LXV.—*Picryl Derivatives of Urethanes and Thiourethanes.*

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IN a paper by one of the authors (Trans., 1902, 81, 436), it was shown that picryl chloride reacted readily with ammonium thiocyanate and alcohols, with the production of the alkyl picryl picriminothiocarbonates.

The formation of these compounds was explained by the interaction of an intermediate additive compound of picrylthiocarbimide and picryl chloride with the alcohols. Another explanation of the reaction which, at the time, seemed less probable, when viewed in the light of other researches on the thiocyanates and the work in this paper, seems, however, to be the true one. It was shown by Dixon (Trans., 1899, 75, 375) that the acidic thiocarbimides, $R \cdot CO \cdot N : C : S$, easily react with the alcohols to form additive compounds, the thiourethanes. When the potassium salts of these substances are treated with alkyl halides, they behave as the tautomeric *pseudothiourethanes*, $R \cdot CO \cdot N : C(SH) \cdot OX$, and pass into acyl iminothiocarbonic esters, $R \cdot CO \cdot N : C(SX') \cdot OX$, the

second alkyl group becoming attached to the sulphur. This explains the formation of the picriminothiocarbonic esters from picryl chloride, thiocyanate, and alcohols. The first formed picrylthiocarbimide unites with the alcohol to form the thiourethane, the tautomeric form of which is again acted on by the picryl chloride, with the production of the picriminothiocarbonate and the liberation of hydrochloric acid—the second molecule of picryl chloride taking the place of the alkyl halide in the foregoing example. According to this explanation, the formation of ethyl picryl picriminothiocarbonate is represented by the following reactions.

The results obtained with *isopropyl*, *tert.*-butyl, and amyl alcohols are described in the present paper.

The reaction with *isopropyl* alcohol is not so complete as in the previous cases. There was a considerable amount of unchanged picryl chloride, and the yield was less than usual. This is probably due to the spatial influence of the two methyl groups in preventing the formation of the thiourethane. With *tert.*-butyl alcohol, this effect is very marked. Even after boiling for an hour under a reflux apparatus, most of the picryl chloride was unchanged, and the sole products isolated were picryl sulphide and picryl thiocyanate, both in rather small quantity. This behaviour of *tert.*-butyl alcohol is very similar to that noticed by Lewis (Proc., 1903, 19, 41) in the case of the reaction between *tert.*-butyl chloride and sodium phenoxide, which gives rise to *tert.*-butylphenol and not the phenyl *tert.*-butyl ether. The amyl compound was obtained by boiling together lead thiocyanate, picryl chloride, benzene, and amyl alcohol. The reaction proceeded normally and gave a moderate yield. Attempts were made to produce the capryl compound, but without result. The bulk of the picryl chloride remained unchanged and very small quantities of picryl thiocyanate and picryl sulphide were isolated.

It seemed of interest to try whether cyanate would react in an analogous manner. The results obtained are quite in accordance with the foregoing explanation of the thiocyanate reaction.

When potassium cyanate is boiled with an alcoholic solution of picryl chloride, two substances are formed.

(1) A substance sparingly soluble in alcohol, having a high melting point, and resembling the picriminothiocarbonates except in colour, which proved to be ethyl picryl picriminocarbonate, $\text{PiN}\cdot\text{C}(\text{OPi})\cdot\text{OEt}$.

(2) A much more fusible substance, moderately easily soluble in alcohol, which was found to be the urethane, $\text{PiN}\cdot\text{C}(\text{OH})\cdot\text{OEt}$.

The ethoxy-group was estimated by Zeisel's method, and the substance was shown to give picramide on hydrolysis. Moreover, it was identical with the compound, melting at 144°, obtained by Romburgh (*Rec. trav. chim.*, 1891, 10, 138) on nitrating phenylurethane. This leaves no doubt as to its constitution.

The formation of these substances is represented by the following equations : $\text{Pi}\cdot\text{N}\cdot\text{C}\cdot\text{O} + \text{EtOH} = \text{Pi}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{OEt} \\ \text{OH} \end{smallmatrix}$; $\text{Pi}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{OEt} \\ \text{OH} \end{smallmatrix} + \text{Pi}\cdot\text{Cl} = \text{Pi}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{OEt} \\ \text{OPi} \end{smallmatrix} + \text{HCl}$.

Methyl alcohol under similar conditions also yielded two compounds, the red potassium picrylmethylurethane, $\text{Pi}\cdot\text{N}\cdot\text{C}(\text{OK})\cdot\text{O}\cdot\text{CH}_3$ (soluble with difficulty in alcohol), and also the free urethane; the former was transformed into the urethane by crystallisation from a mixture of acetic acid and alcohol. This again was identical with Roxburgh's compound melting at 192° (*loc. cit.*).

In addition to these compounds, similar urethanes were prepared from *n*-propyl, *isopropyl*, *isobutyl*, and *amyl* alcohols. *tert*-Butyl alcohol again behaved abnormally. Picramide was obtained in comparatively large quantities and there was some unchanged picryl chloride, but no urethane was isolated.

The behaviour of these picrylurethanes in solution is rather interesting. The substances themselves and their petroleum, chloroform, and carbon tetrachloride solutions are colourless, but when dissolved in water or alcohol the solutions are intensely yellow. One drop of dilute acid makes the weak solutions colourless, and in the case of water the substance is at once "salted out." When carbon dioxide is passed into a weak alcoholic solution, the colour gradually changes, but is not completely destroyed. On boiling and cooling, the yellow colour again becomes more intense. These marked colour changes, combined with the fact that the substances are excessively weak acids, and therefore not appreciably ionised, seem to indicate that the substances are tautomeric, the solid substances and the petroleum solutions probably containing the urethane proper, $\text{Pi}\cdot\text{NH}\cdot\text{CO}\cdot\text{OX}$, whilst other solvents, such as water, alcohol, ether, contain the *pseudourethane*, $\text{Pi}\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{OX}$.

The production of these urethanes as intermediate compounds between picrylcarbimide and the iminocarbonates confirms the foregoing view with regard to the analogous reaction in the case of thiocyanates.

EXPERIMENTAL.

isoPropyl Picryl Picriminothiocarbonate.

Five grams of picryl chloride and 1.6 grams of ammonium thiocyanate were separately dissolved in the smallest possible amount of

isopropyl alcohol and the hot solutions mixed. Precipitation took place immediately with violent frothing, and an oil which separated became solid on cooling and was collected, washed with water, and then with alcohol; it was then extracted with 20 c.c. of boiling alcohol and the residue crystallised from 40 c.c. of a mixture of alcohol and acetic acids (1 : 2), filtering from a small quantity of insoluble impurity, the yield of partially purified product being 2.5 grams. After a second crystallisation, it was obtained pure.

0.2299 gave 0.3016 CO_2 and 0.0430 H_2O . $\text{C} = 35.78$; $\text{H} = 2.08$.

0.2064 „ 31.2 c.c. moist nitrogen at 16.5° and 770 mm. $\text{N} = 17.83$.

$\text{C}_{16}\text{H}_{11}\text{O}_{13}\text{N}_7\text{S}$ requires $\text{C} = 35.49$; $\text{H} = 2.03$; $\text{N} = 18.11$ per cent.

The substance forms light yellow, glistening plates melting at 147° , which are insoluble in water, somewhat sparingly so in alcohol and in ether, and easily dissolve in benzene or glacial acetic acid.

Amyl Picryl Picriminothiocarbonate.

Ten grams of picryl chloride were mixed with 14 grams of lead thiocyanate and boiled on the water-bath for one hour with a mixture of 80 c.c. of amyl alcohol and 120 c.c. of benzene. The solution was filtered from lead chloride and excess of thiocyanate and the solid residue extracted with benzene, the extracts being mixed with the filtered solution of the product, and the whole liquid then diluted and distilled in steam. The residual solid was washed with alcohol and dried, the yield of the crude product being 9.5 grams. After crystallisation from acetic acid and alcohol (1 : 1), 6 grams of pure substance were obtained.

0.1795 gave 0.2497 CO_2 and 0.0450 H_2O . $\text{C} = 37.93$; $\text{H} = 2.78$.

0.1871 „ 27.0 c.c. moist nitrogen at 17° and 772 mm. $\text{N} = 17.03$.

$\text{C}_{18}\text{H}_{15}\text{O}_{13}\text{N}_7\text{S}$ requires $\text{C} = 37.97$; $\text{H} = 2.64$; $\text{N} = 17.23$ per cent.

The compound consists of minute, light yellow, glistening plates melting constantly at 138.5° ; the melting point remaining unchanged after several crystallisations; it is insoluble in water, rather sparingly soluble in alcohol or ether, easily so in acetic acid or benzene.

Picryl Thiocyanate.

Fifteen grams of picryl chloride and 4.8 grams of ammonium thiocyanate were dissolved separately in the least possible quantity of *tert.*-butyl alcohol and the hot solutions mixed; the precipitate which immediately separates was found to consist, for the most part, of unchanged picryl chloride. It was boiled with water, washed with

alcohol, and then extracted carefully with about 30 c.c. of alcohol and acetic acid (1 : 1). As soon as the melted substance gave place to a light, powdery material, it was filtered off rapidly. The residual crude product, which melted at 221°, was a mixture of picryl sulphide and picryl thiocyanate and weighed 3.5 grams. This mixture was now extracted repeatedly with small quantities of alcohol and acetic acid, until the extracts yielded no crystals on cooling. The residue was purified by dissolution in excess of benzyl alcohol and reprecipitation by alcohol. It weighed one gram, and consisted of an almost white powder with a faint yellow tinge, insoluble in water or ether and practically insoluble in acetic acid, benzene, or alcohol. It dissolves readily in acetone or benzyl alcohol, separating from the latter in microscopic, needle-shaped crystals. The substance does not melt, but darkens at about 285°.

0.1607 gave 0.1837 CO₂ and 0.0162 H₂O. C = 31.18; H = 1.12.

0.1741 „ 31.0 c.c. moist nitrogen at 20° and 760 mm. N = 20.61.

0.2145 „ 0.1902 BaSO₄. S = 12.18.

C₇H₂O₆N₄S requires C = 31.11; H = 0.74; N = 20.74; S = 11.85 per cent.

The crystals obtained by extracting the crude product were found to be picryl sulphide; when recrystallised, they melted at 226°, and did not depress the melting point of the substance prepared according to Willgerodt's method. It was rather remarkable that, when boiled with caustic potash, picryl sulphide yielded ammonia and also alkali nitrite. The production of ammonia was found to be due to the interaction of nitrite and potassium picrate formed in the reaction, as these substances, when boiled with potash, were found to yield ammonia.

Picrylmethylurethane.

Nine grams of picryl chloride and 3 grams of potassium cyanate were mixed with 90 c.c. of methyl alcohol, heated on the water-bath for 3 hours in a reflux apparatus, and filtered hot; the filtrate, on cooling, deposited yellow crystals, which were washed with water and recrystallised from ethyl alcohol and acetic acid (2 : 1). The long needles obtained, which were almost colourless, melted at 192° and seemed to be identical with Romburgh's compound (*loc. cit.*).

The red residue was insoluble in alcohol, but dissolved easily in glacial acetic acid, changing colour, and depositing the same colourless crystals, the yield being 7 grams. As it was important to demonstrate that this really was the picrylurethane, it was analysed and the methoxy-group determined by Hewitt's modification of Zeisel's method (*Trans.*, 1902, 81, 319).

0.2004 gave 0.2476 CO_2 and 0.0400 H_2O . $\text{C} = 33.71$; $\text{H} = 2.18$.

0.1909 „ 33.8 c.c. moist nitrogen at 25° and 750 mm. $\text{N} = 19.75$.

$\text{C}_8\text{H}_6\text{O}_8\text{N}_4$ requires $\text{C} = 33.57$; $\text{H} = 2.09$; $\text{N} = 19.58$ per cent.

0.2236 gave 0.1671 AgI . $\text{OMe} = 9.86$.

$\text{C}_8\text{H}_6\text{O}_8\text{N}_4$ requires $\text{OMe} = 10.08$ per cent.

Hydrolysis of the substance by hydrochloric or acetic acid yielded picramide melting at 188° .

The red residue, which was insoluble in alcohol, was recrystallised from water; it was found to contain potassium, the analysis corresponding with the mono-potassium salt described by Romburgh (*loc. cit.*).

0.3595 gave 0.0975 K_2SO_4 . $\text{K} = 12.16$.

$\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$ requires $\text{K} = 12.04$ per cent.

This salt was partially hydrolysed by water, and was distinctly alkaline to litmus.

The conductivity of the methylurethane was determined. Owing to the small solubility at the ordinary temperature, the indications were too small to be of value. It was therefore taken in saturated solution at 75.6° . This gave $\mu_{580} = 4.33$, whilst a solution of the potassium salt in a saturated solution of the methyl compound under the same conditions gave $\mu_{110} = 207.2$. This indicates that the acid is weaker than carbonic acid, giving $\mu_\infty = 590$, and $\text{K} = 0.0793$.

Ethyl Picryl Picriminocarbonate and Picrylethylurethane.

Nine grams of picryl chloride were mixed with 3 grams of potassium cyanate and 70 c.c. of absolute alcohol, the whole being boiled in a reflux apparatus for 3 hours and then filtered while hot. The residue, which amounted to 0.6 gram, was washed with alcohol and water in order to remove potassium cyanate; it was practically insoluble in alcohol, ether, or water; easily soluble in benzene, and also in glacial acetic acid, from which it crystallised in minute, heavy, almost colourless crystals melting at 222° .

0.1972 gave 0.2560 CO_2 and 0.0342 H_2O . $\text{C} = 35.40$; $\text{H} = 1.93$.

$\text{C}_{15}\text{H}_9\text{O}_{14}\text{N}_7$ requires $\text{C} = 35.23$; $\text{H} = 1.76$ per cent.

The hot filtrate deposited the picrylethylurethane (*loc. cit.*) either in plates or needles, which were shown to be dimorphous, both forms of crystals melting at 147° ; the yield was 6 grams. The needles separate from dilute alcoholic solution, and the plates from concentrated solutions. As with the other urethanes, the aqueous and alcoholic solutions are intensely coloured, but are decolorised by the addition of one drop of dilute acid.

0.2076 gave 0.2764 CO_2 and 0.0521 H_2O . $\text{C} = 36.30$; $\text{H} = 2.79$.

0.1694 „ 26.8 c.c. moist nitrogen at 14° and 770 mm. $\text{N} = 18.46$.

$\text{C}_9\text{H}_8\text{O}_8\text{N}_4$ requires $\text{C} = 36.00$; $\text{H} = 2.66$; $\text{N} = 18.66$ per cent.

0.1399 gave 0.1101 AgI. $\text{OEt} = 15.19$.

$\text{C}_9\text{H}_8\text{O}_8\text{N}_4$ requires $\text{OEt} = 15.00$ per cent.

Picryl-n-propylurethane.

Five grams of picryl chloride, 1.6 grams of potassium cyanate, and 17 c.c. of *n*-propyl alcohol with 20 c.c. of benzene were boiled together for 3 hours. The benzene and *n*-propyl alcohol were distilled off in steam, and the solid residue recrystallised from a mixture of ethyl alcohol and glacial acetic acid (3:1). Well-defined, almost colourless needles melting at 139° were obtained, the yield being 3 grams. The substance is slightly soluble in water or light petroleum, moderately so in alcohol or ether, easily so in benzene, glacial acetic acid, or alcohol.

0.3356 gave 0.4682 CO_2 and 0.0979 H_2O . $\text{C} = 38.06$; $\text{H} = 3.24$.

0.2245 „ 33.8 c.c. moist nitrogen at 15° and 760.5 mm. $\text{N} = 17.63$.

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{N}_4$ requires $\text{C} = 38.23$; $\text{H} = 3.19$; $\text{N} = 17.83$ per cent.

Picrylisopropylurethane.

A mixture of 2.5 grams of picryl chloride, 0.8 gram of potassium cyanate, and 20 c.c. of isopropyl alcohol was boiled for two hours in a reflux apparatus and then cooled; the crystalline product, which was collected, washed with hot water and alcohol, weighed 2.2 grams. When crystallised from a mixture of acetic acid and alcohol (1:1) and then from dilute acetic acid, it forms long, white, lustrous needles melting at 177.5° , which are slightly soluble in hot water, forming a yellow solution. The substance is easily soluble in acetic acid and in benzene, moderately so in alcohol or ether, somewhat sparingly so in light petroleum. When boiled with caustic potash, ammonia is evolved. If to the yellow aqueous solution a drop of dilute acid is added, it is immediately decolorised and the substance is salted out.

0.1907 gave 0.2673 CO_2 and 0.0574 H_2O . $\text{C} = 38.22$; $\text{H} = 3.34$.

0.2070 „ 31.6 c.c. moist nitrogen at 16.5° and 754 mm. $\text{N} = 17.62$.

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{N}_4$ requires $\text{C} = 38.22$; $\text{H} = 3.19$; $\text{N} = 17.84$ per cent.

Picrylisobutylurethane.

Five grams of picryl chloride and 1.6 grams of potassium cyanate were boiled on the water-bath for two hours with a mixture of 20

c.c. of *isobutyl* alcohol and 20 c.c. of benzene. The mixture was then distilled in steam and the residue crystallised from a mixture of alcohol and acetic acid. On cooling, the solution became nearly solid. The product when collected and washed with alcohol, weighed 2·3 grams; it was crystallised from dilute acetic acid, and separated in nearly colourless, lustrous needles with a faint yellow tinge (m. p. 134°). It is moderately soluble in hot water, giving a yellow solution, and dissolves easily in acetic acid, alcohol, or benzene. It is moderately soluble in light petroleum or ether. When boiled with caustic potash solution, ammonia and *isobutyl* alcohol are evolved, but the substance may be crystallised practically unchanged from sodium carbonate solution. The solutions in water, alcohol, ether, acetic acid, and benzene are all somewhat yellow, particularly the aqueous and alcoholic solutions. The solution in light petroleum, however, is quite colourless. On the other hand, the addition of one drop of hydrochloric or acetic acid to the alcoholic or aqueous solution removes the colour. Carbon dioxide also produces this effect, but the colour returns on expelling the gas.

0·2396 gave 0·3530 CO₂ and 0·0842 H₂O. C = 40·18; H = 3·90.

0·1955 „ 29·0 c.c. moist nitrogen at 15° and 752 mm. N = 17·20.

C₁₁H₁₂O₈N₄ requires C = 40·25; H = 3·66; N = 17·08 per cent.

Picrylamylurethane.

Five grams of picryl chloride and 1·6 grams of potassium cyanate were mixed with 40 c.c. of amyl alcohol and heated on the water-bath for 12 hours; on cooling, the whole mass solidified. The excess of amyl alcohol was removed by distillation in steam and the residue crystallised several times from a mixture of ethyl alcohol and glacial acetic acid (1:1) and finally from ethyl alcohol alone; the yield was 2·5 grams. The needle-shaped, somewhat yellow crystals, which melted at 131°, were moderately soluble in hot water or light petroleum and easily so in alcohol, benzene, ether, or acetic acid. As in the case of the other urethanes, the solution in light petroleum is colourless, whilst the other solutions are more or less yellow, particularly the aqueous and alcoholic solutions.

0·2689 gave 0·4139 CO₂ and 0·1088 H₂O. C = 42·11; H = 4·49.

0·1964 „ 28·4 c.c. moist nitrogen at 22° and 754·3 mm. N = 16·25.

C₁₂H₁₄O₈N₄ requires C = 42·11; H = 4·09; N = 16·38 per cent.

tert.-Butyl alcohol behaved abnormally, as before; when treated in the usual way, picramide alone was obtained in somewhat large quantity.

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