[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

Phototropic and Thermotropic Anils from 5-Bromosalicylaldehyde

BY C. M. BREWSTER AND L. H. MILLAM

This article is a record of further investigation of anils with a view to increasing the number of compounds exhibiting phototropy and thermotropy. While over three hundred anils have been examined and the majority found to be thermotropic, only twenty-two are reported to be phototropic.[1] The condensation products of aldehydes and primary amines called anils have the general formula R—CH═N—R′. Fifteen of the anils previously reported to be phototropic are derivatives of salicylaldehyde. We have found three new phototropic anils, one a derivative of salicylaldehyde and two of 5-bromosalicylaldehyde. The introduction of the negative bromine atom in salicylaldehyde inhibited to some extent the tendency toward forming phototropic anils, and when two bromine atoms were introduced the resulting anils no longer exhibited phototropy.

In the following table, the plus sign indicates that the anil is phototropic; it is followed by reference number to the literature. The zero indicates that the anil has been examined but is not phototropic. Where a reference number appears at the head of a column only, this applies to the other compounds in the column.

It is apparent that anils of aldehydes having the hydroxyl group para to the aldehyde group may be phototropic, as well as those with the hydroxyl group in the ortho position, and we are studying further examples in this series. The anils from *p*-bromoaniline show phototropy, whether the hydroxyl group is ortho or para to the aldehyde group. Replacement of the ortho hydroxyl group by an ortho nitro group inhibits the phototropy. If the para bromine atom of the amine is replaced by chlorine, the resulting anil is not phototropic.

There is a great variation in the time required for the reversible change due to light or dark. With 5-bromosalicylidene-α-naphthylamine there is a discernible darkening on exposure to sunlight for as short an interval as five minutes, and this fades to the original pale yellow color after the compound is kept in the dark for an hour. However, salicylidene-β-naphthylamine requires an hour's exposure to sunlight to change from yellow to red, and the compound does not change back to the yellow color unless kept in the dark for some weeks. Prolonged exposure to actinic light, however, induces permanent polymorphic change in some of the anils. No indication of phosphorescence or triboluminescence was observed.

Of the twenty-eight new anils which we have prepared, twenty-two were

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(1) Excellent summaries of the work on phototropy may be found in articles by Stobbe, *Chem. Z.*, **44**, 340 (1920); and by Chalkley, *Chem. Rev.*, **6**, 207 (1929).

TABLE I

PHOTOTROPIC ANILS

	Aldehydes					
Amines	Salicylidene-	o-Nitrobenzylidene-	4-Hydroxybenzylidene-	2-Hydroxy-3-methoxybenzylidene-	3,5-Dibromosalicylidene-	5-Bromosalicylidene-
Aniline	+[a]	0[c]	0[f]	0[d]	0[h]	0[i]
o-Bromoaniline	+[d]	0	0	0		0
m-Bromoaniline	+[d]	0	0	0		
p-Bromoaniline	+[d]	0	+	0	0	+
o-Chloroaniline	+[b]	+	0	0		0
m-Chloroaniline	0[b]	+	0	0		0
p-Chloroaniline	0	0	0	0		0
m-Toluidine	+[a]	0	0	0		0
o-Anisidine	+[d]	0	+	0		0
p-Anisidine	+[d]	0	0	0		0
1,3,4-Xylidine	+[b]	0	0	0		
1,2,4-Xylidine	0[a]	+	+	0		0
1,2,5-Xylidine	0[a]	0	0	+		0
α-Naphthylamine	0[a]	0	0		0	+
β-Naphthylamine	+[b]	0	0	0	0	0
m-Aminobenzoic acid	+[e]	0	0			
p-Aminobenzoic acid	+[b]	0	0			0
m-Phenylenediamine	+[d]	0			0	
p-Aminoethylbenzoate	+[g]					
o-Aminocinnamic acid	+[g]					
p-Toluidine	+[i]	0	0	0	0	0

[a] Senier and Gallagher, *J. Chem. Soc.*, **113**, 28 (1918). [b] Senier and Shepheard. *ibid.*, **95**, 441 (1909). [c] Senier and Clarke. *ibid.*, **105**, 1917 (1914). [d] Senier, Shepheard and Clarke, *ibid.*, **101**, 1950 (1912). [e] Stobbe, *Ber. Verhandl. sächs. Akad. Wiss. Leipzig.* **74**, 161 (1922). [f] Senier and Forster, *J. Chem. Soc.*, **105**, 2462 (1914). [g] Gallagher. *Bull. soc. chim.*, [4] **29**, 683 (1921). [h] Brewster, THIS JOURNAL, **46**, 2463 (1924) [i] See experimental part of this article.

found to be thermotropic, changing to a deeper color when heated to a temperature near the melting point. On cooling, the lighter color is restored, though this change usually takes place more slowly than that produced by heat. The restoration of the lighter color may also be brought about in some instances by recrystallization, or by dissolving in dilute alkali and reprecipitating with acids.

Experimental Part

5-Bromosalicylaldehyde.—This compound has been prepared by direct action of bromine on salicylaldehyde,[2] and also by bromination in glacial acetic acid.[3] We found that by mixing solutions of bromine and of salicylaldehyde in carbon tetrachloride. and keeping the mixture at the temperature of the steam-bath for an hour, a purer product was obtained. The solution was diluted with three volumes of ligroin, and on cooling beautiful silky crystals separated. After recrystallization from the same solvents. the product melted at 105° corr.

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(2) Piria, *Ann.*, **30**, 171 (1839).

(3) Auwers and Bürger, *Ber.*, **37**, 3934 (1904).

TABLE II

Name of compound: R = 5-Bromosalicylidene-	Formula	Color and form	Solvent for cryst.	P	Th	M. p. corr., °C.	Analyses, %	
							Calcd.	Found
R-*o*-toluidine[a]	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Yellow needles	Alcohol	0	+	86.5	Br, 27.55	Br, 27.56
R-*m*-toluidine[b]	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Golden plates	Alcohol	0	0	103	Br. 27.55	Br. 27.36
R-*p*-toluidine	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Yellow plates	Alcohol	0	+	163.5	Br. 27.55	Br. 27.76
R-*α*-naphthylamine	$HOC_6H_3BrCH{=}NC_{10}H_7$	Pale yellow needles	Alcohol	+	+	109.5	Br. 24.51	Br. 24.88
R-*β*-naphthylamine[c]	$HOC_6H_3BrCH{=}NC_{10}H_7$	Yellow needles	Bz. + ligroin	0	+	157	Br. 24.51	Br. 24.77
R-*p*-phenetidine	$HOC_6H_3BrCH{=}NC_6H_4OC_2H_5$	Yellow-green needles	Alcohol	0	+	156	Br. 25.00	Br, 24.82
R-*o*-anisidine	$HOC_6H_3BrCH{=}NC_6H_4OCH_3$	Orange needles	Alcohol	0	+	110	Br. 31.25	Br. 31.08
R-*p*-anisidine	$HOC_6H_3BrCH{=}NC_6H_4OCH_3$	Yellow plates	Alcohol	0	+	156	Br, 31.25	Br, 31.32
R-*p*-aminoazobenzene	$HOC_6H_3BrCH{=}NC_6H_4N{=}NC_6H_5$	Yellow-brown scales	Alc., red. from nitrobz.	0	0	212	Br. 21.05	Br. 20.82
R-2-aminoazo-5-toluene	$HOC_6H_3BrCH{=}N(2)CH_3(1)C_6H_3$-$N(5)N(2)C_6H_4CH_3(1)$	Orange-red needles	Nitrobz. + alc.	0	+	212	Br, 19.58	Br. 19.27
R-*o*-aminophenol	$HOC_6H_3BrCH{=}NC_6H_4OH$	Golden-brown scales	Alcohol	0	+	192.5	Br. 27.36	Br. 27.39
R-*p*-aminophenol	$HOC_6H_3BrCH{=}NC_6H_4OH$	Orange plates	Alcohol	0	+	239	Br. 27.36	Br, 27.58
R-amino-2,5-xylene	$HOC_6H_3BrCH{=}NC_6H_3(CH_3)_2$	Yellow plates	Alcohol	0	+	67	Br, 26.25	Br. 26.04
R-amino-2,4-dimethylbenzene	$HOC_6H_3BrCH{=}NC_6H_3(CH_3)_2$	Light orange needles	Alcohol	0	+	131.5	Br, 26.25	Br, 26.21
R-*p*-aminobenzoic acid	$HOC_6H_3BrCH{=}NC_6H_4COOH$	Brilliant orange needles	Alcohol	0	+	282	Br, 25.00	Br. 25.27
R-*m*-nitraniline	$HOC_6H_3BrCH{=}NC_6H_4NO_2$	Orange-red rosets	Bz. + ligroin	0	0	169	Br, 24.91	Br. 24.70
R-*p*-nitraniline	$HOC_6H_3BrCH{=}NC_6H_4NO_2$	Light orange needles	Bz. + ligroin	0	+	205	Br. 24.91	Br. 25.05
R-aniline[d]	$HOC_6H_3BrCH{=}NC_6H_5$	Orange plates	Alcohol	0	+	122.5		
R-*o*-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Light orange needles	Alcohol	0	+	88	Br. 25.76 Cl. 11.41	X, 36.96
R-*m*-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Glistening yellow scales	Alcohol	0	+	127.5	Br, 25.76 Cl. 11.41	Br, 25.51 Cl, 11.52
R-*p*-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Yellow needles	Alcohol	0	+	158	Br. 25.76 Cl. 11.41	Br. 25.18 Cl. 11.51
R-*o*-bromoaniline	$HOC_6H_3BrCH{=}NC_6H_4Br$	Dark orange needles	Alcohol	0	0	78	Br, 45.04	Br, 44.85
R-*p*-bromoaniline	$HOC_6H_3BrCH{=}NC_6H_4Br$	Lustrous yellow leaflets	Bz. + ligroin	+	+	178	Br, 45.04	Br. 44.92
R-2,4-dichloroaniline	$HOC_6H_3BrCH{=}NC_6H_3Cl_2$	Orange needles	Bz. + ligroin	0	+	148	Br. 23.19 Cl, 20.58	X. 43.51
R-2,5-dichloroaniline	$HOC_6H_3BrCH{=}NC_6H_3Cl_2$	Pale yellow needles	Alcohol	0	+	139	Br. 23.19 Cl. 20.58	X. 43.47
Bis-R-*p*-phenylenediamine	$(HOC_6H_3BrCH{=})_2N_2C_6H_4$	Lustrous yellow plates	Nitrobz. + alc.	0	+	277	Br, 33.75	Br. 33.58
Bis-R-*m*-toluylenediamine	$(HOC_6H_3BrCH{=})_2N_2C_6H_3CH_3$	Pale cream plates	Nitrobz. + alc.	0	+	186	Br. 32.75	Br, 32.92
Bis-R-dianisidine	$(HOC_6H_3BrCH{=})_2(NC_6H_3OCH_3)_2$	Brick-red needles	Nitrobenzene	0	0	279	Br, 25.96	Br. 25.78
Bis-R-*o*-tolidine	$(HOC_6H_3BrCH{=})_2(NCH_3C_6H_3)_2$	Orange needles	Nitrobenzene	0	+	242	Br. 27.68	Br. 27.80
Bis-R-benzidine	$(HOC_6H_3BrCH{=}(NC_6H_4)_2$	Yellow scales	Nitrobenzene	0	+	345	Br. 29.08	Br. 28.93
R-phenylhydrazone[e]	$HOC_6H_3BrCH{=}NNHC_6H_5$	Pearly scales	Alcohol	+	+	151		
Salicylidene-*p*-toluidine	$HOC_6H_4CH{=}NC_6H_4CH_3$	Yellow needles	Alcohol	+	+	95	N. 6.63	N, 6.43
Salicylidene-*p*-bromoaniline[f]	$HOC_6H_4CH{=}NC_6H_4Br$	Light yellow needles	Alcohol	+	+	110	Br. 28.95	Br. 29.06

[a] A second form, glistening yellow plates, melting at 165°, was obtained when the materials were melted directly without a solvent. [b] A. Senier and P. Gallagher, *J. Chem. Soc.*, **113**, 28 (1918). [c] A. Senier and F. G. Shepheard, *J. Chem. Soc.*, **95**, 1945 (1909). [d] Haarmann, *Ber.*, **6**, 339 (1873). [e] Auwers and Bürger, *ibid.*, **37**, 3934 (1904). [f] Senier, Shepheard and Clarke, *J. Chem. Soc.*, **101**, 1950 (1912).

Anal. Calcd. for $C_7H_5O_2Br$: Br, 39.77. Found: Br, 39.93.

The anils studied in this investigation are described in Table II. Of these, twenty-eight compounds have been prepared for the first time, as far as we have been able to ascertain. Most of the compounds are readily formed by heating alcoholic solutions of the aldehyde and base; others require prolonged heating in the solvent. A few were formed only on direct heating, without a solvent. The phototropic and thermotropic properties of each compound are indicated in the table.

The anils formed from *m*-nitraniline, *p*-nitraniline, *p*-bromoaniline, 2,4-dichloroaniline, and *p*-phenylenediamine with 5-bromosalicylaldehyde were obtained only on direct fusion without a solvent. The *p*-aminoazobenzene derivative of 5-bromosalicylaldehyde, first obtained from alcohol in the yellow-brown form, on recrystallization from nitrobenzene changes to the red modification. When the red modification is dissolved in acetone and precipitated by addition of alcohol, the yellow-brown modification is again obtained.

Summary

1. A series of twenty-eight new anils, derivatives of 5-bromosalicylaldehyde, has been prepared.
2. Three new instances of phototropy are reported.
3. Twenty-two of the anils are thermotropic.
4. A number of the compounds appear to exist in two forms.

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Asymmetric Syntheses. II. The Action of Optically Active Nitrates on Cyclic Ketones

BY R. L. SHRINER AND E. A. PARKER

The condensation of 4-methylcyclohexanone with *d*- or *l*-2-octyl nitrite in the presence of sodium ethylate gave an optically active sodium salt of the oxime.[1] This reaction constituted a new type of asymmetric synthesis since the optically active octyl group was split off during a reaction which created an asymmetric carbon atom in the molecule. A second example of this type of asymmetric synthesis has been found in the condensation of 4-methylcyclohexanone and optically active alkyl nitrates.

Previous investigators have shown that alkyl nitrates in the presence of potassium ethylate readily condense with fluorene,[2] phenylacetic ester,[3] α-tetralone[4] and cyclohexanone.[5] In each case the product was the potassium salt of a nitro compound. In the present investigation the potassium salt of a nitro compound was likewise produced in accordance with the reaction

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(1) Pezold and Shriner, THIS JOURNAL, **54**, 4707 (1932).

(2) Wislicenus and Waldmüller, *Ber.*, **41**, 3336 (1908).

(3) Wislicenus and Grützner, *ibid.*, **42**, 1930 (1909).

(4) Straus and Ekhard, *Ann.*, **444**, 164 (1925).

(5) Wieland, Garbsch and Chavau, *ibid.*, **461**, 295 (1928).