CCCLXXXIII.—*Studies in the Penthian Series. Part II. Penthian-4-one.*

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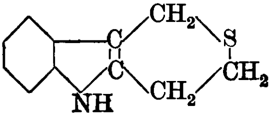
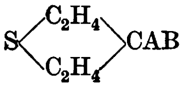
PENTHIAN-4-ONE (J., 1927, 194) has been further investigated.

The *phenyl-*, p-*bromophenyl-*, and p-*nitrophenyl-hydrazones* of the ketone have been prepared. The first two were readily converted by means of the Fischer indole transformation into *penthienoindole* (I) and 8-*bromopenthienoindole* respectively.

(I.)





(II.)

Oxidation of the ketone by hydrogen peroxide yields a crystalline sulphone, *penthianone dioxide*, but a sulphoxide was not isolated nor could a sulphilimine be obtained.

Substances of the general formula (II) are of special importance because of the stereoisomerism to be expected among their derivatives: several compounds of this type have been prepared. For instance, penthianone is converted through its crystalline *cyanohydrin* into *penthian-4-ol-4-carboxylic acid* (A = OH, B = CO_2H); and by means of the appropriate organo-magnesium compounds into 4-*phenylpenthian-4-ol* (A = OH, B = Ph) and the corresponding 4-*benzylpenthian-4-ol*, each of which yields a *sulphone* and a *phenylurethane*. Other derivatives of these substances are of special stereochemical interest and form the subject of the following paper.

EXPERIMENTAL.

Preparation of Penthianone.—Ethyl thiodipropionate was made from β-chloropropionic acid (overall yield, 76%) and converted into the ketone (average yield, 22%).

Penthianone is monoclinic with $a : b : c = 1{\cdot}9196 : 1 : 1{\cdot}8781$ and $\beta = 96° 10'$. Measurements of eight selected crystals (from ether) gave the following mean angular co-ordinates :—

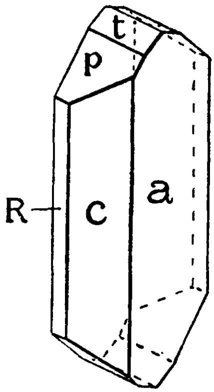
	$a(100)$.	$c(001)$.	$r(\bar{1}01)$.	$p(\bar{1}11)$.	$t(\bar{1}21)$.
ϕ	0° 0′	*83° 50′	*131° 13′	131°	131°
ρ	90° 0′	90° 0′	90° 0′	*35° 18′	19° 25′

The typical habit is shown in Fig. 1 (which has been drawn with the *b* axis vertical), *a* and *c* being large. No marked cleavage was detected.

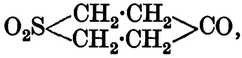
A straight extinction is found on the face *a*. In convergent polarised light the crystals are biaxial and an optic axis emerges almost perpendicular to *a*, the optic axial plane being coincident with *b*(010).

Action of Hydrogen Peroxide on Penthianone.—By oxidation in glacial acetic acid solution with hydrogen peroxide (1 equiv.) a substance (presumably the sulphoxide) of m. p. 113° (from toluene) was obtained on one occasion, but the preparation could not be repeated.

FIG. 1.



Penthianone.

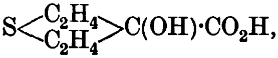
Addition of excess (2½ mols.) of hydrogen peroxide to the ketone in a little acetic acid and evaporation of the latter, a crystal of sodium acetate being added to remove mineral acid, yielded the *sulphone*,  $O_2S<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CO$, which crystallised from toluene in colourless needles, m. p. 170° (Found: C, 40·5; H, 5·4. $C_5H_8O_3S$ requires C, 40·6; H, 5·4%).

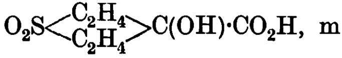
Phenylhydrazones and their Conversion into Penthienoindoles.—The ketone reacted rapidly with aryl hydrazines in ethyl-alcoholic solution. The *phenylhydrazone*, best obtained pure by using a deficit of the reagent, separated from ethyl alcohol in pale buff, granular crystals, m. p. 119° (Found: N, 13·8. $C_{11}H_{14}N_2S$ requires N, 13·6%). It was converted by boiling for 2 hours in glacial acetic acid solution into *penthienoindole* (I), which crystallised from light petroleum (b. p. 120°) in pale yellow, granular crystals, m. p. 157° (Found: N, 7·5. $C_{11}H_{11}NS$ requires N, 7·4%). This substance was not affected by 2 hours' boiling with acetic anhydride.

*Penthianone-*p*-nitrophenylhydrazone* crystallised from ethyl alcohol in orange needles, m. p. 156° (Found: N, 16·7. $C_{11}H_{13}O_2N_3S$ requires N, 16·7%). It was recovered unchanged after 2 hours' boiling in glacial acetic acid.

The p-*bromophenylhydrazone* formed brown needles, m. p. 144°, from ethyl alcohol (Found: N, 10·1; Br, 28·25. $C_{11}H_{13}N_2BrS$ requires N, 10·1; Br, 28·1%). Heated in boiling glacial acetic acid for ½ hour, it yielded 8-*bromopenthienoindole*, which crystallised from light petroleum (b. p. 120°) in pale yellow needles, m. p. 162° (depressed to 112—130° by addition of the hydrazone) (Found: Br, 29·85. $C_{11}H_{10}NBrS$ requires Br, 29·85%).

Conversion of Penthianone into Penthianolcarboxylic Acid.—The ketone (5 g.) was dissolved in water, with the addition of sodium bisulphite (from 5·68 g. of sodium sulphite dissolved in water and saturated with sulphur dioxide), and cooled in ice and a solution of potassium cyanide (2·8 g.) was added. If the solutions were concentrated, part of the cyanohydrin was precipitated. After 1½ hours the product was removed in ether and the extract was washed with a little bisulphite solution and then with brine. The ethereal solution, dried over sodium sulphate, was evaporated; the residue crystallised on standing. *Penthianone cyanohydrin*, thus obtained, crystallised from light petroleum in long needles, m. p. 63° (Found: N, 9·7. C_6H_9ONS requires N, 9·8%). It was sparingly soluble in water or ligroin but readily soluble in most other solvents.

The cyanohydrin was heated on the steam-bath with concentrated hydrochloric acid for 6 hours and the solution was diluted and extracted with ether. The product from the dried extract soon solidified and was then recrystallised from benzene. *Penthianolcarboxylic acid*,  $S<^{C_2H_4}_{C_2H_4}>C(OH)\cdot CO_2H$, was thus obtained in silvery plates, m. p. 133°, fairly readily soluble in water and sparingly soluble in cold benzene or light petroleum. The acid was prepared in larger quantities by hydrolysing the crude cyanohydrin (yield, 80% from the ketone) (Found: S, 19·6; equiv., 161·5. $C_6H_{10}O_3S$ requires S, 19·75%; equiv., 162).

The acid was oxidised by boiling it for ½ hour with hydrogen peroxide (2½ mols.) in glacial acetic acid; the acetic acid was then removed in steam, and the solution evaporated. The solid residue was the *sulphone*,  $O_2S<^{C_2H_4}_{C_2H_4}>C(OH)\cdot CO_2H$, m. p. 208°, which crystallised from ethyl acetate in fine needles (Found: S, 16·4. $C_6H_{10}O_5S$ requires S, 16·5%).

Action of Magnesium Phenyl Bromide on the Ketone.—The ketone (15 g. in 240 c.c. of ether) was added gradually to an ice-cooled and mechanically stirred solution of magnesium phenyl bromide (from 3·9 g. of magnesium and 24 g. of bromobenzene in 180 c.c. of ether). To the mixture, after standing over-night, ice and a slight excess of hydrochloric acid were added. The ethereal layer with further ethereal extracts was dried over potassium carbonate and evaporated. The product solidified on standing and was recrystallised from light petroleum. 4-*Phenylpenthian*-4-*ol* (II; A = OH, B = Ph), thus obtained, formed colourless granular crystals, m. p. 78° (yield, 15 g. or 58%) (Found: C, 68·0; H, 7·25. $C_{11}H_{14}OS$ requires C, 68·0; H, 7·3%). It was converted by heating at 100° for 2 hours with phenylcarbimide into the *phenylurethane* (II; A = O·CO·NHPh, B = Ph), which crystallised from xylene in colourless needles, m. p. 186·5—188° (Found: N, 4·8. $C_{18}H_{19}O_2NS$

requires N, 4·5%). Heated in glacial acetic acid with hydrogen peroxide (2½ mols.), phenylpenthianol was converted into the *sulphone*, which separated from ethyl acetate in colourless prismatic needles, m. p. 197° (Found : C, 58·1 ; H, 6·2. $C_{11}H_{14}O_3S$ requires C, 58·4 ; H, 6·2%).

Action of Magnesium Benzyl Chloride on the Ketone.—Penthianone (15 g. in 240 c.c. of ether) was added gradually to an ice-cooled and well-stirred solution of magnesium benzyl chloride (from 19·2 g. of benzyl chloride, 3·9 g. of magnesium, and 180 c.c. of ether). The solid product and the ethereal solution were separately decomposed with ice and acid. The material recovered from the ethereal layer was contaminated with dibenzyl and did not readily yield the pure benzylpenthianol. That from the solid addition compound often remained as an oil until it was cooled in the ice-chest and inoculated with a crystal of the pure product. 4-*Benzylpenthian*-4-*ol* (II ; $A = OH$, $B = CH_2Ph$), thus obtained (yield, 26%), crystallised from light petroleum in colourless needles, m. p. 51° (Found : C, 68·8 ; H, 7·5. $C_{12}H_{16}OS$ requires C, 69·2 ; H, 7·7%). It yielded a *phenylurethane*, which crystallised from xylene in colourless needles, m. p. 194—195·5° (Found : N, 4·5. $C_{19}H_{21}O_2NS$ requires N, 4·3%), and by oxidation with hydrogen peroxide in excess a *sulphone*, which was obtained from ethyl acetate in elongated plates, m. p. 152·5° (Found : C, 59·9 ; H, 6·6. $C_{12}H_{16}O_3S$ requires C, 60·0 ; H, 6·7%).

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