[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Olefins and Diolefins from Allylic Chlorides

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Irrespective of *cis–trans* isomerism, which will not be considered here, most allylic chlorides exist in two forms. Crotyl chloride, for instance, is a mixture of a primary chloride, $CH_3CH{=}CHCH_2Cl$, and a secondary chloride, $CH_2{=}CHCHClCH_3$. This permits the synthesis of two olefins by the reaction with a Grignard derivative, three diolefins by condensation on magnesium, or ten diolefins by condensation of two different allylic halides. In practice there are limitations which the present paper aims to show by a quantitative examination of the reaction products. Some compounds are highly favored, and some do not appear.

In addition to allyl chloride and methallyl chloride obtained from commercial sources, the allylic chlorides described in Table I were prepared and used as indicated in the experimental part.

TABLE I

ALLYLIC CHLORIDES

Allylic chloride	B. p., °C.	d^{20}_4	n^{20}_D	Other references
1-Chloro-2-butene	83	0.9316	1.4352	Present work
	84	.9282	1.4350	(1)
	84		1.4287 (21°)	(2)
	84		1.4350	(3)
3-Chloro-1-butene	63	.9001	1.4153	Present work
	64	.8978	1.4149	(1)
	64–8		1.3957 (21°)	(2)
	64		1.4150	(3)
4-Chloro-2-pentene	57 (200 mm.)	.9004	1.4328	Present work
	100 (772 mm.)	.9004	1.4322	(4)
2-Chloro-2,5-dimethyl-3-hexene and 4-Chloro-2,5-dimethyl-2-hexene	45–60 (15 mm.)		1.45 to 1.46	Present work

The following experiments were performed to synthesize olefins and diolefins:

(1) **The secondary form of crotyl chloride** (3-chloro-1-butene) was treated with magnesium in ether, to give 7% of 3,4-dimethyl-1,5-hexadiene (A), 57% of 3-methyl-1,5-heptadiene (B) and 3% of 2,6-octadiene (C). The balance of the reagent was recovered unreacted. The relative quantities of A:B:C were as 2:19:1, or 10.4, 85 and 4.5%, respectively, instead of A exclusively.

(2) **The primary form of crotyl chloride** (1-chloro-2-butene), treated in an identical fashion, gave 4% of A, 50% of B, and a small amount of C, instead of C exclusively.

(3) **The crude mixture of the two forms of crotyl chlorides**, treated in the same way, yielded 3% of A, 60% of B, and 4% of C. The relative amounts were as 1:20:1 or 4.5, 89.5 and 6%, respectively.

The three reactions gave substantially the same relative amounts of diolefins. The physical properties of these appear in Table II. The relative amounts obtained are in contrast with those reported for crotyl bromide.[5] When this bromide was reacted with magnesium, a mixture of the three possible diolefins, A, B and C, was reported to be obtained with a 90% yield, and it was claimed that in the mixture B and C were present in roughly equal proportion, while A appeared in only minute quantities. Diolefins B and C were identified by permanganate oxidation, while A was identified by means of its Raman spectrum.

(4) **A mixture of crotyl chlorides and allyl chloride**, in equimolecular proportions, was allowed to react with magnesium under ether. This operation gave 10% of 1,5-hexadiene (D), 10% of 3-methyl-1,5-hexadiene (E), 34% of 1,5-heptadiene (F), 21% of B, and 1% of C. If any quantity of A was formed it could not be detected. The relative amounts of D:E:F:B:C were then as 1:1:3.4:2.1:0.1 or 13, 13, 45, 28 and 1%, respectively.

(5) **Mixture of Crotyl Chlorides and Butylmagnesium Chloride.**—The crotyl chloride was added to a solution of butylmagnesium chloride in ether, and yielded a mixture of 6% of B, 9% of 3-methyl-1-heptene (G), and 85% of 2-octene (H). The relative amounts of B:G:H were then as 1:1.5:14. This relationship was not altered by reversing the order of addition of the reagents, nor by substituting the individual crotyl chlorides for the mixture of isomers.

(6) **Allyl chloride**, condensed by means of magnesium, gave a 60% yield of 1,5-hexadiene, (D).

(7) **Allyl chloride and methallyl chloride** condensed together over magnesium gave 12% of D, 47% of 2-methyl-1,5-hexadiene (J) and 30% of 2,5-dimethyl-1,5-hexadiene (K) together with some recovered chloride, mostly allyl.

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(1) Baudrenghien, *Bull. soc. chim. Belg.*, **31**, 160 (1922).

(2) Ganguly, *J. Ind. Chem. Soc.*, **13**, 580 (1936).

(3) Kharasch, *J. Org. Chem.*, **2**, 489 (1937).

(4) Baudrenghien, *Bull. classe sci. Acad. roy. Belg.*, [5] **15**, 53 (1929).

(5) Lespieau and Heitzmann, *Bull. soc. chim.*, [5] **3**, 273 (1936).

TABLE II

OLEFINS AND DIOLEFINS

	Compound	F. p., °C.	B. p., °C.	*n*	*d*	*MR* calcd.	*MR* obsd.	Other references
A	3,4-Dimethyl-1,5-hexadiene		101.8	1.4211	0.7304	38.21	38.26	5
B	3-Methyl-1,5-heptadiene	Glass	111.0	1.4240	.7291	38.21	38.56	5
C	2,6-Octadiene		124.5	1.4336	.7441	38.21	38.53	5
D	1,5-Hexadiene		59.4	1.4040	.6916	28.97	29.05	7
E	3-Methyl-1,5-hexadiene		80.0	1.4116	.7103	33.59	33.66	
F	1,5-Heptadiene		93.7	1.4200	.7186	33.59	33.87	8
G	3-Methyl-1-heptene			Not isolated, see comments				
H	2-Octene	− 94.04	125.2	1.4130	.7192	38.67	38.83	9
J	2-Methyl-1,5-hexadiene	−128.88	88.1	1.4184	.7198	33.59	33.70	10
K	2,5-Dimethyl-1,5-hexadiene	− 75.6	114.3	1.4293	.7423	38.21	38.29	10
L	1-Octene	−102.11	121.6	1.4090	.7150	38.67	38.73	11
M	6-Methyl-1-heptene	Glass	113.19	1.4068	.7119	38.67	38.71	12
N	2-Methyl-1-heptene	− 90.1	119.3	1.4123	.7206	38.67	38.77	13
P	4-Methyl-2-heptene	Glass	113.5	1.4096	.7150	38.67	38.81	14
Q	2,2,5-Trimethyl-3-hexene		114	1.416				
R	2,4,5-Trimethyl-2-hexene		128.4	1.4268	.7403	43.30	43.66	

(8) **Allyl chloride and *n*-amylmagnesium chloride** gave 1-octene (L), with an 80% yield.

(9) **Allyl chloride and isoamylmagnesium chloride** gave a 60% yield of 6-methyl-1-heptene (M).

(10) **Methallyl chloride** condensed with itself over magnesium to give a 65% yield of K.

(11) **Methallyl chloride and butylmagnesium chloride** gave 2-methyl-1-heptene (N), contaminated with 2-methyl-2-heptene obtained from rearrangement of the former by the magnesium chloride present. The amount of rearrangement depends greatly on the temperature during the condensation, and the working up of the products.

(12) **Piperylene hydrochloride and propylmagnesium chloride** gave a single olefin, 4-methyl-2-heptene (P). This establishes the fact that the piperylene hydrochloride must be represented as 4-chloro-2-pentene, a formula which does not call for an allylic isomer.

It is well to contrast this reaction to the condensation of 1-bromo-2-pentene,[6] which is isomeric with piperylene hydrobromide and whose formula calls for an allylic rearrangement form, 3-bromo-1-pentene. Condensed over magnesium, it gave 5 cc. of 3,4-diethyl-1,5-hexadiene, 62 cc. of 3-ethyl-1,5-octadiene and 28 cc. of 3,7-decadiene.

(13) **Diisocrotyl hydrochloride and methylmagnesium chloride** yielded two olefins, namely, a small amount of 2,2,5-trimethyl-3-hexene (Q) and a larger amount of 2,4,5-trimethyl-2-hexene (R). The ratio Q:R is as 1:5.

The observed physical properties of the olefins and diolefins are indicated in Table II, where the boiling points are at 760 mm., the densities are $d^{20}{}_4$ and the indices $n^{20}{}_D$ Abbe.

The compounds not mentioned in the literature were identified as follows: (E) hydrogenated to 3-methylhexane, b. p. 92.0°; *n* 1.3889; *d* 0.6868; *MR*. calcd. 34.53; *MR*. obsd. 34.50;[15] (G) obtained as a mixture with B. The boiling points of G and B differ by less than 1°, and the constituents could not be separated by distillation. The ratio B:G was determined by refractive index measurement and by double bond titration; both methods gave the same results. Hydrogenation of the mixture gave only 3-methylheptane, f. p. −120.8°; b. p. 119.1°; *n* 1.3988; *d* 0.7055; *MR*. calcd. 39.07; *MR*. obsd. 39.14.[16] (K) Hydrogenated to 2,5-dimethylhexane, f. p. −91.49°; b. p. 109.3°; *n* 1.3929; *d* 0.6939; *MR*. calcd. 39.14; *MR*. obsd. 39.19.[17] (P) Ozone oxidation gave α-methylvaleric acid whose ethyl ester b. p. 152–153°; *n* 1.4026. (Q) Hydrogenated to 2,2,5-trimethylhexane, b. p. 123.0°; *n* 1.3998; *d* 0.7075; *MR*. calcd. 43.76; *MR*. obsd. 43.84.[18] (R) Hydrogenated to 2,3,5-trimethylhexane, f. p. glass; b. p. 130.3°; *n* 1.4063; *d* 0.7218; *MR*. calcd. 43.76; *MR*. obsd. 43.70.[19]

Remarks

The same proportions of olefins or diolefins were obtained from either isomer of crotyl chloride as well as from the crude mixture of both. This parallels results reported by Young.[20]

When an allylic chloride reacted with a Grignard reagent, the proportion of olefin generated, which corresponds to the primary form of the allyl halide, was larger than that which corresponds to the secondary form, and the proportion from secondary predominated over tertiary. Similar observations were made in the case of dimethylbutadiene hydrobromide,[19] and isoprene hydrobromide.[21]

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[6] Prevost, *Bull. soc. chim.*, **49**, 1368, 1372 (1931).

[7] Cortese, THIS JOURNAL, **51**, 2266 (1929).

[8] Slotterbeck, Ph.D. Dissertation, Ohio State University, 1936.

[9] Gibson, Dissertation, Ohio State University, 1938.

[10] Frank, Ph.D. Dissertation, Ohio State University, 1937.

[11] Waterman and deKok, *Rec. trav. chim.*, **53**, 725 (1934).

[12] Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918).

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[14] Dietrich, Ph.D. Dissertation, Ohio State University, 1933.

[15] Edgar and Calingaert, THIS JOURNAL, **51**, 1483, 1544 (1929).

[16] Timmermans, *Bull. soc. chim. belg.*, **30**, 62 (1921).

[17] Timmermans and Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932).

[18] Brooks, Cleaton and Carter, *J. Research Nat. Bur. Standards*, **19**, 319 (1937).

[19] Cline, Ph.D. Dissertation, Ohio State University, 1939.

[20] Young, THIS JOURNAL, **54**, 404 (1932); **58**, 104, 289, 441 (1936); **59**, 2051, 2441 (1937); **60**, 847, 900 (1938).

[21] Rudel, Ph.D. Dissertation, Ohio State University, 1938.

Experimental

Preparation of Crotyl Chloride.—Commercial muriatic acid (700 g.) was first concentrated by leading 200 g. of dry hydrogen chloride into it, at ice temperature. This concentrated acid (200 g.) was cooled with an ice–salt mixture, and commercial butadiene (one mole) was distilled from a tank onto it. The bottle was stoppered with a neoprene stopper held in place by a lead screw cap, and rotated around a horizontal shaft for fifteen to twenty hours, to produce a vigorous mixing of the two layers. At the end of this time, any unreacted butadiene had polymerized and gave the aqueous layer a very viscous appearance. The top layer (purple to black) was decanted and distilled. It is not advisable to concentrate the hydrochloric acid to use it more than twice. The mixture invariably contained 65% of primary chloride and 35% of secondary chloride. Yields were computed as 70 to 75% but are actually about 10% higher, because commercial butadiene of mediocre quality was used. Both isomers were affected by one year of storage in a refrigerator; in both cases, the index of refraction rose by 25 to 30 units of the fourth decimal which was regarded as an indication that polymerization rather than isomerization had taken place.

Piperylene Hydrochloride.—Dry hydrogen chloride was passed through crude commercial piperylene, to yield 60 to 70% of addition product. Actual yields were about 15 to 20% higher. The addition took place in the 1,4-position and yielded exclusively 4-chloro-2-pentene. This compound exists only in one form, because its allylic rearrangement gives an identical product.

Diisocrotyl Hydrochloride.—Anhydrous hydrogen chloride was passed through cooled 2,5-dimethyl-2,4-hexadiene ("diisocrotyl") until the proper increase in weight was reached. Unabsorbed gas was removed by suction, after which the product distilled in a 45 to 60° range at fifteen mm. The mixture of isomeric chlorides was stable in the cold, and decomposed little at room temperature but too much to allow a separation by fractional distillation. The 1,4-addition of hydrogen chloride yields 2-chloro-2,5-dimethyl-3-hexene, whose allylic rearrangement generates 4-chloro-2,5-dimethyl-2-hexene.

Condensations.—All the condensations, with Grignard reagents as well as on magnesium, were performed in a copper reaction vessel, externally cooled by a water jacket. A powerful multi-bladed steel stirrer was used, and the condensation products were always stirred overnight to ensure the completion of the reaction. This method permitted a much more efficient control of the temperature than that which prevails in the customary glass devices. In general, 300 to 400 cc. of ether was used per mole of organic halide. This creates a very pasty reaction mass, and makes the use of a powerful stirrer indispensable. Identical results were obtained in glass, copper and steel equipment.

Quantities.—Amounts of hydrocarbon synthesized ranged from one mole to several liters. This made it possible to effect a complete purification in almost every case.

Distilling Columns.—Adiabatic packed columns (glass helices) were used, with total reflux and partial take-off. The reflux ratios were from 50 to 75.

Note.—This work is a part of the American Petroleum Institute Pure Hydrocarbon Program, operated as Project No. 31 of The Ohio State University Research Foundation. It was presented at the Atlantic City meeting of the American Chemical Society, September, 1941.

Summary

Several allylic chlorides have been prepared. They have been condensed with Grignard reagents to synthesize olefins and condensed with themselves or with each other to synthesize diolefins. All products have been described and listed in tables. The proportions of the different products in the reactions have been ascertained. The configurations of the olefins and diolefins have been established.

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Fluorinated Derivatives of Propane. IV*

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This article presents the synthesis of two tetrafluorotetrachloropropanes, and uses the new information to correct an error in a previous paper.[1] The previous paper claimed that in the treatment of $CHCl_2CCl_2CCl_3$ with antimony trifluoride, the first three substitution steps were $CHCl_2CCl_2CCl_2F$, $CHCl_2CCl_2CClF_2$, and $CHCl_2CClFCClF_2$. This is correct and has now been verified. The fourth derivative was given incorrectly as $CHCl_2CClFCF_3$; actually it is $CHClFCClFCClF_2$.

The formulas of the monofluoride, $CHCl_2CCl_2CCl_2F$, and that of the difluoride, $CHCl_2CCl_2CClF_2$, have been demonstrated before.[2] The formula $CHCl_2CClFCClF_2$ was adopted[1] as the most plausible one for the trifluoride. This is here shown to be correct. The trifluoride could only be represented by A, B or C, because it was obtained from the known difluoride, $CHCl_2CCl_2$-

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* Original manuscript received January 23, 1941.

[1] Henne and Renoll, THIS JOURNAL, **61**, 2489 (1939).

[2] Henne and Ladd, *ibid.*, **60**, 2491 (1938).