BRIEF COMMUNICATIONS

REACTION OF ARYLDIAZONIUM SALTS WITH ACETONE OXIME

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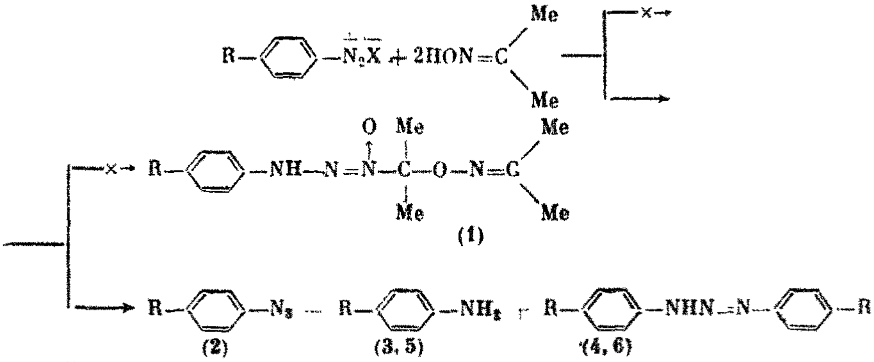
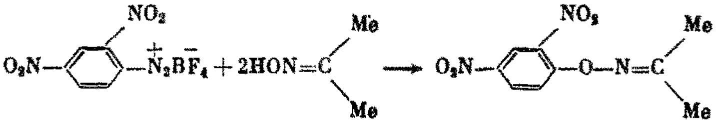
The reaction of aryl diazonium salts containing electron-withdrawing substituents in the aromatic ring with acetone oxime leads to the formation of nitrogen-containing products instead of the expected functional derivatives of 1-alkyl-3-aryltriazene 1-oxides. The structure of these products is a function of the number and chemical nature of the substituents in the diazo component.

Keywords: *aryldiazonium, triazene, triazene oxide, acetone oxime.*

The reaction of aryldiazonium salts with aldoximes and ketoximes is a method for the synthesis of functional derivatives of 1-alkyl-3-aryltriazene 1-oxides (**1**, R = H, Me, OAlK, CO_2H, NO_2), whose structure, however, has been demonstrated rigorously by x-ray diffraction structural analysis only for (**1**, R = H) [4]. Our attempts to reproduce the synthesis of triazene oxide (**1**, R = NO_2) by this method were unsuccessful. The major products of the reaction 4-nitrophenyldiazonium chloride and tetrafluoroborate with acetone oxime are 4-nitrophenyl azide (**2**), 4-nitroaniline (**3**), and 1,3-bis(4′-nitrophenyl)triazene (**4**). The use of 4-bromophenyldiazonium tetrafluoroborate in this reaction also led to the formation of 4-bromoaniline (**5**) and 1,3-bis(4-bromophenyl)triazene (**6**) instead of the expected product (**1**, R = Br). Finally, the only product identified in the reaction of 2,4-dinitrophenyldiazonium tetrafluoroborate with acetone oxime was the 2,4-dinitrophenyl ether of acetone oxime (**7**).



X = BF_4, R = Br (5), (6); X = Cl, BF_4; R = NO_2 (2), (3), (4).



(7)

Thus, the reaction of aryldiazonium salts with ketoximes apparently cannot serve as a general method for the synthesis of triazene 1-oxides **1**. In the case of diazonium salts containing electron-withdrawing substituents in the aromatic ring, the formation of other nitrogen-containing products predominates. The structure of these products is a function of the number and nature of the substituents in the diazo component.

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The structures of the products were demonstrated by IR and PMR spectroscopy and mass spectrometry as well as the comparison of the melting points of **2-7** with reported values [5-8].

EXPERIMENTAL

A sample of 4.2 mmoles diazonium salt was added to 8.5 mmoles acetone oxime and 8.8 mmoles $NaOAc \cdot 3H_2O$ in 20 ml 1% acetic acid at 0°C. The mixture was maintained for 1.5 h. The products were separated by thin-layer chromatography on silica gel. p-$NO_2C_6H_4N_2{}^+BF_4{}^-$ gave *p*-nitrophenyl azide (**2**) in 29% yield, mp 72-74°C [8], *p*-nitrophenylaniline (**3**) in 17% yield, mp 146-148°C, and 1,3-bis(*p*-nitrophenyl)triazene (**4**) in 25% yield, mp 241-243°C [6]. IR spectrum (ν, cm^{-1}): 1340 (NO_2), 1480, 1520 (NO_2), 1600 (Ar), 3200 (NH). Mass spectrum, *m/z* (*I*, %): M^+ 287 (9), 259 (3), 150 (55), 138 (19), 122 (100), 92 (29), 76 (30). p-$BrC_6H_4N_2{}^+BF_4{}^-$ gave *p*-bromoaniline (**5**) in 37% yield, mp 61-63°C and 1,3-bis(*p*-bromophenyl)triazene (**6**) in 33% yield, mp 146-148°C [5]. IR spectrum (ν, cm^{-1}): 820, 1390, 1440, 1485, 1515, 1600 (Ar), 3210 (NH). Mass spectrum, *m/z* (*I*, %): M^+ 353 (5), 355 (11), 357 (5), 325 (2), 327 (4), 329 (2), 183 (62), 185 (65), 155 (100), 157 (100), 76 (23). $2,4$-$(NO_2)_2C_6H_3N_2{}^+BF_4{}^-$ gave the 2,4-dinitrophenyl ether of acetone oxime (**7**) in 55% yield, mp 85-86°C [7].

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