The Reaction between 2,5-Dimethyl-2,4-hexadiene and Chlorine. *trans*-2,5-Dichloro-2,5-dimethyl-3-hexene and 4,5-Dichloro-2,5-dimethyl-2-hexene

Lewis F. Hatch[1] and Mohamed S. Matar

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

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The liquid phase reaction between 2,5-dimethyl-2,4-hexadiene and chlorine yields the following compounds: 4,5-dichloro-2,5-dimethyl-2-hexene (by 1,2 addition), *trans*-2,5-dichloro-2,5-dimethyl-3-hexene (by 1,4 addition), 3,4,5-trichloro-2,5-dimethyl-1-hexene (*threo* and *erythro*), and 1,4,5-trichloro-2,5-dimethyl-2-hexene. These compounds are not the same as those previously reported. A kinetic study was made of the allylic rearrangement of *trans*-2,5-dichloro-2,5-dimethyl-3-hexene to 4,5-dichloro-2,5-dimethyl-2-hexene,

The addition of chlorine to 2,5-dimethyl-2,4-hexadiene (1) in chloroform has been reported by Tishchenko, Abramova, and Yarzhemskaya[2] to give 3,4-dichloro-2,5-dimethyl-1,5-hexadiene (2) as the primary product and 3,6-dichloro-2,5-dimethyl-1,4-hexadiene (3) and 1,6-dichloro-2,5-dimethyl-2,4-hexadiene (4) as secondary products. Sharefkin and Pohl[3] have reported the preparation of 2,5-dichloro-2,5-dimethyl-3-hexene from **1**.

The dichloro compounds produced by the reaction between chlorine and **1** in carbon tetrachloride have now been identified as *trans*-2,5-dichloro-2,5-dimethyl-3-hexene (5) and 4,5-dichloro-2,5-dimethyl-2-hexene (6) in a 2:3 ratio. Identification was made by their infrared spectra and by their nuclear magnetic resonance spectra. The same compounds and in essentially the same ratio were obtained when chloroform, trichloroethylene, or *n*-hexane was used as the solvent. Pure **5** was obtained from the mixture by low-temperature crystallization. The spectrum of **6** was obtained from a mixture of **5** and **6** that was synthesized by the reaction between *trans*-2,5-dimethyl-3-hexene-2,5-diol and thionyl chloride.[4]

The formation of compounds **5** and **6** can be accounted for by the 1,2 addition and 1,4 addition of chlorine to **1**. The product distribution from the addition of chlorine to this diene appears to be kinetically controlled, since no appreciable isomerization of the allylic chlorides would be expected at the temperature used for the addition. The fact that the 1,2-addition product is kinetically favored over the 1,4-addition product indicates that the transition state leading to the 1,2-addition product is more sterically favored.

Three trichloro compounds were isolated. One was identified as 1,4,5-trichloro-2,5-dimethyl-2-hexene (7) and the other two, tentatively, as the 3,4,5-trichloro-2,5-dimethyl-1-hexenes (*threo* and *erythro*) (8).

The reaction between lithium aluminum hydride and compounds **2**, **3**, and **4** would be expected to give one product—*trans*-2,5-dimethyl-2,4-hexadiene.[5] This reaction with **5** gave 2,5-dimethyl-2-hexene (70%) by SN2 and SN2′ reactions and *trans*-2,5-dimethyl-3-hexene (30%) by SN2 reactions. A mixture of **5** and **6** gave the same products in a ratio that indicated that pure **6** would have given 94% 2,5-dimethyl-2-hexene by SN2′ reactions and 6% 2,5-dimethyl-3-hexene. The formation of 2,5-dimethyl-3-hexene from **6** can be accounted for by assuming some allylic rearrangement of **6** and **5** during the reaction. These data provide further evidence that the dichloro compounds obtained in this investigation are not the same as those reported by Tishchenko and coworkers[2] for the chlorination reaction under similar reaction conditions.

Table I

Thermodynamic Functions and Rate Constants for the Isomerization of *trans*-2,5-Dichloro-2,5-dimethyl-3-hexene (5) to 4,5-Dichloro-2,5-dimethyl-2-hexene (6)

Temp, °K	329.4	353.3	372.4
A. Thermodynamic Functions			
6,%	40.6	47.8	53.0
K_{eq}	0.673	0.895	1.13
ΔF, kcal, mol	0.259	0.078	0.089
ΔS, eu	7.31	8.21	8.91
ΔH, kcal/mol	2.66	2.98	3.23
B. Rate Constants			
k_1, hr^{-1}	0.014 ± 0.001	0.12 ± 0.01	0.73 ± 0.06
k_{-1}, hr^{-1}	0.020 ± 0.002	0.13 ± 0.01	0.65 ± 0.05

The allylic rearrangement of **5** to **6** was studied kinetically at 56.2, 80.1, and 99.2° to obtain fundamental data for this reaction. Thermodynamic data and rate data for the unimolecular isomerization are given in Table I. Specific rate constants, defined as $k = X_e/at \ln [X_e/(X_e - X)]$, were determined from a plot of $\ln X_e/(X_e - X)$ *vs.* time, where X is the molar concentration of **5** at time t, a is the initial molar concentration of **5**, and X_e is the molar concentration of **5** at equilibrium. Equilibrium constants, defined as $K_{eq} = [6]/[5]$ and equal to k_1/k_{-1} at a given temperature, were also required for these calculations.[6]

Rate data permitted calculation of the following approximate data: activation energy $E_a = 21$ kcal/mol; entropy of activation $\Delta S^{\neq} = -21$ eu; ΔH, for all three temperatures, 21 kcal/mol.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra measurements were made by use of a Beckman IR-5

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[1] To whom correspondence should be addressed: University of Texas at El Paso, El Paso, Tex. 79999.

[2] D. Tishchenko, A. Abramova, and E. Yarzhemskaya, *Zh. Obshch. Khim.*, **27**, 227 (1957); *J. Gen. Chem. USSR*, **27**, 253 (1957).

[3] J. G. Sharefkin and S. H. Pohl, *J. Org. Chem.*, **29**, 2050 (1964).

[4] J. D. Roberts, W. G. Young, and S. Winstein, *J. Amer. Chem. Soc.*, **64**, 2157 (1942).

[5] L. F. Hatch and G. Bachmann, *Chem. Ber.*, **97**, 132 (1964); L. F. Hatch and R. E. Gilbert, *J. Org. Chem.*, **24**, 1811 (1959); L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959); C. W. Jefford, S. N. Mahajan, and J. Gunsher, *Tetrahedron*, **24**, 2921 (1968).

[6] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 19–20.

spectrophotometer. The nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as the internal reference. Mass spectral analyses were made by using a Consolidated 21110 C high-resolution mass spectrometer. Gas chromatographic analyses were made using a Research Specialties Model 60-30 instrument with temperature programming (Model 611-60). A 6 ft × 0.25 in. o.d. column packed with 10% by weight Carbowax 6000 on 60–80 mesh Chromosorb W was used. Element analyses were made by Clark Microanalytical Laboratory, Urbana, Ill.; The Clayton Biochemical Institute, Microanalytical Laboratory, Austin, Tex.; and Galbraith Laboratories Inc., Knoxville, Tenn. These chloro compounds are relatively unstable toward hydrogen chloride elimination, which accounts for discrepancies in element analyses.

Chlorination of 1.—A solution of chlorine (142 g, 2.00 mol) in carbon tetrachloride (1500 ml) was added slowly to redistilled **1** (220 g, 2.00 mol, furnished by Eastman Chemical Products, Inc.) in carbon tetrachloride (500 ml). The reaction temperature was maintained at 0–4°. On completion of chlorine addition, the reaction was dried over sodium sulfate. Because rearrangement of the two dichlorides (**5** and **6**) occurs at high vpc column temperatures, temperature programming was used at 55–140° during vpc analyses. Compounds **5** and **6** were detected at 65 and 70° after 4 and 6 min, respectively. A typical vpc analysis follows: 47% **6**, 31% **5**, 13% **7**, 6% **8a**, and 3% **8b**. Two peaks (**8a** and **8b**) were obtained for **8**, but the trichlorides were not characterized as to *thero* and *erythro* isomers.

***trans*-2,5-Dichloro-2,5-dimethyl-3-hexene (5).**—This compound was separated from its allylic isomer **6** by crystallization at −25°. Recrystallization of **5** from Skellysolve B at −5° produced white crystals, mp 35°. The ir spectrum of this compound had a peak at 969 cm^{-1}, which indicated a *trans* structure. Absence of a carbon–carbon double bond stretching peak (*ca.* 1660 cm^{-1}) indicated a symmetrical structure around the double bond. The nmr spectrum (CCl_4) follows: τ 4.14 (s, HC=CH), and 8.31 [s, $CCl(CH_3)_2$]. These signals have a relative intensity of 1:6.

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.05; H, 7.79; mol wt, 180.0472. Found: C, 53.2; H, 7.9; mol wt, 180.0478 (mass spectrum).

4,5-Dichloro-2,5-dimethyl-2-hexene (6).—This compound was obtained by trapping on a preparative vpc column from the chlorination reaction mixture. The best separation gave a mixture containing 87% the desired compound **6** and 13% its isomer **5**. The ir spectrum of this mixture has a characteristic absorption at 1672 cm^{-1} which indicates an unsymmetrical carbon–carbon double bond. The nmr spectrum follows: τ 4.59 (d, C=CH), 5.37 (d, CHCl, allylic), 8.19–8.26 [m, $C{=}C(CH_3)_2$], and 8.39 [s, $CCl(CH_3)_2$].

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.05; H, 7.79; Cl, 39.16; mol wt, 180.0472. Found: C, 53.21; H, 7.69; Cl, 39.15; mol wt, 180.0476.

The Trichloro-2,5-dimethylhexenes (7 and 8).—Three trichloro compounds were isolated from the reaction mixture by use of a vpc preparative column, and one was identified as **7**. The ir spectrum of each of the diasteroisomers (**8a** and **8b**) has a strong absorption at 917 cm^{-1} ($CR_1R_2{=}CH_2$ out-of-plane deformation). The ir spectrum of **7** does not show a strong band in this area, which indicates the absence of a terminal methylene group. The elemental analyses of **8b** indicated appreciable loss of chlorine between isolation and analysis. The ir spectra and indices of refraction were obtained on samples immediately after vpc separation.

1,4,5-Trichloro-2,5-dimethyl-2-hexene (7) gave the following data: $n^{25}{}_D$ 1.5045; nmr (CCl_4) τ 4.27 (d, C=CH), 5.40 (d, CHCl, allylic), 6.00 (s, CH_2Cl), 8.10 (d, $C{=}CCH_3$), and 8.30 [s, $CCl(CH_3)_2$].

Anal. Calcd for $C_8H_{13}Cl_3$: C, 44.85; H, 6.07. Found: C, 44.83; H, 5.89.

Compound **8a** gave the following data: $n^{25}{}_D$ 1.4938; nmr (CCl_4) τ 4.75 (s, $C{=}CH_2$), 5.00 (d, CHCl, allylic), 5.80 (d, CHCl), 8.11 (s, $C{=}CCH_3$), and 8.27 [s, $CCl(CH_3)_2$].

Anal. Calcd for $C_8H_{13}Cl_3$: C, 44.54; H, 6.08; Cl, 49.06. Found: C, 44.58; H, 6.07; Cl, 49.34.

Compound **8b** gave the following data: $n^{25}{}_D$ 1.4947; nmr (CCl_4) τ 4.8 (s, $C{=}CH_2$), 4.95 (d, CHCl, allylic), 5.75 (d, CHCl), 8.00 (s, $C{=}CCH_3$), and 8.2–8.3 [m, $CCl(CH_3)_2$].

Anal. Calcd for $C_8H_{13}Cl_3$: mol wt, 214.0083. Found: mol wt, 214.0087 (mass spectrum).

***trans*-2,5-Dimethyl-3-hexene-2,5-diol.**—This diol was prepared by the sodium in liquid ammonia reduction of 2,5-dimethyl-3-hexyne-2,5-diol (Farchan Research Laboratories). The olefin diol was recrystallized from hot toluene, mp 98° (lit.[7] mp 101.5°). The ir spectrum of this compound had the same characteristic absorption peaks as reported for *trans*-2,5-dimethyl-3-hexene-2,5-diol.[8]

Mixture of 5 and 6.—*trans*-2,5-Dimethyl-3-hexene-2,5-diol (4.32 g, 0.030 mol) was dissolved in 130 ml of dry ether. Thionyl chloride (7.85 g, 0.066 mol), dissolved in 60 ml of dry ether, was added dropwise to the alcohol at room temperature. The mixture was refluxed for 2 hr and then analyzed by vpc. Only two peaks were obtained and they had identical retention times with those of the two dichloride peaks from the addition of chlorine to **1**. The ir spectrum of the mixture had the same characteristics as the spectrum of the dichlorides from the addition of chlorine to **1**.

Reduction of Dichlorides by Lithium Aluminum Hydride.—Both **5** and a mixture of **5** and **6** were treated with lithium aluminum hydride in a previously described manner.[5] The products of these reactions are given in the Discussion. The vpc analyses were made using the column described by Smith and Ohlson.[9]

Isomerization Study.—The isomerization of **5** to **6** was carried out at 56.2, 80.1, and 99.2° by thermostating solutions of known concentrations of **5** in *n*-decane. *n*-Decane was used as the solvent because its high boiling point minimized loss due to evaporation and because there is no absorption of this solvent at the ir region used for analysis.

The course of the isomerization was followed by ir spectra analyses of the equilibrating solution at suitable time intervals. Compound **5** has characteristic absorptions at 969 and 1250 cm^{-1} that are suitable for quantitative analysis, and the compounds obeyed Beer's law over the entire concentration range used. Isomer **6** has characteristic absorption at 1672 cm^{-1}, but this band is not intense enough to be used for analysis. Solutions of known concentrations of both isomers were prepared using carbon tetrachloride and *n*-decane as solvents. The absorbance of each isomer was the same regardless of the solvent. The data are given in Table I.

Registry No.—**1**, 764-13-6; **5**, 22966-70-7; **6**, 22929-07-3; **7**, 22929-08-4; **8a**, 22966-71-8; **8b**, 22966-72-9.

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[7] J. R. Johnson and O. H. Johnson, *J. Amer. Chem. Soc.*, **68**, 2615 (1940).

[8] K. Griesbaum, A. A. Oswald, and W. Naegele, *J. Org. Chem.*, **29**, 1887 (1964).

[9] B. Smith and R. Ohlson, *Acta Chem. Scand.*, **13**, 1253 (1959).