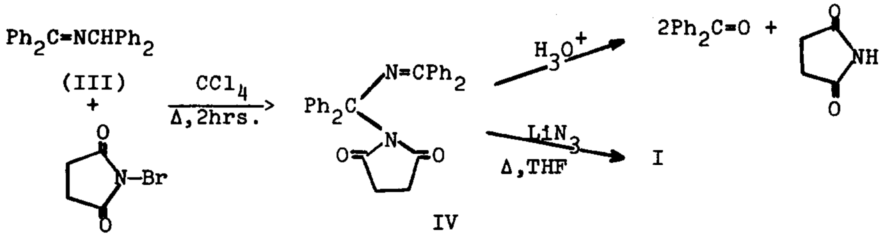
The synthesis of N-benzhydrylidene azidobenzhydrylamine (I)[1] is inherently limited to the symmetrically substituted products (reaction 1a). Our investigation of the chemistry and reactions [2,3] of I required a more flexible and hopefully more general route to this type of compounds.



(1)

N-Benzhydrylidene chlorobenzhydrylamine (IIa, X=Cl) a potential precursor of I, has been obtained from the reaction of lithium diphenylketimine with diphenyldichloromethane at -196° in unstated yields.[4,5] The complexity of the procedure coupled with the need for a convenient and readily available precursor of I prompted the search for an alternate synthesis.

It was felt that the bromo analogue, N-benzhydrylidene bromobenzhydrylamine (IIb, X=Br) could be prepared directly by the allylic bromination of N-benzhydryl diphenylketimine(III)[6] with N-bromosuccinimide. When III was heated under reflux with an equimolar amount of N-bromosuccinimide in carbon tetrachloride for 2 hrs., a moisture sensitive solid was obtained. Two crystallizations from benzene gave colorless crystals, mp. 176-178° (very faint Beilstein test). The compound was too sensitive for the preparation of an analytical sample. Attempted crystallization of the 176-178° sample from benzene gave succinimide and bis-diphenylketimino diphenylmethane.[5] However, the infrared spectrum which had absorptions at ~ 1780 and 1735 (with shoulder [C=O] and 1645 cm^{-1} [>C=N-] in addition to the expected aromatic bands, clearly indicated that the succinimyl moiety was present and that the >C=N- had been retained. This, coupled with the results of the acid catalyzed hydrolysis of the compound to benzophenone and succinimide,[7] suggested that it was N-benzhydrylidene succinimidobenzhydrylamine(IV). Further support for this assignment was provided by the reaction of crude IV with lithium azide

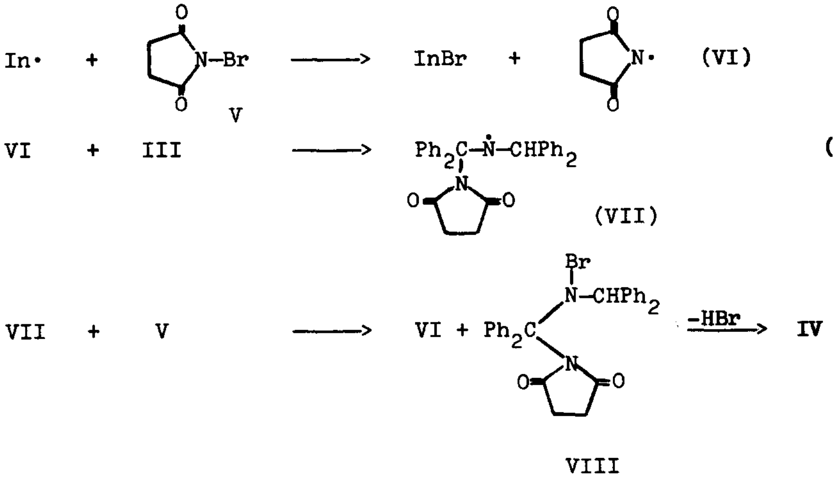


(2)

to give a 40% yield of I.

The substitution of the succinimido group at the allylic position is unprecedented as far as we are aware. It is difficult to rationalize this result in terms of the Bloomfield or the Goldfinger mechanisms.[8,9] The former ascribes to the succinimidyl radical the role of hydrogen abstractor whereas the succinimidyl radical is not at all involved in the Goldfinger mechanism. Since N-bromosuccinimide (NBS) has been reported to undergo ionic reactions, the reaction of NBS with III was carried out in the presence of a catalytic amount of azo-bis-isobutyronitrile (ABIN). The dramatic increase in the yield of the IV (as determined by the 91% yield of I) strongly suggests a radical reaction.

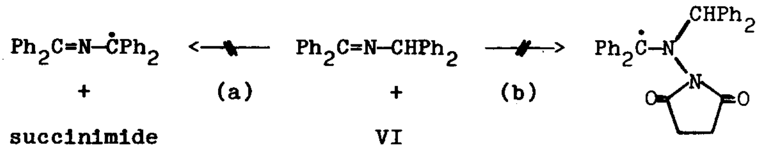
Recent results[8] have tended to favor the Goldfinger mechanism which essentially assigns to NBS the role of a low, constant source of molecular bromine. However, the participation of the succinimidyl radical has been proposed in certain reactions.[10,11] We would like to suggest that in our case, the succinimidyl radical (VI) attacks the carbon of the imine group to yield the radical VII which rapidly abstracts a bromine atom from NBS to regenerate VI and to give the N-bromoamine (VIII). Elimination of hydrogen bromide from VIII finally leads to IV.



(3)

The addition of the bromo and succinimido moieties to >C=C<, has been reported previously.[8,11] A more closely related example of the addition-elimination process postulated above, has been suggested by Schmid and Leutenegger[12] to explain the formation of 9-succinimido acridine from the reaction of acridine with NBS. However, in none of these reports[11,12] was any positive suggestion made as to the detailed steps of the addition.

Besides the unusual course of our reaction itself, there are two points which deserve comments. The first is the generation of hydrogen bromide in the last step of the reaction. If this is indeed true as it appears to be,. then it becomes apparent that the "radical reactions" of NBS (with In• and VII) must be very much faster than its interaction with hydrogen bromide to give bromine (Goldfinger mechanism[8]). Secondly, it may be wondered why the succinimidyl radical adds at the carbon atom of the imino group (to give the non-stabilized nitrogen radical VII) instead of adding at the nitrogen atom or abstracting the allylic hydrogen (Bloomfield mechanism). The formation of VII is probably the result of steric and electronic factors. Indeed, not only is attack at nitrogen (reaction 4b) inherently unfavorable because of coulombic repulsion between the two nitrogens but also the N–N bond which would result, is weaker than the C–N bond (attack at C) by ∿ 30 kcal/mole.



(4)

Removal of the allylic proton (reaction 4a) to give the azallylic radical would require attack of the succinimidyl radical at a very sterically hindered center.

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*Fellow of the Alfred P. Sloan Foundation. To whom inquiries are to be directed.

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