Table II

Addition of Butadiene to Alkyl Aromatic Hydrocarbons[a]

Alkyl aromatic	Addition product (1:1)	Yield,[b] %	B.p., °C. (mm.)	Cyclodehydrogenation product	M.p., °C.
Toluene	5-Phenyl-2-pentene	80	199–201[c]	1-Methylnaphthalene	Liq.
o-Xylene	5-(*o*-Tolyl)-2-pentene	90	223–225	1,5-Dimethylnaphthalene	81–82
p-Xylene	5-(*p*-Tolyl)-2-pentene	91	108–112 (10)	1,7-Dimethylnaphthalene	116–118[d]
Ethylbenzene	5-Phenyl-2-hexene	87	71–74 (1)	1,4-Dimethylnaphthalene	142–143[d]
Durene	5-(2,4,5-Trimethylphenyl)-2-pentene	35	80–83 (1)	. . .	. . .
2-Methylnaphthalene	5-(2-Naphthyl)-2-pentene	19	123–137 (3)	. . .[e]	. . .

[a] Potassium (2.5 g.) on CaO (100 g.) support. [b] Based on butadiene used. [c] W. C. Warner and J. R. Shelton [*Ind. Eng. Chem.*, **43**, 1160 (1951)] give b.p. 84.5–85.0° (13 mm.). [d] Picrate. [e] See Experimental.

(185 g., 1.74 moles) over a period of 3 hr. at 108–110°. Distillation gave 132 g. (87%) of 5-phenyl-2-hexene, b.p. 71–74° (1 mm.). A gas chromatographic analysis resolved the product into equivalent amounts of its *cis* and *trans* isomers. An n.m.r. spectrum of this olefin showed a singlet at τ 2.88, multiplets at 4.5–4.8, 7.6–8.0, 8.35, 8.60, a sextet at 7.27 (J = 6.5 c.p.s.), and a doublet at 8.79 (J = 6.5 c.p.s.), with relative areas of 5:2:2:3:1:3, respectively, assigned to the aromatic, vinyl (C-2,3), β-methylene (C-4), methyl (C-1), α-hydrogen (C-5), and α-methyl protons.

1,4-Dimethylnaphthalene.—A sample of 5-phenyl-2-hexene was cyclized and dehydrogenated[14] as in the preparation of 1,5-dimethylnaphthalene (above). The product was a yellow oil which was purified by elution chromatography over activated alumina. The picrate had m.p. 142–143° (lit.[12] m.p. 143°).

5-(2,4,5-Trimethylphenyl)-2-pentene.—Butadiene (29 g., 0.54 mole) was bubbled through a mixture of a potassium catalyst and 133 g. of durene (m.p. 79.5–80.0°) over a period of 2.5 hr. at a temperature of 155–125°. A liquid product (10 g.) was collected in the cold trap during the reaction, and it was found to be almost entirely butadiene. Distillation, after work-up, yielded 25 g. (35%) of 5-(2,4,5-trimethylphenyl)-2-pentene, b.p. 80–83° at 1 mm. A gas chromatographic analysis of the distillation product showed 5% durene in addition to the *cis* and *trans* isomers. A low-voltage mass spectrum gave mass 188 as the major peak; mass 242 was the major peak in the distillation residue (10.3 g.). The infrared spectrum of the product gave the characteristic olefin peaks at 6.00, 6.07, 7.10, and 10.32 μ, with substitution bands at 8.30, 9.07, 9.76, and 11.45 μ. The n.m.r. spectrum of this olefin showed a broad singlet at τ 7.88, and multiplets at 3.17–3.3, 4.45–4.7, 7.25–7.66, and 8.3–8.5, with relative areas of 11:2:2:2:3, respectively, assigned to three aromatic methyl plus β-methylene (C-4), aromatic, vinyl (C-2,3), α-methylene (C-5), and methyl (C-1) protons. The areas of the broad singlet and a multiplet at its base [τ 7.66–8.1, assigned to β-methylene (C-4)] were added together because of overlapping.

5-(2-Naphthyl)-2-pentene.—Butadiene (32.3 g., 0.60 mole) was bubbled through a mixture of sodium catalyst and 229 g. (1.61 moles) of 2-methylnaphthalene (m.p. 34.5–35.0°) over a period of 3 hr. at a temperature of 124–130°. During the course of the reaction 16.3 g. of a liquid product consisting of mostly butadiene was collected in a cold trap. Distillation, after work-up, gave 11 g. (19%) of 5-(2-naphthyl)-2-pentene,[15] b.p. 123–137° at 1–3 mm. A low-voltage mass spectrum gave mass 196 as the major peak. A vapor phase chromatograph showed a trace of 2-methylnaphthalene together with the *cis* and *trans* isomers. The infrared spectra gave the characteristic olefin peaks at 6.00, 6.10, 7.11, and 10.31 μ. The n.m.r. spectrum of this olefin showed multiplets at τ 2.2–3.0, 4.4–4.7, 7.1–7.42, 7.42–7.9, and 8.30–8.55, with relative areas of 7:2:2:2:3, respectively, assigned to aromatic, vinyl (C-2,3), α-methylene (C-5), β-methylene (C-4), and methyl (C-1) protons.

Acknowledgment.—We would like to thank R. L. Urban for running the reactions using hydrogen fluoride, D. S. Baugher for the mass spectral results, H. C. Williams for the n.m.r. spectra, and D. L. Kerr for the infrared spectra and help in the experimental work. The authors wish to thank the Sun Oil Company for permission to publish these results.

---

(14) After 4 hr. the dehydrogenation reaction was sampled and it was found to contain 26% (calculated by v.p.c. area method) of 5,8-dimethyl-1,2,3,4-tetrahydronaphthalene. Its structure was determined by a collection of a vapor phase chromatographic cut and comparison of its infrared spectrum with an authentic sample.[3] At the end of another 4 hr. this compound was no longer present.

(15) A similar experiment using 3.5 g. of potassium supported on 58 g. of sodium oxide gave a 23% of product.

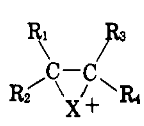
Use of Alkene Chloronium Intermediates in Organic Synthesis. Two New Reactions of Alkene Chloronium Ions

Gene Sumrell,[1] Ronald G. Howell, Bert M. Wyman, and Mack C. Harvey

Research Laboratory, El Paso Natural Gas Products Company, El Paso, Texas

Received July 24, 1964

A number of new chlorinated esters and ethers and one new amide have been prepared utilizing "three-component reactions" involving an olefin, chlorine, and a third material capable of reacting with the intermediate chloronium ion. Two hitherto unreported reactions of alkene chloronium ions were noted and investigated. They were (1) cleavage of the ether linkage, and (2) substitution of the benzene nucleus.



I

Roberts and Kimball[2] postulated a positively charged cyclic halonium intermediate (I) to explain the products obtained from a variety of chlorination and bromination reactions of ethylene compounds. Lucas and Gould,[3] in a classical paper on chlorohydrin formation and reactions, gave convincing evidence to support the existence of such an intermediate in these and related

---

(1) To whom inquiries should be directed at Southern Regional Research Laboratory, P. O. Box 19687, New Orleans, La. 70119.

(2) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937); see also S. Winstein and H. J. Lucas, *ibid.*, **61**, 2845 (1939).

(3) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

TABLE I

CHLOROALKYL ESTERS (RCOOR′)[a]

R	R′	Formula	B.p., °C. (mm.)	n^{25}D	Calcd., % C	Calcd., % H	Calcd., % Cl	Found, % C	Found, % H	Found, % Cl
CH_3	$CH(CH_3)CH_2Cl$	$C_5H_9ClO_2$	58–60 (25)	1.4213[b]	...	...	...	...	...	...
CH_2Cl	$CH(CH_3)CH_2Cl$	$C_5H_8Cl_2O_2$	76–77 (5)	1.4538	35.11	4.72	41.46	35.30	4.77	41.30
$CHCl_2$	$CH(CH_3)CH_2Cl$	$C_5H_7Cl_3O_2$	81–83 (6)	1.4628	29.22	3.43	51.78	29.50	3.50	51.85
CCl_3	$CH(CH_3)CH_2Cl$	$C_5H_6Cl_4O_2$	79–81 (5)	1.4683	25.03	2.52	59.11	25.30	2.80	59.30
CH_3	$CH(C_2H_5)CH_2Cl$	$C_6H_{11}ClO_2$	65–70 (20)	1.4260[c]	...	...	...	...	...	...
CH_3	$CH(CH_3)CHClCH_2Cl$	$C_6H_{10}Cl_2O_2$	71–72 (4)	1.4533	38.94	5.45	38.32	39.20	5.60	38.20
CH_3	$C(CH_2Cl)_2CH_3$	$C_6H_{10}Cl_2O_2$	59–60 (4)	1.4502	38.94	5.45	38.32	39.00	5.40	38.20
CH_3	$CH(C_6H_5)CH_2Cl$	$C_{10}H_{11}ClO_2$	111–112 (3)	1.5164	60.46	5.58	17.85	60.20	5.90	18.20
CH_3	2-CCH[d]	$C_8H_{13}ClO_2$	85–86 (6)	1.4658[e]	...	...	...	...	...	...
CH_2Cl	2-CCH[d]	$C_8H_{12}Cl_2O_2$	132–133 (10)	1.4860	45.52	5.73	33.60	45.70	6.10	33.90
$CHCl_2$	2-CCH[d]	$C_8H_{11}Cl_3O_2$	139–140 (11)	1.4919	39.13	4.52	43.32	39.40	4.80	43.10

[a] See Experimental for procedures and yields. [b] Lit.[14] b.p. 147–149° (745 mm.), n^{20}D 1.4223. [c] Contaminated with the 2-chlorobutyl isomer, see ref. 18. [d] 2-CCH = 2-chlorocyclohexyl. [e] Lit.[21] b.p. 100–100.3° (12 mm.), n^{20}D 1.4644.

reactions where a negative group (such as halogen, hydroxyl, alkoxy, phenoxy, or acyloxy) enters a molecule on a carbon adjacent to another carbon attached to chlorine. This reactive chloronium intermediate is readily formed when an olefin and elemental chlorine are allowed to react in the liquid phase and, in the absence of other reactive materials, adds a chloride ion from the back side of one of the carbons involved in the cyclic structure to give the *trans* dichloride as the principal product. A competing side reaction, if α-hydrogens are present, is elimination of a proton to give a chlorinated olefin,[4] which may in turn further react with chlorine in a similar manner to that of the starting olefin.

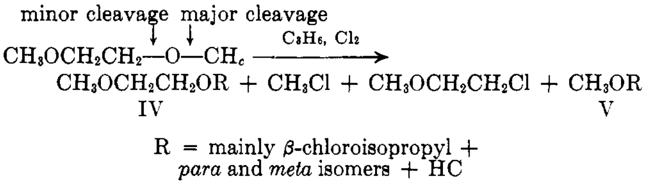
In the presence of water the alkene chloronium intermediate readily adds a hydroxyl group to the back side of one of the carbons yielding the chlorohydrin.[2] Other materials (such as alcohols, phenols, carboxylic acids, acid anhydrides, etc.) capable of providing a negative group may similarly react, and utility has been made of the ionic intermediate resulting from the initial reaction of chlorine and an olefin to carry out a number of "three-component reactions" in which a chlorinated alkyl group is inserted into the molecule to give a variety of chlorinated ethers, esters, and amides.[5]

In the course of an investigation involving the conversion of lower olefins to other materials of potentially greater economic value, we carried out a number of reactions in which a lower olefin and chlorine were allowed to react with a third material. A number of the resulting compounds are new and are described along with the procedures in the Experimental section (also see Table I). Some of these reactions were carried out in solvents presumed at the time to be inert. In two cases reaction with the solvent was noted and further investigated. Since these reactions were unexpected and do not appear to be mentioned in the literature they are reported here.

One of the reactions involved cleavage of the ether linkage by the alkene chloronium intermediate to introduce a chlorinated alkyl group in the ether in place of one of the original alkyl groups, the latter leaving as

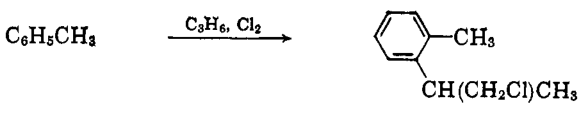
$$\begin{array}{l} ROR + R'CH{=}CH_2 + Cl_2 \longrightarrow \\ \qquad \underset{\text{II}}{ROCH(CH_2Cl)R'} + \underset{\text{III}}{ROCH_2CHClR'} + RCl \end{array}$$

alkyl chloride. Product II was the major product in each of three experiments carried out and III was a minor product. The use of n.m.r. spectroscopy allowed the ratio of these two isomers to be determined. In one instance the ether cleaved was 1,2-dimethoxyethane. Methyl chloride and the analog of II were the major products, with only minor cleavage between the methoxy group and the 2-methoxyethyl residue.



$$\begin{array}{l} \overset{\text{minor cleavage}\ \downarrow}{CH_3OCH_2CH_2}{-}\overset{\downarrow\ \text{major cleavage}}{O{-}CH_c} \xrightarrow{C_3H_6,\ Cl_2} \\ \qquad \underset{\text{IV}}{CH_3OCH_2CH_2OR} + CH_3Cl + CH_3OCH_2CH_2Cl + \underset{\text{V}}{CH_3OR} \end{array}$$

R = mainly β-chloroisopropyl + *para* and *meta* isomers + HC



VI

The other new reaction noted in this investigation was substitution of the benzene nucleus. This reaction was detected as the result of difficulty in purifying the products from several runs in which chlorine and propylene were allowed to undergo a "three-component reaction" with a third material in benzene solution. Ultimately, β-chlorocumene was isolated and identified from these runs in yields of 3–5% based on the propylene used. A run carried out in toluene gave a 10% yield of substitution products which proved to be predominantly the *ortho* isomer (VI). None of the 2-chloropropyl isomers were detected among the products of the substitution of benzene or toluene with the propylene chloronium ion. Similarly, only the β-chloroisopropyl esters resulted from the reaction of this ion with a number of acids, and no detectable amount of the straight-chain ester.[6]

---

(4) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948), and references cited therein.

(5) See (a) F. C. Weber, G. F. Hennion, and R. R. Vogt, *ibid.*, **61**, 1457 (1939), and references cited therein; (b) T. L. Cairns, P. J. Graham, P. L. Barrick, and R. S. Schrieber, *J. Org. Chem.*, **17**, 751 (1952); (c) A. I. Titov, F. L. Maklyaev, and V. G. Kuz'min., *Zh. Obshch. Khim.*, **25**, 744 (1955); *Chem. Abstr.*, **50**, 2420 (1956).

(6) We have no explanation at present for these anomalous results since isomers were formed from reaction at both the primary and secondary carbons on ether cleavage, and it is well known that both isomers occur on chlorohydrin formation; see R. C. Elderfield, *et al.*, *J. Am. Chem. Soc.*, **68**, 1517 (1946).

Experimental[7]

Cleavage of 1,2-Dimethoxyethane.[8]—A mixture of 300 ml. of 1,2-dimethoxyethane and 84 g. (1 mole) of sodium bicarbonate was placed in a 1-l. three-necked flask which was fitted with a stirrer, thermometer, Dry Ice–acetone condenser, and two gas inlet tubes. The temperature was maintained at 40–45° by mild cooling while 1 mole each of chlorine and propylene was added concurrently during 2 hr.[9] The former was added by manually lowering a dewar containing Dry Ice and acetone from a cold trap containing liquid chlorine. The propylene was added from a stainless steel bomb at such a rate as to maintain a mild reflux. The mixture was stirred for 0.5 hr. after the additions were complete. It was then cooled to 5° to reduce evaporation and the liquid phase (335 g.) was decanted from the salt. Gas chromatographic analysis indicated the presence of 0.31 mole of methyl chloride, 0.05 mole of 2-methoxyethyl chloride, 0.20 mole of propylene dichloride, 0.06 mole of 2-methoxypropyl chloride (V), 0.07 mole of propylene chlorohydrin, 0.32 mole of **1-methoxy-2-(1-chloro-2-propoxy)ethane** (IV),[10] 0.01 mole of 1,2,3-trichloropropane, and 0.03 mole of 1-methoxy-2-(1,3-dichloro-2-propoxy)ethane.[11] This reaction mixture was stripped of solvent and other low-boiling components under the column to 50° at water pump pressure and the residue was fractionated. There was obtained 46 g. of IV distilling at 52–53° (6 mm.), $n^{25}\text{D}$ 1.4265.[13]

Anal. Calcd. for $C_6H_{13}ClO_2$: C, 47.21; H, 8.59; Cl, 23.23. Found: C, 46.90; H, 8.50; Cl, 23.50.

Continuation of the fractionation gave 5.8 g. of **1-methoxy-2-(1,3-dichloro-2-propoxy)ethane** at 65–66° (2 mm.), $n^{25}\text{D}$ 1.4482.[12]

Anal. Calcd. for $C_6H_{12}Cl_2O_2$: C, 38.52; H, 6.47; Cl, 37.91. Found: C, 38.60; H, 6.46; Cl, 37.40.

The n.m.r. spectrum for the above compound was consistent for the structure named. A singlet at 3.3 p.p.m. was assigned to the hydrogens of the methoxy group. Another singlet at 3.65 p.p.m. was assigned to the four methylene hydrogens. A doublet at 3.55 p.p.m. (J = 7 c.p.s.) was assigned to the four hydrogens of the chloromethyl groups. This doublet was part of a complex multiplet centered at 3.6 p.p.m. which integration of the area showed to represent five hydrogens. Therefore, the secondary hydrogen on the dichloroisopropoxy grouping was assigned to this area. It was not possible to determine the coupling constant for this hydrogen.

Cleavage of Diethyl Ether. A. By Propylene Chloronium Ion.—One mole of chlorine and 1 mole of propylene were added during 2 hr. to 300 ml. of diethyl ether, using mild cooling to keep the temperature at 20–25°. The mixture was then cooled to 5° and washed with sodium carbonate solution; the organic layer (329 g.) was separated and analyzed by gas chromatography. The data indicated the presence of 0.30 mole of ethyl chloride, 0.07 mole of allyl chloride, 0.61 mole of propylene dichloride, 0.32 mole of 1-chloro-2-ethoxypropane (contaminated with the isomeric 1-ethoxy-2-chloropropane[12]), 0.01 mole of 1,3-dichloro-2-ethoxypropane, and approximately 0.01 mole of a mixture of isomeric bis(chloropropyl) ethers. Fractionation of the mixture gave 35 g. of material distilling at 110–111° (665 mm.), $n^{25}\text{D}$ 1.4102 [lit. for 1-chloro-2-ethoxypropane,[14] b.p. 30.3° (25 mm.), $n^{25}\text{D}$ 1.4103].

B. By Butylene Chloronium Ion.—Another run was carried out similar to that described in A except 1-butene was used in place of propylene. Gas chromatographic analysis of the organic phase (332 g.) indicated the presence of 0.22 mole of ethyl chloride, 0.52 mole of 1,2-dichlorobutane, 0.25 mole of 2-ethoxybutyl chloride,[15] and 0.05 mole of mixed chlorobutyl ethers.

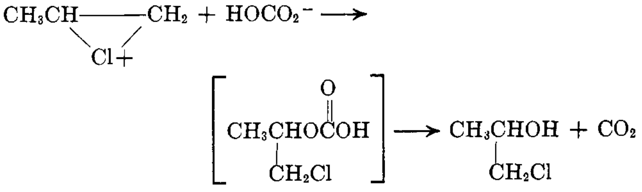
Isolation of β-Chlorocumene from a Propylene Chloronium Ion Reaction in Benzene.—To a mixture of 120 g. (2 moles) of glacial acetic acid and 300 ml. of benzene was added concurrently during 2 hr. at 40–45° 1 mole each of chlorine and propylene. The mixture was then washed with sodium carbonate solution to remove hydrogen chloride and excess acetic acid, and the organic phase (300 g.) was separated and dried over sodium sulfate. Gas chromatographic analysis indicated the presence of 0.01 mole of allyl chloride, 0.65 mole of propylene chloride, 0.23 mole of β-chloroisopropyl acetate, 0.03 mole of 1,2,3-trichloropropane, 0.01 mole of β,β′-dichloroisopropyl acetate, and 0.04 mole of β-chlorocumene. Fractionation of the mixture gave 28 g. of β-chloroisopropyl acetate at 59–60° (25 mm.), $n^{25}\text{D}$ 1.4213 [lit.[16] b.p. 147–149° (745 mm.), $n^{20}\text{D}$ 1.4223], followed by an intermediate cut, and then 6 g. of β-chlorocumene at 71–72° (6 mm.), $n^{25}\text{D}$ 1.5216 [lit.[17] b.p. 79–80° (9 mm.), $n^{25}\text{D}$ 1.5210].

These samples of β-chloroisopropyl acetate and β-chlorocumene were carefully studied by gas chromatography and n.m.r. for the presence of the respective 2-chloropropyl isomers, but in neither case was the other isomer detected. The n.m.r. spectrum for

---

[7] Melting and boiling ranges are uncorrected. Fractionations were carried out using a 60-cm. Podbielniak-type column with heated jacket and partial reflux head similar to that described by J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 238. Gas chromatographic studies were done with an F & M Model 720 chromatograph using a 6-ft. column (0.25-in. i.d.) packed with 20% Dow 9N9 nonionic surfactant on Chromasorb P of 30–60 mesh, and a thermal conductivity detector. The column temperature was 200° and the carrier gas was helium. The n.m.r. data were obtained on a Varian A-60 spectrometer. Carbon tetrachloride was used as the solvent and the chemical shift values are with respect to internal tetramethylsilane at zero p.p.m. Infrared spectroscopic studies were done on a Beckman IR-4 spectrophotometer with sodium chloride optics using thin films of the liquids. The reaction mixtures were routinely analyzed by gas chromatography before fractionation. Yields given are in area per cent under the curves. The products were trapped and identified by infrared and n.m.r. spectroscopy. Where the resulting spectra have special significance they are discussed briefly.

[8] The initial objective of this experiment was to investigate the possibility of preparing propylene chlorohydrin *via* an organic bicarbonate intermediate. It is not clear whether the small amount of chlorohydrin which did form resulted *via* this route or not.



[9] The procedure for the addition of chlorine and propylene presented here is descriptive of the method used for all additions of chlorine and gaseous olefin.

[10] Containing some of the 2-chloro-1-propoxy isomer.[11]

[11] This is the expected product from cleavage of 1,2-dimethoxyethane by the chloronium ion formed by allyl chloride, an expected product of the chlorination of propylene.[4] A small amount of the product from cleavage of both methyl groups by propylene chloronium ion was also detected in the reaction mixture.[12] Many other materials were detected in trace amounts in this reaction mixture, but were not isolated for identification.

[12] At this point a residue of 11.2 g. of material, $n^{25}\text{D}$ 1.4487, remained and was studied by gas chromatography. The major component present in over 50% concentration, was trapped and studied by n.m.r. The spectrum was consistent for bis(1-chloromethylethoxy)ethane which would be expected from cleavage of both methyl groups from 1,2-dimethoxyethane by propylene chloronium ions. An attempt to fractionate this residue at 2 mm. resulted in decomposition and no pure cut of the above named compound was obtained.

[13] This material was a mixture of 1-methoxy-2-(1-chloro-2-propoxy)-ethane (from reaction at the secondary carbon of the chloronium ion) and 1-methoxy-2-(2-chloro-1-propoxy)ethane (from reaction at the primary carbon) in the ratio of 6:1. A singlet in the n.m.r. spectrum falling at 3.3 p.p.m. was assigned to the methoxy grouping (present in both isomers) and another singlet falling at 3.5 p.p.m. was assigned to the four equivalent methylene hydrogens (also present in both isomers). A doublet centered at 1.2 p.p.m. (J = 7 c.p.s.) was assigned to the methyl group of the major product. A doublet centered at 1.5 p.p.m. (J = 7 c.p.s.) was assigned to the methyl group of the minor product. These latter two doublets did not overlap and since each represents a methyl group containing three hydrogens, the integrals of these two areas provided values for the respective amounts of each product present. The ratio of these areas was 6:1. The remaining three hydrogens in these isomers gave overlapping multiplets and it was not possible to determine their coupling constants.

[14] F. B. Tutwiler and C. D. Cook, *J. Org. Chem.*, **24**, 425 (1959), ref. 7. Our material gave only one peak when passed through the gas chromatographic column, but when studied by n.m.r., it was clearly discernible that the two isomers, 1-chloro-2-ethoxypropane and 1-ethoxy-2-chloropropane, were both present, the ratio being approximately 7:1.

[15] Mixed with the isomeric 2-chlorobutyl ethyl ether. Fractionation gave 33 g. of material distilling at 135–138° (665 mm.), $n^{25}\text{D}$ 1.14180 [L. C. Swallen and C. E. Board, *J. Am. Chem. Soc.*, **52**, 651 (1930), report 2-ethoxybutyl chloride to have b.p. 138–139°]. The n.m.r. spectrum of this material was confused because of overlapping bands, but clearly indicated the presence of 10 hydrogens. The material gave only one peak with our 6-ft. chromatographic column, but was resolved in a 200-ft. capillary column (0.01-in. i.d. stainless steel coated with Dow 9N9 nonionic surfactant) into the two components with 2-chlorobutyl ethyl ether comprising 13.4% of the mixture and 2-ethoxybutyl chloride the other 86.6%.

[16] C. F. Irwin and G. F. Hennion, *ibid.*, **63**, 858 (1941).

[17] G. B. Bachman and H. M. Hellman, *ibid.*, **70**, 1773 (1948).

β-chlorocumene contained a doublet at 1.4 p.p.m. ($J = 7$ c.p.s.) to which was assigned the methyl group. The chloromethyl group contained nonequivalent hydrogens which gave a complex multiplet at 3.46 to 3.66 p.p.m. A seven-line multiplet centered at 3.00 p.p.m. ($J = 7$ c.p.s.) was assigned to the single hydrogen on the asymmetric carbon. A singlet at 7.2 p.p.m. was assigned to the hydrogens on the aromatic ring.

The n.m.r. spectrum of β-chloroisopropyl acetate consisted of a singlet at 2.0 p.p.m., assigned to the acetate methyl group; a doublet centered at 3.6 p.p.m. ($J = 6$ c.p.s.), assigned to the remaining methyl group; and a complex seven-line multiplet centered at 5.05 p.p.m. ($J = 6$ c.p.s.), assigned to the methine hydrogen.

Reaction of the Propylene Chloronium Ion with Toluene.—To 300 ml. of toluene was added concurrently during 2 hr. at 40–45° 1 mole each of chlorine and propylene. The mixture was stirred for 0.5 hr. and washed with sodium carbonate solution; the organic phase (376 g.) was dried over sodium sulfate and studied by gas chromatography and infrared and n.m.r. spectroscopy. The data indicated the presence of 0.04 mole of allyl chloride, 0.84 mole of propylene dichloride, 0.02 mole of 1,2,3-trichloropropane, and 0.10 mole of a mixture of β-chloroisopropyl-substituted toluenes. The predominant isomer was the *ortho*-substituted product (strong absorption bands in the infrared at 740 cm.$^{-1}$), with much less of the *para* isomer (infrared absorption at 830 cm.$^{-1}$), and a very small amount of the *meta* isomer (infrared absorption at 790 cm.$^{-1}$).

The n.m.r. spectrum of this mixture of isomers showed a single line at 2.3 p.p.m. to which was assigned the methyl group attached to the benzene ring. A doublet centered at 1.32 p.p.m. ($J = 7$ c.p.s.) was assigned to the other methyl group. As in the case of β-chlorocumene, the two hydrogens in the chloromethyl grouping were nonequivalent and were represented by a complex multiplet at 3.4 to 3.63 p.p.m. A seven-line multiplet centered at 3.00 p.p.m. ($J = 7$ c.p.s.) was assigned to the single hydrogen on the asymmetric carbon. The four aromatic hydrogens were split into a doublet centered at 7.05 p.p.m. ($J = 3$ c.p.s.).

β-Chloroisopropyl Chloroacetate (Illustrating Method A.).—To a mixture of 94.5 g. (1 mole) of chloroacetic acid and 300 ml. of chloroform was added concurrently 1 mole each of chlorine and propylene during 2 hr. with mild cooling to keep the reaction mixture at 40–50°. The mixture was stirred for 0.5 hr., then cooled to 5° and washed with sodium carbonate solution to remove the hydrogen chloride and unreacted chloroacetic acid. The organic phase (395 g.) was separated, dried, and studied by gas chromatography and infrared and n.m.r. spectroscopy. The data indicated the presence of 0.01 mole of allyl chloride, 0.73 mole of propylene chloride, 0.02 mole of 1,2,3-trichloropropane, and 0.22 mole of β-chloroisopropyl chloroacetate. The solvent and lower boiling components were removed under the column at water pump pressure and the residue was fractionated, yielding 35 g. of product at 76–77° (5 mm.), n^{25}_{D} 1.4538.

β-Chloroisopropyl Dichloroacetate.—A run was carried out by method A using 1 mole each of dichloroacetic acid, chlorine, and propylene, and 300 ml. of chloroform. Analysis of the organic phase (574 g.) indicated the presence of a trace of allyl chloride, 0.80 mole of propylene dichloride, 0.02 mole of 1,2,3-dichloropropane, and 0.16 mole of β-chloroisopropyl dichlorodiacetate. Fractionation of this mixture gave 31 g. of ester distilling at 81–83° (6 mm.), n^{25}_{D} 1.4628.

Relative Reactivities of the Propylene Chloronium Ion with Acetic, Chloroacetic, and Dichloroacetic Acid.—Chlorine (1 mole) and propylene (1 mole) were added by method A to a mixture of 1 mole each of acetic, chloroacetic, and dichloroacetic acid (no solvent used on this run). The mixture was cooled to 5° and added to a solution of 2 moles of sodium carbonate in 600 ml. of water. The organic phase (136 g.) was separated and analyzed by n.m.r. spectroscopy. This analysis was possible because the hydrogens in the acid grouping of the ester are isolated and equivalent and fall as a single line with a different chemical shift for each ester. The singlet for the acetate ester fell at 2.05 p.p.m., that for the chloroacetate at 4.05 p.p.m., and that for the dichloroacetate at 6.0 p.p.m. The areas for these three absorptions for the above reaction mixture were in a ratio of 3:2:1, corresponding to identical molar amounts of the three esters in the reaction mixture, and corresponding to identical reactivities of these three acids with the propylene chloronium ion. Further analysis by gas chromatography indicated the presence of 0.07 mole of each of the three esters, 0.70 mole of propylene dichloride, 0.02 mole of 1,2,3-trichloropropane, and minor amounts of other by-products.

β-Chloroisopropyl Trichloroacetate.—Another run was carried out similar to the one described in the paragraph above except that 3 moles of acetic acid and 1 mole of trichloroacetic acid comprised the mixture in the reaction flask. Gas chromatographic analysis of the organic phase (130 g.), after removal of the unreacted acids as described in the previous experiment, indicated the presence of 0.66 mole of propylene dichloride, 0.22 mole of β-chloroisopropyl acetate, 0.02 mole of 1,2,3-trichloropropane, 0.06 mole of β-chloroisopropyl trichloroacetate, and minor amounts of other materials which were not isolated for identification. Fractionation of the mixture gave 14.2 g. of the trichloroacetate at 79–81° (5 mm.), n^{25}_{D} 1.4683.

β-Chloroisopropyl Acetate (Illustrating Method B.).—To a mixture of 300 g. of glacial acetic acid and 98 g. (1 mole) of potassium acetate was added concurrently 1 mole each of propylene and chlorine during 2 hr. with mild cooling to maintain the temperature at 40–50°. The mixture was stirred for 0.5 hr. and poured with stirring into a beaker containing a solution of 318 g. (3 moles) of sodium carbonate in 900 ml. of water. Benzene (100 ml.) was added to the mixture to facilitate separation. The organic phase was separated and the aqueous layer was extracted three times with 50-ml. portions of benzene. The extracts were added to the main product, and the material was dried over sodium sulfate and studied by gas chromatography and infrared and n.m.r. spectroscopy. The data indicated the presence of 0.01 mole of allyl chloride, 0.30 mole of propylene dichloride, 0.62 mole of β-chloroisopropyl acetate, 0.01 mole of 1,2,3-trichloropropane, 0.02 mole of β,β′-dichloroisopropyl acetate, and 0.03 mole of β-chloroisopropyl chloroacetate.[18] Fractionation of this mixture gave 82 g. of β-chloroisopropyl acetate at 58–60° (25 mm.), n^{25}_{D} 1.4213.[19]

Reaction of 1-Butene Chloronium Ion with Acetic Acid.—A run was carried out by method B as described above except that 1-butene was used in the place of propylene. Analysis of the reaction mixture as described indicated the presence of 0.33 mole of 1,2-dichlorobutane, 0.42 mole of 1-chloromethylpropyl acetate, 0.14 mole of 2-chlorobutyl acetate, 0.02 mole of 1,2,3-trichlorobutane, 0.04 mole of 1-methyl-2,3-dichloropropyl acetate, and minor amounts of several other materials which were not isolated for identification. Fractionation gave 80 g. of a mixture of 1-chloromethylpropyl acetate and 2-chlorobutyl acetate at 65–70° (20 mm.), n^{25}_{D} 1.4260.[20] After an intermediate cut, 7 g. of **1-methyl-2,3-dichloropropyl acetate** was obtained at 71–72° (4 mm.), n^{25}_{D} 1.4533.

The n.m.r. spectrum for this compound was consistent for the structure named. It consisted of a singlet at 2.03 p.p.m., assigned to the three hydrogens of the acetate group; a doublet centered at 3.2 p.p.m. ($J = 7$ c.p.s.), assigned to the 1-methyl group; a doublet centered at 3.78 p.p.m. ($J = 6$ c.p.s.), assigned to the two hydrogens of the chloromethyl group; a complex multiplet centered at 5.25 p.p.m., which was assigned to the hydrogen on the 1-carbon; and another complex multiplet centered at 4.2 p.p.m., which was assigned to the hydrogen on the 2-carbon.

Reaction of Isobutylene Chloronium Ion with Acetic Acid.—Another run was carried out as described for method B except that isobutylene was used in the place of propylene and ammonium acetate was used in the place of potassium acetate. Analysis of the reaction mixture as described indicated the presence of the following.[21]: 0.01 mole of 3-chloro-2-methylpropene, 0.03 mole of

---

[18] Small amounts of esters of chloroacetic acid were detected on several runs in which the reactant was acetic acid. It is believed that the chloroacetate esters arose from direct chlorination of the acetate ester which was the main product. The work was done in an internally lighted laboratory with some diffuse sunlight from a small window. No attempt was made to shield any of the reaction mixtures from the light normally present in the room. It is believed that the β,β′-dichloroisopropyl esters which formed in small amounts in most of these runs invariably resulted from reaction of the acid in question with the chloronium ion of allyl chloride.

[19] β,β′-Dichloroisopropyl acetate has been reported by W. Bockemuller and F. W. Hoffman [*Ann.*, **520**, 165 (1935)] to distil at 81° (15 mm.). We are not able to separate it on this fractionation from β-chloroisopropyl chloroacetate, the latter reported elsewhere in this paper.

[20] (a) A. Bruylants, *et al.* [*Bull. Soc. chim. Belges*, **61**, 366 (1952); *Chem. Abstr.*, **47**, 11125 (1953)], have reported 1-chloromethylpropyl acetate to have b.p. 101–102° (100 mm.), n^{20}_{D} 1.4270, and (b) S. J. Cristol and K. R. Eilar [*J. Am. Chem. Soc.*, **72**, 4356 (1950)] have reported 2-chlorobutyl acetate to have b.p. 158–162° (630 mm.), n^{25}_{D} 1.4255. We were not able to separate these two isomeric products in our column.

[21] The diversity of products formed on this run amazed us, but all are predictable from the known reactions of olefins on low-temperature chlorination in a liquid phase.[4]

1-chloro-2-methylpropene, 0.04 mole of *t*-butyl acetate, 0.12 mole of isobutylene dichloride, 0.08 mole of 1,3-dichloro-2-methylpropene, 0.21 mole of 2-chloro-1,1-dimethylethyl acetate, 0.01 mole of 2-chloro-2-methylpropyl acetate, 0.02 mole of 2-methyl-1,1,2-trichloropropane, 0.07 mole of 2-methyl-1,2,3-trichloropropane, and 0.05 mole of 1,1-bis(chloromethyl)ethyl acetate. The only pure material isolated on fractionation of this mixture was a cut of 8.5 g. of **1,1-bis(chloromethyl)ethyl acetate** distilling at 59–60° (5 mm.), $n^{25}D$ 1.4502. The n.m.r. spectrum for this compound consisted of a simple three-line spectrum since all hydrogens are on isolated carbons. The acetate methyl group fell at 2.0 p.p.m., the two equivalent chromethyl groups fell at 3.9 p.p.m., and the remaining methyl group gave a line falling at 1.6 p.p.m.

2-Chlorocyclohexyl Acetate.—A run was carried out as described for method B employing cyclohexene (all added at the start) as the olefin and using sodium acetate in the place of potassium acetate. The salt was filtered from the reaction mixture and acetic acid was removed to a pot temperature of 80° at water pump pressure. The residue was treated with 50 ml. of water to dissolve the remaining salt. The organic phase was separated, dried over sodium sulfate, and fractionated, yielding 37 g. (24%) of *trans*-1,2-dichlorocyclohexane at 56–57° (6 mm.), $n^{25}D$ 1.4878 [lit.[22] b.p. 88–89° (30 mm.), $n^{20}D$ 1.4904]; 103 g. (58%) of 2-chlorocyclohexyl acetate at 85–86° (6 mm.), $n^{25}D$ 1.4658 [lit.[23] b.p. 100–100.3° (12 mm.), $n^{20}D$ 1.4644]; and 15 g. (7%) of impure 2-chlorocyclohexyl chloroacetate at 116–118° (5 mm.), $n^{25}D$ 1.4849.[24]

2-Chloro-1-phenylethyl Acetate.—A run was carried out as described above for cyclohexene, except that styrene was used as the olefin. Fractionation gave 18 g. (13%) of β-chlorostyrene at 80–82° (10 mm.), $n^{25}D$ 1.5741 [lit.[25] b.p. 89–92° (15 mm.), $n^{18}D$ 1.5781]; 67 g. (38%) of styrene dichloride at 90–92° (4 mm.), $n^{25}D$ 1.5492 [lit.[26] b.p. 90° (4 mm.), $n^{15}D$ 1.5544]; and 85 g. (43%) of 2-chloro-1-phenylethyl acetate at 111–112° (3 mm.), $n^{25}D$ 1.5164.

2-Chlorocyclohexyl Chloroacetate.—A mixture of 2 moles of cyclohexene and 1 mole of chloroacetic acid was maintained at 40–45° (warming initially to dissolve the acid, and then mild cooling) while 1 mole of chlorine was added during 3 hr. After the addition was complete, a solution of 70 g. of sodium carbonate in 150 ml. of water was cautiously added. The organic phase was separated, dried, and the excess cyclohexene was removed at water pump pressure. The residue was fractionated, yielding 84 g. (55%) of *trans*-1,2-dichlorocyclohexane at 65–67° (10 mm.), $n^{25}D$ 1.4872; an intermediate cut of 10 g., $n^{25}D$ 1.4930; and then 53 g. (25%) of 2-chlorocyclohexyl chloroacetate at 132–133° (10 mm.), $n^{25}D$ 1.4860.

2-Chlorocyclohexyl Dichloracetate.—A run was carried out as described in the preceding paragraph except that dichloroacetic acid was used in place of the chloroacetic acid. Fractionation gave 83 g. (54%) of *trans*-1,2-dichlorocyclohexane at 66–67° (10 mm.), $n^{25}D$ 1.4881; an intermediate cut of 19 g., $n^{25}D$ 1.4890; and 61 g. (25%) of 2-chlorocyclohexyl dichloroacetate at 139–140° (11 mm.), $n^{25}D$ 1.4919.

N-(β-Chloroisopropyl)acetamide.[27]—To a mixture of 200 ml. of chloroform and 82 g. (2 moles) of acetonitrile were added concurrently 1 mole of chlorine and 1 mole of propylene during 2 hr. with mild cooling to maintain the temperature at 40–45°. After the additions were complete, the mixture was maintained below 20° while a solution of 53 g. of sodium carbonate in 300 ml. of water was added (initially very exothermic!); then the organic phase was separated and dried, and the solvent and propylene dichloride were removed at water pump pressure. The residue was fractionated, yielding 37 g. (27%) of the amide at 108–110° (2 mm.), $n^{25}D$ 1.4778. This material was a very viscous colorless liquid which froze with fracturing when cooled in Dry Ice and melted at −11°.

Anal. Calcd. for $C_5H_{10}ClNO$: C, 44.29; H, 7.43; Cl, 26.15; N, 10.33. Found: C, 44.00; H, 7.10; Cl, 25.80; N, 9.90.

The n.m.r. spectrum for the above compound was consistent for the structure named and consisted of a broad band centered at 7.8 p.p.m., representing one hydrogen, and assigned to the amide hydrogen; a doublet centered at 1.3 p.p.m. (J = 7 c.p.s.), assigned to the methyl group of the N-alkyl grouping; a doublet centered at 3.6 p.p.m. (J = 7 c.p.s.), assigned to the two hydrogens of the chloromethyl group; a complex multiplet centered at 4.2 p.p.m. (J = 7 c.p.s.), representing one hydrogen and assigned to the methine group; and a singlet at 2.05 p.p.m., assigned to the three hydrogens of the acetyl grouping.

---

[22] H. C. Stevens and O. Grummit, *J. Am. Chem. Soc.*, **74**, 4876 (1952).

[23] S. J. Lapporte and L. L. Ferstandig, *J. Org. Chem.*, **26**, 3684 (1961).

[24] The pure material is reported elsewhere in this paper.

[25] F. Bergmann, A. Kalmus, and E. Breuer, *J. Am. Chem. Soc.*, **80**, 4543 (1958).

[26] M. F. Handley, U. S. Patent 2,776,982 (1957); *Chem. Abstr.*, **51**, 8143 (1957).

[27] This experiment was repeated using 1 mole of acrylonitrile (and no acetonitrile or propylene) to see if this material could serve as both the olefin and nitrile in preparing a chlorinated amide. No such product was detected in the reaction mixture, the major product being 2,2,3-trichloropropionitrile. It was obtained in 82% yield based on the unrecovered acrylonitrile, b.p. 60–61° (25 mm.), $n^{22}D$ 1.4655. The n.m.r. spectrum of this material consisted of a single line falling at 4.2 p.p.m., assigned to the two equivalent hydrogens on the 3-carbon. *Anal.* Calcd. for $C_3H_2Cl_3N$: Cl, 67.14. Found: Cl, 67.00.

Valence Tautomerism of Vinyl-Substituted Three-Membered Heterocycles. II. Conversion of N-Ethyl-2,3-divinylaziridine to N-Ethyl-4,5-dihydroazepine

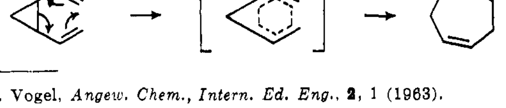
E. L. STOGRYN AND S. J. BROIS

Special Projects Unit, Esso Research and Engineering Company, Linden, New Jersey

Received July 27, 1964

Cyclization of 3-ethylamino-4-hydroxy-1,5-hexadiene, obtained from the aminolysis of 1,2-divinylethylene oxide, gave rise to a mixture of *trans*-N-ethyl-2,3-divinylaziridine and its valence isomer, N-ethyl-4,5-dihydroazepine. The origin of the azepine VI was established by the isolation and ring closure of the *erythro* IIa and *threo* IIb, amino alcohols. The *erythro* isomer cyclized to yield only *trans*-aziridine V. Even at room temperature the *cis*-aziridine isomerized to azepine VI as rapidly as it was generated from the *threo*-amino alcohol IIb.

Small strained carbocycles, with *cis*-oriented olefinic groups are subject to thermally induced ring expansions[1-3] by a Cope[4]-type rearrangement mechanism. Replacement of one of the vinyls by unsaturated hetero atoms, *e.g.*, isocyanate, does not destroy the lability of the small ring toward enlargement. Accordingly, lactams are formed by the thermolysis of *cis*-2-vinylcyclopropyl isocyanate.[1,5] Recent reports have extended the scope of valence isomerization of strained rings systems to include small heterocycles. These



---

[1] E. Vogel, *Angew. Chem., Intern. Ed. Eng.*, **2**, 1 (1963).

[2] E. Vogel, *ibid.*, **1**, 53 (1962).

[3] W. E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).

[4] For recent reviews of the Cope rearrangement, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1962, p. 505; S. J. Rhoads, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers Inc., New York, N. Y., 1963, p. 684.

[5] W. E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).