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Azomethine Dyes. II. Color and Constitution of Acylacetamide Azomethine Dyes

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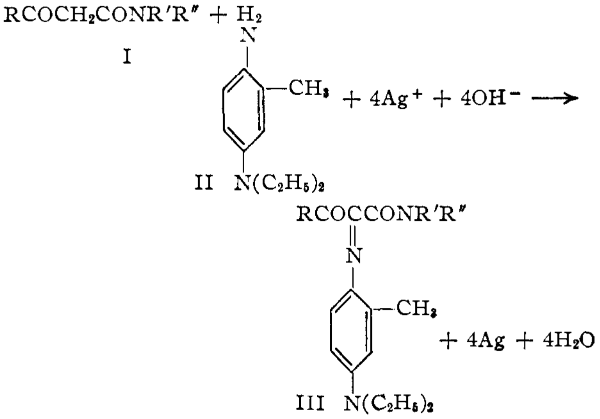
The synthesis and properties of a number of α-acylacetamides and the azomethine dyes derived from them are reported. The azomethine dyes are formed by oxidative condensation of the α-acylacetamides with 4-amino-3-methyl-N,N-diethylaniline. The effects of substituents and of changes in solvent on the absorption spectra of these dyes are interpreted on the basis of electronic and steric factors and hydrogen-bonding.

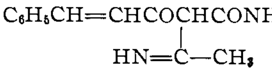
Introduction

A preceding investigation[1] dealt with the relation between color and structure of some magenta azomethine dyes derived from 5-pyrazolones. The present paper is concerned with a similar study of azomethine dyes (III) derived from acylacetamides, which are widely used as yellow-image dyes in color photography.[2]

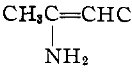


The α-acylacetamides (I) were prepared by condensing β-ketoesters with amines in boiling xylene.[3] Some vinylogs, *i.e.*, α-cinnamoylacetanilides (IV), not accessible in this manner, were prepared by solvolysis of iminoacyl compounds (V)[4] formed by acylation of β-aminocrotonanilides (VI) with cinnamoyl chloride.

$C_6H_5CH{=}CH{-}COCH_2CONHC_6H_5$
IV



$$C_6H_5CH{=}CHCO\underset{\displaystyle HN{=}C{-}CH_3}{\underset{|}{C}H}CONHC_6H_5$$
V

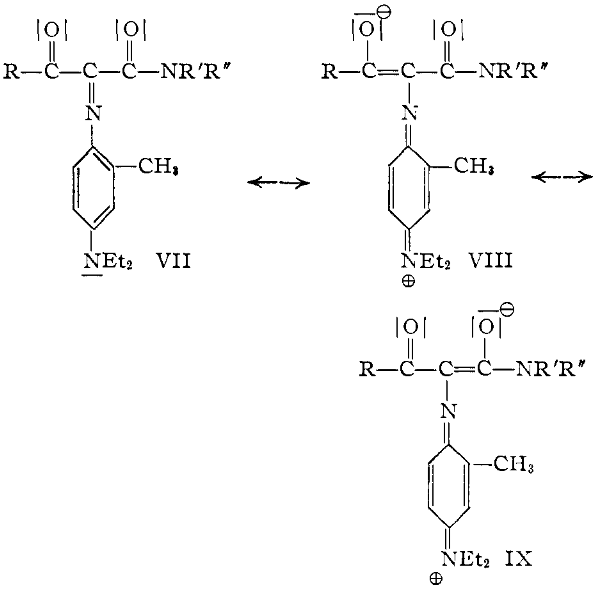


$$CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}{=}CHCONHC_6H_5$$
VI

The azomethine dyes (III) were prepared from the acylacetamides (I) and 4-amino-3-methyl-N,N-diethylaniline (II), using potassium ferricyanide (method A) or silver chloride (method B)[5] as the oxidant. The dyes were purified by chromatography and crystallization, and their absorption spectra in the visible region were determined in cyclohexane, *n*-butyl acetate and methanol.[6]

Discussion

Position of the Absorption Maximum.—The absorption in the visible region by the dyes under consideration can be attributed essentially to the resonance system VII, VIII, IX. Structure VII can be expected to make the preponderant contribution to the resonance hybrid representing the ground state; it differs from the other major contributing structures VIII and IX by the aromaticity of the *p*-phenylenediamine moiety and by the absence of charge separation. When absorption of visible light or near-ultraviolet radiation raises the molecule to a higher-energy level, the polarized (ionic) structures VIII and IX make larger contributions to the excited state.[7] Structural changes which render the polarized structures more stable therefore decrease the energy difference between the ground and excited states and would be expected to cause a bathochromic shift. Structural changes which destabilize the polarized structures



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[1] G. H. Brown, B. Graham, P. W. Vittum and A. Weissberger, THIS JOURNAL, **73**, 919 (1951).

[2] (a) R. M. Evans, W. T. Hanson, Jr., and W. L. Brewer, "Principles of Color Photography," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 259. (b) P. W. Vittum and A. Weissberger, *J. Phot. Sci.*, **2**, 81 (1954).

[3] C. J. Kibler and A. Weissberger, *Org. Syntheses*, **25**, 7 (1945).

[4] E. Benary and W. Kerckhoff, *Ber.*, **59**, 2549 (1926).

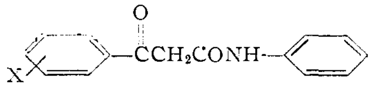
[5] P. W. Vittum and G. H. Brown, THIS JOURNAL, **68**, 2235 (1946).

[6] Data on similar yellow dyes which comprise moieties of polymeric systems [J. O. Corner and E. L. Martin, *ibid.*, **76**, 3593 (1954)] cannot be compared with our results, since Corner and Martin used a different developer (N,N-diethyl-*p*-phenylenediamine) and determined the absorption curves of photographic images and not of dyes in solution.

[7] A. Maccoll, *Quart. Revs.*, **1**, 39 (1947).

TABLE I

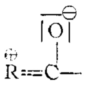
PROPERTIES OF AZOMETHINE DYES DERIVED FROM

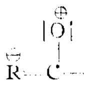


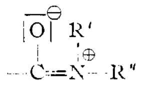
X	M.p., °C.	λ_{max}, mμ Cy-clo	Bu-Ac	Me-OH	$\epsilon_{max} \times 10^{-4}$ Cy-clo	Bu-Ac	Me-OH	ε Cy-clo	Bu-Ac	Me-OH	Analyses, % Calcd. C	H	N	Found C	H	N	Method
H	164–165	424	433	448	1.7	1.6	1.5	0.15	0.20	0.34	75.5	6.6	10.1	75.6	6.8	9.9	B
o-CH_3	146–147	424	434	450	1.7	1.6	1.6	.16	.21	.35	75.9	6.8	9.8	75.8	6.9	9.8	B
2,4,6-$(CH_3)_3$	149–150	439	446	466	1.3	1.8	2.4	.46	.24	.36	76.4	7.3	9.2	76.8	7.5	9.1	A
o-OCH_3	153–154	415	420	434	1.1	1.0	1.1	.27	.31	.38	73.1	6.6	9.5	73.3	6.2	9.4	B
m-OCH_3	144–145	425	434	448	1.7	1.6	1.5	.14	.20	.34	73.1	6.6	9.5	73.0	6.6	9.6	B
p-OCH_3	127–128	422	430	446	1.8	1.6	1.6	.13	.20	.31	73.1	6.6	9.5	73.2	6.4	9.5	B
p-Cl	148–149	427	436	455	1.7	1.6	1.5	.17	.25	.36	69.7	5.8	9.4	70.0	5.7	9.8	A
m-NO_2	169–170	434	443	472	1.5	1.4	1.5	.28	.38	.40	68.1	5.7	12.0	68.3	5.5	12.0	A
p-NO_2	167–168	420	430	460	1.7	1.5	1.4	.34	.42	.57	68.1	5.7	12.2	68.4	5.5	12.5	B
p-NH_2	192–193	422	426	444	..	1.4	1.5	.14	.18	.27	72.9	6.6	13.1	73.2	7.0	13.1	B
p-$NHCOCH_3$	274–275	..	432	447	..	..	..	..	.19	.36	71.5	6.4	12.0	71.3	6.4	12.3	B
p-$NHCOC_6H_5$	211–212	..	433	446	..	1.6	1.4	..	.24	.38	74.4	6.1	10.5	74.5	5.9	10.5	B
p-$NHSO_2C_6H_5$	204–205	..	434	447	..	1.6	1.5	..	.21	.32	67.6	5.7	9.9	68.1	5.7	10.3	B

or stabilize the non-polarized structure increase the energy difference between ground and excited states and would be expected to cause a hypsochromic effect.

In discussing the effect of changes in R, R′ and R″ on the absorption, it must be kept in mind that, in structures VIII and IX, electronic effects can be transmitted across the bonds linking R or N, respectively, to $CO^{\ominus}$ by an inductive effect only; an RC or CN double bond required for mesomeric effects is impossible in these structures. This restriction does not apply to structures not involving polarization of the chromophoric system, *e.g.*, VII. In evaluating the effect of changes in R, R′ and R″, the following contributing structures may become important: 1. Structures which inhibit contributions from structures VIII and IX


X


XI


XII

2. Structures possible with or without polarization of the chromophoric system


XIII

Under no conditions can the effects of electron-*donating* substituents in R′ or R″ be transmitted to the N atom by a mesomeric mechanism.

Increased contributions by structures XII and X or XI will lower the energy of the ground state, interfere with contributions from structures VIII and IX and cause a hypsochromic effect. Increased contributions by structures X or XI will cause a shift in the same direction, although in one case electron-donating and in the other case electron-accepting substituents are involved.

Figure 1 shows the crowding of the dye molecule. For maximum interaction of the structures which contribute to a resonance hybrid, coplanarity of the groups connected by bonds with double-bond character is required; steric hindrance of coplanarity will diminish the contributions of the polarized structures. This applies to VIII and IX as well as to X–XIII. The contributing structures X–XII diminish freedom of rotation about the C–CO and R′R″N–CO bonds, respectively; increased contributions of XII and X or XI will make it more difficult for the respective CO groups to assume coplanarity with the remainder of the chromophoric system since the bonds to the bulky R and NR′R″ groups are more rigid than those in the other structures.

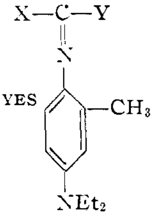
Higher polarity of the solvent facilitates charge separation and shifts the absorption of all the dyes to longer wave lengths. The magnitude of this effect is correlated with the dielectric constant of the solvent ($\epsilon_{25°}$ = 2.02 for cyclohexane, 4.94 for butyl acetate, 32.6 for methanol); its mechanism can be visualized as solvation in which neutralization of electric fields by oriented solvent dipoles and/or hydrogen-bonding play a role.

In the following interpretation of the spectra, restraint is exercised because the number of contributing structures and the additional complications caused by crowding of the molecule and by solvent effects might make a greater elaboration of details too arbitrary.

Table I shows the effect of substituents in the benzoyl moiety (R = aryl). In methanol, *p*-Cl, *m*-NO_2 and *p*-NO_2 have bathochromic effects; these substituents decrease the electron density at the ring carbon linked to –CO, which may increase the contribution of VIII and lower the energy of the excited state. The bathochromic effect of *p*-Cl is small; the mesomeric electron-donating nature of chlorine will increase the contribution of X, an effect which, by itself, would cause a hypsochromic shift. In cyclohexane and in butyl acetate *p*-NO_2 has a small hypsochromic effect, as have *o*- and *p*-methoxy and *p*-NH_2. This indicates increased contributions of X or XI under the influence of these groups. In methanol, the electron-attracting effect of NO_2 appears to be increased, probably by hydrogen-bonding of the NO_2 group with the solvent, so that the greater stabilization

TABLE IIA

PROPERTIES OF AZOMETHINE DYES



X	Y	M.p., °C.	λ_{max}, mμ Cy-clo	BuAc	Me-OH	$\epsilon_{max} \times 10^{-4}$ Cyclo	Bu-Ac	Me-OH	Analyses, % Calcd. C	H	N	Found C	H	N	Method
CH_3CO	$CONHC_6H_5$	104–105	423	433	448	1.5	1.6	1.9	69.5	7.9	10.6	69.5	8.0	10.5	B
C_6H_5CO	$CON(CH_3)C_6H_5$	138–139	448	457	474	0.9	1.2	1.7	75.9	6.8	9.8	76.2	6.5	9.8	B
C_6H_5CO	$CONH_2$		409	414	430		1.3	1.3							B
C_6H_5CO	$CONHCH_3$	153–154	405	413	433	1.1	1.0	1.1	71.8	7.2	12.0	72.2	7.6	11.7	B
C_6H_5CO	$CON(CH_3)_2$		434	446	465	1.1	1.3	1.9	72.3	7.4	11.5	72.3	7.7	11.8	
C_6H_5CO	C_6H_5CO	122–123	446	461	478	1.2	1.5	1.7	78.4	6.6	7.0	78.0	6.8	7.0	

TABLE IIB

PROPERTIES OF AZOMETHINE DYES DERIVED FROM

X	Y	M.p., °C.	λ_{max}, mμ Cy-clo	Bu-Ac	MeOH	$\epsilon_{max} \times 10^{-4}$ Cy-clo	Bu-Ac	MeOH	s Cy-clo	Bu-Ac	MeOH	Analyses, % Calcd. C	H	N	Found C	H	N	Method
H	H	131–132	420	440	Un-stable	0.7	1.1	Un-stable	0.40	0.50	Un-stable	76.4	6.6	9.6	76.6	6.5	9.6	B
H	*o*-OCH_3	141–142	414	427	454	1.3	1.6	1.6	.37	.34	0.45	74.1	6.7	8.9	74.1	6.6	8.9	B
p-OCH_3	*o*-OCH_3	166–167	414	427	450	1.3	1.1	1.1	.35	.30	.43	72.1	6.7	8.4	72.0	6.7	8.5	B

of VIII outweighs the effect caused by an increased contribution of XI. 2,4,6-Trimethyl substitution has a large bathochromic effect. Since the effect of mono-*o*-methyl substitution is small, we are inclined to ascribe the large bathochromic effect to steric causes. Steric interference with coplanarity of the chromophoric system would result in decreased stability of VIII and should therefore cause a hypsochromic shift. If, however, the steric interference reduces the contribution of X, the CO group will be freer to become coplanar with the rest of the chromophoric system (Fig. 1), and the bathochromic effect observed should result.

Replacement of benzoyl by acetyl (Table IIA) does not change λ_{max}, indicating a similar stabilization of structure X, by C_6H_5 and by CH_3, in which probably hyperconjugation of CH_3 plays a role. A very small hypsochromic shift by cinnamoyl (Table IIB) in cyclohexane solution may be attributed to a reduction in steric hindrance for structure X. Solvation of the vinyl system in butyl acetate may render it electron accepting and explain the bathochromic effect. *o*-Methoxy substitution in the cinnamoyl ring, as in the benzoyl derivative, results in a shift of λ_{max} to shorter wave lengths.

Substitution in the anilide ring (III, R′ = aryl) follows a similar pattern (Table III); electron-attracting groups, acting to stabilize structures XIII and to destabilize structure XII, will favor structure IX and produce bathochromic effects. Electron-donating groups (*o*- and *p*-methoxy and dimethylamino) cause very small hypsochromic shifts. At variance with substitution in the benzoyl ring, an electron-attracting substituent in the anilide ring will never interfere with polarization of the chromophoric system but will enhance it through lowering of the electron density of the amide nitrogen. One methyl group has little or no effect on the absorption. Two *o*-methyl or *o*-methoxy groups, however, cause strong hypsochromic effects, presumably because they destabilize for steric reasons structures XIII and, therefore, increase the relative contribution of structure XII.

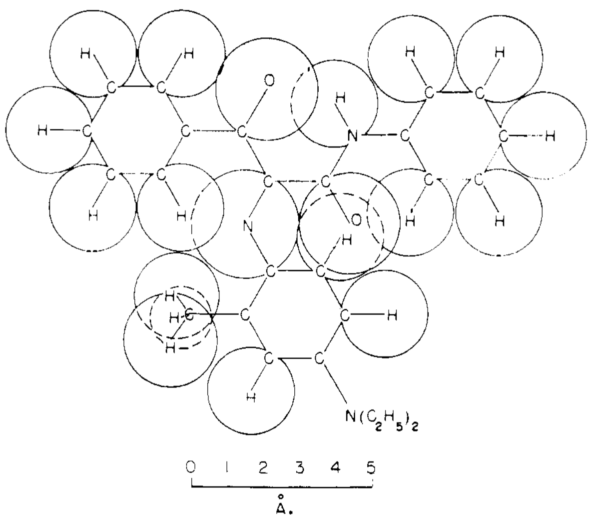
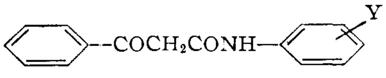


Fig. 1.—Scale drawing of α-benzoyl-α-(4-diethylamino-2-methylphenylimino)-acetanilide. The covalent bond radii and van der Waals' radii are those given by Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y.

In Fig. 2 are plotted reciprocals of λ_{max} for dyes substituted in the anilide ring (Table III) against

Table III

Properties of Azomethine Dyes Derived from



Y	M.p., °C.	λ_{max}, mμ			$\epsilon_{max} \times 10^{-4}$			s			Analyses, % Calcd.			Found			Method
		Cy-clo	Bu-Ac	Me-OH	Cy-clo	Bu-Ac	Me-OH	Cy-clo	Bu-Ac	Me-OH	C	H	N	C	H	N	
H	164–165	424	433	448	1.7	1.6	1.5	0.15	0.20	0.34	75.5	6.6	10.1	75.6	6.8	9.9	B
o-CH_3	142–143	425	434	447	1.7	1.8	1.7	.16	.19	.32	75.9	6.8	9.8	75.6	6.7	9.6	B
m-CH_3	156–157	426	434	450	1.6	1.6	1.5	.15	.21	.34	75.9	6.8	9.8	75.6	6.8	9.9	B
p-CH_3	152–153	425	434	448	1.7	1.6	1.6	.16	.21	.34	75.9	6.8	9.8	75.8	6.8	10.0	B
2,6-$(CH_3)_2$	148–149	411	417	438	1.3	1.2	1.1	.20	.28	.40	76.2	7.1	9.5	76.0	7.1	9.4	B
o-OCH_3	162–163	421	432	447	1.7	1.9	2.0	.16	.17	.25	73.1	6.6	9.5	72.7	6.8	9.1	B
m-OCH_3	151–152	427	436	451	1.8	1.7	1.6	.14	.20	.35	73.1	6.6	9.5	73.4	6.6	9.5	B
p-OCH_3	148–149	422	430	448	1.6	1.5	1.5	.18	.23	.35	73.1	6.6	9.5	72.8	6.3	9.5	B
o-Cl	163–164	432	442	453	2.0	2.2	2.1	.14	.18	.26	64.7	5.8	9.4	69.8	5.7	9.6	B
m-Cl	119–120	430	438	453	1.9	1.6	1.6	.15	.22	.35	69.7	5.8	9.4	69.6	6.0	9.1	B
p-Cl	165–166	430	438	452	1.8	1.7	1.5	.15	.22	.33	69.7	5.8	9.4	69.6	5.8	9.1	B
o-Br	165–166	431	440	452	1.9	2.0	2.0	.15	.19	.29	63.4	5.3	8.5	63.7	5.4	8.8	B
m-Br	132–133	430	438	452	1.9	1.6	1.6	.15	.22	.36	63.4	5.3	8.5	63.8	5.5	8.7	B
p-Br	170–171	431	437	452	1.9	1.7	1.6	.14	.22	.31	63.4	5.3	8.5	63.8	5.5	8.6	B
p-I	183–184	430	438	452	2.0	1.7	1.7	.14	.21	.33	57.9	4.9	7.8	58.1	4.6	7.6	B
o-NO_2	193–194	452	460	470	1.9	1.9	1.9	.16	.23	.32	68.1	5.7	12.2	68.1	5.6	12.0	B
m-NO_2	149–150	434	441	455	1.9	1.7	1.6	.16	.24	.36	68.1	5.7	12.2	68.2	5.7	12.1	B
p-NO_2	178–179	440	451	462	2.4	2.1	2.0	.15	.21	.32	68.1	5.7	12.2	68.2	5.4	12.2	B
m-CN	152–153	433	440	454	2.0	1.7	1.6	.15	.22	.35	73.9	6.0	12.8	73.8	6.3	12.8	A
p-CN	191–192	438	446	458	..	1.9	1.7	.15	.22	.32	73.9	6.0	12.8	74.0	5.9	13.1	B
o-NMe_2	126–127	423	433	448	1.7	1.9	2.0	.14	.17	.25	73.7	7.1	12.3	73.5	7.2	12.2	A
m-NME_2	164–165	420	430	447	1.6	1.8	1.4	.19	.24	.33	73.7	7.1	12.3	73.3	7.0	12.6	A
p-NME_2	160–161	421	431	450	1.6	1.7	1.6	.28	.31	.40	73.7	7.1	12.3	73.6	6.8	12.6	A
o-$NHCOC_6H_5$	218–219	436	438	451	S. sol.	1.7	1.6	.18	.23	.33	74.4	6.1	10.5	74.7	5.9	10.3	A
m-$NHCOC_6H_5$	.....	428	434	450	S. sol.	1.1	1.1	.16	.23	.33	74.4	6.1	10.5	74.5	6.3	10.1	A
p-$NHCOC_6H_5$	201–202	430	435	452	S. sol.	1.5	1.4	.18	.21	.33	74.4	6.1	10.5	74.9	6.5	10.2	A
m-$NHSO_2C_6H_5$	204–205	429	435	450	S. sol.	1.6	1.5	.20	.22	.34	67.1	5.7	9.8	67.6	6.0	9.9	A
p-$NHSO_2C_6H_5$	215–216	Ins.	436	452	Ins.	1.7	1.6	Ins.	.22	.34	67.6	5.7	9.8	67.9	5.8	9.8	A
m-$COCH_3$	154–155	430	436	453	1.8	1.6	1.5	0.16	.24	.33	73.8	6.4	9.2	74.1	6.4	9.2	A
p-$COCH_3$	184–185	434	442	456	2.1	1.9	1.8	.14	.21	.33	73.8	6.4	9.2	74.1	6.4	9.1	A
o-CO_2CH_3	181–182	432	441	454	1.6	1.8	1.7	.16	.22	.32	71.3	6.2	8.9	71.6	6.2	9.1	B
p-CO_2CH_3	171–172	432	441	455	2.1	1.9	1.8	.16	.21	.34	71.3	6.2	8.9	71.5	6.6	9.3	A
3,5-$(CO_2CH_3)_2$	173–174	432	439	454	..	1.6	..	.16	.24	.35	68.0	6.0	7.9	68.1	6.1	8.0	A
o-$CONHC_6H_5$	264–265	..	438	452	..	1.8	..	..	.19	.31	74.4	6.1	10.5	74.6	6.2	10.6	A
m-$CONHC_6H_5$	132–133	430	436	451	1.8	1.7	1.6	.15	.22	.34	74.4	6.1	10.5	74.4	5.8	10.6	A
p-$CONHC_6H_5$	221–222	434	440	455	..	1.9	1.8	.17	.22	.30	74.4	6.1	10.5	74.8	6.2	10.2	A
o-$SO_2NHC_6H_5$	166–167	438	442	456	1.8	1.9	1.8	.24	.23	.33	67.5	5.7	9.8	67.1	5.6	10.1	A
m-$SO_2NHC_6H_5$	191–192	433	439	454	..	1.7	1.7	.18	.23	.34	67.5	5.7	9.8	67.7	5.8	9.9	A
p-$SO_2NHC_5H_5$	229–230	Ins.	443	457	Ins.	1.8	1.7	Ins.	.21	.33	67.5	5.7	9.8	67.7	5.9	9.8	A
o-OC_6H_5	145–146	428	437	450	1.9	2.1	2.0	0.12	.16	.26	76.0	6.2	8.3	76.2	6.1	8.2	A
o-SCH_3	146–147	427	437	450	1.8	1.9	1.9	.15	.19	.31	70.6	6.4	9.1	70.6	6.4	9.5	B
m-CO_2H	238–239	..	434	447	..	1.5	1.5	..	.22	.34	70.9	5.9	9.2	70.5	6.0	9.3	A
o-F	186–187	428	439	449	..	..	..	.15	.18	.30	72.4	6.1	9.7	72.1	5.9	9.7	B
o-CF_3	151–152	433	442	453	2.1	2.2	2.1	.16	.20	.29	67.3	5.4	8.7	67.4	5.7	8.4	B
2,5-$(OCH_3)_2$	185–186	423	433	449	1.9	2.1	2.2	.15	.19	.27	71.0	6.6	8.9	71.0	6.4	8.9	A
2,5-$(OC_2H_5)_2$	150–151	422	434	450	1.8	2.0	2.0	.16	.19	.28	78.1	8.0	6.5	77.8	7.8	6.4	A
2,4-$(OCH_3)_2$	183–184	420	430	447	..	1.9	2.0	.17	.19	.28	71.0	6.6	8.9	71.4	6.8	9.2	A
2,6-$(OCH_3)_2$	193–194	411	420	439	..	1.3	1.4	.22	.25	.36	71.0	6.6	8.9	71.2	6.5	8.7	A

Hammett's σ-constants.[8] The straight lines were fitted to the data by the least-squares method. Their equations are: (1) in cyclohexane, $10^3/\lambda_{max} = 2.345-0.0564\sigma$; (2) in butyl acetate, $10^3/\lambda_{max} = 2.304-0.0554\sigma$; and (3) in methanol, $10^3/\lambda_{max} = 2.222-0.0345\sigma$, if λ_{max} is measured in mμ. For electron-attracting substituents, the values of σ are positive and λ_{max} is shifted toward longer wave lengths. For electron-releasing substituents, $\sigma < 0$, and λ_{max} shifts toward smaller values.

The marked hypsochromic effect on replacement of the phenyl ring in the anilide derivative by a methyl group or hydrogen (Table IIA) indicates that the phenyl ring acts as an electron acceptor; compared with methyl or hydrogen, phenyl stabilizes structures XIII and therefore increases the stability of structure IX. N-Methylation has a strong bathochromic effect. In view of the proximity of the amide hydrogen to the oxygen of the RCO group shown by Fig. 1, one might assume hydrogen bonding between amide hydrogen and carbonyl oxygen. Such hydrogen bonding should, however, stabilize VIII, and elimination of the chelation should cause a hypsochromic shift. The bathochromic shift observed can be explained by a decreased contribution of structure XII because of steric hindrance. It is noteworthy that the absorption of the methylanilide dye is very similar to that of the dibenzoylmethane dye, indicating a large reduction in the methylanilide dye of the contribution of structure XII.

The effects of substituents on both phenyl nuclei are roughly additive, as shown by Table IV.

It should be mentioned that geometrical isomerism about the C=N bond, if it should exist,

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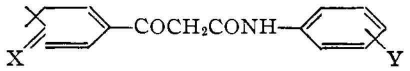
(8) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

TABLE IV

PROPERTIES OF AZOMETHINE DYES DERIVED FROM



X	Y	M.p., °C.	λ_{max}, mμ			$\epsilon_{max} \times 10^{-4}$			s			Analyses, % Calcd.			Found			Method
			Cyclo	Bu-Ac	Me-OH	Cyclo	Bu-Ac	Me-OH	Cyclo	Bu-Ac	Me-OH	C	H	N	C	H	N	
H	H	164–165	424	433	448	1.7	1.6	1.5	0.15	0.20	0.34	75.5	6.6	10.1	75.6	6.8	9.9	B
o-OCH$_3$	*o*-NO$_2$	148–149	445	452	460	1.4	1.4	1.4	.15	.29	.35	64.4	5.8	11.5	66.6	5.9	11.2	B
p-OCH$_3$	*p*-OCH$_3$	165–166	420	430	446	1.8	2.0	2.1	.13	.15	.24	71.0	6.6	8.9	71.3	6.6	9.0	A
o-OCH$_3$	*m*-NO$_2$	187–188	428	432	443	..	1.2	1.1	.25	.26	.37	66.4	5.8	11.5	66.4	5.4	11.7	B
p-NO$_2$	*o*-OCH$_3$	213–214	416	429	444	1.8	1.9	1.8	.36	.32	.41	66.4	5.8	11.5	66.7	6.1	11.8	B
p-NH$_2$	*o*-OCH$_3$	201–202	..	425	442	..	2.0	1.9	..	.13	.25	70.7	6.6	12.2	70.5	6.8	12.5	B
p-NO$_2$	*o*-NMe$_2$	159–160	414	427	443	1.8	1.9	1.9	.34	.25	.41	67.0	6.2	14.0	67.2	6.2	13.7	B

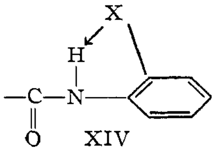
would influence some of the steric effects just discussed. Our observations, however, do not demonstrate the presence of this geometrical isomerism.

Extinction and Shape of the Absorption Curves.—Chemical constitution is better understood in its effect on the position of the absorption maximum than in its effect on extinction and shape of the absorption curve. These parameters are, however, of great importance in color photography, and some correlations can be made. The maximum extinction coefficient, ϵ_{max}, of a dye depends on the probability of the corresponding electronic transitions. Among the factors which determine this probability are the change in dipole moment accompanying the transition and the ability of the molecule to adopt the planar conformation required for excitation.[9] The change in dipole moment is not known from other data, but an effect of structural change on ϵ_{max} can be recognized, depending upon whether that change hinders or facilitates the adoption of a planar conformation of the molecule.

The anilide ring in the aroylacetanilide dyes has an intensifying (hyperchromic) effect on the absorption; ϵ_{max} of the benzoylacetanilide dye (Tables I and III) is about 20% larger than that of the benzoylacetamide dye (Table IIA). Introduction of two *o*-methyl groups in the anilide ring, however, more than obliterates this effect; the extinction coefficient of the dye from α-benzoyl-2,6-dimethylacetanilide (Table III) is lower than that of the benzoylacetamide dye and the absorption is broadened. Steric interference of the two *o*-substituents will diminish the contribution by XIII, and the electron-donating nature of methyl will stabilize XII. The latter structure is antagonistic to IX, and the observed hypochromic (and hypsochromic) effect of the *o*-methyl groups can be expected since the transition to the excited state is rendered more difficult.

N-Methylation of the anilide dye causes a hypochromic effect in cyclohexane and in butyl acetate solution, but increases the extinction coefficient in methanol (λ_{max} in all solvents is shifted to longer wave lengths). The methyl group can be expected to interfere sterically with structure XII. This will increase the relative importance of IX in agreement with the bathochromic effect observed in all three solvents and the hyperchromic effect in methanol. The hypochromic effect in the less polar solvents is not understood.

Polar substituents in the anilide ring have a hyperchromic effect in cyclohexane, but the magnitude of the effect diminishes as the polarity of the solvent is increased, except in the case of *o*-substituents. Figure 2 shows that the relative effects of *m*- and *p*-substitution on λ_{max} are greater in butyl acetate or cyclohexane than in methanol, which may be connected with the proton-donating nature and the polarity of the alcohol. *o*-Substituents with lone pairs of electrons should stabilize a more nearly planar conformation[10] through hydrogen bond formation with the adjacent amide group, as shown in structure XIV. Similar chelation has been proposed by Ungnade[11] to explain certain features of the ultraviolet absorption spectra of substituted acetanilides. This chelation seems to make these substituents less susceptible to disturbances by the solvent as shown by the large hyperchromic effect in methanol (Table III).



XIV

As a measure of the slope of an absorption curve on the long wave length side, which is very important in color photography, we define

$$s = D_{(\max + 60)}/D_{\max}$$

where $D_{(\max + 60)}$ and $D_{\max}$ are optical densities of the dye at λ_{max} + 60 mμ and λ_{max}, respectively; the sharpest curves have the smallest values of s. Values of s are reported in Tables I, IIB, III and IV. Since the band width depends on the vibrational and rotational transitions superimposed upon the electronic transition for any given electronic transition, the absorption curve should be the steeper, the fewer the vibrational and rotational transitions. Those substituents in the *ortho*-position of the anilide ring which form the chelated structures XIV should therefore narrow the absorption band and give smaller values of s. This is shown in Table III by the s-values for methanol solutions of the *o*-halo, *o*-alkoxy and *o*-alkylamino compounds. The effect is less pronounced for solutions in butyl acetate and absent in cyclohexane. The band widths and values of s are larger in the more polar solvents, presumably because solvation of the dye introduces new infrared fre-

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[9] E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

[10] A. Weissberger, *J. Org. Chem.*, **2**, 245 (1937).

[11] H. E. Ungnade, THIS JOURNAL, **76**, 5133 (1954).

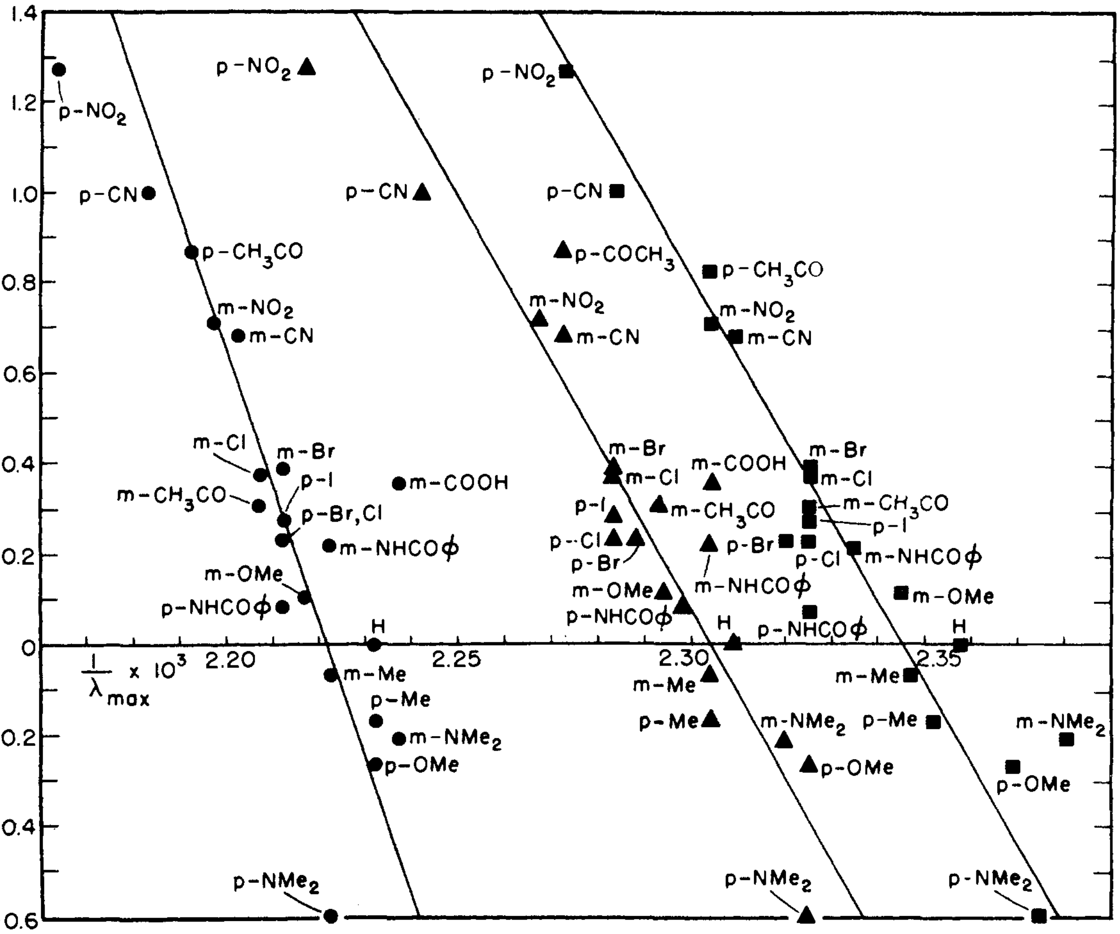

Fig. 2.—Plot of $1/\lambda_{max}$ (λ_{max} in mμ) *vs.* Hammett's σ-constants for azomethine (III) dyes substituted in the anilide ring; solvents: ■, cyclohexane; ▲, butyl acetate; ●, methanol.

quencies. It appears that this solvation does not interfere with the chelation XIV. It would be difficult to understand, however, why the chelating substituents do not cause an increase of sharpness of the dyes in cyclohexane, unless the chelation itself interferes with the solvation in methanol, *i.e.*, solvation takes place on the acetamido group.

Experimental

The requisite **β-ketoesters** were synthesized by previously described methods (see Table VA for references). **Anilines** needed for condensation with the β-ketoesters were generally prepared by low-pressure hydrogenation of nitro-compounds over Raney nickel rather than by the chemical methods of reduction given in the reference of Table VB. 2,4-Dimethoxyaniline[12] was obtained by hydrogenation of 2,4-dimethoxyazobenzene. *o*-Fluoroaniline was prepared by degradation of *o*-fluorobenzamide with sodium hypobromite. This reaction has been reported not to occur,[13] but gave good yields when carried out in the presence of a wetting agent (Nekal A).

***o*-Fluoroaniline from *o*-Fluorobenzamide.**—A mixture of 13 g. (0.09 mole) of *o*-fluorobenzamide and 0.5 g. of Nekal A wetting agent was added, with good stirring, to a solution containing 15 g. (0.37 mole) of sodium hydroxide and 15 g. (0.09 mole) of bromine in 325 ml. of water. The addition was carried out at room temperature, and stirring was continued at this temperature for 30 min. after addition. The mixture was heated at 70° (over a steam-bath) for 1 hr. The product was removed from the reaction mixture by steam distillation until 65 ml. of distillate was obtained, at which point 25 ml. of 40% sodium hydroxide solution was added, and steam distillation was resumed until a total volume of 200 ml. of distillate had been collected. The organic material in the distillate was extracted with benzene (100 ml. plus 2 times in 50 ml.). The combined extracts were washed with water and dried over magnesium sulfate. Fractional distillation gave 8 g. (77%) of product; colorless oil, b.p. 169–170°.

Aroylacetanilides (Tables VA, VB and VC) were prepared by condensation of equimolar amounts of β-ketoester and aniline in boiling xylene.[3,14]

Amino-substituted aroylacetanilides obtained by hydrogenation of the corresponding nitro compounds in ethanol over Raney nickel at two or three atmospheres hydrogen pressure were converted to amides with acid chlorides in sodium acetate-acetic acid solution.

Cinnamoylacetanilides (Table VI). **A. Synthesis of Aminocrotonanilides.**—**β-Aminocrotonanilide** and **β-amino-2-methoxycrotonanilide** were prepared by the method of Knorr[15] by reaction of acetoacetanilide and acet-*o*-anisidide, respectively, with concentrated aqueous ammonia in ethanol. The yield of β-aminocrotonanilide, m.p. 145–146° out of alcohol, was 93%. β-Amino-2-methoxycrotonanilide separated as an oil, which solidified after standing 15 months; m.p. 60–62°, yield 76%.

B. Acylation of the Crotonanilides. α-Cinnamoyl-α-(1-iminoethyl)-acetanilides (V).—The procedure of Benary and Kerckhoff[4] was employed. **α-Cinnamoyl-α-(1-iminoethyl)-acetanilide**, bright-yellow prisms, m.p. 200–201° out of

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[12] J. Bechold, *Ber.*, **22**, 2374 (1889).

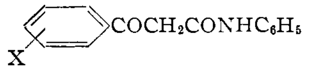
[13] G. Schiemann and H. G. Baumgarten, *ibid.*, **70B**, 1416 (1937).

[14] C. R. Hauser and G. A. Reynolds, This Journal, **70**, 4250 (1948).

[15] L. Knorr, *Ber.*, **25**, 775 (1892).

TABLE VA

PROPERTIES OF AROYLACETANILIDES

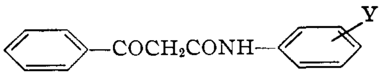


X	Yield, %	Recrystd. from	M.p., °C.	Analyses, %						Source of β-ketoester
				Calcd.			Found			
				C	H	N	C	H	N	
o-CH$_3$	61	C$_6$H$_6$/petr. eth.	85	..	..	5.5	..	..	5.4	a
2,4,6-(CH$_3$)$_3$	..	Ligroin	97	76.9	6.8	5.0	77.0	7.1	4.9	b
o-OCH$_3$	34	C$_6$H$_6$	116–117	..	..	5.2	..	..	4.8	c
m-OCH$_3$	49	C$_6$H$_6$/petr. eth.	95–96	..	..	5.2	..	..	5.2	d
p-OCH$_3$	80	C$_6$H$_6$	120–121	..	..	5.2	..	..	5.2	e
p-Cl	54	MeOH	136–137	..	..	5.1	..	..	5.0	f
m-NO$_2$	48	EtOH	155–157	63.4	4.3	..	63.8	4.2	..	g
p-NO$_2$[h,i]	84	EtOH	160–161	..	..	..	..	..	..	g,j
p-NH$_2$[h,i,k]	52	EtOH	165–166	..	..	..	..	..	..	
p-NHCOCH$_3$[l]	84	EtOH	206–208	68.9	5.4	..	68.7	5.2	..	
p-NHCOC$_6$H$_5$[m]	65	EtOH	222–224[n]	73.7	5.1	7.8	73.8	5.5	7.9	
p-NHSO$_2$C$_6$H$_5$[o]	35	EtOH	197–200	63.9	4.6	7.1	63.9	4.6	6.7	

[a] A. Haller, *Compt. rend.*, **108**, 1118 (1889). [b] C. F. H. Allen, J. VanAllan and C. V. Wilson, THIS JOURNAL, **66**, 1805 (1944). [c] Eastman Kodak Co. [d] A. Wahl and C. Silberzweig, *Bull. soc. chim. France*, [4] **11**, 25 (1912). [e] Fries Bros., New York, N. Y. [f] L. Thorp and E. R. Brunskill, THIS JOURNAL, **37**, 1258 (1915). [g] C. Bülow and E. Hailer, *Ber.*, **35**, 915 (1902). [h] B. Eistert, *Ann.*, **556**, 91 (1944). [i] H. Krzikalla, B. Eistert, R. Schmitt and H. Kracker, German Patent 597,589 (1934). [j] W. H. Perkin, Jr., and G. Bellenot, *J. Chem. Soc.*, **49**, 440 (1886). [k] From α-(4-nitrobenzoyl)-acetanilide by hydrogenation over Raney nickel. [l] From α-(4-aminobenzoyl)-acetanilide and acetic anhydride in acetic acid. [m] From α-(4-aminobenzoyl)-acetanilide and benzoyl chloride in sodium acetate–acetic acid. [n] Reported 198–199° (ref. *h*). [o] From α-(4-aminobenzoyl)-acetanilide and benzenesulfonyl chloride in sodium acetate–acetic acid solution.

TABLE VB

PROPERTIES OF AROYLACETANILIDES



Y	Yield, %	Recrystd. from	M.p., °C.	Analyses, %						Source of amine
				Calcd.			Found			
				C	H	N	C	H	N	
H	[a]									
o-CH$_3$	59	MeOH	138–139	75.9	6.0	..	76.3	6.0	..	a
m-CH$_3$	59	EtOH	101–102	..	..	5.5	..	..	5.5	a
p-CH$_3$	37	C$_6$H$_6$	131–132	75.9	6.0	..	75.7	6.0	..	a
2,6-(CH$_3$)$_2$	60	EtOH	151–152	76.4	6.4	..	76.7	6.5	..	a
o-OCH$_3$	53	MeOH	84–86	71.4	5.6	..	71.6	5.4	..	a
m-OCH$_3$	63	C$_6$H$_6$	84–85	71.4	5.6	..	71.2	5.7	..	a
p-OCH$_3$[b]	74	C$_6$H$_6$	127–128	71.4	5.6	..	71.1	5.5	..	a
o-Cl[c]	48	EtOH	135–137	..	..	5.1	..	..	4.9	a
m-Cl	35	...	115–117	..	..	5.1	..	..	5.2	a
p-Cl[b]	34	MeOH	154–156	..	..	5.1	..	..	5.1	a
o-Br	41	EtOH	123–125	56.7	3.8	4.4	56.9	3.9	4.3	a
m-Br	54	EtOH	118–120	56.7	3.8	4.4	57.0	3.9	4.5	a
p-Br	25	EtOH	170–172	56.7	3.8	4.4	56.8	3.8	4.5	a
p-I	17	EtOH	176–178	49.4	3.3	3.8	49.6	3.4	3.8	a
o-NO$_2$	40	MeOH	109–110	63.4	4.3	9.9	63.2	4.1	9.8	a
m-NO$_2$	53	EtOH	137–138	..	..	9.9	..	..	9.9	a
p-NO$_2$	36	C$_6$H$_6$	179–180	..	..	9.9	..	..	9.9	a
m-CN	65	MeOH	158–159	73.0	4.6	10.6	73.3	4.3	10.6	a
p-CN	68	EtOH	153–155	73.0	4.6	10.6	72.8	4.7	11.1	a
o-N(CH$_3$)$_2$	63	Ligroin	74–76	72.3	6.4	9.9	72.0	6.4	10.0	d
m-N(CH$_3$)$_2$	68	EtOH	138–140	72.3	6.4	9.9	72.4	6.4	9.9	e
p-N(CH$_3$)$_2$	43	C$_6$H$_5$CH$_3$	202–204	72.3	6.4	9.9	72.1	6.5	10.1	a
p-NH$_2$[f,g]	52	EtOH	158–159	..	..	11.0	..	..	11.2	..
o-NHCOC$_6$H$_5$	33	EtOH	168–170	73.7	5.1	7.8	73.0	5.0	8.1	h
m-NHCOC$_6$H$_5$[i]	67	EtOH	145–146	..	..	7.8	..	..	7.8	j
p-NHCOC$_6$H$_5$[k]	73	HAc	227–228	..	..	7.8	..	..	7.8	l
m-NHSO$_2$C$_6$H$_5$[m]	51	MeOH	157–159	..	..	7.1	..	..	7.0	..
p-NHSO$_2$C$_6$H$_5$[n]	62	EtOH	187–188	63.9	4.6	7.1	64.7	4.6	7.1	o
m-COCH$_3$	19	EtOH	121–123	72.6	5.4	5.0	72.5	5.2	5.0	a
p-COCH$_3$	71	EtOH	163–165	72.6	5.4	5.0	72.5	5.3	5.2	a
o-CO$_2$CH$_3$	44	MeOH	110–112	68.7	5.1	..	68.5	5.2	..	a
p-CO$_2$CH$_3$	30	MeOH	167–169	68.7	5.1	4.7	69.2	5.4	4.7	a
3,5-(CO$_2$CH$_3$)$_2$	68	C$_6$H$_6$	164–166	64.2	4.8	..	64.5	5.0	..	p
o-CONHC$_6$H$_5$	67	*n*-BuOH	183–185	73.7	5.1	7.8	73.8	5.2	8.0	q

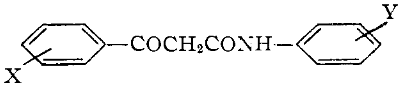
TABLE VB (*Continued*)

Y	Yield, %	Recrystd. from	M.p., °C.	Analyses, % Calcd. C	H	N	Found C	H	N	Source of amine
m-$CONHC_6H_5$	56	*n*-BuOH	180–181	73.7	5.1	7.8	74.0	5.2	8.2	[r]
p-$CONHC_6H_5$	57	Pyridine	231–233	73.7	5.1	7.8	73.9	5.0	8.1	[s]
o-$SO_2NHC_6H_5$	68	EtOH	162–164	63.9	4.6	7.1	64.0	4.7	7.4	[t]
m-$SO_2NHC_6H_5$	46	EtOH	188–190	63.9	4.6	7.1	64.2	4.5	7.2	[u]
p-$SO_2NHC_6H_5$	[a]	...	.....	..	..	..	..	..	..	..
o-OC_6H_5	55	C_6H_6	124–125	76.1	5.2	4.2	76.3	5.3	4.2	[v]
o-SCH_3	34	C_6H_{12}	89–90	67.5	5.3	4.9	67.8	5.8	4.9	[w]
m-CO_2H	53	HAc	210–212	..	..	5.0	..	..	4.9	[a]
o-F	30	C_6H_{12}–C_6H_6	103–105	70.0	4.7	5.5	70.3	4.7	5.7	[x]
o-CF_3	15	EtOH	103–105	62.5	3.9	4.6	..	..	..	[y]
2,5-$(OCH_3)_2$	68	MeOH	76–78	68.2	5.7	..	68.3	5.6	..	[a]
2,5-$(OC_2H_5)_2$	54	EtOH	118–120	69.7	6.5	..	70.4	6.3	..	[a]
2,4-$(OCH_3)_2$	42	EtOH	80–82	68.2	5.7	4.7	68.6	5.6	4.7	[z]
2,6-$(OCH_3)_2$	49	EtOH	151–153	68.2	5.1	4.7	68.2	5.7	5.0	[aa]

[a] Eastman Kodak Co. [b] R. Andrisano, *Bull. sci. Fascolta chim. ind. Bologna*, **8**, 4 (1950); *C. A.*, **44**, 9675 (1950). [c] I. G. Farbenindustrie A.-G., British Patent 355,709 (1930). [d] H. Rudy and K. Cramer, *Ber.*, **71**, 1234 (1938). [e] A. Groll, *ibid.*, **19**, 198 (1886). [f] A. Weissberger, C. J. Kibler and R. Young; Eastman Kodak Co., U. S. Patent 2,412,700 (1946). [g] Prepared by hydrogenation of α-benzoyl-4-nitroacetanilide in ethanol solution over Raney nickel catalyst at 50 p.s.i. [h] P. Ruggli and J. Rohner, *Helv. Chim. Acta*, **25**, 1533 (1942). [i] Also obtained from α-benzoyl-*m*-aminoacetanilide and benzoyl chloride in sodium acetate–acetic acid solution: m.p. 147–149°, yield 64%. [j] C. A. Bell, *Ber.*, **7**, 497 (1874). [k] Also obtained from α-benzoyl-*p*-aminoacetanilide and benzoyl chloride in sodium acetate–acetic acid solution: m.p. 208–210°, yield 67%. [l] C. E. Spencer, THIS JOURNAL, **65**, 2470 (1943). [m] From α-benzoyl-*m*-aminoacetanilide and benzenesulfonyl chloride in sodium acetate–acetic acid solution. [n] Also prepared from α-benzoyl-*p*-aminoacetanilide and benzenesulfonyl chloride in pyridine–dioxane solution: m.p. 183–184°, yield 48%. [o] G. T. Morgan and F. M. G. Micklethwait, *J. Chem. Soc.*, 87, 73 (1905). [p] B. Beyer, *J. prakt. Chem.*, **25**, 465 (1882). [q] H. Kolbe, *ibid.*, **30**, 467 (1884). [r] C. Engler and L. Volkhausen, *Ber.*, **8**, 34 (1875); A. Piutti, *ibid.*, **16**, 1319 (1883). [s] H. Rivier and S. Kunz, *Helv. Chim. Acta*, **15**, 376 (1932). [t] F. Ullmann and C. Gross, *Ber.*, **43**, 2694 (1910). [u] *Friedländer*, **10**, 807 (1901). [v] F. Ullmann, *Ber.*, **29**, 1878 (1896); C. M. Suter, THIS JOURNAL, **51**, 2581 (1929). [w] M. Claasz, *Ber.*, **45**, 2424 (1912); D. G. Foster and E. E. Reid, THIS JOURNAL, **46**, 1936 (1924). [x] See ref. 13. [y] H. Rouche, *Bull. sci. acad. roy. Belg.*, **13**, 346 (1927); *C. A.*, **22**, 2149 (1928). [z] See ref. 12. [aa] T. Simada and K. Hata, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **35**, 365 (1939); *C. A.*, **33**, 4594⁹ (1939). These authors employed reduction with $SnCl_2$–HCl. The present authors obtained a 68% yield of 2,6-dimethoxyaniline by low pressure catalytic hydrogenation of the nitro compound.

TABLE VC

PROPERTIES OF AROYLACETANILIDES[a]

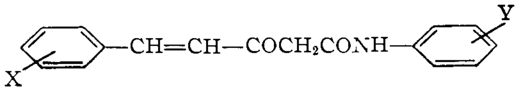


X	Y	Yield, %	Recrystd. from	M.p., °C.	Analyses, % Calcd. C	H	N	Found C	H	N
o-OCH_3	*o*-NO_2	15	C_6H_6	115–117	61.1	4.5	..	61.6	4.2	..
p-OCH_3	*o*-OCH_3	63	EtOH	89–91	68.2	5.7	4.7	68.4	5.9	4.8
o-OCH_3	*m*-NO_2	50	EtOH	125–127	61.1	4.5	8.9	61.3	4.5	8.6
p-NO_2	*o*-OCH_3	68	EtOH	138–140	61.1	4.5	8.9	61.1	4.4	8.9
p-NH_2	*o*-OCH_3	47	CH_3CN	134–136	67.6	5.7	..	67.6	5.7	..
p-NO_2	*o*-$N(CH_3)_2$	65	CH_3CN	135–137	62.4	5.2	12.8	61.8	4.9	12.8

[a] See Tables VA and VB for references to amines and β-ketoesters required for synthesis of these anilides.

TABLE VI

PROPERTIES OF CINNAMOYLACETANILIDES



X	Y	Yield, %[a]	Recrystd. from	M.p., °C.	Analyses, % Calcd. C	H	N	Found C	H	N
H	H	17–22	EtOH	107–108	77.0	5.7	5.3	76.6	6.0	5.3
H	*o*-OCH_3	20	EtOH	120–121	73.2	5.8	4.7	73.5	5.7	4.7
p-OCH_3	*o*-OCH_3	32	EtOH	136–137	70.2	5.9	4.3	70.3	5.7	4.5
p-OCH_3	H	22	EtOH	123–125	73.2	5.8	4.7	73.5	5.9	5.1

[a] For the yield from the imine, see Experimental section.

alcohol, yield 56%; **α-cinnamoyl-α-(1-iminoethyl)-2-methoxyacetanilide**, lemon-yellow powder, m.p. 157–158° out of alcohol, yield 79%; **α-(4-methoxycinnamoyl)-α-(1-iminoethyl)-2-methoxyacetanilide**,[16] m.p. 138–140° out of alcohol, yield 42%; **α-(4-methoxycinnamoyl)-α-(1-iminoethyl)-acetanilide**, yellow crystals out of alcohol, m.p. 146°, 57% yield.

C. Cleavage of the Imino Compounds: Cinnamoylacetanilides (IV). 1. **α-Cinnamoylacetanilide.**[4]—A mixture of 8.0 **g.** (0.026 mole) of crude α-cinnamoyl-α-(1-iminoethyl)-acetanilide and 80 ml. of glacial acetic acid was heated at the boiling point until the imine dissolved. After addition of 40 ml. of water, the mixture was boiled 5 min. The cloudy mixture was allowed to cool slightly, decanted from dark gum and chilled. The light-yellow product was

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(16) The 4-methoxycinnamic acid required for synthesis of this material was prepared according to the procedure given by J. R. Johnson in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 249. The acid chloride was prepared from 4-methoxycinnamic acid and excess thionyl chloride. The excess thionyl chloride was distilled and the residue used directly.

collected on a filter, washed with dilute sodium bicarbonate solution and recrystallized from 50 ml. of 95% ethanol with the addition of Darco. After washing with cold alcohol, the material was recrystallized again from alcohol to give 2.5 g. (38% yield) of pale-yellow product, m.p. 107-108°. Subsequent runs gave 17-22% yields of the anilide.

The other anilides in Table VI were prepared from the corresponding imines in the same manner.

Preparation of the Azomethine Dyes (III) (Tables I-IV). General Procedure.—Method A is carried out as follows: in a 1-l. beaker equipped with a stirrer was placed a solution of 0.01 mole of aroylacetanilide in 200 ml. of 95% ethanol. A solution of 5 g. of sodium carbonate in 50 ml. of water was added, followed by 0.011 mole (2.35 g.) of 4-amino-3-methyl-N,N-diethylaniline hydrochloride in 50 ml. of water. To the stirred mixture was added a solution of 0.04 mole of potassium ferricyanide in 100 ml. of water. Stirring continued for 15 min., and the dye was extracted with 250 ml. of ethyl acetate. The extract was washed several times with water and the solvent removed *in vacuo*. The residue was purified by chromatography over Doucil, with benzene or a mixture of ligroin (b.p. 60–90°) and acetone for development and elution; yield of dye 30-60%.

Method B, the use of silver chloride as the oxidant for preparation of the dyes, has been described previously.[5] The absorption spectra of the azomethine dye solutions, 8×10^{-5} molar concentration, for a 1-cm. thick sample against a water blank, were obtained with a General Electric recording spectrophotometer, using a constant spectral band width of 8 mμ.

Acknowledgment.—The authors thank Mr. E. E. Richardson, of these Laboratories, for the spectrophotometric curves.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

The Bromodesulfonation of Aromatic Sulfonate Salts. I. Sodium 3,5-Dibromo-4-hydroxybenzenesulfonate[1]

BY LAWRENCE G. CANNELL[2]

RECEIVED DECEMBER 20, 1956

The reaction of bromine with sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) to give tribromophenol has been studied in aqueous solution at 25.0°. Ultraviolet and visible spectra show that the reactants combine immediately to give a reaction intermediate which has a 2,6-dibromo-2,5-cyclohexandien-1-one structure. Kinetics (measured iodometrically) give additional support to a mechanism (eqs. 4 and 5) comprised of the formation of the intermediate and Br^- in a fast reversible step which is followed by the first-order decomposition of the intermediate in a rate-determining step. Specifically, the kinetics are zero order in whichever reactant, bromine or I, is in excess and first order in the other. The equilibrium of the first step greatly favors the formation of the intermediate, but the reverse reaction can be demonstrated both kinetically and spectrophotometrically when sodium bromide is added. The significance of these results in regard to the mechanism of electrophilic aromatic substitution is discussed.

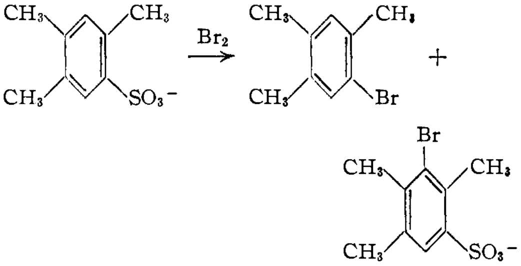
The bromodesulfonation reaction (eq. 1) has been investigated by measuring its reaction kinetics. Previous investigators have found that the reaction is greatly facilitated by amino, methoxy,

$$Br_2 + ArSO_3^- + H_2O \rightarrow ArBr + HSO_4^- + HBr \quad (1)$$

hydroxy or alkyl substituents *ortho* or *para* to the sulfonic acid group, but that these substituents in the *m*-position do not promote bromodesulfonation.[3–7] The reaction, then, appears to be an example of electrophilic aromatic substitution.

Comparable reactions have been reported with chlorine as a desulfonating agent,[8] but molecular iodine does not give the reaction.[9]

That the bromodesulfonation reaction does not proceed by a free-radical mechanism is indicated from the reaction with alkylbenzenesulfonate salts. Here bromination occurs on the aromatic ring and not on the side chain where it would be expected if the reaction takes place by a free-radical mechanism.[12]



(2)

In certain special cases the replacement of a sulfonic acid group by *chlorine* appears to be a free-radical reaction,[13] but these exceptions are charac-

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(1) This paper was presented in part at a symposium on aromatic substitution held by the Division of Organic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956.

(2) Shell Development Co., Emeryville, Calif. National Science Foundation post-doctoral fellow 1955–1956.

(3) R. L. Datta and J. C. Bhoumik, THIS JOURNAL, **43**, 303 (1921).

(4) J. J. Sudborough and J. V. Lakhumalani, *J. Chem. Soc.*, **111**, 41 (1917).

(5) M. S. Van Dorssen, *Rec. trav. chim.*, **29**, 377 (1910); J. Obermiller, *Ber.*, **43**, 4361 (1909).

(6) A. N. Meldrum and M. S. Shah, *J. Chem. Soc.*, **123**, 1982 (1923).

(7) O. Heinichen, *Ann.*, **253**, 267 (1889).

(8) R. L. Datta and H. K. Mitter, THIS JOURNAL, **41**, 2028 (1919).

(9) Bromate,[2,8] iodate[2] or chlorate[2,8] salts in combination with the corresponding hydrohalic acid can also be employed as halogenodesulfonating agents.

(10) T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind.*, **41**, 161-T (1922).

(11) G. Heller, *Ber.*, **46**, 2703 (1913).

(12) W. Kelbe and K. Pathe, *ibid.*, **19**, 1546 (1886); W. Kelbe and H. Stein, *ibid.*, **19**, 2137 (1886).

(13) It was established by Kharasch and Eberly (1940) that, contrary to the claim of Eckert (*Ber.*, **58**, 313 (1925)), α- and β-anthraquinonesulfonic acids do not react with hydrochloric acid in the light to give the corresponding α- and β-chloroanthraquinones if oxygen is rigidly excluded from the system. However, if oxygen is present, the reaction studied by Eckert takes place readily. It was also established that, whereas water solutions of α- and β-anthraquinone sulfonic acids do not react with chlorine in the dark, a ready formation of the corresponding chloroanthraquinones takes place in the light. Results similar to the ones cited above have been obtained with anthraquinone-2,6-disulfonic acid. A free radical mechanism involving chlorine atoms has been postulated to explain these results. It was also established that bromine atoms do not replace sulfonic acid groups under the conditions cited above. A publication dealing with these findings will appear shortly (private communication from M. S. Kharasch).