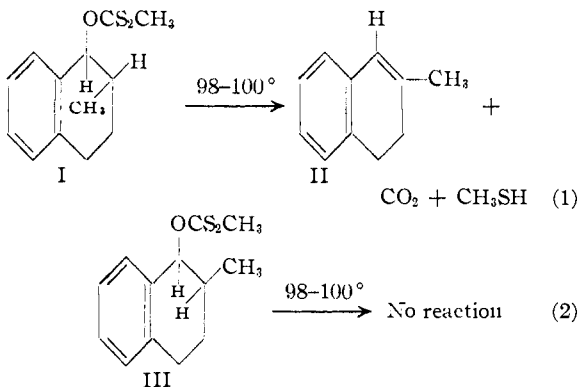


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Studies on the Mechanism of Chugaev and Acetate Thermal Decompositions. III. *cis* and *trans*-2-Methyl-1-indanol

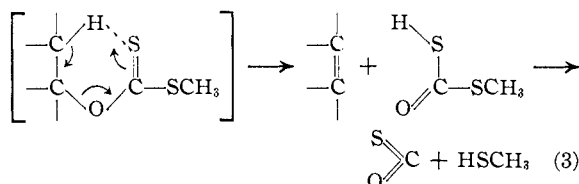
BY ELLIOTT R. ALEXANDER AND ANTON MUDRAK<sup>1</sup>

In the second paper of this series<sup>2</sup> it was shown that, at 98–100°, methyl *trans*-2-methyl-1-tetrahydroxanthate (I) was readily decomposed to 2-methyl-3,4-dihydronaphthalene (II) while the corresponding *cis*-isomer (III) was stable. Similarly, *cis*-2-methyl-1-tetrahydroxanthate was found to be



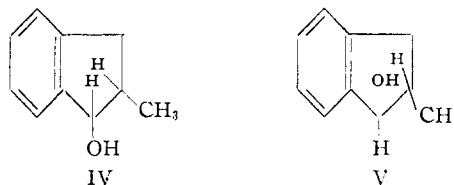
more stable to pyrolysis at 350–550° than *trans*-2-methyl-1-tetrahydroxanthate. Decomposition of the *cis*-isomer, however, was found to lead to 2-methylnaphthalene rather than 2-methyl-3,4-dihydronaphthalene.

Although these experiments support the suggestion that Chugaev<sup>3,4</sup> or acetate<sup>5</sup> thermal decompositions proceed through the formation of a cyclic transition state complex (for example, equation 3), they are not ideal for two reasons. First, in order



to purify methyl *cis*-2-methyl-1-tetrahydroxanthate, a vacuum distillation was necessary. This operation has been reported to convert some xanthates into a form having increased thermal stability.<sup>6</sup> Secondly, in the pyrolysis of *cis*-2-methyl-1-tetrahydroxanthate, the reaction did not simply fail as it had with the corresponding xanthate, but rather the reaction apparently took another course involving simultaneous elimination and dehydrogenation. For an ideal experiment, therefore, the xanthates should be readily isolated from the reaction mixture by crystallization and they should be of such structure that elimination could lead only to one product.

It has been found that the acetates and methyl xanthates of *cis*(IV)- and *trans*(V)-2-methyl-1-



indanol meet these requirements. This paper describes their preparation and a study of their thermal decomposition.

### Experimental<sup>7</sup>

**$\alpha$ -Bromoisobutyryl Bromide.**—The preparation of  $\alpha$ -bromoisobutyryl bromide has been rather poorly described. The following procedure, adapted from that of Berger,<sup>8</sup> was found to be satisfactory.

A mixture of 244 g. (2.77 moles) of isobutyric acid and 25 g. (0.81 mole) of red phosphorus<sup>9</sup> was placed in a 2-liter, 3-necked flask fitted with a reflux condenser, a dropping funnel and an efficient mechanical stirrer. Vigorous stirring was begun and 265 ml. (5.1 moles) of bromine was added at such a rate that the vapors above the solution were never red in color. When about half of the bromine had been added, the mixture was warmed to about 40° and the addition of bromine was continued. A total of about five hours was required for the addition. When all of the bromine had been added, the mixture was heated on a steam-bath until the evolution of hydrogen bromide ceased (20 to 30 hours). The product was then decanted from the viscous residue into a 500-ml. Claisen flask and distilled under reduced pressure. The fraction boiling at 60–75° (23 mm.) was collected (484 g., 76%) and used without further purification in the next step.

**2-Methyl-1-indanone.**—The procedure for the preparation of 2-methyl-1-indanone was essentially that used by Kishner<sup>10</sup> but modified by omitting the alcoholic potassium hydroxide washing operation.<sup>11</sup> Thus from 470 g. (3.56 moles) of anhydrous aluminum chloride, 950 ml. (10.7 moles) of thiophene-free benzene, and 375 g. (1.63 moles) of  $\alpha$ -bromoisobutyryl bromide was obtained 95.1 g. (40%) of 2-methyl-1-indanone, b. p. 80–81° (2 mm.);  $n_D^{20}$  1.5555.<sup>12</sup> The melting points of the semicarbazone,<sup>10</sup> the *p*-nitrophenylhydrazone,<sup>13</sup> the bromo-derivative<sup>14</sup> and the oxime<sup>10</sup> all agreed with the values reported in the literature.

***trans*-2-Methyl-1-indanol.**—A mixture of 43.8 g. (0.3 mole) of 2-methyl-1-indanone, 15 g. of copper-chromium oxide catalyst and 55 ml. of anhydrous ether was hydrogenated at 130° and a pressure of 1800–2600 p.s.i. The theoretical amount of hydrogen was absorbed in 35–40 minutes. The catalyst was removed by filtration and the solvent was evaporated *in vacuo*. The residue crystallized from petroleum ether (42–50°) to give a product melting at 86–88°. The yield in several runs varied from 44 to 63%. An analytical sample was obtained by further recrystallization from petroleum ether, m. p. 88–89°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16. Found: C, 80.97; H, 8.32.

The 3,5-dinitrobenzoate melted at 139–139.5° (90–120° petroleum ether).

(7) All melting points and boiling points are uncorrected.

(8) Berger, *J. prakt. Chem.*, **182**, 294 (1939).

(9) The red phosphorus for this preparation was washed by shaking with several portions of water and dried by heating on a steam-bath under reduced pressure for several hours.

(10) Kishner, *J. Russ. Phys.-Chem. Soc.*, **46**, 1413 (1914).

(11) 2-Methyl-1-indanone can also be prepared by a method recently reported by Fuson and Burckhalter, *This Journal*, **70**, 4184 (1948).

(12) Kishner (ref. 10) reported  $n_D^{20}$  1.5543.

(13) Von Auwers and Aufferberg, *Ber.*, **52**, 92 (1919).

(14) Fuson, Ross and McKeever, *This Journal*, **60**, 2935 (1938).

(1) Colgate, Palmolive-Peet Company, Jersey City, N. J.

(2) Alexander and Mudrak, *This Journal*, **72**, 3194 (1950).

(3) Hüchel, Tappe and Legutke, *Ann.*, **543**, 191 (1940).

(4) Stevens and Richmond, *This Journal*, **63**, 3132 (1941).

(5) Hurd and Blunck, *ibid.*, **60**, 2421 (1938).

(6) McAlpine, *J. Chem. Soc.*, 1114 (1931); 906 (1932); Bulmer and Mann, *ibid.*, 666 (1945).

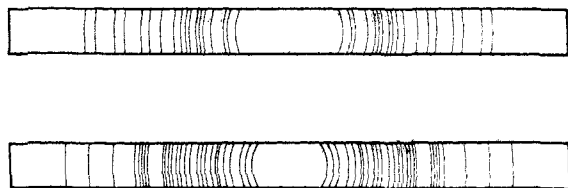


Fig. 1.—X-Ray powder diffraction patterns;  $\text{CuK}\alpha$ ; 40 kv.; 15 M. A.; 8.5 hr.; S. F. D., 7.0 cm.: top, *cis*-2-methyl-1-indanol; bottom, *trans*-2-methyl-1-indanol.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_6$ : C, 59.64; H, 4.12. Found: C, 59.75; H, 4.07.

*trans*-2-Methyl-1-indanol was also prepared in 30% yield by the reduction of 2-methyl-1-indanone with sodium amalgam in ethanol solution following the procedure of Price and Karabinos.<sup>15</sup>

*cis*-2-Methyl-1-indanol.—A mixture of 14.6 g. (0.1 mole) of 2-methyl-1-indanone, 35 ml. of absolute ethanol and 3 g. of Raney nickel was hydrogenated at room temperature and an initial pressure of 45 p.s.i. At the end of 35 hours the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration and the ethanol was evaporated *in vacuo*. The residue was distilled from a short-path distilling flask and the fraction boiling at 62–85° (0.01 mm.) was collected. The product (12.8 g.) solidified on standing at room temperature. Recrystallization from petroleum ether (36–42°) gave 9.7 g. (65%) of *cis*-2-methyl-1-indanol melting at 43–46°. On recrystallization to constant melting point from the same solvent, a product, m. p. 50–51°, was obtained.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{17}\text{O}$ : C, 81.04; H, 8.16. Found: C, 81.22; H, 8.33.

In subsequent runs distillation of the product was found to be unnecessary. After removal of the Raney nickel and ethanol, the residue was dissolved in petroleum ether (42–50°) and crystallization was induced by seeding the cooled solution with some of the pure *cis*-alcohol.

The 3,5-dinitrobenzoate melted at 114.5–115.5° (90–120° petroleum ether).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_8$ : C, 59.64; H, 4.12. Found: C, 59.93; H, 4.24.

The phenylurethan could be recrystallized from the same solvent, m.p. 113–114°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{17}\text{NO}_2$ : C, 76.38; H, 6.41; N, 5.24. Found: C, 76.41; H, 6.31; N, 5.36.

**Isomerization of *cis*-2-Methyl-1-indanol.**—One gram of *cis*-2-methyl-1-indanol, 0.5 g. of copper-chromium oxide catalyst and 15 ml. of absolute ether were shaken at 130° and a pressure of 2400 p.s.i. for 30 minutes in a hydrogenation apparatus. After removal of the catalyst and solvent, the residue was recrystallized once from petroleum ether (38–40°) to give an apparently quantitative yield of product melting at 88–89°. A mixed melting point of this material with a pure sample of *trans*-2-methyl-1-indanol showed no depression.

**Methyl *cis*-2-Methyl-1-indanyl Xanthate.**—This compound was prepared by the method described previously.<sup>16</sup> From 14.8 g. (0.1 mole) of *cis*-2-methyl-1-indanol was obtained 11.1 g. (46%) of crude xanthate. Recrystallization from 95% ethanol gave a product melting at 31–32°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{19}\text{OS}_2$ : C, 60.46; H, 5.92. Found: C, 60.51; H, 5.92.

**Methyl *trans*-2-Methyl-1-indanyl Xanthate.**—This xanthate was prepared by the usual method.<sup>16</sup> From 7.4 g. (0.05 mole) of the *trans*-alcohol was obtained 5.8 g. (48%) of crude xanthate. Recrystallization from 95% ethanol or petroleum ether (42–50°) gave a product melting at 60–61°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{19}\text{OS}_2$ : C, 60.46; H, 5.92. Found: C, 60.56; H, 6.13.

***cis*-2-Methyl-1-indanyl Acetate.**—The procedure which has been previously described<sup>11</sup> was used for the preparation of *cis*-2-methyl-1-indanyl acetate. From 7.4 g. (0.05 mole) of *cis*-2-methyl-1-indanol was obtained 7.6 g. (80%) of the acetate boiling at 77° (0.2–0.3 mm.),  $n_D^{20}$  1.5142.

(15) Price and Karabinos, *THIS JOURNAL*, **62**, 1159 (1940).

(16) Alexander and Mudrak, *ibid.*, **72**, 1810 (1950).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{17}\text{O}_2$ : C, 75.76; H, 7.42. Found: C, 76.00; H, 7.54.

***trans*-2-Methyl-1-indanyl Acetate.**—The acetylation of *trans*-2-methyl-1-indanol was performed in the usual manner.<sup>16</sup> From 14.8 g. (0.1 mole) was obtained 16.8 g. (88%) of the acetate, b. p. 72–78° (0.2–0.3 mm.),  $n_D^{20}$  1.5143.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{19}\text{O}_2$ : C, 75.76; H, 7.42. Found: C, 75.83; H, 7.68.

**Decomposition of the Xanthates.**—The apparatus and procedure used for the decomposition of the xanthates have been described previously.<sup>2,16</sup> The results of the decomposition are shown in Fig. 2.

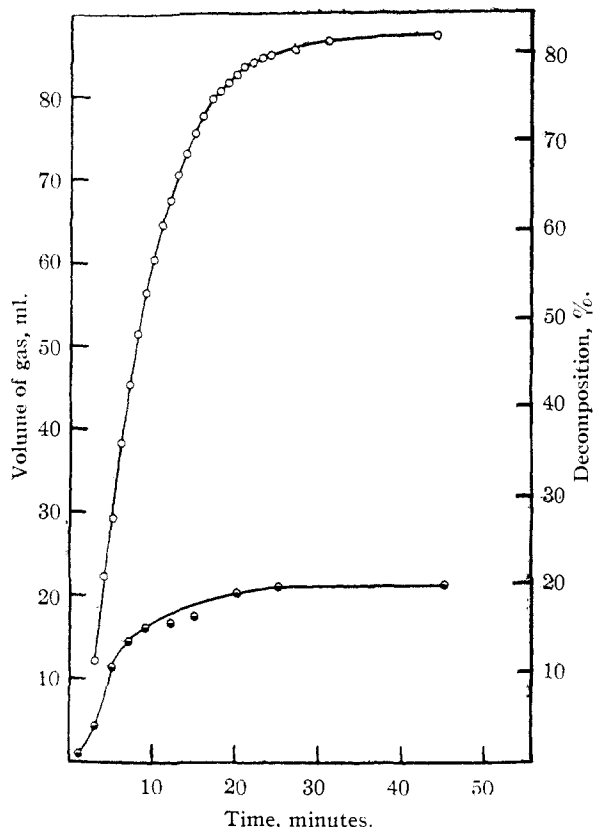


Fig. 2.—Decomposition of the xanthates of *cis*- and *trans*-2-methyl-1-indanol at 98–100°: O, *trans*; ●, *cis*.

The refractive index of the product obtained from the decomposition of *trans*-2-methyl-1-indanyl xanthate varied from 1.5641 to 1.5655 (21°). The material formed a picrate, m. p. 79–80.5°, which showed no depression in a mixed melting point with the picrate of an authentic sample of 2-methylindene.<sup>17</sup>

**Methyl *cis*-2-methyl-1-indanyl Xanthate** decomposed with difficulty. At 300° some 2-methylindene (picrate, m. p. 79–81°) was formed in addition to a considerable amount of high-boiling material which was not investigated further. The picrate showed no melting point depression on admixture with an authentic sample of 2-methylindene picrate.

**Pyrolysis of the Acetates.**—The apparatus and procedure used for the pyrolysis of acetates have already been described.<sup>2,16</sup> The results are summarized in Fig. 3.

The decomposition of *trans*-2-methyl-1-indanyl acetate was almost complete at 450°. The product was 2-methylindene as shown by a mixed melting point of its picrate, 79–80.5°, with the picrate of an authentic sample of 2-methylindene.

A temperature of 650° was required for almost complete decomposition of *cis*-2-methyl-1-indanyl acetate. The product formed a picrate, m. p. 77–79°, which showed no depression in a mixed melting point with the picrate of 2-methylindene.

(17) Koelsch and Johnson, *ibid.*, **65**, 571 (1943).

### Results and Discussion

**Preparation of *cis*- and *trans*-2-methyl-1-Indanol.**—Both the *cis*- and *trans* forms of 2-methyl-1-indanol were prepared by the catalytic hydrogenation of 2-methyl-1-indanone. The *cis*-isomer was obtained when the reduction was performed with Raney nickel at room temperature and at 45 p. s. i. pressure. The reduction required 30 to 40 hours, but the yield of the pure *cis*-alcohol was good (65%).

The *trans*-alcohol was obtained unexpectedly in yields of 44–63% when the reduction was carried out in the presence of copper–chromium oxide at 130° and a pressure of 2000 p. s. i.

Although the stereochemistry of neither of these isomers has been determined by chemical methods, there seems to be no reasonable doubt that they are correct. This conclusion is supported by a number of facts: first, the method of preparation. The isomer we have called *cis* was prepared by the catalytic reduction of an  $\alpha$ -substituted cyclic ketone. There is no case known to us where the low temperature catalytic hydrogenation of such a ketone leads to the preferential formation of a *trans* isomer.<sup>18</sup> The *trans* isomer was prepared by a sodium–alcohol reduction. This method is often employed for the preparation of *trans* 2-alkylcyclohexanols.<sup>19</sup> Second, the *cis* isomer melts lower than the *trans* isomer. While this relationship is not a test in itself, it nevertheless is in the direction which would be expected of molecules such as these in which the ring systems are effectively planar. Third, the data obtained from the powder method of X-ray analysis (Fig. 1) shows that groups of lines which appear in the photographs of both isomers are shifted to larger angles in the case of the isomer we have called *cis*. This indicates closer molecular packing and it is characteristic of the X-ray photographs of *cis* isomers of *cis-trans* pairs.<sup>20</sup> Lastly the *cis*-isomer can be isomerized almost quantitatively to the one we have called *trans*. We know of no instance in which the reverse is true.

**Thermal Decompositions.**—In Fig. 2 is shown a plot against time of the per cent. decomposition at 98–100° of methyl *cis*-2-methyl-1-indanylxanthate and methyl *trans*-2-methyl-1-indanylxanthate. In Fig. 3 is shown a plot of per cent. decomposition against temperature when samples of the corresponding acetates were passed through an electrically heated Pyrex tube packed with glass beads. With both classes of compounds the *cis*-isomers were more stable. At 98–100°, for example, the *trans*-xanthate was 80% decomposed in 25 minutes while the *cis*-xanthate appeared to decompose only to about 20% regardless of the length of time the reaction was allowed to run. Similarly a single pass at 450° through the pyrolysis tube resulted in about 87% decomposition of the *trans*-acetate but only 10% decomposition of the *cis*-acetate.

(18) See for example Skita, *Ann.*, **431**, 1 (1923); Skita and Faust, *Ber.*, **64B**, 2878 (1931).

(19) See for example Price and Karabinos, *THIS JOURNAL*, **62**, 1159 (1940); Godchot and Bedos, *Compt. rend.*, **182**, 394 (1926); and Vavon, Perlin and Horeau, *Bull. soc. chim.*, [4] **51**, 648 (1932).

(20) We are indebted to Dr. G. L. Clark and Dr. Jacob Fuchs for the determination and interpretation of these spectrophotographs.

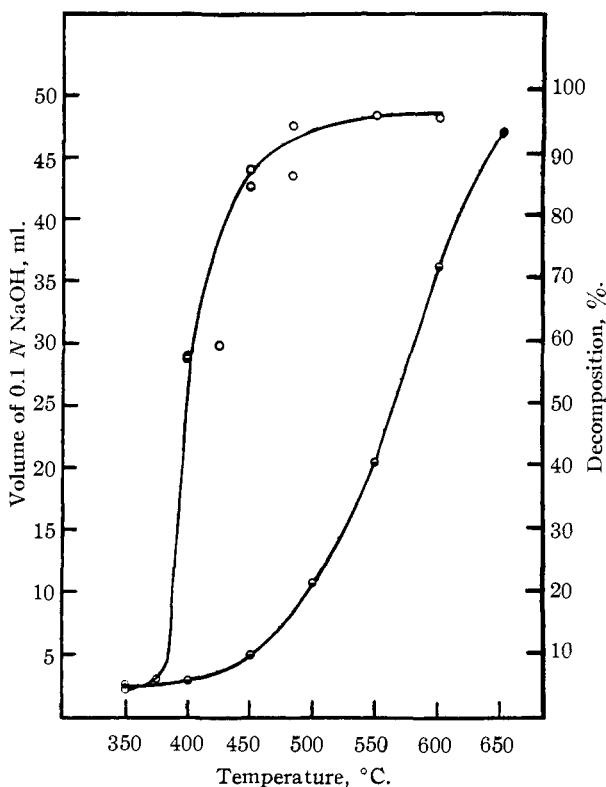


Fig. 3.—Pyrolysis of the acetates of *cis*- and *trans*-2-methyl-1-indanol: O, *trans*; ●, *cis*.

We can conclude, therefore, that these Chugaev and acetate thermal decompositions proceed much more easily when there is a  $\beta$ -hydrogen atom *cis* to the ester linkage. Preferential *cis*-elimination is consistent with the idea of a cyclic transition state complex (equation 3).

It is evident, however, that there must be a path of reaction other than the one involving a cyclic transition state complex by which elimination can proceed. With both the *cis*-acetate and the *cis*-xanthate there is evidence of reaction at low temperatures and with the *cis*-acetate, for example, pyrolysis is almost complete at 650°. Even at this temperature the product is 2-methylindene as shown by a mixed melting point determination of its picrate with that of an authentic sample. Similarly, at 300°, methyl *cis*-2-methyl-1-indanylxanthate gave some 2-methylindene but mostly high boiling material which was not investigated.

The nature of the reaction by which *trans*-elimination occurs is not yet clear. *cis*-Elimination would be expected of a homogeneous unimolecular reaction<sup>21</sup> but we have not yet studied the order of reaction or possible surface effects. From these experiments, however, it would seem that as Chugaev and acetate thermal decompositions are normally carried out, the thermal decomposition of xanthates shows a greater selectivity for *cis*- $\beta$ -hydrogen atoms than does the pyrolysis of acetates.

**Acknowledgment.**—We are indebted to Miss Emily Davis and Miss Rachel Kopel for the microanalyses which are reported.

(21) Barton, *J. Chem. Soc.*, 2174 (1949); Barton and Rosenfelder, *ibid.*, 2459 (1949).

### Summary

Two isomers of 2-methyl-1-indanol have been prepared. One of these, which we believe to be the *cis*-isomer, was obtained by the room temperature hydrogenation of 2-methyl-1-indanone over Raney nickel. The other, which we believe to be the *trans*-isomer, was obtained by hydrogenation of the same ketone at 130° over copper chromium oxide.

A study of the thermal decomposition of *cis*-2-

methyl-1-indanyl acetate and methyl *cis*-2-methyl-1-indanylxanthate has revealed that these compounds are much more stable than the corresponding *trans*-isomers. Decomposition of all of the esters led to 2-methylindene. These results indicate that while a cyclic transition state complex<sup>3,4,5</sup> is probably the preferred intermediate in these reactions, there must be another reaction path by which elimination can occur.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Intermolecular and Intramolecular Cross-Linking in Concentrated Polymer Solutions

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In a number of qualitative studies,<sup>2-4</sup> linear polymer molecules in solution have been cross-linked by chemical reactions to form branched structures and three-dimensional networks. Although the formation of cross bonds was obvious from changes in physical properties and eventual gelation, no information was provided in these earlier investigations concerning the actual number of linkages introduced. The only quantitative studies of the effects of a known number of cross-links on physical properties have been those recently reported by Flory<sup>5</sup> on rubber vulcanized by disazodicarboxylates, in the undiluted state.

In theoretical treatments of the statistics of cross-linking,<sup>6,7</sup> formation of cyclic structures has not been taken into account; in the application of these theories to the linkage of long linear molecules, it must be assumed that each bond is intermolecular, joining two reactive groups on different molecules. It is recognized that some intramolecular bonds are formed, which do not contribute to building up a three-dimensional network, and that the proportion of such intramolecular bonds should be greater if the cross-linking takes place in the presence of an inert diluent. However, there has been no experimental information concerning the actual proportions of intermolecular and intramolecular links.

The present paper describes the introduction of a stoichiometrically known number of cross-links into a solution of linear polymer molecules by quantitative reaction with a cross-linking agent. Since each intermolecular link diminishes the number of molecules by one, while each intramolecular link leaves the number of molecules unchanged, the proportion of intermolecular links can be calculated from the change in number-average molecular weight, and the proportion of intramolecular links

found by difference. The quantity of cross-linking agent employed is sufficiently small so the gel point is not reached.

After preliminary trials with various systems, we chose the reaction between a 1:1 copolymer of styrene and maleic anhydride as the initial linear molecule and a glycol or diamine as the cross-linking agent. This reaction is simple and would be expected to be quantitative. The only solvent found to be suitable was dioxane, which is inert with respect to both polymer and cross-linking agents, and has a dielectric constant sufficiently low so that any occasional hydrolyzed anhydride groups on the polymer remain un-ionized and the complications exhibited by polyelectrolytes with respect to osmotic pressure and viscosity in dilute solution are avoided. Experiments with cross-linking by hexamethylene glycol and benzidine are presented here. Other experiments with hexamethylenediamine gave qualitatively similar results, but are not reported because in this case the reaction was so rapid that it is doubtful whether a homogeneous mixture was achieved before the cross-linking process commenced.

### Materials and Methods

The copolymer of styrene and maleic anhydride (SYHM, Blend 1) was furnished by Union Carbide and Carbon Corporation.<sup>8</sup> It was dissolved in methyl ethyl ketone and fractionated roughly by precipitation with benzene. The first two fractions, A and B, comprising 31 and 29%, respectively, of the original material, were used for cross-linking by benzidine and hexamethylene glycol, respectively. These two cuts did not differ greatly in number-average molecular weight, suggesting that the original material was relatively homogeneous. The fractions were dried by aspiration followed by heating *in vacuo* at 65° for 60 to 70 hours. Although the portions used for cross-linking experiments were not heated above 65° for fear of possible degradation, aliquots heated to 100° *in vacuo* showed a small additional weight loss, and concentrations of solutions made up by weight were expressed in terms of this fully dried material.

Hexamethylene glycol (m. p. 38-41°) was obtained from E. I. du Pont de Nemours and Co., and benzidine (m. p. 127-128°) from H. Rubin.<sup>9</sup> The benzidine was kept under nitrogen. Solutions of the glycol and benzidine were prepared immediately before use. Dioxane was purified by refluxing with hydrochloric acid, neutralization, refluxing

(1) Carbide and Carbon Chemicals Fellow in Physical Chemistry, 1949-1950. Rohm and Haas Co., Philadelphia, Pa.

(2) W. E. Gloor and H. M. Spurlin, *THIS JOURNAL*, **58**, 854 (1936).

(3) R. Signer and P. von Tavel, *Helv. Chim. Acta*, **26**, 1972 (1943).

(4) I. Jullander, *Ark. Kemi Mineral. Geol.*, **21A**, No. 8 (1945).

(5) P. J. Flory, N. Rajjohu and M. Shaffer, *J. Polymer Sci.*, **4**, 225, 435 (1949).

(6) P. J. Flory, *THIS JOURNAL*, **63**, 3083, 3091, 3096 (1941); **69**, 30 (1947).

(7) W. H. Stockmayer, in "High Polymers," edited by S. B. Twiss, Reinhold Publishing Co., New York, N. Y., 1945, p. 61.

(8) We are indebted to Mr. G. M. Powell, Carbide and Carbon Chemicals Division, for this material.

(9) 29 W. 15th St., New York, N. Y.