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RESEARCH IN THE ISOXAZOLE SERIES.

XXXIII.* REACTION OF PHENYLAZOTRIPHENYLMETHANE WITH METHYLISOXAZOLES

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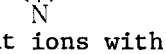
UDC 547.786.1:543.422.25

The thermal decomposition of phenylazotriphenylmethane in 3,5-dimethyl- and 3,4,5-trimethylisoxazole was studied. In 3,5-dimethylisoxazole only the hydrogen atom of the methyl group in the 3 position is replaced by the $(C_6H_5)_3C^{\cdot}$ radical. The activities of the methyl groups of 3,4,5-trimethylisoxazole decrease in the order 3-C > 4-C >> 5-C. The specific direction of the reaction is associated with the orientation of the phenylazotriphenylmethane in the vicinity of the 3-C atom of the isoxazole ring owing to complexing of the azo group with the nitrogen atom. Complexes of 3,5-dimethyl- and 3,4,5-trimethylisoxazole with Eu^{3+} have a similar structure. The structures of the reaction products were established by means of their PMR and mass spectra.

In the course of a study of radical substitution in the isoxazole series we found an unusual reaction of phenylazotriphenylmethane (I). The aim of the present research was to study the specific reaction of azo compound I with methylisoxazoles.

2,5-Addition of $C_6H_5^{\cdot}$ and $(C_6H_5)_3C^{\cdot}$ radicals formed by thermal decomposition of azo compound I to furan was previously described in [2]. Benzene derivatives (even the alkyl homologs) undergo phenylation only in the ring [3]. In contrast to the indicated compounds, 3,5-dimethylisoxazole (II) reacts to give 3-β,β,β-triphenylethyl-5-methylisoxazole (IIa). The reaction must be carried out in a large excess of the isoxazole (≥50 moles), and tetraphenylmethane (III) is formed at a reagent molar ratio of 1:10 because of the "cage effect" [4].

The structure of IIa was established by means of the PMR and mass spectra. Three singlets at δ 2.01, 3.99, and 4.73 ppm with an intensity ratio of 3:2:1 are observed in the PMR spectrum (in $CDCl_3$), along with the signals of aromatic protons at about 7.5 ppm. This sort of spectrum is possible only if substitution took place in one of the methyl groups. The shift to stronger field as compared with the starting isoxazole II of the signals of the protons of the CH_3 group and especially of the 4-H signal (by 1 ppm) constitutes evidence for shielding of the protons by the "umbrella" of the triphenylmethyl group. The choice between the two possible isomeric structures was made on the basis of the mass spectrum, in which one observes a molecular ion peak (m/e 339),† the most intense $(C_6H_5)_3C^+$ fragment ion peak (243), and less intense peaks of  (296) and CH_3CO^+ (43) ions. The spectrum does not contain peaks of fragment ions with mass numbers 285 and 54, which are formed in the fragmentation of the isomeric isoxazole (see [5] for the disintegration of isoxazole derivatives under the influence of electron impact):

*See [1] for communication XXXII.
†Here and subsequently, the numbers pertaining to the ions are the mass-to-charge ratios.

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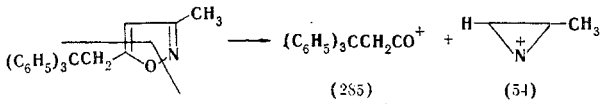
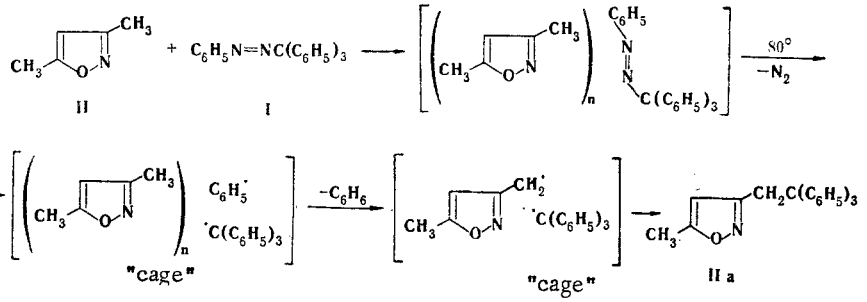


(285) (54)

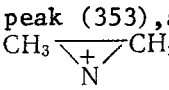
Since the isolated substance could not be freed of hydrocarbon impurities by the usual methods (crystallization or chromatography), it was converted to N-methylisoxazolium picrate, for which a good elementary analysis was obtained.

The following scheme for the formation of isoxazole IIa can be proposed:



II I "cage" "cage" IIa

The probable reason for this specificity of the reaction is the formation of complexes of the azo group with the nitrogen atoms of several molecules of isoxazole II, which leads to orientation of azo compound I in the vicinity of the 3-C atom of the isoxazole ring. The $C_6H_5^{\cdot}$ and $(C_6H_5)_3C^{\cdot}$ radicals formed as a result of the decomposition of the azo compound interact to give III or react with molecules of the solvent if a large excess of the latter is used. Since of the two available radicals the $C_6H_5^{\cdot}$ radical is undoubtedly more active and is, moreover, inclined to attack benzyl hydrogen atoms [6], it is precisely to it that a hydrogen atom is transferred from the methyl group in the 3 position of isoxazole II, whereas the $(C_6H_5)_3C^{\cdot}$ radical recombines with the resulting 3-isoxazolylmethyl radical. The absence of a reaction between isoxazole II and the triphenylmethylradical formed from triphenylchloromethane and zinc dust [7] provides evidence in favor of this scheme.

To confirm the proposed reaction scheme we carried out the thermal decomposition of phenylazotriphenylmethane (I) in 3,4,5-trimethylisoxazole (IV). After removal of isoxazole IV, the mixture of products was recrystallized from ether, and the substance obtained was subjected to mass spectrometric analysis. The mass spectral data provide evidence for the presence in this mixture of tetraphenylmethane (III) and derivatives of isoxazole IV containing a triphenylethyl group in the 3 or 4 position. A molecular ion peak (353), an intense $(C_6H_5)_3C^+$ fragment ion peak (243), and less intense peaks of CH_3CO^+ and  (310) ions are observed in the spectrum. The absence in the spectrum of peaks of fragment ions with masses 285 and 54 proves that substitution in the methyl group attached to 5-C does not occur.

Since the mass spectral data do not make it possible to choose between the two possible isomeric structures, additional information regarding the structures of the reaction products was obtained by means of PMR spectroscopy. According to the PMR spectrum (in $CDCl_3$), the mixture of products contains two isomeric β,β,β-triphenylethyldimethylisoxazoles in a ratio of 2:1. The singlets of two methyl groups at δ 1.02 and 2.13 ppm and of a methylene group at δ 3.85 ppm correspond to the isomer present in higher concentration (IVa); the singlets at δ 1.13 and 2.02 ppm (CH_3) and 3.89 ppm (CH_2), respectively, correspond to the second isomer (IVb). In the spectra of both isomers the signal of one of the methyl groups is shifted to strong field by about 1 ppm, as in the case of the 4-H signal in the spectrum of isoxazole IIa.

To establish the structures of isomers IVa and IVb, the PMR spectra of the mixture of products, as well as of isoxazole IV, which was taken as a model compound, were recorded with the addition of a paramagnetic shift reagent — tris(dipivaloylmethanato)europium [$Eu(DPM)_3$] [8]. In the case of the spectra of model compound IV, for which the assignment of the signals of the CH_3 groups is known [9], the change in the chemical shift of the protons of the 3-CH_3 group under the influence of $Eu(DPM)_3$ (the shift of the signal of this group to weak field) was found to be approximately twice the corresponding changes for the other methyl groups. This makes it possible to conclude that the Eu^{3+} ion is preferably coordinated with the nitrogen atom in the isoxazoles.

In the spectra of the mixture of products recorded with the addition of $Eu(DPM)_3$, of the signals of isomer IVa, the singlet of the methylene group is shifted most strongly to weak field, and, consequently, the $CH_2C(C_6H_5)_3$ substituent in this substance is in the 3 position, i.e., it is 3-β,β,β-triphenylethyl-4,5-dimethylisoxazole. In the case of isomer IVb the singlet of one of the methyl groups undergoes the greatest shift to weak field. Since, according to the mass spectral data, the mixture of products does not contain 5-triphenylethylisoxazole, isomer IVb is evidently 4-β,β,β-triphenylethyl-3,5-dimethylisoxazole. It is interesting to note that the changes in the chemical shifts induced by $Eu(DPM)_3$ for the groups of protons of isomer IVb are considerably more pronounced than for those in the same position relative to the center of coordination of the groups of protons of isomer IVa. The reason for this is probably the steric hindrance to formation of a $Eu(DPM)_3$ complex with isoxazole IVa that is created by the bulky triphenylethyl substituent located close to the coordination center.

Thus in the reaction with phenylazotriphenylmethane the methyl group in the 3 position and, to a lesser extent, the methyl group in the 4 position in isoxazole IV are primarily reactive, and the CH_3 group in the 5 position does not react at all, whereas in the case of homolytic bromination the activities of the CH_3 groups of IV decrease in the order 4-C > 5-C >> 3-C [9]. Consequently, owing to the complexing of the phenylazotriphenylmethane with the nitrogen atom of the isoxazole ring, the direction of radical attack changes.

The reaction described in this paper is very sensitive to the polarity of the C-H bonds of the methyl groups of the isoxazoles: the reaction does not proceed with 3,5-dimethyl-4-chloroisoxazole.

EXPERIMENTAL

The mass spectra were recorded with an MKh-1303 spectrometer equipped with a system for direct introduction of the samples into the ion source at an ionizing-electron energy of 30 eV at 30°.

Mass Spectra of IIa and IVa,b

m/e values (relative intensities of the peaks, %):*

IIa 43 (15.1), 44 (6.1), 165 (65.1), 166 (10.6), 243 (100.0), 244 (22.7), 296 (5.5), 339 (0.2);

IVa,b 43 (8.2, 165 (65.3), 228 (6.1), 243 (100.0), 310 (18.4), 320 (5.7), 353 (0.8).

The PMR spectra were recorded with a HNM-4H-100 spectrometer (JEOL, Japan) with tetramethylsilane as the internal standard.

General Method. A solution of 1.4 g (0.004 mole) of azo compound I in 0.2 mole of isoxazole II or IV was heated at 80° for 5 h until the azo compound disappeared (tested by thin-layer chromatography on Al_2O_3 in benzene). The reaction mixtures from three parallel experiments were combined, the isoxazole was removed by vacuum distillation, and the residue was crystallized from ether.

3-β,β,β-Triphenylethyl-5-methylisoxazole (IIa). Workup of the reaction mixture gave 1.1 g (26%) of IIa with mp 146-148°. 2-Methyl-3-β,β,β-triphenylethyl-5-methylisoxazolium picrate, with mp 204-205°, was obtained from IIa. Found, %: C 64.0; H 4.6; N 9.4. $C_{25}H_{24}O \cdot C_6H_3N_3O_7$. Calculated, % C 63.9; H 4.5; N 9.6.

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4-(5-ARYLVINYL-2-OXAZOLYL)- AND 4-(5-ARYLBUTADIENYL-2-OXAZOLYL)-NAPHTHALIC ANHYDRIDES

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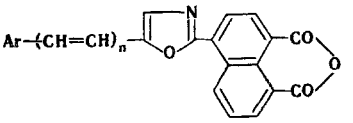
UDC 547.787

4-(5-Arylvinyl-2-oxazolyl)- and 4-(5-arylbutadienyl-2-oxazolyl)naphthalic anhydrides were synthesized by a phosphonate modification of the Wittig reaction from 4-(5-bromomethyl-2-oxazolyl)naphthalic anhydride. The structures of the aryl radicals and the steric hindrance created by some of them have a substantial effect on the absorption and luminescence of these compounds in solution. The introduction of each of the vinylene groups between the aryl and heterocyclic radicals causes approximately identical shifts in the spectra, but the Stokesian shift increases. These effects are reinforced considerably under the influence of electron-donor substituents in the aryl radical. The luminescence maxima of the investigated substances range from 515 to 710 nm, and the absolute quantum yields range from 0.12 to 0.51.

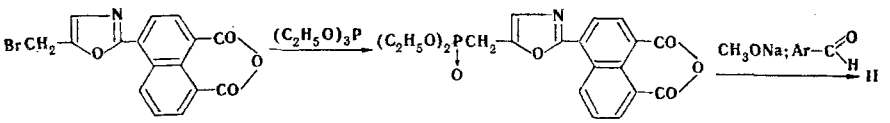
Effective organic luminophores [1, 2] that have found application in the preparation of daylight fluorescent pigments [3] are found among 4-(5-aryl-2-oxazolyl)naphthalic anhydrides (I).



I-III

I n=0; II n=1; III n=2

It was of interest to observe how lengthening of the conjugation chain by the introduction of vinylene groups between the aryl and heterocyclic groupings would affect the spectral luminescence properties of these compounds. For this purpose we obtained II. Their synthesis was accomplished by a phosphonate modification of the Wittig reaction via the scheme



Compounds with two vinylene groups (III) were synthesized via a similar scheme with the application of cinnamaldehyde and p-dimethylaminocinnamaldehyde.

A solution of IIa in toluene absorbs and luminesces over a longer-wavelength range and more intensely than the analogous Ia, which does not contain a vinylene group (Table 1). Lengthening of the chain of conjugated bonds by replacement of the phenyl group by diphenylyl and p-terphenylyl groups or groupings with condensed aromatic rings (IIb-f) leads to a further

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