crystallized from acetone to obtain non-deliquescent colorless needles, m. p. 267–268° (decompn.). *Anal.* Calcd. for $(CH_3)_4N{\cdot}SeCN$: Se, 44.1. Found: Se, 44.15.

Summary

Water-soluble thiocyanate resulted in 10–25% amounts when alkyl and aryl nitriles, amides, or ammonium salts of organic acids, mixed with trimethylamine and sulfur and using methyl alcohol as the reaction medium, were heated at 200–210° for five hours in sealed tubes. A part of this thiocyanate was isolated as tetramethylammonium thiocyanate. On replacing trimethylamine with ammonia in these reactions 10–22% of thiocyanate was produced.

Phenyl thiocyanate was shown to react with trimethylamine to form ionizable thiocyanate.

New compounds prepared and analyzed were: ethyltrimethylammonium thiocyanate, $C_6H_{14}N_2S$; benzyltrimethylammonium thiocyanate, $C_{11}H_{16}N_2S$; and tetramethylammonium selenocyanate, $C_5H_{12}N_2Se$.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

Synthesis of Polyenes. II. Reactions of β-Methylallyl Chloride with Sodamide in Liquid Ammonia

BY M. S. KHARASCH, WALTER NUDENBERG AND E. STERNFELD[1]

The reaction of allyl chloride with sodamide in liquid ammonia to form hexatriene and its polymers has been reported by Kharasch and Sternfeld.[2] This reaction has been further investigated and data bearing on the generality of the reaction

$$2RR'C{=}CR''CH_2Cl + 2NaNH_2 \xrightarrow[NH_3{]}]{[\text{Liquid}} RR'C{=}CR''CH{=}CHCR''{=}CRR' \quad (1)$$

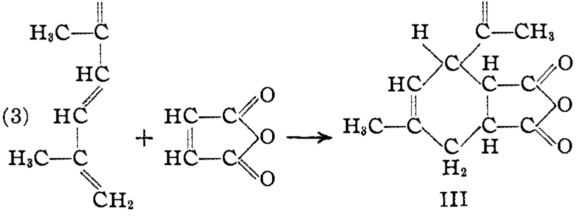
have been obtained from a study of the interaction of β-methylallyl chloride with sodamide in liquid ammonia.

The probability that the conversion of allyl chloride to hexatriene proceeds through the intermediate formation of a chlorohexadiene, was investigated by treatment of two molecular equivalents of allyl chloride with one of sodamide, and careful fractionation of the lower-boiling portion of the product. An approximately 20% yield of a pure chlorohexadiene, b. p. 46–47.5° (96 mm.), n^{20}_D 1.4483, was obtained. Levene and Haller[3] have reported the preparation of 3-chloro-1,5-hexadiene (I) by treatment of allylvinylcarbinol, but have recorded no physical constants other than the rotations of the optically active forms. Further treatment of the purified chlorohexadiene with sodamide yielded butadienyl-2-vinylcyclohexene-3[2] instead of monomeric hexatriene.

$$2H_2C{=}CHCH_2Cl + NaNH_2 \xrightarrow{[\text{Liquid } NH_3]} \left\{\begin{array}{ll} \rightarrow H_2C{=}CHCHClCH_2CH{=}CH_2 & (I) \\ \rightarrow \left\{\begin{array}{l} H_2C{=}CHCH_2CH{=}CHCH_2Cl \quad (IIa) \\ \quad\text{or} \\ H_2C{=}CHCH{=}CHCH_2CH_2Cl \quad (IIb) \end{array}\right. & \end{array}\right. \quad (2)$$

The interaction of equimolecular quantities of β-methylallyl chloride and sodamide in liquid ammonia led to the formation of 2,5-dimethylhexatriene in yields comparable to those of hexatriene obtained from allyl chloride.[2] The product was identified by hydrogenation to 2,5-dimethylhexane, and by condensation with maleic anhydride to form 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride (III)

(3)



III

The physical constants of 2,5-dimethylhexatriene observed in this Laboratory do not agree with those previously reported by Bourguel and Rambaud,[4] who believed they had prepared this compound by treating the glycol, 2,5-dimethyl-2,5-dihydroxy-3-hexene, with dilute hydrochloric acid

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[1] Eli Lilly Fellow. The authors wish to thank the Eli Lilly Company for generous support which made this work possible.

[2] Kharasch and Sternfeld, THIS JOURNAL, **61**, 2318 (1939).

[3] Levene and Haller, *J. Biol. Chem.*, **83**, 185 (1929).

[4] Bourguel and Rambaud, *Bull. soc. chim.*, (4) **47**, 173 (1930).

at 95° for eight days, but who recorded no proofs of the structure or homogeneity of their product.

Treatment of two moles of β-methylallyl chloride with approximately one mole of sodamide in liquid ammonia yielded an intermediate chloro-2,5-dimethylhexadiene, b. p. 33–34° (5 mm.), 160° (752 mm.); $n^{20}_{\rm D}$ 1.4612. Further treatment of this chloride with sodamide gave 2,5-dimethylhexatriene.

Experimental Part

2,5-Dimethylhexatriene.—The method used was essentially that described by Kharasch and Sternfeld.[2] One hundred thirty-five grams (1.5 mole) of redistilled β-methylallyl chloride was added dropwise to one liter of liquid ammonia in a 2-liter unsilvered Dewar flask. Sixty-eight grams (1.7 mole) of sodamide was added intermittently during the addition of the methylallyl chloride. A vigorous reaction ensued after each addition of sodamide. The reaction mixture was stirred for one hour after addition of all the sodamide, then transferred from the Dewar flask to a 2-liter round-bottomed flask. The Dewar flask was rinsed with low-boiling ligroin, and the washings were added to the flask.

The ammonia was evaporated and distilled water and ligroin added to the residue. The layers were shaken and separated. The organic layer was washed with water, and dried over anhydrous sodium sulfate. The ligroin was then removed by distillation through a column containing a tantalum spiral. Distillation of the residue was carried out at 110 mm. on an oil-bath with the use of the tantalum column. A few milliliters distilled at 30–73° (111 mm.) and 22 g. (27%) was collected at 73–75° (110–111 mm.). A portion of material, b. p. 73–75° (110–111 mm.), was redistilled through a Podbielniak column. A constant-boiling fraction, b. p. 90.2° (200 mm.), $n^{21}_{\rm D}$ 1.5150, was taken for analysis.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.88; H, 11.45.

2,5-Dimethylhexatriene boiled at 145° at 747 mm. The melting point was −9°. Heating of the compound near its boiling point for any length of time caused it to become colored and raised its boiling point, indicating rapid polymerization.

The dimethylhexatriene, dissolved in methyl alcohol, underwent smooth hydrogenation in the presence of platinum oxide to yield 2,5-dimethylhexane, b. p. 107.5–108.5° (745 mm.), $n^{21}_{\rm D}$ 1.3925. Gardner and Joseph[5] report b. p. 107–108.5° (755 mm.); $n^{21}_{\rm D}$ 1.3922 for this compound. Egloff[6] gives b. p. 109.3° (760 mm.); $n^{20}_{\rm D}$ 1.39295.

Hydrogenation.—0.0938 gram of dimethylhexatriene, b. p. 58° (51 mm.), in methyl alcohol solution absorbed 53.6 ml. of hydrogen (cor.) (calcd. for C_8H_{12} and 3 double bonds, 58.4 ml. of hydrogen).

By heating of equivalent amounts of 2,5-dimethylhexatriene and maleic anhydride in dry benzene in a sealed tube at 80° for seven hours, 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride (III) was obtained. After three crystallizations from ligroin (b. p. 70–80°) the white crystalline product melted at 115–116°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut. equiv., 103. Found: C, 69.85; H, 7.17; neut. equiv., 107.

Distillation was carried out in some runs at 51 mm., at which pressure 2,5-dimethylhexatriene distilled at 58° to give a product of $n^{20}_{\rm D}$ 1.5122, d^{20}_4 0.7822. The product obtained at this lower temperature and pressure did not polymerize as readily as that obtained at higher pressures. It had the same melting and boiling points at atmospheric pressure.

Preparation of Chloro-2,5-dimethylhexadiene.—Twenty-six grams (0.88 mole) of sodamide was added over a period of one hour to a solution of 93 g. (1 mole) of β-methylallyl chloride in liquid ammonia. After the usual treatment, the following fractions were obtained: 11 g. b. p. 57–67° (50–51 mm.) (2,5-dimethylhexatriene and chloro compounds); 25 g. b. p. 34–36° (6 mm.) of chloro-2,5-dimethylhexadiene and some higher-boiling material which tended to polymerize on distillation at 6 mm.

The chlorodimethylhexadiene was redistilled, boiling at 33–34° (5 mm.); $n^{20}_{\rm D}$ 1.4612. Its boiling point at 752 mm. is 160°.

Anal. Calcd. for $C_8H_{13}Cl$: C, 66.42; H, 9.06; Cl, 24.51. Found: C, 66.12; H, 9.38; Cl, 24.13.

When the chlorodimethylhexadiene was distilled at higher pressures the chlorine analyses were low and the carbon and hydrogen high. The compound tends to lose hydrogen chloride at higher temperatures.

Treatment of the chlorodimethylhexadiene with sodamide in liquid ammonia yielded a liquid, b. p. 58–60° (51 mm.), which, when heated with maleic anhydride in dry benzene, gave the addition product already obtained from 2,5-dimethylhexatriene, m. p. 115–116°. The melting point of a mixture with the known anhydride showed no depression.

Preparation of Chlorohexadiene.—To a solution of 78 g. (1 mole) of allyl chloride in 800 ml. of liquid ammonia was added 24.5 g. (0.5 mole) of sodamide. The mixture was worked up in the usual manner. Upon distillation 12 g. of chlorohexadiene came over at 46–47.5° at 96 mm., $n^{20}_{\rm D}$ 1.4483. It boiled at 115° at 748 mm. with slight decomposition.

Anal. Calcd. for C_6H_9Cl: C, 61.80; H, 7.72; Cl, 30.48. Found: C, 62.35; H, 7.94; Cl, 30.02.

The compound tends to lose hydrogen chloride even at room temperature. On treatment with excess sodamide in liquid ammonia it gave the dimer of hexatriene,[2] b. p. 85–87° (9 mm.), $n^{20}_{\rm D}$ 1.5130.

Of the remaining material from the reaction 15 g. (30%) was chloromethylvinylcyclohexene,[2] b. p. 45–50° (9 mm.), $n^{20}_{\rm D}$ 1.4672.

Absorption Spectra.—Ultraviolet and infrared absorption studies on dimethylhexatriene and the maleic anhydride addition product of hexatriene and dimethylhexatriene were very generously made for us by Drs. Bradley, Richardson,

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(5) Gardner and Joseph, THIS JOURNAL, **61**, 2551 (1939).

(6) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, N. Y., 1939, p. 53.

and Liddel of American Cyanamid Company. We quote from their communication:

"The ultraviolet absorption curve for 2,5-dimethylhexatriene is characterized by three intense narrow absorption bands at 3680, 3830, and 3980 mm.$^{-1}$. We associate these bands with the presence of three conjugated carbon to carbon double bonds in a chain-type aliphatic compound because of their similarity to the corresponding bands found at 3550, 3700, and 3850 mm.$^{-1}$ in the spectrum of α-eleostearic acid. The 130 mm.$^{-1}$ shift toward higher wave numbers (shorter wave lengths) of these bands for the 2,5-dimethylhexatriene is the result of the lower molecular weight of this compound. When the extinction coefficients are compared on a molecular basis the intensity of absorption per molecule is found to be but slightly greater for the α-eleostearic acid as indicated in Table I.

TABLE I

	2,5-Dimethylhexatriene			α-Eleostearic Acid		
		Extinction coefficient[a]			Extinction coefficient[a]	
Band	Wave number	Specific	Molecular	Wave number	Specific	Molecular
I	3680	338.8	36,800	3550	131.8	36,900
II	3830	421.7	45,600	3700	168.0	47,100
III	3980	311.9	33,660	3850	128.8	36,050

[a] The specific extinction coefficient (K) represents the absorption per unit weight of the compound while the molecular extinction coefficient (E_M) represents the absorption per molecule.

$$K = d/Lc \qquad E_M = KM = d/Lc_M$$

where d is the optical density log I_0/I, L is the length in centimeters of the absorption cell filled with solution of concentration c in grams per liter or c_m in moles per liter.

"The infrared spectrum of this compound (dimethylhexatriene) in the region 1000–2000 cm.$^{-1}$ shows those bands which have been observed in similar compounds. The band at 1780 cm.$^{-1}$ is the overtone of the 900 cm.$^{-1}$ C–C band. The infrared absorption due to the conjugated double bond system appears at 1615 cm.$^{-1}$. Since this is the only triply conjugated system we have observed, we cannot say how these differ from double conjugation, if in any manner. The methyl bands appear at 1455 and 1372 cm.$^{-1}$. The terminal $=CH_2$ band appears at 1435 cm.$^{-1}$. Two other weak bands appear at 1319 cm.$^{-1}$ and 1255 cm.$^{-1}$."

The spectroscopic data for the maleic anhydride addition products of hexatriene and 2,5-dimethylhexatriene shows very little evidence for conjugated carbon to carbon double bonds. Accordingly, the structures are those of vinyl and isopropenyl, rather than ethylidene and isopropylidene, tetrahydrophthalic anhydrides, in contradiction to the work of Farmer and Warren.[7]

Summary

1. β-Methallyl chloride reacts with sodamide in liquid ammonia to give 2,5-dimethylhexatriene.

2. A probable intermediate in this reaction, a chloro-2,5-dimethylhexadiene, has been isolated. The corresponding compound from allyl chloride, a chlorohexadiene, also has been obtained.

3. The ultraviolet and infrared absorption spectra of dimethylhexatriene have been determined.

4. Spectroscopic data indicate that the maleic anhydride addition product of hexatriene is 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride, rather than the 3-ethylidene anhydride, as postulated by Farmer and Warren. The corresponding compound from 2,5-dimethylhexatriene is 3-isopropenyl-9-methyl-1,2,3,6-tetrahydrophthalic anhydride.

5. This work is being continued with special attention to the synthesis of non-symmetrical hexatrienes, polyenes, and other classes of unsaturated compounds.

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(7) Farmer and Warren, *J. Chem. Soc.*, 897 (1929).