vent bumping. The total heating time was 1 hr. The reaction mixture was made homogeneous by adding methylene chloride and then the basic fraction was isolated as described;[7a] yield 190 mg. (18%) of violet needles, m.p. 189–191°, which did not require chromatography or recrystallization for purification. This product was the same as the one obtained by *method a* as shown by mixed melting point, ultraviolet, and visible spectra.

When a run lasting 2.5 hr. was made in boiling xylene, the yield of II after chromatography and recrystallization from benzene-petroleum ether mixture was about 3%.

1,4,5,6,7,8-Hexahydro-1-azanaphth[2,1-b]azulene (III). The procedure, reagents, and quantities were the same as for the preparation of I except that 2-naphthylhydrazine hydrochloride (Eastman Kodak Co.) was used in place of the 1-isomer. The yield of light-brown needles, m.p. 114–115°, once recrystallized from 95% ethanol was 9.70 g. (83%). The analytical sample was crystallized from absolute ethanol.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.8; H, 7.22; N, 6.01. Found: C, 86.8; H, 7.57; N, 5.71.

The ultraviolet spectrum of model indole 3,4-benzo-5,6,7,8-tetrahydrocarbazole[14] (VIII) was found to be very similar to that for III except for a slight hypsochromic shift. The infrared spectrum in chloroform was very similar to the infrared spectra for I and VIII. The spectrum for III showed slight maxima at 8.45 and 9.24 μ which were not present for VIII and the latter showed maxima at 7.92, 9.09, and 11.22 μ which were not in the spectrum for III.

1-Azanaphth[2,1-b]azulene (IV). Hexahydronaphthazulene (III) (1.70 g., 0.007 mole) was dehydrogenated by the same technique as was used for the preparation of II by *method a*. Methylene chloride was used to collect the reaction mixture as well as the solvent and developer in the chromatography. The yield of raspberry-red needles, m.p. 201–202°, (lit.[4] m.p. 201°) obtained by crystallization from benzene was 228 mg. (7%).

Anal. Calcd. for $C_{17}H_{11}N$: C, 89.0; H, 4.83; N, 6.11; neut. equiv., 229.3. Found: C, 89.6; H, 4.46; N, 5.83; neut. equiv., 228.9.

As the neutral equivalent was taken with perchloric acid in glacial acetic acid a reddish-orange flocculent solid, m.p. 282–283° (corr.) (73%) formed.

Anal. Calcd. for $C_{17}H_{12}O_4NCl$: C, 61.9; H, 3.67; N, 4.25. Found: C, 62.3; H, 3.81; N, 4.27.

The methiodide derivative for IV, m.p. 329–331° (corr.), (63%) was prepared as was the methiodide for II.

Anal. Calcd. for $C_{18}H_{14}NI$: C, 58.2; H, 3.80; N, 3.77. Found: C, 58.1; H, 3.80; N, 3.59.

Hydrogenation of IV, under conditions similar to those used for II, produced III as shown by mixed melting point and ultraviolet spectra.

1,2-Benzocarbazole (IX). The chloranil method of Barclay and Campbell[16] was used for the dehydrogenation of both 1,2-benzo-5,6,7,8-tetrahydrocarbazole (VII) and 1,2-benzo-3,4-dihydrocarbazole (X).[10,17] The desired product (IX) was readily obtained from the latter but with much difficulty from the former. From VII the product was purified by chromatography (alumina), sublimation, and finally by crystallization from benzene. The white purified products were identical as shown by mixed melting point, ultraviolet, and infrared spectra. The authentic material, m.p. 229–230° (corr.), (lit.[9] 225°) obrained from X had a slightly more narrow melting range than the other product.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.4; H, 5.10; N, 6.45. Found: C, 88.3; H, 5.19; N, 6.34.

MORGANTOWN, W. VA.

(16) B. M. Barclay and N. Campbell, *J. Chem. Soc.*, 530 (1945).

(17) We wish to thank Mr. Edward A. Pacofsky for the preparation of this compound and Mr. Paul Brown for its dehydrogenation as well as the infrared spectra for this paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Halopropargyl Alcohols and Ethers[1]

LEWIS F. HATCH, WILLIAM E. BLANKENSTEIN, AND SHIH HSI CHU

Received July 8, 1957

The following compounds have been prepared and characterized: 2,3-dibromo-2-propen-1-ol, 3-bromo-3-chloro-2-propen-1-ol, 1,1-dibromo-3-ethoxy-1-propene, 1,1-dibromo-3-phenoxy-1-propene, 1-bromo-1-chloro-3-ethoxy-1-propene, 1-bromo-1-chloro-1-propene, 1,3-dibromo-1-chloro-1-propene, 3-bromo-2-propyn-1-ol, 3-chloro-2-propyn-1-ol, 1-bromo-3-ethoxy-1-propyne, 1-bromo-3-phenoxy-1-propyne, 1-chloro-3-ethoxy-1-propyne. The stereochemistry of the addition of bromine to *cis*- and *trans*-1-chloro-1-propene followed by dehydrohalogenation is discussed.

There are only fragmentary reports in the literature on the preparation of halopropargyl alcohols. Lespieau[2] prepared 3-bromo-2-propyn-1-ol by the hydrolysis of the corresponding acetate which in turn was formed by the reaction between 1,3-dibromopropyne and potassium acetate. The yields were very low and the alcohol was impure. 3-Bromo-2-propyn-1-ol has now been prepared by the dehydrobromination of 2,3-dibromo-2-propen-1-ol by potassium amide in liquid ammonia and by the dehydrobromination of 3,3-dibromo-2-propen-1-ol using potassium hydroxide in glycerol.

2,3-Dibromo-2-propen-1-ol was prepared by the addition of bromine to propargyl alcohol in carbon tetrachloride. Apparently only one geometrical isomer was formed and it is assumed to have the *trans* (Br,Br) configuration formed by *trans* addition of the bromine to the triple bond. Several attempts were made to dehydrobrominate this alcohol using alcoholic potassium hydroxide. The yield of 3-bromo-2-propyn-1-ol was very low because of the multiplicity of by-products. The follow-

(1) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-430. Reproduction in whole or in part is permitted for any purpose of the United States Government. This research was also supported in part by grants from the Robert A. Welch Foundation and the Research Corp.

(2) R. Lespieau, *Ann. chim.*, (7)11, 232 (1897).

ing were isolated and identified: propargyl alcohol, acetylene, potassium formate (as formic acid), and bromine.

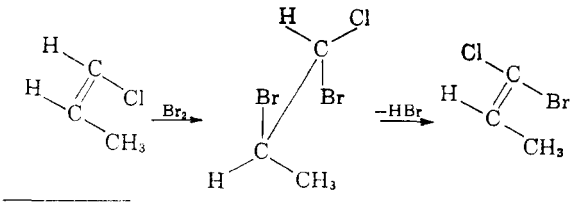
The organic products can be accounted for by the initial production of 3-bromo-2-propyn-1-ol followed by its reaction with potassium hydroxide to form propargyl alcohol. Propargyl alcohol has been reported to decompose to form acetylene and the salt of formic acid in the presence of a strong base.[3] Apparently the formic acid is not formed from formaldehyde by a Cannizzaro reaction, for methanol was not detected in this or previous work.

2,3-Dibromo-2-propen-1-ol was dehydrobrominated successfully by potassium amide in liquid ammonia. Because the yield was low (20%), the dehydrobromination of 3,3-dibromo-2-propen-1-ol was investigated. The 3,3-dibromo-2-propen-1-ol was obtained by the alkaline hydrolysis of 1,1,3-tribromo-1-propene which was made by the reaction between 1,1-dibromo-1-propene and N-bromosuccinimide.[4] The dehydrobromination was effected by the use of 20% potassium hydroxide in glycerol to give a 19% yield of 3-bromo-2-propyn-1-ol.

The ethyl ether of 3-bromo-2-propyn-1-ol was obtained as a by-product (16%) in the reaction between 1,1,3-tribromo-1-propene and sodium ethoxide in ethanol to form 1,1-dibromo-3-ethoxy-1-propene. 1-Bromo-3-phenoxy-1-propyne was obtained in a 17% yield by the dehydrobromination of 1,1-dibromo-3-phenoxy-1-propene. The dibromo-ether was prepared by treatment of 1,1,3-tribromo-1-propene with sodium phenoxide.

3-Chloro-2-propyn-1-ol was prepared from 1-chloro-1-propene by the addition of bromine to form 1,2-dibromo-1-chloropropane[5] which was dehydrobrominated by potassium acetate to 1-bromo-1-chloro-1-propene.[6] The 1-chloro-1-propene was a mixture of the two isomers and contained a high percentage of the *trans* isomer.

The possibility of producing both isomers of 1-bromo-1-chloro-1-propene from the separate isomers of 1-chloro-1-propene was investigated. *Trans* addition of bromine to *cis*-1-chloro-1-propene should give a stereoisomeric 1,2-dibromo-1-chloropropane which on *trans* elimination of the elements of hydrogen bromide should give the *trans* (H,Br) isomer.



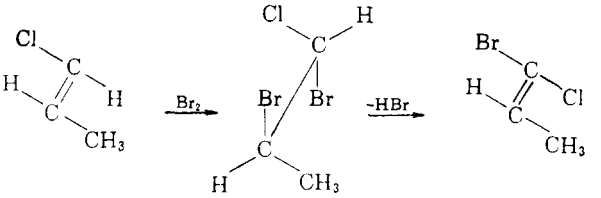
(3) L. Henry, *Ber.*, **8**, 398 (1875); A. F. Thompson and C. Margnetti, *J. Am. Chem. Soc.*, **64**, 573 (1942); L. F. Hatch and A. C. Moore, *J. Am. Chem. Soc.*, **66**, 285 (1944).

(4) L. F. Hatch and S. D. Zimmerman, *J. Am. Chem. Soc.*, **79**, 3091 (1957).

(5) M. Reboul, *Ann. chim.*, (**5**) **14**, 462 (1878).

(6) B. K. Mereshkowsky, *Ann.*, **431**, 231 (1923).

The *trans* isomer of 1-chloro-1-propene should give the *cis*(H,Br) isomer of 1-bromo-1-chloro-1-propene.



The *trans*-1-chloro-1-propene used contained 10% *cis*-1-chloro-1-propene while the *cis* isomer was 99+% pure. Addition to the *cis* isomer was appreciably slower than to the *trans* isomer.

The greater eclipsing effect of bromine compared to chlorine is evident in the dehydrobromination reaction. The addition product from *cis*-1-chloro-1-propene dehydrobrominated less readily to produce *trans*-1-bromo-1-chloro-1-propene(H,Br) than the product from the *trans* isomer to give *cis*-1-bromo-1-chloro-1-propene(H,Br). The extent of the difference in reactivity of the two isomers was determined only in a qualitative manner.

The dehydrohalogenation of the 1-bromo-1-chloro-1-propene from *cis*-1-chloro-1-propene gave only 1-chloro-1-propyne as would be expected with the hydrogen atom and bromine atom in a *trans* position.[7] The unreacted 1-bromo-1-chloro-1-propene, however, had an infrared spectrum identical with that of the product from *trans*-1-chloro-1-propene. The 1-bromo-1-chloro-1-propene from 90% *trans*-1-chloro-1-propene also gave 1-chloro-1-propyne as the only product. *cis*-1-Bromo-1-chloro-1-propene(H,Br) would not be expected to dehydrobrominate by *cis* elimination of the elements of (H,Br) and the reason why *trans*-1-bromo-1-chloro-1-propene(H,Br) is more resistant to dehydrobromination than the *cis*(H,Br) isomer is not known. Apparently either the assignment of configuration is incorrect or the elimination reaction is not the conventional E_2. These possibilities are being investigated.

The *cis*(H,Br) isomer of 1-bromo-1-chloro-1-propene was brominated to 1,3-dibromo-1-chloro-1-propene using *N*-bromosuccinimide. The 1,3-dibromo-1-chloro-1-propene appeared to be produced as a single isomer which isomerized at room temperature in the presence of light. Similar compounds (1,3-dibromopropene) have been observed to isomerize under these conditions.[8] Hydrolysis of the 1,3-dibromo-1-chloro-1-propene appeared to give a single isomer of 3-bromo-3-chloro-2-propen-1-ol which did not isomerize. This alcohol was dehydrobrominated to 3-chloro-2-propyn-1-ol in a 19% yield.

The reaction of 1,3-dibromo-1-chloro-1-propene with sodium ethoxide in ethanol formed a single

(7) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947).

(8) L. F. Hatch and K. E. Harwell, *J. Am. Chem. Soc.*, **75**, 6002 (1953).

TABLE I

PHYSICAL PROPERTIES OF HALOPROPARGYL ALCOHOLS AND ETHERS AND RELATED COMPOUNDS

Compound	B.P., °C. (Mm.)	Index of Refraction			Density			Analysis			
								Bromine		Chlorine	
		20/D	25/D	30/D	20/4	25/4	30/4	Calcd.	Found	Calcd.	Found
$CHBr{=}CBrCH_2OH$	56–58 (1)[a,b]	1.5799	1.5778	1.5754	2.2226	2.2108	2.2035	74.0	74.3 74.3		
$BrC{\equiv}CCH_2OH$	41–42 (1.5)	1.5162	1.5146	1.5119	1.7601	1.7584	1.7544	59.2	58.7 58.7		
$CBr_2{=}CHCH_2OC_2H_5$	58–59 (5)	1.5100	1.5070	1.5050	1.7406	1.7329	1.7264	65.5	65.1 65.6		
$BrC{\equiv}CCH_2OC_2H_5$	50–53 (18)	1.4702	1.4665	1.4670	1.3877	1.3806	1.3683	48.8	48.2		
$CHBrClCHBrCH_3$	59.0 (10)[c]	1.5415	1.5390	1.5360	2.0493	2.0371	2.0254	67.6	67.3	15.0	15.0
$CBrCl{=}CHCH_3$[d]	52–53 (113)	1.4870	1.4841	1.4810	1.6120	1.6024	1.5933	51.4	51.3	22.8	22.8
$CBrCl{=}CHCH_3$[e]	33–34 (55)	1.4864	1.4836	1.4810	1.6030	1.5964	1.5870				
$CBrCl{=}CHCH_2Br$[f]	62.5 (10)	1.5702[f]	1.5680	1.5649[f]	2.1182[f]	2.1099[f]	2.1017[f]	68.4	68.1	15.1	15.0
$CBrCl{=}CHCH_2OH$	45.5–46.0 (1)	1.5281	1.5263	1.5242	1.7908	1.7869	1.7785	46.6	46.5 46.7	20.7	20.6 20.7
$ClC{\equiv}CCH_2OH$	50.5–51.0 (13)	1.4708	1.4690	1.4669	1.2389	1.2342	1.2307			39.2	39.2 39.3
$CBrCl{=}CHCH_2OC_2H_5$	57.5–58.0 (10)	1.4820	1.4799	1.4779	1.4496	1.4422	1.4367	40.6	40.5 40.6	17.8	17.7 17.7
$ClC{\equiv}CCH_2OC_2H_5$	49.5–50.0 (56)	1.4365	1.4340	1.4315	1.0386	1.0368	1.0349			29.9	29.7 29.8
$CBr_2{=}CHCH_2OC_6H_5$	105–107 (1)	1.5936	1.5912	1.5890	1.7400	1.7344	1.7298	54.8	54.2 54.9		
$BrC{\equiv}CCH_2OC_6H_5$	89–93 (2)		1.564			1.415					

[a] R. Lespieau [*Ann. chim.*, [7]**11**, 262 (1897)] gives a b.p. of 205–208° (760 mm.). [b] M.p. 29.5–30.0°. [c] M. Reboul [*Ann. chim.*, [5]**14**, 453 (1878)] gives b.p. 177–177.5°. [d] Prepared from *cis*-1-chloro-1-propene. [e] Prepared from *trans*-1-chloro-1-propene. [f] Thought to be one isomer (*trans*-H, Br). Mangold (D. J. Mangold, Ph.D. Dissertation, The University of Texas, 1954) gives b.p. 39.0–42.0 (5 mm.); n_D^{25} 1.5675.

isomer of 1-bromo-1-chloro-3-ethoxy-1-propene and a small amount of 1-chloro-3-ethoxy-1-propyne. The 1-bromo-1-chloro-3-ethoxy-1-propene was dehydrobrominated to give a 23% yield of 1-chloro-3-ethoxy-1-propyne and no 1-bromo-3-ethoxy-1-propyne. This is in agreement with the results of the dehydrohalogenation of the 1-bromo-1-chloro-1-propenes.

All of the allylic bromides are lachrymators and the allylic alcohols are vesicants. Either the bromochloro olefinic ether or the chloro acetylenic ether caused severe dermatitis.

The infrared spectra[9] of the various compounds are in agreement with the assigned structures. It was not possible to assign definite geometrical configuration from the spectra because the compounds did not possess a hydrogen atom on each of the carbon atoms associated with the double bond.

EXPERIMENTAL

The physical properties and analysis of the compounds prepared during this investigation are given in Table I unless otherwise noted.

3-Bromo-2-propyn-1-ol. This alcohol was prepared from 2,3-dibromo-2-propen-1-ol and 3,3-dibromo-2-propen-1-ol.

From 2,3-dibromo-2-propen-1-ol. 2,3-Dibromo-2-propen-1-ol was prepared in an 87% yield by the addition of bromine to propargyl alcohol in carbon tetrachloride at −15°. Apparently only one isomer was formed and it is assumed to have the *trans* configuration.

Several attempts were made to dehydrobrominate 2,3-dibromo-2-propen-1-ol using alcoholic potassium hydroxide. The following alcohols were used: methyl, ethyl, *n*-propyl, and *n*-butyl. The maximum yield (9%) of 3-bromo-2-propyn-1-ol was obtained using *n*-propyl alcohol. Appreciable quantities of propargyl alcohol, acetylene, and potassium formate were identified as by-products. Bromine was observed during the course of the dehydrobromination reaction but was not identified further. Potassium phenoxide in ethanol gave the same results as alcoholic potassium hydroxide.

2,3-Dibromo-2-propen-1-ol was dehydrobrominated to 3-bromo-2-propyn-1-ol in a 20% yield using potassium amide in liquid ammonia. The operating conditions, mainly salt formation, were partly responsible for the low yield. A 25% yield of propargyl alcohol was obtained.

From 3,3-dibromo-2-propen-1-ol. 1,1,3-Tribromo-1-propene was obtained in a 78% yield by treatment of 1,1-dibromo-1-propene with *N*-bromosuccinimide.[4] It was hydrolyzed to 3,3-dibromo-2-propen-1-ol (72% yield) using a 10% solution of sodium carbonate at 80° for 10 hr.[4] The 3,3-dibromo-2-propen-1-ol was dehydrobrominated to 3-bromo-2-propyn-1-ol using a 20% solution of potassium hydroxide in glycerol. The reaction was carried out at 2 mm. pressure on a steam bath. The bromoacetylenic alcohol distilled as formed and was collected in a cold trap. Distillation under nitrogen gave a fraction boiling at 41–42° (1.5 mm.); lit.[2] b.p. 80–83° (12 mm.). *3,5-Dinitrobenzoate of 2,3-dibromo-2-propen-1-ol:* m.p. 117.5–118°.

Anal. Calcd. for $C_{10}H_6O_6N_2Br_2$: N, 6.83. Found: N, 6.84, 6.82.

3,5-Dinitrobenzoate of 3-bromo-2-propyn-1-ol: m.p. 115–116°.

Anal. Calcd. for $C_{10}H_5O_6N_2Br$: N, 8.51. Found: N, 8.52, 8.51.

(9) Obtained through the courtesy of the Monsanto Chemical Co. and William F. Hamner, Texas City, Tex.

1-Bromo-3-ethoxy-1-propyne. This ether was prepared in a 16% yield when equimolar quantities (1 mole) of 1,1,3-tribromo-1-propene and sodium ethoxide in ethanol were refluxed for 5 hr. There was a 47% yield of 1,1-dibromo-3-ethoxy-1-propene.

1-Bromo-3-phenoxy-1-propyne. This ether was prepared by the dehydrobromination of 1,1-dibromo-3-phenoxy-1-propene. The 1,1-dibromo-3-phenoxy-1-propene was synthesized in a 55% yield from 1,1,3-tribromo-1-propene and sodium phenoxide in ethanol in a manner similar to that used for the preparation of 1,1-dibromo-3-ethoxy-1-propene. The 1,1-dibromo-3-phenoxy-1-propene was dehydrobrominated to 1-bromo-3-phenoxy-1-propyne (17% yield) using potassium hydroxide in glycerol and a procedure similar to the one used for the preparation of 3-bromo-2-propyn-1-ol.

3-Chloro-2-propyn-1-ol. 3-Chloro-2-propyn-1-ol was prepared by a series of reactions which started with the low temperature (−40°) addition of bromine to a commercial mixture of 1-chloro-1-propenes (Columbia Organic Chemicals, Columbia, S. C.). The reaction time was 16 hr. and the yield of *1,2-dibromo-1-chloropropane* was 83%. This material had the following physical properties: b.p. 57.5° (10 mm.); n_D^{20} 1.5385, n_D^{25} 1.5361, n_D^{30} 1.5338; d_4^{20} 2.0397, d_4^{25} 2.0325, d_4^{30} 2.0251. Lit.[5] b.p. 177.0–177.5°.

Anal. Calcd. for $C_3H_5Br_2Cl$: Br, 67.6; Cl, 15.0. Found: Br, 67.3; Cl, 15.0.

The 1,2-dibromo-1-chloropropane was dehydrobrominated to *1-bromo-1-chloro-1-propene* using potassium acetate and the procedure of Mereshkowsky.[6] A 69% yield was obtained and the product had the following physical properties: b.p. 58.5° (198 mm.); n_D^{20} 1.4868, n_D^{25} 1.4838, n_D^{30} 1.4809; d_4^{20} 1.6009, d_4^{25} 1.5920, d_4^{30} 1.5847.

Anal. Calcd. for C_3H_4BrCl: Br, 51.4; Cl, 22.8. Found: Br, 51.3; Cl, 22.8.

The 1-bromo-1-chloro-1-propene was brominated to *1,3-dibromo-1-chloro-1-propene* in a 55% yield using *N*-bromosuccinimide and the usual procedure. The product appeared to have been produced as a single isomer but to have isomerized to a small extent on standing in the light at room temperature. The physical properties given in Table I are for freshly distilled material.

The 1,3-dibromo-1-chloro-1-propene was hydrolyzed to *3-bromo-3-chloro-2-propen-1-ol* using a 10% solution of sodium carbonate at 75° for 18 hr. The reaction products were worked up in the usual manner and a 70% yield of 3-bromo-3-chloro-2-propen-1-ol was obtained. This alcohol was dehydrobrominated to 3-chloro-2-propyn-1-ol using a 25% solution of potassium hydroxide in decyl alcohol at 75° for 2 hr. under 5 mm. Hg pressure. The pressure was reduced to 0.5 mm. Hg and the remaining product and unreacted dihalo alcohol were flashed to a cold trap. Conventional treatment of this material gave a 19% yield of 3-chloro-2-propyn-1-ol. *3,5-Dinitrobenzoate of 3-bromo-3-chloro-2-propen-1-ol:* m.p. 78.0–78.5°.

Anal. Calcd. for $C_{10}H_6O_6N_2BrCl$: N, 7.67. Found: N, 7.60, 7.75.

3,5-Dinitrobenzoate of 3-chloro-2-propyn-1-ol: m.p. 86.0–86.5°.

Anal. Calcd. for $C_{10}H_5O_6N_2Cl$: N, 9.84. Found: N, 9.70, 9.72.

1-Chloro-3-ethoxy-1-propyne. This ether was prepared by the dehydrobromination of 1-bromo-1-chloro-3-ethoxy-1-propene. 1-Bromo-1-chloro-3-ethoxy-1-propene was prepared by a Williamson synthesis from 1,3-dibromo-1-chloro-1-propene and sodium ethoxide in ethanol. The temperature was held at 35° for 2 hr. and at 50° for 1.75 hr. The yield of 1-bromo-1-chloro-3-ethoxy-1-propene was 35%. About a 2% yield of 1-chloro-3-ethoxy-1-propyne was obtained.

1-Bromo-1-chloro-3-ethoxy-1-propene was dehydrobrominated using a 10% solution of potassium hydroxide in decyl alcohol at 60° for 2 hr. under 10 mm. Hg pressure. At the end of the reaction period the remaining material was

flashed to the cold trap at 1 mm. pressure. The products were worked up in the usual manner to give a 23% yield of 1-chloro-3-ethoxy-1-propyne.

cis-1-Bromo-1-chloro-1-propene (H,Br). Bromine was added to a mixture of 90% *trans*-1-chloro-1-propene and 10% *cis*-1-chloropropene (0.77 mole) in carbon tetrachloride (400 ml.) at −10° over a period of 1 hr. followed by 3 hr. at the same temperature. The reaction mixture was worked up in the usual manner and distilled to give a 75% yield of 1,2-dibromo-1-chloropropane boiling at 56° (9 mm.). The physical properties of this compound were the same as those obtained for the 1,2-dibromo-1-chloropropane from *cis*-1-chloro-1-propene and its infrared spectrum was essentially the same.

This 1,2-dibromo-1-chloropropane (0.17 mole) and potassium acetate (0.51 mole) in acetic acid (100 ml.) were heated for 16 hr. at reflux temperature. Work up of the reaction mixture gave a 30% yield of 1-bromo-1-chloro-1-propene. A 56% yield was obtained by using potassium hydroxide (12%) in glycerol at 80° and a pressure of 113 mm. Under these conditions the product flashed to a cold trap as soon as formed. Physical properties of this material are given in Table I.

The *cis*-1-bromo-1-chloro-1-propene (H,Br) was dehydrobrominated by dropping it into a 12% solution of potassium hydroxide in glycerol under nitrogen at a temperature of 76°. There was a 26% conversion and a 25% yield of 1-chloro-1-propyne boiling at 31–31.5° (755 mm.). The identity of the 1-chloro-1-propyne was checked by comparing its infrared spectrum with that of an authentic sample.

trans-1-Bromo-1-chloro-1-propene (H,Br). *cis*-1-Chloro-1-propene with a boiling point of 30.5° at 733 mm. pressure (n_D^{20} 1.4061) was obtained from Columbia Organic Chemicals Co. The material had been purified by distillation through a 100-plate column at a reflux ratio of 100:1. The distillation was made by Arthur Rose, Applied Science Laboratories, Inc., State College, Pa. Gas chromatography indicated a purity of 99+%.

Bromine was added to the *cis*-1-chloro-1-propene in a manner similar to that used for the *trans*-1-chloro-1-propene. Sixty-three hours were required to effect the addition. A 70% yield of 1,2-dibromo-1-chloropropane was obtained. The physical properties were essentially the same as those of the 1,2-dibromo-1-chloropropane from *trans*-1-chloro-1-propane (Table I).

It was not possible to dehydrobrominate this compound with potassium acetate in acetic acid in a manner similar to that used for the bromine addition product of *trans*-1-chloro-1-propene. *trans*-1-Bromo-1-chloro-1-propene(H,Br) was obtained by using potassium hydroxide in glycerol and the same procedure as that used for the production of *cis*-1-bromo-1-chloro-1-propene(H,Br) from the 1,2-dibromo-1-chloropropane from *trans*-1-chloro-1-propene. A 60% yield was obtained.

This 1-bromo-1-chloro-1-propene was not dehydrohalogenated by potassium hydroxide in glycerol under the same conditions used to dehydrobrominate the 1-bromo-1-chloro-1-propene from *trans*-1-chloro-1-propene. It was dehydrobrominated by powdered potassium hydroxide at 130° to give a 33% yield of 1-chloro-1-propyne. No 1-bromo-1-propyne was detected. The unreacted 1-bromo-1-chloro-1-propene was shown by its infrared spectrum to be the same as that of the isomer from *trans*-1-chloro-1-propene.

Infrared spectra. The infrared spectra were obtained using a Baird Associates Double-Beam Recording Infrared Spectrophotometer equipped with sodium chloride optics. The following are the principal bands in microns.

cis-1-Chloro-1-propene: 3.41; 6.10; 6.92; 7.23; 7.60; 10.68; 13.2–13.3; 14.4–14.7.

trans-1-Chloro-1-propene: 3.41–3.45; 6.12; 6.94; 8.09; 10.55; 10.8–10.9; 12.6.

1,2-Dibromo-1-chloropropane (from cis-1-chloro-1-propene): 3.33; 6.91; 7.25; 7.60; 7.99; 8.30; 8.53; 9.51; 9.96; 11.21; 13.08; 13.4–13.9; 14.7.

1-Bromo-1-chloro-1-propene (from cis-1-chloro-1-propene): 3.41; 5.61; 6.17; 6.91; 7.25; 7.87; 9.04; 10.02; 10.2–10.3; 10.73; 11.7–12.1; 12.3–12.4; 14.20.

1-Bromo-1-chloro-1-propene (from trans-1-chloro-1-propene): 3.46; 6.22; 6.97; 7.30; 7.91; 9.10; 10.3–10.4; 11.9–12.1; 12.4.

2,3-Dibromo-2-propen-1-ol: 2.92–3.10; 3.21; 3.41; 3.50; 6.20; 6.90; 8.00; 8.15; 9.4–9.8; 10.42; 12.56; 14.0–14.2.

3-Bromo-3-chloro-2-propen-1-ol: 3.0–3.1; 3.40; 3.48; 6.21; 6.9–7.1; 7.4; 8.2; 9.5–9.9; 11.9–12.2.

1-Bromo-1-chloro-3-ethoxy-1-propene: 3.40; 3.50; 6.21; 6.92; 7.18; 7.42; 7.90; 8.9–9.1; 12.0–12.1.

1,1-Dibromo-3-ethoxy-1-propene: 3.34; 3.47; 6.21; 6.92; 7.31; 7.43; 7.87; 8.29; 9.0–9.1; 9.8; 11.25; 11.9; 12.5–12.8.

1,1-Dibromo-3-phenoxy-1-propene: 3.28; 3.41; 3.48; 6.12; 6.25; 6.68; 6.85; 7.29; 7.70; 8.0–8.3; 8.52; 9.27; 9.63; 9.8; 10.05; 11.32; 11.9; 12.5–12.7; 13.2–13.3; 14.54.

3-Chloro-2-propyn-1-ol: 3.0–3.1; 3.42; 3.48; 4.48; 6.9–7.1; 7.40; 8.18; 9.9–10.1.

3-Bromo-2-propyn-1-ol: 2.9–3.1; 3.43; 3.51; 4.52; 6.9–7.1; 7.41; 8.18; 9.4–9.6; 10.1–10.3; 12.6–12.7.

1-Chloro-3-ethoxy-1-propyne: 3.38; 3.48; 4.45; 6.92; 7.18; 7.42; 7.95; 8.9–9.1; 11.9; 15.1.

1-Bromo-3-ethoxy-1-propyne: 3.35; 3.47; 4.50; 6.72; 6.93; 7.31; 7.42; 7.94; 8.9–9.2; 9.76; 10.01; 11.88.

1-Bromo-3-phenoxy-1-propyne: 2.99; 3.24; 3.39; 3.44; 4.46; 6.22; 6.67; 6.86; 7.25; 7.70; 7.92; 8.1–8.3; 8.49; 9.23; 9.5; 9.7; 10.08; 11.28; 11.99; 12.82; 13.1–13.3; 14.54.

AUSTIN, TEX.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORPORATION]

Catalytic Graphite Inclusion Compounds. II. Potassium Graphite as an Alkylation Catalyst

H. PODALL AND W. E. FOSTER

Received July 8, 1957

Potassium graphite has been found to catalyze both the nuclear and side-chain alkylation of aromatic hydrocarbons with ethylene.

While attempting to catalyze the polymerization of ethylene with potassium graphite, KC_8,[1] in benzene and in toluene, it was found that alkylation of these hydrocarbons occurred instead. A study was therefore undertaken of the potassium graphite-catalyzed alkylation of aromatic hydrocarbons with olefins. The results are shown in Table I.

(1) H. E. Podall, W. E. Foster, and A. P. Giraitis, *J. Org. Chem.*, **23**, 82 (1958).