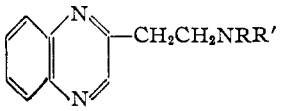
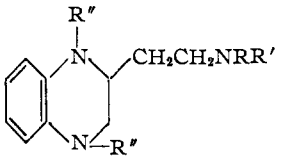
TABLE I

SECTION A



No.	Substituents R	R'	M.p. or b.p., °C.	Mm.	$n^{25}D$	Yield, %	Empirical formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Ia	CH_3	CH_3	109	0.6	1.5806	20.2	$C_{12}H_{15}N_3$	71.64	71.66	7.47	7.37	20.89	20.67
Ib	$C_6H_5CH_2$	C_2H_5	153–155	.15	1.5998	28.8	$C_{19}H_{21}N_3$	78.35	78.02	7.26	7.10	14.42	14.06
Ic	$(CH_2)_5N$		118	.15	1.5869	23.9	$C_{15}H_{19}N_3$	74.69	74.40	7.88	8.19	17.43	17.59
Id	C_2H_5	C_2H_5COO	140	.15	1.5618		$C_{15}H_{19}N_3O_2$	65.93	65.60	6.97	7.24	15.38	15.47

SECTION B



	R	R'	R''	M.p. or b.p., °C.	Mm.								
IIa[a]	CH_3	CH_3	H	120–124	0.2	74	$C_{12}H_{19}N_3$	70.24	70.53	9.37	9.21	20.49	20.16
IIb	C_2H_5	C_2H_5	H	140–142	.2	85	$C_{14}H_{23}N_3$	72.10	71.79	9.88	9.90	18.03	17.85
IIc[b]	$C_6H_5CH_2$	C_2H_5	H	178–185	.2	28	$C_{19}H_{25}N_3$	77.29	77.02	8.48	8.51	14.24	14.07
IIIa[c]	CH_3	CH_3	C_2H_5OCO	173	.7	81	$C_{18}H_{27}N_3O_4$	61.88	61.79	7.74	7.74	12.03	11.58
IIIb	C_2H_5	C_2H_5	C_2H_5OCO	160–164	.2	40	$C_{20}H_{31}N_3O_4$	63.64	63.32	8.28	8.38	11.12	11.29
IVa	CH_3	CH_3	C_2H_5NHCO	127–129[d]		49.6	$C_{18}H_{29}N_5O_2$	62.24	62.10	8.37	8.21	20.17	19.87
IVb	C_2H_5	C_2H_5	C_2H_5NHCO	138–140[d]		51.5	$C_{20}H_{33}N_5O_2$	64.97	65.04	8.88	8.97	18.64	18.59
IVc	CH_3	CH_3	C_6H_5NHCO	191–192[d]		47.7	$C_{26}H_{29}N_5O_2$	70.42	70.45	6.58	6.84	15.76	15.93
IVd	C_2H_5	C_2H_5	C_6H_5NHCO	148–150[d]		25.6	$C_{28}H_{33}N_5O_2$	71.31	71.31	7.06	7.00	14.83	14.72

[a] $n^{25}D$ 1.5750. [b] $n^{25}D$ 1.5943. [c] $n^{25}D$ 1.5322. [d] Melting points.

tered, and the filtrate was concentrated by evaporation under reduced pressure on the steam-bath. The residual oil was fractionated.

1,4-Dicarbethoxy-2-(2-dialkylaminoethyl)-1,2,3,4-tetrahydroquinoxalines (IIIa, IIIb).—A solution of 0.1 mole of 2-(2-dialkylaminoethyl)-1,2,3,4-tetrahydroquinoxaline in 50 ml. of dry pyridine was stirred while a solution of 23.8 g. (0.22 mole) of ethyl chloroformate in 70 ml. of dry benzene was added dropwise. The reaction mixture was cooled occasionally in order to keep the temperature at about 50°. After the addition of reactants was complete the reaction mixture was stirred at room temperature for two hours. Three hundred milliliters of water was added, and the mixture was neutralized with solid sodium bicarbonate. The organic layer was removed, and the aqueous layer was extracted with two 300-ml. portions of benzene. The extracts were combined with the organic layer, and the solvent was removed by evaporation under reduced pressure on the steam bath. The liquid residue was fractionated under reduced pressure.

1,4-Bis-(aryl- or alkylcarbamyl)-2-(2-diethylaminoethyl)-1,2,3,4-tetrahydroquinoxalines (IVa, IVb, IVc, IVd).—A solution of 0.045 mole of the 2-(2-dialkylaminoethyl)-1,2,3,-4-tetrahydroquinoxaline and 0.1 mole of the isocyanate in 100 ml. of dry benzene was refluxed for two hours except in the case of IVc when the reaction mixture was merely heated to boiling. The solvent was removed by evaporation *in vacuo*, and the residue was triturated thoroughly with a mixture of benzene and 60–70° petroleum ether except with IVc. In this case the reaction mixture was cooled. The solid was filtered off and recrystallized from a benzene–petroleum ether (60–70°) mixture in the cases of IVa and IVb and from alcohol in the cases of IVc and IVd.

INDIANAPOLIS 6, INDIANA

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

Restricted Rotation in Aryl Amines. XVI. 4-Substituted 1-Amino-2-methylnaphthalenes

BY ROGER ADAMS AND RAYMOND H. MATTSON[1]

RECEIVED APRIL 19, 1954

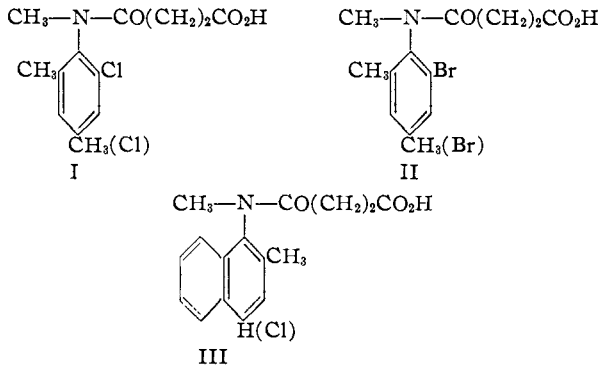
The optically active forms of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene and its 4-chloro and 4-bromo derivatives have been synthesized. The relative racemization rates indicate that the halogen-substituted compounds are less stable than the unsubstituted, thus coinciding with the results found in analogous types of molecules. Nitration of N-benzenesulfonyl-1-amino-2-methylnaphthalene results in the formation of N-benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene.

In several previous papers, the relative rates of racemization of aromatic amines, in which restricted rotation between the nitrogen atom and the ring carbon is present, have been compared. The study of those compounds in which merely a single substituent in a fixed position has been modified has permitted speculation concerning the effect of size of the atom or group and/or of electronic changes upon stability of the molecule.[2] A sub-group in this

(1) An abstract of a thesis submitted by Raymond H. Mattson to the Graduate College of the University of Illinois, 1951, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Eastman Kodak Company Fellow, 1947–1948; 1948–1949.

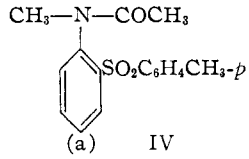
(2) (a) R. Adams and H. W. Stewart, THIS JOURNAL, **63**, 2859 (1941); (b) R. Adams and N. K. Sundholm, *ibid.*, **70**, 2667 (1948); (c) R. Adams and L. J. Dankert, *ibid.*, **62**, 2191 (1940); (d) R. Adams and A. A. Albert, *ibid.*, **64**, 1475 (1942); (e) R. Adams and J. R. Gordon, *ibid.*, **72**, 2454, 2458 (1950).

class which eliminates the steric variable is of particular interest. It comprises molecules in which the substituents on and immediately adjacent to the nitrogen atom are the same from compound to compound. Such compounds may be illustrated by the following pairs, I, II, III.



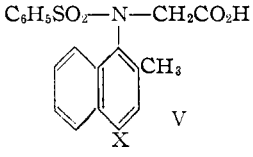
The half-life in boiling *n*-butyl alcohol of N-succinyl-6-chloro-2,4-dimethyl-1-methylaminobenzene (I) is 34 minutes compared with complete racemization in 30 minutes for N-succinyl-4,6-dichloro-2-methyl-1-methylaminobenzene (I). These two compounds showed half-lives in boiling methyl acetate of 63 hr. and 18 hr., respectively.[2e] In the pair illustrated by II, the 4-methyl had a half-life of 3.1 hr. in boiling *n*-butyl alcohol compared with 1.1 hr. for the 4-bromo analog.[2b] In pair III, the 4-unsubstituted compound had a half-life of 5.7 hr. in boiling butanol compared with 4.1 hr. for the 4-chloro derivative.[2d]

A series of similar experiments has been reported on the half-lives of compounds of type IV.[3]



It was established that with variation of the (a) substituent the molecules decreased in stability in the order $OCH_3 > CH_3 > Cl > Br$. These results coincide with those previously mentioned.

A continuation of the study of similar effects is now under investigation and this communication describes the syntheses and relative stabilities of certain molecules of the type shown in V where X may be an electron-attracting or electron-donating atom or group.



Compounds (V) where X = H, Cl and Br have been prepared, resolved and their half-lives determined. Respectively, the following values were found: 4.9, 4.0, 3.7. The first value was obtained in dimethylformamide as a solvent at 118° (b.p. of *n*-butyl alcohol) to be described by Sundstrom in a research, the results of which will be published soon.[4] The solvent for the racemization of the chloro and bromo compounds was boiling *n*-butyl alcohol; the resulting half-lives did not differ essentially from those subsequently obtained in dimethylformamide as solvent at 118°. It is thus seen that in this series, as in the others mentioned, electron-attracting groups cause a decrease in the stability of the optically active forms.

The 4-unsubstituted compound V was prepared from 1-amino-2-methylnaphthalene by benzenesulfonation followed by introduction of a carboethoxymethyl group with ethyl bromoacetate and sodium methylate, then saponification. Synthesis of 1-amino-4-chloro-2-methylnaphthalene was effected by stannous chloride reduction of 2-methyl-1-nitronaphthalene in ethanol and hydrochloric acid solution; the synthesis of 1-amino-4-bromo-2-methylnaphthalene by bromination of 1-acetamino-2-methylnaphthalene followed by hydrolysis of the acetyl group. The substituents on the nitrogen were introduced as previously described for 1-amino-2-methylnaphthalene.

A wider variety of groups in the 4-position of such a molecule as V presented some synthetic difficulties. The best approach appeared to be by the following steps: N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene, reduction of this compound to the amine followed by diazotization and replacement of the diazonium group. 1-Amino-2-methyl-4-nitronaphthalene is a known compound, but it could not be benzenesulfonated by any of the usual methods. The benzenesulfonyl derivative of 1-amino-2-methylnaphthalene was readily prepared and was nitrated to a mononitro derivative. To establish the position of the nitro group as 4, it was reduced to the corresponding amino derivative and benzenesulfonated. This dibenzenesulfonyl derivative proved to be identical with that formed by reduction of the known 1-amino-2-methyl-4-nitronaphthalene followed by introduction of benzenesulfonyl groups on each nitrogen atom.

Acknowledgment.—The authors are indebted to Miss Emily Davis and Miss Rachel Kopel for the microanalyses.

Experimental

All melting points are corrected.

N-Benzenesulfonyl-1-amino-4-chloro-2-methylnaphthalene.—To a solution of 7.3 g. of crude 1-amino-4-chloro-2-methylnaphthalene, prepared as previously described,[2d] in 27 ml. of pyridine was added slowly with cooling and stirring a solution of 7.4 g. of benzenesulfonyl chloride in 10 ml. of pyridine. The mixture was stirred at 0° for one-half hour and then allowed to stand overnight. The mixture was poured into 200 ml. of ice-water and the solid which formed collected and recrystallized three times (twice with Darco) from ethanol. A yield of 6.7 g. of white needles was obtained. Another 3.5 g. of product was recovered from the mother liquors to give a total of 10.2 g. (81%). Recrystallization of the product from 80% acetic acid gave white crystals, m.p. 174–175°.

Anal. Calcd. for $C_{17}H_{14}ClNO_2S$: C, 61.53; H, 4.25. Found: C, 61.29; H, 4.12.

***dl*-N-Benzenesulfonyl-N-carboethoxymethyl-1-amino-4-chloro-2-methylnaphthalene.**—To a solution of 8.2 g. of N-benzenesulfonyl-1-amino-4-chloro-2-methylnaphthalene and 1.5 g. of sodium methoxide in 30 ml. of dry methanol was added a mixture of 4.7 g. of ethyl bromoacetate in 15 ml. of

(3) C. Buchanan and S. H. Graham, *J. Chem. Soc.*, 500 (1950).

(4) R. Adams and K. V. Y. Sundstrom, unpublished results.

dry methanol. The resulting solution was heated under reflux for 2.5 hr. after which time a cake of white crystalline material had formed on the bottom of the flask. The reaction mixture was cooled and poured into 100 ml. of cold water. The white solid which separated was recrystallized 4 times (once with Darco) from ethanol. The yield was 7.5 g. (60%) of fine white needles, m.p. 135–136°.

Anal. Calcd. for $C_{21}H_{20}ClNO_4S$: C, 60.35; H, 4.82. Found: C, 59.76; H, 4.52.

***dl*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene.**—A solution of 15.4 g. of *dl*-N-benzenesulfonyl-N-carboethoxymethyl-1-amino-4-chloro-2-methylnaphthalene, 165 ml. of glacial acetic acid and 125 ml. of 10% sulfuric acid was heated under reflux for 2.5 hours. The mixture was cooled and poured into 1300 ml. of cold water. A white precipitate formed which was somewhat amorphous and retarded filtration. After standing overnight, however, the product was crystalline and was easily collected on a filter. Recrystallization from glacial acetic acid followed by drying over potassium hydroxide at 110° (1 mm.) gave 7.4 g. (52%) of white crystals, m.p. 200–202°.

Anal. Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14. Found: C, 58.68; H, 4.22.

Resolution of *dl*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene.—A solution of 3.00 g. of *dl*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene and 2.266 g. of cinchonine in 130 ml. of 9:1 ethyl acetate–methanol was prepared and filtered. The solution was concentrated to 100 ml. by warming under a current of air. The flask was placed in a refrigerator and after two days the first crop of white granular crystals, 1.565 g., $[\alpha]^{27}D$ +130°, was collected on a filter. Continued fractional crystallization gave another 5 crops of crystals of the following weights and specific rotations: 0.315 g., 128°; 1.226 g., 15°; 0.526 g., 130°; 0.166 g., 13°; and 0.285 g., 22°. All rotations were determined in a 2-decimeter tube using 20-ml. absolute ethanol solutions containing 0.040 g. of the salt. The first two crops were combined and dissolved in an excess of hot 9:1 ethyl acetate–methanol. Fractional crystallization gave two crops, 1.122 and 0.316 g., which showed the same rotation. This was taken as the less soluble salt (*d*B*d*A), m.p. 218–219° dec.

Rotation.—0.040 g. made up to 20 ml. with absolute ethanol at 26° gave αD +0.54°; *l* 2, $[\alpha]^{26}D$ +135°.

Anal. Calcd. for $C_{19}H_{16}ClNO_4S \cdot C_{19}H_{22}N_2O$: C, 66.70; H, 5.60. Found: C, 66.69; H, 5.82.

In view of the erratic nature of the rotations of the successive fractions, the last four crops of crystals from the original fractionation were combined and dissolved in excess hot 9:1 ethyl acetate–methanol. In spite of seeding the initial solution with crystals of the less-soluble salt, fractional crystallization gave three crops of crystals as erratic as those from which they were derived. The weights and specific rotations were, respectively, 1.082 g., 25°; 0.167 g., 130°; 0.473 g., 20°. The first and last of these crops were recrystallized from 9:1 ethyl acetate–methanol to give 1.107 g. of white crystals, m.p. 199–201° dec. This was taken as the more soluble salt.

Rotation.—(*d*B*l*A) 0.040 g. made up to 20 ml. with absolute ethanol at 28° gave αD +0.03°; *l* 2, $[\alpha]^{28}D$ +7.5°.

***d*- and *l*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene.**—The procedure of earlier workers[2a,c,d] for decomposing the alkaloid salts was improved and consequently is described here in detail. A slurry of 0.500 g. of the less soluble salt in 40 ml. of ethanol-free ether was cooled in an ice-bath and to this was added slowly with rapid stirring 20 ml. of 18% hydrochloric acid. The mixture was stirred for about 20 minutes to give two clear layers. About 20 ml. more ethanol-free ether was added to facilitate handling and the aqueous layer separated. The ether solution was washed 3 times with 5% hydrochloric acid and a test with Mayer reagent showed the last wash to be free of cinchonine. (Since the washes are saturated with ether, it is necessary to remove the latter by warming before performing the test for alkaloid in order to avoid a misleading cloudiness caused by dissolved ether.) The ether solution was evaporated to dryness under a current of air. The residue was dissolved in hot glacial acetic acid, the solution filtered, and water added to precipitate the optically active acid. There was obtained 0.247 g. (87%) of the *d*-acid, m.p. 204–205°. A sample recrystallized from 2:1 benzene–cyclohexane gave fine white crystals of the same melting point.

Rotation.—(*d*-acid) 0.040 g. made up to 20 ml. with absolute ethanol at 26° gave αD +0.28°; *l* 2, $[\alpha]^{26}D$ +70°.

Anal. Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14. Found: C, 58.69; H, 4.35.

In the same manner, decomposition of 0.509 g. of the more soluble salt gave, after one recrystallization from 2:1 benzene–cyclohexane, 0.230 g. (79%) of the *l*-acid, m.p. 206–207°.

Rotation.—(*l*-acid) 0.041 g. made up to 20 ml. with absolute ethanol at 28° gave αD −0.29°; *l* 2, $[\alpha]^{28}D$ −72°.

Racemization of *d*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene.—The sample to be racemized was weighed into a 50-ml. ground-joint erlenmeyer flask, 25 ml. of redistilled *n*-butyl alcohol and several carborundum chips introduced into the flask and the contents weighed accurately on an analytical balance. Thorough mixing was effected by swirling and a portion of the solution transferred by means of a pipet to a 2-decimeter polarimeter tube. The rotation of the solution was determined, after which the contents of the polarimeter tube were returned quantitatively to the 50-ml. erlenmeyer flask and the pipet used previously was also washed thoroughly into the flask. The exact time was noted (this was taken as zero time) and the flask placed on a hot plate at medium heat. After about 5 minutes ebullition commenced and was allowed to continue without reflux until the volume of the solution was approximately 15 ml. The hot plate was then adjusted to low heat and a reflux condenser fitted into the flask. After an appropriate interval the time was noted and the solution quenched by plunging the flask into an ice-bath and swirling the contents for about 40 seconds. The flask was wiped dry, placed on the pan of an analytical balance and *n*-butyl alcohol added dropwise to the solution until the weight of the flask and contents was within about 0.002 g. of the original weight. The rotation of the solution at room temperature was determined as before and the cycle repeated until a suitable number of observations had been obtained. The data were plotted on semi-logarithmic paper and the rate constant determined from the slope of the curve in accordance with the relationship, $\ln \alpha = 2kt + c$.

Racemization of a 0.0840-g. sample of *d*-acid in this manner gave 0.596, 0.519, 0.431, 0.371, 0.256, 0.187, 0.130 and 0.063° at 0.0, 1.0, 2.0, 3.0, 5.0, 7.0, 9.0 and 13.0 hr., respectively; rate constant, 8.71×10^{-2} hr.$^{-1}$; half-life period, 3.98 hr. A check with 0.105 g. of acid gave 0.736, 0.630, 0.490, 0.386, 0.280, 0.192, 0.110 and 0.076° at 0.0, 1.0, 2.5, 4.0, 6.0, 8.0, 11.0 and 14.0 hr., respectively; rate constant, 8.52×10^{-2} hr.$^{-1}$; half-life period, 4.07 hr.

N-Benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene.—1-Acetamino-2-methylnaphthalene[5] was brominated according to the method of Shoesmith and Rubli.[6] This latter product was then hydrolyzed[7] to 1-amino-4-bromo-2-methylnaphthalene.

The benzenesulfonation of this last product was carried out as for the corresponding chloro compound. From 19.6 g. of 1-amino-4-bromo-2-methylnaphthalene was obtained 22.9 g. of product; white needles from ethanol, m.p. 183.5–184.5°. Another 2.8 g. of slightly pink needles was recovered from the mother liquor; total yield 25.7 g. (82.4%).

Anal. Calcd. for $C_{17}H_{14}BrNO_2S$: C, 54.26; H, 3.75. Found: C, 54.43; H, 3.93.

***dl*-N-Benzenesulfonyl-N-carboethoxymethyl-1-amino-4-bromo-2-methylnaphthalene.**—From 10 g. of N-benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene was obtained 10.6 g. (86.4%) of the N-carboethoxy derivative by the method used for the corresponding chloro compound; white needles from ethanol, m.p. 134–135°.

Anal. Calcd. for $C_{21}H_{20}BrNO_4S$: C, 54.55; H, 4.36. Found: C, 54.46; H, 4.34.

The *dl*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene.—The procedure for hydrolysis was identical with that for the chloro compound. From 9.8 g. of *dl*-N-benzenesulfonyl-N-carboethoxymethyl-1-

(5) R. Lesser, A. Glasar and G. Aczel, *Ann.*, **402**, 1 (1913).

(6) J. B. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

(7) H. E. Fierz-David, L. Blanger and H. Dubendorfer, *Helv. Chim. Acta*, **29**, 1661 (1946).

amino-4-bromo-2-methylnaphthalene was obtained 8.9 g. (97%) of product; white crystals from 80% acetic acid. These crystals carried acetic acid of crystallization which was removed by drying *in vacuo* over solid potassium hydroxide, m.p. 191.5–192.5°.

Anal. Calcd. for $C_{19}H_{16}BrNO_4S$: C, 52.54; H, 3.71. Found: C, 52.75; H, 3.73.

Resolution of *dl*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene.—Resolution was effected by fractional crystallization of the cinchonine salt of the *dl*-acid in the manner described above for the resolution of *dl*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene. Although two attempts were made using 2.000 g. of *dl*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene and 1.356 g. of cinchonine, successive fractions of the salt could not be obtained for which the specific rotations described a regular pattern. Crops of similar rotation melted over the same temperature ranges and no depression of this range was observed when an intimate mixture of two such crops was melted. Consequently, five fractions, obtained from both attempts at fractional crystallization, weighing 0.223, 0.206, 0.207, 0.318 and 0.283 g. with specific rotations of 128, 118, 125, 120 and 123°, respectively, were combined and dissolved in excess hot 9:1 ethyl acetate–methanol. The solution was filtered and concentrated to 115 ml. when crystals began to appear. The mixture was placed in a refrigerator overnight. There was obtained 0.586 g. of white granular crystals, m.p. 227–228° dec. in a rapidly heated bath. This was taken as the less soluble salt.

Rotation.—(*d*B*d*A) 0.040 g. made up to 20 ml. with absolute ethanol at 27° gave α_D +0.50°; *l* 2, $[\alpha]^{27}D$ +125°.

Anal. Calcd. for $C_{19}H_{16}BrNO_4S \cdot C_{19}H_{22}N_2O$: C, 62.63; H, 5.26. Found: C, 62.84; H, 5.35.

Similarly, three fractions weighing 0.366, 0.280 and 0.375 g. with specific rotations of 10, 8 and 8°, respectively, were combined and dissolved in an excess of hot 9:1 ethyl acetate–methanol and filtered. The filtrate was concentrated to 35 ml. and allowed to stand for 3 days. There was obtained 0.923 g. of white granular crystals, m.p. 221–223° dec. in a rapidly heated bath. This was taken as the more soluble salt.

Rotation.—(*d*B*d*A) 0.041 g. made up to 20 ml. with absolute ethanol at 28° gave α_D +0.03°; *l* 2, $[\alpha]^{27}D$ +7.3°.

***d*- and *l*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene.**—The procedure described above for *d*- and *l*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene was followed. From 0.500 g. of the less soluble salt was obtained 0.213 g. (71.5%) of the *d*-acid. A sample recrystallized from 2:1 benzene–cyclohexane gave fine white crystals, m.p. 212–213°.

Rotation.—(*d*-acid) 0.040 g. made up to 20 ml. with absolute ethanol at 27° gave α_D +0.23°; *l* 2, $[\alpha]^{27}D$ +58°.

Anal. Calcd. for $C_{19}H_{16}BrNO_4S$: C, 52.54; H, 3.71. Found: C, 52.30; H, 3.92.

In the same manner, from 0.500 g. of the more-soluble salt was obtained, after one recrystallization from 2:1 benzene–cyclohexane, 0.104 g. (35%) of fine white crystals, m.p. 211–212°. No attempt was made to collect additional product from the mother liquor.

Rotation.—(*l*-acid) 0.40 g. made up to 20 ml. with absolute ethanol at 28° gave α_D −0.24°; *l* 2, $[\alpha]^{28}D$ −60°.

Racemization of *d*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene.—The procedure described above for the racemization of *d*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene was followed exactly. Racemization of a 0.0907-g. sample gave 0.529, 0.457, 0.363, 0.275, 0.195, 0.153, 0.113, 0.081 and 0.053° at 0.0, 1.0, 2.0, 3.5, 5.0, 6.5, 8.0, 10.0 and 12.0 hr., respectively; rate constant, 9.64×10^{-2} hr.$^{-1}$; half-life, 3.61 hr. A check carried out with 0.084 g. of acid gave 0.676, 0.598, 0.450, 0.374, 0.296, 0.180, 0.146, 0.100 and 0.050° at 0.0, 1.0, 2.5, 3.5, 5.0, 7.0, 9.0, 11.0 and 14.0 hr., respectively; rate constant, 9.16×10^{-2} hr.$^{-1}$; half-life, 3.78 hr.

N-Benzenesulfonyl-1-amino-2-methylnaphthalene.—The procedure described above for N-benzenesulfonyl-1-amino-4-chloro-2-methylnaphthalene was followed. From 20 g. of crude 1-amino-2-methylnaphthalene was obtained 34.3 g. (91%) of slightly pink needles. Five recrystallizations from 80% acetic acid gave a pure product, m.p. 225°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.09. Found: C, 68.75; H, 5.23.

***dl*-N-Benzenesulfonyl-N-carboethoxymethyl-1-amino-2-methylnaphthalene.**—The procedure described for the preparation of *dl*-N-benzenesulfonyl-N-carboethoxymethyl-1-amino-4-chloro-2-methylnaphthalene was used. From 20 g. of N-benzenesulfonyl-1-amino-2-methylnaphthalene was obtained 18.8 g. (73%) of white needles. The product was purified by recrystallization from glacial acetic acid, m.p. 123–124°.

Anal. Calcd. for $C_{21}H_{21}NO_4S$: C, 65.78; H, 5.52. Found: C, 65.91; H, 5.51.

***dl*-N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene.**—The hydrolysis was carried out by the method described for the preparation of *dl*-N-benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene. From 16.4 g. of *dl*-N-benzenesulfonyl-N-carboethoxymethyl-1-amino-2-methylnaphthalene was obtained, after 3 recrystallizations from glacial acetic acid, 12.2 g. (69%) of fine white crystals, m.p. 219–221°. The product was dried *in vacuo* over potassium hydroxide to remove acetic acid of crystallization.

Anal. Calcd. for $C_{19}H_{17}NO_4S$: C, 64.21; H, 4.82. Found: C, 64.19; H, 4.93.

N-Benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene.—To a slurry of 4 g. of N-benzenesulfonyl-1-amino-2-methylnaphthalene in 7.3 ml. of glacial acetic acid was added at 45° with vigorous stirring 1.04 g. of 70% nitric acid. No reaction occurred. When the temperature of the bath was increased to 85°, solution occurred, and brown fumes began to appear. After maintaining for 20 minutes at 65°, the temperature was allowed to drop. In 2.5 hr. yellow needles began to separate. Upon pouring into ice-water, 2.7 g. (58.6%) of product resulted. It was purified by recrystallization from ethanol; yellow crystals, m.p. 155–156°.

Anal. Calcd. for $C_{17}H_{14}N_2O_4S$: C, 59.64; H, 4.12. Found: C, 59.41; H, 4.39.

1-N-Benzenesulfonyl-1,4-diamino-2-methylnaphthalene. A solution of 0.959 g. of N-benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene in 25 ml. of ethanol was reduced with Raney nickel (1/4 tsp.) and hydrogen at 2 atm. pressure and room temperature. The reduction was complete in 1.5 hr. After removing the nickel, the solution was concentrated to 15 ml. The nickel was extracted 5 times with hot ethanol. After concentration of the combined filtrates to 30 ml., 0.427 g. (49%) of pinkish needles separated. The product was purified by crystallization from ethanol containing a few drops of aqueous ammonia. The pure product was white, m.p. 228–229° dec. in a rapidly heated bath.

Anal. Calcd. for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16. Found: C, 65.54; H, 5.31.

N,N′-Dibenzenesulfonyl-1,4-diamino-2-methylnaphthalene. Method A.—A solution of 0.537 g. of 1-amino-2-methyl-4-nitronaphthalene[8] in 25 ml. of ethanol was reduced by the method described for the previous compound. The ethanol solution and extracts of the nickel were treated with 0.6 ml. of concentrated hydrochloric acid and concentrated to 25 ml. Pink platelets, weighing 0.229 g. (35%), separated, m.p. 285° (approx.) with darkening at 255°. This crude hydrochloride was benzenesulfonated immediately.

To a mixture of 0.253 g. of the diamine hydrochloride in 3 ml. of pyridine cooled in an ice-bath, was added with stirring 0.404 g. of benzenesulfonyl chloride in 1 ml. of pyridine. After addition of half of the benzenesulfonyl chloride solution, 2 ml. of pyridine was added. After 0.5 hr. at 0° and 0.5 hr. at room temperature, the reaction mixture was poured into 20 ml. of cold water and acidified with concentrated hydrochloric acid. The precipitate weighed 0.341 g. (73%). After several recrystallizations from ethanol (twice with Darco) white needles resulted, m.p. 236–237° dec.

Method B.—By a similar benzenesulfonation of 1-N-benzenesulfonyl-1,4-diamino-2-methylnaphthalene, the same product was obtained. From ethanol it had the same melting point as the product from Method A and a melting point of the mixture was not depressed.

URBANA, ILLINOIS

(8) V. Vesely and J. Kapp, *Rec. trav. chim.*, **44**, 360 (1925).