bath at 150° for three hours. When the flask was removed from the bath for inspection, the molten contents solidified and would not remelt when heated to 165°. The polymer was suspended in 100 ml. of chloroform and slowly poured into 400 ml. of rapidly stirred methanol. The polymer was washed with methanol and dried for analysis; yield 1.35 g. The original polymer was tough and plastic while the final polymer was rubbery. The new polymer became tacky when heated to 245° and became molten at 320°. The new polymer was 34% soluble in chloroform and the soluble portion had an inherent viscosity of 0.39.

Anal. Calcd. for $C_8H_{14}S_2$: C, 55.12; H, 8.10; S, 36.79. Calcd. for $C_8H_{14}S_4$: C, 40.29; H, 5.92; S, 53.79. Found: C, 49.07; H, 7.29; S, 43.83. Calcd. for $C_8H_{14}S_{2.7}$: C, 48.84; H, 7.17; S, 44.00.

Oxidation of Hexamethylenedithiol with Bromine.—Five ml. of hexamethylenedithiol was added to 50 ml. of 2% MP-635-S[7] solution in a four-ounce polymerization bottle. Three grams of sodium hydroxide was added and the mixture shaken until solution was complete. Then 6 g. of bromine was added and the bottle was capped and shaken on a mechanical shaker for 3 hours. Some polymer formed almost immediately and separated as precoagulant. At the end of the shaking period alum coagulant[7] was added to break the emulsion and the polymer was collected on a filter. The precipitate contained a great deal of inorganic material. By extracting with chloroform and evaporating this solution, about 60% of the theoretical yield of polymer was obtained as a white powder with an inherent viscosity of 0.21.

Anal. Calcd. for $C_6H_{12}S_2$: C, 62.00; H, 10.41; S, 27.59. Found: C, 61.62; H, 9.98; S, 28.11.

[7] C. S. Marvel, V. C. Menikheim, H. K. Inskip, W. K. Taft and B. G. Labbe, *J. Poly. Sci.*, **10**, 39 (1953).

URBANA, ILLINOIS

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

Allylic Chlorides. XXIV. 1,1,3-Trichloro-1-propene, 1,1-Dibromo-3-chloro-1-propene and Related Compounds[1,2]

BY LEWIS F. HATCH AND STANLEY D. ZIMMERMAN

RECEIVED DECEMBER 26, 1956

1,1,3-Trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been prepared by conversion of the dihalopropenes to the corresponding allylic bromides using N-bromosuccinimide, basic hydrolysis of the bromides to the allylic alcohols and treatment of the alcohols with phosphorus trichloride. Relative reactivities of the allylic chlorides with sodium ethoxide in ethanol were determined. The reaction with potassium iodide in acetone gave kinetically anomalous data. The products from this reaction were 1,1-dihalo-3-iodo-1-propenes.

A number of closely related allylic chlorides have been prepared and their relative reactivities toward sodium ethoxide in ethanol and potassium iodide in acetone determined. The ones of interest in the present work are $CY_2{=}\overset{\displaystyle H}{\overset{|}{C}}{-}CH_2Cl$ (Y = H, CH_3) and $CCl_2{=}\overset{\displaystyle Y}{\overset{|}{C}}{-}CH_2Cl$ (Y = F, Cl, CH_3). The introduction of two methyl groups on the *gamma* carbon atom increases the reactivities of the allylic chlorine atom in both reactions. Since the methyl group is electron releasing, it was desirable to determine the effect of electron attracting groups in this position. For this purpose 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been prepared and studied.

Both of these allylic chlorides were prepared by the series of reactions shown in Fig. 1 for 1,1,3-trichloro-1-propene. The allylic chlorides and all of the intermediate compounds are lachrymators and vesicants. The preparation of 1,1,3-trichloro-1-propene by other methods has been reported.[3]

Attempts to prepare both 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene directly by the reaction between N-chlorosuccinimide and the corresponding dihalopropene ($CX_2{=}CHCH_3$) were unsuccessful. No definite product could be separated from either reaction. The oxidation of 1,1-dichloro-1-propene to 3,3-dichloro-2-propen-1-ol using selenium dioxide was attempted under various conditions of temperature and solvent. Apparently no oxidation took place.

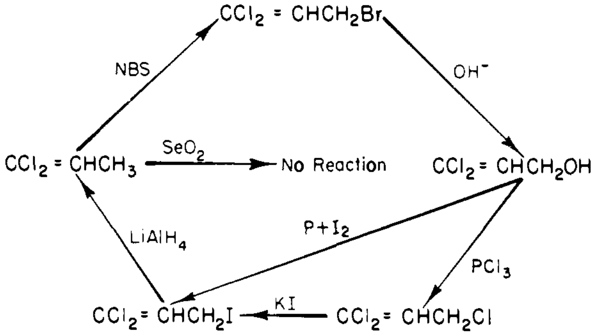

Fig. 1.—1,1-Dichloro-3-halo-1-propenes.

The relative reactivities of the two allylic chlorides with sodium ethoxide in ethanol are given in Table I. The greater reactivity of the dibromo compound is consistent with previous work with the 1,3-dichloropropenes[4] and the 1-bromo-3-chloro-1-propenes.[5] A comparison between the effect of halogen atoms and methyl groups in this position is complicated by the possibility of hydro-

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[1] This research was supported by the Department of Navy at the Defense Research Laboratory, the University of Texas, under contract NOrd-9195.

[2] Presented in part at the 125th National Meeting of the American Chemical Society, Kansas City, Missouri, March, 1954.

[3] (a) A. Kirrman and G. Kremer, *Bull. soc. chim. France*, (5) **15**, 166 (1948); (b) G. W. Hearne, T. W. Evans, H. L. Yale and M. C. Hoff, THIS JOURNAL, **75**, 1392 (1953); (c) A. N. Nesmeyanov, R. Kh. Freidina and V. L. Firstov, *Izvest. Akad. Nauk. U.S.S.R. Otdel Khim. Nauk.*, 505 (1951); (d) United States Rubber Co., Brit. Pat. 660,475 (1951).

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

[5] L. F. Hatch and K. E. Harwell, *ibid.*, **75**, 6002 (1953).

gen atoms of the methyl groups participating in the transition state.[6]

TABLE I

RELATIVE REACTIVITIES OF 1,1,3-TRICHLORO-1-PROPENE AND 1,1-DIBROMO-3-CHLORO-1-PROPENE WITH SODIUM ETHOXIDE IN ETHANOL AT 50°

			1,1,3-Trichloro-1-propene		
Time, hr.	0.50	1.00	1.50	3.00	6.00
Reacted, %	26.3	42.4	51.3	68.2	81.2
k, hr.$^{-1}$ mole^{-1} l.	14.2	14.7	14.0	14.2	14.4
Av. k			14.3 ± 0.2		
Relative reactivity[a]			12.1		
			1,1-Dibromo-3-chloro-1-propene		
Time, hr.	0.10	0.25	0.50	0.75	1.00
Reacted, %	18.7	34.5	52.3	64.0	71.8
k, hr.$^{-1}$ mole^{-1} l.	22.7	23.1	20.1	23.9	22.1
Av. k			22.4 ± 1.0		
Relative reactivity[a]			19.0		

[a] Allyl chloride as 1.00 with k = 1.18.

The kinetic data for the reaction of 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene with potassium iodide in acetone were of such a nature that constant values of second-order rate constants were not obtained. This behavior of polyhalo allylic chlorides has been observed previously.[7] Since these kinetic studies with potassium iodide gave anomalous results, the products from each of the dihalo allylic chlorides were isolated and characterized.

If the reaction of 1,1,3-trichloro-1-propene with iodide ion is an SN2 reaction, there should be a simple exchange of the allylic chlorine atom by an iodine atom.

$$CCl_2{=}CHCH_2Cl + KI \longrightarrow CCl_2{=}CHCH_2I + KCl$$

If the reaction were to proceed by a nucleophilic attack on the γ-carbon atom followed by, or simultaneous with, an allylic rearrangement and expulsion of the allylic chlorine atom from the α-carbon atom (SN2′), then the product would be 3,3-dichloro-3-iodo-1-propene.[8,9]

$$I^- \longrightarrow CCl_2{=}CHCH_2Cl \longrightarrow ICCl_2CH{=}CH_2 + Cl^-$$

The isolation and purification of the reaction products were complicated by the ease of decomposition of the allylic iodide. However, it was possible by distillation at low pressures to obtain a compound of sufficient purity to permit a satisfactory determination of its spectrum, density, index of refraction and boiling point. The spectrum of the compound had an absorption band at 8.7 μ which was indicative of the allylic iodide structure ($CCl_2{=}CHCH_2I$).[10] It did not have an absorption band at 10.1 μ which is characteristic of a monosubstituted ethylene.

This compound also was treated with lithium aluminum hydride, and 1,1-dichloro-1-propene was obtained as the only product.[11] The structure was further established by comparison of the compound with an authentic sample prepared by the treatment of 3,3-dichloro-2-propen-1-ol with red phosphorus and iodine (Fig. 1). The spectrum of the allylic iodide was essentially identical with that obtained for the compound isolated from the reaction with potassium iodide. The physical properties of the two compounds were as close as expected for compounds as unstable as these.

As a further check on the identity of the unknown product from the potassium iodide reaction, its 3,5-dinitrobenzoate was prepared by the use of silver 3,5-dinitrobenzoate and compared with that obtained from an authentic sample of 1,1-dichloro-3-iodo-1-propene as well as with the 3,5-dinitrobenzoates of the corresponding chloride, bromide and alcohol. Mixtures of all possible pairs of these 3,5-dinitrobenzoates in no instance gave a lowering of the melting point.

The compound isolated from the reaction of 1,1-dibromo-3-chloro-1-propene and potassium iodide was shown to be 1,1-dibromo-3-iodo-1-propene in the same manner as that used for the identity of the product from 1,1,3-trichloro-1-propene.

Infrared spectra obtained for the various compounds prepared during this investigation were the same as would have been predicted for the particular compound. It is of especial significance that with the allylic chlorides there was always an absorption at 8.01 μ; with the allylic bromides the absorption was at 8.30 μ and with the iodides at 8.7 μ.[10]

Experimental

3-Bromo-1,1-dichloro-1-propene.—3-Bromo-1,1-dichloro-1-propene was prepared in a 75% yield by the bromination of 2.00 moles of 1,1-dichloro-1-propene (b.p. 76.5–77.0°; n^{25}_D 1.4418; d^{25}_4 1.1675) using N-bromosuccinimide (1.00 mole) and conventional procedures. The 3-bromo-1,1-dichloro-1-propene had the following physical properties: b.p. 45.1° (10 mm.); n^{20}_D 1.5363, n^{25}_D 1.5337, n^{30}_D 1.5310; d^{20}_4 1.7593, d^{25}_4 1.7506, d^{30}_4 1.7421. *Anal.* Calcd. for $C_3H_3BrCl_2$: total halogen, 79.4; Br, 42.1. Found: total halogen, 79.7, 79.5; Br, 41.8, 42.0.

3,3-Dichloro-2-propen-1-ol.—3-Bromo-1,1-dichloro-1-propene (1.00 mole) was hydrolyzed by use of a 7.5% sodium carbonate solution at 65 to 70° for 8 hr. An 85% yield of 3,3-dichloro-2-propen-1-ol was obtained. The dichloroalcohol had the following physical properties: b.p. 75–77° (20 mm.); n^{20}_D 1.4918, n^{25}_D 1.4898, n^{30}_D 1.4879; d^{20}_4 1.3830, d^{25}_4 1.3770, d^{30}_4 1.3718 (lit.[12] b.p. 72° (18 mm.); n^{16}_D 1.4883; d^{16} 1.3617). *Anal.* Calcd. for $C_3H_4Cl_2O$: Cl, 55.9. Found: Cl, 56.1, 56.0.

1,1,3-Trichloro-1-propene.—1,1,3-Trichloro-1-propene was prepared by treating 3,3-dichloro-2-propen-1-ol (0.50 mole) with phosphorus trichloride (0.20 mole) in dry pyridine (0.11 mole) at 65° for 2 hr. A 90% yield was obtained. Physical properties of the 1,1,3-trichloro-1-propene were: b.p. 59.5° (50 mm.); n^{20}_D 1.4958, n^{25}_D 1.4930, n^{30}_D 1.4904; d^{20}_4 1.4030, d^{25}_4 1.3953, d^{30}_4 1.3876 (lit.[3b] b.p. 132–133°; n^{20}_D 1.4962; d^{20}_4 1.3983). *Anal.* Calcd. for $C_3H_3Cl_3$: Cl, 73.2. Found: Cl, 73.4, 73.6.

1,1-Dichloro-3-iodo-1-propene from the Alcohol, Red P and I_2.—A mixture of 3,3-dichloro-2-propen-1-ol (0.50 mole) and red phosphorus (0.10 mole) was stirred vigorously, and cooled while iodine (0.10 mole) was added portionwise and cautiously to the flask. After all of the iodine was added, the mixture was warmed to 70–80° until the iodine coloration of the condensate on the flask walls had disappeared. Then 0.05 mole of iodine was added and heating continued

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[6] J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 855 (1956); L. F. Hatch and P. R. Noyes, THIS JOURNAL, **79**, 345 (1957).

[7] L. F. Hatch and D. W. McDonald, *ibid.*, **74**, 3328 (1952).

[8] A. H. Fainberg and W. T. Miller, Jr., Abstracts of the 119th American Chemical Society Meeting, Boston, Massachusetts, April, 1951.

[9] G. Stork and W. N. White, THIS JOURNAL, **78**, 4609 (1956).

[10] R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

[11] L. F. Hatch and R. E. Perry, Jr., THIS JOURNAL, **71**, 3262 (1949).

[12] F. Kutscher and H. Steudel, *Z. physiol. Chem.*, **39**, 474 (1903).

until once again the iodine coloration was gone. The mixture was cooled and filtered and the filtrate distilled. The 1,1-dichloro-3-iodo-1-propene had the following physical properties: b.p. 34° (1 mm.); n^{20}_{D} 1.6030, n^{25}_{D} 1.5998, n^{30}_{D} 1.5968; d^{20}_4 2.0480, d^{25}_4 2.0401, d^{30}_4 2.0300. *Anal.* Calcd. for $C_3H_3Cl_2I$: total halogen, 83.5; I, 53.6. Found: total halogen, 83.7, 83.7; I, 54.1, 54.0.

Lithium Aluminum Hydride Reduction of 1,1-Dichloro-3-iodo-1-propene from 3,3-Dichloro-2-propen-1-ol, Red P and I_2.—A mixture of 1,1-dichloro-3-iodo-1-propene (0.27 mole) and 10 ml. of ether was stirred rapidly while a suspension of lithium aluminum hydride (0.075 mole) in 20 ml. of ether was added at a rate to produce gentle refluxing. The excess lithium aluminum hydride was destroyed by 2% sulfuric acid and the organic layer was worked up in the usual manner. 1,1-Dichloro-1-propene (b.p. 75–76° (750 mm.); n^{25}_{D} 1.4441) was obtained as the only product.

1,1-Dichloro-3-iodo-1-propene from 1,1,3-Trichloro-1-propene and KI.—1,1,3-Trichloro-1-propene (0.25 mole) was added slowly to 0.25 mole of potassium iodide in 600 ml. of acetone at 10°. The reaction product was worked up in the usual manner and gave 1,1-dichloro-3-iodo-1-propene as the only product. Its physical properties were: b.p. 34.5–35° (1 mm.); n^{20}_{D} 1.6017, n^{25}_{D} 1.5990, n^{30}_{D} 1.5959; d^{20}_4 2.0529, d^{25}_4 2.0440, d^{30}_4 2.0346. *Anal.* Calcd. for $C_3H_3Cl_2I$: total halogen, 83.5; I, 53.6. Found: total halogen, 83.8, 83.9; I, 54.0, 53.7.

Lithium Aluminum Hydride Reduction of 1,1-Dichloro-3-iodo-1-propene from 1,1,3-Trichloro-1-propene and KI.—The same procedure was used as in the reduction of the product obtained from the reaction of 3,3-dichloro-2-propen-1-ol, red phosphorus and iodine. The physical properties of the 1,1-dichloro-1-propene were: b.p. 75–76° (750 mm.); n^{25}_{D} 1.4439.

1,1-Dibromo-3-chloro-1-propene.—A similar series of reactions were carried out for the preparation of 1,1-dibromo-3-chloro-1-propene from 1,1-dibromo-1-propene as used in the preparation of 1,1,3-trichloro-1-propene from 1,1-dichloro-1-propene. The yields and physical properties of the various compounds follow.

1,1-Dibromo-1-propene: b.p. 41.5° (30 mm.); n^{25}_{D} 1.5245.

1,1,3-Tribromo-1-propene: yield 73%; b.p. 62–64° (0.5 mm.); n^{20}_{D} 1.6030, n^{25}_{D} 1.6006, n^{30}_{D} 1.5980; d^{20}_4 2.4408, d^{25}_4 2.4304, d^{30}_4 2.4207. *Anal.* Calcd. for $C_3H_3Br_3$: Br, 86.0. Found: Br, 85.7, 85.7.

3,3-Dibromo-2-propen-1-ol: yield 80%; b.p. 62–64° (0.5 mm.); n^{20}_{D} 1.5652, n^{25}_{D} 1.5633, n^{30}_{D} 1.5611; d^{20}_4 2.1788, d^{25}_4 2.1707, d^{30}_4 2.1632. *Anal.* Calcd. for $C_3H_4Br_2O$: Br, 74.0. Found: Br, 73.5, 73.6.

1,1-Dibromo-3-chloro-1-propene: yield 81%; b.p. 35.5–36.0° (0.6 mm.); n^{20}_{D} 1.5663, n^{25}_{D} 1.5634, n^{30}_{D} 1.5610; d^{20}_4 2.1365, d^{25}_4 2.1260, d^{30}_4 2.1162. *Anal.* Calcd. for $C_3H_3Br_2Cl$: total halogen, 83.3; Cl, 15.1. Found: total halogen, 83.4, 83.6; Cl, 14.7, 14.8.

1,1-Dibromo-3-iodo-1-propene from 3,3-Dibromo-2-propen-1-ol, Red P and I_2: b.p. 50° (0.1 mm.); n^{20}_{D} 1.6737, n^{25}_{D} 1.6708, n^{30}_{D} 1.6681; d^{20}_4 2.7283, d^{25}_4 2.7171, d^{30}_4 2.7060. *Anal.* Calcd. for $C_3H_3Br_2I$: total halogen, 88.0; I, 39.0. Found: total halogen, 88.3, 88.3; I, 39.1, 39.2.

Lithium Aluminum Hydride Reduction of 1,1-Dibromo-3-iodo-1-propene from 3,3-Dibromo-2-propen-1-ol, Red P, and I_2.—1,1-Dibromo-1-propene was the only product; b.p. 40° (29 mm.); n^{25}_{D} 1.5245.

1,1-Dibromo-3-iodo-1-propene from 1,1-Dibromo-3-chloro-1-propene and KI: b.p. 51° (0.2 mm.); n^{20}_{D} 1.6731, n^{25}_{D} 1.6703, n^{30}_{D} 1.6675; d^{20}_4 2.7196, d^{25}_4 2.7082, d^{30}_4 2.6975. *Anal.* Calcd. for $C_3H_3Br_2I$: total halogen, 88.0; I, 39.0. Found: total halogen, 88.1, 88.2; I, 39.1, 39.3.

Lithium Aluminum Hydride Reduction of 1,1-Dibromo-3-iodo-1-propene from 1,1-Dibromo-3-chloro-1-propene and KI.—1,1-Dibromo-1-propene was the only product; b.p. 41° (30 mm.); n^{25}_{D} 1.5247.

3,5-Dinitrobenzoates.—3,5-Dinitrobenzoates of the alcohols and all of the allylic halides were prepared using 3,5-dinitrobenzoyl chloride for the alcohols and the silver salt of 3,5-dinitrobenzoic acid for the halides. All of the alcohol derivatives with each of the corresponding allylic halide derivative showed no melting point depression. The melting point range for the dichloro derivatives was 69.5–70.8° and 90.2–91.2° for the dibromo derivatives. *Anal.* Calcd. for $C_{10}H_6Cl_2N_2O_6$ (from the alcohol): Cl, 22.1; N, 8.73. Found: Cl, 21.8, 22.0; N, 8.94. Calcd. for $C_{10}H_6Br_2N_2O_6$ (from the alcohol): Br, 39.0; N, 6.83. Found: Br, 38.6, 38.8; N, 7.05.

Reaction with Potassium Iodide in Acetone at 20°.—No consistent rate data could be obtained with either 1,1,3-trichloro-1-propene or 1,1-dibromo-3-chloro-1-propene. The weight of potassium chloride formed during the reaction indicated a 66% reaction in 15 minutes and an 88% reaction in 30 minutes.

Reaction of Sodium Ethoxide in Ethanol at 50°.—The procedure was the same as that previously described[4] and the data were calculated using the rate expression for a second-order reaction. The sodium ethoxide solution was 0.09931 molar for the reaction with 1,1,3-trichloro-1-propene (0.1025 molar) and 0.09182 molar for 1,1-dibromo-3-chloro-1-propene (0.1025 molar). A plot of log $b(a-x)/a(b-x)$ *vs.* time gave a straight line for 1,1,3-trichloro-1-propene between 26 and 81% reacted and for 1,1-dibromo-3-chloro-1-propene between 18 and 72% reaction. Selected data are given in Table I. Reaction of the vinyl halogens under these conditions was less than 1%.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Studies of Configuration. III. The Rearrangement of Derivatives of 3- and 4-Methoxycyclohexanecarboxylic Acids[1]

BY DONALD S. NOYCE AND HAROLD I. WEINGARTEN[2]

RECEIVED NOVEMBER 10, 1956

The mechanism of the ether–acid halide rearrangement has been further clarified. The rearrangement of *cis*-3-methoxycyclohexanecarboxylic acid to methyl *trans*-3-chlorocyclohexanecarboxylate by the action of thionyl chloride has been studied. The *trans* isomer does not undergo rearrangement. These facts not only clarify the rearrangement process, but serve as independent evidence for the configuration of the isomers of 3-methoxycyclohexanecarboxylic acid. Similar results are obtained with 4-methoxycyclohexanecarboxylic acid. The cyclic oxonium ion intermediate opens by a process largely SN2 in character, with an additional factor of accelerated reaction in the case of ring-breaking displacement on a five-membered ring. Olefin formation accompanies the rearrangement. The olefin formed, methyl 3-cyclohexene-1-carboxylate is free of isomers, and this suggests that the elimination process is a synchronous reaction not proceeding from the simple carbonium ion.

The cleavage of ethers by acid halides has been investigated sporadically for many years. Benzoyl iodide was shown to cleave ether by Kishner.[3] Acid halides and acid anhydrides cleave ethers in the presence of Lewis acids.[4] These reactions un-

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(1) Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955; previous paper, THIS JOURNAL, **75**, 127 (1953).

(2) Du Pont summer research assistant, 1953; Eastman Kodak Co. Fellow, 1954–1955.

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