

3. Proton attraction by oxygen atoms also occurs in benzoin, ethyl lactate and other molecules.

4. It is suggested that pyrrole molecules exist in solution in a coplanar form, the NH hydrogen being in the plane of the ring, and also (to a smaller extent) in a non-coplanar form. Only the coplanar molecules of carbazole and tetraphenylpyrrole and the non-coplanar molecules of acetylpyrrole occur in appreciable quantities.

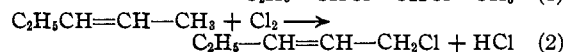
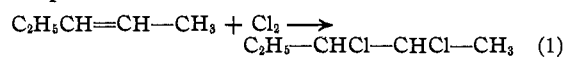
PASADENA, CALIFORNIA RECEIVED NOVEMBER 25, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Induced Substitution of Pentene by Chlorine

BY T. D. STEWART AND BERNHARDT WEIDENBAUM

We have previously<sup>1,2</sup> reported the reactions of chlorine with benzene and *n*-pentane, as induced by ethylene. The present work is a study of the coupled reactions



2-Pentene and chlorine were dissolved separately in carbon tetrachloride, in known concentrations, and measured volumes of the two solutions mixed rapidly.

### Preparation of Materials

Purification of most of the reagents has been described.<sup>2</sup> 2-Pentene (E. K. Co.) was fractionated, and the portion of b. p. 36.2–36.4° was used. 2-Chloropropene was prepared from acetone and phosphorus pentachloride,<sup>3</sup> and distilled at 23.0°. Kahlbaum allyl chloride was used without further purification. 1-Phenyl-2-propene was prepared from phenylmagnesium bromide and allyl bromide.<sup>4</sup> The fraction distilling from 155–157° was used. All reagents were carefully dried.

### Experimental Results

In Table I the concentrations of reagents given refer to the calculated initial concentrations after mixing of the stock solutions. By induction factor is meant the ratio of the moles of chlorine producing hydrogen chloride to the moles of chlorine reacting by addition. Fifteen seconds were allowed for completion of the reaction. From two to four experiments were made at each dilution, varying the order of addition of the reactants.

(1) Stewart and Hanson, *THIS JOURNAL*, **53**, 1121 (1931).

(2) Stewart and Hanson, *ibid.*, **57**, 2036 (1935).

(3) Friedel, *Ann.*, **112**, 236 (1859).

(4) Tiffeneau, *Compt. rend.*, **139**, 482 (1904).

TABLE I

THE RELATIVE AMOUNTS OF SUBSTITUTION AND ADDITION BY CHLORINE REACTING WITH 2-PENTENE IN PURE CARBON TETRACHLORIDE, IN THE ABSENCE OF OXYGEN

Concentration in moles/liter Chlorine	2-Pentene	Induction factor
0.101	0.097	1.23
.0464	.097	1.60–1.64
.101	.051	0.57
.0464	.051	0.88–0.93
.00954	.051	3.04–3.24
.0464	.0097	0.72–0.78

The substitution reaction was favored by a relative increase in the 2-pentene concentration, or by a relative decrease in the chlorine concentration.

Similar results were obtained in the presence of oxygen, *p*-thiocresol and when commercial carbon tetrachloride was used as solvent.

TABLE II

EXPERIMENTS IN THE PRESENCE OF OXYGEN (A), *p*-THIOCREOSOL, 0.018 *M* (B) AND COMMERCIAL CCl<sub>4</sub> (C)

	Concentration in moles/liter Chlorine	2-Pentene	Induction factor
A	0.0104	0.0122	1.11–1.20
	.0064	.0122	2.03
	.0021	.0122	3.22
B	.0104	.0122	1.28–1.31
C	.00954	.0097	1.17–1.32

In Table III are given the results of a series of experiments performed at –10° and at 25.1°. Change of temperature produces little change in the induction factor.

Other attempts to cause a significant change in the induction factor under constant initial concentration of reagents failed; the presence of water, hydrogen chloride and powdered glass, respectively, had no effect.

When 1-phenyl-2-propene was used instead of 2-pentene, the reaction was found to be rapid, but

TABLE III  
EFFECT OF TEMPERATURE

Chlorine 0.0464 <i>M</i> ; time 15 seconds		
Temp., °C.	Moles/liter, 2-pentene	Induction factor
-10	0.0970	1.42-1.48
-10	.0508	0.88-0.90
-10	.0097	0.69-0.70
25.1	.0970	1.46
25.1	.0508	0.79-0.80
25.1	.0097	0.45

the induction factor was only 0.22 with the chlorine and olefin concentrations 0.0975 and 0.119 *M*, respectively, and only 0.76 when they were 0.0097 and 0.119 *M*, respectively. With 2-chloropropene the reaction was very slow and no substitution was observed.

**Identification of Substitution Product.**—450 cc. of 0.0464 *M* chlorine in carbon tetrachloride was added to 450 cc. of 0.498 *M* 2-pentene, at 0°. The induction factor was approximately three. The reaction mixture was then very carefully fractionated in a vacuum jacketed column, 1.5 cm. in diameter and 30 cm. high, packed with fine glass cylinders and surmounted by a head designed for total reflux. At the start the hydrogen chloride and some pentene were collected in a liquid-air trap. The remaining pentene was removed with the bulk of the carbon tetrachloride, and with this and subsequent fractions no further hydrogen chloride was found, indicating stability of the chlorinated pentene. Finally the portion boiling in the range 77–110° was collected, containing some carbon tetrachloride and most of the chloropentene.<sup>5</sup> The residue was then reduced to 2–3 cc. and analyzed for chlorine, since any polychlorinated pentanes would appear as high boiling products. The chlorine content corresponded closely to a dichloropentane.

Samples of the 77–110° fraction were analyzed for olefin with bromine in carbon tetrachloride, for reactive halide with trimethylamine in alcohol, and for total chlorine. The results showed 0.000351 mole of olefin and 0.00035 mole of reactive halide per gram of solution. If but two halides, carbon tetrachloride and mono-substituted pentene were present, the chlorine analysis corresponded to 0.000388 mole of chlorinated pentene per gram of solution.

To determine the position of halogen in the halogenated olefin, the rate of quaternization with

(5) 4-Chloro-2-pentene, b. p. 103–106° (dec.), Reif, *Ber.*, **41**, 2741 (1908); 1-chloro-2-pentene, b. p. 109.5°, Prévost, *Compt. rend.*, **187**, 1052 (1928).

a trialkylamine as suggested by the work of Menschutkin and Wassilieff<sup>6</sup> was used. Probable positions for the chlorine atom in the chloropentene would be  $\alpha$  to the double bond, *i. e.*, on carbons one or four, the former being a primary halide and the latter a secondary halide, and carbons two and three. If the chlorine were on one of the latter, the product would be of the vinyl chloride type. Since these types differ greatly in reactivity, a comparison of the rates of quaternization of excess trimethylamine with the product obtained above, of allyl chloride, of 2-chloropropene, and of carbon tetrachloride was made.

In the presence of the same concentration of amine in ten-fold excess, the pseudo first order specific reaction rate constants in moles per liter at 25° were as follows: the chlorinated 2-pentene, 0.109; 1-chloro-2-propene, 0.045; carbon tetrachloride and 2-chloropropene, no reaction in nine hours. It was shown that the reaction producing chloride ion was quaternary amine formation and not extraction of hydrogen chloride; moreover 90% of the reaction corresponded to the pseudo first order, indicating but one chloropentene present.

The rate of quaternization by the chloropentene was of the same order of magnitude as that of allyl chloride; hence it is probable that the chloropentene is 1-chloro-2-pentene. If it were a secondary halide, 4-chloro-2-pentene, the rate of quaternization would have been much slower, from one-tenth to one-fifth that of allyl chloride.<sup>7</sup>

### Discussion of Results

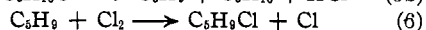
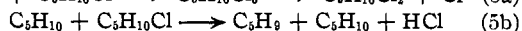
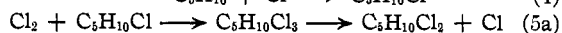
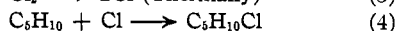
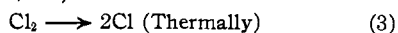
The effect of excess of olefin over chlorine in favoring substitution is of the same order of magnitude as that previously reported in the induced substitution of pentane.<sup>2</sup> Throughout the extended series of experiments there is also some indication that at equal but decreasing concentrations, the induction factor goes through a minimum, being about 1.23 at 0.1 *M*; 0.9 at 0.05 *M*; and 1.2 at 0.0095 *M*. Any eventual explanation must also take into account the independence of the induction factor of inhibitors, surface and especially temperature. Finally, although the data are meager, there is a definite suggestion that when the over-all reaction is slow substitution is low.

The effect of ethylene in quenching the hydro-

(6) Menschutkin and Wassilieff, *Z. physik. Chem.*, **5**, 589 (1890).

(7) Menschutkin, *Z. physik. Chem.*, **5**, 595 (1890); Conant and Hussey, *This Journal*, **47**, 477 (1925).

gen-chlorine chains<sup>2</sup> indicates a very rapid absorption of chlorine atom by the double bond. Moreover, it was concluded<sup>2</sup> that in mixtures of pentane, ethylene and chlorine the pentane was substituted, not ethylene or ethylene dichloride, and that the intermediate which permitted excess of ethylene to favor substitution must contain ethylene itself. Therefore the competitive reactions in the present case may similarly be represented (Eq. 5a, 5b)



with appropriate chain breaking steps. This mechanism also conforms to the ones consistent with the kinetics of the photochlorinations of both pentane and ethylene.

The competitive steps must have nearly the

same activation energy. It would appear highly fortuitous that insensitiveness to temperature would be found, except as the activation energies were very low, as well as equal; therefore the limitation of the effect to rapidly reacting ethylenes may well be expected.

### Summary

Chlorine and 2-pentene react in carbon tetrachloride solution to yield 1-chloro-2-pentene as well as the normal addition product. Substitution is favored by increasing the pentene concentration, addition by increasing the relative concentration of chlorine. The same effect is observed in 1-phenyl-2-propene to a smaller extent, but not at all in the slowly reacting 2-chloropropene. A tentative explanation is suggested, based upon competitive reactions involving a common intermediate.

BERKELEY, CALIFORNIA

RECEIVED JULY 22, 1935

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE RESEARCH LABORATORIES OF SHARP AND DOHME, INC.]

## Reduction of Aldehydes with Aluminum Isopropoxide<sup>1,2</sup>

BY WILLIAM G. YOUNG, WALTER H. HARTUNG AND FRANK S. CROSSLEY

Knowledge of the chemistry of crotyl compounds is much less developed than that of the allyl compounds. Crotyl derivatives are ordinarily obtained from crotyl bromide prepared from methylvinylcarbinol since Bouis reported<sup>3</sup> that alcohols of the type  $\text{RCHOHCH}=\text{CH}_2$  with phosphorus tribromide give bromides of the type  $\text{RCH}=\text{CHCH}_2\text{Br}$ . However, *trans*-crotonaldehyde<sup>4</sup> now commercially available, is a better source for crotyl compounds. Repeated attempts to reduce it to the corresponding unsaturated alcohol by means of zinc and iron,<sup>5</sup> or zinc-copper couple<sup>6</sup> invariably gave low yields of product contaminated with butyl alcohol, and the saturated and unsaturated alcohols and could not be separated.<sup>7</sup> Selective hydrogenation by means of platinum oxide catalyst<sup>8</sup> was successful several times in tenth molar quantities or less, but could not be extended to larger amounts.

(1) This work was aided by a grant from the Board of Research of the University of California.

(2) Presented at the San Francisco meeting of the American Chemical Society, August 19-23, 1935.

(3) Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).

(4) Young, *THIS JOURNAL*, **54**, 2498 (1932).

(5) Liehen and Zeisel, *Monatsh.*, **1**, 823, 840 (1880).

(6) Charon, *Ann. phys. chim.*, [7] **17**, 217 (1899).

(7) Claisen and Tietze, *Ber.*, **59B**, 2344 (1926).

(8) Tuley and Adams, *THIS JOURNAL*, **47**, 306 (1925).

Although Meerwein and Schmidt<sup>9</sup> report the preparation of crotyl alcohol in 60% yields, we have been unable to approach this figure with either aluminum ethoxide or chloromagnesium ethoxide. Our yields were usually little better than by the zinc-copper couple method.

Since polymerization of one of the reaction products, acetaldehyde, was the cause of most of the difficulty, it appeared likely that an alkoxide which oxidizes to a ketone, should prove more effective. Of these, the isopropoxide is the simplest, yielding volatile acetone.

With aluminum isopropoxide, crotyl alcohol has been prepared in satisfactory yields in two different solvents. The quantities that may be prepared at one time are apparently limited only by the size of apparatus.<sup>10</sup>

### Experimental Part

**Aluminum Alkoxides.**—These were prepared from aluminum amalgam and the appropriate alcohol, according to the directions of Child and Adkins.<sup>11</sup> Frequently, the aluminum dissolves with difficulty, but fortunately this

(9) Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

(10) Professor Homer Adkins, working independently in his laboratories at the University of Wisconsin, has obtained similar results. Private communication.

(11) Child and Adkins, *THIS JOURNAL*, **45**, 3013 (1923).