

## FRIEDEL-CRAFTS CHLOROETHYLATION OF HEXAMETHYLBENZENE

Jaromír MINDL<sup>a</sup> and Giovanni Vittorio SEBASTIANI<sup>b</sup>

<sup>a</sup> Department of Organic Chemistry,

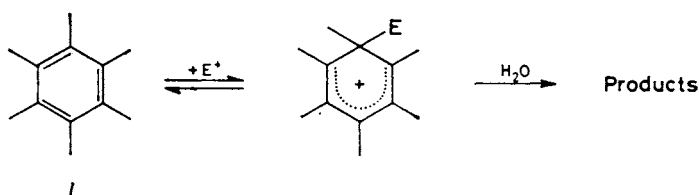
Institute of Chemical Technology, 53210 Pardubice, Czechoslovakia and

<sup>b</sup> Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

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The reaction of hexamethylbenzene (*I*) with 1,2-dichloroethane in the presence of aluminium chloride gives 1-(2-chloroethyl)-1,2,3,4,5,6-hexamethylbenzenium salt (*II*) which is decomposed with water. The decomposition products include hexamethylbenzene (*I*), 3-(2-chloroethyl)-1,2,3,4,5-pentamethyl-6-methylene-1,4-cyclohexadiene (*IIIa*), 5-(2-chloroethyl)-1,2,3,4,5-pentamethyl-6-methylene-1,3-cyclohexadiene (*IIIb*), and 1-(2-chloroethyl)-2,3,4,5,6-pentamethylbenzene (*IV*). The compounds *IIIa* and *IIIb* are rearranged into 1-(3-chloropropyl)-2,3,4,5,6-pentamethylbenzene (*V*).

Electrophilic alkylation reactions in aromatic rings usually proceed as a catalyzed two-step process. The existence of the intermediate  $\sigma$  complex is always proved only indirectly due to the short life time of this complex. On the other hand, the electrophilic reactions of aromatic substrates with bad leaving groups (*e.g.* hexamethylbenzene (*I*)) usually stop at the point of the  $\sigma$  complex which is decomposed with water (Scheme 1)<sup>1</sup>.



SCHEME 1

The aim of the present work is a study of the reaction of hexamethylbenzene with 1,2-dichloroethane in the presence of aluminium chloride, analysis of the reaction products and of the products formed by subsequent hydrolysis. In the context of the problem of "non-conventional" Friedel-Crafts reactions<sup>2</sup>, the second aim was a comparison of the reactivities of hexamethylbenzene with 1,2-dichloroethane and acetanhydride.

## EXPERIMENTAL

*Analytical methods.* The  $^1\text{H}$  NMR spectra were measured with a JEOL JNM-060 HL Spectrometer in  $\text{CCl}_4$  (if not otherwise stated) using tetramethylsilane as the internal standard. The mass spectra were measured with a JEOL JMS-01 SG-2 Spectrometer at the ionization energy of 70 eV (if not otherwise stated). The UV spectra were measured with a Unicam spectrophotometer model SP 800 B, the values of molar absorption coefficients,  $\epsilon$ , are given in  $\text{dm}^{-2} \text{mol}^{-1}$ . The gas chromatographic analyses and isolation of the components from reaction mixtures were carried out with a Fractovap GV apparatus (Carlo Erba). The analytical separations were performed on columns of 2 m length and 3 mm diameter packed with 10% SE-30 or 10% LAC-728 on Chromosorb A 0.20–0.25 mm. The preparative-scale chromatographic separations were performed on columns of 1 m length and 8 mm diameter packed with 10% SE-30 or 10% LAC-728 on Chromosorb A 0.25–0.40 mm. Helium was used as the carrier gas. The liquid chromatography was accomplished on a liquid chromatograph model 900 (Laboratorní přístroje, Prague) with Separon SIX and Separon SIX C18 columns and with the use of 96% aqueous methanol or 0.1% solution of 2-propanol in heptane. The corrected melting points were determined with the use of a Boetius PHMK apparatus (Jena).

*Reagents.* Hexamethylbenzene (*I*) (Fluka), m.p. 162–164°C. 1,2-Dichloroethane (Xenon, Lodž) was dried with calcium chloride and distilled as a fraction boiling from 81.5 to 83.0°C,  $n_{\text{D}}^{20}$  1.4456. 1-Chloromethyl-2,3,4,5,6-pentamethylbenzene, m.p. 80–81°C, was prepared by action of sulphuryl chloride on hexamethylbenzene<sup>3</sup>. Aluminium chloride (Merck) was sublimed before use.

Pentamethylphenylacetic Acid (*IVb*)

A solution of 1.0 g (15 mmol) KCN in 5 ml water was added to a solution of 2.1 g (10.7 mmol) 1-chloromethyl-2,3,4,5,6-pentamethylbenzene in 10 ml dimethyl sulphoxide. The reaction mixture was heated at 130°C in a sealed ampoule and stirred with a magnetic stirrer 5 h. After cooling, the content of the ampoule was mixed with 100 ml water and the separated solid was collected by filtration, washed with water, and submitted to hydrolysis by heating at 130°C with 30 ml conc.  $\text{H}_2\text{SO}_4$  and 50 ml water 10 h. After cooling the solid was collected by filtration and washed with water. The raw product was stirred with 50 ml 5% NaOH at 40°C. The undissolved portion was removed by filtration. The filtrate was acidified with 5% HCl and the separated acid was recrystallized from 50% aqueous ethanol. Yield 1.3 g (59%), m.p. 199–200°C.  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ): 2.2 s, 15 H (3× H-2', 3× H-3', 3× H-4', 3× H-5', 3× H-6'); 3.75 s, 2 H (2× H-1); 10.41 s, 1 H (COOH). The mass spectrum ( $m/z$ ): 206 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 3 400–2 800 (OH); 1 710 (C=O).

2-Pentamethylphenylethanol (*IVa*) and 3-(Pentamethylphenyl)-1-propanol (*Va*)

A solution of 0.2 g acid *IVb* or *Vb* in 5 ml tetrahydrofuran was added drop by drop to a stirred suspension of 0.5 g lithium aluminium hydride in 20 ml tetrahydrofuran within 5 min. The mixture was refluxed 2 h, cooled, diluted with 30 ml diethyl ether, and poured onto a mixture of 10 ml conc. HCl, 100 ml water, and 50 g ice. The organic phase was washed with water, with 5% solution of sodium hydrogen carbonate, again with water, and dried with sodium sulphate. After evaporation of diethyl ether, the product was recrystallized from heptane. Yield 0.13 g *IVa* (69%), m.p. 104.5–106.0°C.  $^1\text{H}$  NMR: 2.15 s, 9 H (3× H-3', 3× H-4', 3× H-5'); 2.20 s, 6 H (3× H-2', 3× H-6'); 2.90 t, 2 H (2× H-2,  $J(1, 2) = 7$ ); 3.60 t, 2 H (2× H-1,  $J(1, 2) = 7$ ). Mass spectrum ( $m/z$ ): 192 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 3 620 (OH). Yield 0.15 g *Va* (80%), m.p.

114–115°C.  $^1\text{H NMR}$ : 1.62–1.68 m, 2 H (2 $\times$  H-2); 2.15 s, 15 H (3 $\times$  H-2', 3 $\times$  H-3', 3 $\times$  H-4' 3 $\times$  H-5', 3 $\times$  H-6'); 2.60–2.72 m, 2 H (2 $\times$  H-3); 3.60 t, 2 H (2 $\times$  H-1,  $J(1, 2) = 7$ ). Mass spectrum ( $m/z$ ): 206 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 3 630 (OH, free).

1-(2-Chloroethyl)-2,3,4,5,6-pentamethylbenzene (*IV*) and 1-(3-Chloropropyl)-2,3,4,5,6-pentamethylbenzene (*V*)

A mixture of 0.1 g alcohol *IVa* or *Va*, 0.5 g  $\text{ZnCl}_2$ , and 10 ml conc. HCl was heated at 130°C in a sealed ampoule 14 h. The mixture was cooled and diluted with 20 ml ether, the organic phase was washed with water, aqueous solution of  $\text{NaHCO}_3$ , and water, and dried with sodium sulphate. Ether was removed by evaporation and the residue was purified by sublimation at 55°C at 133 Pa.  $^1\text{H NMR}$  ( $\text{C}^2\text{HCl}_3$ ): 2.34 s, 9 H (3 $\times$  H-2, 3 $\times$  H-4, 3 $\times$  H-6); 2.39 s, 6 H (3 $\times$  H-3, 3 $\times$  H-5); 3.33 s, 2 H (2 $\times$  H-1'); 3.60 m, 2 H (2 $\times$  H-2'). Mass spectrum ( $m/z$ ): 210 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 714 vs, 623 m (C—Cl); 757 vs ( $\text{CH}_2$ ). Compound *V* was purified by TLC (silica, hexane). Yield 0.05 g (47%), m.p. 47–48°C.  $^1\text{H NMR}$  spectrum: 1.80–1.91 m, 2 H (2 $\times$  H-2'); 2.13 s, 9 H (3 $\times$ , H-3, 3 $\times$  H-4, 3 $\times$  H-5); 2.17 s, 6 H (3 $\times$  H-2, 3 $\times$  H-6); 2.72–2.82 m, 2 H (2 $\times$  H-1'); 3.53 t, 2 H (2 $\times$  H-3',  $J(2', 3') = 7$ ). Mass spectrum ( $m/z$ ): 224 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 660 vs, 735 m (C—Cl); 765 vs ( $\text{CH}_2$ ).

3-(Pentamethylphenyl)propanenitrile (*Vc*)

A solution of 0.9 g (4.3 mmol) 1-(2-chloroethyl)-2,3,4,5,6-pentamethylbenzene (*IV*) in 8 ml dimethyl sulphoxide was mixed with a solution of 0.5 g (10.2 mmol) NaCN in 3 ml water, and the mixture was heated at 130°C in a sealed ampoule with stirring 4 h. After cooling, the mixture was diluted with 100 ml water, and the separated solid was collected by filtration and recrystallized from ethanol. Yield 0.75 (87%), m.p. 109.5–110.5°C.  $^1\text{H NMR}$  spectrum: 2.16 s, 9 H (3 $\times$  H-3', 3 $\times$  H-4', 3 $\times$  H-5'); 2.21 s, 6 H (3 $\times$  H-2', 3 $\times$  H-6'); 2.26 t, 2 H (2 $\times$  H-2,  $J(2, 3) = 6$ ); 3.02 t, 2 H (2 $\times$  H-3,  $J(2, 3) = 7$ ). Mass spectrum ( $m/z$ ): 201 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 2 250 (C $\equiv$ N).

3-(Pentamethylphenyl)propanoic Acid (*Vb*)

A mixture of 0.8 g (4 mmol) 3-(pentamethylphenyl)propanenitrile (*Vc*) and 10 ml 45%  $\text{H}_2\text{SO}_4$  was heated at 130°C in a sealed ampoule 14 h. The product was isolated in a similar way as the acid *IVb* and recrystallized from aqueous ethanol. Yield 0.7 g (80%), m.p. 172–173°C.  $^1\text{H NMR}$  spectrum: 2.20 s, 9 H (3 $\times$  H-3', 3 $\times$  H-4', 3 $\times$  H-5'); 2.25 s, 2 H (3 $\times$  H-2', 3 $\times$  H-6'); 10.6 s, 1 H (COOH). Mass spectrum ( $m/z$ ): 220 ( $\text{M}^+$ ). IR spectrum ( $\text{cm}^{-1}$ ): 3 520 (OH, free), 3 400–2 800 (OH, assoc.); 1 710 (C=O).

Pentamethylisobutyrophenone (*VI*)

A solution of 0.5 ml isobutyryl chloride in 1 ml  $\text{CS}_2$  was mixed with a solution of 0.81 g hexamethylbenzene (*I*) in 5 ml  $\text{CS}_2$  and 0.67 g  $\text{AlCl}_3$ . The mixture was refluxed 10 h. After cooling it was diluted with 10 ml ether and, with stirring, poured into 50 ml water and 10 g ice. The organic phase was washed with water, with 5%  $\text{NaHCO}_3$  solution, and again with water, and dried with sodium sulphate. Ether was evaporated and the residue was dissolved in 2 ml dichloromethane. The solution was purified by column chromatography (silica 0.02–0.04 mm; heptane–ether 20 : 1). Yield 0.22 g (20%), m.p. 38.5–40.0°C.  $^1\text{H NMR}$  spectrum: 1.10 d, 6 H (3 $\times$  H-2', 3 $\times$  H-3,  $J(1, 2') = 7$ ); 2.00 s, 6 H (3 $\times$  H-3', 3 $\times$  H-5'); 2.16 s, 9 H (3 $\times$  H-2', 3 $\times$  H-4', 3 $\times$

H-6'); 2.92 m, 1 H (H-2,  $J(2, 3) = 7$ ). IR spectrum (film,  $\text{cm}^{-1}$ ): 1 690 (C=O). Mass spectrum ( $m/z$ ): 218 ( $\text{M}^+$ ).

#### Preparation and Isolation of Chloromethylation Products from Hexamethylbenzene

A solution of 1.6 g (10 mmol) hexamethylbenzene in 10 ml 1,2-dichloroethane was added to a suspension of 2.6 g (20 mmol)  $\text{AlCl}_3$  in 10 ml 1,2-dichloroethane with stirring, and the mixture was heated to boiling 6 min. A 5 ml sample was taken from the homogeneous reaction mixture (for analysis of the intermediates) and the rest was decomposed by addition of an icy cold solution of 6 ml acetic acid and 4 g sodium acetate in 100 ml water. The organic layer was separated, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated to the volume of 3 ml. This solution was purified by column chromatography (silica, heptane). The eluate was concentrated to 3 ml and injected (by 0.1 ml portions) into the SE-20 column of preparative gas chromatograph. The four fractions isolated were denoted as *I*, *III*, *IV*, and *V*, and the fraction *III* was further separated on a LAC 728 column in a similar way. Yields: 563 mg compound *I*, m.p. 82–83°C, 95 mg liquid compound *IIa*, 29 mg liquid compound *IIIb*, 80 mg compound *IV*, m.p. 57–58°C, and 35 mg compound *V*, m.p. 47–48°C.

**Product analysis.** Purity of the products obtained was verified by gas chromatography on analytical columns SE-30 and LAC-728. Chromatographical and spectral comparison was carried out of the isolated compounds *I*, *IV*, and *V* with the synthesized models (of the same denotation), with 2-chloroethanol, and with methanol. The spectral assignment of compound *IIIa*:  $^1\text{H}$  NMR spectrum ( $\text{C}_6^2\text{H}_6$ ): 0.96 s, 3 H ( $3 \times \text{H-3}$ ); 1.5 s, 6 H ( $3 \times \text{H-1}$ ,  $3 \times \text{H-5}$ ); 1.70 s, 6 H ( $3 \times \text{H-2}$ ,  $3 \times \text{H-4}$ ); 1.87–1.97 m, 2 H ( $2 \times \text{H-1}'$ ); 2.80–2.92 m, 2 H ( $2 \times \text{H-2}'$ ); 4.84 s, 2 H ( $2 \times \text{H-6}$ ). IR spectrum (film,  $\text{cm}^{-1}$ ): 1 660 (C=C); 855 (C=CH<sub>2</sub>); 705 (C–Cl). Mass spectrum ( $m/z$ ): 224 ( $\text{M}^+$ ). UV spectrum (heptane),  $\lambda_{\text{max}}$  (nm): 256,  $\log \epsilon$  5.39. The assignment of *IIIb*:  $^1\text{H}$  NMR spectrum ( $\text{C}_6^2\text{H}_6$ ): 0.98 s, 3 H ( $3 \times \text{H-5}$ ); 1.60 s, 6 H ( $3 \times \text{H-1}$ ,  $3 \times \text{H-3}$ ); 1.70 s, 6 H ( $3 \times \text{H-2}$ ,  $3 \times \text{H-4}$ ); 2.75–2.86 m, 2 H ( $2 \times \text{H-1}'$ ); 3.35–3.45 m, 2 H ( $2 \times \text{H-2}'$ ); 4.78 s, 2 H ( $2 \times \text{H-6}$ ). IR spectrum (film,  $\text{cm}^{-1}$ ): 1 660 (C=C); 855 (C=CH<sub>2</sub>); 700 (C–Cl). Mass spectrum ( $m/z$ ): 224 ( $\text{M}^+$ ). UV spectrum (heptane),  $\lambda_{\text{max}}$  (nm): 308,  $\log \epsilon$  3.69.

The analysis of the intermediates was carried out after extraction of the sample of the reaction mixture with  $2 \times 10$  ml heptane. The heptane layers were combined and concentrated under reduced pressure to a volume of 3 ml. The heptane solution was submitted to GC and HPLC analysis and compared with the model compounds *I*, *IV*, and *V*. A part of the 1,2-dichloroethane phase (containing the intermediate *II*) was used for the  $^1\text{H}$  NMR analysis. Another part of the 1,2-dichloroethane phase was extracted with 37% HCl, and the aqueous extract was used for the measurement of UV spectrum. For the intermediate *II*:  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{H}_3\text{COC}^2\text{H}_3$ ): 1.60 s, 3 H ( $3 \times \text{H-1}$ ); 2.38 s, 6 H ( $3 \times \text{H-3}$ ,  $3 \times \text{H-5}$ ); 2.72 s, 6 H ( $3 \times \text{H-2}$ ,  $3 \times \text{H-6}$ ); 2.80 s, 3 H ( $3 \times \text{H-4}$ ); 3.01 s, 4 H ( $2 \times \text{H-1}'$ ,  $2 \times \text{H-2}'$ ). UV spectrum (HCl, H<sub>2</sub>O)  $\lambda_{\text{max}}$  (nm): 402, 292;  $\log \epsilon$  4.83, 4.93.

The other reactions of hexamethylbenzene with 1,2-dichloroethane or with a solution of acetaldehyde in 1,2-dichloroethane in the presence of aluminium chloride are given in Table I. This table also presents all important variations of the above-described general procedure of treatment of the reaction mixture along with the product analyses carried out by GC after the respective variation.

TABLE I

Effects of the way of treatment of the reaction mixture on proportions of the products *I*, *III*–*V* of the Friedel–Crafts chloroethylation of hexamethylbenzene

Experiment No.	Concentrations mol l <sup>-1</sup>		Relative product ratios, %					<i>IIIa/IIIb</i>	<i>I/IV</i>
	<i>I</i>	AlCl <sub>3</sub>	<i>I</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IV</i>	<i>V</i>		
1 <sup>a</sup>	0.5	1	66	17	4	9	3	4.3	7.4
2 <sup>b</sup>	0.5	1	71	3	1	10	15	3.0	7.1
3 <sup>c</sup>	0.5	1	71	2	—	9	18	—	—
4 <sup>d</sup>	0.5	1	61	19	5	8	7	3.8	7.6
5 <sup>a</sup>	1	0.1	91	6	1	2	—	—	—
6 <sup>a</sup>	1	1	74	13	3	7	3	4.3	—
7 <sup>e</sup>	1	2	65	18	4	9	4	4.5	—
8 <sup>f</sup>	0.5	5	72	13	3	7	5	4.3	—
9 <sup>g</sup>	0.5	1	69	17	4	9	1	4.3	7.7
10 <sup>h</sup>	0.5	1	61	23	6	8	2	3.8	7.7
11 <sup>i</sup>	0.5	1	63	22	5	8	2	4.4	7.8
12 <sup>j</sup>	0.5	1	85	0	0	12	3	—	7.1
13 <sup>k</sup>	0.5	1	65	20	5	8	2	4.0	8.1
14 <sup>l</sup>	0.5	1	66	17	4	9	4	4.3	7.3

<sup>a</sup> The analysis was carried out immediately after the decomposition with water; <sup>b</sup> analyzed 168 h after the decomposition with water; <sup>c</sup> the reaction mixture was heated with decaline at 160°C 3 h; <sup>d</sup> the organic phase after the decomposition with water was heated with maleic anhydride at 50°C 2 h; <sup>e</sup> the reaction was carried out in the presence of acethanhydride; <sup>f</sup> the reaction mixture contained large amount of tarry material; <sup>g</sup> the decomposition with 5% aqueous NaHCO<sub>3</sub>; <sup>h</sup> the decomposition with 10% aqueous NaOH; <sup>i</sup> the decomposition with triethylamine followed by water; <sup>j</sup> the decomposition with conc. HCl; <sup>k</sup> the decomposition was carried out with conc. HCl, whereupon dichloromethane was added and pH value was adjusted at 4.5; <sup>l</sup> the reaction mixture was left to stand at 5°C 24 h.

## RESULTS AND DISCUSSION

In the presence of excess aluminium chloride, hexamethylbenzene (*I*) reacts as a complex with the catalyst and 1,2-dichloroethane. The product exhibits non-equivalent <sup>1</sup>H NMR signals of the methyl groups and corresponds to the 1-(2-chloroethyl)-1,2,3,4,5,6-hexamethylbenzenium salt (*II*). Garmonov<sup>4</sup> found that alkylbenzenes form 1 : 2 complexes with AlCl<sub>3</sub> in the presence of 1,2-dichloroethane, hence we presume Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> to be the anion of the salt *II*. The <sup>1</sup>H NMR spectrum of compound *II* is similar to that of 1-chloromethyl-1,2,3,4,5,6-hexamethylbenzenium salt or heptamethylbenzenium salt which were prepared and studied in a similar

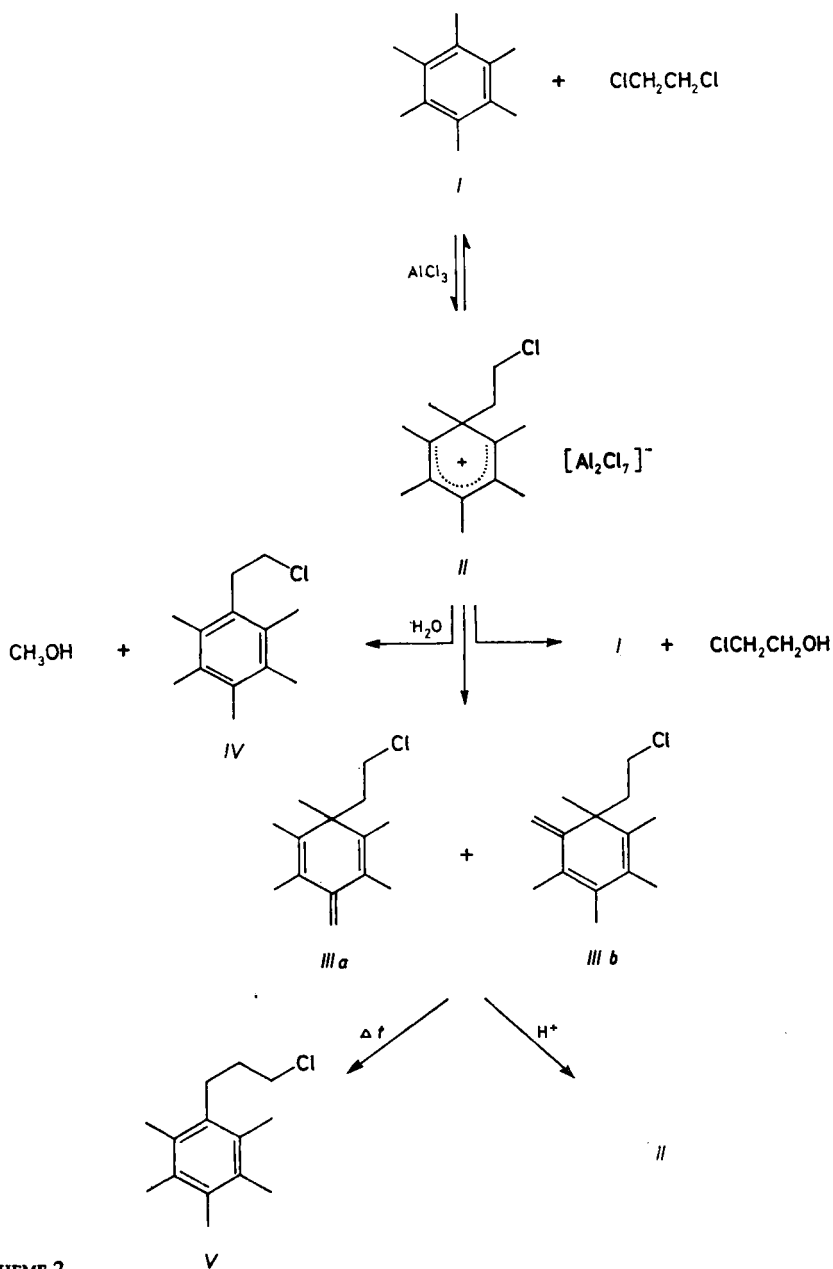
way<sup>5</sup>. Also the UV spectrum of compound *II* in 38% HCl is similar to those of the said salts<sup>6</sup>.

Decomposition of the reaction mixture containing the salt *II* in 1,2-dichloroethane with aqueous acetate buffer of pH 3-4 and subsequent chromatographic separation of the organic phase by means of the gas chromatograph gave five compounds (*I*, *IIIa*, *IIIb*, *IV*, *V*). Their relative amounts were determined by means of gas-chromatographic analysis and are given in Table I (Experiment No. 1). The compound *I* was identified as hexamethylbenzene (by comparison with the authentic sample). As the reaction mixture did not contain free hexamethylbenzene before the decomposition (which was proved by liquid chromatography), we must presume the reverse splitting of the  $\sigma$  complex *II* in aqueous medium to give hexamethylbenzene and 2-chloroethanol (the latter compound was also proved chromatographically) (Scheme 2). A similar splitting of the  $\sigma$  complex was observed by Perrin<sup>7</sup> in the case of electrophilic substitution of 1-substituted-2-naphthols. The compound *IV* was identified as 1-(2-chloroethyl)-2,3,4,5,6-pentamethylbenzene, *i.e.* a substitution product of hexamethylbenzene *I*. Its structure was assigned on the basis of comparison with the authentic sample prepared from 1-chloromethyl-2,3,4,5,6-pentamethylbenzene in four steps (Scheme 3). The compound *IV* formed along with methanol represents another product of the reverse splitting of the  $\sigma$  complex *II* in aqueous medium (Scheme 2).

The ratio of the compounds *IV* to *I* is 1 : 8 and remains constant and independent on the way of treatment of the reaction mixture (Table I, experiments 1, 2, 4–11, 13, 14). Obviously, this ratio reflects the stability of the leaving cations:  $(\text{CH}_2\text{CH}_2\text{Cl})^+ > \text{CH}_3^+$ . Similar conclusions from comparison of the leaving groups were also made by Perrin<sup>7</sup> and Hünig<sup>8</sup>.

It was impossible to perfectly separate the compounds *IIIa* and *IIIb* on preparative scale, which was found by chromatographic analysis. The spectral data given in Experimental correspond to enriched mixtures of 88% *IIIa* with 12% *IIIb* and 78% *IIIb* with 22% *IIIa*. Both compounds dissolve in 38% aqueous HCl. From the spectral characteristics and behaviour in acid medium it is concluded that the compounds represent a pair of the conjugated bases, *i.e.* 3-(2-chloroethyl)-6-methylene-1,2,3,4,5-pentamethyl-1,4-cyclohexadiene (*IIIa*) and 5-(2-chloroethyl)-6-methylene-1,2,3,4,5-pentamethyl-1,3-cyclohexadiene (*IIIb*). Both the compounds are formed by deprotonation of the cation *II* in the ratio 4 : 1 which is practically independent on the way of treatment of the reaction mixture (see experiments 1, 2, 4, 11, 13, 14 in Table I). The higher content of the *IIIa* isomer is connected with lower stability of the conjugated bases type 1,3-cyclohexadiene as compared with the 1,4-isomer<sup>9</sup>. The structure of the conjugated base *IIIb* was attempted to be determined by trapping of its adduct with maleic anhydride under the presumption that the adduct formation will not be affected by the presence of the other components formed by the splitting of the ion *II* (Table I, experiment 4). However, the presence of such compound was

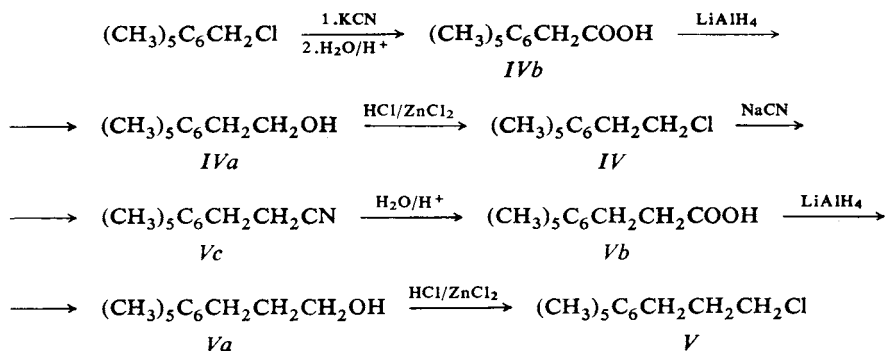
not confirmed chromatographically. The conjugated bases *IIIa* and *IIIb* were also isolated from the reaction mixture by extraction with 38% HCl (Table I, experiment



**SCHEME 2**  
For  $\Delta t$  read  $\Delta T$ .

12). Alkalization of the acid extract gave a mixture containing the compounds *I*, *IIIa*, *IIIb*, *IV*, and *V* proved by means of GC analysis (Table I, experiment 13). The conjugated bases of similar type as *IIIa* and *IIIb* were also observed to be formed from heptamethylbenzenium ion<sup>10</sup> and 1-ethyl-1,2,3,4,5,6-hexamethylbenzenium ion<sup>11</sup>.

The compound *V* was identified as 1-(3-chloropropyl)-2,3,4,5,6-pentamethylbenzene on the basis of comparison with the authentic sample prepared by a four-step synthesis from 1-(2-chloroethyl)-2,3,4,5,6-pentamethylbenzene via the intermediates *Va* – *Vc* (Scheme 3). The presence of compound *V* was not confirmed, if the products of the decomposition with water were immediately analyzed by means of liquid chromatography. Gas chromatography of the same reaction solution revealed a small amount of compound *V*. During long-term standing (and more rapidly by heating), the content of compound *V* increases (Table I, experiments 2 and 3). This is presumed to be due to a slow rearrangement of the CH<sub>2</sub>CH<sub>2</sub>Cl group into the exocyclic double bond in compounds *IIIa* and *IIIb* (Scheme 3). Analogous rearrangement of methyl group was not proved under the given experimental conditions.



SCHEME 3

The variations of the ratio of aluminium chloride to hexamethylbenzene *I* (Table I, experiments 1, 5, 6, 7) showed that the amount of the  $\sigma$  complex *II* in the reaction mixture is decreased at the ratios lower than 2 : 1, whereas excess aluminium chloride (the ratios above 2 : 1) causes consecutive reactions leading to tarry products. In addition, it was found that, in contrast to the course of Friedel–Crafts reactions of lower-alkylated benzenes, the  $\sigma$  complex *II* is quite insensitive to a subsequent electrophilic substitution in the ring. With respect to the fact that mass spectrometry of the hydrolysis products detected no products with  $(m/z) \geq 286$ , it can be also concluded that a substitution of chlorine of the salt *II* by a further hexamethylphenyl group did not take place either. The reason obviously lies in the fact that a formation



of the  $\sigma$  complex with two positive charges is energetically unfavourable. Therefrom it follows that the reaction of hexamethylbenzene with 1,2-dichloroethane under the conditions of the Friedel-Crafts reaction fundamentally differs from the analogous reactions of mono-, di-, and trimethylbenzenes which lead to polymeric 1,2-diarylethanes under the same conditions<sup>12</sup>.

Investigation of the effects of medium on the ratio of the products formed by substitution (splitting of C—C bond) and by elimination (splitting of C—H bond) showed that this ratio depends little on pH and nucleophilicity of the medium, varying from 4.1 (at pH  $\sim$  3.2) to 2.6 (at pH  $\sim$  13.8) (Table I, experiments 1, 9–11). This behaviour indicates that the splitting mentioned proceeds by the monomolecular mechanism.

The attempts at acetylation of hexamethylbenzene (*I*) with acetanhydride in 1,2-dichloroethane medium (Table I, experiment 7) gave no products containing an acetyl group. Results of chromatographical and spectral analyses showed that the reaction product consisted of hexamethylbenzene (*I*) and the known series of the chlorinated hydrocarbons *IIIa*, *IIIb*, and *IV*. This finding indicates that hexamethylbenzene reacts preferably with 1,2-dichloroethane. The acetylation of hexamethylbenzene did not take place even by action of acetyl chloride under different reaction conditions<sup>13</sup>. On the other hand, the reaction of hexamethylbenzene with isobutyryl chloride in carbon disulphide was successful and gave a 20% yield. Similarly, the reaction of hexamethylbenzene with benzoyl chloride in carbon disulphide is also known<sup>14</sup>.

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