

Dehydrogenation-Acetylation of Branched Hydrocarbons  
with Acetyl Chloride and Aluminum Chloride

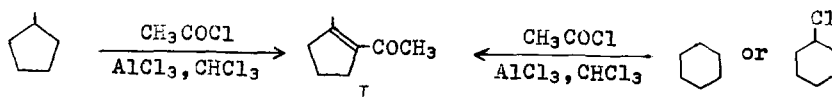
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(Received in Japan 30 July 1968; received in UK for publication 5 September 1968)

We reported the novel rearranged dehydrogenation-acetylation of cyclohexane with acetyl chloride and aluminum chloride where 2-methyl- $\Delta^1$ -cyclopentenyl methyl ketone was obtained as the practically sole component in the 1:1 reaction product. There was obtained a small amount of the 1:2 reaction product (1). Now we wish to report the unrearranged dehydrogenation-acetylation of branched hydrocarbons with acetyl chloride and aluminum chloride. 12.9 g of acetyl chloride (0.3 mole) in 200 ml of chloroform was added into the suspension of 40 g (0.3 mole) of finely powdered aluminum chloride in 100 ml of chloroform. The mixture became homogeneous with stirring and into the resultant solution was added dropwise 25 g of methylcyclopentane in 20 ml of chloroform. After 5 hours stirring, the mixture was poured onto ice-HCl and was extracted with 150 ml of methylene chloride three times. Usual work-up of the organic layer gave 11.3 g of the distillate boiling in the range of 80-89°C at 25 mmHg, which consisted of one major component (89.5% of the above distillate and amounted to 27.4% yield based on methylcyclopentane used) and several minor components by VPC analysis with Silicon DC 550, Apiezon-grease-L and PEG 20,000. The major product, I, was assigned as 1-methyl- $\Delta^1$ -cyclopentenyl methyl ketone on the bases of spectral and chemical behaviors. IR spectrum of I showed the presence of  $\alpha,\beta$ -unsaturated carbonyl function (by characteristic absorption at 1685 and 1620  $\text{cm}^{-1}$ ). This assignment was supported by the observation that I was quantitatively hydrogenated by absorbing one equivalent of hydrogen on the Pd-C catalyst, giving a saturated ketone (IR, 1705  $\text{cm}^{-1}$ ). Nmr spectrum of I gave further support for the structural assignment : 7.89 $\tau$  singlet (3H), 7.97 and 8.00 $\tau$  singlets (3H) and

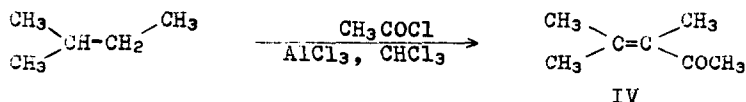
7.2-8.5 $\tau$  multiplet (6H). The structural assignment was consistent with the observation that I gave bromoform and a carboxylic acid on treatment with Br<sub>2</sub>-NaOH. And a conclusive evidence for structural assignment was obtained from its derivation to the corresponding semicarbazone, melted at 220-221°C (recrystallized from aq. methanol, lit. 221°C (2)). Elemental analysis ; found: C=59.92%, H=8.45%, N=22.91% ; calcd. for C<sub>9</sub>H<sub>15</sub>ON<sub>3</sub> C=59.67%, H=8.35%, N=23.20%. I was also obtained from cyclohexane or cyclohexyl chloride on treatment with acetyl chloride and aluminum chloride (1).



On similar treatment of methylcyclohexane (27 g of AlCl<sub>3</sub> and 20 g of acetyl chloride in 150 ml of chloroform and 25 g of methylcyclohexane in 75 ml of chloroform, refluxed for 70 hr.) two ketones, II (48% of the 1:1 products) and III (41% of the 1:1 products) were obtained in 1:1 reaction products (12.8% yield based on the hydrocarbon used). Higher boiling fraction was also obtained which was the bisacetyl derivative. By use of preparative VPC II and III were most efficiently separated and structural determination of them were made by nmr and IR spectra, elemental analysis and mp of the ketone derivative. Thus II (novel) was determined as 2-methyl- $\Delta^2$ -cyclohexenyl methyl ketone ; nmr absorptions (CCl<sub>4</sub> solution): 8.39 $\tau$ , broad single peak (3H) (allylic methyl) ; 7.93 $\tau$ , singlet (3H) (carbonylmethyl) ; 4.41 $\tau$  multiplet (1H) (vinyl) ; 7.80-8.10 $\tau$  multiplet (2H) (allyl) ; 7.05 $\tau$  multiplet (1H) ; 8.05-8.55 $\tau$ , multiplet (4H): IR characteristic absorptions at 1710 and 1655 cm<sup>-1</sup>. And III was identified as 2-methyl- $\Delta^1$ -cyclohexenyl methyl ketone; nmr absorptions (SCL<sub>4</sub> solution): 8.17 $\tau$  singlet with structure (3H), 7.87 $\tau$  singlet (3H), 7.58-8.06 $\tau$  multiplet (4H) and 8.24-8.53 $\tau$  multiplet (4H): The characteristic absorptions at 1683 and 1618 cm<sup>-1</sup>: mp of the semicarbazone, 207-8° (dec.), lit. 207-8° (dec.) (3). In our preliminary experiment, similar result was also obtained from 1-methylcyclohexene.

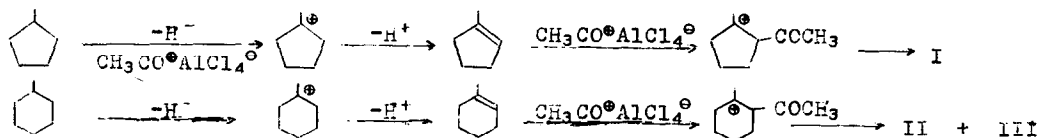


Isopentane (0.35 mole) was similarly treated with acetyl chloride (0.35 mole) and aluminum chloride (0.35 mole) in chloroform. Usual work-up gave 2.6 g of the distillate boiling at 35-50°C at 22 mmHg, which consisted of one major ketone IV (75% of the product) and several minor components by VPC analysis. Practically pure IV was obtained by fractional column distillation. IV was assigned as 1,2-dimethyl- $\Delta^1$ -propenyl methyl ketone from the following spectral and chemical evidence. IR characteristic absorptions at 1690 and 1625  $\text{cm}^{-1}$ . Nmr spectrum ; 7.87 $\tau$  singlet (3H), 8.18 $\tau$  singlet (6H) and 8.25 $\tau$  singlet (3H). The corresponding semicarbazone melted at 184-5°C (lit 186°C (4)). Elemental analysis, found: C=56.51%, H=9.01%, N=24.86%, calcd. for  $\text{C}_8\text{H}_{15}\text{ON}_3$  C=56.80%, H=8.88%, N=24.85%.

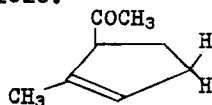


Formation of I, II, III and IV seems to give a general pattern of the reaction of branched saturated hydrocarbons with acetyl chloride in the presence of a Lewis acid (5). The mechanism of the reaction seems to involve hydride abstraction from a hydrocarbon by an acetyl chloride-aluminum chloride complex, as shown in Scheme 1. Cyclohexane and cyclopentane were reported to be abstracted hydride by the Olah's reagent ( $\text{FSO}_3\text{H}-\text{SbF}_5$  or  $\text{HF}-\text{SbF}_5$ ) below 0°C and to be ring-cleaved by protonation above 0°C (6). But in our condition using  $\text{CH}_3\text{CO}^+\text{AlCl}_4^-$  at chloroform reflux temperature, no ring-cleaved product was observed. Possibility of acid-catalyzed isomerization-dehydrogenation of cycloalkane to cycloalkene with aluminum chloride alone preceded the reaction with acetyl cation (7) was excluded by the attempted isomerization of cyclohexane with the saturated solution of aluminum chloride in chloroform. On this treatment, practically no olefin was detected and most of cyclohexane remained unchanged after three hours' refluxing. The other branched hydrocarbons used behaved similarly.

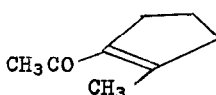
Scheme 1



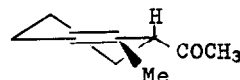
A selective proton-elimination from 2-acetyl-1-methylcyclopentyl cation in contrast with a nonselective proton-elimination from 2-acetyl-1-methylcyclohexyl cation (scheme 1) may be interpreted by relative instability of V (or of the transition state leading to V) compared to I because of 1,3-acetyl hydrogen interaction in the former. A further mechanistic consideration will be made in a full-length article.



V, with considerable  
1,3-Ac-H-interaction



I, no Ac-H interaction



II

Hydride abstraction from simple hydrocarbons by strong Lewis acid was previously observed spectroscopically (6,8). The fate of the carbonium ion thus resulted was said to be an olefin formation (by proton elimination) followed by cationic telomerization (9). Our results showed the example that hydride abstraction was applicable to alkane chemistry on the synthetic viewpoint and the reaction with acetyl chloride will afford the convenient routes to unsaturated ketones having alkyl substituent on the carbon-carbon double bond from the saturated hydrocarbon.

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