

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TENNESSEE AND TULANE UNIVERSITY]

Bis(3-thianaphthenoyl)furoxan

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The action of nitric acid on 3-acetylthianaphthene in acetic acid solvent leads to a product shown to be bis(3-thianaphthenoyl)furoxan (I). Evidence for this structure is (1) similarity of infrared and ultraviolet spectra to the spectra of known furoxans, (2) accelerating effect of nitrite ion on the rate of formation of the product and (3) cleavage of the product with phenylhydrazine to yield 1-(3-thianaphthenoyl)-2-phenylhydrazine (II) and 3-(β -phenylhydrazino)-4-nitroso-5-(3-thianaphthenyl)isoxazole (III). 2-Acetylthianaphthene and 3-acetyl-2-methylthianaphthene were also converted to the corresponding furoxans.

As a part of a continuing program of study of the fundamental chemistry of the thianaphthene ring, we carried out the "nitration" of 3-acetylthianaphthene with concentrated nitric acid in glacial acetic acid solvent at the boiling point of the mixture. There was formed in good yield a light yellow crystalline solid, m.p. 196–197°, which was obviously not a nitro derivative of the 3-acetylthianaphthene. Later Buu-Hoi and Hoan¹ reported the formation of 2-nitro-3-acetylthianaphthene from nitration of 3-acetylthianaphthene with acetic anhydride, fuming nitric acid and glacial acetic acid at 0–5°.

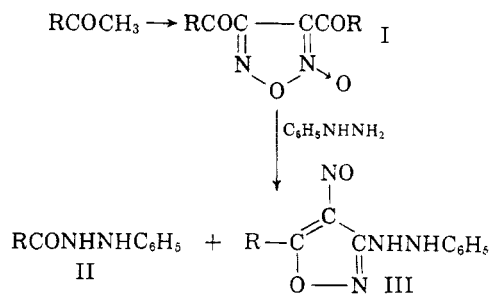
Among several structural possibilities, corresponding to the empirical formula of C₁₆H₅NO₂S for the new compound, was bis(3-thianaphthenoyl)furoxan (I), since diarylfuroxans have been shown to be formed from methyl aryl ketones² and nitric acid. The publication of a study of the infrared spectra of furoxans,³ including some diarylfuroxans, provided good evidence in favor of a furoxan structure for our compound, since bands appeared in its infrared spectrum corresponding to seven bands designated³ as characteristic of furoxans. These are indicated in Table I.

Ultraviolet spectra also furnished some evidence for the furoxan structure. Dibenzoylfuroxan shows a single maximum at 267 m μ in ethanol. The maximum for acetophenone is 242 m μ ⁴ indicating a bathochromic shift of 25 m μ in going from the ketone to the furoxan. A similar shift of 25 m μ is observed in a comparison of 2-acetylfuran (λ_{\max} , 270 m μ) and the corresponding furoxan (λ_{\max} , 295 m μ).⁵ The spectrum of 3-acetylthianaphthene shows a maximum at 304 m μ . Bis(3-thianaphthenoyl)furoxan exhibits a maximum at 330 m μ , representing a bathochromic shift of 26 m μ . The ul-

traviolet absorption maximum for furoxans varies, as would be expected, with the nature of the groups attached. J. H. Boyer and co-workers⁶ report a characteristic furoxan absorption in the range 255–285 m μ , but none of the compounds examined contained a carbonyl group conjugated to the furoxan ring. Dibenzoylfuroxan absorbs in this range but it is expected that the more highly conjugated thianaphthene type would absorb at a longer wave length.

In order to obtain evidence that the action of nitric acid on 3-acetylthianaphthene did not involve the 2-position, we carried out the reaction of 2-methyl-3-acetylthianaphthene with nitric acid. The product of the reaction showed analytical values and infrared absorption bands (Table I) characteristic of the furoxan structure. 2-Acetylthianaphthene was also converted to the corresponding furoxan.

In accordance with observations of other workers^{2,7} that nitrite ion accelerates the rate of



formation of diarylfuroxans from methyl aryl ketones, we observed a marked accelerating effect on the reaction of 3-acetylthianaphthene.

Quist⁸ has reported the formation of two products from the reaction of dibenzoylfuroxan and phenylhydrazine. These are 1-benzoyl-2-phenylhydrazine and 3-(β -phenylhydrazino)-4-nitroso-5-phenylisoxazole. Bis(3-thianaphthenoyl)furoxan underwent

(1) Ng. Ph. Buu-Hoi and Ng. Hoan, *J. Chem. Soc.*, 251 (1951).

(2) See H. R. Snyder and N. E. Boyer, *J. Am. Chem. Soc.*, **77**, 4233 (1955) for some leading references.

(3) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

(4) R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951).

(5) K. Hayes and C. O'Keefe, *J. Org. Chem.*, **19**, 1897 (1954).

(6) J. H. Boyer, U. Toggweiler, and G. A. Stoner, *J. Am. Chem. Soc.*, **79**, 1748 (1957).

(7) G. Ponzio, *Gazz. chim. ital.*, **56**, 490 (1926); *Chem. Abstr.*, **21**, 239 (1927).

(8) W. Quist, *Acta Acad. Aboensis, Math. et Phys.*, **5**, 16 (1928); *Chem. Zentr.*, 1929 I, 892.

TABLE I
 INFRARED DATA

Characteristic ³ Bands (Ranges in μ)	Dibenzoyl- furoxan ^a	Bis(3-thianaph- thenoyl)furoxan	Bis(2-methyl-3- thianaphthenoyl)- furoxan
6.15-6.25		6.23 s	6.20 s
6.78-7.09 (doublet)	6.80 m, 6.90 s	6.83 s, 7.04 s	6.83 m, 7.00 s
7.35-7.69	7.54 s	7.26 m	7.46 m
8.40-8.70	8.51 m	8.35 s	8.42 m
9.71-10.00	9.76 w	9.63 s	9.64 w
10.53-11.11	10.91 s	10.56 w	11.05 w
11.24-11.90	11.20 s	11.90 m	11.70 w

^a s-strong, m-medium, w-weak.

a similar reaction to give the corresponding products II and III.

All of these data indicated that the product from action of nitric acid on 3-acetylthianaphthene was bis(3-thianaphthenoyl)furoxan (I, R = 3-thianaphthenyl).

We have tried on several occasions to repeat the work of Buu-Hoi and Hoan¹ on the formation of 2-nitro-3-acetylthianaphthene by nitration of 3-acetylthianaphthene, but have been unable to obtain a product with the properties they described. We have also carried out the nitration of 3-thianaphthaldehyde in accordance with their directions, and have been unable to isolate the reported 2-nitro-3-thianaphthaldehyde.

EXPERIMENTAL⁹

3-Acetylthianaphthene. Most of the 3-acetylthianaphthene used was supplied by The Texas Co. Some was synthesized by acylation of thianaphthene by the method of Komppa,¹⁰ but a better laboratory procedure in our hands was the reaction of dimethylcadmium and 3-thianaphthenoyl chloride.¹¹ This latter method allowed formation of 3-acetylthianaphthene in 64% yield.

Bis(3-thianaphthenoyl)furoxan. Sixteen grams (0.091 mole) of 3-acetylthianaphthene was dissolved in a solution of 32 ml. of concentrated nitric acid and 80 ml. of glacial acetic acid, and the resulting solution was placed in a 500-ml. round-bottomed flask. The flask was closed and allowed to stand at room temperature overnight. During this period, a yellow crystalline material precipitated from the solution and nitrogen dioxide was evolved. The yellow material was collected on a filter, washed with glacial acetic acid, and after drying weighed 11.4 g. (62%). The crude product melted at 191-193°. The material was best crystallized from a solution composed of water, methyl alcohol, and tetrahydrofuran. The white crystals thus obtained after drying weighed 8.3 g. and melted at 196-197° (λ_{\max} 330 μ ; $\log \epsilon$, 4.06). The significant infrared absorption bands of the product are recorded in Table I.

Anal. Calcd. for $C_{20}H_{10}N_2O_4S_2$: C, 59.1; H, 2.47; N, 6.89; S, 15.8. Found: C, 59.23, 59.22; H, 2.64, 2.50; N, 6.96, 6.93; S, 15.83, 15.59.

The reaction of 3-acetylthianaphthene with concentrated nitric acid is greatly accelerated by the addition of a small

quantity of sodium nitrite. The observation was based on the time required for the first trace of precipitate to form. In the case of the untreated reaction, the time required for the initial precipitation was 8 hr. By the addition of a trace of sodium nitrite, this period decreased to only 1 hr.

2-Acetylthianaphthene. This compound has been reported by Farrar and Levine¹² and Martzoff.¹³ It was best prepared (54% yield) in this work by the action of anhydrous lithium acetate on 2-thianaphthenyllithium.¹⁴ The organolithium compound was prepared by metalation of thianaphthene by *n*-butyllithium.¹⁵

Bis(2-thianaphthenoyl)furoxan. A solution of 6.0 g. (0.034 mole) of 2-acetylthianaphthene and 24 ml. of concentrated nitric acid in 70 ml. of glacial acetic acid was placed in a tightly stoppered flask and allowed to stand for 48 hr. The pressure was released and the precipitated yellow solid (4.55 g.) was removed by filtration. The product melted at 169-174°. Recrystallization raised the m.p. to 176-179° and a small sample recrystallized for analysis melted at 179-180°.

Anal. Calcd. for $C_{20}H_{10}N_2O_4S_2$: C, 59.1; H, 2.47; N, 6.89. Found: C, 58.8, 58.5; H, 2.44, 2.56; N, 6.71, 6.99.

The bis(2-thianaphthenoyl)furoxan showed an infrared spectrum similar to the 3-isomer up to about 7.5 μ and exhibited the "characteristic" aroyl furoxan bands (Table I) above this range.

3-Acetyl-2-methylthianaphthene was prepared by acylation of 2-methylthianaphthene¹⁶ by a procedure apparently better than that reported by Gaertner.¹⁶ Nineteen grams (0.13 mole) of 2-methylthianaphthene was mixed with 12.2 g. (0.12 mole) of acetic anhydride in a 250-ml. flask equipped with a mechanical stirrer and a reflux condenser. The mixture was heated to facilitate solution and then 2.5 g. of anhydrous stannic chloride was added. An exothermic reaction occurred and this was followed by external heating for 1 hr. at a temperature just below the boiling point of the mixture. The reaction mixture was allowed to cool to room temperature and poured into 200 ml. of an ice-water slurry. When the hydrolysis mixture had warmed to room temperature, it was extracted twice with 100-ml. portions of ether. The ethereal extracts were combined and washed with 100 ml. of water and dried over anhydrous sodium carbonate. After removal of the solvent, the residue was distilled *in vacuo* to yield 8.8 g. (39%) of 3-acetyl-2-methylthianaphthene, b.p. 184-188°/23 mm. Recrystallization from hexane yielded 6.5 g. of tan crystals which melted at 67-69°. Gaertner¹⁶ has reported the melting point of 3-acetyl-2-methylthianaphthene to be 69-70°.

(12) M. W. Farrar and R. Levine, *J. Am. Chem. Soc.*, **72**, 4433 (1950).

(13) M. Martzoff, *Compt. rend.*, **234**, 736 (1952).

(14) H. Gilman and P. R. Van Ess, *J. Am. Chem. Soc.* **55**, 1258 (1933).

(15) D. A. Shirley and M. D. Cameron, *J. Am. Chem. Soc.*, **74**, 664 (1952).

(16) R. Gaertner, *J. Am. Chem. Soc.*, **74**, 766 (1952).

(9) Microanalyses are by Galbraith Microanalytical Laboratory, Knoxville, Tenn., and Weiler and Strauss, Oxford, England. All melting and boiling points are uncorrected.

(10) G. Komppa, *J. prakt. Chem.*, **122**, 319 (1929).

(11) D. A. Shirley, *Org. Reactions*, VIII, Chapter 2 (1954).

Bis(2-methyl-3-thianaphthenoyl)furoxan. Two grams (0.010 mole) of 3-acetyl-2-methylthianaphthene was dissolved in a solution of 4 ml. of concentrated nitric acid and 15 ml. of glacial acetic acid. This solution was placed in a 50-ml. Erlenmeyer flask and the flask was stoppered. After only 3 hr. a yellow solid began to precipitate. At the end of 6 hr. the yellow material was collected on a filter. After air-drying the yellow solid weighed 1.3 g. and melted at 162–164°. Recrystallization of the material from a mixture of water, methanol, and tetrahydrofuran yielded yellow crystals which melted at 166–167°, (λ_{\max} 336 $m\mu$; $\log \epsilon$, 4.01). The characteristic infrared bands are recorded in Table I.

Anal. Calcd. for $C_{11}H_7NO_2S$: C, 60.82; H, 3.25; N, 6.44. Found: C, 60.80; H, 3.22; N, 6.36.

Reaction of bis(3-thianaphthenoyl)furoxan with phenylhydrazine. One gram (0.0025 mole) of the furoxan was suspended in 5 ml. of phenylhydrazine in a small flask and heated on a steam bath until an exothermic reaction began. This was noted by the evolution of a gas. Immediately the flask was removed from the source of heat and was allowed to cool slowly to room temperature. The reaction mixture was then poured into a large volume of water. After decanting the water layer, the residue was fractionally crystallized from 95% ethyl alcohol to yield two fractions, 0.20 g. which melted at 233.5–235° and 0.50 g. which melted at 192–193.5°.

The material melting at 233.5–235° was yellow and appears to be 3-(β -phenylhydrazine)-nitroso-(3-thianaphthenyl)isoxazole (III) which is analogous to the product obtained by Quist⁸ from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{17}H_{12}N_4O_2S$: C, 60.71; H, 3.60; N, 16.66; S, 9.52. Found: C, 60.72; H, 3.38; N, 16.2; S, 9.10.

The material melting at 192–193.5° was white and appears to be 1-thianaphthenoyl-2-phenylhydrazine which is analogous to a second product Quist⁸ isolated from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.13; H, 4.51; N, 10.44. Found: C, 67.52; H, 4.59; N, 11.00, 10.80.

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[CONTRIBUTION FROM THE RESEARCH STATION, THE BRITISH PETROLEUM COMPANY LIMITED]

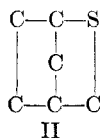
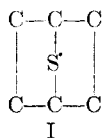
Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. IX. 7-Thiabicyclo[2.2.1]heptane and 6-Thiabicyclo[3.1.1]heptane

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7-Thiabicyclo[2.2.1]heptane and 6-thiabicyclo[3.1.1]heptane have been synthesized and their physical properties recorded.

The presence of thiabicyclo-octanes and -nonanes in the tar oil recovered from the acid used in refining Agha Jari kerosine^{1,2} suggested that thiabicycloheptanes might also be present. Since no compounds have been identified in straight-run distillates with rings containing fewer than five atoms the only thiabicycloheptanes considered were I and II and the synthesis of these compounds was undertaken to obtain their physical properties prior to examining the tar oil for their presence. This paper describes the preparation of I and its isomer, 6-thiabicyclo[3.1.1]heptane (VII), obtained in the course of the synthesis of I.



(1) S. F. Birch, T. V. Cullum, R. A. Dean, and R. L. Denyer, *Ind. Eng. Chem.*, **47**, 240 (1955).

(2) S. F. Birch, T. V. Cullum, and R. A. Dean. Paper presented at a Symposium on Polycyclic Hydrocarbons, Divisions of Petroleum Chemistry and Organic Chemistry, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

One obvious route for the synthesis of I, involving the addition of sulfur dioxide to 1,3-cyclohexadiene followed by hydrogenation of the sulfone and reduction of the product with lithium aluminum hydride (*cf.* 8-thiabicyclo[3.2.1]octane³), was found to be impractical as the initial addition product proved to be entirely polymeric. An attempt to obtain the sulfide by reaction of sodium sulfide with the ditosylate of cyclohexane-1,4-diol was also unsuccessful. The method finally used was based upon the hydrolysis and concomitant cyclization of the chlorocyclohexyl thioacetate V, prepared from 4-chlorocyclohexanol (III) as shown on page 1027.

Since the preparation entailed the addition of thioacetic acid to 4-chlorocyclohexene (IV), besides the required 4-chlorothioacetate the isomeric 3-chlorothioacetate was also produced which resulted in 6-thiabicyclo[3.1.1]heptane being formed as by-product. Separation of the two thiabicycloheptanes was, however, satisfactorily accomplished by

(3) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, Part VII of this series to be published in the *Journal*.