NOTE

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Formation of 2,4-Diarylallophanate from Arylthionocarbamate in an Iodine-DMSO System[†]

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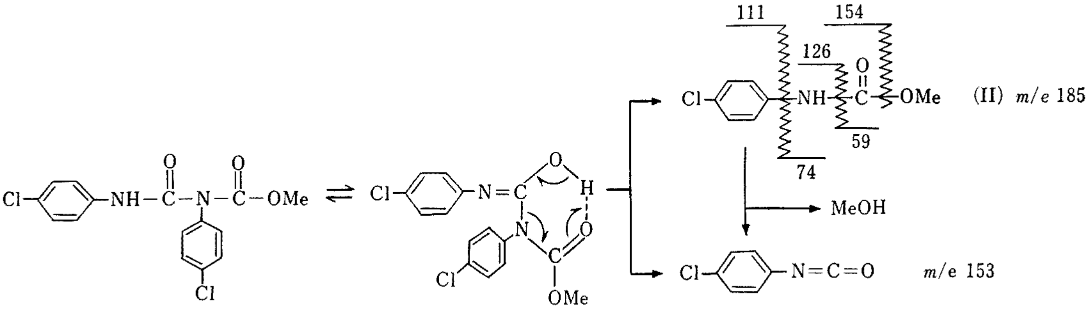
We have recently reported that thionocarbamates are oxidized into sulfur-free carbamates by an iodine-DMSO system.1) During the investigation on the mechanism of the reaction, we detected a by-product which might be valuable in the understanding of the mechanism. We would like to report here on its isolation and structure determination.

When *O*-methyl *p*-chlorothiocarbanilate was treated with the iodine-DMSO system and the reaction mixture was processed as before, we observed, besides the spot of methyl *p*-chlorocarbanilate [*Rf*: 0.15], a spot of a higher *Rf* value [0.41] on a silicic acid-thin layer chromatogram of the reaction mixture. After chromatographic purification, we obtained fine needles of mp 138~139°C in 9.5% yield.

The infrared spectrum of the carbanilate in chloroform showed its N–H stretching vibration at 3435 cm^{-1} in a sharp band. This band was missing in the spectrum of the needles, instead a weak and broad band was observable around 3300 cm^{-1}.

The NMR spectrum of the needles showed the presence of CO_2Me protons (δ 3.72 ppm, 3H, s), aromatic protons (δ 7.05~7.52 ppm, 8H, m) and a strongly deshielded proton (δ 10.86 ppm, 1H br.).



(I) M^+ 338

(I′)

The mass spectrum of the needles showed the presence of two chlorine atoms2) in the molecule [M^+ 338 (16%), (M+2)/M: 68%; (M+4)/M: 14%]. These data suggested that the molecular formula of the compound might be $C_{15}H_{12}O_3N_2Cl_2$. The base peak of the spectrum appeared at *m/e* 185 [(m+2)/m: 43%] and showed the presence of only one chlorine atom in the fragment. We assigned a rearranged molecular ion of molecular formula $C_8H_8O_2NCl$ to the peak. The fragmentation, M^+ 338→*m/e* 185, means the disappearance of 153 (C_7H_4ONCl) mass unit. Among other peaks, the peaks at *m/e* 154 (14%), 153(69%), 149(21%), 140(38%), 126(26%), 125(28%), 111(7%), 99(21%), 90(21%), 74(4%) and 59(23%) were observed.

On the basis of these data, we assigned methyl 2,4-bis(*p*-chlorophenyl)allophanate (I) to the structure of the needles and interpreted some mass fragmentations as follows.

The above mentioned spectral data of the needles are in good agreement with the fact that it has the tautomeric structure, I′.

An authentic sample of the allophanate was prepared according to the method3) of Kogon. The IR, NMR, MS, TLC and mp data of the synthetic sample were all indistinguishable from those of the needles and the identity was confirmed finally by mixture melting point determination.

As the carbanilate (II) was recovered unchanged after 3-hr-heating with iodine in DMSO, it might be concluded that the allophanate was formed not from the final oxidation product, methyl *p*-chlorocarbanilate.

Taking into account the previous results,1) we tentatively would like to propose here the following mechanism for the I_2-DMSO oxidation of thionocarbamates. The formation of alkoxy (arylimino) methoxysulfonium salt (IV) followed by iodide ion-initiated degradation of the salt into the carbamate anion (V) is essential in the mechanism for the formation of both carbamates and allophanates. The Pummerer-type rearrangement4) does not seem to be involved in the present oxidation, since, as described previously,1) DMS was detected in the reaction mixture of bis(methoxyphenyliminomethyl) disulfide (III, Ar=Ph, R=Me) with the iodine-DMSO system. This idea was supported by the fact

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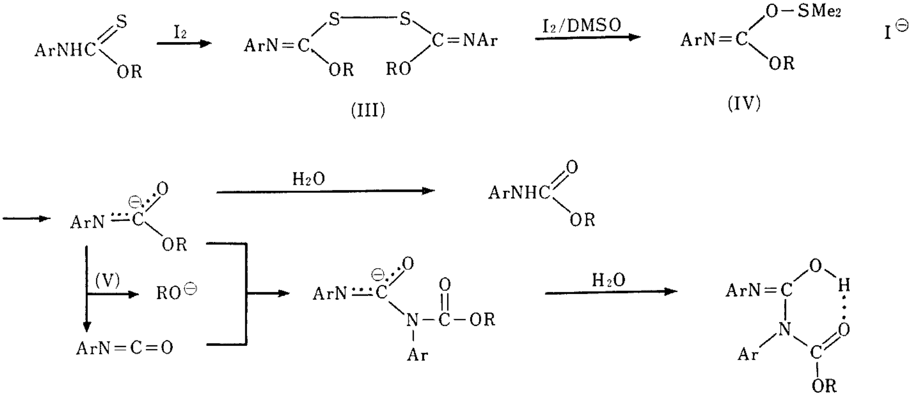
[†] Oxidation of Organic Sulfur Compounds by Iodine in DMSO. Part II. Part I, See Reference 1).



that the allophanate (I) was obtained as a by-product in the oxidation of *O*-methyl *p*-chlorothiocarbanilate.

EXPERIMENTAL

Oxidation of O-methyl p-chlorothiocarbanilate with an iodine-DMSO system and isolation of the by-product

A solution of 5.0 g of *O*-methyl *p*-chlorothiocarbanilate, prepared by our method,⁵⁾ mp 92°C (lit.⁶⁾ 92°C), and 3.15 g (1/2 mole eq) of iodine in 40 ml of DMSO was heated on a water-bath for 3 hr. The mixture was cooled and transferred into a separatory funnel. An aq. sodium thiosulfate (5%, 200 ml) and 100 ml of benzene were added and the mixture was thoroughly shaken. The aq. layer was extracted with additional 100 ml of benzene. The combined extracts were washed successively with 200 ml of 5% sodium thiosulfate and water, and filtered through a small amount of absorbent cotton. After the solvent was evaporated, methanol was added to triturate the residue. The insoluble matter (elemental sulfur) was filtered off and the filtrate was concentrated to give a viscous residue (4.2 g). It was chromatographed over silicic acid (eluent: benzene). The fraction of *Rf* 0.41 (TLC, eluent: benzene) was collected and concentrated *in vacuo*. The residual crude product (0.78 g) was purified by crystallization from ligroin to separate 0.4 g (9.5%) of methyl 2,4-bis (*p*-chlorophenyl)allophanate as fine needles, mp 138~139°C. *Anal.* Found: C, 53.02; H, 3.60; N, 8.18. Calcd. for $C_{15}H_{12}O_3N_2Cl_2$: C, 53.12; H, 3.57; N, 8.26%.

Preparation of an authentic sample of methyl 2,4-bis (p-chlorophenyl)allophanate

The title compound was prepared according to the method³⁾ of Kogon from 0.93 g of methyl *p*-chlorocarbanilate and 0.85 g of *p*-chlorophenyl isocyanate in 100 ml of ligroin in the presence of 0.4 g of cobalt 2-ethylhexanoate (abt. 12% Co; Wako Pure Chem. Ind. Ltd.). After chromatographic purification and crystallization from ligroin, 0.51 g (30%) of pure methyl 2,4-bis-(*p*-chlorophenyl) allophanate, mp 138~139°C, was obtained in fine needles. The spectral data were perfectly identical with those of the by-product. No mixture melting point depression was observed.

Preparation of methyl p-chlorocarbanilate

The title compound was prepared in the usual way from 12.8 g (0.1 mole) of *p*-chloroaniline and 4.7 g (0.05 mole) of methyl chloroformate in 100 ml of benzene. The crude product, on recrystallization from ligroin, gave 7.7 g (83.0%) of pure methyl *p*-chlorocarbanilate, mp 114°C (lit.⁷⁾ 115°C). MS: *m/e* 187 (44%), 185 (M^+, 100%), 153(42%), 140(46%), 125 (32%), 99(29%), 90(17%), 63(20%), 59(24%).

Treatment of methyl p-chlorocarbanilate with iodine in DMSO

A solution of 1.0 g of methyl *p*-chlorocarbanilate and 0.63 g of iodine in 10 ml of DMSO was treated under the same conditions as in the case of *O*-methyl *p*-chlorothiocarbanilate. After the reaction mixture had been worked up, 0.995 g of white crystals, mp 113°C, was obtained. No compounds except the starting carbanilate could be detected on the thin-layer chromatogram of the crystals. The IR spectrum of the crystals in chloroform was perfectly superimposable on that of the starting material.

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