REATIONS OF POLYHALOPYRIDINES.

1. REACTION OF THE ISOMERIC TETRACHLOROCYANO-
PYRIDINES AND PENTACHLOROPYRIDINE WITH SALTS
OF N,N-DIALKYLDITHIOCARBAMIC ACID AND
THE X-RAY STRUCTURAL INVESTIGATION
OF THE REACTION PRODUCTS

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The route of the reaction of the isomeric tetrachloro-2-, -3-, -4-cyanopyridines and of pentachloropyridine with sodium N,N-dialkyldithiocarbamates is determined by the structure of the initial polyhalopyridine. Either substitution of chlorine atoms on the pyridine ring by a dithiocarbamate fragment occurs or subsequent intramolecular processes take place leading to a derivative of 1,3-dithiolo[4,5-c]pyridine or of bis-1,3-dithiolo[4,5-b:4',5'-e]pyridine.

Polychloropyridines are compounds reactive in nucleophilic substitution reactions and are widely used as intermediates in the synthesis of a whole range of agrochemical preparations [1]. Nucleophilic mono- and disubstitution at positions 2 and 4 of the pyridine ring are the most characteristic [2]. Highly reactive reagents [3] or the action of high temperature [4] is required for polysubstitution but reaction may also be accelerated significantly by intramolecular processes [5].

In this paper we report a new method of synthesizing the 1,3-dithiolo[4,5-c]pyridine and bis-1,3-dithiolo[4,5-b:4',5'-e]pyridine systems based on the intramolecular reaction of N,N-dialkyldithiocarbamates of polychloropyridines. Compounds containing these systems possess high biological activity [6].

The reaction of pentachloropyridine (Ia) and of the isomeric tetrachloro-3-, -4-, and -2-cyanopyridines (Ib-d) with sodium N,N-dialkyldithiocarbamates in acetone has been studied under various temperature regimens. It has been shown that in the first case a regioselective nucleophilic monosubstitution occurs at position 4 of the pyridine ring (IIa, c) but the formation of two substances, viz., the products of mono- (IIb) and disubstitution (III), is characteristic of compound (Ic). Compounds (IIa-c) and (III) are stable and are not subject to further conversion on heating (boiling in various solvents).

On reacting sodium dimethyldithiocarbamate with tetrachloro-4-cyanopyridine (Ic) a 2,6-disubstitution occurs with the formation of compound (IV), which on heating is converted in turn into the intermediate (V) and then into compound (VI). Sequential conversions of compound (IV) into (V), and of (V) into (VI) support the scheme given below (see following page).
Fig. 1 Structure of 2,3,5,6-tetrachloro-4-pyridyl N,N-dibenzyldithiocarbamate (IIc).

Fig. 2. Structure of 2,3,6-trichloro-5-cyano-4-pyridyl N,N-dimethyldithiocarbamate (IIb).

Unlike the previous cases compound (Id) is readily converted by hydrates of sodium dialkyldithiocarbamates into 4,7 dichloro-6-cyano-1,3-dithiolo[4,5-c]pyrid-2-one (VII). The composition of the amine portion of the dithiocarbamate does not exert a significant effect on the yield of (VII) or on the reaction conditions (see scheme on following page).

The structures of the compounds synthesized were confirmed by a set of physicochemical methods including x-ray structural analysis and NMR. The structures of the (IIc) and (IIb) molecules are shown in Figs. 1 and 2 respectively. Bond lengths and valence angles are given in the single Table 1 for convenience in making comparisons.