crystalline substance of definite melting point and was quite soluble in water. The tendency of compounds such as V to undergo intra- rather than intermolecular condensation is indicated by the work of E. Fischer.[4] When ornithine was treated with methanolic hydrogen chloride β-aminopiperidone resulted rather than the bimolecular condensation product, bis-(γ-amino-propyl)-diketopiperazine. These facts militated against a possible polymeric structure.

The piperidone, II, was hydrolyzed by refluxing with hydrochloric acid. After neutralization and removal of ammonium chloride, dl-ornithine monohydrochloride was isolated in 97% yield. For identification purposes the amino acid was converted to the dipicrate, m. p. 195.5–196.5°, and to ornithuric acid, m. p. 184–185°.[5]

Experimental

Ethyl α-Acetamido-α-carbethoxy-γ-cyanobutyrate (I).— To a solution of 1 g. of sodium in 500 ml. of absolute alcohol there was added 217 g. (1 m.) of ethyl acetamidomalonate. The resulting slurry was stirred and cooled while 60 g. of acrylonitrile was added dropwise over a period of twenty minutes. The clear solution was allowed to stand at room temperature for one hour. It was chilled and the solid that separated collected on a filter. The filtrate was poured into cold water whereupon a further quantity of material separated. The solids were combined and dried. The yield of ester, m. p. 92–94°, was 256.5 g. (95%).

Anal. Calcd. for $C_{12}H_{18}O_5N_2$: N, 10.37. Found: N, 10.27.

β-Acetamido-β-carbethoxypiperidone (II).— A quantity of 127 g. of the nitrile (I) was dissolved in 400 ml. of alcohol and reduced in the presence of Raney nickel catalyst at 600 lb. initial pressure at 68°. After one and one-half hours the reduction was complete. The catalyst was removed and the filtrate concentrated *in vacuo* to a small volume. It was chilled thoroughly and filtered. The solid was washed with a small quantity of cold alcohol and then with ether. The yield of glistening white prisms, m. p. 136–138.5°, was 96 g. (90%). A sample was crystallized from ethanol, m. p. 138.5°.

Anal. Calcd. for $C_{12}H_{22}O_5N_2$: C, 52.54; H, 8.09; N, 10.21. Calcd. for $C_{10}H_{16}O_4N_2$: C, 52.62; H, 7.07; N, 12.28. Found: C, 52.86; H, 7.28; N, 12.12.

Ornithine Monohydrochloride.— A quantity of 22.8 g. (0.1 mole) of the piperidone was refluxed with 100 ml. of concentrated hydrochloric acid for four hours and then evaporated to dryness. The residue was taken up in 60 ml. of alcohol and treated with 14 ml. of concentrated ammonium hydroxide. After cooling in ice for one hour the solid was collected. It was suspended in 150 ml. of alcohol, boiled for several minutes, filtered, and washed with two 20-ml. portions of alcohol. After drying, the amino acid melted at 225° and weighed 16.4 g. (97.4%).

dl-Glutamic Acid.— The nitrile (I) (23.5 g.) was refluxed with 75 ml. of concentrated hydrochloric acid for six hours. The solution was then taken to dryness. The residue was taken up in water (25 ml.) and neutralized to pH 3 with concentrated ammonium hydroxide. After purification by the method of Dunn and Stoddard,[6] there was obtained 8.4 g. (66%), m. p. 199°.

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(4) Fischer, *Ber.*, **42**, 4886 (1909).

(5) Adamson, *J. Chem. Soc.*, 1564 (1939), reported the m. p. of ornithine dipicrate as 198–200° and the m. p. of ornithuric acid as 186–187°.

(6) Dunn and Stoddard, *J. Biol. Chem.*, **121**, 527 (1937).

The Copolymerization of Styrene and Maleic Anhydride

BY TURNER ALFREY AND EDWARD LAVIN

The general theory of vinyl copolymerization recently has been discussed by several investigators.[1,2,3] The essential feature of such copolymerization reactions is that four distinct chain propagation processes are involved. A monomer of type A can add to an active chain-end of type A; a monomer B can add to such an active chain; a monomer A can add to a B chain end, and a monomer B can add to a B chain end. These four processes are governed by the propagation rate constants: k_2^{aa}, k_2^{ab}, k_2^{ba}, k_2^{bb}. The chemical composition and chain structure of the copolymer is determined by two ratios of these rate constants: $\alpha = k_2^{ab}/k_2^{aa}$; $\beta = k_2^{bb}/k_2^{ba}$. A monomer mixture containing the two monomers in the molar ratio (B/A) yields an initial copolymer with the molar ratio b/a, below:

$$\frac{b}{a} = \frac{B}{A} \cdot \alpha \cdot \frac{\beta B + A}{\alpha B + A} \quad (1)$$

The essential correctness of equation (1) has been experimentally verified in a number of cases.[2,4]

Certain symmetrically substituted ethylenic compounds—maleic anhydride, maleic esters, etc.—exhibit a very special polymerization behavior. These monomers do not polymerize alone or at least polymerize only very slowly to yield products of low polymerization degree. In the presence of an ordinary vinyl monomer, however, they often *co-polymerize* very readily and may actually accelerate the polymerization rate. The most reasonable explanation of this apparent anomaly—and indeed the only explanation which also explains the other effects described in this note—is the following: Such monomers have practically no tendency to add to free radicals of similar structure but will add readily to free radicals of the ordinary vinyl type. Whether this is the result of steric or electronegativity effects, it is impossible to say.

When a vinyl monomer (A) such as styrene is copolymerized with a monomer of the maleic anhydride type (B), the normal set of four propagation processes is reduced to 3, since k_2^{bb} is effectively zero. In this special case, the equations relating polymer composition and monomer composition take on a very simple form, since $\beta = 0$. The simplified equation can best be written

$$\frac{a}{b} = 1 + \frac{1}{\alpha} \cdot \frac{A}{B} \quad (2)$$

Equation (2) indicates that (if B is known to be a monomer of the class possessing a vanishing k_2^{bb}) a single experiment at one monomer ratio will

(1) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205–209 (1944).

(2) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

(3) Wall, *ibid.*, **66**, 2050 (1944).

(4) Alfrey, Merz and Mark, Paper presented at A. C. S. meeting, New York, 1944.

determine α and hence, the composition of co-polymer resulting from any other monomer mixture. We have recently found that for the system styrene–maleic anhydride α has a value of about 24.

Experimental

Styrene monomer (Dow N-100) and maleic anhydride (Eastman 1226) were copolymerized in solution in thiophene-free benzene, using benzoyl peroxide as catalyst. While the monomer ratio in the charge was varied, the total concentration of monomers was maintained at 2.0 moles per 1500 g. of benzene solution. The mix was refluxed with vigorous stirring. As soon as a small amount of copolymer formed, the batch was cooled and the copolymer filtered. Except in the last two experiments, the copolymer precipitated in the form of very fine white particles. The polymer was purified by boiling three times in benzene in the ratio of 1 part polymer to 50 parts benzene and the yield determined as closely as possible. After exhaustive vacuum drying, the copolymers were hydrolyzed and dissolved in 0.2 N sodium hydroxide. The maleic anhydride content was determined by electrometric titration.

The resulting data are shown in Table I. In equation (2) "A" and "a" stand for styrene monomer and styrene in the initial copolymer, respectively, and "B" and "b" stand for maleic anhydride monomer and maleic anhydride in the initial copolymer.

TABLE I

Monomer		Copolymer				Calcd.
Mol., % styr.	Mol., % m. a.	Mol., % styr.	Mol., % m. a.	% Yield	α	mol. % m. a.
5	95	50.1	49.9	2.8	11.5	49.9
50	50	51.1	48.9	...	21.7	49.0
83.3	16.7	55.0	45.0	1.9	23.0	45.3
90.9	9.1	57.6	42.4	1.7	28.8	41.3
95.0	5.0	65.7	34.3	1.9	22.2	35.8
95.0	5.0	61.1	38.9	2.9	37.5	35.8

In the determination of the constant, the following sources of error are known: (1) When the molecular ratio of styrene to maleic anhydride in the copolymer is close to 1.0, the calculated constant is unreliable, since small errors in maleic anhydride determination cause the value of α to vary enormously. (2) When the concentration of maleic anhydride is very low in the initial charge (see last two runs), we do not obtain a true initial copolymer because the yield necessary for analysis causes a large change in the ratio of the monomers in the charge. However, by calculating from the yield what the monomer ratio is at the end of the reaction and averaging this with the initial monomer ratio, a better value for the monomer ratio in the charge is obtained for the calculation of α. (3) The copolymers of the last two batches did not retain their particle size in boiling benzene but agglomerated to a soft gel-like mass. This could be due to their high styrene content or to low molecular weight. The per cent. maleic anhydride in the last batch, which is a repeat on the next to last batch, differs beyond the experimental error in analysis. A reasonable explanation for this difference is that the purification technique of boiling the resin in benzene is not reliable with a resin which swells in boiling benzene. In view of these sources of error, a reasonable estimate for α would be 24 ± 5. Using $\alpha = 24$, the mole per cent. maleic anhydride in the initial copolymer has been calculated. The results are shown in the last column of Table I and can be compared with the observed values of column 4.

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The Methylation of p-Methoxy Dibenzoylmethane

BY CHARLES L. BICKEL

In 1926, Bradley and Robinson[1] attempted to methylate p-methoxydibenzoylmethane. Their experiments, inadequately described, were unsuccessful and they concluded that the direct methylation of this diketone was not a likely probability. The above authors then condensed ethyl benzoate and p-methoxypropiophenone in the presence of sodamide to give a yellow solid, melting at 56.5° and giving both a copper salt and an intense ferric chloride coloration. This compound was assumed to be the methyl derivative of p-methoxydibenzoylmethane, I, and the

$$\underset{\displaystyle C_6H_5\!-\!CO\!-\!\overset{\displaystyle |}{C}H\!-\!CO\!-\!C_6H_4OCH_3\text{ -}p}{\overset{\displaystyle CH_3}{}} \qquad \text{I}$$
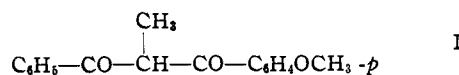
results of alkaline hydrolysis of this substance were compared with those of p-methoxydibenzoylmethane itself.

In 1928, Weygand[2] was unsuccessful in an attempt to prepare I by the action of methyl iodide on the sodium derivative of the diketone, using acetone as a solvent. However, the potassium derivative of the diketone, treated with methyl iodide in ether–benzene solution, gave a colorless solid, melting at 72° and giving neither a copper salt nor a ferric chloride coloration. This substance was converted into an enolic compound by the action of sodium methylate and iced sulfuric acid, and the 72° keto form was regenerated by ordinary recrystallization. The 72° compound has the properties which one would ascribe to I while the properties of the 56.5° compound prepared by Bradley and Robinson are not in agreement with the structure of I.

In order to compare unsymmetrical beta diketones with their methyl derivatives,[3] the author recently set out to methylate the beta diketones by means of silver oxide and methyl iodide[4] in anhydrous ether. p-Methoxydibenzoylmethane can be methylated in this way with no more difficulty than is experienced in the case of dibenzoylmethane, except for the fact that p-methoxydibenzoylmethane is much more insoluble in ether and tends to crystallize on the walls of the flask above the boiling ether. Acetone was therefore substituted for ether as the solvent and the above difficulty was overcome.

The chief product of the reaction of methyl iodide with p-methoxydibenzoylmethane in the presence of silver oxide is the 72° compound previously reported by Weygand. The yield is at least as good and the method is much simpler. The identity of the substance prepared by Bradley and Robinson is as yet obscure but it is

(1) Bradley and Robinson, J. Chem. Soc., 129, 2360 (1926).
(2) Weygand, Ber., 61, 688 (1928).
(3) As yet unpublished.
(4) Abell, J. Chem. Soc., 101, 992 (1912).