Tetrahedron Letters No. 20, pp 1647 - 1650, 1976. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS AND THE ANTIAROMATIC CHARACTER OF DIBENZ[b,f,1]AZAPENTALENES[1]

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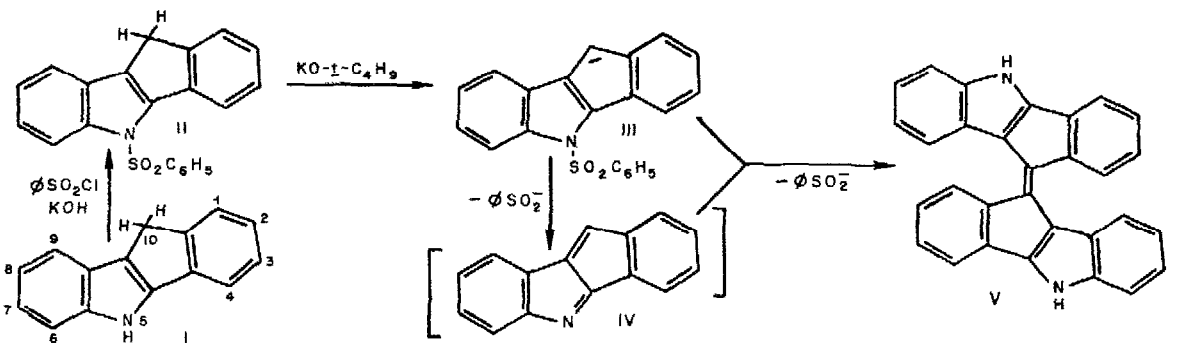
(Received in USA 7 November 1975, received in UK for publication 5 April 1976)

By displaying the variegated chemical and physical consequences of cyclic conjugation, unsaturated heterocyclic compounds have proved invaluable in developing the concept of aromaticity. Indeed, considerable attention recently has been given to exploring the implications of the converse concept, antiaromaticity,[2] for the synthesis and reactivity of heterocyclic counterparts of carbocyclic systems. Syntheses of the nitrogen analogues of the known, but unstable pentalene nucleus[3] have been motivated by the desire to see whether the properties of such azapentalenes depend on the position of the nitrogen atom.[4] By recourse to electron-donating substituents, which stabilize even the parent pentalenes,[3] 2-azapentalenes[4,5] and quaternary salts of 3a-azapentalenes[6] have now been prepared. But claims for the synthesis of benz- or dibenz-azapentalenes[7,8,9] have either been discredited[8,10] or rest on inadequate evidence.[11] In view of this, we wish to report the first synthesis of the dibenz[b,f,1]azapentalene nucleus and to present evidence concerning its antiaromatic character.

Since attempts to obtain benz[b,1]azapentalene by the dehydrogenation of 2,3-dihydrocyclopent[b]indole did not yield monomeric products,[8,10] such dehydrogenations were applied to 5,10-dihydrodibenz[b,f,1]azapentalenes in hopes of obtaining a more stable azapentalene.

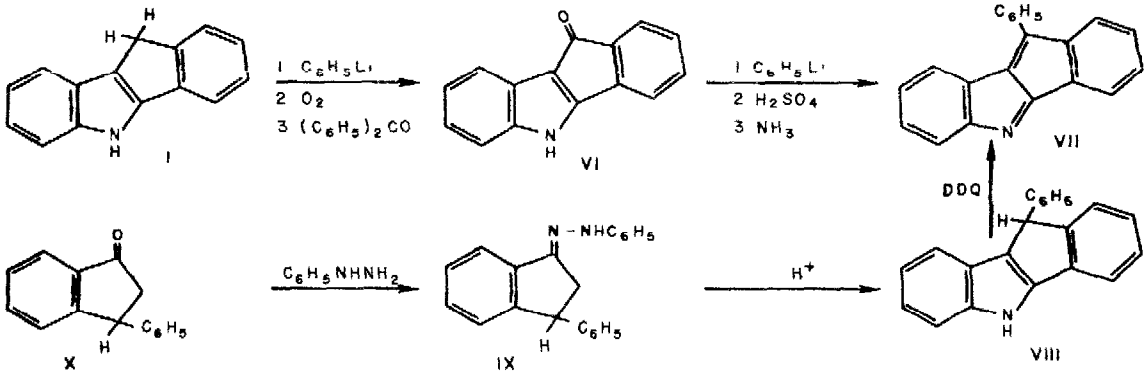
SCHEME I



But attempts to dehydrogenate I with DDQ or by a combination of N-benzenesulfonylation (I → II) and elimination (II → IV) gave only dimeric products, the product from II (100% yield) was a deep purple solid, (m.p. 220°, dec., ir· 3400 cm^{-1} (N-H), nmr (DMSO-d_6) 6.65-7.99 ppm (m, TMS); ms at 70 eV mass (relative abundance). 407 (54), 406 (P, 90), 404 (41), 203 (52) and 202 (100)), whose properties are in accord with the structure of bi(5,10-dihydrodibenz[b,f,1]azapentalen-10-ylidene) (V). The attack of the carbanion III at C_{10} of the intermediate IV, followed by prototropic shifts and the expulsion of the $C_6H_5SO_2$ anion would be a reasonable route to V (Scheme I).

The blocking of the C_{10} position, however, did permit the isolation of a monomeric dibenzazapentalene. Thus, the 10-phenyl derivative (VII) was prepared by two different routes· either by the DDQ dehydrogenation of VIII (ca. 100% yield) or by the addition of phenyllithium to ketone VI (55% yield) and subsequent dehydration. For the first approach, precursor VIII (m.p. 228-230°) was obtained in 60% yield by the Fischer indole cyclization of the phenylhydrazone (IX) of 3-phenyl-1-indanone (X).[12] In the second method, the indeno-indole (I) was converted into its blood-red dianion (10 pi-electrons) by phenyllithium, treated with oxygen to generate a 10-hydroxylate group and then allowed to transfer hydride ion to benzophenone. The resulting bright-red ketone VI, although formed in modest yield, was difficult to obtain by any conventional approach[13] (m.p. 333-336°, ir 3300 (N-H), 1657 (C=O) and 736 cm^{-1} (ortho C_6H_4); nmr (DMSO-d_6) 7.0-7.85 ppm (m, TMS), ms at 70 eV 220 (21), 219 (100), and 190 (31)) (Scheme 2).

SCHEME 2

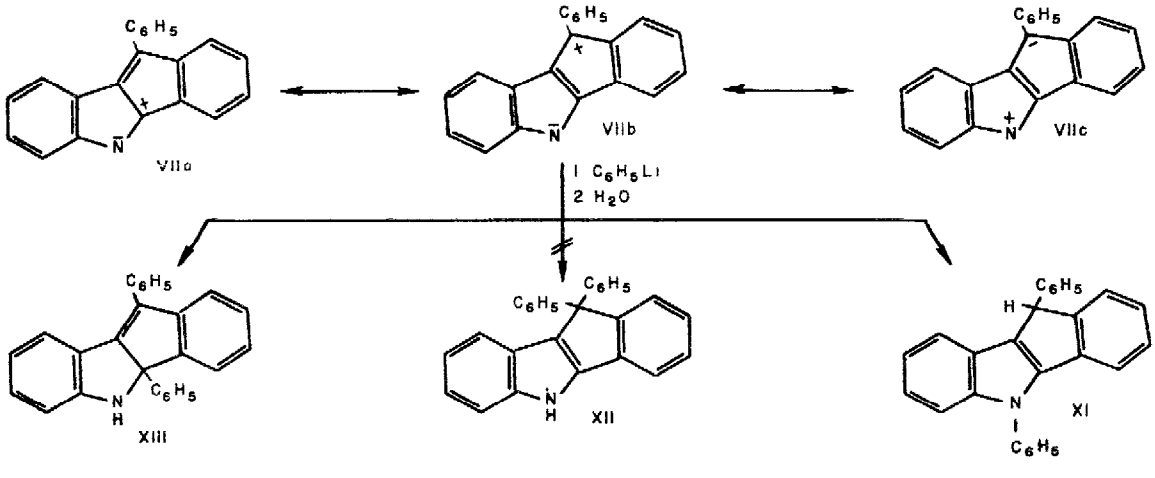


The phenyldibenz[b,f,1]azapentalene (VII), as obtained from either procedure, possessed identical properties. golden-brown solid, m.p. 160-161°, ir 1610, 1560, 1225 and 755 cm^{-1}; nmr ($CDCl_3$) 6.55-8.17 ppm (m, TMS), ms at 70 eV 280 (18), 279 (100). With an azapentalene system in hand, it was of interest to learn what influence the azapentalene delocalization would exert on the polarity of the carbon-nitrogen bond (VIIa-VIIc). To this end, VII was treated with an excess of phenyllithium in ethyl ether. After hydrolysis and column chromatographic separation on silica gel, two pure products were obtained in a 1 1 ratio and total yield of 66%. These derivatives were shown by elemental and mass spectral analysis to be

isomers of diphenyldihydrodibenzazapentalene 1) compound XI, colorless solid, m.p. 192-193°, ir 1597, 1507, 748, 724 and 700 cm^{-1}, nmr ($CDCl_3$) 4.95 (s, 1H) and 6.68-7.58 ppm (m, 18H); ms at 70 eV· 357 (100), 356 (33) and 280 (22), and 2) compound XIII, deep yellow solid, m.p. 184-185°, ir 3385 (N-H), 1600, 757, 747, 706 and 695 cm^{-1}, nmr ($CDCl_3$) 6.12-8.0 ppm (m), ms at 70 eV 357 (80), 356 (12) and 280 (100). Compounds XI and XIII were treated individually with phenyllithium and shown not to interconvert. Moreover, the geminal diphenyl isomer XII (m.p. 258-259°) was synthesized independently from the Fischer indole reaction on the phenylhydrazone of 3,3-diphenyl-1-indanone[12] and by tlc examination was ruled out as a product of the reaction of VII with phenyllithium. Accordingly, by spectral data the phenylation products, XI and XIII, can be assigned the structures of 5,10-diphenyl-5,10-dihydrodibenz[b,f,1]azapentalene and 4b,5-diphenyl-4b,5-dihydrodibenz[b,f,1]azapentalene, respectively. Phenylation of VII on either of the benzenoid rings would yield products displaying both N-H and saturated C-H spectral absorptions.

The previously reported additions of organolithium reagents to C=N or C=C-C=N linkages can be readily rationalized in terms of a transition state involving attack by the negatively polarized carbon of the RLi reagent on electron-deficient sites.[14,15] The observation of both N- and C-phenylations with VII suggests, therefore, that in the transition state the usual polarization

SCHEME 3



of the C=N linkage (VIIa) does not predominate, but that the contribution by resonance structure VIIc is of equal importance. The absence of XII among the products may be due to steric hindrance to attack at C_{10}, rather than to a smaller contribution for resonance structure VIIb. This unusual N-phenylation of VII can be viewed as evidence for the destabilizing effect of antiaromaticity on the expected polar resonance structures such as VIIa and VIIb. Although both structures do have their negative charge on nitrogen, the positive charge is then part of an antiaromatic moiety, namely a substituted cyclopentadienyl cation system.[2] Such destabilization in the transition state for phenyllithium addition seems to enhance the importance of the

polarization depicted in VIIc. Insofar as product stability may also influence the reaction course, N-phenylation is further favored by its leading to a 10 pi-electron or aromatic anion (anion of XI).

ACKNOWLEDGMENT

The authors are grateful to the Public Health Service for the support of this research through Grant CA-10743.

REFERENCES AND NOTES

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11. Reference 9 reports that the treatment of I with trityl perchlorate yields the N-trityl perchlorate salt of IV, but no molecular weight measurement is given. From our attempted dehydrogenations of I, which lead to dimers, we judge that the previous product must have been dimeric.
12. Satisfactory elemental and spectral data were obtained on all the intermediates in these preparations.
13. Attempted oxidations of I or II with the Jones reagent or with N-bromosuccinimide, followed by silver acetate treatment in glacial acetic acid, were unsuccessful.
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