

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

Restricted Rotation in Aryl Amines. XIX. Effect of Substituents in the 4-Position on the Optical Stability of 1-Amino-2-methylnaphthalene Derivatives

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Five new 4-substituted derivatives of *N*-benzenesulfonyl-*N*-carboxymethyl-1-amino-2-methylnaphthalene have been prepared, resolved and the half-lives of racemization of the active forms determined. Electron donating substituents decrease and electron withdrawing substituents increase the rate of racemization of the optically active compounds. A new method for synthesizing aromatic phenylmercapto compounds is reported.

Previous papers in this series^{2,3} have reported the effect of substituents in the 4-position on the rate of racemization of optically active *N*-benzenesulfonyl-*N*-carboxymethyl-1-amino-2-methylnaphthalenes (I), where X = nitro, chloro, bromo, iodo, hydrogen, benzenesulfonamido, acetamido, hydroxyl and amino.

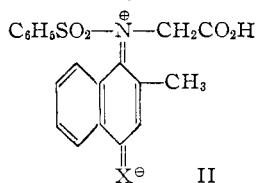
This series has now been extended to include the following groups: X = cyano, phenylmercapto, benzenesulfonyl, methyl and methoxyl. Racemization rates were determined in dimethylformamide solution at 118° (boiling point of *n*-butanol). The average half-lives of two duplicate experiments are given below. The experimental error was probably 0.3 hour.

Substituent X	Half-life, hr.
CN	0.62
NO ₂	0.66, 0.42 ³
C ₆ H ₅ S	1.7
C ₆ H ₅ SO ₂	1.9
H	4.6, 4.9 ³
CH ₃	5.4
CH ₃ O	8.0

The data presented above as well as those reported previously^{2,3} definitely indicate that strong electron withdrawing groups in the 4-position greatly accelerate the rate of racemization, whereas strong electron donors significantly retard it.

The groups on the nitrogen in the 1-position as well as those in the positions *ortho* to it are identical in all the compounds and thus the strictly steric factors are constant. As a consequence the electronic or other effects of the *para* substituent on the optical stability of the various analogs can be studied.

It has been postulated that the racemization process proceeds in two ways, (1) by the gradual slipping of the groups on the nitrogen past the ring interfering groups and (2) through a planar transition state represented by the resonance form II.



(1) An abstract of a thesis submitted by H. H. Gibbs to the Graduate college of the University of Illinois, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Cincinnati Chemical Co. Fellow, 1953-1954; Dow Chemical Co. Fellow 1954-1956.

(2) R. Adams and R. H. Mattson, *THIS JOURNAL*, **76**, 4925 (1954).

(3) R. Adams and K. V. Y. Sundstrom, *ibid.*, **76**, 5474 (1954).

When the second way supplements the first more rapid racemization would be expected. Since the attainment of the configuration II involves the passage of the lone pair of electrons on the nitrogen into the ring, substituents in the 4-position which have a powerful attraction for these electrons would greatly facilitate the formation of this resonance form. On the other hand, groups in the 4-position which have a tendency to repel electrons would retard formation of this resonance structure.

The experimental data are in agreement with this postulation. Previously, the only strong electron acceptor group which had been studied was the nitro which, as predicted, greatly accelerated the racemization rate. This has now been found to be the case for the cyano and benzenesulfonyl groups which are also strongly electron withdrawing.

The presence of a phenylmercapto group appears to give an anomalous result for it acted in the same way as the strongly electron-accepting groups. This was surprising in view of the fact that the Hammett sigma value for this group (sigma = +0.075)⁴ indicates that it should be very weakly electron-withdrawing. Surprising, too, is the fact that no significant difference in the half-lives of racemization was found between the phenylmercapto and benzenesulfonyl compounds. The Hammett sigma value for the benzenesulfonyl group (sigma = +0.95)⁴ indicates that there should be a substantial difference in the effects of these two groups on the optical stability of the two compounds. Assuming that the experimental data are not at fault, it appears that factors other than those which have been normally considered are influencing the rate of racemization, at least of the phenylmercapto derivative.^{4a}

The electron donating property of the methyl and methoxyl groups is illustrated by the decreased rate of racemization. The effect of the methoxyl is not far different from that of the amino group.

All of the compounds in this investigation except the methyl (I, X = CH₃) were synthesized from 2-methylnaphthalene. The latter was nitrated in the 1-position followed by reduction and

(4) H. H. Szmant, Private Communication.

(4a) The phenylmercapto group has been observed to have an electron-withdrawing like character in other instances. In the study of adducts to substituted quinone diimides, the phenylmercapto group in the 2-position acted like an electron withdrawing group in that it caused the same orientation as the benzenesulfonyl group and a different orientation from that encountered when an electron-donating group was present in the same position. This matter is discussed briefly in an article by R. Adams and M. D. Nair, *THIS JOURNAL*, **78**, 5932 (1956).

benzenesulfonation to give N-benzenesulfonyl-1-amino-2-methylnaphthalene. Nitration yielded the 4-nitro derivative which was then condensed with ethyl bromoacetate and hydrolyzed to yield N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene (I, X = NO₂). This compound was reduced to N¹-benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride and then esterified. The salt of the amino ester was diazotized and hydrolyzed to give the phenolic acid (I, X = OH). The phenolic acid was esterified with methanol and sulfuric acid and then allowed to react with dimethyl sulfate at steam-bath temperature. In this process the phenolic hydroxyl was methylated and the methyl ester saponified. Subsequent acidification yielded the methoxy acid (I, X = CH₃O).

The 4-unsubstituted compound was prepared merely by allowing N-benzenesulfonyl-1-amino-2-methylnaphthalene to react with methyl bromoacetate followed by hydrolysis to the acid.

The cyano group was introduced by allowing cuprous cyanide to react with N-benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene which was prepared by direct bromination of N-benzenesulfonyl-1-amino-2-methylnaphthalene. Subsequent reaction with methyl bromoacetate followed by hydrolysis yielded the 4-cyano acid (I, X = CN).

For introducing the phenylmercapto group into the aromatic ring, it was found that cuprous thiophenolate, prepared by allowing cuprous oxide to react with thiophenol, reacted smoothly at 200–220° in a pyridine-quinoline mixture with N-benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene to replace the bromine by the phenylmercapto group. This compound was then alkylated with methyl bromoacetate and hydrolyzed to the 4-phenylmercapto acid (I, X = C₆H₅S). From this product the corresponding 4-benzenesulfonyl analog was synthesized by hydrogen peroxide oxidation.

The 4-methyl derivative (I, X = CH₃) was prepared from 1,3-dimethylnaphthalene, in turn derived from succinic anhydride and *m*-xylene by the method of Evans and Smith.⁵ Nitration yielded 1-nitro-2,4-dimethylnaphthalene. This was reduced to the amine, benzenesulfonated, alkylated with methyl bromoacetate and hydrolyzed. The presence of the amino group in the 1-position was established first by oxidizing the aminodimethylnaphthalene to *o*-phthalic acid and second by a comparison of its ultraviolet spectrum with that of 1-amino- and 2-amino-naphthalene.

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Experimental

All melting points are corrected.

General Procedure for Alkylating N-Benzenesulfonyl-1-amino-2-methylnaphthalenes with Methyl Bromoacetate.—To a solution of the N-benzenesulfonyl-1-amino-2-methylnaphthalene and 1.1 molar equivalents of sodium in 10 parts of absolute ethanol was added 1.1 molar equivalents of

methyl bromoacetate. The solution was heated under reflux for 20–24 hours. To the hot solution water was added to the cloud-point and the product allowed to crystallize. The data for the individual esters are listed in Table I.

General Procedure for Hydrolyzing N-Benzenesulfonyl-N-carbomethoxymethyl-1-amino-2-methylnaphthalene.—A solution of the N-benzenesulfonyl-N-carbomethoxymethyl-1-amino-2-methylnaphthalene in 18 parts of glacial acetic acid and 10 parts of 10% sulfuric acid was heated under reflux for 5–10 hours. The product which crystallized out on cooling was separated by filtration and washed with water. The data for the individual acids are listed in Table II.

Esterification of N¹-Benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene Hydrochloride.—A mixture of 30.0 g. of N¹-benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride in 1000 ml. of absolute ethanol and 10 ml. of concd. sulfuric acid was heated under reflux for 23 hours. The hot cherry colored solution was poured into 6 l. of cold water. The light pink solid which crystallized was separated by filtration, washed with water and recrystallized from a 2:1 ethanol-water mixture to a constant m.p. 155–156°. The yield was 22.6 g. (62%). The analysis of this product did not agree with the calculated values but the product was pure enough for subsequent reactions.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-hydroxy-2-methylnaphthalene.—To 500 ml. of a 1:1 hydrochloric acid cooled to 0–5°, was added with mechanical stirring 5.0 g. of the salt of N¹-benzenesulfonyl-N¹-carboethoxymethyl-1,4-diamino-2-methylnaphthalene obtained as above. To this suspension 0.95 g. of sodium nitrite dissolved in 50 ml. of cold water was added dropwise over a period of 20 minutes. After the excess nitrite had been decomposed by the addition of a little solid sulfamic acid the mixture was filtered to remove insoluble impurities and then added drop by drop over a period of 2 hours to 2.5 l. of boiling 10% aqueous sulfuric acid. The mixture was cooled to 94° by the addition of cold water and then filtered through a fluted filter paper. Upon cooling, a pale pink crystalline solid precipitated which was separated by filtration. The yield was 2.94 g. (79%). Recrystallization of the product from a 3:1 water-ethanol mixture gave light pink needles, m.p. 224–225° dec. (lit.³ m.p. 204–205°).

Anal. Calcd. for C₁₉H₁₇NO₅S: C, 61.44; H, 4.62; N, 3.77. Found: C, 61.40; H, 4.92; N, 3.64.

Infrared analysis indicated a phenolic OH band at 3395 cm.⁻¹ and an acidic OH band at 2600 cm.⁻¹.

N-Benzenesulfonyl-N-carbomethoxymethyl-1-amino-4-hydroxy-2-methylnaphthalene. Method A.—To a suspension of 2.0 g. of N-benzenesulfonyl-N-carboxymethyl-1-amino-4-hydroxy-2-methylnaphthalene cooled to 0–5° in 25 ml. of methanol was added an ethereal solution of diazomethane in excess. After 15 minutes a few drops of glacial acetic acid were added to decompose the excess diazomethane. The ether was evaporated at room temperature by an air jet, and the methanolic solution was then heated to the boiling point and 10 ml. of hot water added. This caused an immediate turbidity which resulted in the deposition of a cherry red colored oil. The oil was crystallized from a 3:1 petroleum ether (b.p. 60–110°)–benzene mixture. The yield was 1.39 g. (65%). Repeated recrystallization from a petroleum ether–benzene mixture gave pure product, m.p. 170–170.5°.

Infrared analysis indicated a phenolic OH band at 3393 cm.⁻¹.

Anal. Calcd. for C₂₀H₁₉NO₅S: C, 62.47; H, 4.97; N, 3.64. Found: C, 62.57; H, 5.25; N, 3.38.

Method B.—A solution of 10.0 g. of N-benzenesulfonyl-N-carboxymethyl-1-amino-4-hydroxy-2-methylnaphthalene in 500 ml. of absolute methanol and 5 ml. of concd. sulfuric acid was heated under reflux for 24 hours. The orange solution was then diluted with 500 ml. of cold water and cooled. The light pink crystalline material was separated by filtration, washed with water and recrystallized from benzene; m.p. 170–171°. The yield was 7.2 g. (70%).

Melting point of a mixture with the ester obtained by diazomethane methylation showed no depression.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-methoxy-2-methylnaphthalene.—To a suspension of 4.80 g. of N-benzenesulfonyl-N-carbomethoxymethyl-1-amino-4-hydroxy-2-methylnaphthalene in 3.14 g. of dimethyl sulfate and 18.5 ml. of methanol was added 2.78 g. of potassium hy-

(5) R. F. Evans and J. C. Smith, *J. Inst. Petrol.*, **37**, 80 (1951).

dioxide dissolved in 12 ml. of water. The reaction was exothermic. The amber colored solution was heated under reflux on a steam-bath for one hour. The solution was cooled, diluted with 5 volumes of water and acidified with 1:1 hydrochloric acid. The crude product was separated by filtration, washed with water and recrystallized from a 2:1 methanol-water mixture. The yield was 3.5 g. (71%). Recrystallization from an 1:1 ethanol-water mixture yielded a pure white crystalline product, m.p. 223-225°.

Anal. Calcd. for $C_{20}H_{19}NO_6S$: C, 62.47; H, 4.97; N, 3.64. Found: C, 62.21; H, 4.98; N, 3.74.

Infrared analysis indicated less than 1% phenolic OH band. There was an acidic OH band at 2650 cm^{-1} . It showed a slightly positive phosphomolybdic acid test for phenols.

2,4-Dimethyl-1-nitronaphthalene.—A solution of 20.0 g. of 1,3-dimethylnaphthalene⁶ in 50 ml. of glacial acetic acid was cooled and stirred in an ice-bath until crystals of acetic acid appeared. To this mixture 12.8 g. of 70% nitric acid was added dropwise over a 10-minute period. When addition of the nitric acid was half complete a yellow solid began to precipitate. After standing at room temperature for one hour, the product was separated by filtration, washed with glacial acetic acid and recrystallized from ethanol; m.p. 84-84.5°. The yield of yellow needles was 15.0 g. (58%).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.76; H, 5.50; N, 6.56.

1-Amino-2,4-dimethylnaphthalene.—A suspension of 23 g. of Raney nickel catalyst in a solution of 30.0 g. of 2,4-dimethyl-1-nitronaphthalene in 500 ml. of absolute methanol was heated to ca. 60° and 28 g. of 85% hydrazine hydrate dissolved in 28 ml. of absolute methanol was added dropwise over a 45-minute period. The heat of the reaction was sufficient to keep the mixture refluxing. After heating on the steam-bath for an additional 45 minutes, the solution was filtered and the catalyst washed with two 10-ml. portions of methanol. The light amber filtrate was poured into an excess of water and crystallization allowed to proceed. The white crystalline amine weighed 24.6 g. (96%). It was purified by crystallization from a 1:1 methanol-water mixture; m.p. 71-71.5°.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.27; H, 7.35; N, 8.37.

The position of the amino group was determined by oxidation of the amine with 50% nitric acid to *o*-phthalic acid, identified as phthalanil. This indicated the amino group was on the ring containing the two methyl groups. A comparison of the ultraviolet spectrum of the unknown aminodimethylnaphthalene with the spectra of 1-amino- and 2-aminonaphthalene indicated that the amino group was definitely in the 1- and not in the 2-position.

N-Benzenesulfonyl-1-amino-2,4-dimethylnaphthalene.—A solution of 24.6 g. of 1-amino-2,4-dimethylnaphthalene in 100 ml. of pyridine was cooled to 10° in an ice-bath. To this was added 27.9 g. of benzenesulfonyl chloride over a 20-minute period. After standing at room temperature for an additional 2 hours, during which time some solid material precipitated, the mixture was poured into 1.5 l. of cold water. The cream colored amorphous product was separated by filtration, washed with water and recrystallized from glacial acetic acid; m.p. 211-211.5°. The yield was 40.2 g. (90%) of a white crystalline product.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.50. Found: C, 69.25; H, 5.54; N, 4.42.

N-Benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene.—To a mechanically stirred suspension of 75.0 g. of N-benzenesulfonyl-1-amino-2-methylnaphthalene in 775 ml. of glacial acetic acid was added drop by drop over a period of 30 minutes 50.3 g. of bromine dissolved in 30 ml. of glacial acetic acid. After being heated on the steam-bath for another 30 minutes, it was cooled overnight, the product separated by filtration and washed with glacial acetic acid. After one recrystallization from ethanol, 63.9 g. (67%) of woolly white needles were obtained, m.p. 182.5-183.5° (lit.² m.p. 182-183°). Melting point of a mixture with a sample first prepared by Mattson² showed no depression.

N-Benzenesulfonyl-1-amino-4-cyano-2-methylnaphthalene.—To a mixture of 20.0 g. of N-benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene and 6.16 g. of cuprous cyanide was added 7 ml. of pyridine. The mixture was heated on a Wood's metal bath at 200-220° (bath tempera-

ture) for 23 hours. The flask was then cooled slightly and the dark brown viscous mass washed out with pyridine. Addition of the pyridine solution to a mixture of ice and concd. hydrochloric acid caused formation of a dark brown amorphous precipitate. This was separated by filtration, washed with water and extracted with six 200-ml. portions of diethyl ether. The combined amber ether extracts were evaporated to dryness on the steam-bath and the resulting cream colored amorphous residue recrystallized from ethanol (Darco); m.p. 183-184°. The yield was 8.04 g. (47%).

Anal. Calcd. for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.28; H, 4.42; N, 8.64.

Cuprous Thiophenolate.—A suspension of 41.3 g. of freshly precipitated cuprous oxide,⁶ 70.0 g. of thiophenol and 280 ml. of absolute ethanol was vigorously stirred and refluxed under nitrogen for 3 hours. The color of the mixture gradually changed from deep red to light tan. The product was separated by filtration and washed thoroughly with ethanol. There was obtained 82.0 g. (82%) of a light tan colored amorphous powder. Attempts to obtain an analytically pure sample by dissolving in pyridine and precipitating again with water failed. The compound so purified charred at ca. 280°.

Infrared analysis indicated the following monosubstituted benzene bands: C=C (str) 1582 and 1478 cm^{-1} ; CH(rock) 1444 cm^{-1} ; CH(wag) 729 and 682 cm^{-1} .

N-Benzenesulfonyl-1-amino-2-methyl-4-phenylmercaptanaphthalene.—A mixture consisting of 25.0 g. of N-benzenesulfonyl-1-amino-4-bromo-2-methylnaphthalene, 12.6 g. of cuprous thiophenolate, 50 ml. of pyridine and 50 ml. of freshly distilled quinoline was heated on a Wood's metal bath. At first, the temperature was 140° (bath temperature 160°). Enough solvent was evaporated to raise the inside temperature to 185° (bath temperature 205°). Heating was continued for 10 hours during which time the reaction mixture changed from a reddish orange to a dark brown color. The mixture was poured into ice and concd. hydrochloric acid and the contents of the flask washed out with pyridine. The tan colored amorphous precipitate was separated by filtration, washed with water and extracted repeatedly with diethyl ether. The combined ether extracts were evaporated to dryness on a steam-bath and the light cream colored residue recrystallized from ethanol; m.p. 196.5-197.5°. The yield was 18.3 g. (68%).

Anal. Calcd. for $C_{23}H_{19}NO_2S_2$: C, 68.12; H, 4.72; N, 3.45. Found: C, 68.39; H, 4.80; N, 3.49.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-benzenesulfonylnaphthalene.—A solution of 3.47 g. of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-phenylmercaptanaphthalene (see Table II), 90 ml. of glacial acetic acid and 17 ml. of 30% hydrogen peroxide was heated under reflux for a period of one hour. It was then poured into ice-water and allowed to stand overnight in the refrigerator. A milky colloidal suspension formed which was easily broken by the addition of a few drops of concd. hydrochloric acid. The white amorphous precipitate was separated by filtration, washed with water and recrystallized from a 1:1 acetic acid-water mixture. The yield was 2.19 g. (59%). Two recrystallizations from a 1:1 ethyl acetate-petroleum ether (b.p. 60-110°) mixture gave a pure white crystalline product, m.p. 216-216.5°.

Anal. Calcd. for $C_{28}H_{21}NO_6S_2$: C, 60.59; H, 4.27; N, 2.83. Found: C, 60.89; H, 4.31; N, 2.57.

Resolution of the Various Acids.—The cinchonidine salts of the N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalenes were prepared by dissolving the acid and alkaloid in ethyl acetate, a mixture of ethyl acetate and methanol or methanol alone. Crystallization of the first salt fraction at times took several days although seeds of this salt induced crystallization of the subsequent salt fractions in a much shorter time. The first fractions were recrystallized to approximately constant rotation. The characteristics of the salts are described in Table III.

Isolation and Racemization of Optically Active Acids.—Regeneration of the optically active acid from its alkaloid salt was accomplished by adding the pure salt to a cold (0-5°) mechanically stirred aqueous solution of 1:1 hydrochloric acid and allowing the slurry to stir for two hours. The solid was separated by filtration, washed free of alkaloid with

(6) A. King, "Inorganic Preparations," D. Van Nostrand Co., New York, N. Y., 1936, p. 39.

TABLE I

N-BENZENESULFONYL-N-CARBOMETHOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENES										
4-Substituent	Solvn. purif.	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	MeOH	123.5-124	77	C ₂₀ H ₁₉ NO ₄ S	65.02	65.03	5.18	5.07	3.79	3.70
CH ₃	Pet. ether (b.p. 60-110°)	123-123.5	81	C ₂₁ H ₂₁ NO ₄ S	65.77	66.01	5.52	5.53	3.64	3.89
CN	MeOH	131.5-132.5	72	C ₂₁ H ₁₈ N ₂ O ₄ S	63.94	63.80	4.60	4.63	7.10	7.13
C ₆ H ₅ S ^a

^a Ester could not be isolated in crystalline form.

TABLE II

N-BENZENESULFONYL-N-CARBOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENES										
4-Substituent	Solvn. purif.	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	AcOH-H ₂ O	218-219 ^a	84
CH ₃	AcOH	209.5-210	92	C ₂₀ H ₁₉ NO ₄ S	65.02	64.94	5.18	5.41	3.79	3.62
CN	AcOH	195.5-196.5	82	C ₂₀ H ₁₈ N ₂ O ₄ S	63.14	63.22	4.24	4.27	7.37	7.36
C ₆ H ₅ S	EtOH	238-238.5	49	C ₂₆ H ₂₁ NO ₄ S ₂	64.77	64.58	4.57	4.78	3.02	2.80
NO ₂	AcOH	209.5-210.5 ^b	98

^a Melting point of a mixture with the 4-unsubstituted acid prepared by Mattson² showed no depression. ^b Melting point of a mixture with the 4-NO₂ acid prepared by Sundstrom³ showed no depression.

TABLE III

RESOLUTION OF N-BENZENESULFONYL-N-CARBOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENES ^a										
4-Substituent	Solvn. prepn.	Solv., ml./g. acid	Solvn. purif.	M.p., °C.	Wt., g.	Solvent ^c	-α _D ^b , deg.	-[α] _D , deg.	Temp., °C.	
CN	AcOEt-MeOH 95:5	40	EtOH	190-191	0.0320	DMF	0.63	98.5	23	
NO ₂	AcOEt	12	AcOEt-MeOH 95:5	177-178	.0235	EtOH	.30	76.6	30	
C ₆ H ₅ S	AcOEt-MeOH 50:1	11	AcOEt-MeOH 95:5	164-164.5	.0296	EtOH	.53	89.4	30	
C ₆ H ₅ SO ₂	AcOEt	23	AcOEt-MeOH 9:1	200-201	.0248	EtOH	.15	38.3	30	
H	AcOEt-MeOH 95:5	118	AcOEt-MeOH 9:1	209.5-210	.0278	EtOH	.68	122.1	29	
CH ₃	AcOEt-MeOH 95:5	65	AcOEt-MeOH 95:5	206.5-207	.0465	EtOH	1.08	116.1	25	
CH ₃ O	EtOH ^d	85	MeOH	222-223	.0320	DMF	0.33	51.6	25	

^a In all cases only the less soluble salt is described. ^b A 1-cm. tube was used in all cases. ^c The salt was made up to 5 ml. in all cases. ^d Absolute ethanol used for preparation, purification and rotation.

TABLE IV

RACEMIZATION OF N-BENZENESULFONYL-N-CARBOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENES												
4-Substituent	Opt. act. acids, m.p., °C.	Wt., g.	-[α] _D ²⁰ , deg.	0	0.25	-α _D ²⁰ after indicated hours heating, ^a in deg.				3.00	Half-life, ^f hr.	
CN	185-186	0.1417	82.4	0.79	0.56	0.43	0.33	0.24	..	0.10	..	0.62 ^b
NO ₂ ^d	105-110	.2509	35.5	.89	0.63	.51	.40	.30	0.19	0.66
C ₆ H ₅ S	192-193	.1532	41.7	.64	..	.53	..	.44	.34	.28	0.21	1.7
C ₆ H ₅ SO ₂	145-150	.2733	19.1	.53	0.51	.46	.44	.40	.34	1.9
H ^e	191-192	.1519	82.4	1.25	..	1.17	..	1.08	1.02	.96	.80	4.6 ^c
CH ₃	179-180	.1511	72.8	1.10	..	1.04	..	0.99	0.91	.86	.74	5.4
CH ₃ O	202-203	.1401	54.2	0.76	..	0.74	..	0.72	0.70	.67	.61	8.0

^a Racemization carried out in DMF at the boiling point of *n*-butanol (118°). ^b This compound was also racemized in DMF at the temperature of boiling methyl acetate (57°). The half-life value found was 13.5 hr. ^c This compound was also racemized as a solution in *n*-butanol at the boiling point of *n*-butanol (118°). The half-life value found was 5.8 hr. ^d This compound was also racemized by Adams and Sundstrom.³ They reported a half-life value of 0.42 hr. and resolution via the cinchonine salt, giving upon regeneration the optically active acid, α_D²⁰ +30.0°. ^e This compound was also racemized by Adams and Sundstrom.³ They reported a half-life value of 4.9 hr. and resolution via the cinchonine salt, giving upon regeneration the optically active acid, α_D²⁰ +91.0°. ^f The values given are the average of two runs.

10% hydrochloric acid and then free of chloride with distilled water. The racemization technique was the same as that previously reported.³ The characteristics of the acids

and the rate data for one of the two runs carried out for each compound are described in Table IV.

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