REACTIONS OF TRICHLOROMETHYLDIALKYLAMINES WITH 2-METHYLBENZOTHIAZOLE, 2-METHYLBENZOXAZOLE, AND THEIR SALTS*

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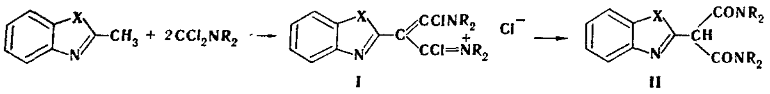
Trichloromethyldialkylamines react with nitrogen heterocyclic compounds containing an active methyl group or with their salts to give 2-heteryl-1,1,3,3-tetrachloro-1,3-bis(dialkylamino) propanes, which are hydrolyzed by water to heterylmalonamides. Cyanine dyes containing a dimethylcarbamoyl group in the α position relative to the polymethine chain were obtained.

Trichloromethyldialkylamines react relatively readily with various types of compounds containing active methylene groups [2]. Čiernik [3] recently demonstrated that dichloromethyldimethylamine reacts with nitrogen-containing heterocyclic bases with a methyl group in the 2 and 4 positions and that the final products may be starting compounds for the synthesis of dyes.

We have found that trichloromethyldialkylamines also react with nitrogen heterocyclic bases containing active methyl groups – 2-methylbenzothiazole, 2-methylbenzoxazole, and their hydrochlorides – to give I.



I, II X=S, O; R=CH_3, C_2H_5

We were unable to isolate these compounds in the individual state, inasmuch as they hydrolyze in air, and the reaction is accompanied by considerable resinification. Hydrolysis of I with aqueous potassium carbonate solution gives N,N,N',N'-tetraalkylamides of heterylmalonic acids (II). (See scheme on the following page.)

2,3-Dimethylbenzothiazolium p-toluenesulfonate reacts with trichloromethyldimethylamine in a 1 : 2 ratio to give 2-(β-dimethylamino-β-chlorovinyl)-3-methylbenzothiazolium chloride (III). Treatment of III with water and sodium perchlorate gives 2-(dimethylacetamido)-3-methylbenzothiazolium perchlorate (IV).

Quaternary salt IV undergoes condensation with 1,3,3-trimethyl-2-formylmethyleneindoline to give trimethylidynecyanine V (λ_{max} 537 nm), while styryl VI (λ_{max} 510 nm) is formed by the action of p-dimethylaminobenzaldehyde.

As expected [4], the introduction of a dimethylcarbamoyl group into the α position of the polymethine chain induces a small hypsochromic shift of the absorption maxima in the dyes (λ_{max} 542 and 530 nm [5, 6], respectively, for dyes V and VI, which do not contain a dimethylcarbamoyl group).

EXPERIMENTAL

Benzothiazolylmalonic Acid N,N,N',N'-Tetramethyldiamide. A 0.05-mole sample of 2-methylbenzothiazole was added to a solution of 0.1 mole of trichloromethyldimethylamine in 70 ml of dichloroethane,

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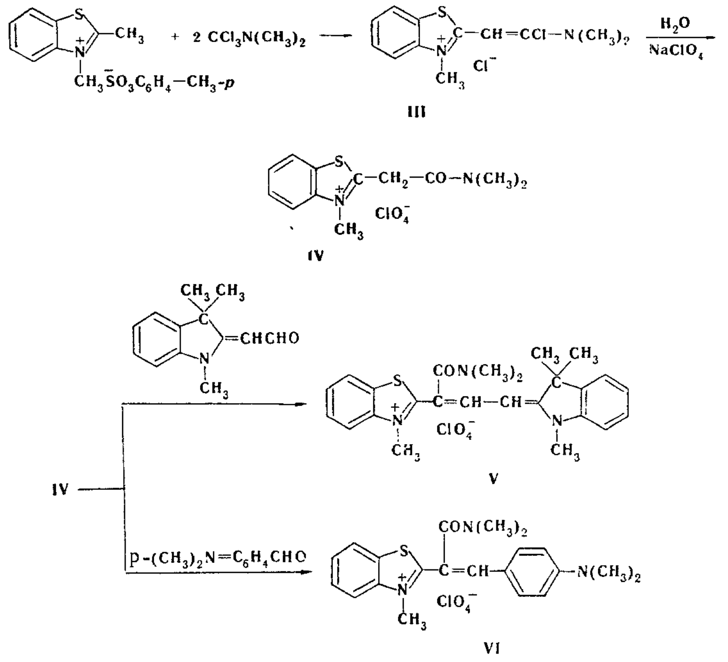

and the mixture was refluxed for 4 h (until hydrogen chloride evolution ceased). The dichloroethane was removed by vacuum distillation, and the residue (a viscous mass) was added to 30 ml of a 30% potassium carbonate solution. The resulting oil was extracted with 30 ml of benzene, the benzene was removed by distillation, and the residue was vacuum distilled to give 2-methylbenzothiazole (35%) with bp 90° (10-12 mm). The residue was a mixture of crystals and oils. It was washed successively with acetone and water and dried. The yield of amide II, with mp 130-131° (from ethanol), was 35%. Found: S 11.2%. $C_{14}H_{21}N_3O_2S$. Calculated: S 11.0%.

Benzothiazolylmalonic Acid N,N,N',N'-Tetraethyldiamide. This compound was similarly obtained from 0.05 mole of trichloromethyldiethylamine and 0.02 mole of 2-methylbenzothiazole hydrochloride. The yield of this amide, with mp 125-126° (from ether), was 20%. Found: N 12.1%. $C_{18}H_{25}N_2O_2S$. Calculated: N 12.1%.

2-(Dimethylacetamido)-3-methylbenzothiazolium Perchlorate (IV). A 0.03-mole sample of 2,3-dimethylbenzothiazolium p-toluenesulfonate was added with stirring to a solution of 0.06 mole of trichloromethyldimethylamine in 50 ml of methylene chloride, after which the mixture was refluxed for 5 h. The resulting precipitate was separated and mixed with 10 ml of a 30% potassium carbonate solution. The aqueous solution was evaporated on a water bath, and the precipitated crystals were removed by filtration and dissolved in alcohol. A saturated aqueous solution of sodium perchlorate was added to the alcohol solution, and the precipitated IV was separated and dried to give 11% of a product with mp 190-191° (from ethanol). Found: S 9.5%. $C_{12}H_{14}ClN_2O_5S$. Calculated: S 9.3%. p-Toluenesulfonyl chloride (25%) was obtained from the first filtrate after removal of the methylene chloride by distillation.

Benzoxazolylmalonic Acid N,N,N',N'-Tetraethyldiamide. A mixture of 0.03 mole of 2-methylbenzoxazole hydrochloride, 0.06 mole of trichloromethyldiethylamine, and 50 ml of dichloroethane was refluxed and stirred for 5 h. The dichloroethane was then removed by vacuum distillation, and the residue was mixed with 20 ml of a 30% potassium carbonate solution. The organic layer was separated and mixed with 20 ml of ether, and the ether mixture was refluxed for 30 min. The solution was cooled, and the precipitated crystals were removed by filtration to give 18% of the amide with mp 126° (from ether). Found: N 12.9%. $C_{18}H_{25}N_3O_3$. Calculated: N 12.7%.

2-[1-Dimethylcarbamoyl-3-(1,3,3-trimethyl-2-indolinylidene)propenyl]-3-methylbenzothiazolium Perchlorate (V). A mixture of 0.2 mmole of perchlorate IV and 0.2 mmole of 1,3,3-trimethyl-2-formylmethyleneindoline was refluxed in 5 ml of acetic anhydride. The solution was cooled, and ether was added to precipitate the dimethylidynecyanine (V). A product with mp 234° (from ethanol) and λ_{max} 537 nm, was obtained in 77% yield. Found: S 5.9%. $C_{25}H_{28}ClN_3O_5S$. Calculated: S 6.2%.

2-(1-Dimethylcarbamoyl-2-(p-dimethylaminophenyl)-2-ethenyl]-3-methylbenzothiazolium Perchlorate (VI). A mixture of 0.3 mmole of IV and 0.3 mmole of p-dimethyl-aminobenzaldehyde was refluxed in a solution of 5 ml of acetic anhydride for 1 h. The crystals were removed by filtration to give a product with mp 189° (from ethanol) and λ_{max} 510 nm in 90% yield. Found: S 7.2%. $C_{25}H_{24}ClN_2O_5S$. Calculated: S 7.1%.

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