doubtedly is some meta displacement but it is believed that this is relatively small and would not seriously change the value recorded.

Discussion of Experimental Results

From the data which are now available it may be safely concluded that a halogen meta to the nitro group does increase the mobility of the halogen in the para position. Also when piperidine is used as the reagent for reactive halogen, a steric effect seems to be of importance. Drake and McElvain[5d,e] have shown that with piperidine a rate determining factor in the halogen replacement reaction is the ability of the reagent to approach the carbon carrying the halogen. In the authors' work this is very noticeable from Table I, if the compounds are examined from the standpoint of groups 1, 2 and 3; 4, 5 and 6; 7, 8 and 9. In these three groups it is the dihalogenated compound which is the most reactive, and it would appear that the iodine atom has both an activating and steric effect. The decided decreased activity of the trihalogenated compounds is undoubtedly due to the steric factors associated with the structure of the compounds.

Regarding the last four compounds it is difficult to say whether it is the increased activating effect, or the decreased steric effect of the chlorine or bromine atoms, which is responsible for the slightly increased halogen displacement of the trihalogenated compounds.

Concerning the steric factor it might be supposed that this would be less noticeable if a reagent such as a phenolate instead of piperidine were used. Preliminary work which has been done using phenol in methyl ethyl ketone and potassium carbonate indicates the plausibility of this supposition. In the compounds 4, 5 and 6 it has been found that expressing the reactivity of compound 4, the least reactive, by unity, the reactivities of 5 and 6 are represented by 16 and 42.

Summary

A quantitative study of the removal of the para halogen using piperidine, from thirteen halogenated nitrobenzenes has been made. The results indicate that meta halogen increases the mobility of the para halogen. There is also a steric factor to be considered. This work is being continued.

EDMONTON, ALBERTA RECEIVED MAY 3, 1935

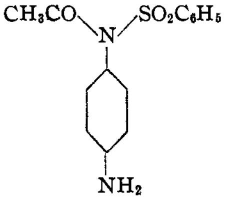
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Anomalous Mutarotation of Amine Salts of *d*-Camphor-10-sulfonic Acid. Attempted Resolution of Tri-substituted Nitrogen Compounds

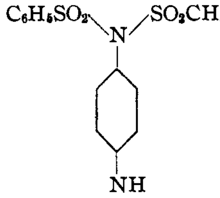
BY R. S. SCHREIBER AND R. L. SHRINER

The concept of a tetrahedral nitrogen atom predicts the existence of optical isomers of compounds of the type RR'R''N. However, the actual isolation of the *d*- and *l*-forms depends on their stability and the failure to resolve such compounds may be due to very rapid racemization. If the configuration of such a molecule could be fixed by some means, then resolution should be possible. It seemed plausible that heavy negative groups, such as acyl or sulfonyl, would be less mobile than alkyl or aryl groups which were attached to the nitrogen atom in compounds whose resolution has been attempted.[1] Kipping and Salway[2] studied the resolution of a compound with one acyl radical, but no studies have been made on the resolution of imides.

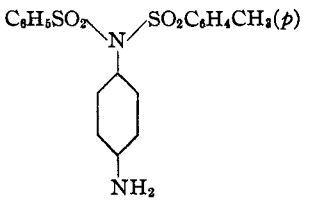
Accordingly, the following unsymmetrically substituted *p*-phenylenediamine derivatives were prepared, then treated with *d*-camphor-10-sulfonic



I



II



III

---

[1] For references, see the recent books on "Stereochemie" by Freudenberg (1933); Goldschmidt (1933); Wittig (1930).

[2] Kipping and Salway, *J. Chem. Soc.*, **85**, 446 (1904).

acid (Reychler's acid), and the salts isolated. It is worth pointing out that, in these compounds, salt formation takes place by means of the free *p*-amino group, and hence there is less likelihood that salt formation would disturb the spacial arrangement about the tertiary nitrogen atom.

These salts were shown by analysis to consist of one mole of the base and one mole of the *d*-camphor-10-sulfonic acid. Upon studying the optical rotation of these salts it was discovered that methanol, ethanol or chloroform solutions of these compounds exhibited *mutarotation.* The curves in Fig. 1 indicate their behavior.

The mutarotation of salts of this type might be due to the formation of diastereoisomers of the two forms of the amine

$$dl\mathrm{B} + d\mathrm{A} \rightleftharpoons d\mathrm{B}d\mathrm{A} + l\mathrm{B}d\mathrm{A}$$

with the *d*-camphor-10-sulfonic acid, and hence indicate that a resolution was taking place. However, removal of the solvent gave a salt identical in melting point and rotation with the original which *again mutarotated in the same manner.* Direct decomposition of solutions of the salts with alkali at 0° gave only the optically inactive compounds I, II and III.

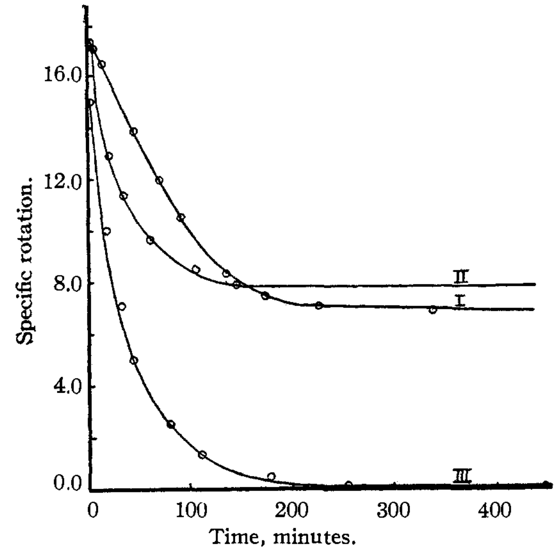


Fig. 1.—Mutarotation of salts of Reychler's acid.

Hence, control experiments were run using the *d*-camphor-10-sulfonic acid salts of other amines,

TABLE I

MUTAROTATION OF AMINE SALTS OF *d*-CAMPHOR-10-SULFONIC ACID

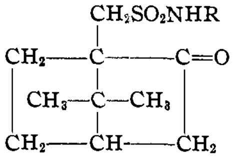
No.	*d*-Camphor-10-sulfonic acid salts	Grams of salt per 100 cc. of solvent	Solvent[a]	Time (min.) to reach constant value	Specific rotations at 25° Initial	Final
I	$\begin{matrix}C_6H_5SO_2\\CH_3CO\end{matrix}\!\!>N{-}C_6H_4NH_2(p)$	1.33	$CHCl_3$	335	+17.3	+ 6.8
		1.2	C_2H_5OH	95	+18.3	+13.3
		10.0	$CHCl_3$		+16.6	+ 9.2
II	$\begin{matrix}C_6H_5SO_2\\CH_3SO_2\end{matrix}\!\!>N{-}C_6H_4NH_2(p)$	1.33	$CHCl_3$	169	+16.9	+ 8.6
		1.2	C_2H_5OH	142	+17.1	+ 7.9
		5.0	$CHCl_3$	480	+17.0	+11.5
III	$\begin{matrix}C_6H_5SO_2\\C_6H_5SO_2\end{matrix}\!\!>N{-}C_6H_4NH_2(p)$	1.2	CH_3OH $CHCl$	185	+15.0	+ 7.9
		1.2	CH_3OH $CHCl_3$	113	+15.8	+ 0.8
		6.0	$CHCl_3$ CH_3OH	127	+13.7	− 4.8
IV	$\begin{matrix}C_6H_5SO_2\\(p)CH_3C_6H_4SO_2\end{matrix}\!\!>N{-}C_6H_4NH_2(p)$	1.2	$CHCl_3$ CH_3OH	250	+15.0	0.0
		3.0	$CHCl_3$ CH_3OH	307	+13.0	− 4.0
V	$C_6H_5SO_2NHC_6H_4NH_2(p)$	1.2	C_2H_5OH	2880	+23.3	− 8.3
		1.2	CH_3OH	3101	+18.8	− 3.8
		5.0	CH_3OH	2000	+19.3	−12.5
VI	$CH_3CONHC_6H_4NH_2(p)$	1.2	C_2H_5OH	3292	+27.5	− 7.9
		1.2	CH_3OH	2607[b]	+22.9	− 2.5
		10.0	CH_3OH	2000[c]	+24.6	−18.4
VII	$H_2NC_6H_4NH_2(p)$	1.2	CH_3OH	720[b]	+29.2	−10.0
		1.12	C_2H_5OH	150[b]	+35.3	..
		1.66	CH_3OH	1440[b]	+29.1	−52.5
VIII	$O_2NC_6H_4NH_2(p)$	2.4	CH_3OH	18	+23.3	+20.0
		1.6	CH_3COCH_3	162	+22.5	+18.1
		10.0	CH_3OH	2200	+21.5	+15.5
IX	$C_6H_5NH_2$	2.4	CH_3OH	3000	+29.2	+ 2.5
		1.00	$CHCl_3$	2700	+35.5	+ 5.5
		10.00	CH_3OH	3000	+28.6	− 5.6

[a] Solvents used were absolute methyl and ethyl alcohols. An equal mixture by volume of $CHCl_3$ and CH_3OH was used for the mixed solvent. [b] Solution became too dark to read further. [c] Crystals separated out here in tube.

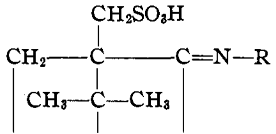
and in each case mutarotation was observed. The essential data are summarized in Table I, which shows the initial and final rotations in different solvents at different concentrations for a variety of amines.

Examination of the data in Table I shows that mutarotation occurred in different solvents and that the final values were dependent on the solvent and concentration, but no direct correlation exists which would explain the anomalous mutarotations. The fact that salts of *p*-phenylenediamine, *p*-nitraniline and aniline (VII, VIII and IX, Table I) mutarotated does show that an asymmetric nitrogen atom is *not* involved in the phenomenon. In each case in Table I, evaporation of the solvent gave the original salt which again mutarotated in the same manner.

The first hint which led to the explanation of these mutarotations came as the result of examination of the salt of *p*-aminoacetanilide (VI). When methyl alcohol solutions of this salt were allowed to stand four days a precipitate appeared which was filtered. It melted at 375-380°, whereas the original salt melted at 208-210°. Its specific rotation in a mixture of absolute methyl alcohol and chloroform was $[\alpha]^{25}\text{D}$ $-192.5°$, whereas the original salt had a dextrorotation of $+24.5°$. Analysis of this precipitate for sulfur and nitrogen showed the loss of one molecule of water. The same compound was also obtained by heating the original salt at 210° for thirty minutes. Two structures which suggest themselves as possibilities are the amide (IV) and the ketimine V.

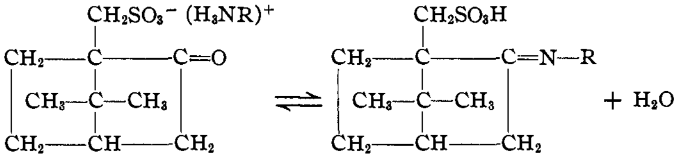


IV



V

The aniline salt (IX), which melted at 184-186°, and had $[\alpha]^{25}\text{D}$ $CHCl_3$ $+ 37.5°$, could also be dehydrated to a compound with m. p. 294-295°, and $[\alpha]^{25}\text{D}$ $-170.5°$. Its analysis indicated the loss of a molecule of water from the salt. Moreover, this dehydrated product was acidic and could be titrated, giving a good neutral equivalent. Formula IV, being a monosubstituted sulfonamide, is also soluble in alkali, but such sulfonamides do not in general give good neutral equivalents. Hence, the ketimine structure affords an adequate interpretation of the analytical data and, in addition, the mutarotations of the salts observed are probably due to the establishment of an equilibrium between the salt VI, and the ketimine or anil (VII).



VI VII

Since anil formation involves the liberation of a molecule of water, the above equilibrium should be profoundly affected by the presence of water in the solvent. In fact, if water was used as the solvent, no mutarotation was observed for the salts VII and IX which were the only ones soluble in that solvent.

The effect of water on the mutarotation was further established by adding small amounts of water to solutions of the salt and of the anil of aniline *d*-camphor sulfonate in chloroform. The curves in Fig. 2 show the effect of addition of small amounts of water to a chloroform solution of the salt, aniline *d*-camphor-10-sulfonate (Curve A) and to the anil (Curve B). It will be noted that the addition of a small amount of water to the anil after the initial mutarotation had reached equilibrium caused a very rapid mutarotation to the same final value as given by the salt. The slow mutarotation of the anil in the chloroform is due to the traces of moisture which the solvent and compound absorbed during weighing, solution and filling of the polariscope tube.

A search of the literature revealed that anomalous mutarotations of *d*-camphor-10-sulfonic acid salts of amino- and diaminobenzoylbromomesitylene were observed by Hyde and Adams[3] during their studies on the mutarotation of substituted diphenyls, but the observations were not explained. Lesslie and Turner[4] also noted the separation of a product from solutions containing the salt of 2-phenylnaphthalene-1,3-diamine with Reychler's acid, but did not characterize the compound. Although many previous investigators had made salts of *d*-camphor-10-sulfonic acid, the mutarotation phenomenon was not observed, either because water was used as the solvent for determining the rotations, or because

---

[3] Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928).

[4] Lesslie and Turner, *J. Chem. Soc.*, 1517 (1929).

the readings were not taken over a sufficiently long period of time. A further study of these salts is being made in order to establish definitely the structure of the dehydration products.

The present investigation indicates that caution must be used in deducing from mutarotation data *alone* that resolution of a racemic compound by means of Reychler's acid is taking place. It is always necessary to decompose the salt and determine the optical activity of the base. Decomposition of the salts and anils described in this paper always gave the optically inactive *p*-phenylenediamine derivatives (I, II and III). Hence, anil formation did not involve any selective reaction of one form of the tertiary nitrogen compound.

Experimental

N-Acetyl-N-4-nitrophenylbenzenesulfonamide.—Twenty-five grams of acetic anhydride was added, all at once, to 58 g. of N-4-nitrophenylbenzenesulfonamide[5] dissolved in 200 cc. of dry pyridine, and the mixture was stirred for about three hours at room temperature. During this time the acetyl derivative is precipitated. It is then filtered and recrystallized from an acetone-alcohol mixture. The yield was 56 g., or 87% of the theoretical value; m. p. 198–199°.

Anal. Calcd. for $C_{14}H_{12}O_5N_2S$: N, 8.75; S, 10.00. Found: N, 8.95; S, 9.86.

N-Sodium N-4-Nitrophenylbenzenesulfonamide.—Two hundred grams of N-4-nitrophenylbenzenesulfonamide was dissolved in 2500 cc. of 5% sodium hydroxide, and the solution evaporated to approximately 800 cc. On standing overnight, the sodium salt precipitated in long yellow needles. These were filtered, washed with ether and dried at 110° for twelve hours. The yield was 210 g., or 97% of the theoretical value; m. p. 409–410°, bloc Maquenne.

Anal. Calcd. for $C_{12}H_9O_4N_2SNa$: Na, 7.66; S, 10.66. Found: Na, 7.64; S, 10.44.

N-Methanesulfonyl N-4-Nitrophenylbenzenesulfonamide.—Fifty-four grams of N-sodium N-4-nitrophenylbenzenesulfonamide was mixed with 75 g. of methanesulfonyl chloride, and the mixture allowed to stand at room temperature for sixteen hours with occasional shaking. The mixture was then refluxed for fifteen minutes and poured into 500 cc. of 15% sodium hydroxide to decompose the excess sulfonyl chloride. The insoluble N-methanesulfonyl N-4-nitrophenylbenzenesulfonamide was filtered, washed well with water and recrystallized from an acetone-alcohol mixture after decolorizing with norite. The faintly yellow solid was produced in a yield of 33 g., or 51% of the theoretical value; m. p. 170–171.5°.

Anal. Calcd. for $C_{13}H_{12}O_6N_2S_2$: N, 7.86; S, 17.97. Found: N, 7.96; S, 17.84.

N-4-Methylphenylsulfonyl N-4-Nitrophenylbenzenesulfonamide.—Ninety grams of N-sodium N-4-nitrophenylbenzenesulfonamide was suspended in 550 cc. of acetone, and to this mixture was added 60 g. of *p*-toluenesulfonyl chloride. The solution was refluxed vigorously for sixteen hours, then diluted with two liters of water and made strongly alkaline with sodium hydroxide to destroy any unreacted sulfonyl chloride. The insoluble disulfonyl compound was filtered, washed well with water and recrystallized as a light yellow solid from acetone. The yield was 95 g. or 73% of the theoretical value; m. p. 188–189°.

Anal. Calcd. for $C_{19}H_{16}O_6N_2S_2$: N, 6.48; S, 14.81. Found: N, 6.60; S, 14.80.

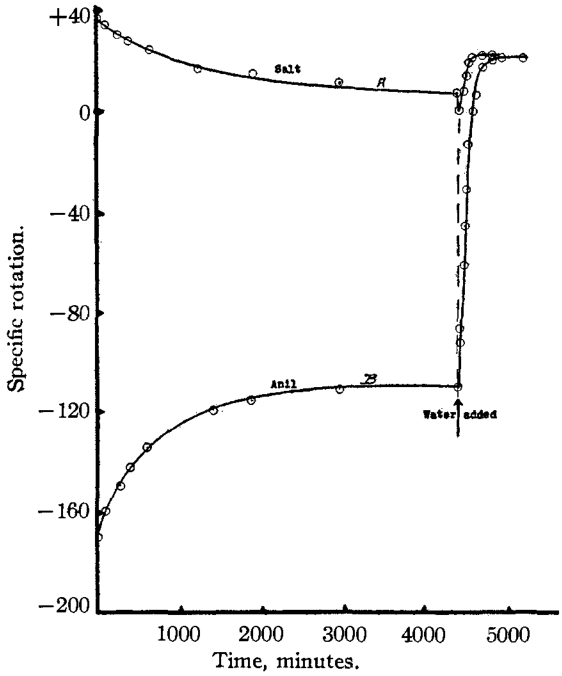


Fig. 2.—Effect of water on mutarotation of the aniline salt and anil of Reychler's acid.

N-Phenylsulfonyl N-4-Nitrophenylbenzenesulfonamide.—(a) One hundred grams of N-sodium N-4-nitrophenylbenzenesulfonamide was treated with 60 g. of benzenesulfonyl chloride in 500 cc. of acetone. This reaction was carried out in exactly the same manner as in the preparation of N-4-methylphenylsulfonyl N-4-nitrophenylbenzenesulfonamide. However, this compound was a white solid. The yield was 105 g. or 75% of the theoretical value; m. p. 213°.

(b) This disulfonyl compound can also be prepared in 5 to 7% yields by heating *p*-nitroaniline with excess benzenesulfonyl chloride on a steam-bath for about a day.

Anal. Calcd. for $C_{18}H_{14}O_6N_2S_2$: N, 6.70; S, 15.31. Found: N, 6.58; S, 15.17.

Preparation of Amino Compounds.—The above nitro compounds were reduced catalytically using platinum oxide and hydrogen in absolute alcohol[6] as the solvent. The reductions proceeded rather slowly, requiring from twelve to twenty hours for completion, due to the slight insolubility of these nitro compounds in alcohol. The reduced compounds were all recrystallized from absolute alcohol

---

[5] E. Lellmann, *Ber.*, **16**, 595 (1883); St. Opolski, *ibid.*, **40**, 3534 (1907).

[6] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

Table II

	M. p., °C.	Color	Yield, %	Analyses, % Calcd. N	Calcd. S	Found N	Found S
$\begin{matrix}H_2NC_6H_4\\H\end{matrix}\!>\!N{-}SO_2C_6H_5$	171–172	Light yellow	87	...	...	Ref. 7	...
$\begin{matrix}H_2NC_6H_4\\C_6H_5SO_2\end{matrix}\!>\!N{-}SO_2C_6H_5$	166–177	White	88	7.21	16.49	7.54	16.52
$\begin{matrix}H_2NC_6H_4\\CH_3C_6H_4SO_2\end{matrix}\!>\!N{-}SO_2C_6H_5$	168–169[a]	Light yellow	88	6.96	15.92	7.23	15.82
$\begin{matrix}H_2NC_6H_4\\CH_3SO_2\end{matrix}\!>\!N{-}SO_2C_6H_5$	163–164	Light yellow	83	8.59	19.63	8.50	19.41
$\begin{matrix}H_2NC_6H_4\\CH_3CO\end{matrix}\!>\!N{-}SO_2C_6H_5$	162–163	Light yellow	93	9.65	11.03	10.08	10.82

[a] Melts at 154–156° when rapidly heated, but solidifies and melts again at 168–169°. If the melting point bath is heated slowly, no change is noticed.

Table III

No.	*d*-Camphor-10-sulfonic acid salts of amines	M. p., °C.	Yield, %	Analyses, % Calcd. N	Calcd. S	Found N	Found S
I	$\begin{matrix}C_6H_5SO_2\\CH_3CO\end{matrix}\!>\!N{-}C_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	174–177 207–208[a]	84	5.36	12.26	5.24	12.27
II	$\begin{matrix}C_6H_5SO_2\\CH_3SO_2\end{matrix}\!>\!N{-}C_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	153–156 195–196[a]	86	5.02	17.20	5.13	17.04
III	$\begin{matrix}C_6H_5SO_2\\C_6H_5SO_2\end{matrix}\!>\!N{-}C_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	210–218 244–245[a]	90	4.51	15.47	4.63	15.39
IV	$\begin{matrix}C_6H_5SO_2\\CH_3C_6H_4SO_2\end{matrix}\!>\!N{-}C_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	212–218 230[a]	81	4.41	15.14	4.46	14.99
V	$C_6H_5SO_2NHC_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	196–198 230[a]	89	5.83	13.33	5.86	13.20
VI	$CH_3CONHC_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	188–194 208–211[a]	90	7.33	8.38	7.10	8.34
VII	$H_2NC_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H$	176–180 210[a]	80	8.23	...	8.00	...
VIII	$O_2NC_6H_4NH_2{\cdot}C_{10}H_{15}OSO_3H{\cdot}3H_2O$	155–157	75	6.60	...	6.63 6.68	...
IX	$C_6H_5NH_2{\cdot}C_{10}H_{15}OSO_3H$	184–186	87	4.31	9.85	4.04	9.85

[a] M. p. on bloc Maquenne.

and decolorized several times with norite. Prolonged heating on recrystallization should be avoided since it causes these phenylenediamine derivatives to darken considerably. The melting points and analyses are summarized in Table II.

Preparation of Amine Salts of *d*-Camphor-10-Sulfonic Acid.—These salts were prepared by dissolving 0.01 molar amounts of the amine and acid in separate portions of hot solvent, usually ethyl acetate, then mixing both portions and allowing to stand. Crystallization usually took place immediately or on standing for a few hours. All the salts were then recrystallized by solution in absolute ethyl alcohol and then adding an equal volume of the ethyl acetate. They were dried over phosphorus pentoxide in a vacuum of about 100 mm. at 80° for several hours. The analyses are given in Table III.

The results of the mutarotation studies of the salts of *d*-camphor-10-sulfonic acid have been listed in Table I. The rotations were all carried out in 2-decimeter tubes, and at temperatures of 25 ± 1°. In order to conserve space, only the initial and final values are given, but in every case, if the rotation is plotted against the time, a smooth curve is obtained similar to those in Fig. 1, falling rapidly at first, and finally tapering off to a constant value.

Dehydration of *p*-Aminoacetanilide-*d*-camphor-10-sulfonate.—Thirty grams of *p*-aminoacetanilide-*d*-camphor-10-sulfonate was dissolved in 150 cc. of warm absolute methyl alcohol and allowed to stand four days, after which time no further crystallization appeared to take place. These crystals were filtered, washed with acetone and ether, then dried over phosphorus pentoxide for twelve hours at 80° in a vacuum of about 100 mm. The yield was 9.5 g., m. p. 375–380° (bloc Maquenne). Evaporation of the mother liquor to about 100 cc. and allowing to stand again for several days produced a second crop of crystals, yield 6.3 g. Further evaporation on down to dryness produced only the unchanged original salt.

---

(7) Morgan and Micklethwait, *J. Chem. Soc.*, **87**, 80 (1905).

Anal. Calcd. for $C_{18}H_{24}O_4N_2S$: N, 7.69; S, 8.79. Found: N, 7.56; S, 8.74, 8.66.

This dehydrated compound was also produced by heating 5 g. of *p*-aminoacetanilide-*d*-camphor-10-sulfonate to 220° for about thirty minutes. This compound also melted at 375–380° (bloc Maquenne).

Anal. Calcd. for $C_{18}H_{24}O_4N_2S$: N, 7.69; S, 8.79. Found: N, 7.87; S, 8.74.

Dehydration of Aniline-*d*-camphor-10-sulfonate.—A weighed sample of the aniline salt was heated in an oven at 200° for three hours. This material was then weighed again and found to have lost weight equivalent to one mole of water. Calcd.: 5.54%. Found: 5.70%.

This anil was then dissolved in chloroform, treated with norite several times to decolorize, and the anil precipitated by adding petroleum ether to the boiling chloroform solution. The yield was 76 g., or 87% of the theoretical value; m. p. 294–295° (bloc Maquenne).

Anal. Calcd. for $C_{16}H_{21}O_3NS$: N, 4.56; S, 10.42. Found: N, 4.59; S, 10.25.

A neutral equivalent was determined for this anil whose calculated molecular weight was 307; found, 306.3.

The original aniline salt may also be titrated. The calculated molecular weight is 325; found, 322.3.

The rotations of the anil were determined in the same solvents as the aniline salt for comparative purposes. It will be noted that, in the same solvent, both reached the same equilibrium point (see Fig. 2).

Summary

The salts of *d*-camphor-10-sulfonic acid and primary amines exhibit slow mutarotation in anhydrous solvents.

The salts aniline-*d*-camphor-10-sulfonate and *p*-aminoacetanilide-*d*-camphor-10-sulfonate, which are *dextro*rotatory, have been dehydrated, leading to the formation of *levo*rotatory compounds which have been characterized as anils.

The mutarotation phenomenon hence appears to be due to the establishment of an equilibrium between the *d*-salt and the *l*-anil.

URBANA, ILLINOIS RECEIVED MAY 3, 1935

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

Hexa-*p*-alkylphenylethanes. The Effect of the *p*-Alkyl Group on the Dissociation of the Ethane

BY J. W. COPENHAVER, MAX F. ROY AND C. S. MARVEL

The observation[1] that increasing the size of the alkyl groups from *t*-butyl to *t*-hexyl in a hexaalkylethinylethane definitely weakened the central ethane linkage led us to believe that the weight of the attached groups may have an important role in the dissociation of other ethanes into free radicals. In order to put this theory to test, we have undertaken the present study of hexa-*p*-alkylphenylethanes.

Saturated alkyl groups were used in order to avoid, as far as possible, any significant change in the unsaturated character of the aryl group. The *p*-alkyl group was used in order to introduce the least amount of steric hindrance effect. Moreover, it was felt that a series of *p*-alkylaryl groups differing by one methylene group would differ very little in any property save weight.

In this communication we describe the preparation of a series of hexa-*p*-alkylphenylethanes in which the alkyl group varies from ethyl to butyl. The ethanes were prepared by treating the triarylchloromethanes with molecular silver as described by Gomberg.[2] The chlorides were synthesized by the usual reactions. The chief difficulties in the synthetic work came in connection with the preparation of the necessary *p*-bromoalkylbenzenes and in the crystallization of the tri-*p*-alkylphenylchloromethanes.

The *p*-bromoalkylbenzenes were prepared by several reactions. Treatment of *p*-bromophenylmagnesium bromide with two moles of an alkyl sulfate or *p*-toluenesulfonate gave about a 40–60% yield of bromoalkylbenzene. *p*-Bromoethylbenzene was most readily prepared from ethyl sulfate by this method. *p*-Bromo-*n*-propylbenzene and *p*-bromoisobutylbenzene were more easily prepared by treating *p*-bromophenylmagnesium bromide with allyl bromide and methylallyl chloride followed by reduction of the unsaturated derivatives. *p*-Bromoisopropylbenzene, *p*-bromo-*s*-butylbenzene and *p*-bromo-*n*-butylbenzene were most readily prepared by condensing *p*-bromophenylmagnesium bromide with acetone, ethyl methyl ketone and *n*-butyraldehyde followed by dehydration of the carbinols and reduction of the resulting unsaturated hydrocarbons.

---

(1) Davis and Marvel, THIS JOURNAL, **53**, 3840 (1931).

(2) Gomberg and Cone, *Ber.*, **37**, 1626 (1904); **39**, 3286 (1906).