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Abstract

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SYNTHESIS AND PROPERTIES OF MIXED ESTERS OF PHENYLIMIDODITHIOCARBONIC ACID

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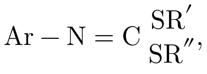
The synthesis of new derivatives of carbon disulfide is of considerable interest in connection with the search for highly effective plant-protection agents. Representatives of these substances are used as fungicides, insecticides, and even herbicides. Such a broad spectrum of action is to some extent connected with the structural and compositional features of the molecule in various forms of carbon disulfide derivatives. The area of compounds under consideration is limited by the valence structure of carbon $\equiv C <$, just as the area of organophosphorus insecticides is defined by the structure

$$= P-;$$

nevertheless, it may be asserted that the possibilities for the synthesis of new compounds here are still far from exhausted, and that the dependence of properties on the composition and structure of the molecule has not been sufficiently clarified.

It is known that an unsymmetrical structure of the molecule, and its greater dipole moment, often correspond to comparatively higher insecticidal activity.

Therefore, first of all, a series of mixed diesters of phenylimidodithiocarbonic acid was synthesized and characterized. These esters correspond to the general formula:



$$\mathrm{Ar-N=C}\genfrac{}{}{0pt}{}{\mathrm{SR'}}{\mathrm{SR''}},$$

where R′ and R″ are different alkyl radicals, and Ar is a phenyl or aryl residue of varying complexity. They had not been described in the literature.

One accessible route for the synthesis of such esters may proceed by the alkylation reaction of the corresponding dithiourethanes. The most probable should be considered the alkylation of one of the tautomeric forms of the dithiourethanes ($^{1-3}$), namely form II, which is highly characteristic of aromaticly substituted compounds:

$$C_6H_5\underset{\mathrm{I}}{NH \cdot} CS - SR' \rightleftarrows C_6H_5 \cdot \underset{\mathrm{II}}{N} = C \genfrac{}{}{0pt}{}{SR'}{SH} \qquad (1)$$

As our experiments showed, the equilibrium state of both tautomeric forms (I and II) was shifted toward the formation of phenyl-

imidodithiocarbonic acid (II′) in the presence of an equivalent amount of alkali:

$$C_6H_5NH{-}CS{\cdot}SR' + NaOH \rightarrow H_2O + C_6H_5{-}N{=}C \genfrac{}{}{0pt}{}{SR'}{SNa} \qquad (2)$$

II′

The formation of the thioether salt (II′) is accompanied by migration of the hydrogen of the amide nitrogen and its transition into the ionic state. The thioether salts of alkali metals are comparatively stable; they are readily soluble in alcoholic and aqueous media. From these solutions, on oxidation with iodine, diphenyldialkylisothiuram disulfides were isolated; their formation is possible only from the imide form (II) of dithiourethane, according to the equation:

$$2\,C_6H_5NC(SR')SNa + J_2 \rightarrow 2NaJ + \left(C_6H_5N{=}C \genfrac{}{}{0pt}{}{SR'}{S}\right)_2 \qquad (3)$$

In contrast to this, dithiourethanes in form I are insoluble in water and apparently do not directly take part in alkylation reactions.

Alkylation of thioether salts in alcoholic media makes it possible to obtain mixed esters of a specified composition in high yields and under mild reaction conditions. The latter circumstance is of essential importance, since the starting dithiourethanes are often thermally insufficiently stable. The synthesis was carried out in an alcoholic solution of the dithiourethane containing the calculated amount of alkali or sodium alcoholate in accordance with equations (2) and (4):

$$C_6H_5{-}N{=}C \genfrac{}{}{0pt}{}{SR'}{SNa} + X{-}R'' \rightarrow C_6H_5{-}N{=}C \genfrac{}{}{0pt}{}{SR'}{SR''} + NaX \qquad (4)$$

where X is a halogen (Cl, Br, or J). Thus, all components of the reaction were taken in equimolecular ratio. Usually, after introduction of the alkyl halide, the reaction mixture was heated and stirred. The reaction mixture was then kept in a closed state. On dilution with water, a layer of oil separated, which was removed; the alcohol and the precipitate of the alkali-metal halide passed into the aqueous layer. After repeated washing with water and drying of the oily substances, isolation of each ester in the individual state was carried out by distillation in vacuo. Thus, under comparable conditions, the alkylation reactions of the methyl ester of phenyldithiocarbamic acid with ethyl iodide, allyl bromide or chloride, *n*-propyl bromide, and isopropyl—

Table 1

No.	Formula	*M*	B.p., °C, mm Hg	d_{25}^{25}	n_D^{25}	MR_D, calc.	MR_D, found	Yield, %
1	$\genfrac{}{}{0pt}{}{C_2H_5S}{CH_3S}{>}C{=}NC_6H_5$	211,34	176/17	1,134	1,6185	64,79	64,80	78
2	$\genfrac{}{}{0pt}{}{C_3H_5S}{CH_3S}{>}C{=}NC_6H_5$	223,35	185/17	1,131	1,6223	68,94	69,53	67
3	$\genfrac{}{}{0pt}{}{n{-}C_3H_7S}{CH_3S}{>}C{=}NC_6H_5$	225,37	183/17	1,111	1,6065	69,41	69,70	84
4	$\genfrac{}{}{0pt}{}{u{-}C_3H_7S}{CH_3S}{>}C{=}NC_6H_5$	225,37	175/17	1,153	1,6040	69,41	67,25	56
5	$\genfrac{}{}{0pt}{}{n{-}C_4H_9S}{CH_3S}{>}C{=}NC_6H_5$	239,40	194/17	1,087	1,5953	74,02	75,01	81
6	$\genfrac{}{}{0pt}{}{u{-}C_4H_9S}{CH_3S}{>}C{=}NC_6H_5$	239,40	186/17	1,091	1,5950	74,02	74,62	73

···with bromoethyl, *n*-butyl bromide, and isobutyl bromide. The constants of the substances obtained and their yields are given in Table 1. Under the same conditions, the alkylation of the ethyl and allyl esters of phenyldithiocarbamic acid with methyl iodide was studied. In this case the yields of compounds No. 1 and No. 2 (see Table 1) practically coincide with the yields obtained by the first variant of the synthesis. The mixed diesters of phenylimidodithiocarbonic acid are colorless, transparent, viscous liquids with a characteristic odor. They are readily soluble in ether, benzene, and other organic solvents, but insoluble in water. Their hydrolysis proceeds with difficulty upon prolonged heating with water. On boiling with acidic solutions of salts of heavy metals, they form characteristic precipitates of mercaptides.

Experimental Part

1. Ethyl methyl diester of phenylimidodithiocarbonic acid. In a three-necked flask of 150 ml capacity, fitted with a stirrer, reflux condenser, thermometer, and dropping funnel, 40 ml of methanol were placed and 2.5 g of metallic sodium were dissolved in it, followed by 20 g of the methyl ester of phenyldithiocarbamic acid. To the colorless solution, with stirring and external cooling by water, 17 g of ethyl iodide were gradually added. The solution, at first transparent, gradually deposited a suspension and then a precipitate of sodium iodide. At the same time self-heating occurred. After an hour and a half, the cooling was replaced by heating for two hours at 40–50° on a water bath. During this time a layer of oil separated. The reaction mixture was left in a closed state. After two days, the oil obtained was repeatedly washed with water until a negative test for halogen ion was obtained, and, after drying over sodium sulfate, 21.8 g of product were obtained. The substance distilled over from 175 to 177° at a pressure of 17 mm of mercury. Collected: 18.1 g (yield 78.7%).

$C_{10}H_{13}NS_2$. Found, %: N 6.68; 6.71; S 30.12; 30.25
Calculated, %: N 6.63; S 30.34.

The specific gravity, refractive index, and molecular refraction are given in Table 1.

Other mixed diesters were obtained by an analogous method.

2. Allyl methyl diester of phenylimidodithiocarbonic acid. To a solution of 2.76 g of sodium in 44 ml of methanol were successively added 22 g of methyl phenyldithiocarbamate and 14.5 g of allyl bromide. 24.1 g of an oily liquid were obtained, which distilled over from 184 to 186° (17 mm). Yield: 17.9 g, or 66.8%.

$C_{11}H_{13}NS_2$. Found, %: N 6.23; 6.44; S 28.52; 28.59
Calculated, %: N 6.27; S 28.71.

3. *n*-Propyl methyl diester of phenylimidodithiocarbonic acid. From a solution of 3.5 g of sodium in 56 ml of methanol, with 28 g of the methyl ester of phenyldithiocarbamic acid and 18.8 g of *n*-propyl bromide, 29.5 g of substance were obtained, distilling over from 182 to 184° (17 mm). Yield of diester: 28.3 g, or 83.7%.

$C_{11}H_{15}NS_2$. Found, %: N 6.51; 6.42; S 28.31; 28.38
Calculated, %: N 6.23; S 28.45.

4. Isopropyl methyl diester of phenylimidodithiocarbonic acid. From a solution of 2.52 g of sodium, 20 g of methyl phenyldithiocarbamate in 40 ml of anhydrous methanol, and 13.5 g of isopropyl bromide, 19.8 g of substance were obtained. Distillation from 173.5 to 175.5° (17 mm) gave a yield of diester of 13.6 g, or 56.2%.

$C_{11}H_{15}NS_2$. Found, %: N 6.43; 6.39; S 28.52; 28.39
Calculated, %: N 6.23; S 28.45.

5. ***n*-Butyl methyl diester of phenylimidodithiocarbonic acid.** From 18 g of the methyl ester of phenyldithiocarbamic acid and 13.5 g of *n*-butyl bromide in a solution of 2.26 g of sodium and 36 g of methanol, 23.2 g of substance was isolated. After distillation at 193 to 195° (17 mm), the yield of the diester was 19 g, or 81.2%.

Found, %: N 5.91; 5.74; S 26.65; 26.48
$C_{12}H_{17}NS_2$. Calculated, %: N 5.86; S 26.78.

6. **Isobutyl methyl diester of phenylimidodithiocarbonic acid.** From a solution of 3.02 g of sodium, 24 g of the methyl ester of phenyldithiocarbamic acid, and 18 g of isobutyl bromide in 48 ml of anhydrous methanol, 27.7 g of substance was obtained, distilling from 184.5 to 187.5° (17 mm). Yield 22.8 g, or 73.1%.

Found, %: N 6.11; 6.03; S 26.51; 26.45
$C_{12}H_{17}NS_2$. Calculated, %: N 5.86; S 26.78.

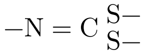
Insecticidal properties of mixed diesters

Tests carried out during the last two years at the Institute of Zoology and Phytopathology of the Ministry of Agriculture showed that the mixed diesters of phenylimidodithiocarbonic acid possess high fumigation activity against various pests of agricultural crops, including those living in the soil. We give some average data from a series of experiments.

Thus, after a 3-hour exposure at a concentration of 15 mg/l, the percentage mortality of the granary weevil on the 2nd and 7th days increases in the following order: carbon disulfide (0–57); dichloroethane (0–65); diester No. 6 (see Table 1) (0–87); diester No. 3 (52–94); diester No. 4 (25–100*); diester No. 2 (50–100); diester No. 5 (66–100); diester No. 1 (100–100); this indicates their high fumigation activity in comparison with that of carbon disulfide and dichloroethane.

The nematocidal activity against the potato nematode (*Heterodera rostochiensis*) of diester No. 1 is higher than that of the ethyl ester of dimethyldithiocarbamic acid. After the dust of diester No. 1 was introduced into soil heavily infested with nematodes, at the rate of 30 g/m^2 of active ingredient, cysts on the potato roots and emergence of larvae were completely absent, whereas for the standard the number of cysts on the roots was 1 and the emergence of larvae was 31.

Thus, high insecticidal activity is observed in certain derivatives of carbon disulfide that contain in their molecule the group



$$-N=C\begin{matrix}S-\\S-\end{matrix}$$

The phytocidal action in the droplet-liquid state is exhibited by all members of the series of mixed diesters of phenylimidodithiocarbonic acid, which was established by the formation, at the point of application on the green surface of the leaf, of a localized burn. For diester No. 2, an expansion of the burn zone was observed owing to penetration of the substance into the plant:

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* For all diesters the active concentration was 1.5–2.0 mg/l.

Note: Figure translations are in progress. See original paper for figures.