CONCLUSIONS

1. Sulfonation and chlorosulfonation of 2,3-dichloro-1,4-naphthoquinone in the 6 position of the naphthoquinone has been effected by heating with oleum or with chlorosulfonic acid.

2. The corresponding 6-sulfonamide derivatives of 2,3-dichloro-1,4-naphthoquinone have been obtained by the action of ammonium carbonate or morpholine on the 6-sulfonyl chloride under mild conditions.

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REACTION OF o-AMINOTHIOPHENOL WITH 1-BROMO-2-ACYLACETYLENES

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UDC 542.91:547.564

o-Aminothiophenol (ATP) reacts with unsaturated carbonyl compounds, simultaneously with the C=O group and with the C=C bond, with the formation of seven-membered rings [1-3]. In the reaction of ATP with ethynyl ketones, 2,4-substituted 1,5-benzothiazepines, 2-acylmethyl-4,5-benzothiazolines, and 3-acylvinyl-2-acylmethyl-4,5-benzothiazolines are formed, depending on the ketone structure, solvent, and catalyst [4, 5].

The present paper reports a study of the reaction of ATP with 1-bromo-2-acylacetylenes (Ia, b). The mercapto group is a stronger nucleophile than the amino group [6, 7] and hence it might be expected in the first instance to form an S-monoadduct. In fact, the reaction mechanism appears to be the direct nucleophilic substitution of Br at the ethynyl carbon [8, 9] with the formation of the hydrobromide of 1-acyl-2-(2'-aminophenylthio)acetylenes (IIa, b). The reaction is carried out in anhydrous benzene at 0°C or in ether at −10°C without a catalyst and with a molar ratio of Ketone (I) to ATP = 1:1 and 2:1. In all cases, the products (IIa, b) were isolated in 50-60% yield, and their structures were confirmed by their infrared and mass spectra.

When the ketones (Ia, b) are reacted with ATP in 1:1 molar ratio in the presence of a catalyst such as Et_3N or KOH in methanol, ketenemercaptals (IIIa, b) are obtained in 30-42% yield. With a molar ratio of ketone (I) to ATP = 1:2, the yields of (IIIa, b) become 40 and 60%, respectively.

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*Deceased.

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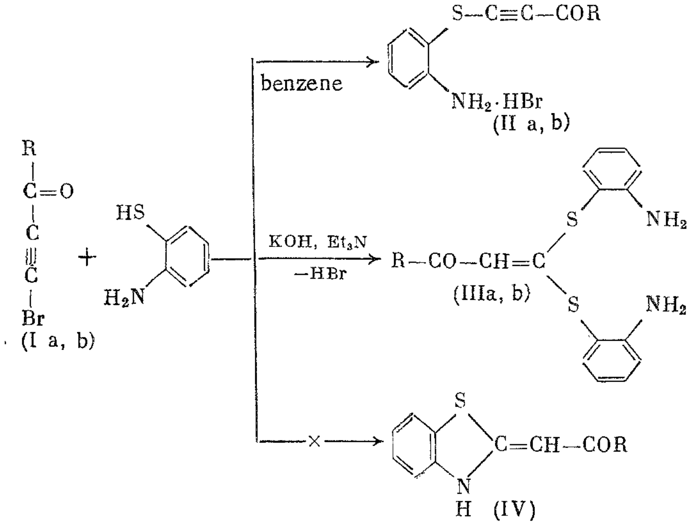
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 858-861, April, 1985. Original article submitted January 26, 1984.

0568-5230/85/3404-0778$09.50

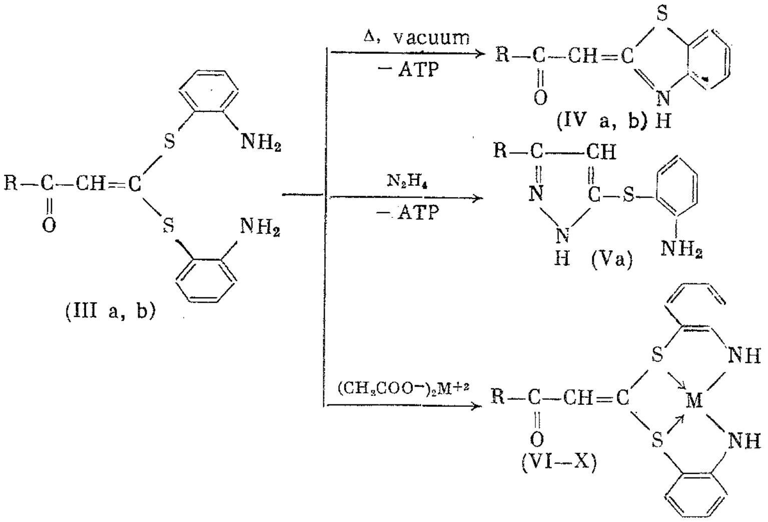
Under the above conditions, and also in the presence of glacial acetic acid, the formation of the possible 2-aceylmethylene-4,5-benzothiazolines (IV) is not observed.



R = Ph (a); α-C_4H_3S (b).

The mass spectra of (IIIa, b) showed peaks due to fragments corresponding to 2-benzomethylene-4,5-benzothiazoline (IVa) and 2-thenoylmethylene-4,5-benzothiazoline (IVb). Apparently, on heating compounds (IIIa, b) in vacuum they undergo intramolecular cyclization with separation of ATP.

Heating of the ketenemercaptal (IIIa) with hydrazine hydrate in EtOH leads to the formation of the corresponding 3,5-substituted pyrazole (Va) and is accompanied by the splitting off of a molecule of ATP.



R = Ph (a); α-C_4H_3S (b); R = Ph, M = Co (VI); R = Ph, M = Cu (VII); R = Ph, M = Zn (VIII); R = Ph, M = Cd (IX); R = α-C_4H_3S; M = Co (X).

Reaction of the ketenemercaptal (IIIa) with the acetates of Co, Cu, Zn, and Cd, and of (IIIb) with Co acetate in aqueous MeOH with heating yields metal complexes with the composition ML (M = metal, L = ligand). Comparison of the spectra of the free ligands (IIIa and IIIb) with the prepared complexes (VI)-(X) indicates that coordination is taking place on the N and S atoms. Deprotonation of the NH_2 group occurs, as shown by the presence of only one band for NH at 3230-3300 cm^{-1} in the infrared spectrum, whereas for the free ligands (IIIa, b) bands are observed at 3320-3325 and 3420-3425 cm^{-1}.

Significant differences between the infrared spectra of the metal complexes and those of the uncoordinated ligands are also observed in the region below 1610 cm^{-1}: bands due to C—S are observed at 750-780 cm^{-1} (705-708 cm^{-1} for the free ligands), to C=C at 1530-1547 cm^{-1} (1588-1600 cm^{-1}), and to conjugated carbonyl at 1600-1610 cm^{-1} (1625-1635 cm^{-1}).

TABLE 1. Data for Compounds Prepared

Compound	Yield, %	mp, °C	Molecular formula	Found/calc., % C	H	N	S
(IIa) *	53	99–100	$C_{15}H_{12}BrNOS$	53,44 53,89	3,41 3,59	4,22 4,19	9.51 9,58
(IIb)	50	102–104	$C_{13}H_{10}BrNOS_2$	45.65 45,88	2.80 2,94	4,40 4,12	18.62 18,82
(IIIa)	42	145–146	$C_{21}H_{18}N_2OS_2$	66.57 66,66	4 88 4,76	7,38 7,40	16.81 16,93
(IIIb)	31	146–148	$C_{19}H_{16}N_2OS_3$	59.70 59,37	4.26 4,16	7.68 7,27	24,96 25.00
(Va)	52	121–122	$C_{15}H_{13}N_3S$	67.07 67,41	5,09 4,88	15.53 15.73	11.65 11.98
(VI)	86	256–257	$CoC_{21}H_{16}N_2OS_2$	57,44 57,93	3.82 3,68	6.78 6,44	14.75 14.71
(VII)	82	172–174	$CuC_{21}H_{16}N_2OS_2$	57.11 57,27	3,67 3,64	6,18 6,36	14.28 14,58
(VIII)	73	272–274	$ZnC_{21}H_{16}N_2OS_2$	56,98 57,14	3.41 3,62	6.09 6,35	14,28 14,51
(IX)	69	258–260	$CdC_{21}H_{16}N_2OS_2$	51.55 51,64	3.40 3,28	6.02 5,74	13.21 13,11
(X)	66	295–298	$CoC_{19}H_{14}N_2OS_3$	51.76 51.70	3,11 3,17	6.42 6,35	21.46 21,77

*Found: Br 24.28%. Calculated: Br 23.95%.

The Co chelates (VI) and (X) and the Cu chelate (VII) are only slightly soluble in $CHCl_3$, Me_2CO, and MeOH and freely soluble in DMSO and DMF. The Zn chelate (VIII) and that of Cd (IX) dissolve only in DMSO and DMF.

EXPERIMENTAL

Infrared spectra were run on a UR-20 instrument in KBr discs, NMR spectra on a Tesla 480B in $CDCl_3$ (TMS reference), and mass spectra on an MX-1303 mass spectrometer using 30- and 70-eV ionizing potentials with the ionization chamber at 100-150°C.

1-Benzoyl-2-(2'-aminophenylthio)acetylene Hydrobromide (IIa). To a solution of 1.05 g (5 mmoles) of ketone (Ia) in 10 ml anhydrous benzene at 0°C was added, gradually, a solution of 0.62 g (5 mmoles) o-ATP in 10 ml anhydrous benzene and the mixture stirred for 10 min. The crystalline precipitate was filtered off, washed on the filter with anhydrous benzene and Et_2O, and dried in vacuum. Yield, 0.88 g (53%) (IIa), rose-colored crystals (see Table 1).

When the above reaction was carried out in anhydrous ether at −10°C, the yield of (IIa) was 1.0 g (60%). IR spectrum (ν, cm^{-1}): 702 (C—S), 1632 (C=O), 2135 (C≡C), 2950 ($-NH_3^+$). Mass spectrum, m/z (rel. intensity, %): 253 (75), 149 (45), 125 (65), 108 (20), 105 (100), 93 (55), 81 (40), 77 (65).

1-Thenoyl-2-(2'-aminophenylthio)acetylene Hydrobromide (IIb). The method was similar to the preceding, using 0.77 g (3.6 mmole) (Ib) and 0.45 g (3.6 mmole) ATP. Yield 0.6 g (50%) (IIb). IR spectrum (ν, cm^{-1}): 705 (C—S), 1635 (C=O), 2142 (C≡C), 2980 ($-NH_3^+$).

1,1-Bis(2'-aminophenylthio)-2-benzoylethylene (IIIa). To a solution of 0.63 g (5 mmole) o-ATP in 20 ml MeOH at −15°C was added 0.6 ml (6 mmole) Et_3N and then, dropwise, with stirring, a solution of 1.05 g (5 mmole) of ketone (Ia) in 20 ml MeOH. Stirring was continued for 15 min at about 20°C after all the (Ia) had been added, and the crystalline precipitate was then filtered off, washed on the filter with cold MeOH, and dried in vacuum. Yield 0.8 g (42%) (IIIa).

When the reaction was carried out under the same conditions in the presence of an equivalent amount of KOH, the yield of (IIIa) amounted to 40%, and when using MeONa, to 45%.

With a molar ratio of (Ia):ATP = 1:2, 1.8 g (60% yield) of (IIIa) was obtained. IR spectrum (ν, cm^{-1}): 705 (C–S), 1590 (C=C), 1630 (C=O), 3320, 3422 (NH_2). NMR spectrum ($CDCl_3$; δ, ppm): 6.51 s (1H, CH=), 4.38 s (4H, NH_2), 6.75-7.42 m (13 H, arom. protons). Mass spectrum m/z (rel. intensity, %): 253 (45), 176 (60), 125 (45), 105 (100), 77 (60).

1,1-Bis(2'-aminophenylthio)-2-thenoylethylene (IIIb). This was prepared by a method analogous to the preceding (IIIa) from 0.63 g (5 mmole) of o-ATP, 1.08 g (5 mmole) ketone (Ib), and 0.6 ml Et_3N. Yield 0.6 g (31%). With a molar ratio of ketone:ATP = 1:2, the yield was 1.5 g (29%) of (IIIb). IR spectrum (ν, cm^{-1}): 705 (C–S), 1586 (C=C), 1635 (C=O), 3320, 3425 (NH_2). NMR spectrum ($CDCl_3$; δ, ppm): 6.5 s (1 H, CH=), 4.43 s (4 H, NH_2), 6.82-7.74 m (11 H, arom. protons). Mass spectrum m/z (rel. intensity, %): 259 (50), 176 (55), 125 (45), 111 (100), 83 (45).

Reaction of (IIIa) with Hydrazine Hydrate. A mixture of 0.38 g (1 mmole) of the ketenemercaptal (IIIa), 3 ml hydrazine hydrate, and 50 ml EtOH was heated to boiling and stirred for 3 h. The solvent was partially evaporated and the residue cooled to 20°C and poured into water. The thick mass which was deposited was extracted with ether, the solvent evaporated, and the residue dried in vacuum. Yield 0.14 g (52%) of 3-(2'-aminophenylthio)-5-phenylpyrazole (Va).

Cobalt Chelate of 1,1-Bis(2'-aminophenylthio)-2-benzoylethylene (VI). To a solution of 0.38 g (1 mmole) (IIIa) in 60 ml MeOH at boiling point was added, gradually, with stirring, a solution of 0.25 g (1 mmole) cobalt acetate tetrahydrate in 10 ml water. The mixture was stirred for 4 h at boiling point and cooled to 0°C. The precipitated solid was filtered off, washed three times with water, and dried in vacuum. Yield 0.38 g (86%) of the cobaltochelate (VI); blue crystals. Compounds (VII)-(X) were prepared in a similar manner (see Table 1).

CONCLUSIONS

The reaction of o-aminothiophenol with 2-benzoyl- or 2-thenoyl-1-bromoacetylenes gives, depending on conditions, hydrobromides of 1-acyl-2-(2'-aminophenylthio)acetylenes and 1,1-bis(2-aminophenylthio)-2-acylethylenes. The latter can act as ligands in the formation of coordination complexes of metals (Co, Cu, Zn, Cd).

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