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# The Synthesis of Dibenzo[*b*,*f*][1,5]diazocine

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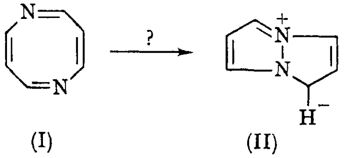
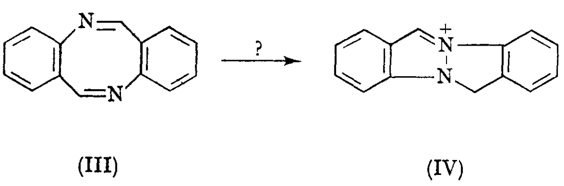
THE synthesis of 1,5-diazocines (I) has been the object of a research effort in our laboratories for the past few years and has resulted in the synthesis of some tetrahydro-diazocines.[1]

The interest in preparing the 1,5-diazocine lies in the possibility that it might isomerize to the aromatic diazapentalene (II). It has been suggested that this might well occur exothermically.

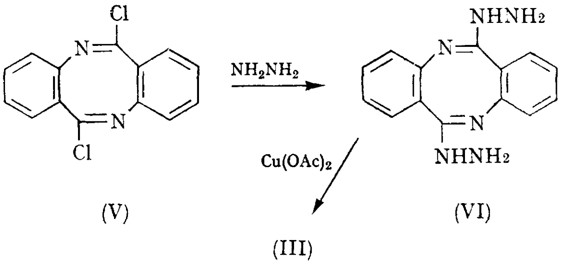


In fact, the synthesis of the diazapentalene (II) has recently been described by two different groups.[2] Since this compound was prepared from pyrazole derivatives, the N–N bond is already pre-formed, and the question of the existence of the isomerization of (I) to (II) could not be answered. If this type of isomerization is indeed possible,[3] then we would expect that the transformation (III) → (IV) would also occur.



Consequently it became of considerable interest to prepare either the diazocine (I) or the dibenzo-analogue (III).[4] This would have to be accomplished by a reaction sequence that does not involve intermediates which already contain the N–N linkage.

The synthesis of dibenzo[*b*,*f*][1,5]diazocine (III) or of its isomer (IV), was accomplished by the following sequence of reactions.



The preparation of the dichloro-compound (V) has been described previously.[5] The structure of the compound (III) or (IV) rests upon the following evidence:

(1) The mass spectrum confirms the molecular weight, as well as the molecular formula. The parent ion (*m*/*e* 206) readily loses 2 molecules of HCN in two consecutive steps (*m*/*e* 179 and 152). The resulting ion, possibly a dibenzocyclobutadienyl ion, would not be as readily rationalizable as being formed from structure (IV) as it is from structure (III).

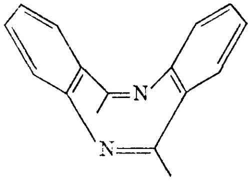
(2) The chemical shift of the nonbenzenoid protons (τ 1·47) of the compound is very similar to that of the methine proton of benzalaniline (τ 1·64). If the compound had the diazapentalene structure (IV), the nonbenzenoid protons would appear at a position much more deshielded than the methine proton of benzalaniline since they would be part of an aromatic system which could maintain a ring current. This argument is further substantiated by a comparison of the chemical shifts of the olefinic protons of *trans*- (τ 2·90) and of *cis*- (τ 3·45) stilbene with those of dibenzo[*a,e*]cyclo-octatetraene (τ 3·29).

(3) The infrared spectrum of the compound (III) or (IV) has a strong absorption peak at 6·08 μ. The C=N absorption of benzalaniline appears at 6·16 μ, in the region typical for a conjugated C=N grouping.

If the compound had structure (IV), the C=N bond would certainly absorb at a wavelength of at least that of the C=N absorption of benzalaniline. Thus, the infrared spectrum again points to the structure (III) as that of the compound in question.

(4) Finally, a comparison of the n.m.r. spectrum of the compound with that of compound (V) offers additional support to the assigned structure (III).

The presence of the chlorine atoms in structure (V) in place of the nonbenzenoid protons would be expected to have a deshielding effect upon the benzenoid proton "*peri*" to the substituent. On the other hand, the chlorine atom in compound (V) would be expected to have essentially no effect on the "*peri*"-benzenoid proton since the substituent is at an angle of at least 60° (see structure IIIa) with respect to the proton in question and is, furthermore, not part of an extended conjugated system.



(IIIa)

A comparison of the n.m.r. spectra shows the validity of the latter argument, and we conclude that the compound is dibenzo[*b,f*][1,5]diazocine (III).

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[1] W. W. Paudler, G. R. Gapski, and J. M. Barton, *J. Org. Chem.*, 1966, **31**, 277; W. W. Paudler and A. G. Zeiler, *ibid.*, 1967, **32**, 2425.

[2] S. Trofimenko, *J. Amer. Chem. Soc.*, 1966, **88**, 5588; T. W. G. Solomons and C. F. Voigt, *ibid.*, p. 1992.

[3] Dibenzotetraazapentalenes have recently been prepared and shown to be aromatic (R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, 1967, **89**, 2618).

[4] The 6,12-diphenyl analogue, which might possess the carbon skelton of either (III) or (IV), has recently been described (W. Metlesics, R. Tavares, and L. H. Sternbach, *J. Org. Chem.*, 1966, **31**, 3356).

[5] F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 1954, 3429.