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REACTION OF CHLORO-SYMM-TRIAZINES WITH THIOACETIC ACID

N. P. Petukhova, V. P. Sergeeva, and E. N. Prilezhaeva UDC 541.124:542.91:547.873:547.299

Derivatives of symm-triazine containing sulfur functions are commonly used as pesticides which are less persistent and less mobile in the soil than chloro-symm-triazines [1].

In the present work, we studied the reaction of 2-chloro-4-isopropylamino-6-ethylaminosymm-triazine (Ia), 2-chloro-4,6-bis(diethylamino)-symm-triazine (Ib), and 2,4,6-triclorosymm-triazine (cyanogen chloride) (Ic) with thioacetic acid (TAA) under nucleophilic conditions. 2-Chloro-symm-triazines (Ia) and (Ib) do not react with an equimolar amount of TAA in acetone at 20-40°C in the presence of pyridine or collidine, while they react with a slight excess of the sodium salt of TAA in ethanol to give virtually quantitative yields of thiols (IIIa) and (IIIb) instead of the expected thioacetates (IIa) and (IIb). By analogy, (Ic) and three equivalents of AcSNa give a 90% yield of trithiol (IIIc). The initially formed symmtriazinyl thioacetates (IIa-c) apparently undergo facile alcoholysis by the action of the solvent to the corresponding thiols (IIIa-c).

An attempt to obtain triazinyl acetates by the action of 2-chloro-4,6-bis(alkylamino)and 2-chloro-4,6-bis(dialkylamino)-symm-triazines with ACOK in DMF [2] also led to the corresponding 2-hydroxy derivatives, presumably through the unstable acetates. Hydroxy-symmtriazines were also obtained upon the phosphorylation of (Ic) and its derivatives [3], but the intermediate phosphates in this case are more stable and they may be detected by IR spectroscopy and, sometimes, isolated.



The reaction temperature depends on the activity of the chlorine atom in the starting symm-triazines, in accord with the data on the hydrolysis of aminochloro-symm-triazines [4, 5]. Thus, the complete replacement of chlorine in (Ic) proceeds at 20°C, while heating to 40°C is required for chloride (Ia) and less active (Ib) reacts only at 70-75°C.

Another method for the synthesis of thioacetates is the acylation of thiols [6], although the acylation of 2,4,6-trihydroxy-symm-triazine proceeds only with difficulty [7],

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1432-1434, June, 1986. Original article submitted October 25, 1985.

and only the product of the reaction of its silver salt with PhCOCl was isolated. Our attempts to carry out the reaction of the silver salts of thiols (IIIa-c) with AcCl or to acylate (IIIa-c) in the presence of  $\text{Et}_3N$  or pyridine at 20°C were unsuccessful. In both cases, the starting thiols were isolated after work-up of the reaction mixtures.

Since the physical constants for thiols (IIIa) and (IIIc) isolated in this work differed from the literature values [8, 9] and these constants were unknown for (IIIb), their structures were confirmed by convergent synthesis through the isothiuronium salts by the preparation of disulfide derivatives (IVa) [10] and trimethylthio derivatives (V) [9] as well as by elemental analysis, mass spectrometry, and IR spectroscopy. The mass spectra of thiols (IIIa-c) contain strong molecular ion peaks, while their IR spectra have triazine ring bands at 1610-1400 cm<sup>-1</sup>.

#### EXPERIMENTAL

The reactions were carried out in absolute solvents. Cyanogen chloride and 2-chloro-4-isopropylamino-6-ethylamino-symm-triazine were purified by recrystallization from acetone, and a sample of 2-chloro-4,6-bis(diethylamino)-symm-triazine was obtained according to Hoffmann [9].

The mass spectra were taken on a Varian MAT CH-6 spectrometer and the IR spectra were taken on a UK-20 spectrophotometer in KBr pellets.

<u>2-Mercapto-4-isopropylamino-6-ethylamino-symm-triazine (IIIa).</u> a) A sample of 10 g (0.046 mole) (Ia) was added to a solution of 2.8 g (0.07 mole) NaOH and 5.3 g (0.07 mole) TAA in 50 ml ethanol, and the mixture was stirred for 4 h at 40°C. The precipitate was filtered off and ethanol was distilled off to yield 8.6 g (87%) (IIIa), mp 255-256°C (from methanol), 213°C [8]. Mass spectrum, m/z: 213 (100%) M<sup>+</sup>. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3430, 3230 (NH). Found: C 45.01; H 7.05; N 32.78; S 15.58%. Calculated for C<sub>8</sub>H<sub>15</sub>N<sub>5</sub>S: C 45.05; H 7.09; N 32.83; S 15.03%.

b) A mixture of 10 g (0.046 mole) (Ia), 3.5 g (0.046 mole) thiourea, and 1 ml HCl in 70 ml 1-propanol was heated at reflux for 4 h, and then 7.8 g (0.14 mole) 50% aqueous KOH was added and the mixture was heated at reflux for an additional 1 h. A portion of the alcohol was distilled off, and the residue was diluted with water, acidified by the addition of 1 N HCl to pH 5-6, and the precipitate was separated to yield 6.0 g (61%) (IIIa), 254-255°C (from methanol). The mixed melting point of samples of thiol (IIIa) obtained by methods a and b was not depressed.

<u>2-Mercapto-4,6-bis(diethylamino)-symm-triazine (IIIb).</u> A sample of 10 g (0.04 mole) triazine (Ib) was added to a solution of 2.4 g (0.06 mole) NaOH and 4.5 g (0.06 mole) TAA in 50 ml ethanol, heated at reflux for 3 h, and then treated as in the above procedure to yield 6.9 g (70%) (IIIb), mp 155.5-156°C (from acetone). Mass spectrum, m/z: 255 (100%) M<sup>+</sup>. Found: C 51.92; H 8.35; N 27.45; S 12.54%. Calculated for  $C_{11}H_{21}S_5S$ : C 51.73; H 8.29; N 27.42; S 12.55%. A sample of thiol (IIIb) did not give a depressed mixed melting point with the thiol obtained from the corresponding isothiuronium salt.

<u>2,4,6-Trimercapto-symm-triazine (IIIc)</u>. A sample of 10 g (0.054 mole) (Ic) was added to a solution of 7.1 g (0.18 mole) NaOH and 13.5 g (0.18 mole) TAA in 50 ml ethanol and stirred for 4 h at about 20°C. Similar work-up yielded 8.6 g (90%) of a yellow product with mp > 310°C. Mass spectrum, m/z: 177 (100%) M<sup>+</sup>. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2530 (SH). Found: C 20.21; H 1.59; N 23.66; S 54.43%. Calculated for C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S<sub>3</sub>: C 20.33; H 1.71; N 23.70; S 54.26%. Thiol (IIIc) obtained through the isothiuronium salt had mp > 310°C.

<u>Di(4-isopropylamino-6- ethylamino-symm-triazinyl)</u> Disulfide (IVa). This compound was obtained as described by Pearlman and Banks [7]. A yield of 0.85 (80%) product was obtained, mp 185-187°C (from ethanol). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3440, 3270 (NH). Mass spectrum, m/z: 424 (65%) M<sup>+</sup>. Found: C 45.29; H 6.69; N 33.10; S 15.05%. Calculated for C<sub>16</sub>H<sub>28</sub>-N<sub>10</sub>S<sub>2</sub>: C 45.29; H 6.65; N 32.99; S 15.10%.

<u>2,4,6-Trimethylthio-symm-triazine (V).</u> A mixture of trithiol (IIIc) and 0.91 g (23 mmoles) NaOH in 10 ml water was heated in water until completely dissolved, cooled, and then 2.29 g (18 mmoles) dimethyl sulfate was added. The precipitate was separated and washed with aqueous ethanol to give 1.18 g (95%) (V), mp 186-187°C (from acetic acid [8]). Mass spectrum, m/z: 219 (100%) M<sup>+</sup>. Found: C 32.74; H 4.01; N 18.98; S 43.95%. Calculated for  $C_6H_9N_3S_3$ : C 32.85; H 4.13; N 19.16; S 43.85%.

## CONCLUSIONS

The reaction of cyanogen chloride and 2-chloro-4,6-bis-(alkylamino)- and 2-chloro-4,6-bis(dialkylamino)-symm-triazines with sodium thioacetate gave the corresponding symm-triazinethiols.

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TRIPLET EXCIPLEXES OF CHLORANIL WITH METHYLATED BENZENES

P. P. Levin and V. A. Kuz'min

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Quinones in the triplet state form short-lived triplet exciplexes (TE) with aromatic electron donors in liquid solutions [1, 2]. Studies have been carried out mainly on the TE of quinones with aromatic amines, which are strong electron donors [1-3]. It is of interest to study the properties of the TE of quinones with relatively weak electron donors such as aromatic hydrocarbons.

In the present work, we studied the nature and kinetics of the formation and annihilation of the TE arising upon the quenching of the triplet state of chloranil (C) by methylated benzenes (D) in CCl<sub>4</sub> and benzene.

## EXPERIMENTAL

The absorption spectra and kinetics for the annihilation of the intermediates were recorded using a pulse photolysis unit with a nitrogen laser, resolving time of the system was 8 nsec. All the measurements were carried out in deoxygenated solutions at about 20°C. The solvents were purified by distillation. Samples of chloranil and the methylbenzenes were recrystallized and sublimed in vacuum.

# RESULTS AND DISCUSSION

The flash photoexcitation of 0.001 M chloranil in benzene and CCl<sub>4</sub> leads to the formation of a triplet species with absorption spectrum shown in Fig. 1 and first-order annihilation kinetics with rate constants  $(k_0)$  of  $1.0 \cdot 10^5$  and  $4.0 \cdot 10^4$  sec<sup>-1</sup>, respectively. The absorption spectrum of <sup>3</sup>C in benzene differs from that in CCl<sub>4</sub> by the existence of absorption at  $\lambda \ge 600$  nm (see Fig. 1) due to the formation of a triplet complex of chloranil with benzene, viz., a nonpolar TE, whole absorption spectrum has a charge transfer band in the long-wavelength region. Similar long-wavelength absorption for <sup>3</sup>C was observed in other electron-donor solvents [4, 5].

The introduction of methylated benzenes is accompanied by an increase in the rate constant for the annihilation of triplet chloranil. The corresponding dependence on the concentration of D is nonlinear and reaches saturation at a rather high concentration of D, indicating the formation of TE by the following reaction:

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