mately half of the lines are observed, corresponding to the central, most intense portion of the spectrum. The less intense lines, located at the peripheries of the spectrum, could not be detected, since the spectrum lost resolution as the concentration of the salt III was increased. The biradical and monoradical were of comparable stability: both decomposed at room temperature in solution over a period of 1-2 days.

Electronic spectrum (in $CH_3CN$), $\lambda_{max}$: I, 226 and 317, nm; II, 222, 321, 370 (sh), and 762 nm; III, 218, 322, 370 (sh), and 762 nm.

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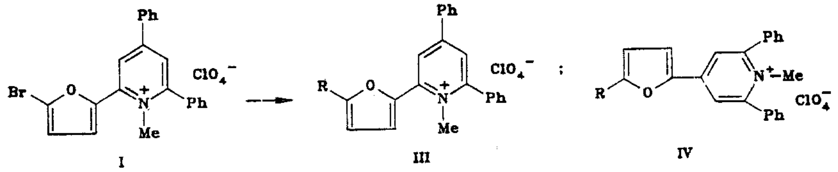
# PHOTONUCLEOPHILIC SUBSTITUTION OF HALOGEN IN (5-BROMOFURYL-2)-PYRIDINIUM DERIVATIVES

V. M. Feigel'man, Ya. R. Timyanskii, V. N. Novikov,
O. A. Zubkov, M. I. Knyazhanskii, and V. S. Pustovarov

UDC 547.722.4'727'821.3:
541.144

We have found that halogen atoms can be readily displaced by nucleophiles in 2-(5-bromofuryl-2)-1-methyl-4,6-diphenylpyridinium(I) and 4-(5-bromofuryl-2)-1-methyl-2,6-diphenylpyridinium (II) perchlorates upon irradiation in light.



R= o- and p-tolyl, morpholino, piperidino

The reactions were carried out in acetonitrile solution in the presence of excess nucleophile in a pyrex photoreactor irradiated with a mercury DRT-220 lamp. The irradiation time was varied from 30 min to 2 h, while the extent of reaction was monitored spectrophotometrically. After removal of solvent the reaction products III and IV were isolated in near qualitative yields. Reaction with toluene resulted in the formation of a mixture of o- and p-tolyl substituted isomers in a ca. 2:3 ratio. This was established based on the integrated intensity ratio of the proton signals for the o- and p-methyl groups in the PMR spectra of compounds III [2.58 (o-$CH_3$) and 2.40 (p-$CH_3$) ppm] and IV [2.29 (o-$CH_3$) and 2.00 (p-$CH_3$) ppm].

Reactions of compound I with morpholine and piperidine, as well as of cation II with piperidine, occur at very slow rates in the dark, and are significantly accelerated upon exposure to light. Photosubstitution of halogen also takes place upon treatment of compounds I and II with benzene, p-xylene, mesitylene, furan, and sylvan (α-methylfuran). The corresponding p-bromophenyl substituted pyridinium derivatives do not participate in these types of halogen photosubstitution reactions.

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0009-3122/87/2310-1145 $12.50

1-Methyl-2-(5-piperidinofuryl-2)-4,6-diphenylpyridinium Perchlorate. mp 131-133°C (dec.). UV spectrum: $\lambda_{max}$ 478 nm (log ε 4.44).

1-Methyl-2-(5-morpholinofuryl-2)-4,6-diphenylpyridinium Perchlorate. mp 130-132°C (dec.). UV spectrum: $\lambda_{max}$ 467 nm (log ε 4.35).

1-Methyl-4-(5-piperidinofuryl-2)-2,6-diphenylpyridinium Perchlorate. mp 152-154°C (dec.). UV spectrum: $\lambda_{max}$ 480 nm (log ε 4.68).

1-Methyl-4-(5-morpholinofuryl-2)-2,6-diphenylpyridinium Perchlorate. mp 162-164°C (dec.). UV spectrum: $\lambda_{max}$ 470 nm (log ε 4.53). All of the compounds were purified by recrystallization from isopropyl alcohol. The results of elemental analysis for C, H, N, and Cl, as well as the PMR spectral data were consistent with the proposed structures.

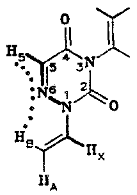
# TRANSFER OF LONG-RANGE SPIN—SPIN COUPLING BETWEEN PROTONS IN 1,3-DIVINYL-6-AZAURACIL VIA A HYPERVALENT N...H BOND

A. V. Afonin, Z. V. Stepanova, V. K. Voronov, and A. V. Vashchenko

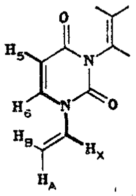
UDC 543.422.25:547.854.4:541.553

Long-range spin—spin coupling of protons is widely used in structural investigations of organic molecules [1]. There are two main pathways for transmission of long-range spin—spin coupling in PMR spectra, namely, via a system of bonds across a stereospecific fragment, and across space in the case of spatially proximate interacting protons.

In the case of 1,3-divinyl-6-azauracil (I), we have detected the feasibility of transmission of long-range spin—spin coupling between the 5-H and B-H protons via a third different pathway. This conclusion is based on a comparison of long-range proton spin—spin-coupling between the ring and 1-vinyl group in 1,3-divinyluracil II and its 6-aza analog I. Both molecules exhibit long-range spin—spin coupling via 5 bonds, between the 5-H and X-H protons (0.55 and 0.45 Hz, respectively). This interaction is transmitted predominantly via a system of σ-bonds across a planar zig-zag-shaped fragment [1].



I



II

${}^5J_{5X}=0{,}55$ Hz, ${}^6J_{5B}=0{,}25$ Hz; ${}^5J_{5X}=0{,}45$ Hz, ${}^5J_{6B}=0{,}35$ Hz

A similar fragment array appears in molecules I and II in the case of an s-trans(O)-conformation of the 1-vinyl group. For molecule II this conformation furthermore results in spatial proximity of the 6-H and B-H protons, which makes it possible to consider the observed interaction between these nuclei (0.35 Hz) as occurring through space.

The similarity in the electronic and three-dimensional structures of molecules I and II would be expected to be reflected in an identical character of long-range spin—spin coupling transmission across bonds, as has in fact been observed in the case of the 5-H and X-H protons. However, long-range spin—spin coupling between the 5-H and 6-H protons occurs across 6 bonds and, because of the distance separating them, these protons cannot interact through space, and is present, in fact, in only one of these compounds, namely molecule I

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