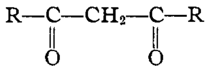
TABLE II

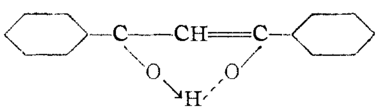
GENERAL FORMULA 

$R{-}\underset{\displaystyle O}{\overset{}{C}}{-}CH_2{-}\underset{\displaystyle O}{\overset{}{C}}{-}R^1$

VIII, R and R^1 = phenyl
IX, R = *p*-bromophenyl; R^1 = phenyl
X, R = phenyl; R^1 = mesityl
XI, R = *p*-methoxyphenyl; R^1 = mesityl
XII, R = *m*-nitrophenyl; R^1 = mesityl
XIII, R = *p*-nitrophenyl; R^1 = mesityl

These β-diketones like the α-diketones did exhibit absorption at 3.4 and 6.25 μ which is characteristic of CH and phenyl absorption.

Thus we have negative evidence, the disappearance of bands at 2.95 and 6 μ, for the chelated structure of the β-ketones. It is difficult to indicate the presence of the O–H–O band since it too absorbs at about 3.4 μ.



However, the O–D–O band[8] appears at about 4.35 μ, and it is the plan of the authors to prepare β-diketones with the labile hydrogen replaced by deuterium and study them spectroscopically in an attempt to establish definitely that the enols of the β-diketones are chelated.

[8] R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 534 (1938).

DEPARTMENT OF CHEMISTRY
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Boiling Point and Composition of Methanethiol–Isobutane Azeotrope

BY F. R. BROOKS AND A. C. NIXON

RECEIVED AUGUST 18, 1952

Recently Denyer, Fidler and Lowry[1] predicted the boiling point and composition of an azeotrope between methanethiol and isobutane by extrapolation from the boiling points and azeotropic compositions of other thiols and hydrocarbons. We recently had occasion to determine the boiling point of this azeotrope and find that the azeotrope has a boiling point of −13.0° and contains 17.5 mole % of the thiol; corresponding values of −16.5° and 12.5 mole % were predicted by Denyer, *et al.* The difference between the observed and predicted values may reflect the deviation which commonly occurs with the first member of a series or it may be due to uncertainty in our determination. Our data were obtained by distillation of mixture of 19.6 mole % methanethiol (Eastman Kodak Co. white label) in isobutane (Phillips 99.9% pure). The distillation was carried out in standard (Podbielniak) low temperature distillation apparatus, which is equivalent to about 25 theoretical plates, at a reflux ratio of about 50:1. Several cuts were taken after the temperature had leveled out and after intermittent periods of total reflux operation. We estimate that the data are good to ±0.5° and ±0.5 mole %.

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[1] Denyer, Fidler and Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

Eight-membered Carbocycles. IV. Reduction of Cycloöctatetraene

BY L. E. CRAIG, R. M. ELOFSON AND I. J. RESSA

RECEIVED SEPTEMBER 2, 1952

Since it has been shown that cycloöctatetraene can be determined quantitatively by polarographic analysis,[1] the electrolytic reduction of cycloöctatetraene at a mercury cathode was investigated. Reduction was found to proceed smoothly in neutral and alkaline solutions in the presence of the tetramethylammonium ion. Without the tetramethylammonium ion, the reduction was found to be much less efficient, a fact which is in agreement with the polarographic findings.[1]

The product of the electrolytic reduction was shown by elementary analyses and by the absorption of three molar equivalents of hydrogen to give cycloöctane to be cycloöctatriene. Chromatographic examination of the product showed that two materials were present, one to the extent of about three times the other. The ultraviolet absorption spectrum of the material present in the larger amount was essentially identical with that reported by Cope and Hochstein[2] for 1,3,6-cyclooctatriene. The ultraviolet absorption spectrum of the mixture produced by electrolytic reduction indicates that it is a mixture of about 75% 1,3,6-cycloöctatriene and 25% 1,3,5-cycloöctatriene, which is in agreement with the composition indicated by the chromatographic separation.

During the course of the work, isomerization of 1,3,6-cycloöctatriene to 1,3,5-cycloöctatriene during slow distillation was encountered. The alkali-catalyzed isomerization as reported by Cope and Hochstein[2] was confirmed by treating with ethanolic sodium ethoxide and following the isomerization by means of the ultraviolet absorption spectra. The curves of Fig. 2 clearly indicate that the one product is being formed at the expense of the other. It, therefore, seems probable that 1,3,6-cyclooctatriene is the product formed upon electrolytic reduction and that the 1,3,5-cycloöctatriene is formed by isomerization. The formation of bicyclic hydrocarbons in the reduction appears to be negligible because of the high (84%, distilled) yield of cycloöctane obtained on hydrogenation.

Cycloöctatrienes have also been reported to be produced from cycloöctatetraene by the addition of lithium followed by treatment with methanol,[2,3] by reduction with sodium in liquid ammonia,[3] and by reduction with sodium and methylaniline in ether.[4] Ziegler and Wilms[4] suggested that the first product of the reduction with sodium and *m*-ethylaniline in ether is bicyclo[4,2,0]-3,7-octa-

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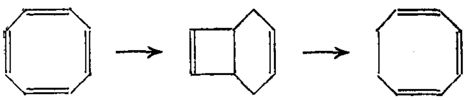
[1] R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

[2] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

[3] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[4] K. Ziegler and H. Wilms, *ibid.*, **567**, 1 (1950).

diene (I) which rearranges on heating to 1,3,5-cycloöctatriene (II). In a reduction carried out with "intense cooling," Ziegler and Wilms reported



I II

the formation of I and its reduction to bicyclo[4,2,0]octane. In our work, the product formed by reduction in this manner at room temperature was a mixture of 1,3,6-cycloöctatriene (about 57%) and 1,3,5-cycloöctatriene (about 43%). The formation of any appreciable quantity of bicyclic hydrocarbons did not appear to occur.

Reduction of cycloöctatetraene with sodium and alcohol was carried out with the expectation that products similar to those produced in the above reductions would be obtained. The product, however, was found to absorb two molar equivalents of hydrogen to give cycloöctane. Ozonolysis experiments clearly indicated that the product again was not a single compound. A refined distillation resulted in the separation of two products which were shown by comparison of physical constants with those reported by elementary analyses and by ozonolysis to be 1,4-cycloöctadiene and 1,5-cycloöctadiene. A small amount of lower boiling product was obtained which absorbed oxygen rapidly from the air. It was not possible to identify it and it is probable that it was either 1,3-cycloöctadiene or a bicyclic hydrocarbon.

Reduction of cycloöctatetraene was attempted with zinc and acetic acid and with lithium aluminum hydride. Reduction occurred to a limited extent in each case. The ultraviolet absorption curves of the products obtained by subtracting the absorption due to the unreacted cycloöctatetraene present suggest that the products were trienes, although the absorption maxima were displaced toward shorter wave lengths.

Acknowledgment.—We are indebted to Dr. H. Hemmendinger for determination of the ultraviolet spectra, to Dr. F. W. Mitchell for the microchromatographic examinations, to Dr. C. W. Gould for quantitative hydrogenation, to Dr. L. J. Lohr for distillations in the Podbielniak column, and to Mr. L. J. Frauenfelder and Mr. R. L. Edsberg for analyses.

Experimental[5]

Electrolytic Reduction of Cycloöctatetraene.—A solution of 100 g. of tetramethylammonium bromide in one liter of 50% ethanol was placed in a 2-liter resin pot, the bottom of which was covered with mercury to serve as a cathode. A porous electrolysis cup containing 300 g. of 20% sodium hydroxide as anolyte was suspended in the catholyte medium and a steel anode attached. Connection was made to the cathode by mercury-filled glass tubing with a platinum wire sealed into the end immersed in the mercury. To the catholyte was added 100 g. of cycloöctatetraene and the resin pot was covered and fitted with a condenser to prevent loss by evaporation and a stirrer to produce agitation. The resin pot was immersed in ice and the electrolysis carried out with a current of 6 to 8 amperes (20 volts applied) for ten hours with the catholyte–cycloöctatetraene mixture being agitated. The catholyte was then extracted exhaustively with low boiling petroleum ether, the combined extracts dried over anhydrous sodium sulfate, the solvent removed and the residue distilled at reduced pressure through a short glass helix-packed column. The product (74 g.) was collected at 73–75° (80 mm.), n^{25}D 1.5146.[6] See Fig. 1 for the ultraviolet absorption spectrum. *Anal.* Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.24; H, 9.78.

A 10.6-g. sample of the product absorbed 100% of three molar equivalents of hydrogen in the presence of Adams catalyst to give an 84% yield of cycloöctane, b.p. 147.5–148°, n^{25}D 1.4546, m.p. 9–11° (about 98% purity[2]).

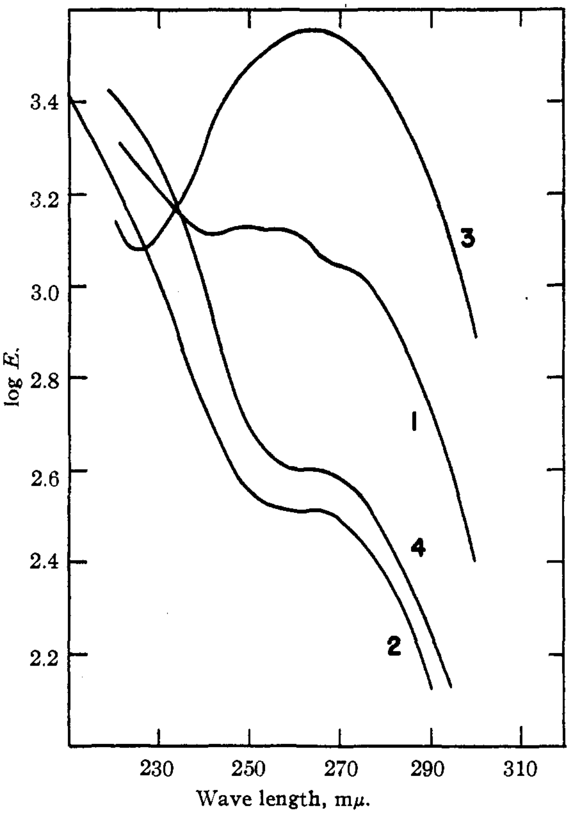


Fig. 1.—Ultraviolet absorption spectra: curve 1, electrolytic reduction product of cycloöctatetraene; curve 2, material separated from electrolytic reduction product by chromatography; curve 3, 1,3,5-cycloöctatriene[3]; curve 4, 1,3,6-cycloöctatriene containing 4–6% of 1,3,5-cycloöctatriene.[3]

A small sample of the electrolytic reduction product was examined by chromatography on a micro scale with activated charcoal as the absorbent and methanol as the solvent. The concentration of the material in the effluent liquid was followed continuously by index of refraction changes. The refractive index curves indicated that the product consisted of two materials, one present to the extent of about three times the other. The material which was present in the larger amount passed through the column first and its ultraviolet absorption spectrum was obtained (see Fig. 1). This absorption curve is nearly identical with that reported for 1,3,6-cycloöctatriene containing 4–6% of 1,3,5-cycloöctatriene.[2] The ultraviolet absorption curve of the entire electrolytic reduction product ϵ_{265} 1175, indicates that it is composed of about 75% 1,3,6-cycloöctatriene and 25% 1,3,5-cycloöctatriene (based on values of ϵ_{265} 3600 for 1,3,5-cycloöctatriene and ϵ_{125} 320 for 1,3,6-cycloöctatriene).

Treatment of Cycloöctatriene Mixture with Alcoholic Sodium Ethoxide.—To a solution of sodium ethoxide prepared by adding 2 g. of metallic sodium to 50 cc. of absolute

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[5] All melting points and boiling points are uncorrected, unless otherwise indicated.

[6] Reported (ref. 2) for 1,3,6-cycloöctatriene, b.p. 68° (60 mm.), n^{25}D 1.5046; for 1,3,5-cycloöctatriene, b.p. 72.5° (60 mm.), n^{25}D 1.5215.

ethanol was added 21 g. of the electrolytic reduction product. The solution was heated on a steam-bath at reflux for 30 minutes, cooled, poured into 50 cc. of cold water and the mixture extracted exhaustively with petroleum ether. After drying the combined extracts and removing the solvent, the cycloöctatriene was distilled, 19 g., b.p. 74–76° (80 mm.), $n^{25}\mathrm{D}$ 1.5165. The ultraviolet absorption spectrum is reported in Fig. 2. This material (17 g.) was again treated as above with reflux being maintained for ten hours. Upon working up in the same manner, the product was collected at 75–77° (80 mm.), $n^{25}\mathrm{D}$ 1.5228. The ultraviolet absorption spectrum is also contained in Fig. 2.

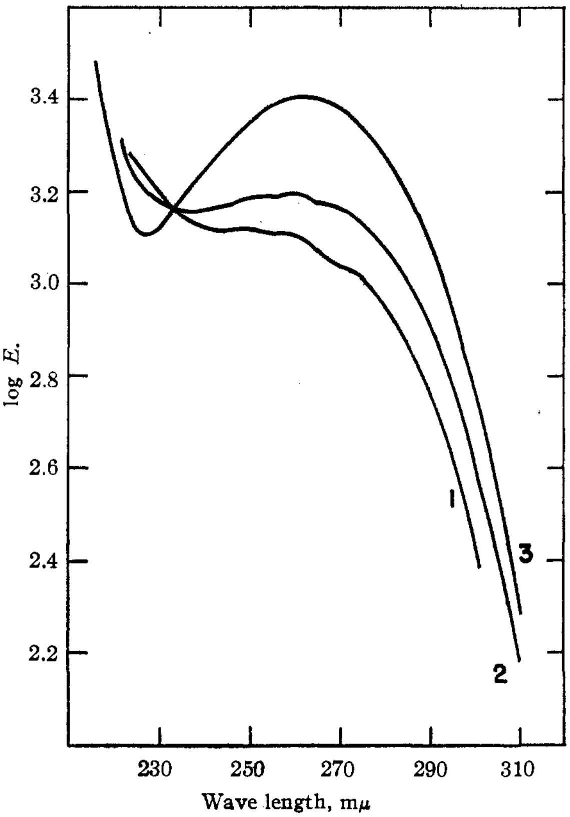

Fig. 2.—Ultraviolet absorption spectra of electrolytic reduction product of cycloöctatetraene: curve 1, as recovered; curve 2, after refluxing 30 min. in the ethanolic sodium ethoxide; curve 3, after 10 hr.

Reduction of Cycloöctatetraene with Sodium and N-Ethylaniline in Ether.—To a stirred solution of 20.8 g. of cycloöctatetraene and 72.7 g. of N-ethylaniline in 350 ml. of absolute ether was added 10.1 g. of sodium in small pieces. The sodium was added over a period of 2 hours and the temperature was kept below 25°. After stirring for an additional two hours, 290 ml. of water was added slowly with external cooling. The ether layer was removed under reduced pressure leaving 19.7 g. of residue, $n^{25}\mathrm{D}$ 1.5092, which was shown by polarographic analysis to contain 1.2% unreacted cycloöctatetraene. Assuming no other material to be present, the ultraviolet absorption spectrum (ϵ_{265} 1780) indicated that the product contained 57% 1,3,6-cycloöctatriene and 43% 1,3,5-cycloöctatriene.

A 13.1-g. sample of the product absorbed 88% of three molar equivalents of hydrogen in the presence of Adams catalyst to give 10.2 g. (74%) of cycloöctane, b.p. 150–151°, $n^{25}\mathrm{D}$ 1.4563, m.p. 10–12.5°.

Reduction of cycloöctatetraene as above with aniline and with piperidine in place of the ethylaniline proceeded in a similar manner, although somewhat longer reaction periods were required. When the ether was omitted, no reduction occurred and the sodium was largely unreacted even after 24 hours.

Reduction of Cycloöctatetraene with Sodium in Alcohol. I.—Into a 1-liter, three-necked flask fitted with a stirrer and reflux condenser were placed 500 ml. of absolute ethanol and 55 g. (0.53 mole) of cycloöctatetraene. To this solution was added in small portions 70 g. (3 moles) of metallic sodium. The heat of the reaction caused reflux of the ethanol and gentle reflux was maintained by the rate of addition. After all had been added, reflux was maintained for an additional hour. To the cooled mixture was added with cooling 300 ml. of cold water and the resulting mixture was extracted with four 100-ml. portions of low boiling petroleum ether. The extracts were dried over anhydrous sodium sulfate, the ether removed and the residue distilled crudely to give 44.8 g. (81%) of product, b.p. 141–149°, $n^{25}\mathrm{D}$ 1.4859. Refractionation through a short glass-helix packed column gave material with b.p. 147–149°, $n^{25}\mathrm{D}$ 1.4857.

A 10-g. sample of the product in the presence of Adams catalyst absorbed 102% of two molar equivalents of hydrogen to give cycloöctane (9.4 g., 91%), b.p. 148–150°, $n^{25}\mathrm{D}$ 1.4550, m.p. 10–11°.

A 5-g. sample of the product in methylene chloride was treated with bromine until color persisted. Removal of the solvent under reduced pressure left a very viscous residue from which separated 1.5 g. of crystalline product on treatment with low boiling petroleum ether, m.p. 127–128°. Elementary analyses indicated that the product was a tetrabromocycloöctane. *Anal.* Calcd. for $C_8H_{12}Br_4$: C, 22.44; H, 2.81; Br, 74.72. Found: C, 22.34; H, 2.73; Br, 75.04.

Several samples of the reduction product were subjected to ozonolysis and the ozonide oxidized according to the directions indicated below, but it was not possible to isolate any pure dicarboxylic acid. The apparent mixture of dicarboxylic acids produced suggested that the reduction product was a mixture.

II.—A 50-g. sample of cycloöctatetraene was reduced by the above procedure (500 ml. of ethanol, 55 g. of sodium) and the product isolated in the same manner. The product (55 ml.) was carefully fractionated (reflux ratio 30:1) through a 6 ft. × 11 mm. Podbielniak column with tetralin as a chaser. Three materials were collected: A, 8.5 ml., b.p. 140.5° (cor.) (737 mm.), $n^{25}\mathrm{D}$ 1.4865; B, (1,4-cycloöctadiene,[7] 22.5 ml., b.p. 143.2° (cor.) (737 mm.), $n^{25}\mathrm{D}$ 1.4858; and C, (1,5-cycloöctadiene),[8] 22 ml., b.p. 150.8° (cor.) (757 mm.), $n^{25}\mathrm{D}$ 1.4908. *Anal.* Calcd. for C_8H_{12}: C, 88.81; H, 11.19. Found: for A: C, 83.50; H, 9.82. For B: C, 88.50; H, 11.51. For C: C, 88.64; H, 11.35.

In quantitative microhydrogenations, materials A, B and C absorbed 105.9, 92.8 and 99.7%, respectively, of two molar equivalents of hydrogen.

Samples (1.1 g.) of materials A, B and C were ozonized in 75 ml. of ethyl acetate at −20°, the ethyl acetate removed under reduced pressure and the residue heated on a steam-bath for four hours with 25 ml. of acetic acid and 15 ml. of 30% hydrogen peroxide. The solutions were evaporated to dryness under reduced pressure, the residue dissolved in 10 ml. of saturated sodium carbonate and the solution extracted with two 10-ml. portions of ether. The water layer was acidified with concentrated hydrochloric acid and the resulting solution (white precipitate formed from material C) extracted with one 25-ml. and five 10-ml. portions of ether. Ether extracts were dried and evaporated to dryness.

It was not possible to isolate any pure material from the organization of A. The elementary analysis of material A indicated that it had absorbed oxygen before it was examined. The oxygen-containing compounds might be responsible for the impurities in the ozonolysis product. A might be bicyclic or it might be 1,3-cycloöctadiene.[9]

From the ozonolysis as carried out as above, B gave 1.35 g. of white powder, m.p. 92–119°. This material was separated into benzene-insoluble and benzene-soluble portions. Recrystallization of the benzene-insoluble material from water gave a small amount of material m.p. 135–137°

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[7] Reported for *cis*-1,4-cycloöctadiene (ref. 5), b.p. 145.1° (758 mm)., $n^{20}\mathrm{He}$ 1.4895.

[8] A. C. Cope and W. J. Bailey, THIS JOURNAL, **70**, **2305** (1948), reported b.p. 148–149° and $n^{25}\mathrm{D}$ 1.4905 and Ziegler and Wilms (ref. 4) reported b.p. 150.8° (755 mm.) and $n^{20}\mathrm{He}$ 1.4936 for 1,5-cycloöctadiene.

[9] Ziegler and Wilms (ref. 4) reported b.p. 142.7° (754 mm.), $n^{20}\mathrm{He}$ 1.4930, and A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950), reported b.p. 48° (25 mm.), $n^{25}\mathrm{D}$ 1.4940 for 1,3-cycloöctadiene.

(malonic acid melts at 136°). Two recrystallizations of the benzene-soluble material gave a very small amount of solid, m.p. 93–95°, mixed m.p. with a sample of glutaric acid, m.p. 94–96°.

C, from the above ozonolysis, gave 1.35 g. of white solid, m.p. 179–185°. After recrystallization from water it melted at 186–189°, mixed m.p. with a sample of succinic acid 187–189°.

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β-2-Pyrrole-ethylamine

BY WERNER HERZ

RECEIVED SEPTEMBER 5, 1952

In view of the appearance of two recent articles in which the synthesis of β-2-pyrrole-ethylamine from ethyl 2-pyrroleacetate is described,[1,2] we wish to report work carried out in this Laboratory which led to this amine and related substances *via* a different and very convenient route.

As outlined below we have utilized our earlier discovery that Mannich bases derived from pyrrole readily serve as alkylating agents.[3] 2-Dimethylaminomethylpyrrole methiodide, available from pyrrole in 80–85% yield,[4] was treated with sodium cyanide in aqueous solution and the resulting nitrile, obtained in 52% yield, was reduced to the amine using lithium aluminum hydride. This sequence of reactions obviates the difficulties caused during the last step by the relative insolubility of the amide in ether and appears to be generally applicable, as exemplified by the preparation of β-2-(N-methylpyrrole)-ethylamine.

The physiological properties of these amines are now being investigated and will be reported elsewhere.

Acknowledgment.—This work was supported in part by a grant from the United States Public Health Service. We wish to thank Dr. H. J. Barrett of the Electrochemicals Division, du Pont de Nemours and Company, Inc., for the generous gift of chemicals.

Experimental[5]

2-Pyrroleacetonitrile.—2-Dimethylaminomethylpyrrole was prepared in 87% yield by the Mannich reaction[4] and was converted to the methiodide by dropwise addition to excess methyl iodide with stirring and cooling to avoid the formation of by-products.[6] The freshly prepared methiodide, wt. 34 g. (91%), which quickly turns dark on standing, was heated on the steam-bath for 1.5 hours with 17 g. of sodium cyanide and 200 ml. of water. The dark mixture was cooled and thoroughly extracted with ether. Fractionation of the dried ether extracts yielded 7.1 g. (52%) of product, b.p. 110–115° (2 mm.). The analytical sample boiled at 102–103° (1.1 mm.), n^{23}D 1.5230.

Anal. Calcd. for $C_6H_6N_2$: C, 67.92; H, 5.70. Found: C, 67.70; H, 5.82.

β-2-Pyrrole-ethylamine.—A solution of 36 g. of the nitrile in 400 ml. of anhydrous ether was added dropwise with stirring to 17 g. of lithium aluminum hydride in one liter of ether. The mixture was worked up as recommended by Amundsen and Nelson.[7] On distillation there was obtained 24.5 g. (66%) of a rather viscous basic substance, b.p. 90–98° (2 mm.). The analytical sample boiled at 91–92° (1.7 mm.).

Anal. Calcd. for $C_6H_{10}N_2$: C, 65.40; H, 9.16. Found: C, 65.28; H, 9.01.

The orange picrate, m.p. 154.5–155° (dec.), lit.[1] 156°, was prepared by mixing alcoholic solutions of the amine and picric acid and heating. Crystals separated only after dilution with water and prolonged chilling.

β-2-(N-Methylpyrrole)-ethylamine.—The yield of 2-N-methylpyrroleacetonitrile[3b] was improved considerably by carrying out the reaction on a steam-bath. From 201 g. of 2-dimethylaminomethyl-N-methylpyrrole methiodide there was obtained 36 g. (42%) of the nitrile and 11.6 g. (12%) of crude 2-N-methylpyrroleacetamide. Lithium aluminum hydride reduction of the nitrile in the manner described above yielded on fractional distillation 19.7 g. (53%) of a basic substance which decomposed slowly at room temperature and readily absorbed carbon dioxide from the air; b.p. 70–75° (1.5 mm.). The analytical sample boiled at 70–71° (1.5 mm.), n^{24}D 1.5248.

Anal. Calcd. for $C_7H_{12}N_2$: N, 22.55. Found: N, 22.39.

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[1] K. Eiter, *Monatsh.*, **83**, 252 (1952).

[2] W. Kutscher and O. Klamerth, *Z. physiol. Chem.*, **289**, 229 (1952).

[3] (a) W. Herz, K. Dittmer and S. J. Cristol, THIS JOURNAL, **70**, 504 (1948); (b) W. Herz and J. L. Rogers, *ibid.*, **73**, 4923 (1951).

[4] W. Herz, K. Dittmer and S. J. Cristol, *ibid.*, **69**, 1698 (1947).

[5] Melting points are uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[6] C. Schöpf and J. Thesing, *Angew. Chem.*, **63**, 377 (1951); J. Thesing and F. Schülde, *Ber.*, **85**, 324 (1952).

[7] L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

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Metachromasy of Rhodamine 6G Produced by Polyvinyl Sulfate

BY M. KOIZUMI AND N. MATAGA

RECEIVED SEPTEMBER 12, 1952

In the course of the study of metachromasy, we have found that the system Rhodamine 6G and K-polyvinyl sulfate (PVSK) (of which sulfonation degree is 61%) shows a very interesting type of concentration effect which differs from the result reported recently by Levine and Schubert.[1]

The main features of our experimental results can be summarized as follows. (a) The absorption spectrum of the aqueous Rhodamine 6G solution has a peak at 526 mμ accompanied by a small shoulder at 500 mμ in the range of lower concentration, but the shoulder at 500 mμ grows gradually as the concentration increases, the peak at 526 mμ declining at the same time. These results are the same as those reported by other investigators and the peaks at 526 mμ and at 500 mμ can be attributed, respectively, to the monomer (M-band) and the dimer (D-band)[2] (*cf.* Fig. 1).

(b) When PVSK is added step by step to the aqueous Rhodamine 6G solution of a definite concentration, the D-band grows quite rapidly, at first, accompanied with the reduction of M-band, but when the quantity of the added PVSK reaches a certain critical value, the M-band begins to grow again (*cf.* Fig. 2), though the turning point is not so sharp and varies with the dye concentration. Such behaviors are always observed at any concentration of dye between 5 × 10^{-6} mole/liter and 5 × 10^{-5} mole/liter. It is to be added that although position of the M-band does not change at

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[1] A. Levine and M. Schubert, THIS JOURNAL, **74**, 91 (1952).

[2] W. L. Levshin, *Acta Physicochim. U.R.S.S.*, **1**, 684 (1935).