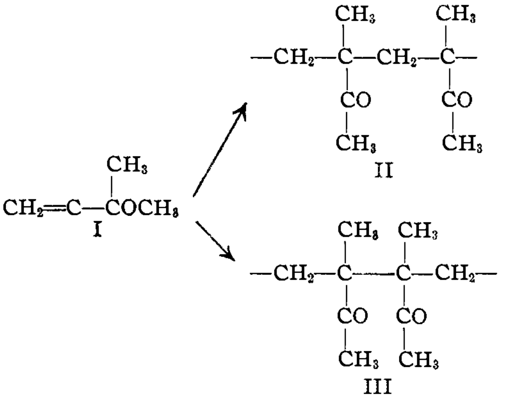
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Structure of Vinyl Polymers. XII.[1] The Polymer of Methyl Isopropenyl Ketone

By C. S. Marvel, E. H. Riddle,[2] and J. O. Corner[3]

The object of the present investigation was to determine whether the polymer of methyl isopropenyl ketone (I) had the monomer units joined together in a "head to tail" (II) or "head to head, tail to tail" (III) manner. Since the polymer of methyl vinyl ketone has the "head to tail" type of structure,[4] the same arrangement might be expected for the methyl isopropenyl ketone polymer as well.

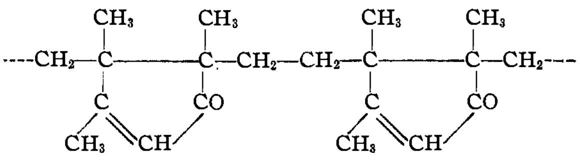


Methyl isopropenyl ketone has long been known to polymerize readily.[5] Staudinger and Ritzenthaler[5d] report that slow polymerization at room temperature gives a glass-like mass with a molecular weight of about 120,000 which is insoluble in carbon disulfide, carbon tetrachloride, benzene, tetralin and decalin but soluble in acetone, dioxane and pyridine. By activating the monomer with ultraviolet light, a polymer of about 40,000 molecular weight was obtained.[5d]

In confirmation of these reports, we have found that methyl isopropenyl ketone can be readily polymerized either by activation with ultraviolet light or by catalysis with 1% of benzoyl peroxide at 25°. The second process is slightly slower than the first and results in material of slightly higher molecular weight. The polymer is readily obtained as a white solid by slowly dropping its acetone solution into water (at least 100 cubic centimeters of water for each gram of polymer) with good agitation. Using Staudinger's viscosity constants for this polymer, the product from ultraviolet light catalysis was found to have a molecular weight of about 11,200. The polymer prepared by use of 1% benzoyl peroxide as a catalyst had a molecular weight of about 36,000. When polymerization was carried out at 60° in acetone solution, the molecular weight was about 6000; and at 60° without a solvent, about 12,000. In all cases our polymers seemed to have a much lower molecular weight than have been previously reported.[5d]

When the polymer of methyl isopropenyl ketone, prepared in the presence of ultraviolet light, was heated to 270–300°, it lost water readily, and no serious degradation of the carbon chain took place. The distillate contained water, a little monomer and some dimer[5d] with insignificant amounts of higher boiling organic compounds. The residual polymer was a dark brown mass readily soluble in acetone. This solubility indicated that the polymer was still essentially linear. Analysis of this residue showed that 63% of the oxygen originally present in the polymer was removed by the pyrolysis. Pyrolysis at 360° over a five-hour period gave the same results.

The loss of more than 50% of the oxygen from the polymer of methyl isopropenyl ketone on pyrolysis indicates that the polymer may have the "head to tail" structure (II). The water must be lost by an internal aldol condensation. In the case of a "head to head, tail to tail" polymer (III), this reaction could give five-membered cyclic ketone rings along the chain (IV) and these would be isolated in such a way that further condensation to remove more than 50% of the oxygen would have to involve cross-linking of chains, in which case the product would be expected to be insoluble in acetone.



IV

On the other hand, the "head to tail" structure (II) would lead to six-membered rings along the

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(1) For the eleventh paper see This Journal, **62**, 3499 (1940).

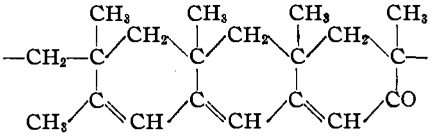
(2) Monsanto Fellow in Chemistry, 1940–1941.

(3) Monsanto Fellow in Chemistry, 1941–1942.

(4) Marvel and Levesque, This Journal, **60**, 280 (1938).

(5) (a) German Patent, 309,224; *Friedl.*, **13**, 643 (1917); (b) British Patents 404,317, 408,063 (1934); (c) U. S. Patent 2,005,295 (1935); (d) Staudinger and Ritzenthaler, *Ber.*, **67**, 1773 (1934).

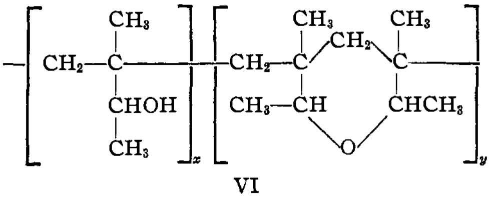
chain and these cyclic ketone units could undergo further loss of water to form complex polynuclear units (V) in a linear polymer structure. In the case of the polymer of methyl vinyl ketone,[4] pyrolysis removed 79–85% of the oxygen as water. In a random aldol type of condensation in such a molecule, as is represented by a "head to tail" polymer from methyl vinyl ketone or methyl isopropenyl ketone (overlooking steric factors), it has been calculated[6] that the loss of oxygen as water should take place to the extent of $^{1}/_{2}e$ or 81.6%. By similar calculation it was estimated[6a] that a polymer of random structure should lose 68.8% of its oxygen as water, while a "head to head" polymer would lose exactly 50% of its oxygen as water.



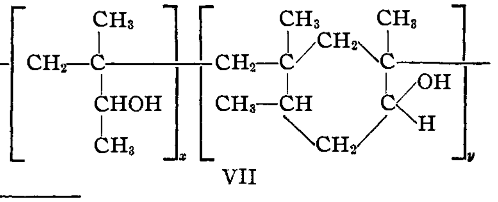
V

The greater degree of steric hindrance in the methyl isopropenyl ketone polymer may be responsible for the less complete condensation reaction, or it is possible that there is a random arrangement of the units which is responsible for the intermediate loss of water in this case.

Further evidence that the polymer of methyl isopropenyl ketone has the "head to tail" structure was obtained by catalytic reduction of the polymer over Raney nickel.[7] During reduction at 175° and 2000 pounds pressure in dioxane solution, a considerable amount of oxygen was removed from the polymer. The composition of the reduction product corresponded very closely to that of a polymer of type VI or VII in which ring closure has occurred to the extent of 86.47%. This is the extent to which ring closure may occur when the cyclic molecule produced is incapable of further reaction.[6b] To obtain VII, it would be necessary for hydrogenation to occur as soon as aldol condensation produced a cyclic ketone or further loss of oxygen would have resulted (see formula V).



VI



VII

To distinguish between those two possibilities (VI and VII) the compound was acetylated and also chloroacetylated. The acetyl derivative was analyzed for acetyl groups and the chloroacetyl derivative for chlorine. These experiments showed conclusively that the reduction product was the mixed alcohol-ether (VI).

Experimental

Polymerization of Methyl Isopropenyl Ketone.—The polymerizations were carried out with methyl isopropenyl ketone, b. p. 45–46° (40 mm.), prepared by the condensation of formaldehyde with methyl ethyl ketone, followed by dehydration with oxalic acid.[8] Boron fluoride always produced a black insoluble polymer and cadmium chloride gave no polymer. Catalysis with benzoyl peroxide and activation with ultraviolet light both produced a polymer. The experiments are summarized in Table I.

TABLE I

POLYMERIZATION OF METHYL ISOPROPENYL KETONE

Monomer, g.	Solvent (Acetone)	Catalyst	Temp., °C.	Time of standing	Yield, g.	Mol. wt. based on viscosity of acetone soln.
14	20	None	60	10 days	5	6,050
18	None	None	60	8 days	4	12,000
60	200	1% Bz_2O_2	60	2 weeks	20	5,000
16	None	1% Bz_2O_2	25	5 weeks	10	36,000
40	None	None	25	5 weeks	4	25,900
20	30	1% Bz_2O_2	25	5 weeks	6	12,200
100	None	Ultraviolet light	25	5 weeks	75	11,200

Pyrolysis of Polymer.—Fifteen grams of polymer was placed in a 250-cc. Claisen flask bearing a capillary tube through which a slow stream of nitrogen was passed. The side-arm of the distilling flask was led into a large test-tube immersed in an acetone–solid carbon dioxide-bath. The polymer was quickly heated to 270° and the pressure reduced to 5 mm. Over a period of five hours the temperature of the heating bath was gradually raised to 300°. The pressure was then allowed to come to normal and the flask cooled to room temperature.

The brown residue was dissolved in 300 cc. of hot acetone and this solution was poured into an equal volume of water. The polymer which precipitated was filtered off and dried. For analysis this brownish powder was dried under reduced pressure at 100° for eight hours.

Anal. Found: C, 84.28; H, 8.72.

A second 36-g. sample was pyrolyzed for five hours at 360°. The residual polymer was treated as above.

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(6) (a) F. T. Wall, private communication. (b) Flory, private communication, see also THIS JOURNAL, **61**, 1518 (1939).

(7) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

(8) Morgan, Megson and Pepper, *J. Soc. Chem. Ind.*, **57**, 885 (1938).

Anal. Found: C, 84.34; H, 8.04.

The distillates were redistilled. The first portion boiled at 80–85° and was an azeotrope of water and methyl isopropenyl ketone. The second fraction was water, boiling at 98–100°. A very small third fraction boiling at 55–60° (3 mm.) was evidently the dimer, 2,6-dimethylocten-1-dione-3,7, which forms when methyl isopropenyl ketone is heated to 100°.[5d]

Reduction of the Polymer of Methyl Isopropenyl Ketone.—To a solution of 25 g. of polymer (mol. wt. 11,200 by viscosity determination) in 600 cc. of dioxane was added 90 g. of Raney nickel. The mixture was shaken in a hydrogen atmosphere at 175° and 2000 pounds pressure for about seventeen hours until there was no further absorption of hydrogen. After cooling the mixture, the bomb was opened, the catalyst filtered, and the clear solution was poured slowly into a large volume of water. The reduction product separated and was collected on a filter. It was further purified by solution in methyl ethyl ketone and reprecipitated by pouring this solution into twice the volume of water. The product was then dried. The yield was 19 g. of a white powdery material melting over a range of 195–205°.

Anal. Calcd. for Formula VI or VII (86.47% ring closure): C, 76.71; H, 11.68. Found: C, 76.02, 75.84; H, 11.39, 11.39.

One attempt to reduce the polymer in dioxane at 200° caused a violent decomposition of the dioxane and the safety plug of the bomb blew out.

Chloroacetylation of Reduction Product.—Three and one-half grams of the reduction product was treated with 28 cc. of chloroacetyl chloride and 5 cc. of pyridine at room temperature for twenty-four hours. The mixture was poured into water, the polymer filtered, dissolved in methyl ethyl ketone and reprecipitated by pouring the solution into water. This was repeated three times, and then the polymer was washed with water until the washings gave no test for chlorine. The product was dried at 70° and then weighed 2.6 g. It was a white powdery material melting at 195–205°.

Anal. Calcd. for chloroacetyl derivative of VI: C, 71.41; H, 10.47; Cl, 5.42. Calcd. for chloroacetyl derivative of VII: C, 60.48; H, 8.04; Cl, 16.57. Found: C, 72.38, 72.70; H, 10.98, 10.68; Cl, 3.67, 3.47.

Acetylation of Reduction Product.—Two grams of the reduction product was treated with 20 cc. of acetic anhydride and 20 cc. of dry pyridine at room temperature for thirty-six hours. The mixture was diluted to 200 cc. with methyl ethyl ketone and poured into water. The polymer was filtered and purified by reprecipitating twice from methyl ethyl ketone solution and finally washing with water. The product was dried at 70° and then weighed 1.4 g. It was a white powdery material melting at 190–200°.

Anal. Calcd. for acetyl derivative of VI: C, 72.08; H, 10.14; CH_3CO-, 23.90. Calcd. for acetyl derivative of VII: C, 75.33; H, 11.28; CH_3CO-, 6.93. Found: C, 75.47; H, 11.35; CH_3CO-, 6.84.

The analysis for acetyl groups was carried out by the method of Matchett and Levine.[9]

Summary

The polymer of methyl isopropenyl ketone has been shown to have a "head to tail" type of structure.

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(9) Matchett and Levine, *Ind. Eng. Chem., Anal. Ed.*, **13**, 98 (1941).

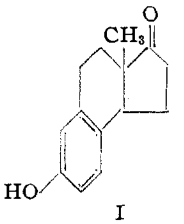
URBANA, ILLINOIS RECEIVED SEPTEMBER 24, 1941

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Synthesis of an Analog of the Sex Hormones

BY W. E. BACHMANN AND DONALD G. THOMAS

In connection with our investigations on the synthesis of sex hormones and related compounds[1] we have prepared 6-hydroxy-2-methyl-3′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (I). We were interested in determining the estrogenic activity of this compound in view of similarity in structure with estrone (II).



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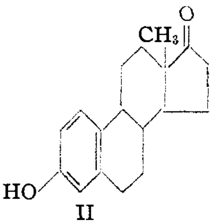

II

The compound was synthesized in *cis-* and *trans-*forms from 6-methoxy-1-tetralone by the procedure employed for the preparation of the desoxy derivative.[2] Since the actual configurations have not been determined the two forms have been designated by the prefixes α and β. The α-form was inactive in 5 mg. doses but the β-form induced the estrus response when injected into ovariectomized rats in 5 mg. doses.

We are grateful to Miss Helen C. McRae of the Department of Gynecology and Obstetrics of this University for these tests and to the Horace H. Rackham School of Graduate Studies for a generous grant which made possible this investigation.

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[1] For the most recent article in this series see Bachmann and Holmes, THIS JOURNAL, **63**, 2592 (1941).

[2] Bachmann and Thomas, *ibid.*, **63**, 598 (1941).