extracted with dry benzene from which 1.4 g. of white crystals could be obtained, m.p. 118–19°, lit. m.p. 122; yield 52.3%.

Reaction of α-chlorodibenzyl sulfone with peracetic acid. A. To a solution of 0.5 g. of α-chlorodibenzyl sulfone in 15 ml. of glacial acetic acid was added 1 ml. of 40% peracetic acid. After letting the reaction mixture stand at room temperature for 24 hr., it was poured into 25 g. of crushed ice and filtered to recover a quantitative amount of the chlorosulfone that did not depress the melting point of pure starting material.

B. The above experiment was repeated using exactly the same quantities and the reaction mixture was saturated with hydrogen chloride gas and allowed to stand for 24 hr. at room temperature. In this case also a quantitative yield of the starting material was recovered by using the above procedure for isolation.

Reaction of benzyl mercaptan with peracetic acid. To 5.6 g. of benzyl mercaptan (0.045 mole) in 100 ml. of glacial acetic acid was slowly added 25 ml. of 40% peracetic acid with cooling and constant shaking. The mixture was saturated with hydrogen chloride gas for a period of 10 min. and set aside for 24 hr. Upon pouring the mixture into crushed ice 0.3 g. of solid was obtained which did not depress the melting point of an authentic sample of α-phenylmethanesulfonyl chloride, m.p. 92–93°. Evaporation of the aqueous solution in vacuum gave a deliquescent solid which was treated with a solution of 2 g. of sodium hydroxide in 10 ml. of water to obtain 7.5 g. of crystals upon evaporation. Treatment of 5 g. of this compound with 5.4 g. of phosphorus pentachloride in phosphorus oxychloride according to Johnson and Ambler[10] gave 2.8 g. of α-phenylmethanesulfonyl chloride.

Reaction of I with benzyl phenyl sulfone. To a solution of 19.5 g. (0.084 mole) of benzyl phenyl sulfone in 100 ml. of dry chloroform in a flask provided with a calcium chloride tube was added 23 g. (0.084 mole) of I. No reaction seemed to have occurred even after the mixture was allowed to stand for a week. It was then filtered to remove unchanged I and from the filtrate 18.2 g. of benzyl phenyl sulfone (m.p. 145–46°) was recovered.

Reaction of I with diphenylmethyl chloride. To a solution of 5 g. (0.025 mole) of diphenylmethyl chloride in 50 ml. of carbon tetrachloride was added 6.8 g. of I. No apparent reaction occurred. The mixture was allowed to stand at room temperature for 8 days. The unchanged I was filtered (4.0 g.) and the filtrate distilled in vacuum to give 1.2 g. of iodobenzene b.p. 40–45°/0.05 mm. and 4.6 g. of unchanged diphenylmethyl chloride b.p. 110–15°/0.05 mm. The recovered diphenylmethyl chloride did not give a precipitate with 2,4-dinitrophenylhydrazine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOPE COLLEGE]

A Study of the Condensation of Thianaphthene with Formaldehyde

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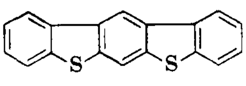
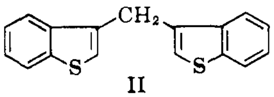
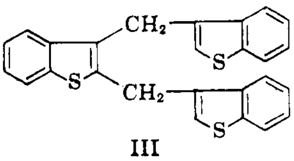
The condensation of thianaphthene with formaldehyde is promoted by hydrogen chloride, aluminum chloride and boron trifluoride catalysts. Evidence is presented that the products obtained consist of di(3-thianaphthenyl)methane (II) and 2,3-di(3-thianaphthenylmethyl)thianaphthene (III) besides higher molecular weight compounds of unknown structure. The ratio in which the above compounds are formed varies with the catalyst used as well as with the reaction time. Compound II was also prepared by the reaction of 3-chloromethylthianaphthene and 3-thianaphthenylmagnesium bromide. The infrared spectrum and the melting point of the dibromide derivative were identical with those of the thianaphthene-formaldehyde condensation product. The isomeric compound, 3-(2-thianaphthenylmethyl)thianaphthene (IV) was prepared and its properties compared with those of II.

This reaction seemed of interest since the expected methylene compounds were unknown and it was hoped that the greater reactivities of the 2- and 3- positions over positions in the benzene nucleus would increase the tendency toward the formation of relatively simple compounds. It was thought possible that compounds such as the following (I) might be obtained since the aluminum chloride catalyzed condensation of benzene and formaldehyde yields large amounts of anthracene as well as diphenylmethane.[1] Also it was of interest to obtain some accurate information about the isomer distribution in these reactions since few careful studies of electrophilic substitution involving thinaphthene have been undertaken. The reported study was undertaken to determine the conditions necessary for and the nature of the products from the reaction between thianaphthene and formaldehyde.

The results using hydrogen chloride, aluminum


I


II


III

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[1] G. B. Frankfort and V. Kopatnur, *J. Am. Chem. Soc.*, 36, 1529 (1914).

chloride, and boron trifluoride as catalysts were similar. Distillation of the product gave clear viscous sirups. Fraction A boiled near 200°(0.3 mm.) and fraction B boiled near 300° (0.3 mm.) and set to a brittle glass at about 50°. An undistillable residue remained in the flask which in some reactions was the major product. It was a brittle glass, softening at a somewhat higher temperature than fraction B. None of these fractions could be made to recrystallize.

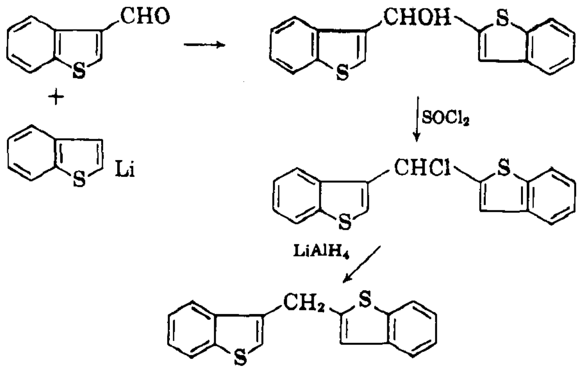
When gaseous hydrogen chloride was used as a catalyst, with chloroform as a solvent, the yield of fractions A and B did not exceed 30% even on prolonged treatment. The main product was 3-chloromethylthianaphthene.

Aluminum chloride in a mixture of carbon disulfide and chloroform gave the highest per cent conversion to fraction A (50%), but it also led to the formation of more tarry materials than did the other catalysts. The product from this as well as from the hydrogen chloride catalyzed reaction always contained a small amount of solid material, m.p. 301–302°, the elemental analysis of which was consistent with that calculated for structure I. This solid was not obtained in the boron trifluoride catalyzed condensation.

The boron trifluoride catalyzed reaction was studied in more detail since it was more convenient, no tarry residues remained, and the catalyst had no effect on thianaphthene itself. The relative amounts of fractions A and B obtained depended upon the reaction time. The conclusions arrived at with regard to the composition of fractions A and B apply to the reaction catalyzed by boron trifluoride etherate.

Composition of Fraction A. The elemental analysis and molecular weight indicated that this material was a dithianaphthenylmethane. Bromination of the product in chloroform yielded a dibromide melting at 197°. An authentic sample of di(3-thanaphthenyl)methane was prepared by the reaction of 3-thianaphthenylmagnesium bromide with 3-chloromethylthianaphthene. The infrared spectrum of this compound was identical with the spectrum of fraction A, and there was no depression in the melting point on admixture of the dibromide derivatives.

To determine more precisely the isomeric purity of A, 3-(2-thianaphthenylmethyl)thianaphthene was prepared by the route shown. It was found to be a solid, m.p. 78.5°, and yielded a dibromide, m.p. 130.5°. A comparison of its infrared spectrum with that of the dithianaphthenylmethane from the boron trifluoride condensation showed that not more than a few per cent of the 2,3- isomer could be present in fraction A. A strong peak in the spectrum of the 2,3- isomer at 12.2 μ was absent in the spectrum of fraction A.



IV

Composition of Fraction B. Assignment of structure III to fraction B is based on the following evidence: The elemental analysis and molecular weight are in agreement and when B was desulfurized with Raney nickel, a liquid hydrocarbon was obtained, the analysis and molecular weight of which agreed with that calculated for 2,4,7-triphenyloctane, the expected compound if structure III is correct.

It was at first suspected that B might possess structure I or possibly the dihydro form of this compound. Were this the structure of B, then *m*-diphenylbenzene,[2] m.p. 85°, b.p. 363°, or 1,3-diphenylcyclohexane,[3] b.p. 196–198° (16 mm.), should have been obtained upon Raney nickel treatment. Our hydrocarbon was neither, since it was a liquid, b.p. 190–200° (3 mm.), and was unaffected by heating with selenium; 1,3-diphenylcyclohexane is converted to *m*-diphenylbenzene by selenium treatment.[3] Furthermore treatment of di-(3-thanaphthenyl)methane with trioxane and boron trifluoride etherate led only to a glassy substance which could not be distilled. An intermolecular methylene bridge is apparently introduced in preference to an intramolecular linkage even when no thianaphthene is available for reaction.

In experiments in which di(3-thianaphthenyl)-methane or thianaphthene were treated in the usual way with boron trifluoride etherate, in the absence of formaldehyde, the starting materials were recovered unchanged showing that none of the products identified or the undistillable glasses were formed by the simple polymerization of these known compounds.

From the data shown in Table I, it appears that fraction B arises from the reaction of di(3-thianaphthenyl)methane and thianaphthene with formaldehyde since the amounts of these two compounds recovered decrease as B increases.

Although it seems likely that fraction B consists mainly of III, especially since the dithianaphthenylmethane from which it apparently arises has been shown to possess structure II, it was not possible to demonstrate conclusively the isomeric purity

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[2] C. A. Wardner and A. Lowy, *J. Am. Chem. Soc.*, **54**, 2510 (1932).

[3] C. D. Nenitzescu and E. Curaneanu, *Ber.*, **70**, 346 (1937).

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM BORON FLUORIDE CATALYZED REACTIONS AT VARIOUS REACTION TIMES

Time	Thianaphthene	Fraction A	Fraction B
13 hr.	46	24	10
1 day	15	20	20
6 days	0	5	50

of the material. It could not be caused to recrystallize even after several distillations or after chromatography on aluminum. Attempts at preparing derivatives by bromination and hydrogen peroxide oxidation were likewise unsuccessful. It was recovered essentially unchanged after heating with selenium. However, when 3-hydroxythianaphthene reacted with di(2-thianaphthenyl)methane, with boron trifluoride catalyst, a fairly good yield of material was obtained the infrared spectrum of which was identical with that of fraction B. This experiment gives support that fraction B is probably 2,3-di(thianaphthenylmethyl)thianaphthene.

EXPERIMENTAL

Reaction catalyzed by boron trifluoride etherate. Twenty grams (0.15 mole) of thianaphthene, 4.5 (0.05 mole) of trioxane, and 24 g. (0.18 mole) of boron trifluoride etherate was dissolved in 90 ml. of absolute ether and stirred for a time at room temperature. With longer reaction periods, viscous sirups precipitated which were dissolved in benzene. The catalyst was decomposed with ice water and the ether layer was washed successively with sodium bisulfite, dilute sodium hydroxide, and water. Three fractions were obtained upon distillation of the dried ether layer.

(1) b.p. 45–60° (0.3 mm.), thianaphthene: (2) b.p. 190–200° (0.3 mm.).

Anal. Calcd. for $C_{17}H_{12}S_2$: C, 72.81; H, 4.32; S, 22.87; mol. wt., 280. Found: C, 72.69; H, 4.57; S, 23.09; mol. wt., 290 (f.p. in benzene).

(3) b.p. 280–300° (0.3 mm.), a light yellow liquid which set to a brittle glass, softening at about 50°.

Anal. Calcd. for III, $C_{26}H_{18}S_3$: C, 73 00; H, 4.24; S, 22 70; mol. wt., 427. Found: C, 72.70; H, 4.45; S, 22.60; mol. wt. 448 (f.p. in benzene).

Di(3-thianaphthenyl)methane. 3-Thianaphthenylmagnesium bromide was prepared by refluxing 30 g. (0.14 mole) of 3-bromothianaphthene[4] with 3.6 g. (0.15 mole) of magnesium turnings suspended in 200 ml. of anhydrous ether containing a small amount of methyl iodide as a catalyst. After 3 hr. 20 g. (0.11 mole) of 3-chloromethylthianaphthene[5] was added and the refluxing continued for 24 hr. After the addition of water the ether layer was separated, dried, and distilled yielding 11.7 g. of a clear, viscous sirup, b.p. 180–205° (0.3 mm.). A 1-g. sample of the product was dissolved in chloroform and treated with an equal weight of bromine to give a dibromide in the form of white needles, m.p. 197–198°.

Anal. Calcd. for $C_{17}H_{10}S_2Br_2$: S, 14.64; Br, 36 47. Found: S, 14.94; Br, 36.42.

2-Thianaphthenyl-3-thianaphthenylcarbinol. 2-Thianaphthenyllithium[6,7] was prepared by the addition of 13.4 g. of thianaphthene to a solution of 8.4 g. (0.10 mole) of phenyllithium in 200 ml. of ether. The mixture was refluxed for 30 min., cooled, and treated with 16.2 g. (0.10 mole) of 3-thianaphthenecarboxaldehyde. The solution was refluxed for an additional 2 hr. before water was added to hydrolyze the lithium salt. The ether layer was dried and concentrated to give a viscous sirup which could not be induced to crystallize. Vacuum distillation yielded 11.3 g. of liquid, b.p. 230–240° (0.4 mm.). This liquid set to a taffy-like material upon cooling. The pale yellow crystals obtained by repeated recrystallization from alcohol still melted over a wide range (90–110°).

2-Thianaphthenyl-3-thianaphthenylchloromethane. To 10 g. (0.034 mole) of impure carbinol there was added 8.3 g. (0.07 mole) of thionyl chloride. After the first vigorous reaction had subsided, the mixture was heated in a water bath for 1 hr. The excess thionyl chloride was distilled *in vacuo* to give crude 2-thianaphthenyl-3-thianaphthenylchloromethane.

3(2-Thianaphthenylmethyl)thianaphthene. IV. The crude chloromethane was suspended in ether and added to a solution of 1.2 g. of lithium aluminum hydride in 100 ml. of ether. The solution was heated under reflux for 4 hr. and then allowed to stand for 8 hr. The excess hydride was decomposed with water and the aluminum hydroxide was dissolved by adding hydrochloric acid. The ether layer was separated, dried, and distilled to yield 5.4 g. of viscous sirup, b.p. 200–215° (0.3 mm.). Crystals formed after the sirup had been allowed to stand overnight. Repeated recrystallizations from petroleum ether (b.p. 00–00°) gave an analytical sample in the form of pale yellow needles, m.p. 78.5–79°.

Anal. Calcd. for $C_{17}H_{12}S_2$: C, 72.81; H, 4.32; S, 22.87. Found: C, 72.88; H, 4.38; S, 22.65.

A bromine derivative obtained in the same way as for the the 3,3- isomer melted at 130.5–131°.

Anal. Calcd. for $C_{17}H_{10}S_2Br_2$: S, 14.64; Br, 36.47. Found: S, 14.40; Br, 36.50.

Desulfurization of Fraction B. Ten grams of the glassy solid was dissolved in 500 ml. of tetrahydrofuran which contained 75 g. of Raney nickel,[8] and shaken vigorously at the boiling point for 1 hr.[9] The Raney nickel was removed by filtration and the tetrahydrofuran solution was concentrated. The residue was distilled *in vacuo* to yield 5 g. of viscous oil, b.p. 190–200° (0.3 mm.).

Anal. Calcd. for $C_{26}H_{30}$; mol. wt., 342.5; C, 91.17; H, 8.83. Found: mol. wt. 330 (f.p. in benzene); C, 90.80; H, 9.10.

Treatment of di-(3-thianaphthenyl)methane with trioxane and boron trifluoride etherate. A mixture of 7.4 g. (0.027 mole) di(3-thianaphthenyl)methane, 1.2 g. of trioxane, and 8 g. of boron trifluoride etherate was dissolved in 30 ml. of absolute ether and stirred at room temperature for 2 days. A large amount of sirupy material separated during this period. The reaction mixture was worked up as described previously and an attempt was made to distill the residue. Although only 0.5 g. of di(3-thianaphthenyl)methane was recovered, essentially no material with the characteristics of fraction B was collected. At 360° some glassy material began to distill accompanied by considerable decomposition. The residue in the distillation flask consisted of a glass much like the residues from the previous reactions.

Reaction of 3-Hydroxymethylthianaphthene with di(3-thianaphthenyl)methane. To 7.2 g. (0.044 mole) of 3-hydroxymethylthianaphthene[6] (prepared by the lithium aluminum hydride reduction of 3-thianaphthenecarboxylic acid) in 25 ml. of ether there was added 12.2 g. (0.044 mole) of di(3-thianaphthenyl)methane and 7.0 g. of boron trifluoride etherate. The mixture was stirred at room temperature for 2 days. Benzene was added to dissolve the sirupy material which had precipitated and then water to decompose the

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(4) J. Szmuszkovicz and F. J. Modest, *J. Am. Chem. Soc.*, **72**, 571 (1950).

(5) W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

(6) F. F. Blicke and D. Sheets, *J. Am. Chem. Soc.*, **71**, 2856 (1949).

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

(8) R. Monzingo, S. H. Harris, and K. Volkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

(9) F. F. Blicke and D. Sheets, *J. Am. Chem. Soc.*, **71**, 4001 (1949).

excess boron fluoride. The organic layer was dried, the solvent removed, and the residue distilled to give a small amount of dithianaphthenylmethane and 6.6 g. of material, b.p. 290–315° (0.2 mm.). The product was redistilled to remove traces of di(3-thianaphthenyl)methane. The infrared spectrum potassium bromide of the final product was identical with the spectrum potassium bromide of fraction B.

Reaction of thianaphthene and trioxane with aluminum chloride as catalyst. A mixture of 134 g. (1 mole) of thianaphthene and 18 g. 0.5 mole) of trioxane was dissolved in a mixture of 100 ml. of chloroform and 100 ml. of carbon disulfide. The temperature was kept at 0–10° and 42. g. of powdered anhydrous aluminum chloride was added with stirring over the course of 10 hr. The temperature was then maintained at about 10° and stirring was continued for 4 days. The reaction mixture became very black and nearly solid. After the addition of ice water to decompose excess aluminum chloride, the mixture was filtered to remove the tarry solids. The filtrate was washed with dilute sodium hydroxide and water and dried over magnesium sulfate. The solvent was removed and the residue was distilled to give 3 g. of thianaphthene and 71 g. (50%) of di(3-thianaphthenyl)methane, b.p. 200–220° (1 mm.). The melting point for and the analysis of the dibromide were the same as for those of the dibromide obtained in the analogous boron trifluoride catalyzed reaction. When the impure di(3-thianaphthenyl)methane was allowed to stand for a time, a small amount of crystals appeared in the viscous sirup. A little ether was added to make the mass more fluid, and the crystals were collected. Recrystallization from dioxane yielded pearly leaflets, m.p. 300–302°.

Anal. Calcd. for compound I, $C_{18}H_{10}S_2$: C, 74.47; H, 3.48; S, 22.04. Found: C, 75.19; H, 3.11; S, 22.00.

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HOLLAND, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Kinetics of the Reactions of Phenyl Isocyanate with Thiols[1]

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The base-catalyzed reactions of phenyl isocyanate with 1-butanethiol, 2-butanethiol, and 2-octanethiol in various solvents at 25° were studied to elucidate the mechanism. The slight catalytic effect of the product on the initial second-order reaction was shown to require the amide hydrogen, since *n*-butyl-*N*,*N*-diphenyl thiolcarbamate had no effect. The rate of reaction depended primarily upon the concentration and type of amine catalyst and the polarity of the solvent. The catalytic ability of an amine was generally proportional to its base strength; however, a steric requirement was also apparent. A mechanism is proposed which includes a spontaneous reaction, a base-catalyzed reaction, a product-catalyzed reaction, and a product-base-catalyzed reaction. From kinetic equations based on this mechanism rate constants were calculated, which compare favorably with experimental data.

It has been shown previously[2] that the reactions of phenyl isocyanate with thiols in the presence of triethylamine follow approximate second order kinetics during the early stages. As the reactions progress there is an increase in the rate, which was attributed to catalysis by the thiolcarbamate produced during the reaction. It was the purpose of this work to continue the study of the base-catalyzed reaction of phenyl isocyanate with thiols in order to propose a mechanism and to derive a rate equation. Many studies have been made on the kinetics of the reactions of isocyanate with alcohols[3–5] and with amines,[6] but the thiol reaction has not been thoroughly investigated.

The major portion of this work was done with phenyl isocyanate and 1-butanethiol in various solvents with several base catalysts. The study also included the reaction of the isocyanate with the secondary thiols, 2-butanethiol and 2-octanethiol. The triethylamine-catalyzed reaction between phenyl isocyanate and 1-butanethiol at 25° was shown[2] to produce a single product, *n*-butyl thiolcarbanilate. This product was found to be inactive toward phenyl isocyanate under these conditions. Similarly, the reaction between phenyl isocyanate and 2-butanethiol produced only the secondary butyl thiolcarbanilate.

The kinetic results obtained from the reactions of phenyl isocyanate with 1-butanethiol, 2-butanethiol, and 2-octanethiol at various isocyanate to thiol ratios and at various concentrations of triethylamine in toluene are summarized in Table I. The second order rate curves (Fig. 1) for several reactions of phenyl isocyanate with 1-butanethiol

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[1] From the Ph.D. Thesis of John F. Glenn and the M.S. Thesis of Edward G. Lendrat, University of Delaware, 1960. Presented at the 138th meeting of the American Chemical Society, New York, N. Y., September 1960. Received by the *J. Am. Chem. Soc.*, July 13, 1960.

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[3] (a) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947); (b) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9 (1949); (c) J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958); (d) L. L. Ferstandig and R. H. Scherrer, *J. Am. Chem. Soc.*, **81**, 4838 (1959).

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[6] (a) J. W. Baker and D. N. Bailey, *J. Chem. Soc.*, **1957**, 4652 (1951). (b) NOTE ADDED IN PROOF: A recent paper on thiols is by Y. Iwakura and H. Okada, *Can. J. Chem.*, **38**, 2418 (1960).