[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Polycondensation of α-Methylacrolein

BY EVERETT E. GILBERT[1] AND JOHN J. DONLEAVY

It was shown by von Pechmann and Röhm[2] that in the presence of sodium methylate, methyl acrylate polycondenses to give a 10% yield of α-methyleneglutaric ester together with an uninvestigated higher fraction. A similar dimerization also was observed[3] in the case of methyl crotonate when an ether solution of this compound was exposed to the action of sodium methylate. Michael[4] obtained the same dimer by the action of sodium upon an ether solution of the ester.

In a discussion of the probable mechanism of the reaction, von Pechmann suggests that a molecule of sodium methylate first adds to the heteroconjugate system of a molecule of acrylic ester, thus producing the sodium enolate of a saturated molecule containing an active methylene group. In the presence of the strongly alkaline catalyst, a Michael reaction was thought to occur between this saturated molecule and an acrylic ester molecule. Loss of sodium methylate led to the formation of α-methyleneglutaric ester as the final product.

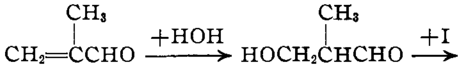
The purpose of this article is to record a similar type of polycondensation for α-methylacrolein. This investigation was conducted in connection with a study of the Michael polycondensation of various alpha, beta-unsaturated compounds being undertaken in this Laboratory. In this case the reaction occurred easily in the presence of dilute aqueous alkali. This extreme ease of reaction may be explained in part by the greater activation of the aldehyde group as compared to the ester grouping of ethyl acrylate. In addition, the final molecules produced from the methylacrolein contained no olefinic bonds, the addendum (water) being incapable of removal except by ring formation when stage II has been reached. A parallel is found in the dimerization of methyl vinyl ketone in the presence of dilute aqueous alkalies to produce octanol-8-dione-2,6.[5] A similar reaction, to be reported subsequently, has been observed in the case of acrolein.

Three polymers were isolated and identified—a trimer, a tetramer, and a pentamer. All three contained a molecule of water introduced during the polycondensation. They gave an immediate precipitate with Tollens' reagent, a delayed but positive test with Schiff's reagent, and an immediate precipitate of manganese dioxide when treated at room temperature with neutral aqueous permanganate. All three fractions yielded yellow 2,4-dinitrophenylhydrazones. As may be seen from Table I, the increases in refractive index and density from the trimer through the pentamer are approximately linear. A similar gradation was observed in the colors—the lowest fraction being colorless, the middle slightly yellow, and the top fraction a deeper shade of yellow. The three fractions were viscous oils, the viscosity increasing through the pentamer. All fractions possessed a mild and slightly spicy odor.

TABLE I

Fraction		Low	Middle	High
B. p.	°C.	113–118	159–164	175–180
	Mm.	12	12	9
	Bath., °C.	135–140	195–210	200–210
d^{20}_{20}		1.017	1.062	1.096
$n^{20}\text{D}$		1.4441	1.4657	1.4867
$Mk\text{D}$	Calcd.	59.41	78.01	96.61
	Found	59.61	77.73	96.60
Mol. wt.	Calcd.	228	298	368
	Found	237	288	371
Carbon, %	Calcd.	63.12	64.43	65.18
	Found	62.80	64.64	65.55
Hydrogen, %	Calcd.	8.77	8.73	8.70
	Found	8.94	8.86	9.00

The mechanism of the polycondensation is probably as follows. A molecule of water is first added to a molecule of α-methylacrolein, thus forming a β-hydroxyaldehyde containing the necessary active hydrogen. A series of Michael reactions then occurs, leading to the formation of the products isolated. Both of these processes are of a type known to occur with remarkable ease in the presence of alkalies. These reactions may be expressed as follows



$$\underset{\text{I}}{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CHO} \xrightarrow{+HOH} HOCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCHO \xrightarrow{+I}$$

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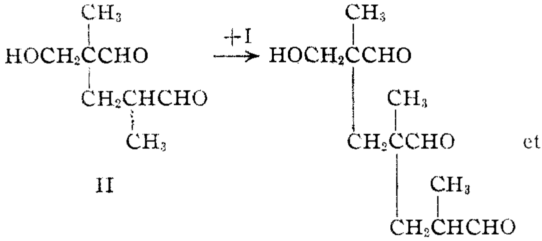
[1] This communication describes work done by Everett E. Gilbert in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] H. von Pechmann and O. Röhm, *Ber.*, **34**, 427 (1901).

[3] H. von Pechmann, *ibid.*, **33**, 3323 (1900).

[4] A. Michael, *ibid.*, **33**, 3766 (1900).

[5] Farbenfabriken vorm Freidr. Bayer and Co. in Elberfeld, German patent, 227,177 (1910).



Experimental

The α-methylacrolein was purchased from the Shell Development Co. It was of about 98% purity and contained 0.05% hydroquinone as an antioxidant. Since it was desired to avoid polymerization produced by peroxides, and since the hydroquinone did not appear to inhibit the polycondensation, it was used as received without further purification.

Thirty-three grams of methylacrolein was mixed with 200 cc. of distilled water. About 50 cc. of ethyl alcohol was added to promote solution and ten cc. of 4% aqueous sodium hydroxide. A brown flash of color appeared which disappeared upon shaking. In about ten minutes turbidity appeared and a yellow oil began to settle. Heat was evolved; the flask was cooled by bathing in cold running water. After allowing the flask to stand for one hour (during which time it was shaken frequently), the solution was extracted three times with ether, and the extract was dried over sodium sulfate. The ether was removed and the oil was fractionated under reduced pressure. In the preliminary distillation three fractions were collected as follows:

(1)	Bath 165–170° (15 mm.)	141.1 g.
(2)	Bath 195–210° (10 mm.)	3.6 g.
(3)	Bath 225–250° (10 mm.)	7.6 g.

The total yield of crude oils was 71.3% of the theoretical Other experiments gave similar results.

Upon redistillation the above fractions were found to consist almost entirely of the pure polymers. The properties were determined from these purified fractions. The molecular weights were determined in freezing benzene. These and other data are listed in Table I.

Preparation of the Tri-2,4-dinitrophenylhydrazones of the Polymers.—The method employed was essentially that suggested by Shriner and Fuson.[6] An equivalent of dinitrophenylhydrazine for each aldehyde group was employed. Yellow tridinitrophenylhydrazones were obtained in each case. The derivative of the trimer separated from the reaction mixture even when boiling. Cooling was resorted to in the other cases to obtain crystallization of the derivatives. They were then recrystallized from benzene. The tridinitrophenylhydrazone of the trimer decomposed to a red liquid at 173–174° (uncorr.), but the other two derivatives decomposed indefinitely as the temperature was raised above 100°.

Anal. Trimer. Calcd. for $C_{30}H_{32}N_{12}O_{13}$: N, 21.8. Found: N (Dumas), 21.4. Tetramer. Calcd. for $C_{34}H_{38}N_{12}O_{14}$: C, 48.65; H, 4.53; N, 20.0. Found: C, 48.60; H, 4.82; N, 20.4. Pentamer. Calcd. for $C_{38}H_{44}N_{12}O_{16}$: N, 18.5. Found: N, 18.5.

Summary

α-Methylacrolein polycondenses by the Michael reaction in the presence of dilute aqueous alkali. A trimer, a tetramer, and a pentamer were isolated and characterized.

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[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 148.

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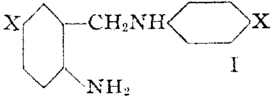
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

A Study of the Conversion of Para-substituted Methylene-bis-arylamines and Trimeric Methylene-arylamines to Substituted 2-Aminobenzylarylamines

BY T. R. MILLER AND E. C. WAGNER

Aminobenzylarylamines of type I may be prepared from para-substituted amines through the reactions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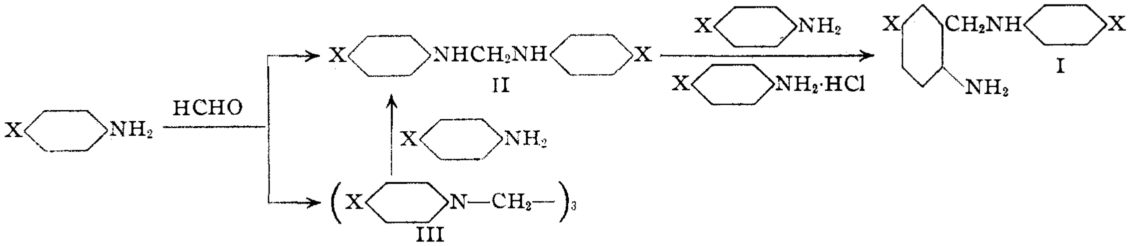

The only published procedure[1] is cumbersome, as it requires mechanical stirring of a mixture of methylene-*p*-toluidine, *p*-toluidine and *p*-toluidine hydrochloride for forty-eight hours at 20°, in the presence of enough nitrobenzene to yield a mass which is finally liquid. The mild conditions specified (which greatly prolong the reaction period) are clearly intended to exclude or minimize

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[1] German Patent 105,797; *Friedl.*, **5**, 84; v. Walther and Bamberg, *J. prakt. Chem.*, [2] **71**, 153 (1905).