

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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KNOXVILLE, TENN.

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

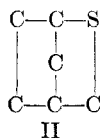
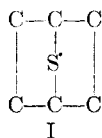
Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. IX. 7-Thiabicyclo[2.2.1]heptane and 6-Thiabicyclo[3.1.1]heptane

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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.



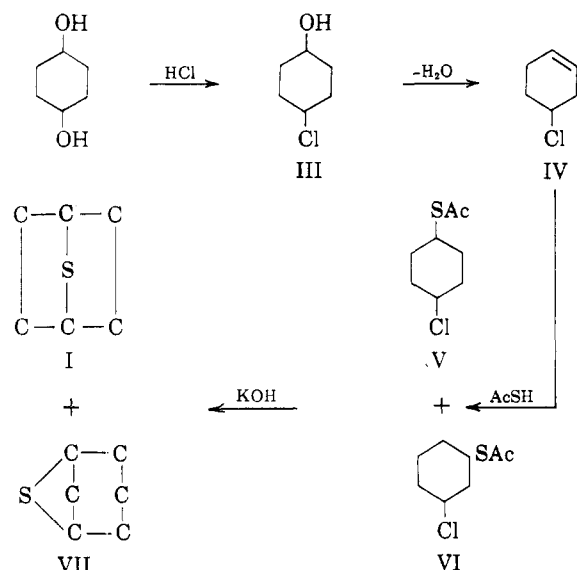
(1) S. F. Birch, T. V. Cullum, R. A. Dean, and R. L. Denyer, *Ind. Eng. Chem.*, **47**, 240 (1955).

(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*.



fractional distillation in the presence of isopropylcyclohexane. 2-Naphthalenesulfonic acid was chosen for the dehydration of III since the work of Vogel,⁴ Bousset⁵ and Kohler *et al.*⁶ indicated that this would give IV uncontaminated with isomeric chlorocyclohexenes. The reaction of thioacetic acid with IV was very erratic. On occasions only some 25% reaction occurred even when radical-forming compounds were present and/or the mixture was irradiated with light from tungsten-filament or ultraviolet lamps. On other occasions the mixture reacted spontaneously when the reactants were mixed and a theoretical yield was obtained. This spontaneous reaction frequently took place in the receiver when unreacted materials were recovered by distillation from the product of an incomplete reaction. No explanation of the unpredictable course of this reaction has been obtained, but the most likely theory appears to be that an inhibitor can be formed by a side-reaction and that this, if formed in sufficient quantity, almost entirely stops the reaction. However, despite this, the final yield of thioacetates was 86%. Hydrolysis of the product gave a mixture of the two thiabicycloheptanes (I and VII), cyclohexanethiols, and some polymeric material. Since a Walden inversion would be expected to occur at the cyclization stage³ and the sulfides exist only in the *cis* form (*cf.* the thiabicyclo [3.2.1] octanes³), it is presumed that the sulfides were formed from the *trans*-thioacetates and the by-products were mainly derived from the *cis*-thioacetates.

Separation of the mixture of sulfides was attempted by crystallization. This was unsuccessful since both were solids and were present in roughly equal amounts. Fractional distillation was rejected because of the practical difficulties associated with

the distillation of solids with high melting points. Distillation in the presence of isopropylcyclohexane, however, proved completely successful in separating the two sulfides since the lower boiling component formed an azeotrope (this was predicted from previous experience⁷) while the higher boiling did not and remained in the residue. The azeotrope was not obtained free from the entrainer since the boiling points were very close but complete separation was obtained by continuing the distillation until a negligible amount of sulfide was present in the distillate. The sulfides were separated from the hydrocarbon by adsorption on silica gel and finally purified by crystallization from acetic acid. The properties of the two thiabicycloheptanes are recorded in Table I; the infrared spectra were obtained in the range 2–15 μ .⁸

TABLE I

PHYSICAL PROPERTIES OF THE SULFIDES

Sulfide	M.P., °C.	B.P.		n_D^{20}
		°C.	Mm.	
7-Thiabicyclo[2.2.1]-heptane	127.5–128.5	164	765	1.517 ^a
6-Thiabicyclo[3.1.1]-heptane	93.5–95.5	175	775	1.519 ^a

^a By proportion from the values of solutions in di-*n*-butyl sulfide.

At this stage it was not known with certainty which of the two isomers had the structure of I although some indication had been obtained from the relative stabilities of the mercuric salt complexes. Attempts to separate the sulfides by crystallization and regeneration of the mercuric chloride derivatives of the mixture gave only an intractable plastic solid from which a small amount of mercaptan-containing oil was obtained on regeneration; on the other hand, extraction of a pentane solution of the mixed sulfides with aqueous mercuric acetate solution followed by regeneration of the extract gave one sulfide only, identical with the lower boiling compound. Since the residual aqueous liquors contained a mercapto alcohol it was assumed that the higher boiling compound was the 6-thiabicyclo[3.1.1]heptane and that this formed unstable mercuric salt derivatives owing to the sulfur atom being in a 4-membered ring (*cf.* thiacyclobutane⁹). The correctness of this assumption was shown when a small amount of a mixture of 6-thiabicyclo[3.1.1]heptane and 7-thiabicyclo [4.1.0] heptane (X) (cyclohexene sulfide¹⁰) was prepared by the

(7) D. H. Desty and F. A. Fidler, *Ind. Eng. Chem.*, **43**, 905 (1951).

(8) To be submitted to the API Research Project 44 for inclusion in their catalog of spectral data.

(9) E. Grischkevitch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, **47**, 880 (1916).

(10) E. E. van Tamelen, *J. Am. Chem. Soc.*, **73**, 3444 (1951).

(4) A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

(5) A. Bousset, *Bull. soc. chim.*, **6**, 983 (1939).

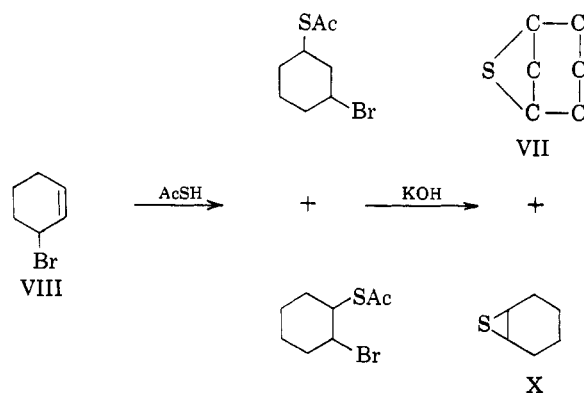
(6) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

TABLE II
MELTING POINTS AND ANALYSES OF THE DERIVATIVES OF THE SULFIDES

Compound	Formula of Derivative	M.P., °C. (Corrected)	Analyses					
			Calcd.			Found		
			C	H	S	C	H	S
7-Thiabicyclo[2.2.1]-heptane	C ₆ H ₁₀ Cl ₂ HgS	186.5-187.5 dec.	18.7	2.6	8.3	18.6	2.7	8.4
	C ₆ H ₁₀ O ₂ S	253-254 ^a	49.3	6.9	21.9	49.4	7.0	22.2
	C ₇ H ₁₃ IS	138-139 dec. ^a	32.8	5.2	12.5	33.0	5.1	12.5
6-Thiabicyclo[3.1.1]-heptane	C ₆ H ₁₀ O ₂ S	171.5-172.5	49.3	6.9	21.9	49.5	6.7	21.8

^a Sealed tube.

method shown below. The infrared spectrum of the mixture, which was semi-solid at room temperature, was obtained and comparison of this spectrum with those of the pure sulfides showed that the higher boiling sulfide was present to the extent of at least 50% and that the lower boiling one could not be detected. 6-Thiabicyclo[3.1.1]heptane was ob-



served to decompose to some extent at its atmospheric boiling point with the formation of a white solid insoluble in the usual solvents. Further evidence of the instability of this sulfide was obtained when it was found that a sample which had been degassed and sealed under vacuum was partly converted into non-volatile material under the influence of daylight. The original sulfide gave a positive result in the acrylonitrile test for free radicals,¹¹ indicating that in the absence of oxygen, which presumably normally acts as an inhibitor, 6-thiabicyclo[3.1.1]heptane undergoes a light-initiated radical polymerization. Thiacyclobutane itself has been found to behave similarly in the absence of oxygen¹² but rough comparative tests with this compound showed that, although it was more effective in polymerizing acrylonitrile, it was not nearly so susceptible to self-polymerization as VII. 6-Thiabicyclo[3.1.1]heptane is readily decomposed by concentrated sulfuric acid, polymeric

material again being formed (*cf.* thiacyclobutane¹³).

7-Thiabicyclo[2.2.1]heptane was characterized by means of the usual derivatives. No further attempt was made to prepare the mercuric chloride complex of 6-thiabicyclo[3.1.1]heptane; with methyl iodide the sulfide gave only an oil but the sulfone was obtained by the usual method. The melting points and analyses of the derivatives are recorded in Table II.

7-Thiabicyclo[2.2.1]heptane has not so far been detected in those fractions of the tar oil in which, from its boiling point, it might be expected to occur. It is interesting to note that Rossini and his co-workers have recently shown¹⁴ that a hydrocarbon having this ring structure is probably present in the representative petroleum of A.P.I. Research Project 6.

EXPERIMENTAL

All melting points are corrected. All sublimations were carried out under reduced pressure. Microanalyses are by Dr. Ing. A. Schoeller, Kronach/Oberfranken, Bambergerstrasse 20, Germany.

4-Chlorocyclohexanol (III) (b.p. 96-106°/10 mm., n_D^{20} 1.4947) was obtained in average yield of 60% from 1,4-cyclohexanediol.¹⁵

4-Chlorocyclohexene (IV). 4-Chlorocyclohexanol (108 g.) and 2-naphthalenesulfonic acid (5 g.) were heated in an oil-bath at 200-240° and the distillate was taken off through a short, glass-packed column. The organic layer was dried over calcium chloride and the fraction, b.p. 88-93°/130 mm., n_D^{20} 1.4822 (48 g., 51%) was taken as 4-chlorocyclohexene, leaving a residue of polymeric material.

Chlorocyclohexyl thioacetates (V and VI). (a) Portions (*ca.* 0.2 mole) of 4-chlorocyclohexene were mixed with thioacetic acid (*ca.* 0.3 mole, b.p. 86-87.5°/763 mm., n_D^{20} 1.4646-1.4648) and the mixtures were allowed to stand for various periods (2-20 hr.), under various conditions of temperature (20-90°) and illumination (daylight, 100-watt tungsten-filament lamp, ultraviolet), and in one instance a trace of azobisisobutyronitrile was added as a radical source. Reaction was not vigorous under any of these conditions and only moderate yields (20-45%) of addition products (b.p. 106-112°/3 mm.) were obtained. Complementary amounts of unreacted materials were recovered as forerunnings, and these usually reacted spontaneously in the receiver giving

(13) D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

(14) B. J. Mair, P. E. Eberly, Kun Li, and F. D. Rossini. Paper presented at the Symposium quoted in Ref. 2.

(15) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

(11) J. H. Baxendale, M. G. Evans, and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946); *cf.* S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Pet.*, **39**, 206 (1953).

(12) W. E. Haines, G. L. Cook, and J. S. Ball, *J. Am. Chem. Soc.*, **78**, 5213 (1956).

further quantities (20–70%) of the required addition products, but sometimes the reaction went to completion only after a second recovery of unreacted materials. (b) 4-Chlorocyclohexene (0.3 mole) was distilled under nitrogen (50 mm.) into an ice cooled flask and thioacetic acid (0.45 mole) was distilled under nitrogen (50 mm.) into the same receiver. On removal of the ice, vigorous reaction occurred spontaneously and it became necessary to cool the mixture to moderate the reaction. The mixture was allowed to stand half an hour after the reaction appeared to have ceased and was then distilled giving 55 g. (98%) of thioacetate. In a second preparation carried out under these conditions, reaction was not vigorous and only 60% of addition product was obtained initially. The recovered starting materials reacted spontaneously to give a further quantity of thioacetate: total yield 91%.

Redistillation of the combined products from (a) and (b) gave an 86% yield of the thioacetates, b.p. 98–102°/2 mm., n_D^{20} 1.5195.

Preparation of 7-thiabicyclo[2.2.1]heptane (I) and 6-thiabicyclo[3.1.1]heptane (VII). The thioacetate mixture (274 g.) was added dropwise during 30 min. to refluxing aqueous ethanolic caustic potash (KOH, 770 g.; EtOH, 1925 ml.; H₂O, 1925 ml.), refluxing then being continued for 2 hr. The reaction mixture was distilled until thiol began to come over in appreciable quantities and the distillate was then diluted with water and extracted with *n*-pentane. The extracts were shaken with iodine and 10% aqueous caustic potash until free from thiol, and sublimation of the solid left on evaporation, gave a mixture of 7-thiabicyclo[2.1.1]heptane and 6-thiabicyclo[3.1.1]heptane (66 g., 41%) melting at 105–108°. Infrared spectroscopy showed the composition to be 42% and 58%, respectively.

Further distillation of the aqueous residues from the thioacetate hydrolyzate and extraction of the distillate with *n*-pentane gave 42 g. of material b.p. 30°/27 mm.–150°/3 mm. The alkali soluble portion (20 g.) of the fraction (25 g.) b.p. 62–64°/27 mm., had b.p. 78–79°/47 mm., n_D^{20} 1.5177. This was probably a mixture of cyclohexene thiols.

Anal. Calcd. for C₈H₁₀S: C, 63.1; H, 8.8; S, 28.1. Found: C, 63.0; H, 8.7; S, 27.8.

2,4-Dinitrochlorobenzene derivative, m.p. 106–107° from ethanol.

Anal. Calcd. for C₁₂H₁₂N₂O₄S: C, 51.4; H, 4.2; S, 11.4; N, 10.1. Found: C, 51.9; H, 4.5; S, 11.3; N, 10.0.

Separation of 7-thiabicyclo[2.1.1]heptane (I) and 6-thiabicyclo[3.1.1]heptane (VII) by azeotropic distillation. A quantity (15.8 g.) of the mixture of the sulfides (m.p. 105–108°) was dissolved in isopropylcyclohexane (600 ml., b.p. 83°/81 mm., n_D^{20} 1.4909; purified by percolation over silica gel) and this mixture was distilled at reduced pressure (81 mm.) through a 40-plate, glass-packed column until several consecutive fractions of n_D^{20} 1.4911, b.p. 82.8°/81 mm. were obtained (initial fractions had n_D^{20} 1.4946≐ca. 5% sulfide and b.p. 79.5°/81 mm.). The distillate fractions were combined (total 400 ml.) and percolated over silica gel (170 g., 28–200 mesh), using *n*-pentane (100 ml.) to displace the isopropylcyclohexane, and ethanol to elute the sulfide. The 7-thiabicyclo[2.2.1]heptane was separated in the usual way and sublimed to give 5.5 g. (83% recovery based on that present in the original mixture) of m.p. 123–126°. 6-Thiabicyclo[3.1.1]heptane (7.0 g., 76% recovery), separated in the same manner from the distillation residue, was crystallized from glacial acetic acid to a constant melting point of 93.5–95.5°.

Anal. Calcd. for C₈H₁₀S: C, 63.1; H, 8.8; S, 28.1. Found: C, 62.7; H, 9.1; S, 28.2.

Isolation of 7-thiabicyclo[2.1.1]heptane (I) by mercuric acetate treatment. A solution of 0.4 g. of the mixture of sulfides in *n*-pentane (5 ml.) was extracted with four 5-ml. portions of aqueous mercuric acetate [Hg(OAc)₂, 500 g.; H₂O, 1500 ml.; HOAc, 25 ml.]. The combined extracts were added to refluxing aqueous sodium sulfide [30 ml. of 1:1 (w/w)/-

Na₂S·9H₂O:H₂O] and the regenerated sulfide was sublimed to give a solid (ca. 0.1 g.) melting at 126–127°. Continuous ether extraction of the aqueous sodium sulfide liquors for 16 hr. resulted in isolation of ca. 0.1 g. of an unpleasant smelling mobile oil (n_D^{20} 1.5256) the infrared spectrum of which indicated it to be a mercapto alcohol.

Anal. Calcd. for C₈H₁₂OS: C, 54.5; H, 9.2; S, 24.2. Found: C, 54.8; H, 8.8; S, 23.8.

A further quantity (11.4 g.) of 7-thiabicyclo[2.2.1]heptane was obtained by this treatment and purified to a constant melting point of 127.5–128.5° by crystallization of its mercuric chloride complex (31 g.) followed by crystallization of the regenerated sulfide from glacial acetic acid.

Anal. Calcd. for C₈H₁₀S: C, 63.1; H, 8.8; S, 28.1. Found: C, 63.3; H, 8.9; S, 27.8.

Preparation of VII and 7-thiabicyclo[4.1.0]heptane (X). 3-Bromocyclohexene (14.5 g., b.p. 75–79°/30 mm.), prepared¹⁶ in 51% yield from cyclohexene and *N*-bromosuccinimide, was distilled in a nitrogen atmosphere under reduced pressure into an ice cooled flask containing thioacetic acid (8.5 g.) similarly distilled under nitrogen. Since there was no apparent reaction on allowing the mixture to warm to room temperature it was allowed to stand for several days, during which time there was slow evolution of hydrogen bromide, and it was then distilled under reduced pressure. The fraction (4.0 g., 19%) boiling over the range 72–100°/0.5 mm. (mostly at about 90°/0.5 mm.), n_D^{20} 1.539–1.543, was refluxed for 1 hr. with aqueous ethanolic caustic potash (KOH, 20 g.; EtOH, 50 ml.; H₂O, 50 ml.). Distillation of the material obtained by *n*-pentane extraction of the aqueous ethanolic distillate from the hydrolyzate gave 0.12 g. (6%) of an oil which gradually solidified.

Properties of 6-thiabicyclo[3.1.1]heptane. A sample of 6-thiabicyclo[3.1.1]heptane which had been degassed and sealed under vacuum in a Pyrex U-tube was allowed to stand in diffuse daylight for several hours. One limb of the tube was then cooled in liquid nitrogen and, while most of the solid readily sublimed into this limb, a portion was found to be comparatively nonvolatile. The limb containing the 6-thiabicyclo[3.1.1]heptane thus freshly sublimed was sealed off, while still maintaining the vacuum, and this was exposed to strong sunlight for 1 hr. At the end of this period the sulfide had been converted almost entirely to an amorphous, opaque, nonvolatile solid. This on further standing in the dark, was transformed to a translucent material which appeared to be semisolid. A sample of thiacyclobutane similarly degassed and sealed was exposed to strong sunlight for several hours and to diffuse daylight for several days, but even then the sample readily distilled to a liquid nitrogen-cooled portion of the tube, leaving only a small nonvolatile oily residue.

Both 6-thiabicyclo[3.1.1]heptane and thiacyclobutane gave positive results in the acrylonitrile test¹¹ for radical formation. After a few hours in strong sunlight, a considerable amount of white solid polymer had formed in the tube containing the nitrile to which 6-thiabicyclo[3.1.1]heptane had been added: the nitrile which had been treated with thiacyclobutane was converted almost entirely to solid polymer over the same period.

The sulfide was completely removed from a solution of 6-thiabicyclo[3.1.1]heptane (0.19 g.) in *n*-pentane (2 ml.) by shaking with concentrated sulfuric acid (1 ml.) for about 10 min. The acid layer assumed a yellow color and there was formation of sulfur dioxide. After standing for 2 hr., the acid layer was added dropwise to a cooled solution of potassium hydroxide (2.5 g.) in ice water (10 ml.) covered by a layer of *n*-pentane (10 ml.). Only about 20% of the original sulfide was recovered by evaporation of the *n*-pentane extracts.

Derivatives of the sulfides. The mercuric chloride complex, methiodide, and sulfone of 7-thiabicyclo[2.2.1]heptane were prepared in the usual way. An attempt to prepare the methiodide of 6-thiabicyclo[3.1.1]heptane gave an oil but a solid sulfone was obtained by the usual method. The melting point and analysis of this sulfone is given in Table II

together with the melting points and analyses of the 7-thiabicyclo[2.2.1]heptane derivatives.

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(16) E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950).

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SUNBURY-ON-THAMES, ENGLAND

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES OF AMHERST COLLEGE]

Reaction of *N*- and *O*-Alkylchelidamic Acids with Thionyl Chloride¹

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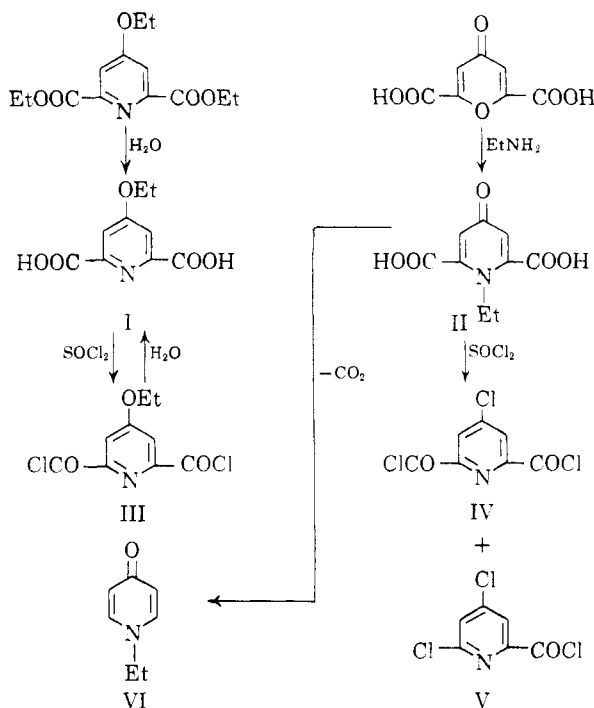
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The reactions of *N*-alkyl-4-pyridone-2,6-dicarboxylic acids and of the isomeric 4-alkoxy-pyridine-2,6-dicarboxylic acids with thionyl chloride are described. The latter yield the expected 4-alkoxy-pyridine-2,6-dicarboxylic acid chlorides while the former furnish mixtures of 4-chloropyridine-2,6-dicarboxylic acid dichloride and 4,6-dichloropicolinic acid chloride. Derivatives of the various acids are described and some of their physical constants are presented. Also included is the description of *N*-ethyl-4-pyridone.

In a recent publication² we described the reaction of sodium ethoxide with diethyl 4-chloropyridine-2,6-dicarboxylate which gave diethyl 4-ethoxy-pyridine-2,6-dicarboxylate. On hydrolysis of this ester the corresponding acid (I) was obtained. Since its melting point did not agree with the one reported in the literature³ the isomer *N*-ethyl-4-pyridone-2,6-dicarboxylic acid (II) was prepared for comparison from 4-pyridone-2,6-dicarboxylic acid and ethylamine. Although the formation of the two acids presents in itself some evidence for their constitution, additional proof of structure seemed to be desirable. Their reaction with thionyl chloride was found to serve this purpose. However no conclusions can be drawn as to the structure of the acid prepared by the British authors³ since their work was not repeated.

On treatment with thionyl chloride, the compound obtained by hydrolysis of diethyl 4-ethoxy-pyridine-2,6-dicarboxylate gave smoothly the corresponding acid chloride (III) which could be converted to the original acid and to the amide and anilide. On the other hand, the isomer *N*-ethyl-4-pyridone-2,6-dicarboxylic acid (II) gave under comparable conditions a mixture of two products. In addition to the expected⁴ 4-chloropyridine-2,6-dicarboxylic acid dichloride (IV) 4,6-dichloropic-

olinic acid chloride (V) was isolated as the predominant product. Both acid chlorides were characterized by hydrolysis to the parent acids and by conversion to several derivatives.



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(1) This investigation was supported by a grant (CY-2924) from the National Institutes of Health, U. S. Public Health Service, to Professor G. W. Kidder, whom the author wishes to thank for his continued interest in this work.

(2) D. G. Markees and G. W. Kidder, *J. Am. Chem. Soc.*, **78**, 4130 (1956).

(3) J. N. Collie and G. Bishop, *J. Chem. Soc.*, **127**, 962 (1925).

(4) See e.g. H. Maier-Bode and J. Altpeter, *Das Pyridin und seine Derivate in Wissenschaft und Technik*, Wilhelm Knapp, Halle (Saale) 1934, p. 147.

The literature describes several similar reactions in the pyridine series. It was observed that *N*-methyl-5-methoxy-4-pyridone-2-carboxylic acid reacts with thionyl chloride to give 4,6-dichloro-5-methoxypicolinic acid chloride.⁵ An earlier report,⁶ however, indicates that the corresponding nor-acid, 5-methoxy-4-pyridone-2-carboxylic acid furnishes 4-chloro-5-methoxypicolinic acid chloride under

(5) K. Heyns and G. Vogelsang, *Ber.*, **87**, 1377 (1954).

(6) T. Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).