Nucleophilic Substitution in Nitrofluorenone

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Abstract—The reaction of 2,4,5,7-tetranitrofluorenone with amines, thiols, and phenol in a polar aprotic solvent led to the preferable substitution of the nitro group in the position 2, and in the reaction of 2,4,7-trinitrofluorenone first the nitro group in the position 4 was replaced. The different regioselectivity is due evidently to the steric hindrances to the nucleophilic attack on the atom C4 caused by the nitro group in the position 5 of tetranitrofluorenone.

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Polynitrofluorenone are used as efficient sensitizers for electrophotography [1]. The nucleophilic substitution of nitro groups in nitrofluorenone is a simple way to the modification of their structure. The comparison of the reactions of tetranitro- and trinitrofluorenone with O-, N-, and S-nucleophiles provides a possibility to conclude on the dependence of the substitution regioselectivity on the structure of the reagent and the substrate.

It was formerly established that in 2,4,5,7-tetranitrofluorenone (I), 2,4,7-trinitrofluorenone (II) [2], and also in the 2,4,7-trinitrofluorenone-5-carbonitrile [3] in HMPA at room temperature the nitro group in the position 4 is replaced by the hydroxy group with the formation of 4-hydroxy-2,5,7-trinitrofluorenone (III), 4-hydroxy-2,7-dinitrofluorenone (IV), and 4-hydroxy-2,7-dinitrofluorenone-5-carbonitrile respectively. The heating of tetranitrofluorenone in HMPA results in the formation alongside 4-hydroxy-substituted (III) of the isomeric 2-hydroxy-4,5,7-trinitrofluorenone, and the heating of the 2,4,7-trinitrofluorenone-4-carbonitrile provides only the 4-hydroxy derivative. Presumably the nucleophilic agent attacking the nitro group is water contained in HMPA. Adding water to dry HMPA accelerates the reaction.

Whereas at the hydrolysis in HMPA at room temperature in 2,4,5,7-tetranitrofluorenone (I) only the nitro group in the position 4 is exchanged for the hydroxy group, at the action of amines, thiols, phenol in the polar aprotic solvents the nitro group in the position 2 is substituted.

As a result of the reaction with dimethylamine in DMF without heating within 3 days 2-dimethylamino-4,5,7-trinitrofluorenone (Va) was obtained with insignificant impurity of 4-dimethylamino-2,5,7-trinitrofluorenone. At the use of the appropriate secondary amines 2-diethylamino-4,5,7-trinitrofluorenone (Vb) and 2-dibutylamino-4,5,7-trinitrofluorenone (Ve) were synthesized.

The reaction of 2,4,5,7-tetranitrofluorenone (I) with butane-1-thiol in DMSO at heating or in HMPA at room temperature gave 2-butylsulfonyl-4,5,7-trinitrofluorenone (VII) [4]. At boiling tetranitrofluorenone (I) in DMSO 2-methylsulfanyl-4,5,7-trinitrofluorenone (Vc) formed because of the thermal decomposition of the solvent [5]. In the reaction of fluorenone I with thiophenol also the nitro group in the position 2 suffered the substitution to afford 2-phenylsulfanyl-4,5,7-trinitrofluorenone (VII) in a 78% yield. At heating compound I with phenol in HMPA at 100°C 2-phenoxy-4,5,7-trinitrofluorenone (VII) was obtained. The reactions with thiols and phenol do not require the presence of a base usually added to increase the nucleophilicity. This fact demonstrates the high electron-deficiency of the polynitrofluorenone.

Compounds Va, Vla possess the properties of sensitizers for the organic electrophotographic layers [6, 7].

The boiling of 2,4,7-trinitrofluorenone (II) in DMSO led to the formation of a mixture of 4-methylsulfanyl-2,7-dinitrofluorenone (VIII) and 2-methylsulfanyl-4,7-dinitrofluorenone (IX) in the ratio ~4:1. Treating 2,4,7-trinitrofluorenone (II) with excess butanethiol
in DMSO at room temperature in the course of 2 days resulted in the formation of a mixture of 4-butylsulfanyl-2,7-dinitrofluorenone (VIIIb) and 2-butylsulfanyl-4,7-dinitrofluorenone (IXb) in the ratio 3:1 and an overall yield 74%. In the reaction of trinitrofluorenone II with thiophenol exclusively the nitro group in the position 4 underwent the substitution, and the sole reaction product was 4-phenylsulfanyl-2,7-dinitrofluorenone (VIIIc) (yield 87–89%).

The position of the substituent arising at the replacement of the nitro group by the nucleophile was established from the 1H NMR spectra. At the exchange in the position 2 for an electron-donor group the doublet signals of the protons located in the position 1 appear in essentially stronger field than the signals of the same protons at the substitution in the position 4 when in the ortho-position to them remains the electron-acceptor nitro group. The corresponding chemical shifts in 2-dimethylamino-substituted Va and its 4-dimethylamino-substituted isomer are observed at 7.38 and 7.55 ppm, in 2-methylsulfanyl-substituted IXa and its isomer VIIIa, at 7.98 and 8.32 ppm, in 2-butyl-substituted IXb and its isomer VIIIb, at 7.99 and 8.35 ppm. The doublet signals from the protons in the position 3 for these isomeric pairs are observed at 7.67 and 7.79, 8.30 and 8.42, 8.31 and 8.51 ppm respectively. In the combination with the interpretation of the other signals in the 1H NMR spectra (see Experimental) it is possible to distinguish between the substitution in the position 2 or 4. The structure of 4-phenylsulfanyl-substituted compound VIIIc was established by X-ray analysis [8].

Therefore in 2,4,5,7-tetranitrofluorenone (I) the hydroxy group substituted predominantly the nitro group in the position 4, and dialkylamino-, alkylsulfanyl-, phenylsulfanyl-, and phenoxy groups replace the nitro group in the position 2. In 2,4,7-trinitrofluorenone (II) prevalingly the nitro group in the position 4 is substituted. The regioselectivity of the nucleophilic substitution in the polynitrofluorenone depends on the relative reactivity of the certain position occupied by the nitro group, and on its spatial accessibility which in its turn is governed by the extent of shielding of the site of the attack and by the volume of the attacking species. In the absence of steric hindrances the position 4 is obviously more active, and the substitution with water occurs just in this place.