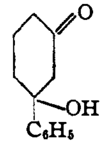
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

The Reaction of β-Cyclohexanedione (Dihydroresorcinol) and its Ethyl Enol Ether with Phenylmagnesium Bromide

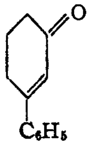
BY G. FORREST WOODS AND IRWIN W. TUCKER

The reaction of dimedone with phenylmagnesium bromide has been previously investigated.[1] We have now studied the corresponding reaction of dihydroresorcinol (I) whose structure is very similar to that of dimedone.

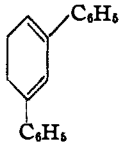
Three products (II, III, and IV) and a tar were isolated after decomposing the Grignard complex.



II

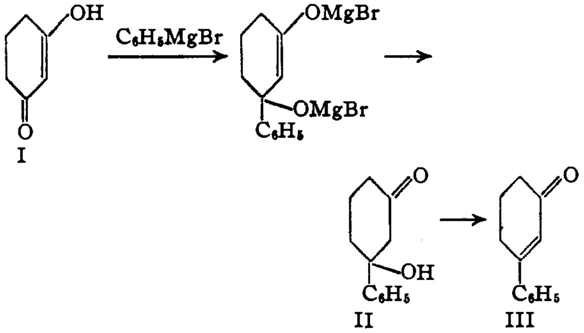


III

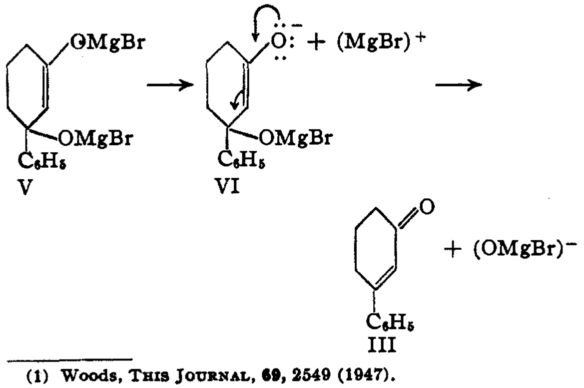


IV

The first two substances, II and III, are readily accounted for by the mechanism proposed by Kohler and Erickson[2] for the reaction of strongly enolic β-diketones with Grignard reagents as shown below applied to dihydroresorcinol



The formation of 1,3-diphenylcyclohexadiene-1,3 (IV), however, is difficult to explain. Although this substance would obviously be the product of a double addition of phenylmagnesium bromide to dihydroresorcinol in the β-diketonic form, this concept is hardly acceptable since dihydroresorcinol is known to be strongly enolic.[3] A more reasonable mechanism is shown

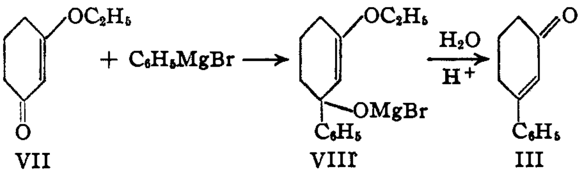


If it is assumed that some degree of ionization exists in the magnesium enolate bond of structure (V) leading to structure (VI), then (VI) stabilizes itself by the ejection of the (O-Mg-Br)⁻ ion, which had been activated by both the phenyl group and the ethylenic link, along with a concurrent electron shift. Thus, 3-phenyl-Δ^2-cyclohexenone (III) is generated and then reacts with phenylmagnesium bromide, the addition product subsequently losing water to give IV. In this connection it is interesting to note that the hydrocarbon (IV) was obtained in higher yield almost to the exclusion of the other products by continued refluxing of the Grignard solution after displacement of the ether with benzene. The tar formed in the reaction of dihydroresorcinol with phenylmagnesium bromide is assumed to be a polymer of 1,3-diphenylcyclohexadiene-1,3, a substance which contains both butadiene and styrene-like structures.

We wished to prove the structure of 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3 by an independent mode of synthesis, and to obtain a good preparative method for these substances. The preparation of the ethyl enol ether of dihydroresorcinol and the subsequent reaction of this substance with phenylmagnesium bromide accomplished the above two points.

The white crystalline silver salt of dihydroresorcinol was obtained by mixing dihydroresorcinol and silver nitrate in water and adjusting the *p*H of the solution. The silver salt thus prepared readily reacts with ethyl iodide in refluxing benzene to yield the ethyl enol ether of dihydroresorcinol.[4] We found this method of preparation superior to the reaction of dihydroresorcinol with sodium ethylate and ethyl iodide, with diethyl sulfate and aqueous sodium hydroxide, or with absolute ethyl alcohol and sulfuric acid. This last method was the mode of preparation of the ethyl enol ether of dimedone.[5]

Dihydroresorcinol ethyl enol ether (VII) reacts with phenylmagnesium bromide to yield 3-phenyl-Δ^2-cyclohexenone (III) as shown



The intermediate product (the keto alcohol from VIII) was not isolated and it was found, as had been anticipated from previous work, that the

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[1] Woods, THIS JOURNAL, **69**, 2549 (1947).

[2] Kohler and Erickson, *ibid.*, **53**, 2301 (1931).

[3] (a) Blout, Eager and Silverman, *ibid.*, **68**, 566 (1946); (b) Schwarzenback and Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[4] Merling, *Ann.*, **278**, 28 (1894).

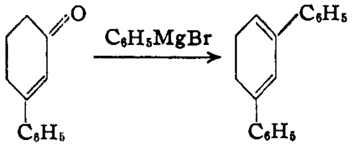
[5] Crossley and Renouf, *J. Chem. Soc.*, **93**, 640 (1908).

enol ether linkage of VIII was readily cleaved and the molecule dehydrated on treatment with dilute sulfuric acid under the conditions of steam distillation. The product, obtained in 80–85% yield, was identical with the 3-phenyl-Δ^2-cyclohexenone obtained by the reaction of dihydroresorcinol with phenylmagnesium bromide.

3-Phenyl-Δ^2-cyclohexenone (III) had previously been synthesized by Abdullaho[6] by the condensation of phenyl vinyl ketone with acetoacetic ester and the subsequent hydrolysis and decarboxylation of the condensation product. The constants of our product and its derivatives are in good agreement with his. Further, 3-phenyl-Δ^2-cyclohexenone is readily converted to *m*-phenylphenol by dehydrogenation over palladium–charcoal[7] or hydrogenated with palladium-charcoal to 3-phenylcyclohexanone.

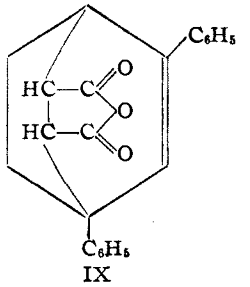
The fact that substance II, 3-phenylcyclohexane-3-ol-1-one, was readily dehydrated by refluxing in benzene in the presence of a trace of iodine to yield 3-phenyl-Δ^2-cyclohexenone establishes the structure of the former.

The structure of substance IV, 1,3-diphenylcyclohexadiene, was established by its synthesis from 3-phenyl-Δ^2-cyclohexenone (III) and phenylmagnesium bromide in good yield and superior quality



III IV

This substance was identical with the corresponding product obtained from the reaction of dihydroresorcinol with phenylmagnesium bromide. That this structure was correct was also shown by the conversion of 1,3-diphenylcyclohexadiene by dehydrogenation over palladium–charcoal to the known *m*-diphenylbenzene[8] and by the isolation of an adduct, for which the structure IX is written, from the Diels–Alder reaction of 1,3-diphenylcyclohexadiene-1,3 with maleic anhydride.



IX

Experimental

Reaction of Phenylmagnesium Bromide with Dihydroresorcinol.—An ethereal solution (1400 ml.) of phenylmagnesium bromide from 1.0 mole of bromobenzene and magnesium turnings was prepared in the pot of a Soxhlet extractor. Finely ground dihydroresorcinol[9] (28 g., 0.25 mole) was introduced into the extraction thimble and the extraction process continued until only a small residue (3 g.) remained unextracted. The Grignard complex solution, which set to a solid on cooling in an ice-bath, was hydrolyzed with dilute aqueous ammonium chloride. The ether solution, dried over anhydrous magnesium sulfate, concentrated to 300–500 ml. and chilled, gave 8 g. of solid which was recrystallized from acetone–petroleum ether (80–100°). This product was 3-phenylcyclohexan-3-ol-one (II) and melted at 155–155.5°. *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.77; H, 7.42. Found: C, 75.94, 75.89; H, 7.70, 7.58.

The ethereal filtrate, after the removal of the above product, was then distilled under reduced pressure. Two substances (III and IV) were obtained after the removal of bromobenzene and biphenyl. Impure 3-phenyl-Δ^2-cyclohexenone (III) was collected which distilled over the range of 106–185° (10 mm.). The main portion of this material distilled from 165–185° (10 mm.). The yield was 15–20 g. This material, which solidified on cooling, yielded coarse white crystals upon recrystallization from petroleum ether (30–60°) which melted at 64.5–66.0°. *Anal.* Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.55, 83.64; H, 7.22, 7.17.

The second product, 1,3-diphenyl-cyclohexadiene-1,3 (IV), distilled over the range of 130–190° (0.2 mm.). The main fraction (5 g.) distilled at 176° (0.2 mm.). This substance was decolorized with norite and crystallized from petroleum ether (30–60°). Upon further recrystallization white crystalline platelets were obtained which melted at 98–99°.[10] *Anal.* Calcd. for $C_{18}H_{16}$: C, 93.10; H, 6.94. Found: C, 93.14, 92.97; H, 6.62, 6.65.

In subsequent reactions 3-phenylcyclohexan-3-ol-1-one (II) was not isolated since it was readily converted in the following operations to 3-phenyl-Δ^2-cyclohexenone (III), a desired product. The original ethereal solution from the Grignard complex was made acid with dilute sulfuric acid and subjected to steam distillation. In this manner the troublesome impurities of bromobenzene and biphenyl were readily eliminated, since 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3 are only slightly volatile with steam.

Conversion of 3-Phenylcyclohexan-3-ol-1-one to 3-Phenyl-Δ^2-cyclohexanone.—3-Phenylcyclohexan-3-ol-1-one (II) (0.6 g.) was refluxed in toluene (25 ml.) after the addition of a small crystal of iodine. The toluene was removed by distillation under reduced pressure and the residue dissolved in ether and decolorized with norite. The product was recrystallized from petroleum ether which was added after removal of most of the ether. This material melted at 64.5–66.0° and gave no depression in a mixed melting point determination with a sample of 3-phenyl-Δ^2-cyclohexenone obtained previously as above.

Preparation of Dihydroresorcinol Ethyl Ether[11] (VII).—Dihydroresorcinol[9] (50 g.) and silver nitrate (76 g.) were dissolved in 400 ml. of water. To this solution was added dropwise with stirring 1.0 *M* sodium hydroxide until the *p*H of the solution was 5.5–6.0. During this process silver oxide precipitated locally but gradually redissolved while silver dihydroresorcinate precipitated in a white crystalline form. Excessive amounts of sodium hydroxide caused a noticeable darkening of the precipitate and a subsequent lowering in yield of the ultimate product.

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(6) Abdullaho, *J. Indian Chem. Soc.*, **12**, 62 (1935).

(7) Horning and Horning, This Journal, **69**, 1359 (1947).

(8) France, Heilbron and Hey, *J. Chem. Soc.*, 1288 (1939).

(9) "Organic Syntheses," Vol. 27, John Wiley and Sons, New York, N. Y., p. 21.

(10) This product becomes contaminated readily with either the substances of polymerization or with some *m*-terphenyl (from the oxidation of the diphenylcyclohexadiene). Thus this melting point is obtained only with difficulty.

(11) The development of this method of preparation of the ethyl enol ether of dihydroresorcinol was done by Mr. Bernard Armbrecht. The details given by Merling (*Ann.*, **278**, 28 (1894)) are so brief as to amount only to an indication of procedure.

The silver salt of dihydroresorcinol was isolated by suction filtration and pressed reasonably free of water. The moist precipitate (80–85 g.) was placed in a three-neck flask to which was fitted a mechanical stirrer, a separatory funnel, and a moisture receiving tube itself connected to a reflux condenser. Benzene (300 ml.) was introduced into the three-neck flask and the mixture refluxed with stirring until all the water was removed. To the benzene solution was then added 0.5 mole of ethyl iodide and the refluxing and stirring continued for fifteen minutes. The solution, after removal of the silver iodide by suction filtration, was subjected to distillation under reduced pressure. Ethyl enol ether of dihydroresorcinol (36 g. 51%) distilled at 95–105° (1 mm.). In this preparation it was found that the yield of the ethyl enol ether was not favored by any excess of ethyl iodide while the yield was adversely affected by longer refluxing periods of ethyl iodide with the silver salt of dihydroresorcinol in benzene.

Preparation of 3-Phenyl-Δ^2-cyclohexenone (III) from Dihydroresorcinol Ethyl Ether.—Dihydroresorcinol ethyl ether (70.0 g.) dissolved in 300 ml. of ether was added slowly with stirring to a solution (600 ml.) of phenylmagnesium bromide prepared from bromobenzene and magnesium (0.75 mole). The Grignard complex was decomposed with dilute sulfuric acid. This mixture was subjected to steam distillation until all the bromobenzene and most of the biphenyl had been removed. The residue in the steam pot was extracted with ether. The ether solution was washed with dilute sodium bicarbonate and water, decolorized with norite, and dried over magnesium sulfate. After removal of most of the ether by heating on a steam-bath, the residue was dissolved in petroleum ether (30–60°). This solution deposited white to pale yellow-colored crystals (71 g., 87%) which upon recrystallization melted at 64.5–66° and which gave no depression in a mixed melting point determination with the previously obtained samples of this compound.

The oxime of this product was prepared in the usual manner and recrystallized from alcohol–water. The melting point of the product so obtained was 102–111° and only upon repeated recrystallizations from both alcohol–water and ether–petroleum ether was a product melting at 113.5–118° obtained. Abdullaho[6] reported a melting point of 117–118° for this substance. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 76.98; H, 7.00. Found: C, 76.95, 77.25; H, 6.59, 6.58.

The red 2,4-dinitrophenylhydrazone of 3-phenyl-Δ^2-cyclohexenone prepared in the usual manner melted at 228–230°. *Anal.* Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58. Found: C, 61.21, 61.60; H, 4.17, 4.22.

The semicarbazone of 3-phenyl-Δ^2-cyclohexenone which was prepared in the usual manner and recrystallized from alcohol melted at 227–229° with decomposition. *Anal.* Calcd. for $C_{13}H_{15}ON_3$: C, 68.10; H, 6.59. Found: C, 67.89; H, 6.23.

The *p*-nitrophenylhydrazone of 3-phenyl-Δ^2-cyclohexenone prepared in the usual manner melted at 182.5–185°. *Anal.* Calcd. for $C_{18}H_{17}N_3O_2$: C, 70.35; H, 5.71. Found: C, 70.16, H, 5.67. Abdullaho[6] reported a melting point of 184–185° for this substance.

Reduction of 3-phenyl-Δ^2-cyclohexenone (3.0 g.) was accomplished in ethyl alcohol at atmospheric pressure and room temperature with palladium–charcoal. The hydrogenation was arrested after a 5% excess of hydrogen calculated for saturation of one ethylenic link had been adsorbed. After removal of the catalyst one half of the solution was used for the preparation in the usual manner of the semicarbazone of 3-phenylcyclohexanone which melted at 163.5–164.5° after recrystallization from alcohol–water.[12] *Anal.* Calcd. for $C_{13}H_{17}ON_3$: C, 67.51; H, 7.41. Found: C, 67.35; H, 7.03. The remaining half of the above solution was used to prepare the 2,4-dinitrophenylhydrazone of 3-phenylcyclohexanone, which was yellow and which melted at 183–186°. *Anal.* Calcd. for $C_{18}H_{18}O_4H_4$: C, 61.01; H, 5.12. Found: C, 61.14, 61.20; H, 5.18, 5.51.

Preparation of 3-Phenylphenol from 3-Phenol-Δ^2-cyclohexenone.—The procedure for dehydrogenation and isolation of the phenol is essentially that of Horning.[7] 3-Phenyl-Δ^2-cyclohexenone (2.0 g.), palladium–charcoal catalyst[13] (0.7 g. 5% Pd), and 15 ml. of cymene were heated under reflux for approximately ninety minutes. This solution upon cooling was filtered and the filtrate extracted three times with Claisen solution (30 ml.). The Claisen solution was extracted once with benzene and then with petroleum ether (30–60°). The alkaline solution was then diluted with an equal volume of water and acidified with concentrated hydrochloric acid. The solid phenol was extracted with ether and the extract dried over magnesium sulfate. Upon evaporation of most of the ether and addition of petroleum–ether (30–60°), 1.25 g. of 3-phenylphenol crystallized on standing. This product after recrystallization from water was a white solid melting at 73.5–74.5°.[14] *Anal.* Calcd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84:95, 84.71; H, 6.00, 6.00.

The phenylurethan of 3-phenylphenol was prepared in the usual manner and recrystallized from petroleum ether (90–100°) to which benzene was added to effect solution. The white crystalline product melted at 135–135.5°. *Anal.* Calcd. for $C_{19}H_{15}O_2N$: C, 78.87; H, 5.23. Found: C, 79.19; H, 5.54.

Preparation of 1,3-Diphenylcyclohexadiene-1,3 (IV).—To a solution of phenylmagnesium bromide prepared from 18.3 g. of bromobenzene and 2.8 g. of magnesium in 100 ml. of ether was added 10 g. of 3-phenyl-Δ^2-cyclohexenone dissolved in 100 ml. of ether. After addition of the ketone the reaction mixture was refluxed for thirty minutes, cooled in an ice-bath, and decomposed with cold 6% sulfuric acid. The ether extract was washed with aqueous sodium carbonate and with water and finally dried over anhydrous magnesium sulfate. On evaporation of the ether, 14 g. of solid residue was obtained which corresponds to a theoretical yield of 1,3-diphenylcyclohexadiene-1,3. This material, recrystallized from 95% ethanol, gave 9 g. of product (67%) melting at 96–98°. Recrystallization of this material from ethanol and decolorization with charcoal yielded colorless plates melting at 98–99°. *Anal.* Calcd. for $C_{18}H_{16}$: C, 93.10; H, 6.94. Found: C, 93.14, 92.97; H, 6.65, 6.62.

Maleic Anhydride Adduct of 1,3-Diphenylcyclohexadiene-1,3 (IX).—Maleic anhydride (1.1 g.) and 1,3-diphenylcyclohexadiene-1,3 (2.5 g.) were heated for four hours at 130–150°. The product on cooling was pulverized and warmed with 300 ml. of 10% sodium hydroxide solution. The small residue which remained undissolved was removed by filtration. The alkaline filtrate was acidified to congo red with hydrochloric acid. The precipitate was removed after cooling by filtration and redissolved in acetone and decolorized with Norite. The product (2.0 g.) crystallized upon cooling after the addition of water to the acetone solution, m. p. 149–151.5°. *Anal.* Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.17, 80.22; H, 5.70, 5.60.

Preparation of *m*-Diphenylbenzene from 1,3-Diphenylhexadiene-1,3.—1,3-Diphenylcyclohexadiene-1,3 (2.0 g.) in 15 ml. of cymene was heated under reflux in the presence of 0.7 g. of 5% palladized charcoal for three hours, following which time most of the cymene was removed by distillation. The final portion of cymene was removed by using low pressure distillation. The residue was dissolved in hot ethyl alcohol and the catalyst removed by filtration. On cooling, the filtrate deposited *m*-terphenyl (1.3 g.) which was isolated by filtration, m. p. 86.5–86.8°. This product gave no depression with an authentic sample kindly furnished us by Dr. C. F. H. Allen. *Anal.* Calcd. for $C_{18}H_{14}$: C, 93.88; H, 6.12. Found: C, 94.02; H, 6.25.

Summary

1. The reaction of dihydroresorcinol with

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[12] A melting point of 167° has been reported for this substance (Boyd, Clifford and Probert, *J. Chem. Soc.*, **117**, 1383 (1920)).

[13] "Organic Syntheses," Vol. 26, 1946, p. 77.

[14] Jacobsen and Loch (*Ber.*, **36**, 4085 (1903)) reported 78°, and Errera and La Spada (*Gazz. chim. ital.*, **35**, II, 552) reported 75° for the melting point of this substance.

phenylmagnesium bromide has been shown to yield 3-phenylcyclohexan-3-ol-1-one, 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3. A mechanism by which the latter substance could be formed is discussed.

2. The syntheses of 3-phenyl-Δ^2-cyclohexenone from the ethyl enol ether of dihydroresorcinol and of 1,3-diphenylcyclohexadiene-1,3 from 3-phenyl-Δ^2-cyclohexenone, are reported.

3. 3-Phenylphenol and *m*-terphenyl are conveniently prepared by the catalytic dehydrogenation, using palladized charcoal, of 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3, respectively.

COLLEGE PARK, MARYLAND RECEIVED JANUARY 28, 1948

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Partition of Acrylonitrile between Styrene and Water

BY WENDELL V. SMITH

A satisfactory discussion of the emulsion copolymerization of styrene and acrylonitrile requires a knowledge of the partition of the acrylonitrile between the water phase and the oil phase, since acrylonitrile is appreciably water soluble. Fordyce and Chapin[1] have compared the composition of the copolymer of styrene and acrylonitrile obtained in emulsion polymerization with that obtained in bulk polymerization and have found the emulsion copolymer to be consistently richer in styrene by a small amount than the bulk polymer produced from the same initial monomer composition. They have suggested that this difference may be due solely to the decrease in acrylonitrile content of the oil phase resulting from the water solubility of the acrylonitrile. The present investigation, which provides the data necessary to test this suggestion, has been carried out primarily to aid in discussing the emulsion copolymerization of these two monomers.

Under the conditions employed in emulsion polymerization, the ternary system, styrene–acrylonitrile–water, can be described sufficiently by specifying the compositions of two liquid phases, one of which may be called the aqueous phase, and the other the oil phase. A good approximation may be made by neglecting the solubility of styrene in the aqueous phase, also a fair approximation is obtained by neglecting the solubility of water in the oil phase (this is a good approximation when the oil phase is rich in styrene but becomes progressively less satisfactory as the acrylonitrile content of the oil phase increases).

Suppose that the system consists of

a volumes acrylonitrile
s volumes styrene
w volumes water

At equilibrium the oil phase will contain practically all the styrene and a_s volumes of acrylonitrile while the water phase will contain practically all the water and a_w volumes of acrylonitrile, where

$$a = a_s + a_w \qquad (1)$$

It is convenient to define a partition coefficient, α, by the relation

$$\alpha = \frac{a_s}{a_s + s} \cdot \frac{a_w + w}{a_w} \qquad (2)$$

Experimentally this partition coefficient may be determined by equilibrating a styrene–acrylonitrile solution of known composition with water and determining the resulting change in acrylonitrile content of the oil phase. If this change in acrylonitrile content is represented by

$$\Delta A = \frac{a}{a + s} - \frac{a_s}{a_s + s}$$

and if the equilibrium acrylonitrile content of the oil phase is represented by

$$A_s = a_s/a_s + s$$

then equations 1 and 2 give

$$\alpha = A_s\left[1 + \left(\frac{w}{a + s}\right)\frac{(1 - A_s)}{\Delta A}\right] \qquad (3)$$

After having determined α it is then possible to reverse the calculation and obtain the equilibrium composition of any mixture of water and oil phase. This may be done by rearranging equation 3 to obtain the quadratic

$$A_s^2 - [R(\alpha - s/a + s) + 1]A_s + R\alpha a/a + s = 0 \qquad (4)$$

where $R = (a + s)/(a + s + w)$. The most convenient method of solving equation 4 for A_s is by successive approximation. Since the first term is small, a first approximation for A_s may be obtained by neglecting A_s^2 and estimating α from Fig. 1 and an estimated value of A_s. From this first approximation a new value of α may be obtained from Fig. 1 and the small correction due to the first term may be calculated. Then a second approximation for A_s may be calculated from equation 4. This may be continued to give any degree of approximation warranted by the experimental work.

One other problem which is treated in the experimental section is that of calculating the acrylonitrile content of a water solution by equilibrating the water solution with styrene and determining A_s, the equilibrium acrylonitrile content of the

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(1) Reid G. Fordyce and Earl C. Chapin, THIS JOURNAL, 69, 581 (1947).