The Thiocyanation of Retene

ERLING FREDERIKSEN and SV. LIISBERG

Leo Pharmaceutical Products Copenhagen, Denmark

Only few cases of thiocyanation of polynuclear hydrocarbons are described in the literature¹, and no examples of thiocyanation of simple phenanthrene derivatives are known.

Since the bromination and the chlorination of retene (1-methyl-7-isopropylphenanthrene) always lead to very complex mixtures of halogen derivatives², and since it is known that the thiocyanation reaction, although very similar to halogenation, is more specific³, we have found it interesting to investigate the thiocyanation of this hydrocarbon.

In our experiments the thiocyanation was carried out using solutions of free thiocyanogen in different solvents under various conditions, and we found that when chloroform, carbon tetrachloride, carbon disulphide, glacial acetic acid and ether were used, no thiocyanation took place. We found, however, that dry benzene was a suitable solvent, and that illumination from a mercury lamp was of great importance. The optimal temperature was found to be about 40° C.

The main reaction product was obtained in a yield of about 70 % of the theoretical as white crystals, and the analysis showed it to be a mono thiocyanoretene.

When treated with ethanol in the presence of sodium ethoxide it gave a thiourethane, while morpholine gave a thiourea derivative and hydrazines substituted thiosemicarbazides. All these reactions show that the reaction product is an *iso* thiocyanoretene.

When the compound was heated with a mixture of ethanol and conc. hydrochloric acid, hydrogen thiocyanate was liberated, and a white crystalline precipitate was formed. This new compound which was free from nitrogen and sulphur, was sparingly soluble in most organic solvents, and the melting point was rather high (245° C).

Analysis showed it to be a hydrocarbon, and we found that the molecular weight was about three times the molecular weight of retene.

This result is similar to that of Wood and Fieser working with thiocyanomethyl cholanthrene¹.

From this reaction it was natural to assume that an unsaturated hydrocarbon was formed as an intermediate product, but we did not succeed in isolating such a compound from the reaction mixture, and we did not find it possible to depolymerize the trimeric hydrocarbon into a dehydroretene by heating since all attempts in that direction led to the formation of retene and a mixture of unknown hydrocarbons.

It was possible, however, to prepare a highly unsaturated hydrocarbon (m.p. 171.5-172.4° C) by treating the *iso* thiocyanoretene with a tertiary amine.

This hydrocarbon gave on heating with alcoholic hydrochloric acid the trimeric hydrocarbon mentioned above, and it added bromine instantaneously to give a dibromoretene. The corresponding iodine derivative could not be made under similar conditions.

Hydrogenation in presence of a palladium catalyst at room temperature and ordinary pressure converted it quantitatively to retene.

From these facts we conclude that the new hydrocarbon is 1-methyl-7-isopropenyl-retene (Formula II). III is then a possible formulation of the trimeric hydrocarbon.

These results are not in harmony with the results of Talvitie and Laakso⁴ who claim that 1-methyl-7-isopropenyl-retene is formed by dehydrogenation of retene at 500° C in the presence of a catalyst, because Talvitie and Laakso's compound melts at 163-164° C and adds iodine very easily to form a diiodide. The dibromide made from Talvitie and Laakso's hydrocarbon melts at 116-117° C⁵ while our dibromide melts at 123-125° C.

The retenyl thiourethane could be converted into the corresponding retenylamine by treatment with alcoholic potassium hydroxide, but the yield was poor and large amounts of the trimeric hydrocarbon were formed. We found it impossible to acetylate the amine, and no hydroxyretene was formed by treatment with sodium nitrite in acid solution. In both cases the trimeric retene derivative was formed.

This instability of the retenyl amine and the corresponding hydroxyretene indicates that the substituents are attached to the 7¹-carbon atom.

All attempts to introduce thiocyanogen in the nucleus of retene and phenanthrene failed.

EXPERIMENTAL

7¹-*iso*-Thiocyano-1-methyl-7-isopropylphenanthrene

To 250 ml of dry benzene solution of free thiocyanogen prepared from 120 g of lead thiocyanate and a little less than the calculated amount of bromine ⁶ was added a solution of 24 g of retene in 100 ml of dry benzene.

The mixture was illuminated from a mercury lamp for 12 hours at 38–40° C. The precipitated polymeric thiocyanogen was then filtered off and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in 300 ml of boiling ethanol, and the solution was treated three times with 1 g of carbon. The resulting colourless solution was then cooled to 0–5° C and allowed to stand at this temperature for 1 hour.

The white crystalline precipitate of *iso* thiocyanoretene was filtered off and dried in the air. Yield 20 g (67 % of the theoretical). M. p. 107.5–108° C (corr.).

$C_{19}H_{17}NS$ (291.2)	Calc.	C 78.5	H 5.91	N 4.82	S 11.0
	Found	» 78.8	» 5.86	» 4.80	» 10.99

N-Retenyl-(7¹)-thiocarbamyl-morpholine

10 g of *iso*-thiocyanoretene was dissolved in 100 ml of dry acetone and 5 g of morpholine was added. After standing at room temperature for a few minutes a white crystalline precipitate was formed.

The compound which is sparingly soluble in most organic solvents was purified by washing with boiling acetone. Yield 9.8 g (76 % of the theoretical). M. p. 163°–164°, 5 C (corr.).

$C_{23}H_{26}ON_2S$ (378.3)	Calc.	C 73.0	H 6.96	N 7.41	S 8.46
	Found	» 72.8	» 6.92	» 7.43	» 8.40

4-Retenyl-(7¹)-thiosemicarbazide

1 g of *iso*-thiocyanoretene was refluxed with a solution of 1 g of hydrazine-hydrate in 8 ml of ethanol for a few minutes. The retenylthiosemicarbazide crystallized from the boiling solution as white needles, which were almost insoluble in most organic solvents. Yield 0.9 g (81 % of the theoretical). M. p. 188–89° C (corr.)

C ₁₉ H ₂₁ N ₃ S (323.2)	Calc.	C 71.0	H 6.23	N 12.91	S 9.72
	Found	» 71.2	» 6.56	» 12.80	» 9.69

N-Retenyl-(7¹)-thiourethane

3 g of *iso*-thiocyanoretene was dissolved in a solution of 1.5 g of sodium in 50 ml of abs. ethanol by gentle heating for a few minutes. The thiourethane separated as white crystals from the hot solution. Recrystallization from acetone. Yield 3.2 g (92 % of the theoretical). M. p. 177–78° C (corr.).

C ₂₁ H ₂₃ ONS (337.2)	Calc.	C 74.8	H 7.41	N 4.16	S 9.50
	Found	» 74.5	» 7.19	» 4.18	» 9.47

7¹-Retenylamine

10 g of retenylurethane was refluxed with a solution of 5 g potassium hydroxide in 200 ml of 90 % ethanol for 24 hours. The solution was then diluted with 600 ml of water and extracted four times with 50 ml of ether. By addition of alcoholic hydrochloric acid the retenylamine hydrochloride was precipitated. Recrystallization from water. Yield 1.8 g (19 % of the theoretical). M. p. 277–80° C (corr.).

C ₁₈ H ₂₀ NCl (285.7)	Calc.	N 4.89
	Found	» 4.88

0.1 g of the hydrochloride was dissolved in boiling water and the solution was made alkaline with sodium hydroxide. The retenylamine separated as white crystals. Recrystallization from ethanol. Yield 0.07 g (81 % of the theoretical). M. p. 120–121° C (corr.).

C ₁₈ H ₁₉ N (249.2)	Calc.	C 87.1	H 7.63	N 5.62
	Found	» 86.6	» 7.55	» 5.61

"Trimeric retene" (C₁₈H₁₆)₃

2 g of *iso*-thiocyanoretene was dissolved in 15 ml of boiling ethanol and 1.5 ml of conc. hydrochloric acid was added. The mixture was refluxed for five hours. A white crystalline precipitate was formed during the refluxing. Yield 1.3 g (81 % of the theoretical). M. p. 244–45° C (corr.).

(C ₁₈ H ₁₆) ₃	Calc.	C 93.1	H 6.89	M. wt. 696
	Found	» 93.0	» 6.98	» » (acc. to Rast) 662

1-Methyl-7-isopropenylphenanthrene

10 g of *iso*-thiocyanoretene was refluxed with 20 ml of dimethylaniline for 3 hours. The reaction mixture was poured into dilute hydrochloric acid and the precipitate was dissolved in ether.

The ethereal solution was dried with calcium chloride, and after filtration evaporated to dryness. The residue was recrystallized three times from ethanol. Yield 3.5 g (44 % of the theoretical; a large amount of the trimeric hydrocarbon was formed). M. p. 171.5–172.4° C (corr.).

$C_{18}H_{16}$ (232.2)	Calc.	C 93.5	H 6.92
	Found	» 93.13	» 7.03

1-Methyl-7¹, 7²-dibromo-7-isopropylphenanthrene

0.23 g of 1-methyl-7-isopropenylphenanthrene was dissolved in 10 ml of dry ether at 0° C. To this solution was added drop by drop a solution of 0.16 g of bromine in 5 ml of ether. The mixture was then evaporated to dryness *in vacuo*. Yield 0.3 g (72 % of the theoretical). M. p. (after recrystallization from ether) 123–125° C (corr.). The compound is unstable, and hydrobromic acid is easily liberated.

$C_{18}H_{16}Br_2$ (392.0)	Calc.	C 55.0	H 4.14	Br 40.8
	Found	» 55.7	» 4.11	» 39.0

Hydrogenation of 1-methyl-7-isopropenylphenanthrene

0.1 g of the dehydroretene was dissolved in 50 ml of dry ether and a suspension of 50 mg palladium catalyst was added. Hydrogen was bubbled through the solution for four hours at room temperature. After filtration and evaporation to dryness the residue was recrystallized from ethanol. Yield 0.09 g. M. p. 97–98° C (corr.). The melting point was not depressed when the product was mixed with retene (melting point 97–98° C).

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