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ACYLATION OF 2-THIOXOQUINAZOL-4-ONES: FORMATION OF 2-ACYLTHIOQUINAZOL-4-ONES

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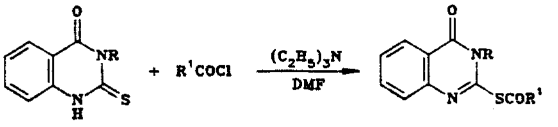
The acylation of 2-thioxoquinazol-4-ones by various acylating agents was studied. The main products are 2-benzoylthioquinazol-4-ones. Minor amounts of the $N_{(3)}$-acylation products are formed.

The aim of the present work was to investigate the acylation of 2-thioxoquinazol-4-ones (I, II) and to seek conditions for selective reaction. The reactions of (I, II) with benzoyl, para-nitrobenzoyl, and ortho-methoxybenzoyl chlorides were realized in an organic solvent and were monitored by TLC. Triethylamine was used as hydrogen chloride acceptor. The choice of solvent is restricted. The triethylammonium salt (I, II) is poorly soluble in low-polarity solvents, and acylation under heterogeneous conditions leads to the formation of a mixture of products from acylation at the $N_{(3)}$ nitrogen atom and at the sulfur atom. The acylation of (I, II) takes place most selectively in DMFA, which dissolves the salts (I, II) well.



I, II

IIIa-d, IVa-c

I, III R=H; II, IV R=CH_3; III, IVa $R^1=C_6H_5$, b $R^1=p\text{-}NO_2C_6H_4$, c $R^1=m\text{-}NO_2C_6H_4$, $R^1=o\text{-}CH_3OC_6H_4$

In addition to the 2-benzoylthioquinazol-4-ones (IIIa-d, IVa-c), according to TLC, the reaction mixture contains the products from acylation of (I) at the $N_{(3)}$ atom, but their content does not exceed 3-5%. These substances (they did not separate from the solution) are separated from the isomeric compounds (IIIa-d, IVa-c) during recrystallization. The $N_{(3)}$- and S-acylated thioxoquinazolones were identified by comparison of their mobilities during TLC. Compounds (II-IV) have similar R_f values (Table 1), which are always 0.20 lower than for the corresponding $N_{(3)}$ isomers. During the acylation of (Ia) with benzoyl chloride, in addition to the isolated isomer (IIIc), the product from acylation at the $N_{(3)}$ atom, identified

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TABLE 1. 2-Benzoylthioquinazol-4-ones (IIIa-d, IVa-c) and 3-Benzoylthioquinazol-4-one (V)

Compound	mp, °C (acetonitrile)	R_f*	M (mass spectrum)	Found, %			Molecular formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
III^a	210—212	0,53	282	64,0	3.6	9.8	$C_{15}H_{10}N_2O_2S$	63.8	3.5	9.9	53
IIIb	175—176	0,55	327	54.9	2.8	13.1	$C_{15}H_9N_3O_4S$	55.0	2.7	12.8	45
IIIc	170—172	0.46	327	54.7	2.8	12.6	$C_{15}H_9N_3O_4S$	55.0	2.7	12.8	60
IIId	200—202	0.47	312	61.0	3.8	8.8	$C_{16}H_{12}N_2O_3S$	61.5	3.8	8.9	36
IVa	158—160	0.62	358	70.8	3.7	7.8	$C_{21}H_{14}N_2O_2S$	70.4	3.9	7.8	26
IVb	220—222	0.46	403	62,4	3.2	10.0	$C_{11}H_{13}N_3O_4S$	62,5	3.2	10.4	38
IVc	268—270	0.45	383	68.2	4.0	7.4	$C_{22}H_{16}N_2O_3S$	68.0	4.1	7.2	24
V	139—140	0,75	282	64,2	3,4	10,0	$C_{15}H_{10}N_2O_2S$	63,8	3,5	9.9	60

*In system A for compounds (IIIa-d, IVa-c), in system B for (V).

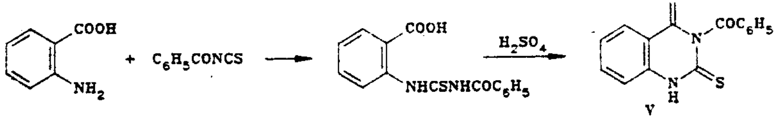
by TLC in comparison with an authentic sample produced by an alternative synthesis, was always present in the reaction sphere.

Compounds (IIIa-d, IVa-c) are colorless high-melting crystals. They are unstable to hydrolysis and are converted by reaction with water into the initial compounds (I, II) and the corresponding acid, and this is typical of the S-acyl derivatives of the pyrimidine series [1]. The low yields of (III, IV) (Table 1) are evidently explained by the high lability of these compounds.

The structure of 3-benzoylthioquinazol-4-one (V), which was detected in the solution in minor amounts, was confirmed by an alternative synthesis from ammonium thiocyanate, benzoyl chloride, and anthranilic acid.

The acyl derivatives of heterocycles containing exocyclic sulfur and oxygen atoms isomerize comparatively readily into each other [2]. We investigated the possibility of the mutual transformation of compounds (IIIa) and (V). The individual compounds (IIIa) and (V) were boiled in dry DMFA for 5 h. The formation of the isomeric products was not observed (TLC).

$$NH_4SCN + ClC(O)C_6H_5 \longrightarrow C_6H_5CNCS + NH_4Cl$$



V

Unlike compound (IIIa), compound (V) is hydrolytically stable (Table 1). The structures of compounds (IIIa-d, IVa-c) were confirmed by IR and mass spectrometry. In addition to the characteristic absorption bands in the region of 1660-1715 cm^{-1} for $C_{(4)}$=O, observed in the spectra of the initial compounds (I, II), their IR spectra contain an absorption band for the C=O group of the benzoyl fragment. This confirms the acylation of the 2-thioxoquinazol-4-ones.

The benzoyl derivatives of 2-thioxoquinazol-4-one are stable to electron impact and give a strong molecular ion peak (10-22% of the intensity of the maximum peak in the spectrum), and this confirms the entry of the benzoyl group into the molecules of (I, II). The presence of the fragment ions $[M - CSCOC_6H_4R^1]^+$ in the spectrum indicates that (I, II) are acylated at the exocyclic sulfur atom.

Thus, the acylation of 2-thioxoquinazol-4-ones by aromatic acid chlorides takes place selectively at the exocyclic sulfur atom.

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a UR-20 spectrometer. The mass spectra were obtained on an MX-1303 mass spectrometer. The TLC was performed on Silufol UV-254 plates in the 4:1 benzene—acetonitrile (A) and 4:1 benzene—acetone (B) systems.

2-Benzoylthioquinazol-4-one (IIIa). To a solution of 1.78 g (0.01 mole) of (I) in 20 ml of DMFA, while stirring, over 15 min we added 1.01 g (0.01 mole) of triethylamine. We then added dropwise 1.41 g (0.01 mole) of benzoyl chloride so that the temperature of the reaction mass did not exceed 20°C. The mixture was stirred for 1 h. The precipitated triethylamine hydrochloride was filtered off, the DMFA was distilled under vacuum, the residue was recrystallized from acetonitrile, and 1.51 g (53%) of (III) was obtained; mp 210-212°C. IR spectrum, cm^{-1}: 1625 (C═N), 1655 (C═O), 1740 (C═O). Mass spectrum, m/z (%): M$^+$ 282 (7), 254 (9), 253 (8), 178 (20), 132 (7), 122 (16), 105 (100), 77 (67).

Compounds (IIIb-d, IVa-c) were obtained similarly (Table 1).

3-Benzoyl-2-thioxoquinazol-4-one (V). To 50 ml of concentrated sulfuric acid we added 3.0 g (0.01 mole) of 1-(o-carboxyphenyl)-3-benzoylurea in portions. The mixture was left at 20°C for 24 h and was then poured with cooling into 50 ml of a saturated solution of sodium acetate. The precipitate was filtered off, washed with water, and dried in air, and 1.7 g (60%) of compound (V) was obtained; mp 139-140°C (from alcohol). IR spectrum, cm^{-1}: 1630 (C═N), 1658 (C═O), 1735 (C═O). Mass spectrum, m/z (%): M$^+$ 280 (8), 252 (9), 176 (20), 130 (6), 120 (17), 103 (100), 89 (10), 75 (69).

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ELECTROCHEMICAL OXIDATION OF SUBSTITUTED 1H-1,2-DIAZAPHENALENES

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It was shown by cyclic voltammetry and electrolysis at controlled potential at a platinum electrode and also by TLC and UV spectroscopy that the electrochemical oxidation of substituted 1H-1,2-diazaphenalenes in anhydrous acetonitrile takes place in a single one-electron stage with the formation of a stable radical-cation. The oxidation potentials of a series of derivatives of 1H-1,2-diazaphenalene and the parameters of the equation for the correlation of these potentials with the Taft substituent constants were determined.

1H-1,2-Diazaphenalenes belong to the excess-π peri-heterocyclic compounds. Possessing a high-lying HOMO, the excess-π heterocycles are distinguished by considerable susceptibility to oxidation [1]. Cyclic voltammetry at a standard platinum microelectrode was used for a quantitative assessment of the capacity of compounds of the 1H-1,2-diazaphenalene series for oxidation. The investigated substances are given in Table 1.

As seen from Table 1, at a platinum electrode in acetonitrile solutions compounds (I-X) give one well-defined electrooxidation wave, the half-wave potentials of which lie in the range of 0.5-1.1 V. Figure 1 shows the cyclic current—voltage curve for compound (I), recorded with a potential sweep rate of 1 V/sec. The clear anodic peak and the presence of a cathodic peak comparable with the anodic peak in magnitude show that the oxidation process is reversible. The peak current is limited by the diffusion rate with an insignificant contribution from the adsorption component, as demonstrated by the value of the rate criterion (the slope of the straight line against the logarithm of the peak current and the logarithm of the potential sweep rate), which is equal to 0.60 for the anodic peak and 0.64 for the cathodic peak [2]. The high degree of reversibility in the electrode process is also con-

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