INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXV. Structure and Properties of Methylated 1-Benzazolyl-3, 5-diphenylformazans*

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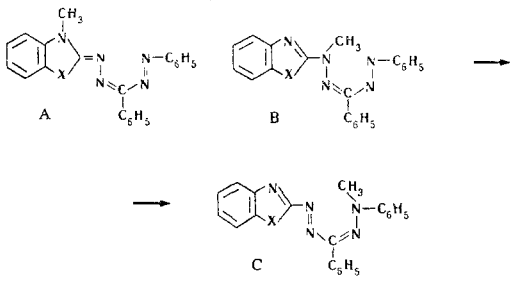
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 5, pp. 882–884, 1969

UDC 547.787.3'789.6'883

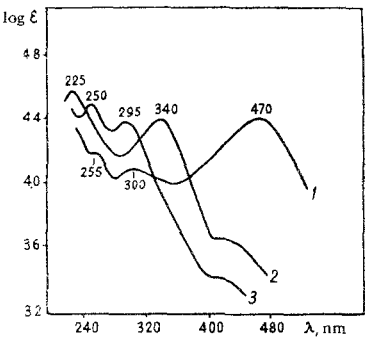
The methylation of 1-benzazolyl-3, 5-diphenylformazans (I–III) with methyl iodide takes place at the nitrogen atom of the heterocycle and the methyl derivatives obtained do not undergo oxidation to free radicals—verdazyls. On methylation with diazomethane, 1-(benzimidazol-1'-yl)-3, 5-diphenylformazan (I) and 1-benzoxazolyl-3, 5-diphenylformazan (III) form analogous methyl derivatives. In contrast to this, on methylation with diazomethane 1-benzothiazolyl-3, 5-diphenylformazan (II) is converted into a methyl derivative which, in benzene solution, undergoes spontaneous oxidation to 1-benzothiazolyl-3, 5-diphenylverdazyl (VII).

As has been shown by Kuhn et al. [2, 3], the methylation of arylformazans gives methyl derivatives which undergo spontaneous oxidation in the air and are converted into stable free radicals—verdazyls. Verdazyls of heterocyclic formazans have not hitherto been known. In this paper we give the results of an investigation of the methylation of heterocyclic analogs of triphenylformazan and of the structure of the products obtained. In view of tautomerism and the possibility of the occurrence of the reaction with migration of the reaction center, methylation could form the isomers A, B, and C. Of these, only B and C can be expected to form free radicals.



IV X=NCH$_2$C$_6$H$_5$; V X=S; VI X=O

When compounds I–III were methylated with methyl iodide in alcoholic alkali, the monomethyl derivatives IV–VI were obtained. It can be seen from a comparison of their electronic spectra (figure) that they all have two well-defined maxima in the UV region and a maximum or a shoulder in the visible region. The methyl derivative of I (IV) has an absorption maximum in the visible region similar to that of I itself (470 and 474 nm, dioxane), i.e., replacement of hydrogen by methyl has no influence on the structure of the chromophore. In the UV region, the spectrum of IV (λ_{max} 255, 300 nm) is similar both to that of I and to that of the "model" 1-benzyl-2-imino-3-methylbenzimidazoline (λ_{max} 262, 305 nm) [1]. It was reported previously that I has an open structure and the mobile hydrogen is on the nitrogen of the benzimidazole moiety. All this gives grounds for considering that the methylation of compound I under these conditions takes place at the nitrogen of the heterocycle with the formation of a product of structure A.



Electronic spectra (in dioxane): 1) IV; 2) V; 3) VI.

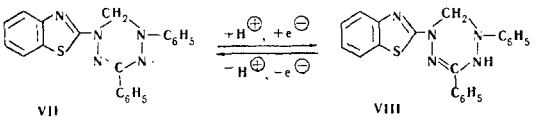
In the case of II and III, the methyl derivatives have far higher colors than the formazans themselves (figure) (V has a shoulder in the 400–420 nm region and VI a small shoulder in the 400–410 nm region, while in the corresponding formazans these are at 470 and 430 nm). The hypsochromic shift of the absorption maximum on methylation is explained by the fact that II and III, in contrast to I, have a chelate structure [1]. Since neither V nor VI undergoes oxidation to radicals, it may be assumed that methylation with methyl iodide takes place at the nitrogen of the heterocyclic ring in II and III, as well.

It is known [4, 5] that in the case of heterocyclic amino derivatives exhibiting a capacity for tautomerism, two types of derivatives can be obtained on methylation with diazomethane. The methylation of I and III with diazomethane yielded the same methyl derivatives as methylation with methyl iodide (IVA and VIA) incapable of oxidation to radicals.

The methylation of II with diazomethane at room temperature in benzene gave a deep green solution which exhibited paramagnetic properties (the formation of a paramagnetic green solution also accompanies the methylation of triphenylformazan [2]). This solution can stand for a long time without change. Evaporation of the benzene and crystallization from isopropanol yielded a crystalline, almost black, paramagnetic substance, corresponding in elementary composition to VII. To confirm the structure of VII, we obtained

*For part XXIV, see [1].

the leuco base VIII corresponding to it. Evaporation of a benzene solution and treatment of the resinous residue with a mixture of dimethylformamide, ethanol, and water, yielded a brown substance which gave no EPR signals either in benzene solution or in the form of crystals. The elementary analysis of the substance corresponded to the leuco base of the radical VIII and the IR spectrum had a ν_{NH} band in the 3165 cm^{-1} region. When a benzene solution of VIII was shaken with PbO_2, the coloration changed from yellow-brown to green and an EPR signal similar to that given by the initial green benzene solution appeared. All this confirms the structure of the brown product isolated as VIII and the green product as VII.



VII VIII

Thus, only by the diazomethane methylation of II, containing the most aromatic heterocycle, benzothiazole, is it possible to obtain B or C, which passes into the leuco base and then spontaneously oxidizes to the radical. In contrast, the methylation of I and III, regardless of the nature of the methylating agent, gives only A, incapable of spontaneous oxidation to verdazyls.

EXPERIMENTAL

Product of the methylation of II (VA). A solution of 1 g of II in 80 ml of ethanol was treated with 5 ml of 30% NaOH and 3 ml of methyl iodide, and the mixture was boiled for 2 hr, after which the color had changed from crimson to red-brown. The ethanol was distilled off and the precipitate that had deposited was twice purified by the reprecipitation of an ethanolic solution with water. Red crystalline powder, mp 66-68° C. Found, %: C 66.78; H 4.33; N 18.30; S 9.0. Calculated for $C_{21}H_{17}N_5S \cdot (1/2)H_2O$, %: C 66.28; H 4.50; N 18.40; S 8.46.

Product of the methylation of III (VIA). This was obtained in a similar manner to VA, but at room temperature. Brown powder, mp 90-93° C. Found, %: C 70.60; H 5.22; N 19.02%. Calculated for $C_{21}H_{17}N_5O$, %: C 70.95; H 4.82; N 19.70.

Product of the methylation of I (IVA). Obtained in a similar manner to VIA. Red-brown powder, mp 115-118° C. Found, %: C 74.91; H 5.61; N 19.09. Calculated for $C_{28}H_{24}N_6$, %: C 75.65; H 5.44; N 18.91.

Product of the methylation of II with diazomethane (VII). A benzene solution of diazomethane obtained from 5 g of nitrosomethylurea was added to a solution of 1.8 g (0.005 mole) of II in benzene. On standing at room temperature for 4 days, the dark red solution acquired an intense green coloration and paramagnetic properties. After the evaporation of the benzene, a resinous residue remained which, after crystallization from isopropanol, gave an almost black product with mp 108-110° C. The EPR spectrum was taken on an RE-1301 instrument (in benzene). Found, %: C 64.40; H 4.47. Calculated for $C_{21}H_{16}N_5S \cdot H_2O$, %: C 64.90; H 4.63. The recrystallization of this compound from a mixture of dimethylformamide, ethanol, and water gave a nonparamagnetic brown crystalline product, mp 73-75° C. Found, %: C 67.98; H 5.36. Calculated for $C_{21}H_{17}N_5S$, %: C 67.92; H 4.60.

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