Experimental[5]

N-(D-Ribityl)-3,4-dimethylaniline (III). Method A. From 4-Nitro-*o*-xylene (I).—A mixture of 12 g. of D-ribonolactone, 10 g. of 4-nitro-*o*-xylene, and 3 cc. of *N* potassium hydroxide in 100 cc. of ethanol was hydrogenated at 60° and 100 atmospheres pressure with 1 g. of Adams platinum oxide catalyst. After twenty-four hours 50 cc. of ethanol was added and the mixture warmed to dissolve any precipitated product. The catalyst was separated by filtration and the solution cooled to 10°. After crystallization had taken place the product (3 g.) melting at 140–142° was filtered. Recrystallization from ethanol afforded further purification.

Method B. From 3,4-Dimethylaniline.—To a solution of ethanol (5000 cc.) containing 875 g. of D-ribonolactone and 730 g. of 3,4-dimethylaniline, was added 150 cc. of *N* potassium hydroxide. Fifty grams of Adams platinum oxide catalyst suspended in 290 cc. of distilled water was added and the mixture hydrogenated for thirty hours at 75° under a pressure of 2000 lb. per sq. in. The solution was then heated gently on a steam-bath until the material which crystallized was dissolved. The platinum black was filtered from the warm solution under a stream of carbon dioxide. After cooling the filtered solution, the crystals of N-(D-ribityl)-3,4-dimethylaniline (855 g.) were filtered off and washed with about 200 cc. of acetone. Recrystallized from ethanol, the product (792 g.) melted at 141–142°.

N-(3,4-Dimethylphenyl)-D-glucamine.—A mixture of 24 g. of D-glucono-δ-lactone, 20 g. 3,4-dimethylaniline, 4 cc. of 0.5 *N* potassium hydroxide and 2 g. of Adams platinum oxide catalyst in 160 cc. of ethanol was hydrogenated for seventy-two hours at 80° under a pressure of 2000 lb. per sq. in. The mixture was then warmed to dissolve the gel which had formed and filtered from the catalyst. The solution was evaporated to dryness *in vacuo* and the residue (30 g.) recrystallized four times from methanol. The needles melted at 134.5–135.5°. Kuhn and Birkofer[4] give the melting point as 131°.

Anal. Calcd. for $C_{14}H_{23}O_5N$: C, 58.91; H, 8.12; N, 4.91. Found: C, 58.94; H, 8.05; N, 5.00.

N-*p*-Tolyl-D-glucamine.—Forty-four grams of D-glucono-δ-lactone and 36.3 g. of *p*-toluidine were dissolved in 200 cc. of ethanol to which had been added 20 cc. of 0.5 *N* potassium hydroxide. Two and one-half grams of Adams platinum oxide catalyst was added and the mixture shaken with hydrogen under 2000 lb. pressure at 65° for seventy-two hours. The catalyst was filtered off and the filtrate evaporated to dryness *in vacuo*. The residue (weight *ca.* 35 g.) was shaken with ether and water. The aqueous layer was separated and evaporated to a small volume *in vacuo*. The crystals which formed were filtered off and recrystallized from methanol. The product, which had a tendency to form a gel in solution, melted at 123°.[4]

Anal. Calcd. for $C_{13}H_{21}O_5N$: C, 57.53; H, 7.80; N, 5.17. Found: C, 57.73; H, 7.90; N, 5.26.

(5) The analyses were carried out under the direction of Dr. Al Steyermark of these laboratories. All melting points were taken with an uncalibrated set of Anschütz thermometers.

Summary

1. A synthesis of N-aryl-glycamines is described which consists in the catalytic hydrogenation of aldonic acid lactones in the presence of arylamines.

2. The reaction described is of importance in the preparation of N-(D-ribityl)-3,4-dimethylaniline, an intermediate in the synthesis of riboflavin, from D-ribonolactone and 3,4-dimethylaniline.

NUTLEY, N. J. RECEIVED APRIL 30, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure and Activity of Sulfanilamides[1,2]

BY F. G. BORDWELL, AVIS B. COLBERT[3] AND BARRE ALAN

Fuson[4] has brought attention to the fact that the effect of a functional group is transmitted almost undiminished through a vinyl group (—CH=CH—). For this reason it would be expected that the amino group and sulfamyl group (SO_2NH_2) in 2-(*o*- and *p*-aminophenyl)-ethene-1-sulfonamide (VI and VII, R = H) would bear the same chemical relationship to one another as in sulfanilamide. It is therefore of interest to compare the bacteriostatic effect of compounds in these two series with that of sulfanilamide.

The synthesis outlined was used to prepare simple vinylogs of sulfanilamide. Nitration of 2-phenylethene-1-sulfonyl chloride (I) gave a

$$C_6H_5CH{=}CHSO_2Cl \longrightarrow \underset{\text{I}}{} \; o \text{ and}$$

$$p\text{-}NO_2C_6H_4CH{=}CHSO_2Cl \longrightarrow \underset{\text{II and III}}{} \; o \text{ and}$$

$$p\text{-}NO_2C_6H_4CH{=}CHSO_2NHR \longrightarrow \underset{\text{IV and V}}{} \; o \text{ and}$$

$$p\text{-}NH_2C_6H_4CH{=}CHSO_2NHR$$
VI and VII

practically quantitative yield of a mixture of nitro sulfonyl chlorides, from which approximately 20% of II and 50% of III were separated by fractional crystallization. Condensation of II and III with ammonia gave the corresponding sulfonamides (IV and V) in good yield. Reduction of the nitro group in IV and V was readily accomplished using ferrous sulfate and ammonia. Acetylation of IV and V followed by reduction of the nitro group gave the corresponding vinylogs of sulfacetamide.

It is possible that the arrangement of groups around the olefinic double bond is important in determining the bacteriostatic effect of these vin-

(1) This investigation was supported in part by a grant from the Abbott Fund of Northwestern University.

(2) Presented at the One-Day Technical Conference of the Chicago Section of the American Chemical Society, Evanston, Illinois, November 16, 1945.

(3) Winthrop Chemical Company Fellow, 1944–1945. Part of the experimental work was abstracted from a thesis submitted by Miss Colbert as partial fulfillment of the degree of Master of Science, June 1945.

(4) Fuson, *Chem. Rev.*, **16**, 1 (1935).

ylogs. There is no way at present of deciding the arrangement in the *para* vinylogs (VII), but in the *ortho* series (VI) the configuration is apparently *trans*. This designation of structure was arrived at by conversion of II to 2-(*o*-aminophenyl)-ethene-1-sulfonic acid, which on diazotization and hydrolysis gave a phenol and no sultone. Previous experience has shown that where the $-NH_3^+$ and $-SO_3^-$ groups are in close proximity, as would be the case for the *cis* isomer, the diazonium salt is converted to a sultone in high yield by hydrolysis. Thus 8-amino-1-naphthalenesulfonic acid[5] and *o*-aminophenylmethanesulfonic acid[6] are converted to 1,8-naphthalene sultone and *o*-phenylmethane sultone, respectively, by this procedure.[7,8]

The vinylogs of sulfanilamide (VI and VII, R = H) and of sulfacetamide (VI and VII, R = $-COCH_3$) were tested *in vitro* for bacteriostatic activity against types I, II and III *pneumococcus*, *Streptococcus pyogenes* and the tubercle bacillus.[9] The compounds showed no ability to inhibit growth of these organisms.

Compound VII (R = H), SN-8800, was submitted for testing as a potential antimalarial and proved to be inactive.

Discussion

The fact that substitution in parts of the sulfanilamide molecule other than the sulfamyl group invariable leads to a considerable loss of bacteriostatic activity has been ascribed to steric factors[10] and to chemical and steric factors.[11]

The steric characteristics of the sulfanilamide vinylog molecules are, of course, much different from those of the active sulfonamides, and the lack of activity of the former may be attributed to differences of this kind. However, it is interesting to note that in the *ortho* sulfanilamide vinylog the average distance between the amino and sulfamyl groups, assuming a *trans* structure, is not much less than in sulfanilamide.

(5) Erdmann, *Ann.*, **247**, 306 (1888).

(6) Marckwald and Frahne, *Ber.*, **31**, 1854 (1898).

(7) This evidence is not absolute since it is possible that change(s) in configuration occurred in going from II to 2-(*o*-aminophenyl)-ethene-1-sulfonic acid and/or from II to VI. However, neither IV, VI or VII (R's = H) is affected by refluxing in a solution of 25% hydrochloric acid for twenty minutes, which points to the more stable (presumable *trans*) configuration for these compounds.

(8) A Referee questioned this reasoning on the basis that the ring closures cited in the literature (footnotes 5 and 6) are for *gamma* sultones while the diazotization and hydrolysis of 2-(*o*-aminophenyl)-ethene-1-sulfonic acid would give a *delta* sultone. To settle this point we have reduced potassium 2-(*o*-nitrophenyl)-ethene-1-sulfonate in aqueous solution with hydrogen using palladium on charcoal and platinum catalysts. In each case the pressure drop practically ceases when the nitro group has been reduced. A diazotization of the amino sulfonic acids, however, gives a small yield of a sultone, m. p. 112–113°, saturated to potassium permanganate, which analyzes correctly for the sultone from 2-(*o*-hydroxyphenyl)-ethane-1-sulfonic acid, indicating that *delta* sultones can be formed in this reaction.

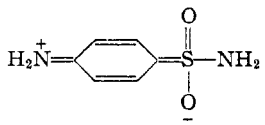
Anal. Calcd. for $C_8H_8O_3S$: C, 52.16; H, 4.38. Found: C, 52.09; H, 4.58.

(9) We wish to thank Dr. C. A. Lawrence of the Winthrop Chemical Company for carrying out these tests.

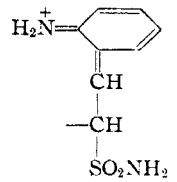
(10) Bell and Roblin, THIS JOURNAL, **64**, 2905 (1942).

(11) Kumler and Daniels, *ibid.*, **65**, 2190 (1943).

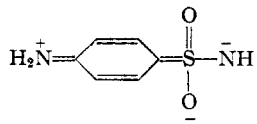
It is somewhat more difficult to understand the inactivity of these vinylogs from a chemical viewpoint. A measurement of the *pKa* value of VI and VII (R = $-COCH_3$) gave values close to that of sulfacetamide[10] confirming the expected similarity in chemical behavior of the $-SO_2NHCOCH_3$ groups in these molecules. If the determining factor in deciding the activity of sulfonamides is the extent to which resonance structures having a coplanar amino group, such as VIII, contribute to the structure of the molecule,[11] the vinylogs should show appreciable activity, since for these molecules it is possible to write structures comparable to VIII and in addition structures such as IX.



VIII



IX



X

As has been previously noted,[12] the hypothesis of Kumler and Daniels[11] is also subject to criticism of a more fundamental nature.[13] Recently Bell, Bone and Roblin[14] have shown that the experimental observation of Kumler and Strait[15] of a greater intensity in the ultraviolet absorption spectrum maximum for sulfanilamide in basic than in neutral solution is in error. The experimental evidence upon which Kumler and Daniels[11] based their assumption that resonance structures, such as X, contribute more to the structure of the sulfanilamide anion than VIII does toward the structure of the undissociated molecule is thereby removed. In view of the proximity of negative charges, X would actually be expected to contribute *less* to the structure of the anion than VIII does to the structure of the undissociated molecule, and since the corrected ultraviolet absorption curves[14] can be interpreted as agreeing with this reasoning,[12] it seems evident that contributions from structures with a coplanar amino group are more important in the undissociated molecule than in the anion. It is thus impossible to reconcile the Kumler and Daniels hypothesis with the widely accepted view that the anion is the active form of the drug.

(12) Bordwell and Klotz, THIS JOURNAL, **66**, 660 (1944).

(13) The inactivity of the vinylogs of sulfanilamide is, of course, negative evidence against the hypothesis, and might be explained from a chemical standpoint by postulating oxidation or reduction reactions at the vinyl group.

(14) Bell, Bone and Roblin, THIS JOURNAL, **66**, 847 (1944). This result has been corroborated by Dr. I. M. Klotz of this Laboratory.

(15) Kumler and Strait, *ibid.*, **65**, 2349 (1943).

It has been previously noted[14] that the lack of correlation between base constants and bacteriostatic activity of sulfamilamide type compounds does not support the Kumler and Daniels hypothesis, and that resonance structures similar to those written by Kumler and Daniels to explain the low activity of sulfanilylurea and 3-sulfanilamido-1,2,4-triazole may also be written for most of the *active* sulfonamides.[12]

Experimental[16,17]

2-(*o* and *p*-Nitrophenyl)-ethene-1-sulfonyl Chlorides (II and III).—To 930 ml. of red fuming nitric acid, (d. 1.59; a mixture of concentrated nitric and sulfuric acids gave similar results) kept at about 0° and mechanically stirred, was added, in 10–15 g. portions, 124 g. (0.61 mole) of powdered 2-phenylethene-1-sulfonyl chloride[18] (in this experiment material of m. p. 89° was used, but in other experiments nearly as good results were obtained with crude material). The addition was completed in thirty minutes, the mixture stirred for two hours longer, poured into 3 liters of ice-water and the solid collected and washed free of acid. The weight of crude dry product was 145 g. (95%).

One hundred and thirty-five grams of the crude nitration mixture was extracted with 2.8 liters of Skellysolve C by heating on the steam-bath for forty-five minutes and decanting the supernatant liquid. Second and third extractions were made in a similar manner using 1.4 and 1 liter of solvent, respectively. The melting points and weights of the crystalline materials separating from the three extracts on cooling were: (1) 18.2 g., m. p. < 90°; (2) 11.5 g., m. p. 100–102°; (3) 10.2 g., m. p. 102–104°. The melting point of the material from the first extract could not be raised by crystallization from Skellysolve C or carbon tetrachloride. It seems likely that some of the *meta* isomer was present here, since mixtures of the *ortho* and *para* isomers were readily resolved by fractional crystallization. After removal of two crops of the *para* isomer from a benzene solution of the residue (see below), extraction of the residue obtained on complete evaporation of the benzene, yielded 8.4 g. more of the *ortho* isomer (II). After crystallization from carbon tetrachloride a total yield of 28 g. (20% based on 2-phenylethene-1-sulfonyl chloride) of product II, m. p. 102–104°, was obtained. For analysis this material was crystallized twice from Skellysolve C and twice from carbon tetrachloride; m. p. 103–105° (cor.).

Anal. Calcd. for $C_8H_6O_4NSCl$: N, 5.67. Found: N, 6.14, 5.72.

A 0.2-g. sample of II was dissolved in 50% acetone and oxidized with potassium permanganate. Working up the reaction mixture gave a 45% yield of an acid which, after crystallization from hexane–benzene, melted at 138–141°, and did not depress the melting point of an authentic sample of *o*-nitrobenzoic acid (m. p. 145°), but gave a large depression in melting point when mixed with a sample of *m*-nitrobenzoic acid (m. p. 140–141°).

The residue from the Skellysolve C extractions was dissolved in 1.3 l. of hot benzene. On cooling 59 g. of the *para* isomer (III) separated and concentration of the solution to 200 ml. gave a second crop. The total yield of product III, m. p. 167–169°, was 72 g. (50% based on I). Recrystallization from benzene raised the melting point to 172–174°.

Anal. Calcd. for $C_8H_6O_4NSCl$: Cl, 14.32. Found: Cl, 14.65, 14.55.

Oxidation of a sample of III with potassium permanganate gave a 70% yield of *p*-nitrobenzoic acid, m. p. and mixed m. p. 235–238°.

(16) Melting points are uncorrected unless otherwise noted.

(17) Microanalyses by Margaret Ledyard and Winifred Brandt.

(18) Bordwell, Suter, Holbert and Rondestvedt, THIS JOURNAL, **68**, 139 (1946).

2-(*o* and *p*-Nitrophenyl)-ethene-1-sulfonamides (IV and V, R = H).—These sulfonamides were prepared by addition of the corresponding sulfonyl chlorides (II and III) to an excess of liquid ammonia.

The *ortho* isomer (IV, R = H) was crystallized from water (about 75 ml./g.); m. p. 145–148°. An 85% yield of crystalline material was obtained.

Anal. Calcd. for $C_8H_8O_4N_2S$: N, 12.28. Found: N, 12.55.

The *para* isomer (V, R = H) was crystallized from 50% acetone. The yield of crystalline product, m. p. 193–194°, was 80%.

Anal. Calcd. for $C_8H_8O_4N_2S$: N, 12.28. Found: N, 12.60.

2-(*o* and *p*-Aminophenyl)-ethene-1-sulfonamides (VI and VII, R = H).—The nitro group in the *ortho* isomer (IV, R = H) was reduced according to the general method of Heidelberger and Jacobs.[19] From 3.6 g. of nitro compound 30 g. of ferrous sulfate heptahydrate, 35 ml. of concentrated ammonia and 175 ml. of water, boiled for five minutes and filtered through a steam jacketed Büchner funnel, was obtained on acidification 2.5 g. (80%) of crude 2-(*o*-aminophenyl)-ethene-1-sulfonamide. The product was crystallized from ethylene chloride and from water; m. p. 150–152°.

Anal. Calcd. for $C_8H_{10}O_2N_2S$: N, 14.13. Found: N, 13.68.

The nitro group of the *para* isomer (V, R = H) was reduced in a similar manner, except that 6 *N* sodium hydroxide was added prior to filtration, and the filtrate carefully acidified to precipitate the sulfonamide. The yield of product after crystallization from water was 60%; m. p. 213–215° (in a preheated bath).

Anal. Calcd. for $C_8H_{10}O_2N_2S$: C, 48.47; H, 5.10. Found: C, 48.48, 48.78; H, 5.20, 5.10.

N¹-(Acetyl-2-(*o*) and *p*-nitrophenyl)-ethene-1-sulfonamides (IV and V, R = —$COCH_3$).—The acetyl derivatives were obtained in 90% yield by refluxing the nitro sulfonamides (IV and V, R = H) for one hour with ten times their weight of acetic anhydride containing a few crystals of *p*-toluenesulfonic acid. The crude products were used without further purification, but for purposes of analysis were recrystallized. The *ortho* isomer was crystallized from ethylene chloride; m. p. 183–184°.

Anal. Calcd. for $C_{10}H_{10}O_5N_2S$: C, 44.40; H, 3.70. Found: C, 44.63; H, 3.75.

The *para* isomer was crystallized from alcohol; m. p. 191–192° (cor.).

Anal. Calcd. for $C_{10}H_{10}O_5N_2S$: C, 44.40; H, 3.70. Found: C, 44.54; H, 4.05.

N¹-Acetyl-2-(*o* and *p*-aminophenyl)-ethene-1-sulfonamides (VI and VII, R = —$COCH_3$).—Reduction of the nitro groups in IV and V (R = $-\overset{\overset{O}{\|}}{C}CH_3$) with ferrous sulfate and ammonia was carried out as above. It was found that the yield and purity of the products were impaired either by use of excess ammonia or by heating prolonged beyond the specified five minutes. The products crystallized from the filtrate on careful acidification with acetic acid. Recrystallization was difficult and was accomplished only by dissolving the products rapidly in ethylene chloride at about 50°, filtering and allowing the solution to cool slowly in the presence of a seed crystal. The *ortho* isomer after crystallization melted at 131–133°, the *para* isomer at 142–143°.

Anal. (*ortho* isomer) Calcd. for $C_{10}H_{12}O_3N_2S$: C, 50.00; H, 5.00. Found: C, 50.04; H, 5.22.

Anal. (*para* isomer) Calcd. for $C_{10}H_{12}O_3N_2S$: C, 50.00; H, 5.00. Found: C, 50.09; H, 5.36.

The *pKa* values for these *ortho* and *para* vinylogs of N¹-acetylsulfanilamide were 6.1 and 6.6, respectively, determined by measuring the *p*H of a half-neutralized sample

(19) Heidelberger and Jacobs, *ibid.*, **39**, 1435 (1917).

in 50% alcohol. Using the curve developed by Bell and Roblin[10] for correcting these values to those in aqueous solution gave figures close to the 5.38 given for N¹-acetylsulfanilamide itself.

Preparation and Diazotization of 2-(*o*-Aminophenyl)-ethene-1-sulfonic Acid.—Hydrolysis and reduction of II was carried out by the method described for the preparation of orthanilic acid.[20] Isolation of the product was made difficult by the surprisingly great water solubility of this aminosulfonic acid. A small amount of the aminosulfonic acid crystallized on slow evaporation of an acid solution in the cold room. It was identified by qualitative tests and analysis.

Anal. Calcd. for $C_8H_9O_3NS \cdot H_2O$: neut. equiv., 217. Found: neut. equiv., 219, 216.

A 0.35-g. sample of this aminosulfonic acid dissolved in acid solution reacted with the theoretical quantity of sodium nitrite solution (end-point determined with starch–iodide paper). Heating the diazonium solution caused a vigorous evolution of nitrogen. The mixture of salts obtained on evaporation of this solution was insoluble in organic solvents and completely soluble in water. The aqueous solution gave a deep blue coloration with ferric chloride solution showing the presence of a phenol.

(20) Wertheim, "Organic Syntheses," Coll. Vol. II, p. 472.

Summary

1. Two simple vinylogs of sulfanilamide and two of sulfacetamide have been prepared and were found to have no bacteriostatic activity *in vitro*.

2. Evidence has been presented to show that the *ortho* vinylogs have a *trans* configuration.

3. The hypothesis of Kumler and Daniels,[11] concerning the relationship between the structure and activity of sulfonamides, has been criticized on several counts.

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[CONTRIBUTION FROM CELANESE CORPORATION OF AMERICA, PLASTICS DIVISION]

Copolymerization: the Composition Distribution Curve

BY IRVING SKEIST

When two or more monomers are copolymerized, the product is a mixture of polymer molecules which vary in composition as well as in chain length. If, *e.g.*, the polymer first formed is richer in one component than the monomer mixture, then some of the polymers formed subsequently must be poorer in that component than the original monomer mixture. Some mixtures of monomers yield a polymer aggregate of fairly uniform composition, while others give a product whose molecules vary so widely in composition that technical usefulness is impaired. Thus it becomes important to know the distribution of compositions in the polymer.

At any instant, the composition of the polymer in a binary mixture is related to the composition of the monomer according to the expression[1,2,3]

$$\frac{\Delta A}{\Delta A + \Delta B} = A_p = \frac{\alpha A^2 + AB}{\alpha A^2 + 2AB + \beta B^2}$$

where A and B are the mole fractions of the two components in the monomer, ΔA and ΔB are the amounts (*e.g.*, moles per unit weight) of the corresponding components which enter the polymer in a differential time interval, A_p is the mole fraction of the first component in the polymer formed during the differential time interval, and α and β are the monomer reactivity ratios[2,3]; α is k_{A*A}/k_{A*B} and β is k_{B*B}/k_{B*A}, where k_{A*B}, for example, is the rate constant for the propagation reaction involving the addition of B monomer to A radical.

For a three-component system, the relation between A_p and A is found similarly from the following set of equations[4,5]

$$\frac{\Delta A}{\Delta B} = \frac{A(A/\beta^a\gamma^a + B/\beta^a\gamma^b + C/\beta^c\gamma^a)\,(A + B/\alpha^b + C/\alpha^c)}{B(A/\alpha^b\gamma^a + B/\alpha^b\gamma^b + C/\alpha^c\gamma^b)\,(A/\beta^a + B + C/\beta^c)} \quad (2a)$$

$$\frac{\Delta A}{\Delta C} = \frac{A(A/\beta^a\gamma^a + B/\beta^a\gamma^b + C/\beta^c\gamma^a)\,(A + B/\alpha^b + C/\alpha^c)}{C(A/\alpha^c\beta^a + B/\alpha^b\beta^c + C/\alpha^c\beta^c)\,(A/\gamma^a + B/\gamma^b + C)} \quad (2b)$$

where β^a, for example, is β for the binary system A-B. The information needed to solve these equations, as well as the equations for systems involving a greater number of monomers, can be obtained entirely from experiments on the binary systems involved.

Integration of equations (1) and (2) should give a relationship between the conversion, or amount of polymer formed, and its composition. These integrations have been performed by Mayo and Lewis[2] and Walling and Briggs.[5] Even in a binary system, the integral is complex; in a ternary system it becomes nearly unmanageable. An attempt to simplify the integral relationship for a ternary system results in an approximate expression which is precise only when the polymer composition is close to that of the feed.

It is the purpose of this paper to present a more convenient method for determining the relationship between conversion and composition, and from this the distribution of compositions, in a polymer of any number of components. The method is applicable to any system for which one knows the relation between composition of monomer and composition of polymer, regardless of whether the system can be described in terms of the monomer reactivity ratios of equations 1 and 2.

(1) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
(2) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).
(3) Wall, *ibid.*, **66**, 2050 (1944).
(4) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944).
(5) Walling and Briggs, THIS JOURNAL, **67**, 1774 (1945).