from diethyl vinyl phosphate were unsuccessful. A soft, tacky homopolymer of divinyl benzenephosphonate was obtained. The vinyl ester group in diethyl vinyl phosphate is stable toward water and dilute hydrochloric acid solution.

Experimental

Diethyl Vinyl Phosphate.—Diethyl 2-chloroethyl phosphate used in the preparation of diethyl vinyl phosphate, was prepared by reaction of diethyl chlorophosphate with ethylene oxide by the general procedure of Daly and Lowe.[6] After this work was completed, Saunders, *et al.*,[7] reported the preparation of diethyl 2-chloroethyl phosphate by reaction of diethyl chlorophosphate with ethylene chlorohydrin.

To a stirred solution containing 387 g. (2.24 moles) of diethyl chlorophosphate and 3.9 g. (0.03 mole) of anhydrous aluminum chloride was added 114 g. (2.6 moles) of ethylene oxide over a period of 8 hours at room temperature. Distillation of the reaction mixture under reduced pressure gave 400 g. (82.5%) of diethyl 2-chloroethyl phosphate, b.p. 115–117° (5 mm.), $n^{25}\text{D}$ 1.4281.

Anal. Calcd. for $C_6H_{14}O_4ClP$: P, 14.32; Cl, 16.37. Found: P, 14.46; Cl, 16.48.

A solution containing 56.1 g. (1.0 mole) of potassium hydroxide, 1000 ml. of ethanol and 216 g. (1.0 mole) of diethyl 2-chloroethyl phosphate was refluxed for 11 hours. The potassium chloride that separated (59 g.) from the reaction solution during this time was removed by filtration. Distillation of the filtrate gave 93 g. (49%) of diethyl vinyl phosphate, b.p. 67° (2.5 mm.), $n^{25}\text{D}$ 1.4040.

Anal. Calcd. for $C_6H_{13}O_4P$: P, 17.20. Found: P, 16.80.

Diethyl vinyl phosphate was recovered unchanged after being refluxed in water and in 1% aqueous hydrochloric acid solution for 3–6 hours. There was no evidence that acetaldehyde or ethanol were liberated by these treatments.

Copolymers of Diethyl Vinyl Phosphate.—These were prepared as follows. A solution containing 1.8 g. of diethyl vinyl phosphate, 1.04 g. of styrene and 0.14 g. of benzoyl peroxide was heated under nitrogen at atmospheric pressure for 42 hours at 80°. A colorless, viscous liquid was formed from which 1.2 g. of a white, solid copolymer was obtained by precipitation of the polymerization product with 50 ml. of methanol. The diethyl vinyl phosphate/styrene copolymer softened at 68° and contained 2.52% phosphorus.

Diethyl vinyl phosphate/methyl methacrylate and diethyl vinyl phosphate/acrylonitrile copolymers containing 1.42% phosphorus and 0.91% phosphorus, respectively, were prepared by substitution of equivalent amounts of methyl methacrylate and acrylonitrile for the styrene in the above procedure. The copolymer with methyl methacrylate softened at 110° and the copolymer with acrylonitrile softened at 210–220°. Diethyl vinyl phosphate did not form a copolymer with vinyl acetate under these conditions.

Diethyl vinyl phosphate did not polymerize when heated for 42–70 hours at 80° in the presence of 2–5% α,α'-azodiisobutyronitrile or benzoyl peroxide, at 125° in the presence of di-(*t*-butyl) peroxide, or at −30° in the presence of 2–4% sodium in liquid ammonia. In each case the monomer was recovered almost quantitatively by distillation of the product.

Divinyl Benzenephosphonate.—Bis-(2-chloroethyl) benzenephosphonate was prepared in 77% yield by reaction of 195 g. (1.0 mole) of benzenephosphonyl dichloride with 132 g. (3.0 moles) of ethylene oxide in the presence of 1.95 g. of anhydrous aluminum chloride. The product was a colorless liquid, b.p. 160° (0.8 mm.), $n^{25}\text{D}$ 1.5235.

Anal. Calcd. for $C_{10}H_{13}O_3Cl_2P$: P, 10.94; Cl, 25.05. Found: P, 11.05; Cl, 25.63.

A mixture containing 87.3 g. (0.31 mole) of bis-(2-chloroethyl) benzenephosphonate and 65.6 g. (0.62 mole) of anhydrous sodium carbonate was heated for 1.5 hours at 105°, 2 hours at 155° and then for 3 hours at 200°. The sodium chloride that separated from the reaction solution was removed by filtration. Distillation of the filtrate gave 40 g. (61.5%) of divinyl benzenephosphonate, b.p. 174° (3.0 mm.), $n^{25}\text{D}$ 1.5258.

Anal. Calcd. for $C_{10}H_{11}O_3P$: P, 14.74. Found: P, 14.96.

The non-volatile residue from the distillation was a viscous liquid polymer of divinyl benzenephosphonate and amounted to 15 g. (23.1%).

Anal. Calcd. for $C_{10}H_{11}O_3P$: P, 14.74. Found: P, 14.90.

Homopolymers.—These ranged from viscous liquids to soft, tacky solids and were obtained by heating divinyl benzenephosphonate at 80° in the presence of 1–3% benzoyl peroxide.

CONTRIBUTION NO. 319, CHEMICAL DEPARTMENT
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.
WILMINGTON, DELAWARE

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[7] B. C. Saunders, G. J. Stacey, F. Wild and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

Studies on the Chemistry of Heterocyclics. XXII. Investigations on the Mechanism of Reactions of 2-Thienyl Halides with Sodium Amide and Sodium Acetylide in Liquid Ammonia

BY ALEXANDER VAITIEKUNAS AND F. F. NORD

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In view of the growing importance of the reactions of sodium amide as well as sodium acetylide in liquid ammonia for the syntheses and elucidation of the structure of natural products[1,2,3] it appeared worthwhile to investigate this reaction in the heterocyclic series. It is known that sodium amide in liquid ammonia gave the corresponding acetylenic carbinols[2d] with furan and tetrahydrofuran derivatives and thiophene-2-aldehyde, 3-methyl-thiophene-2-aldehyde as well as β-2-thienylacrolein readily gave the corresponding acetylenic alcohols with sodium acetylide in liquid ammonia.[4] However, the alkylations carried out by this method are unsuccessful when applied to halides in the benzene series.[5] In view of the greater reactivity of the thiophene nucleus it appeared desirable to investigate the reaction of 2-thienyl halides with sodium acetylide in liquid ammonia to attempt the direct synthesis of 2-thienylacetylene.

Preliminary experiments have indicated that 2-chlorothiophene did not react and the starting material was recovered quantitatively while 2-bromothiophene did react vigorously.[5a] However, the main reaction product obtained was not the expected 2-thienylacetylene, but tetrabromothiophene, the monohalide being converted into a tetrahalo derivative. Subsequent investigations with 2-bromothiophene and 2-iodothiophene confirmed the results of the preliminary experiments and we obtained, in the case of 2-bromothiophene, tetrabromothiophene in a yield of 35 to 50%. In the case of 2-iodothiophene the tetraiodo derivative was obtained in a yield of 50% together with a small amount of di- and triiodothiophene.

It appears that in all the above reactions some electrophilic reagent such as NH_2Br or $CH{\equiv}CBr$

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(1) J. Heilbron, *J. Chem. Soc.*, 386 (1948).

(2) (a) E. R. H. Jones, *ibid.*, 754 (1950); (b) J. B. Armitage, E. R. H. Jones and M. C. Whiting, *ibid.*, 1993 (1952); (c) J. B. Armitage, C. L. Cook and E. R. H. Jones, *ibid.*, 2010 (1952); (d) G. Eglinton, E. R. H. Jones and M. C. Whiting, *ibid.*, 2873 (1952).

(3) H. H. Schlubach and V. Franzen, *Ann.*, **573**, 105 (1951).

(4) A. Vaitiekunas, R. E. Miller and F. F. Nord, *J. Org. Chem.*, **16**, 1603 (1951).

(5) T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *ibid.*, **2**, 9 (1938).

(5a) A. Vaitiekunas and F. F. Nord, *Nature*, **168**, 875 (1951).

might serve as an intermediary brominating agent, or that the reaction might proceed through complex formation, or that the amide ion initiates the reaction. To establish the more probable mechanism the following reactions have been studied: (1) ammonolysis of 2-thienyl halides at the boiling point of liquid ammonia; (2) reactions of 2-bromo- 3-bromo- or 2-iodothiophene, 3-methyl-2-bromothiophene, 2,5-dibromothiophene and 2,3-dibromothiophene with sodium amide and sodium acetylide; (3) reactions of 2-bromothiophene and phenol mixtures with sodium amide and sodium acetylide in liquid ammonia; (4) the effect of non-ionizing solvent; and (5) the effect of ammonium halides.

Results

1. We have found that neither 2-bromothiophene nor 2-iodothiophene are affected by liquid ammonia at its boiling point where the original reactions were carried out. Both thienyl halides used were recovered quantitatively. They are both easily soluble in liquid ammonia at the concentrations used in the above reactions.

2. The reactions of 2,5-dibromothiophene and 2,3-dibromothiophene with sodium acetylide and sodium amide in liquid ammonia were carried out in a manner analogous to that applied to the monohalides. Tetrabromothiophene was obtained in a yield of 35%. Some 2-bromothiophene was isolated despite the fact that the 2,5-dibromothiophene was carefully purified. In the case of 2,3-dibromothiophene which was prepared by a method which excludes the formation of monobromothiophene, some 3-bromothiophene was obtained. When sodium amide alone was used the conversion of φ 2,5-dibromothiophene into tetrahalide gave a yield of 20%.

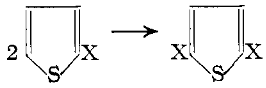
Reactions of 2-bromothiophene, 3-bromothiophene and 2-iodothiophene with sodium amide in liquid ammonia were carried out using freshly prepared sodium amide according to an earlier method.[6] Dibromothiophene and some tribromo product[7] were obtained which were identified by their elemental analysis, refractive indices and boiling points. The dibromothiophene was difficult to purify, probably due to the presence of small amounts of partially hydrogenated decomposition products of the free thiophene. The possibility that such hydrogenation of the thiophene nucleus may take place with decomposition has been recorded recently.[8] Applying the same method to 2-iodothiophene, no triiodothiophene was isolated. We found that using smaller amounts of sodium amide, *e.g.*, 0.2 mole of sodium amide to 1 mole of 2-thienyl halide, the yield of dihalide obtained was much smaller and 70% of the starting material was recovered as recorded in Table I. However, using greater amounts than 1 mole, *e.g.*, 2 moles, of sodium amide to 1 mole of 2-thienyl halide the amount of recovered monohalide was insignificant while the greatest part of monohalide was decomposed probably under partial dehydrohalogenation. No doubt the C–S bond is broken down. The 3-bromothiophene did not react.

TABLE I

EFFECT OF SODIUM AMIDE CONCENTRATION ON THE YIELDS OF THIENYL DIHALIDES

Thienyl halide	Quantity, mole	Sodium amide, moles	Yield in[a] thienyl dihalide, %	Recovered starting material, %
2-Bromothiophene	1	2	18	10
2-Bromothiophene	1	1	36	35
2-Bromothiophene	1	0.2	17	70
2-Iodothiophene	1	2	22	12
2-Iodothiophene	1	1	15	45
2-Iodothiophene	1	0.2	15	65

[a] Calculated according to the equation:



It appears that the initial reaction of 2-bromothiophene as well as of 2-iodothiophene proceeds in an analogous way as with sodium acetylide.

Reactions of 3-methyl-2-bromothiophene with sodium amide in liquid ammonia were performed in a manner analogous to that applied to the monohalides. The dibromo product was formed in a yield of 16.5% only. The methyl group functioning as an electron releasing group did not facilitate the conversion. Analogous results were obtained using sodium acetylide in liquid ammonia.

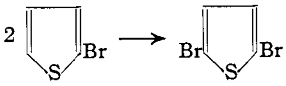
3. Reactions of mixtures of 2-bromothiophene and phenol with sodium acetylide and sodium amide in liquid ammonia: Nitrogen bromide or acetylene bromide might serve as electrophilic agents in these conversions. It is known that nitrogen iodide easily iodinates phenol thus giving the triiodo derivative.[9] When such a reagent serves as intermediary halogenating agent it would be conceivable to obtain some bromo derivative of phenol. However, using different molecular amounts of phenol as recorded in Table II, we were unable to isolate either a mono- or a tribromo derivative of phenol while a conversion of 2-thienyl halide into tetrahalide did take place. The latter reaction took place less readily.

TABLE II

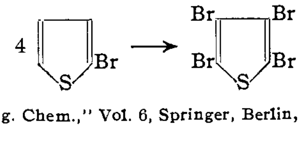
EFFECT OF PHENOL ON THE CONVERSION OF 2-THIENYL HALIDE TO TETRAHALIDE

2-Bromothiophene, mole	Sodium amide (sodium acetylide), mole	Phenol, mole	Recovered monohalide, %	Dihalide,[a] %	Tetrahalide,[b] %
0.1	0.2	0.1	37	50	10
.1	.2	.05	25	21	20
.1	.2	.01	6	12	35

[a] Calculated as dibromoproduct:



[b] Calculated according to the equation:



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(6) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

(7) H. D. Hartough, "The Chemistry of Heterocyclic Compounds, Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 208, 498.

(8) S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 2556 (1951).

(9) Beilstein, "Handbuch der Org. Chem.," Vol. 6, Springer, Berlin, 1923, p. 118.

These observations do not agree with the possible occurrence of intermediary brominating agents such as nitrogen bromide or acetylene bromide. The interference of phenol in this conversion is readily explained by the fact that phenol acting as an acid diminished the concentration of the amide as well as the acetylide ion.

4. While studying the effect of a non-ionizing solvent on the reaction we found that addition of absolute ether to the reaction mixture in amounts of 10% of the total solvent stopped the reaction. The starting materials were recovered and no tetrahalides were obtained.

5. Effect of ammonium halides on the reaction: These are known to react as acids in liquid ammonia and attack the sodium acetylide as well as the amide thus diminishing the acetylide as well as the amide ion concentrations following the equation

$$NaC{\equiv}CH + NH_4X \longrightarrow HC{\equiv}CH + NH_3 + NaX$$

Our present studies indicate that the addition of ammonium chloride as well as of ammonium bromide in amounts of 1 mole of ammonium halide to 1 mole of sodium acetylide or amide interrupts the reaction. In all cases the starting materials were recovered and no tetrahalides were obtained. However, it has to be noticed here that even when ammonium halides were added to the reaction mixture after 3 hours of continuous stirring and shortly prior to the decomposition of the reaction mixture with water no tetrahalides were obtained. This would support the view that the reaction proceeds through a complex formation which under decomposition would give rise to the tetrahalides. Attempts to isolate and to identify such a complex were, however, unsuccessful. It is to be concluded that the presence of sufficient amounts of acetylide as well as of amide ions are necessary for the reaction to proceed.

From the above results we may conclude that: 1, the presence of a sufficient concentration of amide ion is necessary; 2, by means of sodium amide, generally, only monohalides are converted to dihalides, the further conversion to tetrahalides being halted; 3, when dihalides are used as starting materials the conversion with sodium amide proceeds to tetrahalides; 4, the presence of sodium acetylide is indispensable for the conversion of monohalides into the tetrahalides.

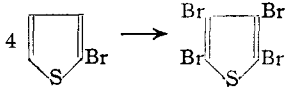
According to these conclusions it could be expected that mixtures of sodium amide and sodium acetylide are capable of converting the monohalides into tetrahalides more readily than sodium acetylide alone. When only the latter is present the amide ion concentration is not effective enough to remove the proton and thus to initiate the reaction. However, the presence of sodium acetylide prevents the decomposition of the thiophene nucleus. Our experiments with 2-bromothiophene confirmed this conclusion. The freshly prepared sodium amide was converted to sodium acetylide to the approximate extent of 25%, 50% and 75% of the total amount of the sodium amide present. The results obtained are shown in Table III.

TABLE III

EFFECT OF MIXTURES OF SODIUM AMIDE AND SODIUM ACETYLIDE ON THE YIELD OF TETRABROMOTHIOPHENE

Sodium amide, %	Sodium acetylide,[a] %	Tetrahalide yield,[b] %
25	75	90
50	50	65
75	25	35
..	100	35

[a] The approximate percentages were calculated by reducing the time required for 100% conversion. [b] Calculated according to the equation:



Discussion

It has been shown earlier[10] that monohalides of benzene, under analogous reaction conditions as outlined above, were converted in liquid ammonia with sodium amide and potassium amide to the corresponding amines. However, we have to consider the different reactivities of the thiophene and benzene nuclei. The former, due to the presence of its sulfur atom, is known to have a smaller effective nuclear charge and a greater electron mobility and is, therefore, capable of reacting in a quite different manner. It is known also that the corresponding thiopheneamines are unstable compounds and can be isolated only as salts. Under the present conditions, the isolation of the corresponding amines would, therefore, not be expected.

The failure of 2-chlorothiophene and 3-bromothiophene to undergo the above conversion reaction can easily be explained considering the higher bond energies of the carbon–chlorine bond or carbon–bromine bond in the 3-position. It is known that the bond energy of the bromine–carbon bond in 2- or 5-position of the thiophene nucleus is lower than that of the corresponding chlorine–carbon bond, *e.g.*, the typical Wurtz syntheses are not reported with the chlorothiophene, while 2-bromothiophene undergoes this reaction.[11]

3-Bromothiophene does not undergo Grignard formation with magnesium in ether[12] while 2-bromothiophene reacts vigorously.

It seems that when the amide ion concentration is too high the dehydrohalogenation reaction prevails, the C–S bond breaks and the decomposition proceeds to the thiol stage and beyond. It is true that in the course of our investigations we failed to isolate any free thiophene when monohalides were used as starting materials; however, we succeeded in isolating monohalides when dihalides served as starting materials. It is very probable that the free thiophene nucleus possessing a negative charge is unstable and before accepting the proton decomposes more readily.

That nitrogen bromide or acetylene bromide could serve as electrophilic brominating agents was disproved by the fact that attempts to isolate bromophenol derivatives were of no avail. It appears therefore that the conversion is initiated by the amide ion and may proceed either *via* formation of a complex which under decomposition with water (or more probably sodium hydroxide) gives

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[10] F. W. Berson, R. E. Wright, Ch. Chandler and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936).

[11] E. Schleicher, *Ber.*, **18**, 3015 (1885).

[12] W. Steinkopf, H. Jacob and H. Penz, *Ann.*, **515**, 135 (1934).

rise to the higher halogenated thiophene derivative. However, the results might also satisfy the consideration of an S_N2 nucleophilic displacement involving solvolysis of the ions taking part in the reaction.

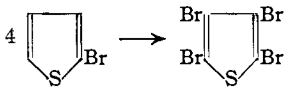
Experimental

Materials.—The 2-bromothiophene (partly) as well as 2-iodothiophene, 3-bromothiophene, 3-methyl-2-bromothiophene, 2,3-dibromothiophene and 2,5-dibromothiophene were prepared according to earlier descriptions[7] while sodium amide and sodium acetylide were obtained by known methods.[6] 2-Chlorothiophene, 2-bromothiophene (partly), phenol, absolute ether, 3-methylthiophene and the ammonium halides used were commercial products.

Ammonolysis of 2-Thienyl Halides at the Boiling Point of Liquid Ammonia.—To 750 ml. of liquid ammonia 0.5 mole of 2-thienyl halide was added dropwise under continuous stirring. The solution was stirred for 3–4 additional hours. Sufficient amount of water was added to the reaction mixture and the halides were extracted with ether. The thienyl halides used were recovered quantitatively.

General Procedure for the Reactions of 2-Thienyl Halides, 3-Bromothiophene, 3-Methyl-2-bromothiophene, 2,3- and 2,5-Dibromothiophene with Sodium Acetylide and Sodium Amide.—The procedure applied was essentially the same as recorded for 2-bromothiophene with sodium acetylide in liquid ammonia.

Reactions of 2-Bromothiophene with Sodium Acetylide in Liquid Ammonia.—To the prepared sodium acetylide (1 mole) in 1.5 l. of liquid ammonia, 1 mole of 2-bromothiophene was added dropwise. The reaction mixture was stirred for 3–4 additional hours and hydrolyzed with water. After extraction with ether there resulted a crystalline substance (45 g., yield 45%) when calculated according to the equation



0.25 mole of 2-bromothiophene was recovered and 6 g. of high boiling oil, a mixture of tri- and dibromothiophene, was obtained. The substance recrystallized from dilute ethanol gave white needles melting at 114°. The molecular weight determined by the Rast method was 380 ± 12. The product was identified as tetrabromothiophene in that it did not depress the melting point on admixture with an authentic specimen prepared according to the method of Volhard and Erdmann.[13]

Anal. Calcd. for C_4Br_4S: C, 12.02; Br, 80.00; S, 8.04. Found: C, 12.31; Br, 80.25; S, 8.44.

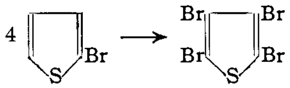
Reactions of 2-Iodothiophene with Sodium Acetylide in Liquid Ammonia.—Eighteen grams of crystalline substance was obtained from 50 g. (0.24 mole) of 2-iodothiophene; yield 50%. It melted at 198° and did not depress the m.p. on admixture with an authentic specimen prepared according to an earlier description.[14]

Anal. Calcd. for C_4I_4S: I, 86.38. Found: I, 86.33.

No starting material was recovered. However, there was isolated 2,5-diiodothiophene (3 g.), m.p. 38°, and probably 2,3,5-triiodothiophene. The latter had a m.p. of 98°.

Anal. Calcd. for $C_4H_2I_2S$: C, 14.33; H, 0.60; I, 75.77. Found: C, 14.5; H, 0.50; I, 75.8. Calcd. for C_4HI_3S: I, 82.42. Found: I, 82.3.

Reactions of 2,5-Dibromothiophene and 2,3-Dibromothiophene with Sodium Acetylide and Sodium Amide in Liquid Ammonia.—(a) When sodium amide was used as a reagent there was obtained from 0.2 mole of 2,5-dibromothiophene: (1) 0.02 mole of 2-bromothiophene, $n^{20}_{\rm D}$ 1.585, showing *Anal.* Calcd. for C_4H_3BrS: C, 29.48; H, 1.84; Br, 49.1. Found: C, 29.61; H, 1.82; Br, 49.52. (2) 3.5 g. (0.011 mole) tribromothiophene which melted at 29°. (3) 7 g. (0.017 mole) of tetrabromothiophene which melted at 114°. According to the equation



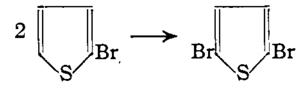
this amounts to a conversion of 18.5%.

(b) When sodium acetylide was used alone there was obtained tetrabromothiophene (m.p. 113°) in a yield of 35% and an analogous amount of 2-bromothiophene to the above described which was identified by its refractive index ($n^{20}_{\rm D}$ 1.5864) and elemental analysis. *Anal.* Calcd. for C_4H_3BrS: Br, 49.1. Found: Br, 49.6.

(c) When sodium amide was used as a reagent there was obtained from 0.1 mole of 2,3-dibromothiophene: (1) 0.01 mole of 3-bromothiophene $n^{20}_{\rm D}$ 1.586, b.p. 157°. *Anal.* Calcd. for C_4H_3BrS: C, 29.48; H, 1.84; Br, 49.1. Found: 29.6; H, 1.82; Br, 49.5. (2) 0.5 g. of tribromothiophene which melted at 43° (probably 2,3,4-tribromothiophene). (3) 5 g. (0.013 mole) of tetrabromothiophene which melted at 113°. This amounts to a conversion of 13%.

(d) When sodium acetylide was used alone, the results were analogous to that of 2,5-dibromothiophene.

Reactions of 2-Bromo, 2-Iodo-, 3-Methyl-2-bromo-, 3-Bromothiophene with Sodium Amide.—(a) From 163.2 g. (1 mole) of 2-bromothiophene there was obtained: (1) 2-bromothiophene, 59 g. (0.36 mole), 35% recovery. (2) 2,5-dibromothiophene, 45 g. (0.188 mole), $n^{20}_{\rm D}$ 1.6380. This amounts to a conversion of 36% according to the equation



Anal. Calcd. for $C_4H_2Br_2S$: C, 19.76; H, 0.83; Br, 66.12. Found: C, 19.76; H, 0.88; Br, 66.40.

(b) Using 1 mole of 2-iodothiophene to 1 mole of sodium amide there was obtained 2,5-diiodothiophene in a yield of 15% which melted at 38° while 45% of 2-iodothiophene was recovered. *Anal.* Calcd. for $C_4H_2I_2S$: C, 14.33; H, 0.60; I, 75.77. Found: C, 14.20; H, 0.5; I, 75.8.

(c) Using 1 mole of 3-methyl-2-bromothiophene to 1 mole of sodium amide there was obtained 21 g. of 3-methyl-2,5-dibromothiophene (b.p. 228°, $n^{20}_{\rm D}$ 1.612). This amounts to a conversion of 16.5%. *Anal.* Calcd. for $C_5H_4Br_2S$: C, 23.6; H, 1.56; Br, 62.67. Found: C, 24.0; H, 1.23; Br, 63.2.

(d) The 3-bromothiophene was recovered quantitatively. When the sodium amide ion concentration was increased to 2 moles to 1 mole of 3-bromothiophene used some decomposition of the latter took place.

Reactions of 2-Bromothiophene with Sodium Amide and Sodium Acetylide Mixtures.—0.2 gram-atom of metallic sodium was dissolved in 450 ml. of liquid ammonia, 0.04 g. of ferric nitrate was added and the mixture stirred for 15 minutes. The dry acetylene gas was bubbled through during a period of 20 minutes. According to the standard procedure developed in other experiments approximately 75% of the sodium amide present was converted to sodium acetylide. 0.1 mole (16.3 g.) of 2-bromothiophene was added dropwise and stirred for 2.5 additional hours. After decomposition with water and extraction with ether there resulted 9.5 g. of tetrabromothiophene which when recrystallized from ethanol melted at 114°; yield 95%.

Reactions of Mixtures of 2-Bromothiophene and Phenol with Sodium Amide and Sodium Acetylide in Liquid Ammonia.—0.2 gram-atom of metallic sodium was converted to sodium amide in liquid ammonia. 0.1 mole of 2-bromothiophene and 0.1 mole of phenol were mixed and added dropwise to the sodium amide solution in liquid ammonia. The phenol was readily dissolved in the halide under absorption of heat. The reaction mixture was stirred for 3–4 additional hours. After decomposition with water the thienyl halides were extracted with ether while the phenol remained in solution as sodium phenolate. The solution of the latter was evaporated under diminished pressure and after acidification the phenol was recovered quantitatively. From the ethereal solution there was obtained 37% (6.05 g.) of recovered 2-bromothiophene and tetrabromothiophene (1 g.) in a yield of 10%.

Reactions of 2-Thienyl Halides with Sodium Acetylide in the Presence of Liquid Ammonia and Absolute Ether or Ammonium Halides.—The halides used were dissolved in absolute ether and then added dropwise to the sodium acetylide solution in liquid ammonia. Absolute ether in amounts of 10% of the total solvent stopped the progress of the reaction. The ammonium halides were added in form of a salt.

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(13) J. Volhard and H. Erdmann, *Ber.*, **18**, 454 (1890).

(14) W. Steinkopf and W. Hanske, *Ann.*, **527**, 247 (1937).

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Interconversion of Hexachlorocyclohexane Isomers

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Because of the insecticidal properties of the γ-isomer, the 1,2,3,4,5,6-hexachlorocyclohexanes have received extensive investigation[1] but the interconversion of the isomers has apparently not been reported. A study of the pure α-, β-, γ- and δ-hexachlorocyclohexane isomers revealed that they are isomerized by heating with anhydrous ferric chloride in sealed tubes under nitrogen at temperatures of 140° or higher. Under these conditions the alpha was the most stable isomer and was isomerized slowly and in low conversion to a mixture of isomers from which delta was isolated and in which beta, gamma and epsilon were indicated by infrared spectrophotometric analysis. The β-isomer was converted readily and almost exclusively to alpha. Gamma was isomerized largely to the α- and δ-isomers; the change in composition of this product mixture with severity of heating suggested that delta was the primary product and was subsequently converted to alpha. Reaction of the pure delta was indeed found to give alpha with a lesser amount of gamma; however, only a small portion of the delta was isomerized. Other Friedel–Crafts type catalysts also promoted isomerization but were usually either less effective or like aluminum trichloride caused extensive degradation with formation of trichlorobenzene. Compositions of typical isomerization products are given in Table I.

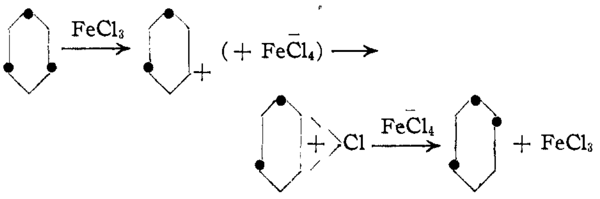
TABLE I

INTERCONVERSION OF HEXACHLOROCYCLOHEXANE ISOMERS

Isomer	Structure[2]	$FeCl_3$, % w. of isomer	Time, hr.	Temp.,[a] °C.	Composition, % w.[b] α	β	γ	δ	Total	Predicted products[e]
α	124/356	100	48	170	87	1.5	0.8	3.7[c]	93[d]	α(12),β(2),γ(4),δ(4),ε = 123/456(2)
β	135/246	8[f]	24	170	77.3	13.0	1.3	2.7	94.3	α(12),β(12)
		5	0.5	310	80.1[c]	10.3	1.0	1.3	92.7	
γ	1245/36	5	12	140	2.8	0.0	60.3	34.1	97.2	α(8),γ(8),δ(8)
		5	12	170	15	0	21	52[c]	88	
		20	122	170	50.0	2.3	4.6	44.0	100.9	
δ	1235/46	20	72	170	15.8	0.0	4.4	68.1	88.3	α(4),β(4),γ(4),δ(8),η = 1234/56(4)

[a] Heated in evacuated, sealed glass tube. [b] By infrared spectrophotometric analysis. [c] Presence confirmed by isolation. [d] Trace of ε-isomer indicated. [e] From displacement with participation from neighboring groups; figures in parentheses are the number of possible transformations out of the total of 24 which would give the indicated isomer. [f] $SbCl_3$, 61%, present as solvent.

The isomerization of the symmetrical β-isomer (135/246) configuration[2] to the α-isomer (124/356) requires the inversion of the positions of the chlorine atoms on any two adjacent carbon atoms. Such a change is highly suggestive of a displacement reaction with participation from a neighboring group as illustrated below.[3] In the formulas a dot represents a chlorine atom above the plane of the ring.



First, a ferric chloride molecule abstracts one of the three chlorine atoms on, for illustration, the top side of the cyclohexane ring. The electron deficient carbon atom then forms a cyclic ion with either of the two identical adjacent carbon atoms and the attached chlorine atom. This chlorine atom and hence the cyclic ion are necessarily on the under side of the cyclohexane ring. Approach to and return of a chlorine atom from the catalyst complex can then be only to the top side of the ring. Return of the chlorine atom to the original carbon atom reforms the β-isomer but return to the neighboring participating carbon atom results in the α-isomer.

Since all carbon atoms in the β-isomer are equivalent, isomerization by this mechanism can give only the α-isomer as a primary product. With the other known isomers in which all carbon atoms are not identical formation of two or more isomers would be expected. Since a carbon atom can participate with each of its two neighboring carbon atoms, four transformations are possible from each carbon atom or a total of 24 from all six. Many of these transformations will of course reform the starting isomer. In this mechanism the positions of both the abstraction and the return of the chlorine atom would be influenced by steric factors and selective formation of one or more isomers would be expected. The products predicted from each of the four isomers and the number of possible transformations giving rise to each product are shown in the table with the experimental results. In investigating the composition of the isomerization mixtures, no thorough attempt was made to isolate minor constituents. Since the spectra and indeed the

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[1] S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

[2] Following Cristol,[1] the numbers above the line indicate the positions of chlorine atoms which lie above a hypothetical planar cyclohexane ring and those below the line lie below the hypothetical planar cyclohexane ring.

[3] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).