zenetetracarboxylic acid (0.12% and called "prehnitic" acid). Since the same conditions produced none of these aromatic acids from cellulose, but 0.83% of the pentacarboxylic acid from a solvent-extracted sprucewood,[25b] the authors suggested that the immediate precursors existed as such in the wood. The present almost negative result for sprucewood suggests that the pentacarboxylic acid they found was an artifact from the alkalinity and high temperature used in their oxidation, and was therefore comparable in origin to that now derived from alkali lignin itself (Table III). In the same way, Horn's[26] isolation of perhaps 0.4% of mellitic acid from a Willstätter lignin might have owed its success to the condensing action of the fuming hydrochloric acid used to prepare the lignin, and to the boiling concentrated nitric acid employed for the oxidation.

The effect of acid reagents upon lignin was recently demonstrated by Richtzenhain,[20] who recovered up to 1.3% of 4,5-dimethoxyphthalic (metahemipinic) acid from methylated samples of Willstätter lignin, ethanol lignins and lignosulfonic acid, but none from methylated sprucewood, by oxidation with hot potassium permanganate solution kept near *p*H 7. Structure (I) must have undergone a nuclear condensation in position 6 to produce the precursor yielding metahemipinic acid. Treatment of the Willstätter lignin with 70% potassium hydroxide at 170° prior to methylation caused the yield of this acid to decrease, and none was isolated from the oxidation of a methylated alkali lignin. These observations might have been connected with further nuclear condensation to the precursors of the benzenepolycarboxylic acids discussed in the present article. It was interesting to note that the same treatment increased Richtzenhain's recoveries of 2,3-dimethoxy-*m*-phthalic (isohemipinic) acid from 0.9% in sprucewood to 6.65% in the alkali lignin, and that some of the lignin in sprucewood was presumably substituted in the fifth position of the structural unit (I). Such a substitution would also explain the origin of 3.9% of *m*-toluic acid isolated after the electrochemical oxidation of a butanol lignin from western hemlock,[27] although, of course, the requisite precursor might have been formed only during the extraction of the lignin with aqueous butanol near 160°.

Acknowledgment.—One of the authors (D.E.R.) wishes to thank The Ontario Paper Co. Limited for the Fellowship, and the Canadian Pulp and Paper Association for other financial assistance, awarded to him during the research.

[26] O. Horn, *Brennstoff-Chem.*, **10**, 364 (1929).

[27] A. Bailey and H. M. Brooks, THIS JOURNAL, **68**, 445 (1946).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XV. Preparation and Properties of the 1,2,3-Trichloropropenes[1]

BY LEWIS F. HATCH, JOHN J. D'AMICO[2a] AND EDWARD V. RUHNKE[2b]

The two isomers of 1,2,3-trichloropropene have been prepared, characterized and their relative reactivities have been determined with potassium iodide in acetone and with sodium ethoxide in ethanol. No relationship between reactivity and configuration was noted for the reaction with sodium ethoxide but with potassium iodide the isomer with the vinyl chlorine atom and the chloromethyl group in the *cis* position was appreciably more reactive. In addition to the 1,2,3-trichloropropenes the following compounds were prepared and characterized: *cis*- and *trans*-3-bromo-1,2-dichloro-1-propene and *cis*- and *trans*-2,3-dichloro-2-propen-1-ol.

1,2,3-Trichloropropene has been reported in the literature as having been prepared by the dehydrochlorination of 1,2,2,3-tetrachloropropane,[3,4] the dehydrobromination of 2-bromo-1,2,3-trichloropropane[4] and by the decarboxylation and dehydrochlorination of $\alpha,\beta,\beta,\gamma$-tetrachlorobutyric acid.[5] With all of these methods of preparation it would be possible to obtain a mixture of both *cis*- and *trans*-1,2,3-trichloropropene, but in no case was any mention made of the separation and identification of these isomers. The present paper describes the preparation and characterization of these two isomeric trichlorides and two closely related pairs of geometrical isomers. The following equations represent the reactions employed in this study.

$$\mathrm{CHCl{=}CClCH_3} + \text{N-bromosuccinimide} \longrightarrow \mathrm{CHCl{=}CClCH_2Br} \quad \text{(I)}$$

$$\mathrm{CHCl{=}CClCH_2Br} + \mathrm{H_2O} \xrightarrow{\mathrm{Na_2CO_3}} \mathrm{CHCl{=}CClCH_2OH} \quad \text{(II)}$$

$$\mathrm{CHCl{=}CClCH_2OH} + \mathrm{PCl_5} \xrightarrow{\mathrm{C_5H_5N}} \mathrm{CHCl{=}CClCH_2Cl} \quad \text{(III)}$$

$$\mathrm{CHCl{=}CClCH_2Cl} + \mathrm{LiAlH_4} \longrightarrow \mathrm{CHCl{=}CClCH_3} \quad \text{(IV)}$$

In reaction I both *cis*- and *trans*-1,2-dichloro-1-propene was brominated separately but for each reaction the product consisted of a mixture of both *cis*- and *trans*-3-bromo-1,2-dichloro-1-propene. The isomerization of the 3-bromo-1,2-dichloro-1-propenes was sufficiently slow, however, to permit their separation and hydrolysis to give good yields of the corresponding dichloroalcohol. The isomers of both 2,3-dichloro-2-propen-1-ol and 1,2,3-trichloropropene did not isomerize.

The configuration of the isomers of 1,2,3-trichloropropene was assigned by relating the trichloride to the corresponding 1,2-dichloro-1-propene of known structure[6] (reaction IV). With each

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[1] For number XIV of this series see L. F. Hatch and J. J. D'Amico, THIS JOURNAL, **73**, 4393 (1951).

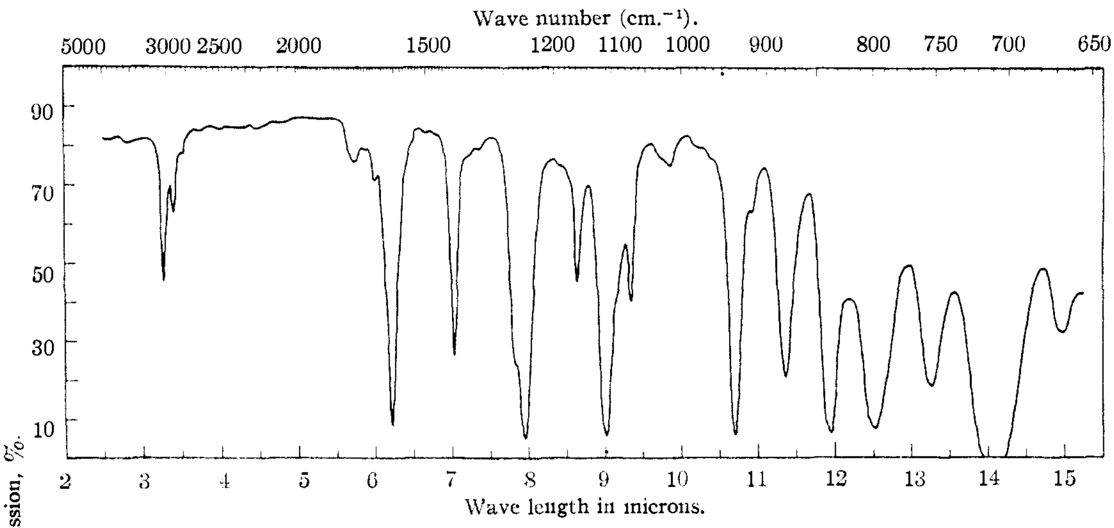
[2] (a) Monsanto Chemical Co., Nitro, West Virginia; (b) Agricultural and Mechanical College of Texas, College Station, Texas.

[3] W. Pfeffer and R. Fittig, *Ann.*, **135**, 357 (1865).

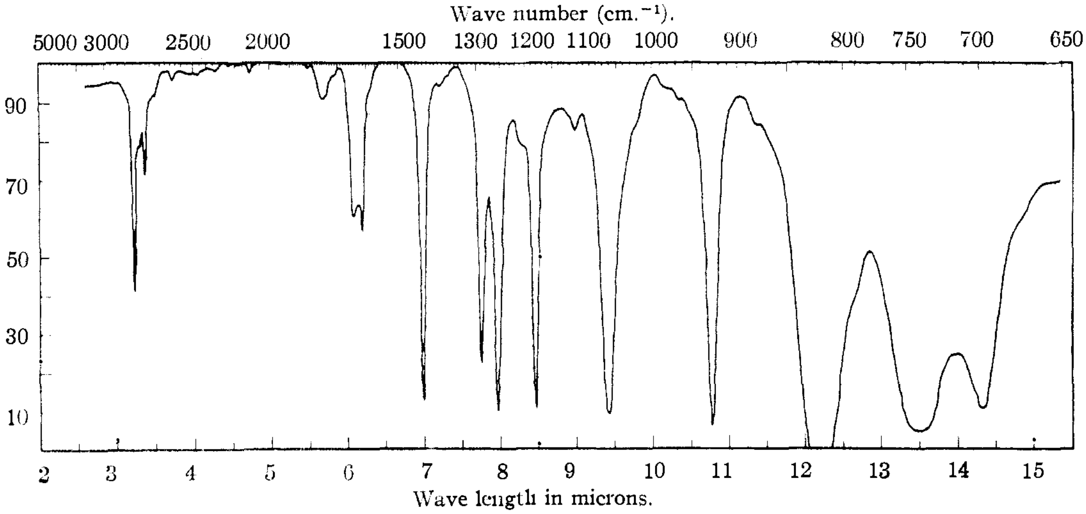
[4] A. Kirrmann and G. Kremer, *Bull. soc. chim.*, 166 (1948).

[5] G. Oestermann, *ibid.*, 254 (1949).

[6] W. H. King and H. A. Smith, THIS JOURNAL, **72**, 3459 (1950); H. J. Bernstein and J. Powling, *ibid.*, **73**, 1843 (1951).



cis-1,2,3-Trichloropropene.



trans-1,2,3-Trichloropropene.

Fig. 1a.

pair the higher boiling isomer had the *cis* configuration. By analogy, the higher boiling isomer of both 2,3-dichloro-2-propen-1-ol and 3-bromo-1,2-dichloro-1-propene would have the *cis* configuration.

Figure 1 gives the infrared spectra for all of the stable compounds prepared in these studies.[7] These spectra show no characteristics which are not in agreement with the assignment of configuration. The spectra of 3-bromo-1,2-dichloro-1-propenes were not obtained because of their tendency to isomerize.

The reactivities of both *cis*- and *trans*-1,2,3-trichloropropene have been determined in the reaction with potassium iodide in acetone at 20° and with sodium ethoxide in ethanol at 50°. In the reaction with sodium ethoxide the replacement of a hydrogen atom on the number 2 carbon atom caused a slight decrease in reactivity over that of 1,3-dichloropropene.[8] Geometrical configuration does not cause a material difference in reactivity.

In the reaction with potassium iodide an electron attracting group (Cl, Br) on the number 2 carbon atom decreases the reactivity and an electron releasing group (CH_3) increases the reactivity when there are two hydrogen atoms on the number 1 carbon atom.[9] With a hydrogen and a chlorine atom on the number 1 carbon atom, however, the reactivity of the allylic chlorine atom is increased by the replacement of the hydrogen atom on the number 2 carbon atom regardless of the nature of the group or atom (CH_3, or Cl).

The role of geometrical configuration is important and consistent within the three pairs of similar geometrical isomers studied (1,3-dichloropropene,[9,10] 1,3-dichloro-2-methylpropene[9,11] and 1,2,3-

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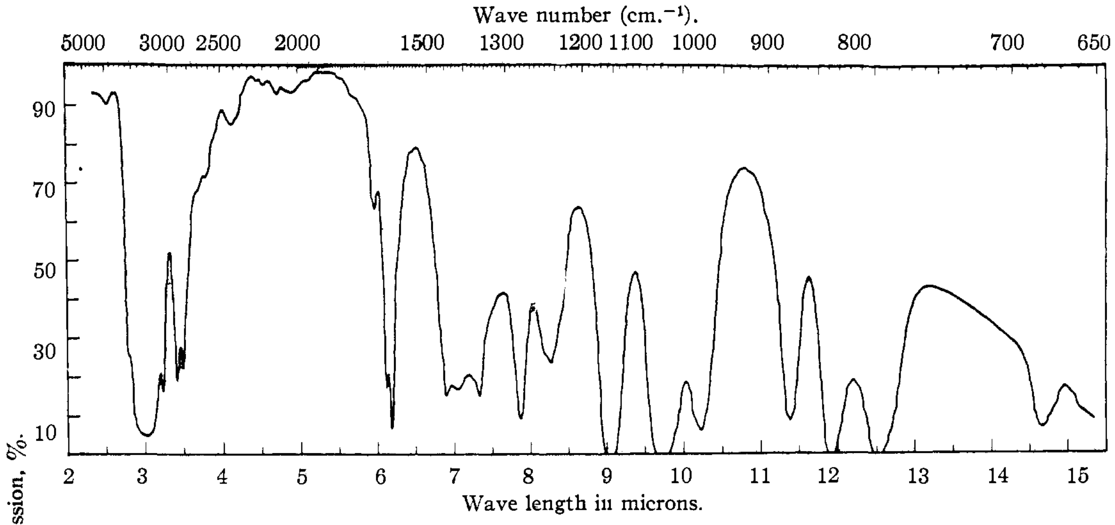
[7] These spectra were obtained through the courtesy of Dr. R. E. Kitson, Polychemicals Department, Chemical Division, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

[8] L. F. Hatch and H. E. Alexander, THIS JOURNAL, **71**, 1037 (1949).

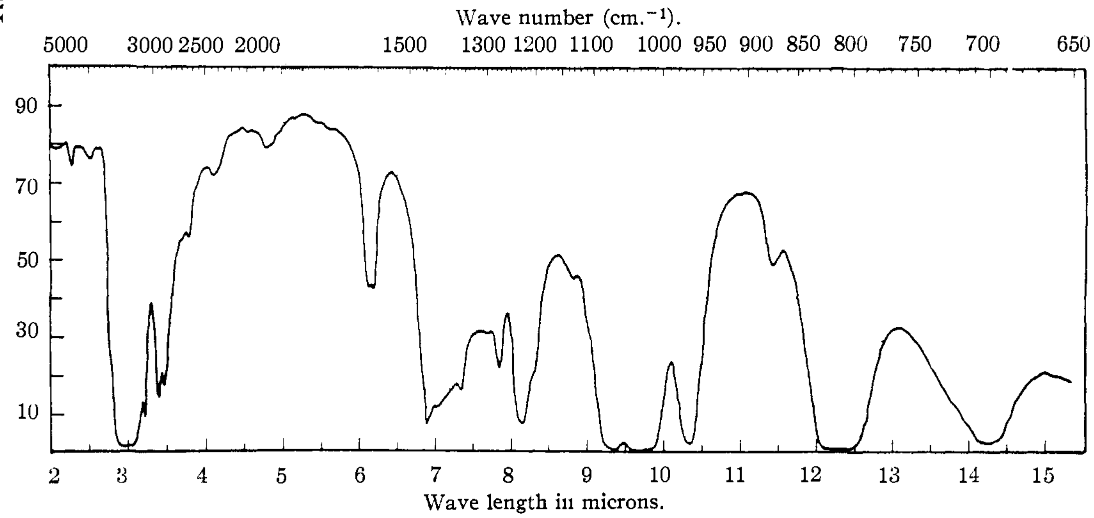
[9] L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

[10] L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

[11] L. F. Hatch, A. N. Brown and H. P. Bailey, *ibid.*, **72**, 3198 (1950).



cis-2,3-Dichloro-2-propen-1-ol.



trans-2,3-Dichloro-2-propen-1-ol.

Fig. 1b.

trichloropropene). With each pair the isomer having the vinyl chlorine atom and the chloromethyl group in the *cis* position was the more reactive. This same relationship between configuration and reactivity has also been noted for the cuprous chloride catalyzed acid hydrolysis of allylic chlorides.[11]

1,2,3-Trichloropropene was also prepared by the dehydrochlorination of 1,2,2,3-tetrachloropropane[3,4] to determine if this method of preparation would yield both isomers. Both isomers were obtained in nearly equal amounts and in good yields.

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Experimental

***cis*- and *trans*-3-Bromo-1,2-dichloro-1-propene.**—A mixture of *cis*- and *trans*-1,2-dichloro-1-propene (Halogen Chemicals, Inc., Columbia, South Carolina) was fractionated to obtain the two isomers (*cis* b.p. 93.0–93.5°, *trans* b.p. 75.0–75.8°). Each isomer was separately brominated with N-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide.[12] The reaction was complete within one hour and the products were worked up in the usual manner. Fractionation of the products through a three-foot glass-helix packed column gave the following yields: from *cis*-1,2-dichloro-1-propene (2.00 moles), 37% *cis*-3-bromo-1,2-dichloro-1-propene and 14% *trans*-3-bromo-1,2-dichloro-1-propene; from *trans*-1,2-dichloro-1-propene (2.50 moles), 22% *cis*-3-bromo-1,2-dichloro-1-propene and 27% *trans*-3-bromo-1,2-dichloro-1-propene.

The bromo compounds slowly isomerized at room temperature to a mixture of the two isomers. The following physical data were obtained on freshly distilled material and may be considered as approximately correct.

***cis*-3-Bromo-1,2-dichloro-1-propene:** b.p. 67–68° (20 mm.); d^{25}_{4} 1.794; $n^{25}\text{D}$ 1.540, $n^{30}\text{D}$ 1.538.

***trans*-3-Bromo-1,2-dichloro-1-propene:** b.p. 57–58° (20 mm.); d^{25}_{4} 1.737; $n^{25}\text{D}$ 1.535, $n^{30}\text{D}$ 1.533.

***cis*- and *trans*-2,3-Dichloro-2-propene-1-ol.**—Each isomer of 2,3-dichloro-2-propen-1-ol was obtained by the hydrolysis of a freshly distilled sample of the corresponding isomer of 3-bromo-1,2-dichloro-1-propene using a 10% molar excess of a 10% solution of sodium carbonate. The hydrolyses were carried out at *ca.* 80° and for a reaction time of 12 hours. The products were worked up in the usual manner and dis-

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[12] C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

tilled through a 16-inch glass-helix packed column. The *cis* isomer (1.24 moles) gave a yield of 74% *cis*-2,3-dichloro-2-propen-1-ol and the *trans* isomer (0.90 mole) gave a 61% yield of the *trans* dichloroalcohol.

***cis*-2,3-Dichloro-2-propen-1-ol:** b.p. 87.0–87.5° (21 mm.); d^{22}_4 1.4020; $n^{22}\mathrm{D}$ 1.4990, $n^{25}\mathrm{D}$ 1.4982.

Anal.[13] Calcd.: Cl, 55.92. Found: Cl, 56.18, 56.25.

***trans*-2,3-Dichloro-2-propen-1-ol:** b.p. 76.0–76.7° (21 mm.); d^{22}_4 1.4014; $n^{22}\mathrm{D}$ 1.5010, $n^{25}\mathrm{D}$ 1.4997.

Anal.[13] Calcd.: Cl, 55.92. Found: Cl, 56.08, 56.10.

***cis*- and *trans*-1,2,3-Trichloropropene.**—The 1,2,3-trichloropropenes were prepared from the corresponding dichloroalcohols using phosphorus trichloride in pyridine.[14,15] The *cis* isomer of the dichloroalcohol (0.93 mole) gave a yield of 53% *cis*-trichloride. A 55% yield of the *trans*-trichloride was obtained from the *trans*-dichloroalcohol (0.48 mole).

***cis*-1,2,3-Trichloropropene:** b.p. 87° (100 mm.); d^{25}_4 1.4238; $n^{25}\mathrm{D}$ 1.5020, $n^{30}\mathrm{D}$ 1.4995.

Anal.[13] Calcd.: Cl, 73.15. Found: Cl, 73.20, 73.37.

***trans*-1,2,3-Trichloropropene:** b.p. 75° (100 mm.); d^{25}_4 1.4057; $n^{25}\mathrm{D}$ 1.4956; $n^{30}\mathrm{D}$ 1.4932.

Anal.[13] Calcd.: Cl, 73.15. Found: Cl, 73.28, 73.36.

Reaction of *cis*- and *trans*-1,2,3-Trichloropropene with Lithium Aluminum Hydride.—Both *cis*- (0.32 mole) and *trans*-1,2,3-trichloropropene (0.22 mole) were treated with lithium aluminum hydride. The reaction was carried out in a manner similar to that described by Hatch and Perry.[10] *cis*-1,2-Dichloro-1-propene (b.p. 93.0°, $n^{25}\mathrm{D}$ 1.4508) was obtained in a 63% yield from *cis*-1,2,3-trichloropropene. *trans*-1,2,3-Trichloropropene gave a 71% yield of *trans*-1,2-dichloro-1-propene (b.p. 75.0°, $n^{25}\mathrm{D}$ 1.4460). With both compounds the conversion was relatively low.

Dehydrochlorination of 1,2,2,3-Tetrachloropropane.—The 1,2,2,3-tetrachloropropane (8.31 moles) was prepared by the addition of chlorine to 9.22 moles of 2,3-dichloro-1-propene (b.p. 92.5) at 10° (90% yield).[4] The 1,2,2,3-tetrachloropropane [b.p. 107–108° (150 mm.); d^{18}_4 1.5000; $n^{18}\mathrm{D}$ 1.4937, $n^{25}\mathrm{D}$ 1.4901; lit.[4] b.p. 165° (760 mm.), 51° (12 mm.); d^{18}_4 1.5000; $n^{18}\mathrm{D}$ 1.494] in 18.8 moles of ethanol was dehydrochlorinated by the slow addition of 8.31 moles of potassium hydroxide at 80°. The reaction products were worked up in the usual manner and distilled through a four-foot glass-helix packed column to give a 26% yield of *cis*-1,2,3-trichloropropene (b.p. 87° (100 mm.), $n^{25}\mathrm{D}$ 1.5020) and 32% yield of *trans*-1,2,3-trichloropropene (b.p. 75° (100 mm.)). There was 11% of unreacted tetrachloride. The product of this reaction reported by Kirrmann and Kremer[4] had the following physical properties: b.p. 32–33° (14 mm.); d^{16} 1.402; $n^{16}\mathrm{D}$ 1.4993.

Infrared Spectra.[7]—The infrared spectra data were obtained in the liquid phase using a Perkin–Elmer model 21 double-beam spectrometer. Sodium chloride optics were used with a cell thickness of 0.037 mm., except for *trans*-2,3-dichloro-2-propen-1-ol which had a cell thickness of 0.040 mm.

Reaction with Potassium Iodide in Acetone.—The usual procedure was used.[6] The reactions were too fast at 20° to permit the calculation of exact kinetic data. The per cent. reacted *vs.* time data are given in Table I. It is estimated that *trans*-1,2,3-trichloropropene reacted about five times faster than the *cis* isomer.

TABLE I

RELATIVE REACTIVITIES OF *cis*- AND *trans*-1,2,3-TRICHLOROPROPENE

Reaction with potassium iodide in acetone at 20°

cis-1,2,3-Trichloropropene

Time, hr.	0.75	1.00	1.25	1.50	1.75
Reacted, %	41.6	46.4	55.7	61.4	64.0

trans-1,2,3-Trichloropropene

Time, hr.	0.267	0.334	0.416	0.500
Reacted, %	62.1	72.6	77.4	84.9

Reaction with sodium ethoxide in ethanol at 50°

cis-1,2,3-Trichloropropene

Time, hr.	4.00	6.00	8.00	10.0	12.0
Reacted, %	25.7	34.1	40.3	45.9	51.6
k, hr.$^{-1}$ mole^{-1} l.	1.96	1.94	1.87	1.87	1.93
Av. k			1.91 ± 0.04		
Relative reactivity[a]			1.61		

trans-1,2,3-Trichloropropene

Time, hr.	2.00	3.00	4.00	5.00	7.00
Reacted, %	22.7	30.4	36.4	42.8	51.3
k, hr.$^{-1}$ mole^{-1} l.	2.75	2.75	2.65	2.72	2.65
Av. k			2.70 ± 0.04		
Relative reactivity[a]			2.27		

[a] Allyl chloride as 1.00 with k = 1.19.

Reaction with Sodium Ethoxide in Ethanol.—A previously described procedure[8] was used for this study and the data were calculated using the rate expression for a second order reaction. The sodium ethoxide solution was 0.04316 M for the reaction with *cis*-1,2,3-trichloropropene (0.03753 M) and 0.05036 M for the reaction with *trans*-1,2,3-trichloropropene (0.03753 M). A plot of log $(b(a - x)/a(b - x)$ *vs.* time gave a straight line for *cis*-1,2,3-trichloropropene between 26 and 52% reacted and between 23 and 51% reacted for the *trans* isomer. The data are given in Table I.

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(13) E. Chablay, *Ann. chim.*, **1**, 510 (1914).

(14) A. Juvala, *Ber.*, **63B**, 1989 (1930).

(15) L. F. Hatch and S. S. Nesbitt, THIS JOURNAL, **72**, 727 (1950).