Anal. (2c)[15] Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14; mol. wt., 226. Found: C, 85.21; H, 14.74; mol. wt. (cryoscopic, benzene), 222.

Summary

The action of sodium on (+)2-chlorooöctane has been found to give octylene (37%), octane (8.5%), (+)3-methylnonane (6.4%), $[\alpha]^{25}D$ + 5.16° and (+)7,8-dimethyltetradecane (3.7%), $\alpha^{23}D$ + 0.96° (homogeneous, 1-dm. tube.) It is suggested that the optically active hydrocarbons are formed by a concerted displacement reaction with accompanying Walden inversion. The known extensive racemization of the same hydrocarbons produced by the action of sodium ethyl on (−)2-bromooctane is interpreted as indicating that this halide reacts with sodium alkyls by a two-stage process involving initial production of a racemizable *s*-octyl carbonium ion.

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RECEIVED APRIL 20, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

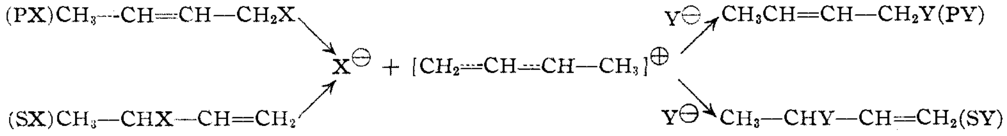
Reactions of Organometallic Compounds with Alkyl Halides. III. On Sodium Ethyl and Butenyl Chlorides

BY STEPHEN E. ULRICH[1] AND JOHN F. LANE

In the first two papers of this series[2,3] it has been shown that interaction of sodium alkyls with an optically active alkyl chloride led to the production of optically active hydrocarbons. On the other hand, with the corresponding alkyl bromide extensively or completely racemized products were obtained. These results have been interpreted[3] as indicating that the displacement of chlorine by alkyl carbanions is a concerted, one step process attended by Walden inversion but little racemization, while displacement of bromine by the same carbanions is a two stage process involving preliminary ionization of the halide to give a racemizable carbonium ion.

The occurrence of this kind of displacement in a medium of low dielectric constant and with an entering anion of high basicity is somewhat surprising. It was, therefore, considered desirable to explore the possibility of its occurring with certain additional halides which are prone to undergo displacement reactions by way of intermediate carbonium ions.

It is well known that allylic halides are of this type. Furthermore, much evidence has been presented[4,5] to substantiate the conclusion that with a pair of allylic isomers, the two stage ionic replacement of one group by another (S_N1) leads from each isomer to the same mixture of products, *e. g.*



$$\begin{array}{l}(PX)CH_3—CH{=}CH—CH_2X \searrow \qquad\qquad\qquad\qquad\qquad \nearrow Y^{\ominus} \; CH_3CH{=}CH—CH_2Y(PY) \\ \qquad\qquad X^{\ominus} + [CH_2{\dots}CH{\dots}CH—CH_3]^{\oplus} \\ (SX)CH_3—CHX—CH{=}CH_2 \nearrow \qquad\qquad\qquad\qquad\qquad \searrow Y^{\ominus} \; CH_3—CHY—CH{=}CH_2(SY)\end{array}$$

while, on the other hand, concerted one stage displacement usually leads to "normal" products (Y + PX → PY + $X^{\ominus}$, S_N2) and sometimes to "inverse" products (Y + PX → SY + $X^{\ominus}$, S_N2'), it never leads to mixtures.

In the present study the isomeric butenyl chlorides, 1-chloro-2-butene (PCl) and 3-chloro-1-butene (SCl), were separately allowed to react in pentane with sodium ethyl. In each case the only clearly isolable product was (chiefly *trans*) 2-hexene (PC_2H_5), although the lower boiling fractions may have contained traces of the isomeric 3-methyl-1-pentene (SC_2H_5). This behavior indicates formation in each case of a mixture of products in which the thermodynamically more stable hexene-2 is predominant.[6] That ionic replacement of chlorine by ethyl should, in this system, lead to a mixture of products resembling the thermodynamically stable one is quite reasonable. This has, indeed, been shown to be true[4a] in the conversion of the corresponding alcohols (POH, SOH) to the bromides by an ionic mechanism.

These results strongly suggest that with these reactive halides the replacement of chlorine by ethyl has not proceeded by the concerted one stage mechanism, but rather by way of a resonating butenyl carbonium ion.

Experimental

Materials.—The isomeric butenyl chlorides were obtained by fractionation, through a 90-cm. Todd column, of the commercial mixture of the Shell Development Company. 3-Chloro-1-butene boiled at 64.9–65.0° (771 mm.)

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[1] American Chemical Society Fellow in Rutgers University, 1946–1949.

[2] Brink, Lane and Wallis, THIS JOURNAL, **65**, 943 (1943).

[3] Ulrich, Gentes, Lane and Wallis, *ibid.*, **72**, 5127 (1950).

[4] (a) Young and Lane, *ibid.*, **60**, 847 (1938); (b) Roberts, Young and Winstein, *ibid.*, **64**, 2197 (1942).

[5] Hughes, *Trans. Far. Soc.*, **37**, 603 (1941).

[6] Am. Pet. Inst., "Selected Values of Properties of Hydrocarbons," Vol. III, Table 8p, gives the following free energies of formation (ΔF_{298}, kcal.): PC_2H_5, *trans*, 18.46, *cis* 19.18, SC_2H_5, 20.28. From these the composition of the thermal equilibrium mixture is estimated to be: PC_2H_5, *trans*, 70.4%, *cis* 26.3%, SC_2H_5, 3.3%.

$n^{20}D$ 1.4149; 1-chloro-2-butene boiled at 85.9-86.1° (762 mm.), $n^{20}D$ 1.4346. The mercury diethyl and pentane ($n^{20}D$ 1.358) used here were prepared as previously described.[3]

Action of Sodium Ethyl on the Isomeric Butenyl Chlorides.—In these experiments the same apparatus and essentially the same technique were employed as described previously[2,3] for the treatment of the 2-halooctanes with sodium ethyl. Data on the amounts of reactants, conditions, and amounts of chloride ion and mercury obtained are summarized in Table I.

TABLE I

REACTANTS, CONDITIONS AND INORGANIC PRODUCTS IN THE REACTIONS OF SODIUM ETHYL WITH BUTENYL CHLORIDES

Compound, butene		3-Chloro-1	1-Chloro-2-
Reactants, mole	Alkenyl halide	0.483	0.486
	Sodium	0.79	0.92
	Mercury diethyl	0.277	0.283
Stirring times at −10, 25°, hr.		5,24	5,24
Inorganic products	Chloride ion, mole	0.473	0.470
	Mercury, mole	0.264	0.287

After decomposition of the reaction mixture with water, in each case the dried pentane solution was treated with sodium over a period of several days until freshly added sodium was no longer discolored. The resulting solutions were then fractionated through the 90-cm. Todd column. Data on the fractionations are given in Tables II and III.

TABLE II

CHARACTERISTICS OF HYDROCARBON PRODUCTS BOILING BETWEEN 37 AND 117° (766 MM.) FROM REACTION OF SODIUM ETHYL WITH 3-CHLORO-1-BUTENE

Fraction	B. p., °C.	Wt., g.	$n^{20}D$	Bromine addn. no.[a]
1	37.0-46.5	4.0	1.3613	4
2	50.0-59.0	2.0	1.3863	126
3	62.7-68.9	2.8	1.3920	185
4	69.0-69.3	3.3	1.3935	
5	69.5	2.7	1.3938	193
6	69.5-69.7	3.6	1.3941	
7	69.7-70.0	1.9	1.3941	
8	70.0-71.0	0.4	1.3960	
9	110-117	0.7	1.4221	
10	Residue	6.2		

[a] Determined by the method of Uhrig and Levin (*Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941)).

TABLE III

CHARACTERISTICS OF HYDROCARBON PRODUCTS BOILING BETWEEN 37 AND 117° (763 MM.) FROM REACTION OF SODIUM ETHYL WITH 1-CHLORO-2-BUTENE

Fraction	B. p., °C.	Wt., g.	$n^{20}D$	Bromine addn. no.
1	37.0-48.2	2.1	1.3658	29
2	49.2-58.0	1.9	1.3825	135
3	58.3-67.8	3.1	1.3902	178
4	68.0-69.0	2.4	1.3932	191
5	69.0-69.2	2.1	1.3938	191
6	69.2-71.0	1.8	1.3944	
7	99.2-121.0	2.0	1.4198	
8	Residue	8.4		

The boiling points and refractive indices of the isomeric 2-hexenes are, respectively,[7] *cis*, 68.6°, 1.3954; *trans*, 67.9°, 1.3935; of 3-methyl-1-pentene, 53.8°, 1.384. If it be assumed that pentane ($n^{20}D$ 1.358) is the saturated contaminant of fractions 2 and 3 in each table, the weights and refractive indices of the unsaturated (C_6H_{12}) portions of these fractions are estimated to be: Table II (2) 1.33 g., $n^{20}D$ 1.40 ± 0.01; (3) 2.73 g., $n^{20}D$ 1.39 ± 0.01; Table III (2) 1.35 g., $n^{20}D$ 1.39 ± 0.01; (3) 2.90 g., $n^{20}D$ 1.39 ± 0.01. The third fractions evidently contain C_6H_{12} only as 2-hexene. The second fractions would appear to contain C_6H_{12} chiefly as 2-hexene. Fractions 4-7 of Table II and 4-6 of Table III are substantially pure 2-hexene, which from the refractive indices appear to be mainly the *trans* form.

Summary

The action of sodium ethyl on 1-chloro-2-butene and on 3-chloro-1-butene has been found to give 2-hexene (chiefly *trans*) as the only clearly isolable product. This has been interpreted as indicating that, with these halides, the replacement of chlorine by ethyl proceeds by way of a resonating butenyl carbonium ion.

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RECEIVED APRIL 20, 1950

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(7) Ref. 6, Table 8a.