Anal. Calcd. for $C_{24}H_{41}NO$: N, 3.90. Found: N, 3.85, 4.01, 3.92.

The anilide showed no depression of m. p. (mixed m. p. 92.5–93.5°) on admixture with authentic stearanilide, m. p. 92.5–93.5° (95.5°).[24]

9,12-Diketostearic Acid.—12-Hydroxy-9-octadecynoic acid (ricinstearolic acid) was prepared from castor oil by the method of Mühle.[25] This substance was converted to 12-hydroxy-9-ketostearic acid by the procedure of Goldsobel.[26] The latter compound was oxidized to 9,12-diketostearic acid with potassium permanganate in acetone, following the method outlined above for oxidation of the tetrahydro derivative, m. p. 102–104°. Crystallization from 50% aqueous acetone, followed by recrystallization from ethyl acetate, gave pure **9,12-diketostearic acid,** m. p. 97.5–98° (96.5°)[5] in a yield of 47%. The ultraviolet spectrum of the substance (Fig. 2) showed a maximum at 275 mμ, log ε = 1.788 (95% ethanol). The infrared spectrum (Fig. 1) resembled that of the diketoacid, m. p. 95–96°, but showed minor characteristic differences, particularly in the region 1000 to 700 cm.$^{-1}$. The substance yielded the reported dioxime, m. p. 111.5–112.5° (112–113°),[5] and pyrrole, m. p. 71–72.5° (73°).[5]

The melting point of 9,12-diketostearic acid was depressed on admixture with the diketoacid, m. p. 95–96° (mixed m. p. 87.5–91°). The mixture of the corresponding dioximes also showed a depression (mixed m. p. 95–108°).

Ozonization.—Ozonized oxygen (10 l./hr.) was passed through an ice-cold solution of the isolate, m. p. 104–104.5° (500 mg.) in 50 ml. of methylene chloride for one hour. Two volumes of water was added to the solution and nitrogen was bubbled through the mixture until the methylene chloride was evaporated. A 20-ml. portion of 30% hydrogen peroxide was added to the resulting suspension, the mixture was boiled for one hour, and the solution was extracted three times with 100-ml. portions of chloroform. Evaporation of the combined extract left 400 mg. of yellow oil with a strong, fatty-acid odor. Vacuum distillation of the oil yielded 36 mg. of a volatile acid, b. p. 80–90° (15 mm.). Comparison of the infrared spectrum of the distillate with that of *n*-valeric acid showed the two to be identical. The distillate yielded an **S-benzylthiuronium salt,** m. p. 154–155°.

Anal.[21] Calcd. for $C_{13}H_{20}N_2O_2S$: N, 10.44. Found: N, 10.23, 10.20.

An authentic sample of the previously unreported **S-benzylthiuronium** *n*-valerate, m. p. 154–155°, was prepared for comparison.

Anal.[21] Calcd. for $C_{13}H_{20}N_2O_2S$: N, 10.44. Found: N, 10.11, 10.17.

The derivatives showed no depression of m. p. on admixture (mixed m. p. 154–155°).

The non-volatile still-residue was extracted with 3 ml. of hot water. The extract was decolorized with charcoal (Darco G-60), and filtered. On cooling, the solution deposited 40 mg. of crystalline solid, m. p. 96–99°. Recrystallization from water raised the m. p. to 101–103°. The infrared spectrum of the substance was found to be identical with that of azelaic acid. The mixed m. p. with an authentic sample of the latter, m. p. 103–105° (106°),[27] showed no depression (mixed m. p. 103–105°). Treatment of the substance with *p*-bromophenacyl bromide yielded a derivative, m. p. 129–130°.

Anal. Calcd. for $C_{25}H_{26}Br_2O_6$: Br, 27.45. Found: Br, 27.56, 27.64.

The mixed m. p. of the derivative with authentic di-(*p*-bromophenacyl) azelate, m. p. 130–131° (130.6°),[28] showed no depression (mixed m. p. 130–131°).

A search for other fragments in the mother liquor resulted only in the isolation of more azelaic acid.

Summary

A crystalline substance, isolated in low yield from tung oil, has been shown to be 9,14-dihydroxy-10,12-octadecadienoic acid.

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[25] Mühle, *Ber.*, **46**, 2091 (1913).

[26] Goldsobel, *ibid.*, **27**, 3121 (1894).

[27] Gantter and Hell, *Ber.*, **14**, 1545 (1881).

[28] Kelly and Kleff, THIS JOURNAL, **54**, 4444 (1932).

STAMFORD, CONNECTICUT RECEIVED JULY 9, 1949

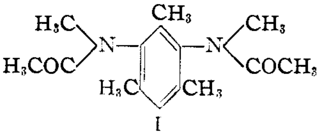
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Aryl Amines. VIII. Ring Nitrogen Derivatives of Diaminomesitylene

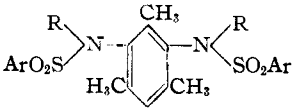
BY ROGER ADAMS* AND JOHN B. CAMPBELL[1]

Stereoisomers of N,N′-dimethyl-N,N′-diacetyldiaminomesitylene (I) could not be obtained.[2] However, *cis* and *trans* isomers due to restricted rotation of the groups about the carbon–nitrogen bond were prepared readily from compounds of the type shown in formula II.[3] When R is a carboxymethyl group, the *trans* isomer was resolved into its optical antipodes.

In the present investigation, a study was made of diaminomesitylene derivatives in which the two nitrogens were incorporated in five-membered ring systems. As a model experiment, disuccinimidomesitylene was synthesized from N,N′-disuccinyldiaminomesitylene by the action of acetic anhydride and sodium acetate. In a similar manner, diaminomesitylene and α,α-dimethylsuccinic anhydride were condensed to the N,N′-di-(α,α-dimethylsuccinyl)-diaminomesitylene and the latter dehydrated to bis-(α,α-



I



II

R = alkyl, benzyl, carboxymethyl
Ar = phenyl or
R = methyl
Ar = phenyl, *p*-tolyl, *p*-bromophenyl

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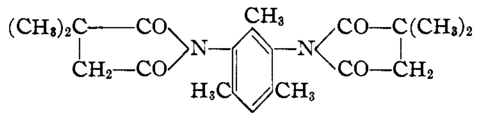
* Harvard University Ph.D. 1912.

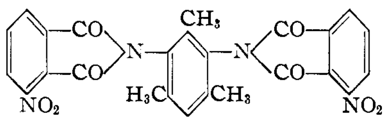
[1] An abstract of a thesis submitted by John B. Campbell to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adams and Chase, THIS JOURNAL, **70**, 4202 (1948).

[3] Adams and Tjepkema, *ibid.*, **70**, 4204 (1948); Adams and Rothstein, *ibid.*, **71**, 1620 (1949).

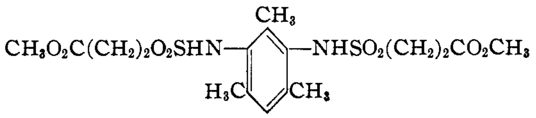
dimethylsuccinimido)-mesitylene (III). No isomers were observed; a 90% yield of a single product resulted. Nitration of III gave a quantitative yield of a single mononitro derivative.

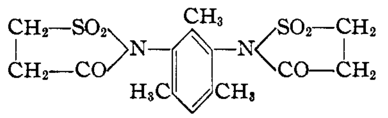

III


IV

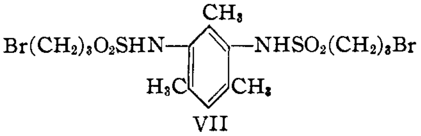
By the reaction of 3-nitrophthalic anhydride with daiminomesitylene, bis-(2-carboxy-6-nitrobenzamido)-mesitylene formed, assuming that the anhydride linkage is opened in the same position as that established when it reacts with ammonia.[4] No solvent could be found for purification, so after extraction to remove starting materials, it was dehydrated to bis-(3-nitrophthalimido)-mesitylene (IV). A 93% yield of a single product resulted.

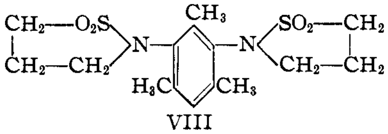
Bis-(propionylsulfimido)-mesitylene (VI) was next prepared. The most suitable conditions for the synthesis involved the heating together without solvent of equimolar quantities of methyl β-chlorosulfonylpropionate and diaminomesitylene to give 62% yield of N,N′-di-(β-carbomethoxyethanesulfonyl)-diaminomesitylene (V). Hydrolysis of the ester groups in V followed by dehydration gave a single product, bis-(propionylsulfimido)-mesitylene (VI).


V


VI

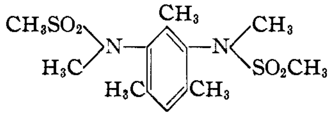
To obtain a molecule more similar to those illustrated by II, a 13% yield of N,N′-di-(γ-bromopropanesulfonyl)-diaminomesitylene (VII) was obtained by heating together equimolar amounts of γ-bromopropanesulfonyl chloride and diaminomesitylene. The product could not be obtained analytically pure but ring closure by means of aqueous alkali afforded the readily purified bis-(N-trimethylenesulfonamido)-mesitylene (VIII) in 94% yield. No isomers were found.

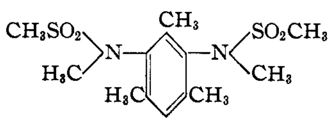

VII


VIII

It thus appears that in compounds III, IV, VI and VIII, despite the varied character of the atoms attached to the nitrogens, restricted rotation is non-existent. The groups attached to the nitrogens are apparently pulled away from the benzene ring and do not collide with the methyl groups of the mesitylene nucleus. Atomic distances and bond angles in molecules of this type have not been measured so that the conclusion has to be drawn merely from the experimental facts observed that the bond angle is smaller when the nitrogen is incorporated in these five-membered rings than when no ring is present.

In order to verify this supposition, N,N′-dimethyl-N,N′-dimethanesulfonyldiaminomesitylene (IX) was prepared which is very similar to compound VIII, but does not contain the nitrogen ring systems. Two isomers were readily obtained, IXa and IXb. It is thus obvious that only very minor differences in structure of such molecules are adequate to modify the mobility of the atoms present.


IXa


IXb

Methanesulfonyl chloride and diaminomesitylene reacted to form N,N′-dimethanesulfonyldiaminomesitylene. Upon methylation of this product in alkaline solution, N,N′-dimethyl-N,N′-dimethanesulfonyldiaminomesitylene was obtained as a mixture of *cis* and *trans* isomers. The higher-melting form (m. p. 209–210°) was assigned structure IXa, the lower-melting form (m. p. 175–178°) structure IXb. The lower-melting form above its melting point is converted into the higher-melting form. Infrared spectra of nitromethane solutions of the two forms indicated the structural differences of the two and showed they were not isomorphic.

Experimental[5]

N,N′-Disuccinyldiaminomesitylene.—A suspension of 6.67 g. of succinic anhydride in a solution of 5 g. of diaminomesitylene in 150 ml. of dry benzene was refluxed for three hours. After cooling, the cream colored product was collected on a filter and washed well with benzene. The yield was 11.16 g. (96%). Two recrystallizations

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[4] Alexander and McElvain, THIS JOURNAL, 60, 2285 (1938).

[5] All melting points are corrected. Those above 200° were taken in an aluminum block.

from 95% ethanol gave small white crystals, m. p. 227-229°.

Anal. Calcd. for $C_{17}H_{22}N_2O_6$: C, 58.27; H, 6.33; N, 8.00. Found: C, 58.46; H, 6.40; N, 8.13.

Disuccinimidomesitylene.—A suspension of 1.18 g. of N,N'-disuccinyldiaminomesitylene and 1 g. of anhydrous sodium acetate in 10 ml. of acetic anhydride was refluxed for three hours and cautiously hydrolyzed with 4 ml. of water. The resulting solution deposited small white needles upon standing a few minutes. After cooling, the product was collected on a filter, washed well with 50% acetic acid solution and dried. The yield was 0.99 g. (93%). After recrystallization from absolute ethanol, the melting point was 295-297°.

Anal. Calcd. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 65.19; H, 5.84; N, 8.99.

N,N'-Di-(α,α-dimethylsuccinyl)-diaminomesitylene.—A solution of 16.5 g. of diaminomesitylene and 27.0 g. of α,α-dimethylsuccinic anhydride[6] in 350 ml. of dry benzene was refluxed for four hours. The resulting mixture was cooled and the light cream colored product collected on a filter, washed well with benzene and dried. The yield was 36.0 g. (84%). Two recrystallizations from 95% ethanol gave white crystals, m. p. 246-247°.

Anal. Calcd. for $C_{21}H_{30}N_2O_6$: C, 62.04; H, 7.44; N, 6.89. Found: C, 61.96; H, 7.50; N, 6.94.

Bis-(α,α-dimethylsuccinimido)-mesitylene.—A suspension of 9.07 g. of N,N'-di-(α,α-dimethylsuccinyl)-diaminomesitylene and 9 g. of anhydrous sodium acetate in 90 ml. of acetic anhydride was refluxed for six hours and then cautiously hydrolyzed with 15 ml. of water. The resulting solution was evaporated to a volume of 35 ml., 25 ml. of boiling water slowly stirred in and the solution cooled slightly. As crystals appeared, an additional 25 ml. of hot water was gradually added. After cooling overnight in the ice box, the product was collected on a filter and washed with a little water. The yield was 7.34 g. (90%) of white crystals. After recrystallization from 95% ethanol the product melted at 211-213°.

Anal. Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.08; H, 7.08; N, 7.56. Found: C, 67.99; H, 7.15; N, 7.78.

Bis-(α,α-dimethylsuccinimido)-nitromesitylene.—To 225 g. of fuming nitric acid (sp. gr. 1.5) maintained at 0° was added 10.2 g. of solid bis-(α,α-dimethylsuccinimido)-mesitylene over a period of fifteen minutes. The resulting solution, after standing at 0° for thirty minutes, was poured onto 1500 g. of cracked ice. The bulky white crystalline precipitate was collected on a filter, washed well with water and dried. The yield was 11.1 g. (97%). After recrystallization from 95% ethanol small white crystals were obtained, m. p. 250-251°.

Anal. Calcd. for $C_{21}H_{25}N_3O_6$: C, 60.71; H, 6.07; N, 10.11. Found: C, 60.90; H, 6.21; N, 10.36.

Bis-(2-carboxy-6-nitrobenzamido)-mesitylene.—A suspension of 3.75 g. of diaminomesitylene and 9.64 g. of 3-nitrophthalic anhydride in 300 ml. of dry benzene was refluxed for six hours, cooled and the light cream colored product collected on a filter, washed well with benzene and dried. A nearly quantitative yield was obtained. The product could be dissolved in only a few high boiling solvents with some accompanying decomposition. It was purified by refluxing with 200 ml. of glacial acetic acid for three hours and filtering while hot. The product then melted at 242-245°. From the acetic acid filtrate a very small amount of bis-(3-nitrophthalimido)-mesitylene, m. p. 276-278°, separated which is described below.

Bis-(3-nitrophthalimido)-mesitylene.—A suspension of 5.05 g. of bis-(2-carboxy-6-nitrobenzamido)-mesitylene and 5 g. of anhydrous sodium acetate in 50 ml. of acetic anhydride was refluxed for five hours and then cautiously hydrolyzed with 12 ml. of water. After standing overnight at room temperature the tan crystalline product was collected on a filter, washed with a few ml. of glacial acetic acid and dried. The yield was 4.36 g. (93%). After two recrystallizations from a 4:1 mixture of ethyl acetate and ethylene chloride, cream colored crystals resulted, m. p. 276-278°.

Anal. Calcd. for $C_{25}H_{16}N_4O_8$: C, 60.00; H, 3.22; N, 11.20. Found: C, 59.88; H, 3.17; N, 11.40.

Methyl β-Chlorosulfonylpropionate.—A solution of 34.3 g. of methyl β-sulfopropionate[7] in 30 ml. of thionyl chloride was refluxed for three hours and the excess thionyl chloride removed under reduced pressure. The residue was distilled through a 10-in. Vigreux column. After a very small forerun there was obtained 27.5 g. (72%) of a nearly colorless viscous oil, b. p. 110-113° (4 mm.).

Anal. Calcd. for $C_4H_7O_4ClS$: C, 25.74; H, 3.78. Found: C, 25.77; H, 3.95.

β-Carbomethoxyethanesulfonanilide.—A solution of 0.5 g. of methyl β-chlorosulfonylpropionate and 0.6 g. of aniline in 15 ml. of dry benzene was refluxed for twenty minutes and filtered from the precipitated hydrochloride. The benzene was removed and the residue recrystallized three times from carbon tetrachloride to yield white needles, m. p. 89°. The product was soluble in 5% aqueous sodium hydroxide.

Anal. Calcd. for $C_{10}H_{13}NO_4S$: C, 49.37; H, 5.38; N, 5.76. Found: C, 49.61; H, 5.33; N, 5.75.

In pyridine or aqueous alkali, the reaction results in the formation of water-soluble products only, which may be sulfonic acids due to rearrangement.

N-(β-Carbomethoxyethanesulfonyl)-diaminomesitylene.—A solution of 3.53 g. of diaminomesitylene and 4.40 g. of methyl β-chlorosulfonylpropionate in 30 ml. of dry benzene was refluxed for two hours and filtered. The filtrate was evaporated to a volume of 15 ml. and 15 ml. of petroleum ether (b. p. 30-60°) was slowly stirred in. The cream colored precipitate was collected on a filter and washed with a few ml. of a 1:1 mixture of benzene and petroleum ether (b. p. 30-60°) and dried. The yield was 2.90 g. (41% based on the sulfonyl chloride used). After two recrystallizations from a 1:1 mixture of benzene and carbon tetrachloride white crystals were obtained, m. p. 133-134°.

Anal. Calcd. for $C_{13}H_{20}N_2O_4S$: C, 51.98; H, 6.71; N, 9.33. Found: C, 51.77; H, 6.70; N, 9.02.

In pyridine or aqueous alkali, only water-soluble products resulted, which may be sulfonic acids due to rearrangement.

N,N'-Di-(β-carbomethoxyethanesulfonyl)-diaminomesitylene.—A solution of 15 g. of diaminomesitylene and 18.7 g. of methyl β-chlorosulfonylpropionate in 30 ml. of chloroform was placed on the steam cone, the chloroform quickly evaporated and the residual cake heated for forty minutes. Then 80 ml. of 5% hydrochloric acid solution was added and the gummy mixture heated and stirred a few minutes to promote crystallization. The cream colored product was collected on a filter, washed well with water and dried. The yield was 14 g. (62% based on the sulfonyl chloride used). After recrystallization from a 1:1 mixture of benzene and ethanol, white crystals resulted, m. p. 140-141°.

Anal. Calcd. for $C_{17}H_{26}N_2O_8S_2$: C, 45.32; H, 5.82; N, 6.22. Found: C, 45.47; H, 5.91; N, 6.22.

The product was unaffected by the reaction of sodium acetate and acetic anhydride.

N,N'-Di-(β-carboxyethanesulfonyl)-diaminomesitylene.—A solution of 10.25 g. of N,N'-di-(β-carbomethoxyethanesulfonyl)-diaminomesitylene in 100 ml. of 15% aqueous sodium hydroxide was allowed to stand two days at room temperature. The solution was then acidified with concd. hydrochloric acid and placed in the ice box overnight. The white crystalline product was collected on a filter, washed with a little cold water and dried. The yield was 9.1 g. (95%). After recrystallization from a 1:1 mixture of ethanol and carbon tetrachloride the product melted at 181-182°.

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[6] Verkade and Hartmann, *Rec. trav. chim.*, **52**, 948 (1933).

[7] Kharasch, Chao and Brown, THIS JOURNAL, **62**, 2393 (1940). No attempt was made to obtain this material in crystalline form.

Anal. Calcd. for $C_{15}H_{22}N_2O_8S_2$: C, 42.64; H, 5.25; N, 6.63. Found: C, 42.87; H, 5.45; N, 6.67.

Bis-(propionylsulfimido)-mesitylene.—A mixture of 2.32 g. of N,N′-di-(β-carboxyethanesulfonyl)-diaminomesitylene, 2.3 g. of anhydrous sodium acetate and 25 ml. of acetic anhydride was refluxed for four hours and then cautiously hydrolyzed with 20 ml. of water. After cooling in the ice box overnight, the cream colored crystalline precipitate was collected on a filter, washed well with water and dried. The yield was 1.58 g. (75%). Two recrystallizations from ethylene chloride gave white crystals, m. p. 308–310° (dec.). No additional crystalline material could be obtained from the filtrate.

Anal. Calcd. for $C_{15}H_{18}N_2O_6S_2$: C, 46.62; H, 4.69; N, 7.25. Found: C, 46.49; H, 4.76; N, 7.45.

γ-Bromopropyl Thiocyanate.—To a stirred refluxing solution of 275 g. of trimethylene bromide in 300 ml. of absolute ethanol was added dropwise over a period of two hours a solution of 66 g. of potassium thiocyanate in 50 ml. of water. The mixture was refluxed for one hour after the addition was complete. Then 300 ml. of water was added and the mixture shaken to dissolve precipitated potassium bromide. The lower layer was separated, dried over anhydrous sodium sulfate and the excess trimethylene bromide removed at the water pump. The residue was distilled through a 12-inch column packed with glass beads to yield 66 g. (54%) of a viscous water-white liquid, b. p. 72° (1.5 mm.), n^{20}_D 1.5350. The material was extremely irritating upon contact with the skin.

Anal. Calcd. for C_4H_6NSBr: C, 26.69; H, 3.36; N, 7.78. Found: C, 26.89; H, 3.41; N, 7.85.

γ-Bromopropanesulfonyl Chloride.—Chlorine was passed into a well-stirred cooled suspension of 79 g. of γ-bromopropyl thiocyanate in 600 ml. of water at such a rate as to keep the temperature below 5°. After one hour the mixture had acquired a permanent yellow-green color and was extracted with 350 ml. of ether. The ether layer was washed with cold dilute sodium sulfite solution and dried over anhydrous sodium sulfate. After removal of the ether, the residue was distilled under vacuum, considerable decomposition occurring during distillation. The lachrymatory product was obtained as a dark yellow viscous oil, b. p. 96–100° (1.5 mm.). The yield was 56.4 g. (58%). No forerun of unreacted thiocyano compound was obtained. Analyses indicated the product was not entirely pure. It was used crude for the subsequent reactions.

N-Trimethylenesulfonamidobenzene.—A solution of 2 g. of the sulfonyl chloride and 5 g. of aniline in 15 ml. of chloroform was warmed to initiate a vigorous reaction. The chloroform was removed on the steam cone and the residue extracted with two 100-ml. portions of 10% hydrochloric acid. The residual oil was warmed and stirred a few minutes with 100 ml. of 5% aqueous sodium hydroxide, whereupon crystallization took place. The product was collected on a filter, washed well with water and recrystallized twice from a mixture of benzene and methylcyclohexane to yield glistening white platelets, m. p. 122°.

Anal. Calcd. for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 55.04; H, 5.86; N, 7.39.

N,N′-Di-(γ-bromopropanesulfonyl)-diaminomesitylene.—A solution of 6.23 g. of γ-bromopropanesulfonyl chloride and 4.22 g. of diaminomesitylene in 15 ml. of chloroform was placed on the steam cone, the chloroform quickly boiled off and the residual cake heated for thirty minutes. Then 80 ml. of 5% hydrochloric acid was added and the mixture warmed and stirred a few minutes. The solution was decanted from the dark gummy residue and the latter washed twice by decantation with water. The gum was then extracted with three 75-ml. portions of boiling benzene. The combined benzene extracts were treated with Darco, evaporated to a volume of 30 ml. and cooled in the ice box overnight. There was obtained 0.92 g. (13% based on the sulfonyl chloride used) of white crystals. After two recrystallizations from benzene, the product melted at 151–152° with softening at 140°. It could not be obtained in a state of analytical purity. The crude product was used directly for further reactions.

Bis-(N-trimethylenesulfonamido)-mesitylene.—A suspension of 1.35 g. of N,N′-di-(γ-bromopropanesulfonyl)-diaminomesitylene in 55 ml. of water containing 6 ml. of ethanol and 0.208 g. of sodium hydroxide was refluxed for two hours and filtered hot. The white crystalline material on the filter was washed with 30 ml. of water and dried. The combined filtrate and wash water were cooled overnight in the ice box and a second crop of less pure crystalline material was obtained. Recrystallization of the latter from absolute ethanol gave 0.09 g. of white crystals. The total yield was 0.87 g. (94%). The two fractions were combined and recrystallized from absolute ethanol to yield a product melting at 285–287°.

Anal. Calcd. for $C_{15}H_{22}N_2O_4S_2$: C, 50.26; H, 6.24; N, 7.82. Found: C, 50.36; H, 6.47; N, 7.75.

N,N′-Di-(methanesulfonyl)-diaminomesitylene.—To a solution of 29 g. of diaminomesitylene in 50 ml. of pyridine was slowly added 58 g. of methanesulfonyl chloride. A vigorous reaction ensued with evolution of heat. The hot solution was allowed to stand fifteen minutes and then 500 ml. of water was added. The mixture was boiled and stirred a few minutes, crystallization taking place. After acidification with hydrochloric acid the mixture was filtered and the crude yellow product washed well on the filter with water. Two recrystallizations from 95% ethanol with the use of Darco gave 34 g. (58%) of white crystals, m. p. 233–235°.

Anal. Calcd. for $C_{11}H_{18}N_2O_4S_2$: C, 43.12; H, 5.92; N, 9.15. Found: C, 43.34; H, 6.11; N, 9.16.

***cis* and *trans* Isomers of N,N′-Dimethyl-N,N′-di-(methanesulfonyl)-diaminomesitylene.**—Three ml. of methyl iodide was added to a solution of 3.06 g. of N,N′-di-(methanesulfonyl)-diaminomesitylene and 1.5 g. of potassium hydroxide in 30 ml. of a 1:1 mixture of methanol and water and the mixture mechanically shaken for sixteen hours. The white crystalline precipitate (A) was collected on a filter, washed with 20 ml. of a 1:1 mixture of methanol and water and dried. The product weighed 3 g., melting over the range 175–206°. The combined filtrate and wash was evaporated to a volume of 25 ml. and cooled in the ice box to yield a second crop (B) of white crystalline material which weighed 0.12 g., and had a m. p. 174–178°. Precipitate A was recrystallized three times from acetone to yield 1.86 g. (56%) of hard white crystals, m. p. 209–210°.

Anal. Calcd. for $C_{13}H_{22}N_2O_4S_2$: C, 46.68; H, 6.63; N, 8.38. Found: C, 46.89; H, 6.79; N, 8.63.

The initial acetone filtrate was evaporated to dryness and the residue, m. p. 173–178°, combined with crop (B). The material was extracted with 150 ml. of ether in a Soxhlet extractor for eight hours. After evaporating the extract to a volume of 25 ml. and cooling, there was collected on a filter 0.63 g. (19%) of white crystals. The product melted incompletely at 175–178°, resolidified and remelted at 208–210°. A clear melt was obtained upon inserting the material in a bath preheated to 180°. Three recrystallizations from methanol did not alter the melting point properties.

Anal. Calcd. for $C_{13}H_{22}N_2O_4S_2$: C, 46.68; H, 6.63; N, 8.38. Found: C, 46.90; H, 6.63; N, 8.53.

Summary

1. The synthesis of disuccinimidomesitylene as a model experiment for the synthesis of diimides of diaminomesitylene was accomplished by the action of acetic anhydride on N,N′-disuccinyldiaminomesitylene.

2. Three diimides of diaminomesitylene, bis-(α,α-dimethylsuccinimido)-mesitylene, bis-(3-nitrophthalimido)-mesitylene and bis-(propionylsulfimido)-mesitylene were synthesized. No evidence for *cis–trans* isomers was found.

3. Bis-(N-trimethylenesulfonamido)-mesitylene was also synthesized. No *cis–trans* isomers were obtained. This is in contrast to N,N′-dimethyl-N,N′-di-(methanesulfonyl)-diaminomesitylene from which *cis–trans* isomers resulted.

4. The lack of *cis–trans* isomerism in bis-(N-trimethylenesulfonamido)-mesitylene has been attributed to bond angle distortions in the molecule due to the five-membered nitrogen ring systems.

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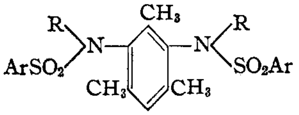
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

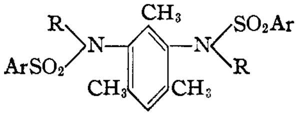
Restricted Rotation in Aryl Amines. IX. Diaminodurene Derivatives

BY ROGER ADAMS* AND NILS K. NELSON[1]

Pairs of isomers (I and II) due to two points of restricted rotation in the molecules have been reported among derivatives of diaminomesitylene.[2]

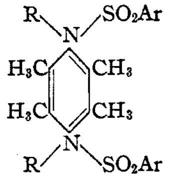


I

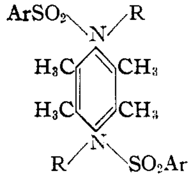


II

In this communication are described similar pairs of isomers obtained from diaminodurene as shown by structures III and IV. In this series the isomers correspond to *cis* and *trans*, each of which has a plane of symmetry. It was assumed that the higher-melting form had the more symmetrical structure, IV. A remarkable difference in physical properties of the members of each pair was noted, much greater than in the mesitylene series. Solubility differences were exemplified by the facile isolation of the less-soluble, higher-melting forms from the mixtures since they were essentially insoluble in hot methanol while the more-soluble lower-melting forms were quite soluble. The differences in melting points of the members of a pair ranged from 75 to 100°. When the lower-melting forms were heated above their melting points, they resolidified. By this treatment they were isomerized to the higher-melting forms.



III



IV

The compounds were made by alkylating N,N′-dibenzenesulfonyldiaminodurene in aqueous methanolic potassium hydroxide with methyl iodide, ethyl bromide and benzyl chloride. The pair of ethyl isomers was also formed by treatment of N,N′-diethyldiaminodurene with benzenesulfonyl chloride. No replacement of one ethyl group as was found in the mesitylene series[2] was observed.

N,N′-Dibenzenesulfonyldiaminodurene was also subjected to cyanoethylation in dioxane solution in presence of Triton B. The product was primarily a monocyanoethylation derivative which upon repetition of the procedure gave essentially a single, high-melting, dicyanoethylated compound. In one experiment which would not be duplicated, dicyanoethylation was obtained in one step and two isomers were formed, the higher-melting corresponding to that resulting from cyanoethylation of the monocyanoethylated derivative and the other melting much lower. The lower-melting was converted to the higher-melting by heating above its melting point. Both isomers were hydrolyzed to the corresponding isomeric acids.

Experimental

Diaminodurene.—A suspension of 44.5 g. of dinitrodurene in 150 ml. of ethanol was reduced under a pressure of 150 atm. of hydrogen with one teaspoonful of Raney nickel catalyst. The temperature rose from 25 to 70° during the course of the reduction. The reaction was complete after four hours.

After addition of 800 ml. of boiling water (which had been boiled for several minutes to liberate any dissolved oxygen) the solution was filtered to remove the catalyst. Small white needles crystallized rapidly when the solution cooled, and after standing thirty minutes, the first crop was removed by filtration, using a rubber dam to exclude air. A second crop, having the same melting point, was obtained when the mother liquor was allowed to stand overnight in an ice box. The yield was 28.7 g. (89%). The melting point was 149–150° (cor.) and was unchanged by crystallization from water.[3] Cain reports m. p. 149°.

N,N′-Dibenzenesulfonyldiaminodurene.—A solution of 17.4 g. of diaminodurene in 50 ml. of pyridine was added slowly to a solution of 47 g. of benzenesulfonyl chloride and 25 ml. of pyridine in a 300-ml. Erlenmeyer flask, while the flask was swirled in an ice–water-bath. After approximately three-fourths of the amine had been added, the reaction product became quite viscous, and it was necessary to add 25 ml. of pyridine. After the addition was completed, the flask was allowed to stand overnight at room temperature. Finely divided yellow crystals precipitated upon standing. The reaction product was poured into 1500 ml. of ice-water, and after standing at room temperature for several hours, the yellow precipitate was removed by filtration.

The product was dissolved in a solution of 40 g. of

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[1] An abstract of a thesis submitted by Nils K. Nelson to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adams and Tjepkema, THIS JOURNAL, **70**, 4204 (1948); Adams and Rothstein, *ibid.*, **71**, 1620 (1949); Adams and Campbell, *ibid.*, **72**, 128 (1950).

[3] Cain, *Ber.*, **28**, 968 (1895).