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A Polymer of Methyl Ethyl Ketone

Metil Etil Keton Polimeri

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Polymerization of substances containing carbonyl group by the action of Al_2O_3, ThO_2, $Ba(OH)_2$, SiO_2, etc. have been investigated. It has been reported that acetaldehyde polymers which were obtained by the action of alumina on acetaldehyde for 10 - 12 hrs, had a degree of polymerization of about 5300 (1). Furukawa et al. (2) indicated that the degree of polymerization increased to 33000 if the reaction was carried out at −70°. Artmeyer (3) obtained a polymer with the degree of polymerization of about 72, by shaking the acetaldehyde with alumina at −70° for 20 hrs. Experimental data have shown that aliphatic ketones also polymerise by the catalytical action of the above mentioned catalysts. In the presence of basic catalysts, ketones of small molecular weight afforded the ketohols (4), according to Kuliev et al. (5), diacetone was obtained when acetone was passed through a layer of chromatographic alumina, while 3-methyl-3-hydroxy-5-heptanone was the product, if methyl ethyl ketone was utilized instead of acetone.

In this work, polymerization conditions and the product obtained from methyl ethyl ketone by flowing it through a layer of alumina (Brockmann Basic), are described.

EXPERIMENTAL

A glass column having a diameter of 4 cm and a length of 25 cm was used. A small piece of cotton and a filter paper disk were placed at lower end of column; then the column was packed with alumina (Brockmann Basic). Methyl ethyl ketone was run through the column at a rate of 0.3 ml/min. The unreacted methyl ethyl ketone

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was removed from the reaction mixture by distillation under reduced pressure. The remaining portion was then distilled in vacuo for further purification of the product.

When methyl ethyl ketone was shaken with alumina in a flask, the same product was obtained, only with a smaller yield compared to the product obtained, by the former technic. Substances such as chloroform or ethanol which might have been present in the reaction media as solvent did not interfere in the reaction; on the other hand, if acidic or neutral alumina was used instead of basic one, the expected product could not be obtained.

The product is a yellow oily substance with a special odor and burning taste. b.p. 155°C; d. 1.30; it is inflammable and miscible with organic solvents in all proportions. It is converted to a resinous form by the action of light and air. It reduces potassium permanganate, iodine, or bromine in neutral solutions.

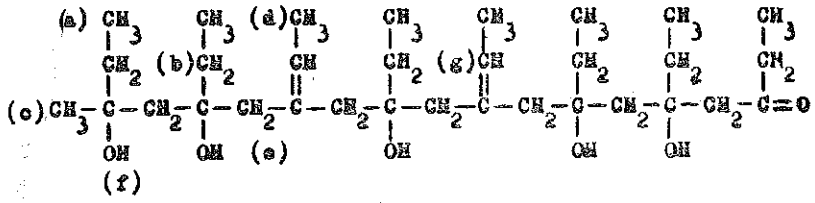
The UV spectrum showed λ_{max}^{EtOH} at 238 mμ (Σ 284000). The IR spectrum (Perkin Elmer 137, liquid film) showed characteristic peaks at 3448 cm^{-1} (OH); 2941 cm^{-1} (streching of aliphatic C-H); 1689 cm^{-1} (C=O); 1400 cm^{-1} (symetrical bending of CH_3—); 1618 cm^{-1} (C=C); 1449 cm^{-1} (asymetrical bending of CH_3—); 1366, 1124 cm^{-1} (C—O streching of tertiary alcohol). The NMR spectrum in $CDCl_3$ (HA 100, TMS as internal standart) showed signals at 0.2 - 1.2 (31 H, triplet and quartet), 1.84 (3 H), 2.14 (6 H, doublet), 2.17 - 2.6 (16 H), 1.4 - 1.7 (6 H) and 6.15 ppm (2 H). The Mass spectrum showed peaks at m/e 126, 115, 97, 73, 69, 57 and 43.

Anal. Calcd. for $C_{32}H_{60}O_6$: C, 71.06; H, 11.18; 0, 17.76. Found C, 71.44; H, 11.06; 0, 17.88.

RESULTS and DISCUSSION

In contact with basic alumina, methyl ethyl ketone is converted to a polymer with a degree of polymerization 8, which gives a resinous substance on standing. Its elementary analysis agrees with a molecular formula of $C_{32}H_{60}O_6$ which indicates a dehydration of the molecule during polymerization. It appears as a single blue violet spot under UV light by TLC. The IR spectrum indicates that the substance is an aliphatic compound with a tertiary alcohol, a carbonyl group and a C=C double bond. The NMR spectrum of the substance indicates that the molecule does not contain an acidic or enolic —OH group; the signals at 0.2 - 1.2 ppm are characteristic of CH_3 and CH_2

protons (a and b in formula); the signal at 1.84 belongs to CH_3 (c protons) attached to a C containing an OH group. As can be seen in the formula, this is the only CH_3 group in the molecule, and this fact is proven by the presence of three-hydrogen integral of these particular signal. The protons of CH_3 (d protons) attached to C=C give signals at 2.14 ppm with an integral value of 6H, which is indicative of only two double bonds in the molecule. The signals at 2.15 - 2.60 of the methylenes (e protons) and at 1.40 - 1.70 of tertiary alcohol groups (f protons) are in concordance with the formula. The protons of the double bonded carbon are found at 6.15 ppm with an integral value of 2H. The absence of a singlet and the presence of a tetret indicate that the CH=group is attached to a CH_3 and that the dehydration in the molecule occured as follows:



The mass spectrum of the compound (Fig. 1) exhibits a base peak at m/e 57 (C_3H_5O) which is a characteristic feature of the methyl ethyl ketones (6). Other fragments are shown in the sheme and m* indicates that the proposed transition is supported by a metastable ion. These facts support the reliability of the proposed formula.

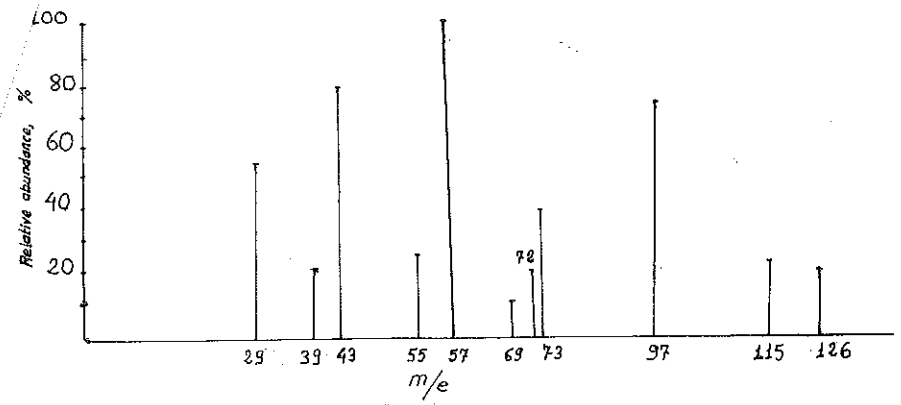
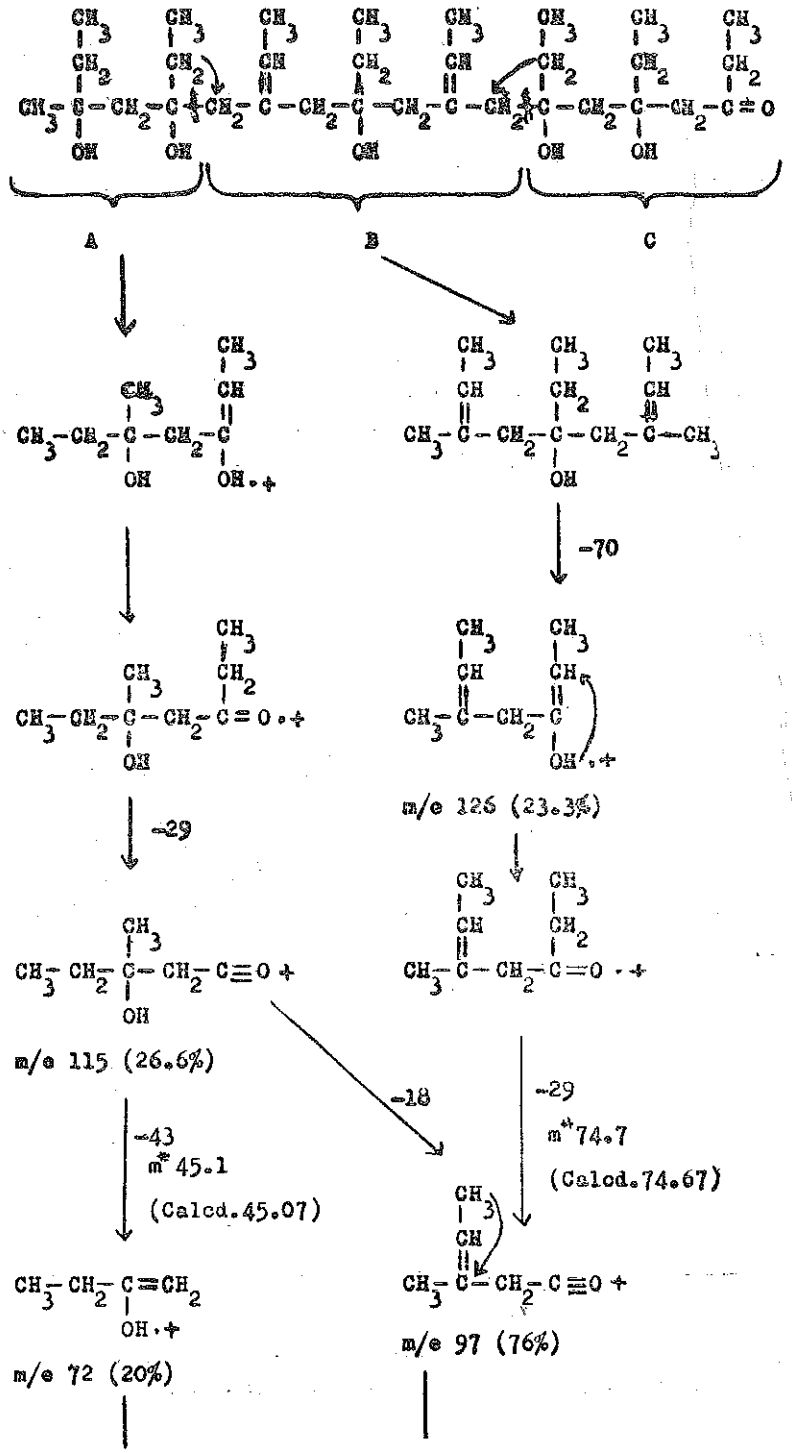
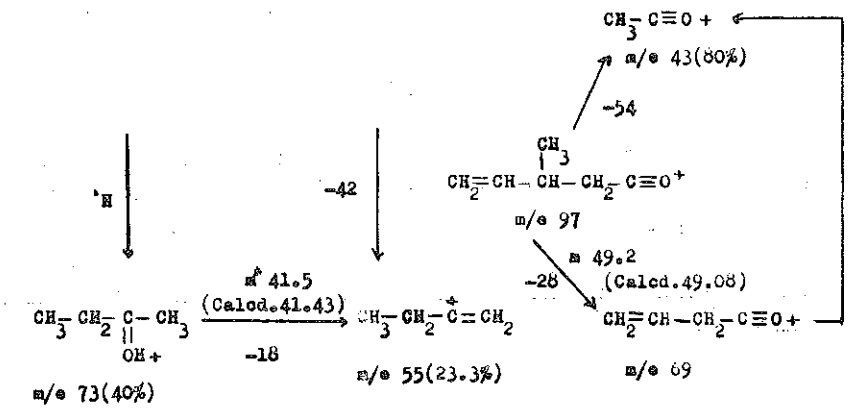
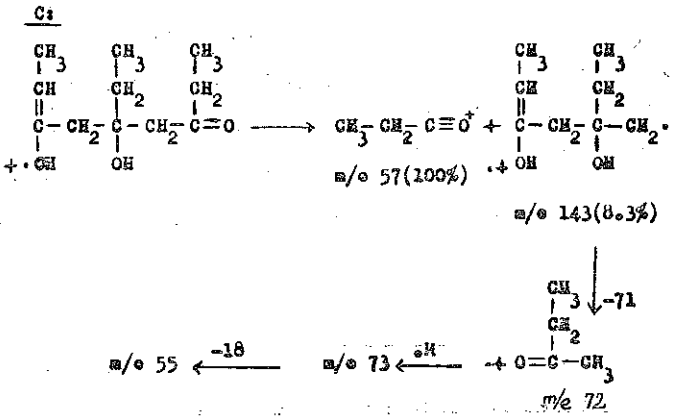


Fig. 1. Mass spectrum of the polymer of methyl ethyl ketone. (the instrument was Operated at 160° and the electron voltage 70eV).


A
B
C
-70
m/e 126 (23.3%)
-29
m/e 115 (26.6%)
-43
m* 45.1
(Calcd.45.07)
-18
-29
m* 74.7
(Calcd.74.67)
m/e 72 (20%)
m/e 97 (76%)





Acknowledgement

The analysis and the NMR spectrum of the compound was kindly determined at Hoffmann-La Roche and the mass spectrum determined by Mr. B. J. Millard at the department of Pharmaceutical Chemistry, School of Pharmacy, University of London.

SUMMARY

Methyl ethyl ketone polymerizes when it is passed through a chromatographic column of alumina, a substance with molecular formule of $C_{32}H_{60}O_6$ is produced with removal of water.

The structure of the oily substance with special odor is confirmed by elementary analysis, IR, NMR and mass spectroscopy.

ÖZET

Metil etil keton, kromatografi için kullanılan bazik aluminyum oksid üzerinden geçirildiğinde polimerleşir, bu esnada molekülden su kaybı ile $C_{32}H_{60}H_6$ bünyesinde bir madde meydana gelir. Yağ kıvamında ve özel kokusu olan maddenin yapısı elementer analiz, IR, NMR ve kütle spektrofotometrik metodlar ve bazı reaksiyonlar yardımıyla aydınlatılmıştır.

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