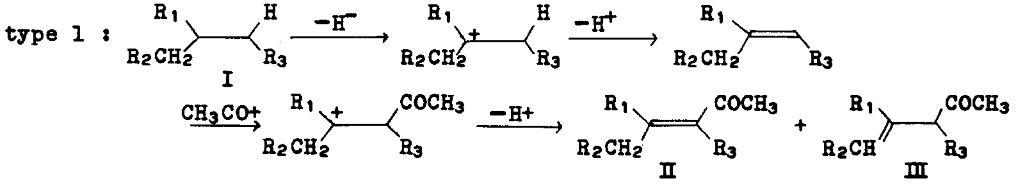
Tetrahedron Letters No.30, pp. 2581-2584, 1969. Pergamon Press. Printed in Great Britain.

FRAGMENTATION-ACETYLATION OF ISOOCTANE WITH ACETYL CHLORIDE-ALUMINUM CHLORIDE COMPLEX

I.Tabushi, K.Fujita, R.Oda
Department of Synthetic Chemistry
Kyoto University, Kyoto, Japan
and
M.Tsuboi
Yonago Technical School
Yonago, Tottori, Japan

(Received in Japan 10 May 1969; received in UK for publication 27 May 1969)

We reported the unrearranged dehydrogenation-acetylation (Type 1) of branched hydrocarbons$^{1)}$ and the rearranged dehydrogenation-acetylation (Type 2) of cyclohexane$^{2)}$ with the acetyl chloride-aluminum chloride complex. Thus the type 1 reactions of isopentane (Ia), methylcyclopentane (Ib) or methylcyclohexane (Ic) gave 1,2-dimethyl-Δ^1-propenyl methyl ketone (IIa), 2-methyl-Δ^1-cyclopentenyl methyl ketone (IIb) or 2-methyl-Δ^1-cyclohexenyl methyl ketone (IIc) and 2-methyl-Δ^2-cyclohexenyl methyl ketone(IIIc), respectively. The type 2 reaction of cyclohexane gave 2-methyl-Δ^1-cyclopentenyl methyl ketone (IV) (Scheme 1).

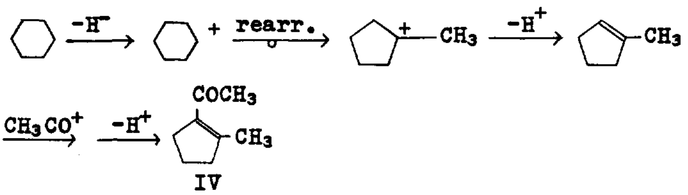


a. $R_1=R_3=CH_3$ $R_2=H$

b. $R_1=CH_3$ $R_2R_3=-CH_2CH_2-$

c. $R_1=CH_3$ $R_2R_3=-(CH_2)_3-$

type 2 :



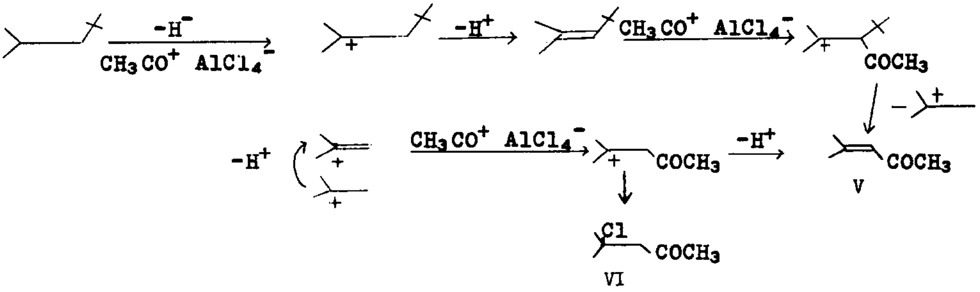
Scheme 1

In this article, We wish to report the new type of the reaction, fragmentation-acetylation (Type 3) of isooctane with the acetyl chloride-aluminum chloride complex. To the authors'knowledge, this type of highly selective fragmentation has not been firmly shown on chemical grounds.

19.6g of acetyl chloride in 20 ml of chloroform was added into the suspension of 33.3g of finely powdered aluminum chloride in 100 ml of chloroform. The mixture became homogeneous with stirring and into the resultant solution was added dropweise 28.5g of isooctane in 20 ml of chloroform. After 12 hours refluxing, the mixture was poured onto ice-HCl and was extracted with methylene chloride. Usual work-up of the organic layer gave 17.9g of isooctane unreacted, 7.6g of the distillate of the boiling range 40-53° at 48 mmHg of which V was the major product and 1.4g of the distillate boiling in the range of 60-105° at 38 mmHg which consisted of V and VI together with some components. The yield of V was ammounted to 80% (mole/mole isooctane consumed). V and VI were assigned to mesityl oxide and 2-chloro-2-methylpropyl methyl ketone, respectively. IR spectrum of V showed the presence of α,β-unsaturated carbonyl function (1700 and 1635 cm^{-1}) and was identical with that of the authentic mesityl oxide in every detail.

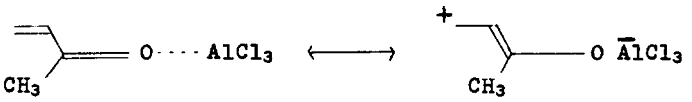
NMR spectrum of V (CCl_4 solution) : τ 4.0 multiplet (1H), τ 7.93 doublet (J was not determined because of superimposition on acetyl CH_3) (3H), τ 7.94 singlet (3H) and τ 8.14 doublet (J=1.5 cps, 3H). Mass spectrum : m/e 98 (parent) and other necessary peaks. NMR spectrum of VI (CCl_4 solution) : τ 7.07 singlet (2H), τ 7.82 singlet (3H) and τ 8.30 singlet (6H). IR characteristic absorption : 1735 cm^{-1}. Mass spectrum : m/e 134 (parent), 119 (p-CH_3), 99 (p-Cl), 98 (p-HCl) and 84 (p-Cl-CH_3).

Formation of V and VI as major products showed that the fragmentation of isooctane skeleton to C_4 skeleton occured under the reaction condition. Similar to the type 1 and 2 reactions, the type 3 reaction seems to involve hydride abstraction from isooctane by the acetyl chloride-aluminum chloride complex as an initiating step (Scheme II).



Scheme II (Type 3 reaction)

In this mechanism, the most interesting point to note is that the highly selective elimination of t-butyl cation from isooctyl or substituted isooctyl cation took place instead of deprotonation. It is explicable by the much greater stability of t-butyl cation and of the much greater bulkiness of t-butyl than proton. Fragmentation of n-heptyl cation by the Olah's reagent (FSO_3H-SbF_5 or HF-SbF_5) to t-butyl cation was observed at room temperature only by nmr spectroscopy, while our results showed that the intermediate was trapped chemically. Our success of chemical trapping seems to be due to the fact that the double bond of the product was not further attacked by the acetyl chloride-aluminum chloride complex presumably because the α,β-unsaturated carbonyl is present in the form of the complex with aluminum chloride complex (VII)[4], which is much less reactive to cationic attack than the uncomplexed olefin.



VII

Every type reaction (Type 1,2 and 3) of an alkane with the acetyl chloride-aluminum chloride complex has the common steps after olefin formation, i,e., the addition of acetyl cation followed by the eliminaton of proton or by the addition of chloride. We have also observed the alternative steps i.e, the addition of acetyl cation followed by the abstraction of hidride to give saturated ketones (Type 4 reaction) for cyclooctane and some other saturated hydrocarbons. The results will be soon published.

References

1. I.Tabushi, K.Fujita and R.Oda, Tetrahedron Letters, 5455 (1968)
2. I.Tabushi, K.Fujita and R.Oda, Tetrahedron Letters, 4247 (1968)
3. G.A.Olah and J.Lukas, J. Am. Chem. Soc., 90, 933 (1968)
4. The complexes of carbonyl compounds with aluminum chloride were shown to have aluminum chloride on carbonyl oxygen ; for example : T.Inukai and T.Kojima, J.Org. Chem., 31, 1121 (1966) for methyl acrylate and M.F.Lampert, J.Chem. Soc., 542 (1962) for ethyl acetate.