2586 © 1980 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **53**, 2586—2591 (1980) [Vol. 53, No. 9

The Dehydrochlorination of *gem*-Dichloroalkane and the Formation of Dienes from the Reactions of Butenes and Cyclohexene with Chlorine through Molten Salt

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(Received January 5, 1980)

The dehydrochlorination of 1,1-dichloropropane and 1,1-dichloro-3-methylbutane was carried out over molten salt catalysts (mainly $ZnCl_2$-containing melts) using a conventional flow system. The *cis*/*trans* ratio (1.8) of the resulting olefins from 1,1-dichlorobutane was found to stand between the ratio (1.4) with 1,1-dichloro-3-methylbutane and the ratio (2.2) with 1,1-dichloropropane; this can be explained by considering the stereochemistry of the adsorbed carbonium ions. The detailed results of the reactions of three butene isomers with chlorine through molten salts were presented. The selective formation of butadiene was explained in terms of the thermally assisted attack of chlorine in the allylic positions of butene, followed by the 1,2- or 1,4-elimination of HCl from chlorobutenes, a process which is strongly assisted by the $ZnCl_2$-containing melts. The reaction of 2-methyl-2-butene and cyclohexene with chlorine through molten salts was also undertaken. The addition of Zn powder to $ZnCl_2$ melts in advance was found to improve the selectivity for the formation of isoprene and cyclohexadiene. Because the HCl evolved reacts instantly with Zn powder to afford $ZnCl_2$ and hydrogen, Zn powder substantially prohibits the addition of HCl to dienes yielding chlorobutenes and chlorocyclohexenes.

In a previous paper,[1] we explained the *cis*/*trans* ratio of the 1-chloro-1-butene produced in the dehydrochlorination of 1,1-dichlorobutane in contact with zinc chloride melts by considering the surface-adsorbed carbonium ion. The former part of this paper will present additional information to support this explanation, using 1,1-dichloropropane and 1,1-dichloro-3-methylbutane as reactants.

The reaction of butenes with chlorine through zinc chloride melts containing alkali chloride has been found to yield butadiene predominantly.[2] The dependence of this reaction on the reaction conditions has been discussed. The selective formation of isoprene and cyclohexadiene from the reaction of 2-methyl-2-butene and cyclohexene with chlorine was also examined. In these cases, the addition of zinc powder to zinc chloride melts improved the yield of these dienes.

Experimental

Catalysts and Reagents. The $ZnCl_2$, $SnCl_2$, CuCl, LiCl, NaCl, KCl, $NaNO_3$, and KNO_3 were all commercially available guaranteed reagents. The nitrogen, argon, chlorine, and hydrogen chloride were dried by passing each gas from commercial cylinders through concd H_2SO_4 and anhydrous calcium chloride. The 1,1-dichloropropane was prepared by the reaction of propionaldehyde with PCl_5 (bp 83—85 °C; 98% pure).[3] The 1,1-dichloro-3-methylbutane was prepared by the reaction of isopropyl chloride and vinyl chloride in the presence of $AlCl_3$ (bp 57 °C/66 mmHg; 99% pure).[4] The addition of HCl to isoprene afforded 3-chloro-3-methyl-1-butene (bp 32 °C/40 mmHg).[5] The 1-chloro-3-methyl-2-butene was obtained by the isomerization[5] of 3-chloro-3-methyl-1-butene in the presence of HCl [bp 61—62 °C/120 mmHg; NMR ($CDCl_3$) 1.70 (6H, CH_3, m), 3.96 (2H, $ClCH_2$, d), 5.34 (H, CH=C, t)]. The 3-chloro-2-methyl-1-butene and 1-chloro-2-methyl-2-butene were separated from a mixture of them obtained by the chlorination[6] of 2-methyl-2-butene using preparative gas chromatography; they were confirmed on the basis of their respective NMR spectra [the former NMR (CCl_4): 1.60 (3H, $ClCHCH_3$, d), 1.84 (3H, $=CCH_3$, s), 4.46 (1H, CHCl, q), 4.74 (1H, HC=, s), 4.92 (1H, HC=, s); the latter NMR (CCl_4): 1.70 (6H, $=CHCH_3$, $=CCH_3$, mc), 3.96 (2H, CH_2Cl, s), 5.34 (1H, $CHCH_3$, q)]. The 3-chlorocyclohexene was prepared by the photoirradiation of a mixture of cyclohexene and *t*-butyl hypochlorite (bp 52—53 °C/25 mmHg; 95% pure).[7] The 4-chlorocyclohexene was obtained by the dehydration[8] of 4-chlorocyclohexanol, which had been synthesized according to the literature (bp 56—57 °C/39 mmHg; 97% pure).[9]

General Procedure. The reaction through molten salts was carried out using an apparatus similar to that described in the previous paper.[1] The salts tested were two ternary mixtures, 60 mol% $ZnCl_2$–20 mol% KCl–20 mol% NaCl ($ZnCl_2$ melts) and 60 mol% CuCl–20 mol% KCl–20 mol% NaCl (CuCl melts), and a binary mixture, 60 mol% $SnCl_2$–40 mol% KCl and 60 mol% CuCl–40 mol% LiCl. The melt of 50 mol% KNO_3–50 mol% $NaNO_3$ was used as a reaction medium, through which chlorination may be supposed to reflect a purely thermal reaction. For the preparation of the anhydrous $ZnCl_2$ melts,[10] a stream of HCl gas was introduced, along with a N_2 stream, at the desired temperature; then dry N_2 was bubbled in in order to eliminate the excess HCl gas. For the other salts, dry N_2 was allowed to flow through the melts until no more H_2O was seen at the exit. A total of 40—70 g of material was used, and the melt height was 8 cm from the tip of the nozzle to the melt surface.

The duration of the reaction was 30 min. After the end of the reactant-feeding, N_2-bubbling was continued for about 1 h in order to recover the reaction mixture remaining in the system. The reaction products were collected at the exit in an ice–water trap. Analysis of the gaseous products was carried out by removing aliquots from the gas stream with the aid of a syringe (every ten minutes after the start of feeding). Both the HCl evolved and the unreacted Cl_2 (in the case of chlorination) were removed prior to sampling by passing the gas stream through a $Na_2S_2O_3$ solution.

Analysis of Reaction Products. The GC column materials used for products analysis were as follows: 1. 10% Pluronic L 84 on Neopak 1 A (60/80 mesh), 2. 30% Propylene Carbonate/Uniport C (30/60 mesh), 3. 15% Silicone DC 550/Celite 545 (60/80 mesh), 4. 20% PEG 20 M/Celite 545 (30/60 mesh), 5. Silica gel (60/80 mesh).

The columns and the operating temperature used for the analysis of the liquid and gaseous products obtained from the respective reaction systems are described below for each reaction system. 1,1-Dichloropropane (liq: 1, 40 °C, Shimadzu GC-3BT; gas: 5, 145 °C, Shimadzu GC-3AH), 1,1-dichloro-3-methylbutane (liq: 1, 70 °C, Shimadzu GC-2C; gas; 5, 145 °C, Shimadzu GC-3AH), butene (liq: 1, 60 °C, Shimadzu GC-3BT; gas: 2, room temp, Shimadzu GC-2C), 2-methyl-2-butene (liq: 1, 50 °C, Shimadzu GC-3BT; gas: 3, 50 °C, Shimadzu GC-3BT), cyclohexene (liq: 4, 110 °C, Shimadzu GC-2C; gas: 5, 145 °C, Shimadzu GC-3AH).

Identification of Products. Both *cis*- and *trans*-1-chloro-1-propene and *cis*- and *trans*-1-chloro-3-methyl-1-butene were separated by preparative gas chromatography, and their structures were confirmed by a comparison of the chemical-shift difference[11] of the olefinic proton between CCl_4 and C_6H_6. Most of the products were confirmed by having the same retention time as that of the reference and by means of the mass spectra of each fraction, obtained using GC-MS (Hitachi-RMU-6 MG type). Table 1 shows the confirmed liquid products (arranged in the order of elution in a gas chromatography) for each reaction system.

Results and Discussion

Dehydrochlorination of 1,1-Dichloropropane and 1,1-Dichloro-3-methylbutane. The results of the dehydrochlorination of 1,1-dichloropropane and 1,1-dichloro-3-methylbutane through $ZnCl_2$–KCl–NaCl, $SnCl_2$–KCl, and CuCl–LiCl are shown in Table 2 and Table 3 respectively. At 450 °C, the 1,1-dichloropropane conversion was approximately double the conversion at 400 °C through $ZnCl_2$ melts and $SnCl_2$ melts. The finding that the gaseous-product yield at 450 °C was more than twice the value at 400 °C suggests an increasing contribution of the thermal reaction at the higher temperature. Such a tendency was also observed in the dehydrochlorination of 1,1-dichloro-3-methylbutane. The dehydrochlorination with the $ZnCl_2$ melts afforded a relatively high conversion in comparison with that of the $SnCl_2$ melts.

The dehydrochlorination of alkyl halides through molten salts containing Lewis acid, such as $ZnCl_2$, $SnCl_2$, and CuCl, has been studied by Kenney,[12] Bailey,[10] and the present authors.[13] An E_1-elimination mechanism has been postulated. Since the carbonium ion formed by chloride abstraction from *gem*-dichlorides is stabilized through the conjugation with another chlorine atom, *gem*-dichloroalkanes also could proceed *via* E_1 elimination. The higher conversion of 1,1-dichloropropane and 1,1-dichloro-3-methylbutane

Table 1. The different kinds of liquid products for different reaction systems

Reaction system	Products
1,1-Dichloropropane	*cis*-1-chloro-1-propene, *trans*-1-chloro-1-propene, 3-chloro-1-propene, [1,1-dichloropropane], 1,2-dichloropropane
1,1-Dichloro-3-methylbutane	isoprene, *cis*-1-chloro-3-methyl-1-butene, *trans*-1-chloro-3-methyl-1-butene, monochloromethylbutenes (4 peaks), [1,1-dichloro-3-methylbutane]
Butene	2-chloro-1-butene, *trans*-2-chloro-2-butene, (*cis*-1-chloro-1-butene),[a] 3-chloro-1-butene, *cis*-2-chloro-2-butene(*trans*-1-chloro-1-butene),[a] 4-chloro-1-butene, 1-chloro-2-butene, *meso*-2,3-dichlorobutane, *dl*-2,3-dichlorobutane, 1,2-dichlorobutane, 3,4-dichloro-1-butene, polychloro compounds
2-Methyl-2-butene	2-methyl-1-butene, [2-methyl-2-butene], isoprene, 2-chloro-2-methylbutane and 3-chloro-3-methyl-1-butene, 3-chloro-2-methyl-1-butene, monochlorobutenes (3 peaks), 1-chloro-2-methyl-2-butene and/or 1-chloro-3-methyl-2-butene, polychloro compounds
Cyclohexene	[cyclohexene], 1,3-cyclohexadiene, 1,4-cyclohexadiene, benzene, monochloromethylcyclopentanes, chlorocyclohexane, 1-chlorocyclohexane, monochlorocyclohexadienes, 4-chlorocyclohexenene, 3-chlorocyclohexene, 1,2-dichlorocyclohexane

a) In the case of 1-butene as the starting material.

Table 2. Dehydrochlorination[a] of 1,1-dichloropropane through molten salts

Molten salts	$ZnCl_2$-KCl-NaCl		$SnCl_2$-KCl		CuCl-LiCl
Reaction temp (°C)	400	450	400	450	450
Recovery (%)	90	84	93	86	91
Conversion (%)	45.7	85.5	28.2	67.2	65.3
Distribution of products (%)					
cis-1-Chloro-1-propene	19.4	42.0	13.6	38.2	37.3
trans-1-Chloro-1-propene	8.8	20.2	5.7	17.6	15.9
3-Chloro-1-propene	3.0	6.9	1.3	2.8	3.6
1,2-Dichloropropane	12.8	11.8	6.2	5.4	6.3
Gaseous products	1.7	4.6	1.3	3.2	1.4
cis/*trans*	2.2	2.1	2.4	2.2	2.3

a) Reactant : Ar = 0.036 : 0.094 mol/h, Duration of reaction: 30 min, Conv % = 100 − reactant in recovered liquid (%), Recovery (%) = (total C number of liquid products/total C number of reactant) × 100.

over the melts containing $ZnCl_2$ can easily be understood, because $ZnCl_2$ may be supposed to abstract chloride from the substrate forming the carbonium ion due to its relatively strong Lewis acidity.

In the case of 1,1-dichloropropane, the *cis/trans* ratio of the resultant 1-chloro-1-propene was observed in the region from 2.1 to 2.4 through three kinds of melts. On the other hand, the *cis/trans* ratio of 1-chloro-3-methyl-1-butene was between 0.9 and 1.4. We have reported on the dehydrochlorination1) of 1,1-dichlorobutane through molten salts, where the quite large ratio of *cis/trans* of 1-chloro-1-butene (1.4—1.8 with $ZnCl_2$ melts) may be explained in terms of the resultant carbonium ion adsorbed on the surface of the melts [illustrated in Fig. 1 (R representing the methyl, ethyl, and isopropyl groups)].

The release of H_b from the carbonium ion (in Fig. 1) as a proton leads to the effective sharing of the free-electron pair at C_2 with the vacant p orbital at C_1. This process affords *cis*-olefin predominantly. If the alkyl group goes on from methyl to isopropyl, the location of the carbonium ion as in Fig. 1, becomes, however, somewhat unfavored because of the increasing steric repulsion between chlorine and isopropyl groups. This leads to the desorption of the carbonium ion from the melts surface, the *cis/trans* ratio of the resulting olefin nearing unity. The finding that *cis/trans* ratio with alkyl group=C_2H_5 (1.8) stands between the ratio with alkyl=CH_3 (2.2) and the ratio with alkyl=$(CH_3)_2CH$(1.4) under the same conditions is in good agreement with the explanation presented above.[14,15] The formation of isoprene from the reaction of 1,1-dichloro-3-methylbutane through $ZnCl_2$ can be explained by considering the rearrangement of the primary monochloro carbonium ion (in Fig. 1) to the more stable secondary and/or tertiary carbonium ion and the subsequent 1,4-dehydrochlorination of the 1-chloro-3-methyl-2-butene produced from the above rearranged carbonium ion.

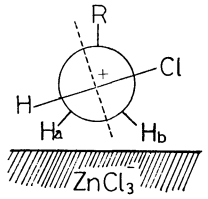


Fig. 1. Molten salts surface-adsorbed carbonium ion. Dotted line shows the vacant p orbital; R=CH_3, C_2H_5 and $(CH_3)_2CH$; Cl atom is linked to C_1, Both H_a and H_b are on C_2.

Reaction of Butene with Chlorine. The reaction of butene with chlorine through the $ZnCl_2$ melts and the CuCl melts is shown in Tables, 4, 5, and 6. The substitution reaction by chlorine probably takes place at the allylic position of butenes (1-butene, *cis*-2-butene, *trans*-2-butene) *via* a radical mechanism whose operation was confirmed in the chlorination of cyclohexane[13]

TABLE 3. DEHYDROCHLORINATION OF 1,1-DICHLORO-3-METHYLBUTANE

Molten salts	$ZnCl_2$-KCl-NaCl[a)]		$SnCl_2$-KCl[b)]		CuCl-LiCl[b)]
Reaction temp (°C)	400	450	400	450	450
Recovery (%)	97	97	71	70	84
Conversion (%)	44.1	80.2	21.5	64.0	75.2
Distribution of products (%)					
Isoprene	4.3	5.8	1.0	1.1	2.3
cis-1-Chloro-3-methyl-1-butene	18.0	31.6	9.3	29.2	27.6
trans-1-Chloro-3-methyl-1-butene	12.9	26.8	7.9	26.7	29.8
Monochlorobutenes	6.3	8.8	1.5	2.6	9.3
Gaseous products[c)]	2.3	5.5	1.1	4.3	4.2
Others	0.3	1.7	0.7	0.1	2.0
cis/trans	1.4	1.2	1.2	1.1	0.9

a) Reactant : Ar=0.11 : 0.056 mol/h, b) Reactant : Ar=0.027 : 0.080 mol/h. c) Mainly propane, propylene.

TABLE 4. REACTION[a)] OF *trans*-2-BUTENE WITH CHLORINE (450 °C)

Molten salts	$ZnCl_2$-KCl-NaCl	CuCl-KCl-NaCl	Gas-phase reaction
Recovery (%)	68	80	68
Conversion (%)	70.1	69.7	60.0
Distribution of products (%)			
1-Butene	0.8	tr	tr
cis-2-Butene	10.4	8.8	11.1
Butadiene	58.9	46.2	14.8
Monochlorobutenes	tr	2.2	27.6
meso-2,3-Dichlorobutane	tr	5.4	5.8
dl-2,3-Dichlorobutane	tr	1.0	2.0
Others	tr	0.9	tr

a) Cl_2/Reactant=0.9, Reactant : Ar=0.10 : 0.15 mol/h.

through the $ZnCl_2$ melts and the CuCl melts. The subsequent dehydrochlorination of the resulting chlorobutenes could be assisted by the melts, yielding butadiene in a high selectivity. Using the $ZnCl_2$ melts, a butadiene selectivity of more than 93% is attained if one does not take account of the degree of isomerization among butenes. With the CuCl melts, considerable amounts of unreacted chlorobutene and dichlorobutane were observed. The effects of the reaction temperature and the Cl_2/butene ratio on the extent of reaction and the degree of selectivity to butadiene were examined with the $ZnCl_2$ melts (Tables 7 and 8). The reactions at 400 °C and 450 °C gave almost the same yields of butadiene in a good material balance. With a Cl_2/feed equal to 1.15, appreciable amounts of carbonaceous material were produced; this led to a poor material balance at a high concentration of chlorine. An inspection of Table 8 reveals that the Cl_2/butene ratio between 0.59 and 0.85 is desirable in view of the material balance and butadiene yield.

There have been reported several dehydrogenation processes of butene for butadiene production. One of them is to use metal oxide catalysts[16] in the presence of oxygen and chlorine-releasing compounds (yield 27%, selectivity, 43% at 700 °C). Another procedure[17] gives a 68.0% yield of butadiene with a 89.3% selectivity (temp 638 °C, HI/butene=0.2, over 5% CeO_2/Al_2O_3). The yield and selectivity of the process presented here compares fairly well with those of the latter process under less severe conditions.

Reaction of 2-Methyl-2-butene with Chlorine. The results of experiments using both the $ZnCl_2$ melts

TABLE 5. REACTION[a] OF *cis*-2-BUTENE WITH CHLORINE (450 °C)

Molten salts	$ZnCl_2$-KCl-NaCl	CuCl-KCl-NaCl	Gas-phase reaction
Recovery (%)	89	79	67
Conversion (%)	73.9	74.9	70.2
Distribution of products (%)			
1-Butene	0.8	tr	tr
trans-2-Butene	14.1	12.5	15.1
Butadiene	59.0	51.2	17.2
Monochlorobutenes	tr	3.4	28.6
meso-2,3-Dichlorobutane	tr	1.4	3.5
dl-2,3-Dichlorobutane	tr	5.4	5.8
Others	tr	1.0	tr

a) Cl_2/Reactant=0.9, Reactant : Ar=0.10 : 0.15 mol/h.

TABLE 6. REACTION[a] OF 1-BUTENE WITH CHLORINE (450 °C)

Molten salts	$ZnCl_2$-KCl-NaCl	CuCl-KCl-NaCl	Gas-phase reaction
Recovery (%)	99	96	95
Conversion (%)	50.4	48.5	36.6
Distribution of products (%)			
trans-2-Butene	2.2	0.6	—
cis-2-Butene	1.8	0.4	—
Butadiene	46.4	38.1	16.0
Monochlorobutenes	tr	7.4	16.5
1,2-Dichlorobutane	tr	1.6	1.7
Others	tr	0.4	2.4

a) Cl_2/Reactant=0.9, Reactant : Ar=0.10 : 0.15 mol/h.

TABLE 7. EFFECTS OF TEMPERATURES[a] ON THE REACTIONS OF BUTENES WITH CHLORINE

Butene	1-Butene			*trans*-2-Butene		
Cl_2/C_4H_8	0.99	0.98	1.0	1.0	1.0	0.95
Temp (°C)	350	400	450	350	400	450
Recovery (%)	97	97	95	85	95	96
Conversion (%)	61.4	65.2	67.2	77.9	81.8	80.4
Distribution of products (%)						
trans-2-Butene	1.1	1.0	1.3	0.6	0.5	0.7
cis-2-Butene	0.8	0.9	1.0	9.4	8.0	8.3
Butadiene	45.2	55.3	60.7	57.8	69.3	71.4
Monochlorobutenes	11.0	6.2	3.6	5.5	2.0	tr
1,2-Dichlorobutane	1.3	0.7	0.2	3.3[a]	1.3[a]	tr[a]
Others	2.0	1.1	0.4	1.3	0.7	tr

a) Reactant : Ar=0.10 : 0.15 mol/h. $ZnCl_2$ melts. b) 2,3-Dichlorobutane

Table 8. Effect of the Cl_2/C_4H_8 ratio on the reactions[a] of *trans*-2-butene with chlorine (450 °C)

Cl_2/C_4H_8	0.30	0.59	0.95	1.15
Recovery (%)	108	112	96	81
Conversion (%)	27.0	57.8	80.4	90.5
Distribution of products (%)				
1-Butene	0.1	1.5	0.7	0.4
cis-2-Butene	8.1	9.5	8.3	4.9
Butadiene	18.8	46.8	71.4	85.2

a) Reactant : Ar = 0.10 : 0.15 mol/h.

Table 9. Reaction[a] of 2-methyl-2-butene with chlorine

Molten salts	$ZnCl_2$	$ZnCl_2$-Zn[b]		
Cl_2/C_5H_{10}	0.58	0.27	0.61	1.1
Recovery (%)	81	88	89	81
Conversion (%)	98.4	32.3	56.9	81.5
Selectivity to diene	11.4	86.7	82.1	64.0
Product distribution (%)				
2-Methyl-1-butene	tr	1.4	2.9	2.2
Isoprene	11.2	28.0	46.7	52.2
2-Chloro-2-methylbutane	66.7	0.2	1.4	4.9
3-Chloro-3-methyl-1-butene	1.1	0.1	0.2	1.1
3-Chloro-2-methyl-1-butene	3.5	1.5	2.9	4.0
Other chloromethylbutenes	12.3	0.1	0.1	1.7

a) Reactant : Ar = 0.091 : 0.10 mol/h. b) $ZnCl_2$-KCl-NaCl-Zn = 46 : 15 : 15 : 24 mol %.

Table 10. Reaction of cyclohexene with chlorine[a]

Molten salts	$ZnCl_2$[b]	$ZnCl_2$-Zn[c]		
Cl_2/C_6H_{10}	0.55	0.26	0.55	1.0
Recovery (%)	90	94	90	81
Conversion(%)	39.3	21.4	46.4	67.5
Selectivity to diene	39.7	78.5	73.9	59.7
Product distribution (%)				
1,3-Cyclohexadiene	15.6	16.8	34.3	40.3
1,4-Cyclohexadiene	3.6	1.8	3.6	5.5
Benzene	5.8	1.4	5.1	14.8
1-Chlorocyclohexene	1.4	0.9	1.5	2.5
3-Chlorocyclohexene	5.5	—	0.1	1.0
4-Chlorocyclohexene	0.5	0.2	0.6	1.8
Chloromethylcyclopentanes	2.3	—	—	0.4
Chlorocyclohexane	1.5	—	—	—
1,2-Dichlorocyclohexane	tr	—	—	—
Others	3.1	0.3	1.2	1.2

a) Cyclohexene : Ar = 0.095 : 0.10 mol/h. b) $ZnCl_2$-KCl-NaCl = 60 : 20 : 20 mol %. c) $ZnCl_2$-KCl-NaCl-Zn = 46 : 15 : 15 : 24 mol %.

and the $ZnCl_2$ melts containing a suspension of Zn powder in the reaction of 2-methyl-2-butene with chlorine are shown in Table 9.

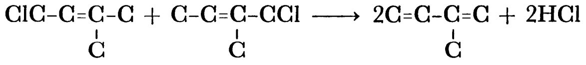
Using the $ZnCl_2$ melts as catalysts, the reaction of 2-methyl-2-butene with chlorine gave small amounts of expected isoprene, along with great quatities of 2-chloro-2-methylbutane. The primary formation of the latter compound was supposed to be due to the addition of the HCl produced to an intermediate product, 2-methyl-2-butene, through the $ZnCl_2$ melts (at 400 °C, 76.9% yield of 2-chloro-2-methylbutane). In order to eliminate the HCl evolved during this reaction and to improve the yield of isoprene, we used $ZnCl_2$ melts containing a suspension of Zn powder instead of $ZnCl_2$ melts. As Table 9 shows, the use of those melts brough about a high yield of isoprene, as expected, and at the same time we found the formation of H_2 in an amount about the same as the quantities calculated on the basis of the following equation: $[H_2 = (\text{isoprene}) + (C_5H_9Cl)/2 - (C_5H_{11}Cl)/2]$.

Based on these findings, this reaction may be outlined as follows:

$$2\,C\text{-}\underset{\displaystyle C}{\underset{|}{C}}\text{=}C\text{-}C + Cl_2 \longrightarrow$$

$$C\text{-}\underset{\displaystyle C}{\underset{|}{C}}\text{=}C\text{-}CCl + C\text{-}C\text{=}\underset{\displaystyle C}{\underset{|}{C}}\text{-}CCl + 2HCl \qquad (1)$$

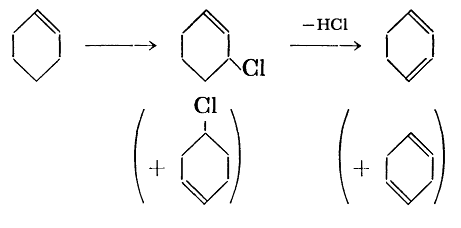
$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2 \qquad (2)$$



$$ClC\text{-}\underset{\displaystyle C}{\underset{|}{C}}\text{=}C\text{-}C + C\text{-}C\text{=}\underset{\displaystyle C}{\underset{|}{C}}\text{-}CCl \longrightarrow 2C\text{=}C\text{-}\underset{\displaystyle C}{\underset{|}{C}}\text{=}C + 2HCl \qquad (3)$$

Appreciable amounts of 1-chloro-2-methyl-2-butene and/or 3-chloro-2-methyl-2-butene were produced with $ZnCl_2$ melts; this was confirmed by means of GC-MS analysis.

Reaction of Cyclohexene with Chlorine. The results of the reaction through the $ZnCl_2$ melts and the Zn-powder-suspended $ZnCl_2$ melts are presented in Table 10. The presence of Zn powder increases the selectivity to cyclohexadiene in the chlorination of cyclohexene. Therefore, in a way similar to the reaction of 2-methyl-2-butene, Zn powder can react with evolved HCl, which otherwise will add to cyclohexene or/and cyclohexadiene, yielding H_2 and $ZnCl_2$. The good agreement of the hydrogen amounts with the calculated value confirms this process to be correct. Under the same conditions, the dehydrochlorination of 3-chlorocyclohexene and 4-chlorocyclohexene (at 400 °C) proceeded with an 85 and 49% selectivity to cyclohexene respectively. Therefore, it may be suggested that the chlorination of cyclohexene proceeds as in the following reaction scheme:



(4)

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