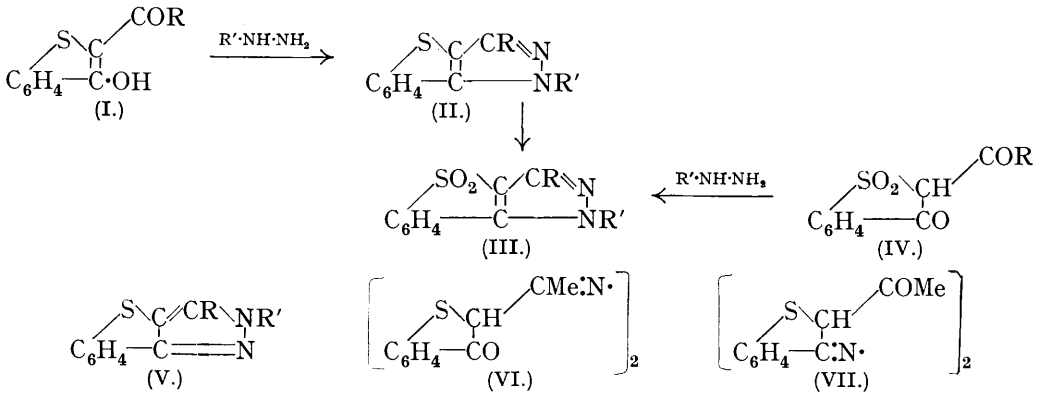
104. *Thionaphthenopyrazoles.*

By W. J. Barry and E. W. McClelland.

3-Hydroxythionaphthens with an acyl group in the 2-position (I) react with hydrazines in acid media to give pyrazoles; *e.g.*, 3-hydroxy-2-acetyl-1-thionaphthen reacts with phenylhydrazine and with *p*-bromophenylhydrazine to give the *thionaphthenopyrazoles* (II : R = Me, R′ = Ph; R = Me, R′ = *p*-C_6H_4Br). Similarily, 3-hydroxy-2-benzoyl-1-thionaphthen (I; R = Ph) reacts with phenylhydrazine to give the *diphenylthionaphthenopyrazole* (II; R = R′ = Ph). The formation of the pyrazoles takes place by way of the corresponding hydrazones, since they are also obtained from the appropriate hydrazones by heating with alcoholic sulphuric acid. 3-Hydroxy-2-acetyl-1-thionaphthen condenses with hydrazine hydrochloride in alcohol to give a small amount of the pyrazole (II; R = Me, R′ = H) and a red substance of high melting point which is presumably a *bis-compound* (VI or VII). When the condensation is effected in acetic acid, the pyrazole alone is obtained.

Oxidation of the sulphur to the sulphone condition in many cyclic systems appears to restrain the tendency to enolisation (compare McClelland, J., 1929, 1588; Cohen and Smiles, J., 1930, 406; Levi and Smiles, J., 1931, 520; McClelland and D'Silva, J., 1932,

227). Therefore it was considered that the dioxides formed by oxidation of the thionaphthenopyrazoles might not be identical with those obtained directly from the thionaphthen dioxides (IV). Oxidation of the thionaphthenopyrazoles gave, however, dioxides identical with those obtained from the corresponding thionaphthen dioxides and the appropriate hydrazines by the method of Cohen and Smiles (*loc. cit.*).



It is evident that the condensation of a phenylhydrazine with a 2-acyl hydroxythionaphthen (I) may yield two isomeric pyrazoles (II and V), but the formation of isomerides has not been detected. Since the bivalent sulphur in the thionaphthen system favours enolisation at the 3-position, the thionaphthenopyrazoles have presumably the structure (II), although the alternative structure (V) cannot be excluded. In order to eliminate this alternative, attempts were made to degrade the thionaphthenopyrazoles but without success. It was found, however, that the corresponding dioxides were susceptible to alkaline reduction, sulphur being eliminated during the process. Thus reduction of the pyrazole dioxide (III; R = Me, R' = H) by sodium amalgam gave 5(3)-phenyl-3(5)-methylpyrazole (Sjollema, *Annalen*, 1894, **279**, 248; Auwers and Stuhlmann, *Ber.*, 1926, **59**, 1048). The pyrazole dioxide (III; R = Me, R' = Ph) reacted with sodium in alcohol to give a small amount of 1 : 5-diphenyl-3-methylpyrazoline (Auwer and Mauss, *Ber.*, 1926, **59**, 611), thus confirming the structure (II) assigned to the thionaphthenopyrazoles. The main product of the reaction is, however, a *substance* (*A*), m. p. 122—124°. The analysis of this material corresponds to a diphenylmethylpyrazole. It is neither 1 : 5-diphenyl-3-methylpyrazole nor 1 : 3-diphenyl-5-methylpyrazole (compare Auwers and Mauss, *loc. cit.*; Drumm, *Proc. Roy. Irish Acad.*, 1930, **40**, *B*, 106). The latter might be expected to result from the pyrazole dioxide if the thionaphthenopyrazole had the structure (V). The material (A) forms a *mononitroso*-compound, and also a *monobromo*-compound which is not identical with 4-bromo-1 : 5-diphenyl-3-methylpyrazole (Drumm, *loc. cit.*).

It being assumed that a new cyclic system has not been formed, consideration of these properties and those recorded in the experimental section suggests that (A) may be 1 : 5-diphenyl-4-methylpyrazole, formed by migration of the methyl group during reduction of the thionaphthenopyrazole dioxide (III; R = Me, R' = Ph). The possibility of an intramolecular rearrangement with the formation of a non-pyrazole cyclic system cannot be excluded.

Experimental.

1-Phenyl-3-methyl-4 : 5-thionaphthenopyrazole (II; R = CH_3, R' = Ph).—A solution of 3-hydroxy-2-acetyl-1-thionaphthen (10 g.) and phenylhydrazine hydrochloride (10 g.) in alcohol (80 c.c.) was refluxed for 3 hours. The *pyrazole* (10 g.), which separated on cooling, crystallised from alcohol in colourless needles, m. p. 120° [Found : C, 72·7; H, 4·4 (Schoeller); N, 10·7. $C_{16}H_{12}N_2S$ requires C, 72·7; H, 4·6; N, 10·6%]. It was also obtained by refluxing 3-hydroxy-2-acetyl-1-thionaphthen and phenylhydrazine in acetic acid for 4 hours.

Oxidation.—The pyrazole (10 g.) in acetic acid (100 c.c.) containing hydrogen peroxide (30 c.c., 100 vol.) was heated at 100° for 1 hour. The material, obtained by dilution, after

purification gave no depression when mixed with 1-phenyl-3-methyl-4 : 5-thionaphthenopyrazole *S*-dioxide.*

1-p-*Bromophenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole* (II; R = CH_3, R′ = *p*-C_6H_4Br).—3-Hydroxy-2-acetyl-1-thionaphthen (5 g.) and *p*-bromophenylhydrazine (5 g.) in alcohol (50 c.c.) were refluxed for 2 hours. Sulphuric acid (1 c.c.) was added, and the refluxing continued for 5 minutes. The *product*, after being washed successively with alkali, acid, and water, crystallised from alcohol in colourless needles, m. p. 159° (Found: C, 55·8; H, 3·7; Br, 23·6. $C_{16}H_{11}N_2BrS$ requires C, 56·0; H, 3·2; Br, 23·3%). 3-*Hydroxy*-2-*acetyl*-1-*thionaphthen*-p-*bromophenylhydrazone*, obtained by heating the components in alcohol for 1½ hours, crystallised from alcohol in brown plates or yellow needles, m. p. 160—161° (Found: C, 52·8; H, 3·7. $C_{16}H_{13}ON_2BrS$ requires C, 53·2; H, 3·6%); it gave the pyrazole when heated with alcoholic sulphuric acid.

1-p-*Bromophenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole Dioxide* (III; R = CH_3, R′ = *p*-C_6H_4Br)—The above pyrazole (1 g.) in acetic acid (20 c.c.) and hydrogen peroxide (5 c.c., 100 vol.) was heated at 100° for 1 hour. The *product*, which crystallised from acetic acid in colourless plates, m. p. 207°, was identical with that obtained from 3-hydroxy-2-acetyl-1-thionaphthen 1 : 1-dioxide (1 g.) and *p*-bromophenylhydrazine (1 g.) by refluxing in alcohol containing sulphuric acid (Found: C, 51·2; H, 3·3. $C_{16}H_{11}O_2N_2BrS$ requires C, 51·2; H, 2·95%).

1 : 3-*Diphenyl*-4 : 5-*thionaphthenopyrazole* (II; R = R′ = Ph).—A solution of 3-hydroxy-2-benzoyl-1-thionaphthen (10 g.) and phenylhydrazine (10 g.) in alcohol (300 c.c.) was refluxed for 10 hours. Sulphuric acid (5 c.c.) was added, and the mixture heated for 2 hours. The material which separated on cooling crystallised from alcohol in colourless needles, m. p. 171° [Found: C, 77·4; H, 4·3 (Schoeller); N, 8·5. $C_{21}H_{14}N_2S$ requires C, 77·3; H, 4·3; N, 8·6%]. The *pyrazole* (1 g.) in acetic acid (20 c.c.) and hydrogen peroxide (5 c.c., 100 vol.), heated at 100° for 1½ hours, gave on dilution a material, which after purification from acetic acid had m. p. 225° alone or mixed with 1 : 3-diphenyl-4 : 5-thionaphthenopyrazole *S*-dioxide.*

Condensation of Hydrazine with 3-*Hydroxy*-2-*acetyl*-1-*thionaphthen*.—A solution of the thionaphthen (5 g.) in alcohol (50 c.c.) and hydrazine hydrochloride (5 g.) was refluxed for 1 hour. The material (*bis-compound*) which separated during the reaction was filtered off. It crystallised from aniline in red needles, m. p. 305° (Found: C, 62·9; H, 4·4; N, 7·7. $C_{20}H_{16}O_2N_2S_2$ requires C, 63·1; H, 4·2; N, 7·4%). This compound was insoluble in acid and alkali and was unaffected by heating with alcoholic sulphuric acid. The filtrate, after removal of the bis-compound, was neutralised with aqueous sodium hydroxide; 3-*methyl*-4 : 5-*thionaphthenopyrazole* (II; R = CH_3, R′ = H) slowly separated. It crystallised from alcohol in colourless needles, m. p. 185° (Found: C, 63·2; H, 4·2. $C_{10}H_8N_2S$ requires C, 63·8; H, 4·3%). The pyrazole alone was obtained when 3-hydroxy-2-acetyl-1-thionaphthen (10 g.) and hydrazine hydrochloride (10 g.) in acetic acid (100 c.c.) were refluxed for 4 hours; the pyrazole hydrochloride which separated on cooling was dissolved in water, and the solution neutralised. The pyrazole is soluble in acid and alkali and forms a silver salt. The *pyrazole dioxide*, obtained in the usual way, crystallised from acetic acid in colourless needles, m. p. 244—246° (Found: N, 13·0. $C_{10}H_8O_2N_2S$ requires N, 12·7%).

Reduction of the Thionaphthenopyrazole Dioxides.—(i) Sodium amalgam (20 g. of 5%) was added to a solution of 3-methyl-4 : 5-thionaphthenopyrazole dioxide (1 g.) in 2*N*-sodium hydroxide (10 c.c.). The mixture was warmed, and kept over-night. The solution was poured into an excess of 2*N*-sulphuric acid, boiled till free from sulphur dioxide, and neutralised. Extraction with ether gave a material, which after crystallisation from water and finally from ligroin had m. p. 123° and gave no depression with 5(3)-phenyl-3(5)-methylpyrazole.

(ii) A solution of 1-phenyl-3-methyl-4 : 5-thionaphthenopyrazole (5 g.) in alcohol (100 c.c.) was refluxed for 3 hours, during which sodium (5 g.) was added portionwise. The solid which separated was filtered off and washed with alcohol. (This material gave Smiles' sulphinic acid test.) It was dissolved in water, and the aqueous solution acidified, boiled till no more sulphur dioxide was evolved, and cooled. The *product* (*A*) crystallised from alcohol in colourless needles, m. p. 122—124° (Found: C, 82·3; H, 5·5; N, 12·0. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%). The filtrate, obtained above, was evaporated to dryness, and the residue treated with water and extracted with ether. The product from the ethereal solution, crystallised from alcohol, melted at 114° alone or at 114—116° with 1 : 5-diphenyl-3-methylpyrazoline and gave an identical colour reaction with sodium nitrite in sulphuric acid.

Properties and Reactions of (*A*).—The substance (A) does not give Knorr's pyrazoline test

* The authors are indebted to Professor Smiles for specimens of these dioxides.

and is insoluble in aqueous alkali. It is basic, forming easily hydrolysable salts with mineral acids and an unstable methiodide, m. p. (*ca.*) 135°. It was recovered unchanged after heating with concentrated hydrochloric acid at 180° for 6 hours and was not susceptible to reducing agents. Bromine in chloroform was added to a solution of (A) in chloroform until decoloration ceased. The solvent was removed, and the residue washed with aqueous sodium carbonate (10%). The product crystallised from acetic acid in colourless needles, m. p. 142—143° [Found : Br, 24·9 (Schoeller). $C_{16}H_{13}N_2Br$ requires Br, 25·5%]. (A) (0·5 g.) was dissolved in sulphuric acid (10 c.c. of 60%) with warming. The solution was cooled, and sodium nitrite (0·2 g.) added. After standing over-night, the mixture was diluted with water and partly neutralised. The solid which separated crystallised from acetic acid in green needles, m. p. 202—203° [Found : N, 16·5 (Schoeller). $C_{16}H_{13}ON_3$ requires N, 16·0%].

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