

On the Reaction of *tert*-Butyl Chloride with Ethylene

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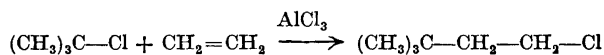
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The reaction between *tert*-butyl chloride and ethylene has been studied. The following four chlorides have been isolated.

- 1-chloro-3,3-dimethylbutane
- 1-chloro-3,3-dimethylpentane
- 1-chloro-3,3,4-trimethylpentane
- 1-chloro-3,3,6,6-tetramethylheptane

A mechanism which explains these products is given for the reaction.

The condensation of some saturated halides with ethylene has been studied by Schmerling¹. With *tert*-butyl chloride the main reaction is



This reaction has now been studied in greater detail. The byproducts obtained in the reaction have been examined and the structure has been proved for three of them.

The reaction was carried out by bubbling pure ethylene at -15° to -20° into pure *tert*-butyl chloride containing about 1.5 % by weight of AlCl_3 . By careful fractionation of the crude chloride mixture obtained in the reaction, the following chlorides have been isolated from the reaction of 132 kg of *tert*-butyl chloride and 47.5 kg of ethylene:

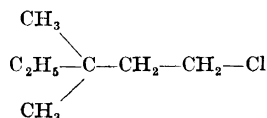
- 3.6 kg (2.7 %) of *tert*-butyl chloride
- 146.9 kg (85.4 %) of the main product $\text{C}_6\text{H}_{13}\text{Cl}$, b.p. $115-122^\circ$
- 1.35 kg (0.7 %) of a chloride $\text{C}_7\text{H}_{15}\text{Cl}$, b.p. $145-150^\circ$
- 12.00 kg (5.7 %) of a chloride $\text{C}_8\text{H}_{17}\text{Cl}$, b.p. $45-50^\circ/8$ mm Hg and
- 1.65 kg (1.2 %) of a chloride $\text{C}_{11}\text{H}_{23}\text{Cl}$, b.p. $82-84^\circ/8$ mm Hg

The yield of the chloride $\text{C}_{11}\text{H}_{23}\text{Cl}$ was calculated on the assumption that two moles of *tert*-butyl chloride is consumed to produce one mole of the chloride $\text{C}_{11}\text{H}_{23}\text{Cl}$.

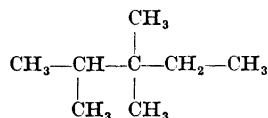
The chlorides mentioned above correspond to 95.7 % of the *tert*-butyl chloride. There were also obtained a residue boiling above $85^\circ/8$ mm weighing 5 kg and several small intermediate fractions having a total weight of 1.5 kg. Gas chromatographic analysis of these intermediate fractions showed that they

consisted of mixtures of the chlorides mentioned above together with a small quantity of a fraction boiling at 72—74°/8 mm Hg, probably a chloride $C_{10}H_{21}Cl$, which could not be obtained in a pure state. The weight of this chloride is about 0.1 % of the total weight of the chlorides.

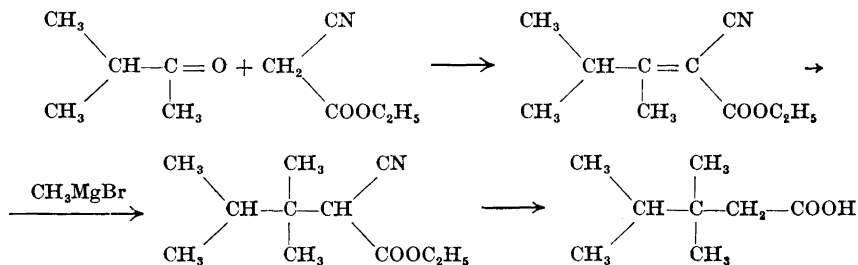
The main product $C_6H_{13}Cl$ has the formula $(CH_3)_3C-CH_2-CH_2-Cl$ ¹ and the chloride $C_7H_{15}Cl$ is identical with the main product obtained from *tert*-amyl chloride and ethylene¹ and has the structure



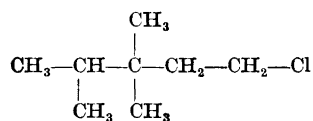
The chloride $C_8H_{17}Cl$ reacts with magnesium to form a Grignard reagent which on treatment with water gives the hydrocarbon



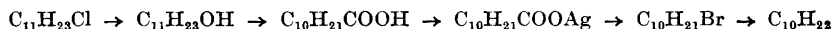
The chloride $C_8H_{17}Cl$ can further be converted to an alcohol $C_8H_{17}OH$ which can be oxidized to an acid $C_7H_{15}COOH$ ³. This acid is identical with that obtained by the reactions



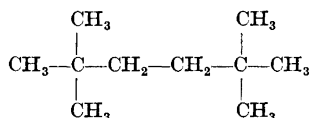
The chloride $C_8H_{17}Cl$ has thus the following structure



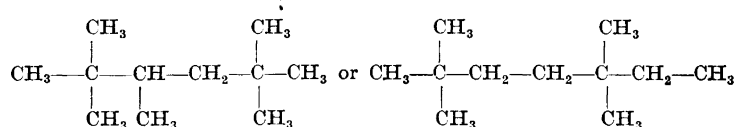
The chloride $C_{11}H_{23}Cl$ reacts with magnesium to form a Grignard reagent which on treatment with water gives a hydrocarbon $C_{11}H_{24}$ which seems not to have been described before. The chloride can be converted to a hydrocarbon $C_{10}H_{22}$ by the following reactions.



This hydrocarbon has the same infrared absorption and boiling point as

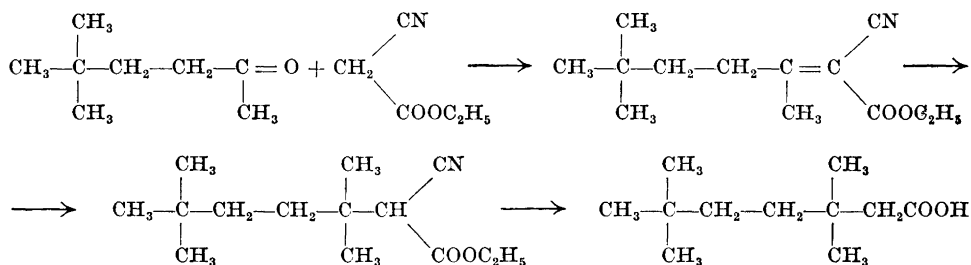


The hydrocarbon C₁₁H₂₄ must then be

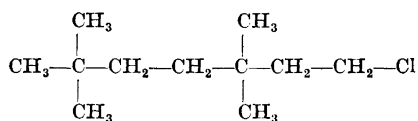


The left hand of these has been described by Moersch and Whitmore³ and has a boiling point, a refractive index and a density which is different from that of the hydrocarbon C₁₁H₂₄ obtained from the chloride C₁₁H₂₃Cl. This hydrocarbon must therefore have the right hand of the two structures given.

The acid C₁₀H₂₁COOH obtained from the chloride C₁₁H₂₃Cl is identical with the acid obtained by the reactions:

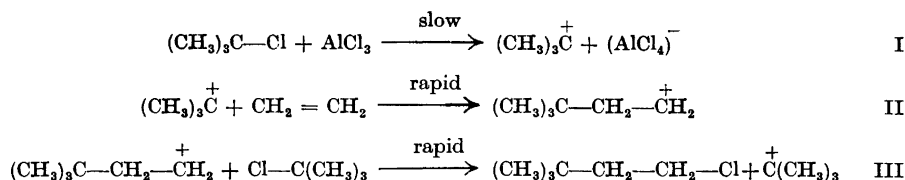


The chloride C₁₁H₂₃Cl has thus the following structure



The fact that the yield of the main product is high, together with the limited number of byproducts obtained in the reaction suggests that a very simple reaction mechanism is most probable. Such a mechanism which explains all the byproducts obtained can in fact be conceived. It is based on the following considerations:

The reaction conditions are such that a carbonium ion mechanism is probable. The reaction has further a definite period of initiation during which it is very slow, followed by a rapid increase in velocity so that the absorption of ethylene becomes as rapid as the rate of addition and the capacity of the cooling bath permits. This indicates that a chain reaction is operating. This chain is probably

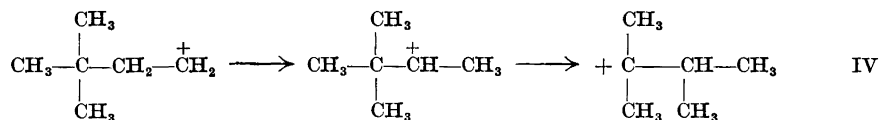


In step I, which is a slow heterogeneous reaction, the reactive component, a carbonium ion, is formed. This is rapidly used up in step II, and regenerated in step III. The mechanism up to this point is just a slight modification of that generally accepted⁴, which however, does not explain the period of initiation.

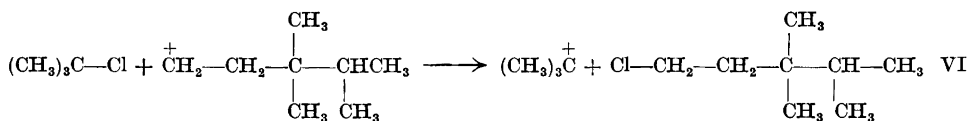
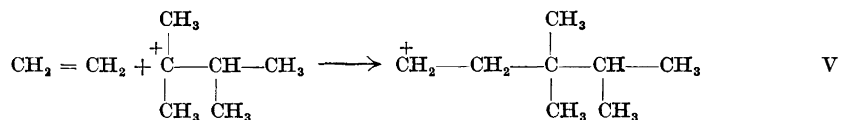
The very important point in the mechanism given above is the existence of the carbonium ion $(\text{CH}_3)_3\text{C}-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$. This is a primary carbonium ion which will undergo rearrangements or other reactions unless the step III is extremely rapid.

The fact that $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CH}_2-\text{Cl}$ is obtained in a 85.4 % yield indicates that step III is in fact extremely rapid. All byproducts obtained can, however, be explained as results of subsequent reactions of the ion $(\text{CH}_3)_3\text{C}-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$.

The ion $(\text{CH}_3)_3\text{C}-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$ may undergo a succession of 1,2-shifts to give a more stable carbonium ion. The most likely succession is:

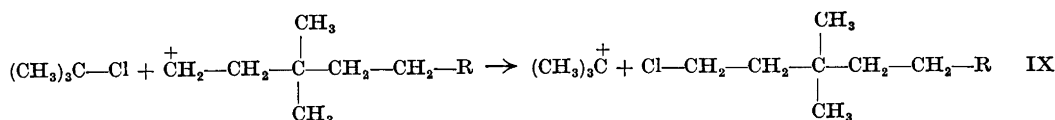
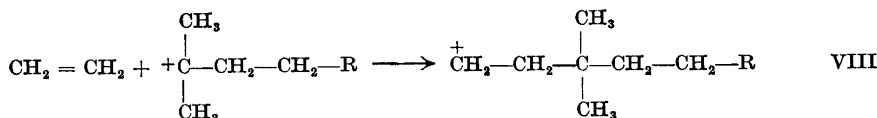
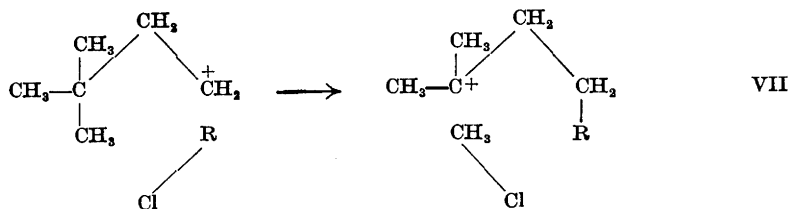


The carbonium ion thus formed can then undergo reactions similar to steps II and III.



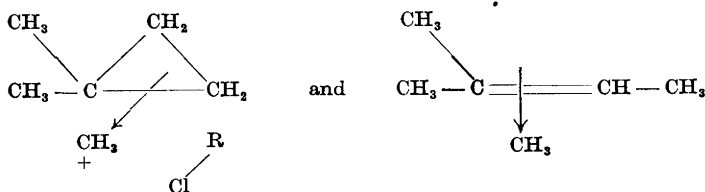
By the reactions IV, V and VI the formation of the main byproduct, the chloride $\text{C}_8\text{H}_{17}\text{Cl}$ is explained.

The formation of the chlorides $\text{C}_7\text{H}_{15}\text{Cl}$ and $\text{C}_{11}\text{H}_{23}\text{Cl}$ means that an uneven amount of carbon atoms are added or lost. Only two chlorides containing an uneven number of carbon atoms could be isolated from the reaction mixture. The reaction is further probably ionic and the chlorides $\text{C}_7\text{H}_{15}\text{Cl}$ and $\text{C}_{11}\text{H}_{23}\text{Cl}$ differ by 4 carbon atoms. All this suggests that a methyl group is lost in the $(\text{CH}_3)_3\text{C}-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$ ion and replaced by an hydrogen atom or a *tert*-butyl group. Such a mechanism may be



When R represents H the chloride $\text{C}_7\text{H}_{15}\text{Cl}$ is formed and when it represents $(\text{CH}_3)_3\text{C}$ the chloride $\text{C}_{11}\text{H}_{23}\text{Cl}$ is formed.

The weakness in the scheme of step VII is that the wrong end of the R-Cl molecule appears to attack the positive charge of the carbonium ion. The point of attack is the significant difference between step III and step VII. The charge distribution in the carbonium ion $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CH}_2^+$ is, however, not so absolutely certain as that given by the conventional formula. Dewar⁵ has *e.g.*, explained the tendency of carbonium ion to rearrange itself by the formation of a π -complex between the migrating group and the rest of the molecule. Whether Dewar's explanation of the carbonium ion rearrangement is correct or not, it indicates the presence of a positive charge on the methyl group and some similarity between this type of reaction and reaction VII, which can be seen from the following formulas:



These represent the hypothetical structures in the steps VII and IV, respectively.

A still closer similarity exists between the mechanism given in step VII and the mechanism for a 1,3-rearrangement⁶. Step VII is in fact an exact intermolecular analogue to the intramolecular 1,3-shift, and can be expressed as a 1,3-substitution.

The halides R-Cl which can be expected to be reactive in step VII and which are present in the reaction mixture are HCl and $(\text{CH}_3)_3\text{C-Cl}$, which exactly correspond to the two halides $\text{C}_7\text{H}_{15}\text{Cl}$ and $\text{C}_{11}\text{H}_{23}\text{Cl}$ which have been found. Whether the chloride $\text{C}_6\text{H}_{13}\text{Cl}$ which is obtained as the main product in the reaction is capable of functioning as R-Cl in step VII is impossible to say. If it can, a chloride $\text{C}_{13}\text{H}_{27}\text{Cl}$ should be present in the high boiling residue. The residue was, however, not examined for this product.

From the formulations given for step VII it follows that CH_3Cl can be expected as a byproduct. No attempts have been made to isolate it from the reaction mixture due to experimental difficulties and the fact that the presence of CH_3Cl can have many explanations and its absence can be explained by subsequent reactions.

EXPERIMENTAL

The reaction between *tert*-butyl chloride and ethylene was performed as described by Brändström⁷ but on a larger scale using 12 kg of *tert*-butyl chloride in each run. 11 such runs were collected and distilled through a 2 m packed column.

The conversion of the chloride obtained into the acid with the same number of carbon atoms has been described by Brändström⁸.

Preparation of 3,3,4-trimethylpentanoic acid. 115 g of ethyl cyanoacetate, 96.5 g of 3-methylbutanon-2, 15.6 g of ammonium acetate, 50 g of glacial acetic acid, and 170 ml of benzene are mixed and refluxed in a 1-litre flask fitted with a water separator. When no more water is obtained, the mixture is cooled and treated in the usual way⁸. The yield is 134 g of ethyl 2-cyano-3,4-dimethylpent-2-enoate, b. p. 115–120°/8 mm Hg.

A Grignard reagent is prepared from 0.3 moles of magnesium, 0.3 moles of methyl iodide and 120 ml of ether. This reagent is added to a mixture of 50 ml of ether, 0.25 moles of ethyl 2-cyano-3,4-dimethylpent-2-enoate, and 0.5 g of Cu_2Cl_2 during 30 min. The temperature is kept below +5° during this operation by cooling. The reaction mixture is then treated in the usual way⁹. The yield is 84 % of ethyl 2-cyano-3,3,4-trimethylpentanoate, b. p. 118–122°/8 mm.

This ester is saponified by refluxing for 1 h with a solution of 21 g of potassium hydroxide in 60 ml of water. The resulting solution is acidified and extracted with benzene. The benzene extract is distilled at ordinary pressure during which operation decarboxylation occurs. The resulting distillate is fractionated under reduced pressure giving a 67 % yield of 1-cyano-2,2,3-trimethylbutane, b. p. 64–65°/10 mm Hg.

A portion of this cyanide is saponified⁹ by refluxing with a solution of potassium hydroxide in ethylene glycol. When the resulting solution is worked up in the usual way, 3,3,4-trimethylpentanoic acid, b. p. 112–113°/8 mm Hg is obtained. This acid is in all respects identical with the acid obtained from the chloride $\text{C}_8\text{H}_{17}\text{Cl}$.

Preparation of 3,3,6,6-tetramethylheptanoic acid. 5,5-Dimethylhexanone-2 is prepared from 4,4-dimethylpentanoyl chloride by acylating diethyl malonate and hydrolysing the resulting diethyl acylmalonate¹⁰.

The diethyl 4,4-dimethylpentanoylmalonate, b. p. 145–155°/10 mm Hg, is obtained in a yield of 89 % and the treatment of this ester with propionic acid and sulphuric acid gives 5,5-dimethylhexanone-2, b. p. 145–157°, in a yield of 76 %.

5,5-Dimethylhexanone-2 is condensed with ethyl cyanoacetate by the method given above⁸, giving the ethyl 2-cyano-3,6,6-trimethylhept-2-enoate, b. p. 145–160°/10 mm Hg, in a yield of 68 %.

This ester is treated with an ether solution of methylmagnesium bromide by the method given above⁹ giving ethyl 2-cyano-3,3,6,6-tetramethylheptanoate, b. p. 145–155°/10 mm Hg, in a yield of 70 %.

This ester is hydrolysed and decarboxylated by the method given above⁹, giving 1-cyano-2,2,5,5-tetramethyl hexane, b. p. 205–215°, in a yield of 64 %.

A portion of this cyanide is hydrolysed by the method given above⁹, giving 3,3,6,6-tetramethylheptanoic acid. This acid is in all respects identical with the acid obtained from the chloride $\text{C}_{11}\text{H}_{23}\text{Cl}$.

Preparation of 2,3,3-trimethylpentane from the chloride $C_8H_{17}Cl$. A Grignard reagent is prepared from 1 mole of the chloride $C_8H_{17}Cl$, 1 mole of magnesium and 200 ml of ether. This reagent is decomposed by cautious addition of water and hydrochloric acid. The layers are separated and distilled giving a 80 % yield of 2,3,3-trimethylpentane, b. p. 112–115°. The structure was established by a comparison of the infrared spectra of the product with that given for 2,3,3-trimethylpentane.

Preparation of 2,2,5,5-tetramethyl hexane. 50.2 g of the dry powdered silver salt of 3,3,6,6-tetramethylheptanoic acid are placed in a dry 250 ml three-necked flask fitted with a stirrer, a reflux condenser and a dropping funnel. The flask is cooled in ice-water and a solution of 9.0 ml of bromine in 40 ml of dry carbon tetrachloride is added during 20 min. The flask is then heated on a water-bath for 3 h.

The reaction mixture is cooled and filtered. The solid is washed with some ether. The combined filtrates are washed with a sodium bisulphite solution and then with a sodium carbonate solution. The ether and carbon tetrachloride are distilled off and the residue fractionated under reduced pressure.

The yield of 1-bromo-2,2,5,5-tetramethylhexane, b. p. 76–78/10 mm Hg, is 60 %.

A Grignard reagent is prepared from 10 g of the bromide above and magnesium which is then treated with hydrochloric acid giving 2,2,5,5-tetramethylhexane, b. p. 134–138°. The structure of this hydrocarbon was established by comparing the infrared spectra with that given for 2,2,5,5-tetramethylhexane.

Preparation of 2,2,5,5-tetramethylheptane from the chloride $C_{11}H_{23}Cl$. A Grignard reagent, prepared from the chloride $C_{11}H_{23}Cl$ and magnesium, is treated with hydrochloric acid giving a 50 % yield of 2,2,5,5-tetramethylheptane, b. p. 161.5–162.5°, $d_4^{20} = 0.7452$, $n_D^{20} = 1.4186$.

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REFERENCES

1. Schmerling, L. *J. Am. Chem. Soc.* **67** (1945) 1152.
2. Brändström, A. *Acta Chem. Scand.* **13** (1959) 610.
3. Moersch, G. W. and Whitmore, F. C. *J. Am. Chem. Soc.* **71** (1949) 819.
4. Alexander, E. R. *Principles of ionic organic reactions*, New York 1950, p. 146.
5. Dewar, M. J. S. *The electronic theory of organic chemistry*, Oxford 1949, p. 211.
6. Bartlett, P. D. in Gilman, H. *Organic Chemistry III*, New York 1953, p. 69.
7. Brändström, A. *Acta Chem. Scand.* **13** (1959) 611.
8. *Organic Syntheses III* (1955) 399.
9. Brändström, A. and Forsblad, I. *Arkiv Kemi* **6** (1954) 561.
10. Walker, H. G. and Hauser, C. R. *J. Am. Chem. Soc.* **68** (1946) 1386.

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