(b) **Isolation of an Unidentified Hydrocarbon.**—To an ether solution of 0.25 mole of phenyl Grignard reagent, 0.05 mole of sulfone II in benzene was added. After standing overnight at room temperature, the ether was removed by distillation and the benzene solution refluxed for three hours. After treating the reaction mixture as in (b) above, the biphenyl fraction was distilled under reduced pressure. After biphenyl, a white solid distilled, b.p. 165° (24 mm.), which weighed 3.5 g. and crystallized from methanol as gleaming plates, m.p. 58–60°. By mixed melting points it was found not to be biphenyl, triphenylethylene[8] (m.p. 68–69°) or 1-*o*-biphenyl-1-phenylethylene[9] (m.p. 59–61°). Analysis gave C 94.5% and H 6.2%. Production of this hydrocarbon could be repeated under the same conditions, but it could not be found among the products after six days at room temperature only. Therefore it was presumed to be the result of the higher temperature reaction of excess Grignard reagent with the primary products and was not further investigated. It was not found in any reaction with phenyllithium.

(8) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 606.

(9) C. K. Bradsher, THIS JOURNAL, **66**, 45 (1944). A sample of this compound was available by courtesy of Dr. Bradsher.

ALMA, MICHIGAN

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

Restricted Rotation in Aryl Amines. XVII. Effect of Varying the 4-Substituent on the Stability of Optically Active N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene

BY ROGER ADAMS AND K. V. Y. SUNDSTROM[1]

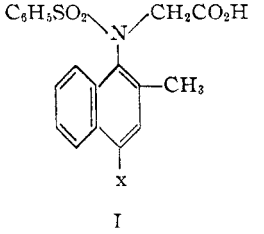
RECEIVED MAY 21, 1954

The influence of sterically non-interfering substituents on the stability of various optically active N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalenes is described. Nine 4-substituted derivatives of this compound have been synthesized and resolved. Electron-withdrawing substituents increase, electron-supplying substituents decrease the racemization rate of these optically active compounds.

In previous work reported on aromatic amines which exhibit restricted rotation, only a few have been synthesized in which the substituents on the nitrogen and in the positions *ortho* to it have been the same from compound to compound. The variation in these molecules has consisted merely of the modification of the substituent in the position *para* to the site of restricted rotation. The comparison of the rates of racemization of the optically active forms of such molecules affords a means of determining the presence and character of factors other than strictly steric which may influence stability.

In the previous paper[2] in this series, compounds of this type have been discussed and the effect of certain electron-attracting groups in the 4-position of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene has been described. The presence of such groups causes a decrease in the stability of the molecules.

This study has now been extended to include ten compounds of type I in which x represents the variable substituent. Racemizations were carried out in dimethylformamide solution at 118° (boiling point of *n*-butyl alcohol). The following half-lives of optical activity were found, where the experimental error, with the exception of the nitro compound, was probably 0.2 to 0.3 hour.

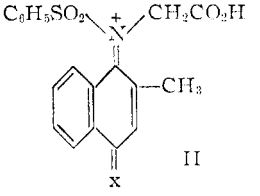


I

Substituent x	Half-life, hours
NO_2	0.42
Cl	3.7; 4.0[2]
Br	3.8; 3.7[2]
I	4.4
H	4.9
$NHSO_2C_6H_5$	3.8
$NHCOCH_3$	5.0
$NHCOC_6H_5$	5.9
OH	8.7
NH_2	9.7

Since the groups which interfere sterically with free rotation about the carbon–nitrogen bond are the same in all of these compounds, the variation in half-life of the optically active forms must be due to the electronic effect of the *para* substituent, x.

Racemization of restricted-rotation isomers probably involves the deformation of atoms and the distortion of bonds since no bonds are broken. The process is usually accepted as proceeding through a planar transition state, and factors which might tend to induce such a state must be considered. Among these factors are resonance forms, such as II, which involve the aromatic nucleus and the lone pair of electrons on the nitrogen. The presence of such forms would lower the energy barrier to racemization by resonance stabilization of the transition state and this would be reflected in an increased rate of racemization. The prevalence of such forms is influenced profoundly by the nature of the substituent, x, in the *para* position relative to the nitrogen. It follows, therefore, that those substituents which favor the formation of such structures should promote racemization; conversely, those which do not should impede racemization.



II

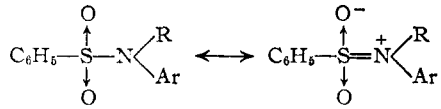
The experimental data agree with this postulation, since resonance according to structure II requires that the substituent x be electron withdrawing. In such compounds (best illustrated by the

(1) An abstract of a thesis submitted by K. V. Y. Sundstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Cincinnati Chemical Co. Fellow, 1951–1952, 1952–1953.

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

nitro derivative) the half-life is short compared to other cases in which the substituent x is electron supplying.

The free electron pair on the pivot nitrogen may be involved in resonance with the benzenesulfonyl system also, as illustrated by structures IIIa and IIIb.



IIIa IIIb

Studies of molecular models show that structure IIIb is much more difficult to construct in a planar configuration than is IIIa. Yet, it is likely that the benzenesulfonyl group competes in some way for the lone pair of electrons on the nitrogen, since the racemization data indicate that the effect of a benzenesulfonamide group is comparable to that of a chlorine or a bromine. Both of the latter are considered electron attracting.

Of all the compounds that were studied, the nitro compound is the only one with a strongly electron-withdrawing group. Resonance structures similar to II are well known in discussions of aromatic nitro compounds. The halogen analogs of I may likewise enter into resonance according to II, but the tendency is weaker than in the case of the nitro. The differences between the half-lives of the chloro, bromo and iodo compounds cannot be considered particularly significant in view of the experimental error in studies of this kind.

Although the 4-benzenesulfonamido group appears to be electron withdrawing, the acetamido and the benzamido derivatives belong on the electropositive side of the unsubstituted compound. The strongly electron-donating hydroxy and amino groups appear to suppress resonance according to II. The ratios of half-lives indicate that the effect of the strongly electron-supplying substituents, amino and hydroxy, is not as important as the effect of the strongly electron-withdrawing nitro.

The compounds in this work were synthesized from 2-methylnaphthalene, which was nitrated in the 1-position followed by reduction to 1-amino-2-methylnaphthalene and benzenesulfonation. Nitration of N - benzenesulfonyl - 1 - amino - 2-methylnaphthalene gave the 4-nitro derivative. N-Benzenesulfonyl-1 - amino - 2 - methyl - 4 - nitronaphthalene was next condensed with ethyl bromoacetate, followed by hydrolysis, which yielded N-benzenesulfonyl - N - carboxymethyl - 1 - amino - 2-methyl-4-nitronaphthalene (compound I in which x = NO_2). This compound was reduced to N^1-benzenesulfonyl - N^1 - carboxymethyl - 1,4 - diamino - 2-methylnaphthalene (compound I in which x = NH_2), from which the rest of the compounds in this study were prepared by substitution of the 4-amino group or by the usual replacement reactions through the diazonium salts.

The compounds in this study are acids and were resolved *via* alkaloidal salts. Cinchonine was found most useful, but cinchonidine and brucine also were used. In the case x = NH_2, the compound is amphoteric, and the optically active isomer was prepared best by catalytic reduction of the optically active nitro compound. The alkaloidal salts were purified by recrystallization and the optically active acids were isolated by decomposition of the salts with hydrochloric acid and extraction with ether.

Racemization studies usually have consisted of intermittent heating of a solution of optically active material, accompanied by observations of rotation and some check for constant concentration. In the present work, a weighed amount of optically active compound was dissolved in a known volume of solvent. The solution was then divided into smaller portions, which were sealed in ampules. The ampules were then heated by immersion in boiling *n*-butyl alcohol for various periods. Some of the compounds under investigation are only sparingly soluble in common solvents, hence dimethylformamide was used. Previous studies in this series have involved racemization in *n*-butyl alcohol solution, which is the reason for the choice of the boiling point of this solvent (118°) as racemization temperature.

Acknowledgment.—The authors are indebted to Mrs. Lucy Chang, Mrs. Esther Fett, Mrs. Jean Fortney, Mrs. Katherine Pih, Miss Emily Davis and Mr. Joseph Nemeth for the microanalyses.

Experimental[3]

N-Benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene.—To a suspension of 104 g. of N-benzenesulfonyl-1- amino-2-methylnaphthalene[4] in 400 ml. of glacial acetic acid, 38 g. of 70% nitric acid was added dropwise with stirring, while the temperature was kept between 85 and 90°. At the end of the addition, a brown solution had formed, which was kept at 80° for one hour and then allowed to cool slowly. The yellow solid, which formed, was collected and recrystallized from ethanol (Norit). The yield was 60 g. (46%), m.p. 155–156° (lit.[4] 156°).

N-Benzenesulfonyl-N-carboethoxymethyl-1-amino-2-methyl-4-nitronaphthalene.—After drying over phosphorus pentoxide 38 g. of N-benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene was added to 200 ml. of absolute ethanol, which had been previously treated with 2.90 g. of sodium. To this solution 22 g. of ethyl bromoacetate and one drop of piperidine were added and the reaction mixture was kept at reflux for 24 hours. Solid sodium bromide was removed by filtration and the solution was reduced by distillation *in vacuo* to about half its original volume, then cooled overnight, yielding a yellow solid, which was collected on a filter, washed with water and recrystallized twice from 95% ethanol. The yield was 35 g. (73%), m.p. 98.5–99°.

Anal. Calcd. for $C_{21}H_{20}N_2O_6S$: C, 58.90; H, 4.71. Found: C, 58.91; H, 4.72.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene.—To a boiling solution of 30 g. of N-benzenesulfonyl-N-carboethoxymethyl-1-amino-2-methyl-4-nitronaphthalene in 250 ml. of glacial acetic acid was added 70 ml. of 10% aqueous sulfuric acid. After boiling for 8 hours, the solution was allowed to cool and a pale green solid crystallized as fine needles. The product was purified by recrystallization from glacial acetic acid, m.p. 209.8–210°. The yield was 27 g. (95%).

Anal. Calcd. for $C_{19}H_{16}N_2O_6S$: C, 57.05; H, 4.01. Found: C, 57.06; H, 4.24.

N^1-Benzenesulfonyl-N^1-carboxymethyl-1,4-diamino-2-methylnaphthalene Hydrochloride.—To a hot solution of 60 g. of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene in 300 ml. of 2.5% aqueous sodium hydroxide was added 80 g. of sodium hydrosulfite in 2 portions, at a 20-minute interval. While the temperature was kept at 90°, 80 g. of sodium acetate in 150 ml. of water was added. When all of the original mustard color had vanished, the heating was discontinued and the solution was allowed to cool to room temperature. A small amount of solid appeared, but addition of 100 ml. of concd. hydro-

(3) All melting points are corrected.

(4) See ref. 2.

chloric acid caused precipitation of the amino acid as hydrochloride. This was used in the following preparations after one recrystallization from 5% aqueous hydrochloric acid. The yield was 40 g. (70%), m.p. 164–165°.

Anal. Calcd. for $C_{19}H_{18}N_2O_4S$: C, 55.60; H, 4.93; N, 6.85. Found: C, 56.08; H, 5.03; N, 7.04.

N¹-Benzenesulfonyl-N¹-carboxymethyl-N⁴-acetyl-1,4-diamino-2-methylnaphthalene.—To a well-stirred suspension of 5 g. of N-benzenesulfonyl-N-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride in 80 ml. of glacial acetic acid was added 1.5 g. of acetic anhydride. The suspension was heated carefully until all the solid material dissolved. The pink crystalline solid, which separated when the solution was poured into 1 l. of ice-water, was recrystallized twice from glacial acetic acid. The yield was 3.5 g. (70%), m.p. 247.5–248°.

Anal. Calcd. for $C_{21}H_{21}N_2O_5S$: C, 61.15; H, 4.88; N, 6.79. Found: C, 61.26; H, 4.77; N, 6.88.

N¹,N⁴-Dibenzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene.—To a solution of 4.0 g. of N¹-benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride in 25 ml. of pyridine was added 1.9 g. of benzenesulfonyl chloride. The reaction mixture became hot and was left for 3 hours to cool. On pouring the pyridine solution into 300 ml. of ice-water, a light brown gum separated. Trituration with absolute ethanol removed color and induced crystallization. By recrystallization from absolute ethanol, 3 g. (60%) of pure material resulted, m.p. 258–258.5°.

Anal. Calcd. for $C_{25}H_{22}N_2O_6S_2$: C, 58.82; H, 4.24; N, 5.49. Found: C, 58.69; H, 4.23; N, 5.56.

N¹-Benzenesulfonyl-N¹-carboxymethyl-N⁴-benzoyl-1,4-diamino-2-methylnaphthalene.—To a solution of 6 g. of N¹-benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride in 50 ml. of pyridine was added 2.2 g. of benzoyl chloride. The reaction mixture became hot. After 2 hours at room temperature, the pyridine solution was poured into 200 ml. of ice-water. A milky suspension formed, which was coagulated by addition of 50 ml. of concd. hydrochloric acid. The crude product was recrystallized from a 3:1 ethanol–acetone mixture. The yield was 4.5 g. (65%), m.p. 172–173°.

Anal. Calcd. for $C_{26}H_{22}N_2O_5S$: C, 65.79; H, 4.68; N, 5.92. Found: C, 65.81; H, 5.52; N, 6.01.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-iodo-2-methylnaphthalene.—The hydrosulfate of N¹-benzenesulfonyl-N¹-carboxymethyl-1,4-diamino-2-methylnaphthalene was prepared by repeated recrystallization of 20 g. of the hydrochloride of the same compound from 10% aqueous sulfuric acid. To a solution of 18 g. of this hydrosulfate in 150 ml. of aqueous sodium hydroxide was added 2.6 g. of sodium nitrite and the mixture was cooled in an ice-bath. The cold solution was poured slowly with stirring into 200 ml. of 10% aqueous sulfuric acid, containing ice. Excess nitrous acid in the resulting red solution was destroyed with sulfamic acid. The solution was then filtered and one-half of it added to a solution of 10 g. of potassium iodide in 50 ml. of water. Evolution of gas and formation of a white precipitate took place at once. After heating for 2 hours on a steam-bath, the precipitate was collected on a filter and recrystallized from glacial acetic acid. The yield was 5.2 g. (41%), m.p. 180–180.5°.

Anal. Calcd. for $C_{19}H_{16}INO_4S$: C, 47.48; H, 3.39; N, 2.88. Found: C, 47.24; H, 3.39; N, 3.00.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-hydroxy-2-methylnaphthalene.—To the other half of the diazonium solution prepared in the preceding experiment was added 50 ml. of 15% aqueous sulfamic acid. The solution was allowed to stand for 4 hours in ice with intermittent stirring, after which it was filtered and added slowly to 2 l. of boiling 10% aqueous sulfuric acid. The formation of colored bodies was prevented by addition of small amounts of dilute aqueous potassium permanganate.[5] The reaction product, which collected at the surface of the reaction mixture, was removed on a filter and recrystallized from a 3:1 ethanol–water mixture. The yield was 3.3 g. (32%), m.p. 204–205°.

Anal. Calcd. for $C_{19}H_{17}NO_6S$: C, 61.50; H, 4.62; N, 3.77. Found: C, 61.25; H, 4.71; N, 4.05.

(5) H. Gies and E. Pfeil, *Ann.*, **578**, 11 (1952).

TABLE I

RESOLUTION OF N-BENZENESULFONYL-N-CARBOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENE AND DERIVATIVES[a]

Subst. (x)	Alkaloid	Solv. prepn.	Solv., ml./g. acid	Solv. purif.	Less-sol salt m.p., °C.	Wt., g.	Rotation in dimethylformamide[b] Vol., ml.	α_D	$[\alpha]_D$	Temp., °C.	Formula salt	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
NO_2	A	AcOEt	300	AcOEt	214–214.5	0.0868	20	+0.9361°	+108.0°	30	$C_{38}H_{38}N_4O_7S$	65.61	65.88	5.53	5.46
Cl	A	$CHCl_3$	28	AcOEt–MeOH 9:1	218–219	.012	5	+ .0339	+140	28	.....	Ref. 4			
Br	A	AcOEt–MeOH 9:1	80	AcOEt	225–227	.0331	5	+ .834	+126	28	.....	Ref. 4			
I	A	EtOH(abs.)	80	EtOH(abs.)	188–188.5	.0158	5	+ .648	+205	25	$C_{38}H_{38}IN_3O_5S$	58.70	58.95	4.94	5.03
H	A	$CHCl_3$	23	AcOEt–MeOH 19:1	200–200.5	.0361	5	+1.11	+158	25	.....	Ref. 4			
$NHSO_2C_6H_5$	A	H_2O	800	EtOH–H_2O 1:1	166.5–167	.0422	5	+0.465	+55.2	30	$C_{44}H_{44}N_4O_7S_2$	65.51	65.48	5.51	5.25
$NHCOCH_3$	B	H_2O	1000	EtOH(abs.)	146–146.5	.0691	5	−1.021	−85.5	25	$C_{44}H_{47}N_4O_8S$	60.49	60.68	5.44	5.40
$NHCOC_6H_5$	C	EtOH–$(CH_3)_2CO$ 1:1	170	EtOH–$(CH_3)_2CO$ 1:1	195–195.5	.0246	5	−0.264	−53.6	30	$C_{45}H_{44}N_4O_8S$	70.32	70.07	5.76	6.01
OH	C	EtOH–H_2O 1:4	170	EtOH(abs.)	159.5–160	.0356	5	−0.367	−51.7	25	$C_{38}H_{39}N_3O_6S$	69.51	69.80	5.99	6.07
NH_2	(Optically active isomer prepared by reduction of active nitro compound)														

[a] In all cases merely the less soluble salt is described. [b] A 1-dm. tube was used in all cases. A = cinchonine; B = brucine; C = cinchonidine.

TABLE II

RACEMIZATION OF N-BENZENESULFONYL-N-CARBOXYMETHYL-1-AMINO-2-METHYLNAPHTHALENE AND DERIVATIVES

Subst. (x)	Opt. act. acids, m.p., °C.	Wt., g.	Vol., ml. DMF	Temp., °C.	$[\alpha]_D$	α_D after indicated minutes of heating[a] 0	15	30	45	60	90	120	180	$t_{1/2}$ hr.
NO_2	216–218	0.568	20	33	+30.0°	+0.853	+0.538	+0.325	+0.247	+0.149		+0.031		0.42[b]
Cl	200–202	.0482	20	28	+71.0	+ .171		+ .158		+ .140	+0.127	+ .117	+0.094	3.7
Br	193–194	.318	20	28	+60.0	+ .953		+ .880		+ .783	+ .731	+ .664	+ .565	3.8
I	180–181	.322	10	25	−15.7	− .505	− .469	− .454		− .427	− .387		− .338	4.4
H	207–208	.523	20	28	+91.0	+3.431		+3.172		+2.985	+2.780	+2.571	+2.251	4.9
$NHSO_2C_6H_5$	263–265	.356	10	25	+27.4	+0.976	+ .920	+0.877		+0.815	+0.720	+0.675	+0.568	3.8
$NHCOCH_3$	248–249	.199	10	25	+24.7	+0.492	+ .470	+ .452		+ .430		+ .390	+ .343	5.0
$NHCOC_6H_5$	172–173	.104	10	30	+103	+1.107	+1.037	+ .945		+ .934	+ .873	+ .841	+ .750	5.9
OH	204–205	.316	20	25	+65.0	+1.028	+0.998	+ .968		+ .934	+ .908	+ .885	+ .814	8.7
NH_2	222–223	1.189	20	30	+15.2	+0.904	+0.885	+ .880	+0.865	+ .845		+ .787	+ .733	9.7

[a] The temperature during racemization was maintained at 118°. [b] This compound was also racemized in DMF at 57° and in boiling methyl acetate (b.p. 57°). The half-life values obtained were essentially identical, 2.12 hr.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-chloro-2-methylnaphthalene.—A solution of 5 g. of N^1-benzenesulfonyl-N^1-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride and 0.85 g. of sodium nitrite in 100 ml. of 5% aqueous sodium hydroxide was cooled in an ice-bath and added slowly to 200 ml. of 10% aqueous hydrochloric acid, containing ice. The excess of nitrous acid was destroyed with a few drops of 15% aqueous sulfamic acid, and the diazonium solution was poured slowly into 100 ml. of a solution of cuprous chloride in hydrochloric acid.[6] Gas was evolved and a solid separated. The solid was recrystallized from glacial acetic acid and dried over potassium hydroxide. The yield was 2.8 g. (60%), m.p. 201–202° (lit.[4] m.p. 201–202°).

N-Benzenesulfonyl-N-carboxymethyl-1-amino-4-bromo-2-methylnaphthalene.—This compound was prepared from 5 g. of N-benzenesulfonyl-N-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride in exactly the same manner as the 4-chloro compound (the preceding experiment). The yield was 3.0 g. (60%), m.p. 191–192° (lit.[4] 191–192°).

N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene.—A solution of diazonium salt was prepared by dissolving 5 g. of N-benzenesulfonyl-N-carboxymethyl-1,4-diamino-2-methylnaphthalene hydrochloride and 0.85 g. of sodium nitrite in 100 ml. of 5% aqueous sodium hydroxide, cooling and adding to 200 ml. of 10% aqueous sulfuric acid. The solution was filtered and a solution of 1.2 g. of sodium hypophosphite in 50 ml. of water was added to the filtrate. The mixture was allowed to stand in a refrigerator for 6 days. A slightly yellow solid was then collected on a filter, recrystallized from glacial acetic acid and dried over potassium hydroxide. The yield was 3.6 g. (75%), m.p. 220–221° (lit.[4] 219–220°).

Resolution and Racemization of N-Benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene.—When a filtered solution of 10.00 g. of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-nitronaphthalene and 7.35 g. of cinchonine in 3 l. of ethyl acetate was kept in a refrigerator for 10 days, a solid formed gradually; weight 6.27 g., m.p. 213–214°, $[\alpha]^{30}D$ +108.0° in dimethylformamide. The solution was concentrated *in vacuo* to 1.9 l. and 7 days later a second crop was collected; weight 2.93 g., m.p. 213–214°, $[\alpha]^{30}D$ +107.0° in dimethylformamide. The two crops were combined and recrystallized from ethyl acetate, yielding 8.3 g. of purified salt, m.p. 214–214.5°.

Rotation.—0.0868 g. made up to 20 ml. with dimethylformamide at 30° gave αD +0.9361; *l* 1, $[\alpha]^{30}D$ +108.0°.

Anal. Calcd. for $C_{38}H_{38}N_4O_7S$: C, 65.61; H, 5.53. Found: C, 65.88; H, 5.46.

To isolate the *d*-acid, 4.0 g. of the purified less-soluble salt was introduced into a 500-ml. separatory funnel containing 150 ml. of diethyl ether, 50 ml. of 20% aqueous hydrochloric acid and ice. The funnel was shaken until all the solid had dissolved. The aqueous layer was removed, and the ether layer was extracted with fresh portions of hydrochloric acid, until the extract gave a negative test for alkaloid with Mayer reagent. The ether layer was then washed with water, the ether evaporated under an air jet and the product dried over sulfuric acid. The yield was 2.0 g. (87%), m.p. 216–217°.

A solution of 0.568 g. of the *d*-acid was made up quantitatively to 20 ml. with dimethylformamide and transferred in 2-ml. portions to glass tubes (15 cm. long, 8 mm. diameter). These were sealed and immersed in boiling *n*-butyl alcohol at the intervals indicated below. At the end of the heating, the tubes were all quenched at the same time in ice-water. They were then allowed to come to room temperature, opened and the contents of each transferred to a 1-dm. polarimeter tube. The unheated sample had αD +0.853°, $[\alpha]^{33}D$ +30.0°; one-quarter hour of heating αD +0.538°, $[\alpha]^{33}D$ +18.9°; one-half hour αD +0.325°, $[\alpha]^{33}D$ +11.8°; three-fourths hour αD +0.247°, $[\alpha]^{33}D$ +8.20°; one hour αD +0.149°, $[\alpha]^{33}D$ +5.27°; two hours αD +0.031°, $[\alpha]^{33}D$ +1.10°.

These values were plotted on semi-logarithmic paper. From the slope of the resulting straight line, typical of a unimolecular rate equation, may be derived the half-life $t_{1/2}$ 0.42 hour.

A second racemization experiment gave data which were in good agreement with the first.

The other compounds in this study were resolved and racemized in a manner similar to that of the nitro compound. The significant data on the resolutions and racemizations are given in Tables I and II.

URBANA, ILLINOIS

(6) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170.