XLIII.—*The Picriminothiocarbonic Esters.*

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A SHORT preliminary note on the picriminothiocarbonic esters has already appeared (*Camb. Univ. Rep.*, 1902, 32, 23, 549), but in view of the publication of a paper dealing with the action of acidic thiocyanates on alcohol (Dixon, *Trans.*, 1902, 81, 168), it seems advisable to publish the work in full. The experiments deal entirely with the action of picryl chloride on thiocyanates and alcohols. The reaction is a remarkable one, and takes place, in most cases, with ease, the products being beautifully crystallised bodies. The first case investigated was the reaction of picryl chloride on ammonium thiocyanate in ethyl alcohol solution.

Ethyl Picryl Picriminothiocarbonate.

Ten grams of picryl chloride dissolved in hot absolute alcohol were mixed with a hot alcoholic solution of 3·2 grams of ammonium thiocyanate. Precipitation immediately took place, and a yellow oil sank to the bottom and later solidified to a yellow solid. The whole mass was filtered on cooling, washed with alcohol, water, and lastly with alcohol again. The yield was 10 grams, and the mother liquor contained free hydrochloric acid. On crystallisation from ethyl alcohol and glacial acetic acid (1:1), 8 grams of the pure substance were obtained. It forms golden-yellow, compact prisms melting at 138°. It is insoluble in water or ether, and sparingly soluble in alcohol, but easily so in benzene or acetic acid. Analysis gave the following results:

0·2049 gave 0·2566 CO₂ and 0·0352 H₂O. C = 34·15; H = 1·91.

0·2152 „ 34·6 c.c. moist nitrogen at 17° and 755 mm. N = 18·53.

0·2107 „ 34·8 c.c. „ 20° „ 759 mm. N = 18·87.

0·2001 „ 0·0910 BaSO₄. S = 6·24.

C₁₅H₉O₁₃N₇S requires C = 34·16; H = 1·71; N = 18·59; S = 6·07 per cent.

The substance probably contains two picryl groups. On boiling it with very concentrated aqueous potash, ammonia was evolved and ethyl alcohol was found in the distillate; it must thus contain an ethoxy-group. This was shown quantitatively by the Zeisel method. The whole apparatus was kept at 85–90°, and an additional bulb containing dilute copper sulphate was interposed to retain the sulphur-

etted hydrogen formed during the reaction. The result shows that one ethoxy-group is present.

0.2575 gave 0.1107 AgI. $\text{OEt} = 8.23$.

$\text{C}_{13}\text{H}_4\text{O}_{12}\text{N}_7\text{S}\cdot\text{OEt}$ requires $\text{OEt} = 8.54$ per cent.

The substance is only oxidised with difficulty, and is recovered practically unchanged after boiling for two hours with a 10 per cent. solution of chromic acid in glacial acetic acid. If boiled for two hours with a mixture of glacial acetic acid and hydrochloric acid, hydrolysis takes place, and after dilution and decolorisation of the resulting liquor, picramide is deposited on cooling in bluish-yellow crystals melting at 188° . The yield of picramide was about 25 per cent. of the ethoxy-compound taken.

These facts gave a clue to the structure of the substance. It must contain two picryl groups, one of which is attached to a nitrogen atom, forming a picrimino-group, $\text{Pi}\cdot\text{N}^{\cdot}$, the other being attached to the sulphur atom. The reaction is doubtless connected with the remarkable property which picryl derivatives possess of forming additive compounds, since neither phenyl thiocyanate nor phenylthiocarbimide reacts with picryl chloride and alcohol. The formation is explained by the equations, picryl thiocarbimide, $\text{Pi}\cdot\text{N}^{\cdot}\text{C}:\text{S}$, being regarded as the first product:

The alternative explanation, involving the formation of a *pseudo*-thiourethane, $\text{Pi}\cdot\text{N}^{\cdot}\text{C}(\text{OEt})\cdot\text{SH}$, by the addition of a mol. of the alcohol to the thiocarbimide, is rendered improbable in view of the fact that picryl chloride is not decomposed by boiling with water or alcohol. Much less likely is it, then, to act on a SH-group. On the other hand, ethyl chlorocarbonate is easily decomposed by water or alcohol. This renders it very probable that the ethyl picrimino-chlorothiocabonate—which in addition contains two strongly acidic picryl groups—will easily react with alcohols.

The hydrolysis to picramide is easily understood from the following equation:

When hydrolysed with potash, the picramide first formed is decomposed by the alkali into ammonia and potassium picrate.

The action of picryl chloride and ammonium thiocyanate has been tried on other alcohols with similar results. It was somewhat unexpected, however, to discover two isomeric methoxy-compounds

easily transformable one to the other. The more stable form, the " β -isomeride," is obtained in the usual way.

Methyl Picryl Picriminothiocarbonates.

Ten grams of picryl chloride were dissolved in hot methyl alcohol and mixed with a solution of 3.2 grams of ammonium thiocyanate in methyl alcohol; immediate precipitation took place, and on cooling the crumbling mass was filtered off. The yield amounted to 9.2 grams, and the mother liquor contained free hydrochloric acid. The crude product may be crystallised from a mixture of glacial acetic acid and methyl alcohol (1:1); it is then obtained in fine, fluffy needles, melting constantly at 169° , which are insoluble in water or ether, slightly soluble in alcohol, and easily so in benzene or glacial acetic acid. Analysis confirmed the view that the substance was *methyl picryl picriminothiocarbonate*:

0.2027 gave 0.2437 CO_2 and 0.0319 H_2O . $\text{C} = 32.78$; $\text{H} = 1.75$.

0.2534 „ 40.8 c.c. moist nitrogen at 14° and 769 mm. $\text{N} = 19.18$.

0.2245 „ 0.1004 BaSO_4 . $\text{S} = 6.14$.

$\text{C}_{14}\text{H}_7\text{O}_{18}\text{N}_7\text{S}$ requires $\text{C} = 32.75$; $\text{H} = 1.37$; $\text{N} = 19.10$; $\text{S} = 6.24$ per cent.

The methoxy-group was determined by the Zeisel method in the usual manner, except for the addition to the apparatus of a bulb of dilute copper sulphate solution to absorb the sulphuretted hydrogen formed. The result indicates that one methoxy-group is present in the molecule:

0.2679 gave 0.1322 AgI . $\text{OCH}_3 = 6.51$.

$\text{C}_{13}\text{H}_4\text{O}_{12}\text{N}_7\text{S} \cdot \text{OCH}_3$ requires $\text{OCH}_3 = 6.04$ per cent.

The α -isomeride which was first discovered is prepared from the β -compound; for this purpose, 5 grams of the β -isomeride are crystallised from 140 c.c. of a mixture of ethyl alcohol and acetic acid (1:1). The crystallisation is carefully watched. Minute, compact prisms are deposited at first. Immediately the β -isomeride begins to separate in fluffy aggregates, the mother liquor is poured off from the crystals, which are washed with alcohol and then with ether. The yield of the α -isomeride obtained by this means amounts to 1.2 grams. The substance consists of compact, golden-yellow prisms, so like the ethoxy-compound in appearance as to be almost indistinguishable from it. It melts at 158° , is insoluble in water or ether, sparingly soluble in alcohol, and easily so in benzene or acetic acid. It is perfectly stable in the dry state and may be preserved for months unchanged, but in contact with solvents it is slowly but completely converted to the β -isomeride. The analyses indicate that the substance is *methyl picryl picriminothiocarbonate*:

0.2042 gave 0.2471 CO₂ and 0.0291 H₂O. C = 33.01 ; H = 1.58.

0.2035 „ 0.2439 CO₂ „ 0.0302 H₂O. C = 32.68 ; H = 1.65.

0.1536 „ 25.3 c.c. moist nitrogen at 18° and 767 mm. N = 19.21.

0.2160 „ 0.0912 BaSO₄. S = 5.80.

C₁₄H₇O₁₃N₇S requires C = 32.75 ; H = 1.37 ; N = 19.10 ; S = 6.24 per cent.

The presence of a methoxy-group was shown quantitatively by the Zeisel method :

0.2106 gave 0.0962 AgI. OCH₃ = 6.03.

C₁₃H₄O₁₂N₇S·OCH₃ requires OCH₃ = 6.04 per cent.

That the two substances are not polymeric was shown by the identity of the molecular weights in benzene solution. Owing to the slight solubility in cold benzene, only one reading could be taken in each determination.

α-Isomeride :

0.1693 gram lowered the freezing point of 21.67 grams of benzene by 0.075°. Mol. wt. = 510.

β-Isomeride :

0.0823 gram lowered the freezing point of 16.73 grams of benzene by 0.048°. Mol. wt. = 502.

The calculated mol. wt. is 513.

These are probably not desmotropic forms, because they are perfectly stable in the dry state. On the other hand, the ease with which they can be transformed, one to the other, in solution shows that they are very probably stereoisomerides of the oxime type. Two isomeric forms are possible, represented by the expressions :

The fact that isomerides of the other homologues have not been prepared is not surprising when the limited means applicable in the particular case of these substances is considered. When melted, they decompose, and even when kept at about 130° for some time they are in most cases completely charred, owing to the high percentage of nitro-groups contained in them.

n-Propyl Picryl Picriminothiocarbonate.

2.5 grams of picryl chloride are dissolved in 10 c.c. of *n*-propyl alcohol and mixed with a hot solution of 0.8 gram of ammonium thiocyanate in 10 c.c. of *n*-propyl alcohol. A flocculent precipitate at once forms. On cooling, this is filtered from the mother liquor—which

is again found to be acid—washed with alcohol, water, and lastly with alcohol again. The yield amounted to 2 grams. The product was crystallised from alcohol and acetic acid (1:1). The pure substance melts at 151–152°. It forms lustrous, golden-yellow leaflets, insoluble in water or ether, sparingly soluble in alcohol, fairly easily so in benzene, and easily so in acetic acid. Analysis indicated that the substance was *propyl picryl picriminothiocarbonate*:

0.1861 gave 0.2408 C_2O and 0.0360 H_2O . $C = 35.29$; $H = 2.15$.

0.2323 „ 36.4 moist nitrogen at 16° and 745 mm. $N = 17.89$.

0.2424 „ 0.1049 $BaSO_4$. $S = 5.94$.

$C_{16}H_{11}O_{13}N_7S$ requires $C = 35.49$; $H = 2.03$; $N = 18.11$; $S = 5.92$ percent.

isoButyl Picryl Picriminothiocarbonate.

2.5 grams of picryl chloride dissolved in 10 c.c. of *isobutyl* alcohol are mixed with a hot solution of 0.8 gram of ammonium thiocyanate in 20 c.c. of *isobutyl* alcohol. The mass becomes almost solid from the deposition of minute plates. On cooling, the precipitate is filtered off from the acid mother liquor. The yield amounts to 2.4 grams. After washing with alcohol, water, &c., the product is crystallised from a mixture of acetic acid and alcohol (1:1). The new substance melts at 173° and consists of golden-yellow, lustrous leaflets, which are insoluble in water or ether, but easily soluble in acetic acid. Analysis showed it to be *isobutyl picryl picriminothiocarbonate*:

0.2288 gave 0.3080 CO_2 and 0.0448 H_2O . $C = 36.72$; $H = 2.17$.

0.1971 „ 29.9 c.c. moist nitrogen at 16° and 765 mm. $N = 17.80$.

0.2194 „ 33.4 „ „ 15° „ 760 mm. $N = 17.83$.

$C_{17}H_{13}O_{13}N_7S$ requires $C = 36.77$; $H = 2.34$; $N = 17.66$ per cent.

Similar compounds have been obtained with *isopropyl*, *allyl*, and *benzyl* alcohols, and the investigation of these is being proceeded with. The ease with which this reaction takes place makes it probable that it will be of use for the characterisation and identification of the lower alcohols; in most cases, it takes place easily, even when the alcohol is diluted with benzene.

In conclusion, I have to thank Dr. G. S. Turpin for his kindness in permitting me to start this work, which is the result of an observation made by him in 1891.

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