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Synthesis and Polymerization of Methacroylacetone

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SUMMARY:

The synthesis of a polymerizable β-diketone, methacroylacetone, by the usual acylation of an ester by a ketone in the presence of sodium methoxide, is described. However, the reaction with acrylic and methacrylic ester yielded important amounts of secondary products, especially substituted cyclohexanediones; a reaction scheme is proposed, which proceeds through an intermediate Michael addition. The monomeric diketone was polymerized and a high polymer (D.P. 235), was obtained which forms metal chelate complexes analogous to that of the monomer.

RESUMÉ

La synthèse d'une β-dicétone polymérisable, la méthacroylacétone, a été effectuée par la méthode habituelle d'acylation d'un ester par une cétone en présence de méthylate de sodium. La réaction avec les esters acrylique et méthacrylipue fournit toutefois des quantités appréciables de produits secondaires, principalement des cyclohexanediones 1.3, substituées en position 2. Un mécanisme de réaction est proposé, suivant lequel la réaction suivrait un processus d'addition de Michael. La dicétone monomérique a été polymérisée et un polymère de DP 235 a été obtenu; ce polymére fournit des complexes chélatés avec les métaux analogues au complexes formés au départ du monomére.

Numerous data on the synthesis of α,β-unsaturated β-diketones are given in the literature[2, 3, 4]); however, most of those are devoted to the preparation of ketones containing cinnamic or crotonic moieties.

A diketone, which could be eventually polymerized has been synthesized by Hurd[5]), by condensation of ethyl acrylate and 2-octanone in the presence of sodium methoxide; the structure proposed by the author for this reaction product was that of the 1-undecene-3,5-dione. Since our

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[2]) C. R. Hauser and alii: "Organic reactions" Vol. VIII, Chapter 3, J. Wiley and Sons, Inc., New York 1954.

[3]) C. R. Hauser, R. S. Yost and B. I. Ringler, J. org. Chemistry **14** (1949) 261.

[4]) B. O. Linu and C. R. Hauser, J. Amer. chem. Soc. **78** (1956) 6066.

[5]) C. D. Hurd and C. C. Kelso, J. Amer. chem. Soc. **62** (1940) 2184.

laboratory was interested in the synthesis of pure⁶) polymeric diketones, the method of **HURD** has been further investigated; unfortunately, it was found surprisingly that the product described by **HURD** could not be polymerized, and therefore would have another structure than that proposed by this author. A systematic study was then undertaken to elucidate its structure⁷) and to synthesize a polymerizable β-diketone.

Experimental

1. *Synthesis of methacroylacetone*

1 M. of dry powdered sodium methoxide was prepared²) in an half-liter three-necked flask fitted with a dropping funnel, a reflux condenser (protected with a Drierite tube) and a sealed stirrer. 1 mole of pure dried methyl methacrylate (with inhibitor) was added to the base under vigorous stirring and cooling. After 10 minutes, 1 mole of dried acetone was added dropwise under vigorous stirring at 0 °C.; the mixture was kept overnight in an icebox and then poured on 200 g. of crushed ice. The aqueous layer was separated, washed with ether, acidified with hydrochloric acid to pH 5, and extracted 4 times with ether.

The ethereal solution was washed with saturated sodium bicarbonate solution, dried over sodium sulphate and the solvent removed.

Two main fractions were separated by rapid distillation of the ethereal extract, one from 40–95 °C. at 18 mm.Hg., the second from 107–117 °C. at 18 mm.Hg.⁸).

The first crude fraction contained principally methacrylic acid and methacroylacetone, while the second one gives on further purification 4- methyl 1.3- cyclohexanedione (yield 5–10%).

In order to isolate the methacroylacetone from its mixture, the first fraction has been diluted with an equal volume of ethanol and poured in a large excess of copper acetate solution, saturated with ammonia. The copper chelate of the diketone falls out; it is filtered off and washed with water. Overall yield 5%. The copper chelate can be recrystallized from 90% ethanol: m.p. 167–167.5 °C. Calculated for $CuC_{14}H_{20}O_4$: Cu 20.1, Found Cu 20.6. The copper chelate was decomposed in the presence of ice-cold 10% sulfuric acid and the mixture extracted three times with ether; the ethereal extracts were washed and dried. Distillation afforded a 90% yield of pure methacroylacetone b.p. 70–72 °C/17 mm.Hg.

Several other methods were applied unsuccessfully to the preparation of this compound. The same procedure, as described above, was followed during the condensation of methylacrylate and methylmethacrylate with methyl-hexyl and methyloctylketone. Products

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⁶) U.S.P. 2,613,200, **RÖHM** and **HAAS**, oct. 7, 1952, described the preparation of a polydiketone from acetone and polyalkylacrylate; however no structural details concerning the polymer obtained were given, and its properties did not correspond exactly to those expected for a polyacroylacetone.

⁷) It is also interesting to note that the properties of the compound obtained by Hauser⁴) by condensation of crotonyl chloride and 2-octanone are different from those of the compound synthesized by **HURD**⁵) from ethyl crotonate and the same octanone.

⁸) Melting points and boiling points are uncorrected.

corresponding to the compound described by HURD[5]) (as acroyloctanone) were isolated by crystallization in ethyl acetate or by high vacuum distillation; they were identified as substituted cyclohexanedione (see further).

Infrared spectra were recorded on a model 21 PERKIN-ELMER double beam spectrometer equipped with a rock salt prism.

The titration of the different diketones were carried out with sodium methoxide in benzene in 1% pyridine solutions. A 1% pyridine solution of thymolphthalein was used as indicator[9]).

The copper content of the chelate complex was determined iodometrically after decomposition of the products in concentrated sulfuric acid[10]).

2. *Polymerization*

Polymerization of the methacroylacetone was carried out in bulk, by heating up for 15 hrs. at 80 °C. in the presence of 1% benzoyl peroxide or for 24 h. at 60 °C. in the presence of 0.5% azobisisobutyronitrile (polymerization occured also in the presence of UV light).

The polymer is dissolved in chloroform and precipitated in ether, then redissolved in dioxane and precipitated in methanol. The white powder is dried at 40 °C. under vacuum. Neutralization equivalent: calc. 126, found 127. The degree of conversion is about 80%.

The copper chelate of the polymer was prepared by mixing a dioxane solution of the polydiketone with an excess of a copper acetate dioxane solution. Saline water was added; the green polymer was filtered off and washed thoroughly with water. Copper content: calcul. 20.1%, found 19,5% (97%).

The polymer gave also a positive test with a solution of ferric chloride (deep violet coloration of the powder).

3. *Copolymerization*

The copolymerization experiments were carried out in benzene solution at 65 °C. in the presence of 0.5% azobisisobutyronitrile during about 5 hrs. The monomers and solvent were previously distilled under a nitrogen atmosphere; nitrogen was also bubbled through the tubes before sealing off. The yields were limited between 5 to 10%. The copolymers are purified by several dissolution and precipitation cycles, in benzene-ligroin or dioxane-alcohol, and thereafter dried at 40 °C. under high vacuum.

The diketone content of the methacroylacetone-styrene copolymer was determined by direct titration in pyridine, while the tyrene content was determined by quantitative infrared spectrometry at 14.30 μ. Both values were found in close agreement.

The methacrylic acid content of the other type of copolymer was determined by differential potentiometric titration in 80% acetone - 20% water solutions, under a nitrogen-atmosphere.

4. *Molecular weight determination*

The degree of polymerization of the polydiketone was determined by the osmotic method in a FUOSS-MEAD type apparatus at 25 ± 0.02 °C. The solvent used was chloroform

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[9]) L. F. AUDRIETH and J. KLEINBERG: "Titrations in Nonaqueous Solvents", J. Wiley and Sons, Inc., New York 1953, p. 128.

[10]) A. VOGEL: "Quantitative Inorganic Analysis", Longmans Green Co., London 1953, p. 343.

pro analysi. Molecular weights were evaluated by plotting reduced osmotic pressure versus concentration and extrapolating to zero concentration (RT constant used for chloroform was 171,000).

The limiting viscosity numbers were determined in a modified UBBELOHDE viscometer[11]) at $25 \pm 0.02\,^{\circ}C$. The solvents were chloroform or water-free dioxane. The unit of concentration used was g./100 ml.

Discussion of Results

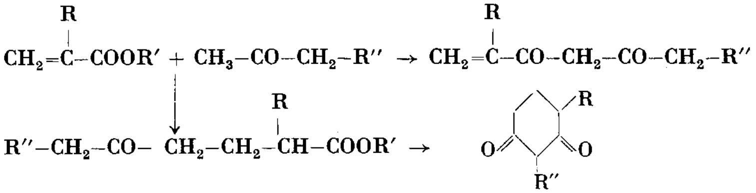
I. Structure of the condensation products

A. Cyclic diketones

Several compounds (including that described by HURD) obtained by condensation of alkyl acrylates or methacrylates with hexyl methyl ketone or octyl-methyl ketone in the presence of the corresponding sodium alkoxide, were investigated by titrimetry in non-aqueous solvents and by infrared spectrometry.

The very weak acidic properties of these products as well as their neutralization equivalent (determined in non-aqueous solvents) agreed very well with the brutto formula proposed by HURD; however the compounds failed to polymerize in the presence of various catalysts such as benzoyl peroxide, azobisisobutyronitrile, and ultraviolet irradiation. This behavior seemed unexplicable for vinyl derivatives in which the terminal double bond is directly conjugated to a carbonyl function (acrylic and methacrylic derivatives). Indeed, the infrared spectra of these compounds did not indicate a conjugated β-diketone structure; moreover any absorption band characteristic of a vinyl or isopropenyl double bond was absent. Further, the enol-content was low, and the intensity of the absorption band corresponding to the chelated carbonyl group was dependent on the dilution: this behavior, characteristic of an intermolecular association for sterically hindered cyclohexanediones, is again unexplicable for chain diketones in which intramolecular hydrogen bonding is largely predominant (chelation)[12]).

A substituted cyclohexanedione structure was therefore attributed to the products obtained; it would result from a MICHAEL condensation reaction followed by an usual intramolecular acylation, as indicated in the following reaction scheme.



$$CH_2{=}\overset{R}{C}{-}COOR' + CH_3{-}CO{-}CH_2{-}R'' \rightarrow CH_2{=}\overset{R}{C}{-}CO{-}CH_2{-}CO{-}CH_2{-}R''$$

$$R''{-}CH_2{-}CO{-}\,CH_2{-}CH_2{-}\overset{R}{CH}{-}COOR' \rightarrow$$

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[11]) V. DESREUX and J. BISCHOFF, Bull. Soc. chim. Belgique **59** (1950) 98.

[12]) M. C. DE WILDE-DELVAUX and PH. TEYSSIÉ, in press.

These results were checked by the hydrolysis of the cyclohexanediones which, in contrast to the open-chain diketones, yield an acid of the same number of carbon atoms as that of the starting product. All the results obtained are summarized in table I.

Tab. 1 Properties of the β-diketones obtained by acylation of (meth)acrylic esters.

Starting Products		Neutral. eq. of dik.		Neutr. eq. of Hydr. pod.		Yield % of diketone	m.p. or b.p.
Ketone	Ester	Theor.	Found	Theor.	Found		
Methyl octyl	Me acrylate	210	208	228	236	18	70-71 °C.
	Me methacrylate	224	220	242	253	28	165-170 °C/10 mm
Methyl hexyl	Me acrylate	182	178	200	207	48	68-69 °C.
Acetone	Me methacrylate	126	118	144	152	8	104-114 °C/17 mm[b]
		126[a]	127	—	—	5	70-72 °C/17 mm

a) Methacroylacetone. b) With some decomposition.

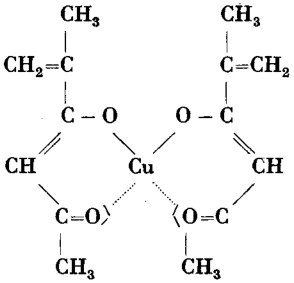
B. Methacroylacetone

A polymerizable open-chain diketone was synthesized by reacting methyl methacrylate with acetone: besides several by-products a low yield of methacroylacetone was obtained which has been isolated as a copper-complex by a systematic investigation of the different fractions.

The reaction seems to follow the same reaction scheme as described above. No improvement of the yield could be obtained by varying the structure of the ester (methyl, ethyl or phenyl methacrylate), the nature of the catalyst (higher alkoxides, sodamide, sodium) or by using methacroyl chloride instead of methyl methacrylate in a procedure analogous to that described by HAUSER[4]).

Moreover, the synthesis of the corresponding acroylacetone (from acetone and methyl acrylate in the presence of sodium methoxide) was unsuccessful; the diketone formed in the reaction medium (as shown by the purple ferric chloride test) polymerized spontaneously during the purification of the product. From the reaction mixture of acetophenone and phenyl methacrylate a 30 % yield of copper complex can be isolated with a degree of purity of 92 %: however its structure could not be completely elucidated.

The neutralization equivalent of the pure methacroylacetone as well as the copper content of its complex correspond very closely to the expected structure (101 and 102 % respectively), the theoretical copper content being calculated on the basis of a tetradentate coordination compound.



The structure of the diketone was also proved by infrared spectrometry: besides the absorption bands characteristic of the keto groups (free at 1720 and 1667 cm^{-1} chelated keto-enol at 1583 cm^{-1}), a C═C double bond absorption (independent of that of the enol form) was found at 1633 cm^{-1}.

The chelated-enol content was very high and has been evaluated to about 90 %. The product gives also an intense purple color test with ferric chloride.

II. Polymerization

Methacroylacetone has been polymerized in bulk or in solution under the influence of benzoyl peroxide, azobisisobutyronitrile or U.V. light. After purification a white powder was obtained; its structure was investigated by the same methods as for the monomer.

This polydiketone was almost exclusively in the enol form, as indicated by a strong absorption at 1605 cm^{-1} [8]), and the lack of the two bands characteristic of the both free keto-groups around 1675 cm^{-1}. This enolization, more complete than in acetylacetone, must be correlated with the more electronegative character of the tertiary substituted carbon atom. As could be expected, the C=C absorption band at 1633 cm^{-1} disappeared entirely from the spectrum.

The neutralization equivalent corresponded to the theoretical value 127 instead of 126 (theor.).

The polymer was soluble in several organic solvents as dioxane, chloroform, acetone, toluene, and in aqueous sodium hydroxide solution; it was insoluble in diethyl-ether, petroleum ether, alcohol and water; it became deeply violet in the presence of ferric ions.

Its molecular weight was evaluated by osmotic measurements (in chloroform solution) to 29,600 (DP = 235). A somewhat unexpected result was the viscometric behavior of this polymer: the limiting viscosity number in dioxane solution was 0.20 (k′ = 0.12) while the extrapolated value in chloroform solution was only 0.03 (k′ = 377), both plots giving quite reproducible straight lives.

The copper chelate complex of the polymer was also prepared. Excepted the 1633 cm^{-1} absorption band corresponding to the C=C double bond, the infrared spectrum of that complex corresponds exactly to the spectrum of the monomeric one. Its copper content amounts to 97 % of the theoretical value: since the reaction between a divalent reagent and a polymeric chain with uniform distribution of the reactive functions is limited to 86 % for statistical reason[13]) intermolecular complexion must take place in this case: this result is enhanced by the insolubility of the polymeric complex, while both the free polymeric diketone and the monomeric copper complex are quite soluble in a wide range of solvents.

The polymeric copper-complex as well as monomeric one can be decomposed by dilute mineral acids (N solution) and yield again the free polydiketone.

Any attempt to polymerize the monomeric copper complex in concentrated solution in the presence of various catalysts, were unsuccessful.

Methacroylacetone has been copolymerized very easily with several monomers, namely styrene, methacrylic and N-vinylpyrrolidone. On account of the high reactivity of its double bond, the molar fraction of methacroylacetone in these polymers was always higher than the molar fraction in the solution of the monomers. Some details concerning these data will be published later.

Conclusion

The β-diketone obtained from methylmethacrylate and acetone was proved unequivocally to be the methacroylacetone, and the chemical properties of this monomer and its polymer were found to be quite similar.

More detailed studies will be published shortly, namely on the determination of the stability of the metal chelate complexes formed by these compounds and also on the kinetic behaviour of this new monomer during polymerization.

Acknowledgment

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[13]) P. J. FLORY, J. Amer. chem. Soc. **61** (1939) 1518.