[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Physical Properties of the Aminoazobenzene Dyes. VII. Absorption Spectra of 4-Aminoazobenzene Dyes in Ethanol[1]

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The visible absorption spectra of approximately sixty azobenzene derivatives in 95% ethanol have been investigated. Of particular interest was the effect of various substituents on the long wave length band associated with a zwitterionic resonance structure. An increasing shift toward the visible is shown by 4-substituted azobenzenes with the following substituents: $H < Me < NHAc < OH < SMe < NH_2 < N(CH_2CH_2Cl)_2 < NHMe < NHEt < NMe_2 < NEt_2$. Substitution of electron acceptor groups in the 4′-position of the 4-aminoazobenzene dyes causes an increasing shift toward the visible in the order: $H < C_6H_5 < SCN < CH{=}CH_2 < Ac < N{=}N{-}C_6H_5 < NO_2$. For the 4-dialkylaminoazobenzene dyes containing either a nitro or acetyl group at the negative end of the molecule there is a gradual shift toward the visible in the order $3' < 2' \ll 4'$. The presence of alkoxy, methylthio, or amino groups at the negative end of the molecule has very little effect on the wave length maximum in 95% ethanol. In naphthalene dyes such as 4-phenylazo-1-naphthol, λ_{max} 409 mμ, as compared to 4-hydroxyazobenzene, λ_{max} 349 mμ, the bathochromic shift is postulated as due to the relatively lower energy of the α-naphthoquinone excited state structure as compared to the *p*-benzoquinone excited state structure of 4-hydroxyazobenzene.

The relative intensity of two adjacent bands in chloro-, methoxy-, methylthio-, and amino derivatives of 4-dialkylaminoazobenzenes is shown to be solvent dependent. In aqueous alcohol 2′-amino-4-dimethylaminoazobenzene shows evidence of spectral fine structure that appears to be absent in the other compounds. On the basis of the spectra it is suggested that this compound exists mainly in a structure which contains a five membered ring involving an intramolecular hydrogen bond between the amino hydrogen and the β-azo nitrogen. The structure involving a six membered ring containing an intramolecular hydrogen bond between the amino hydrogen and the α-azo nitrogen is believed to be present also.

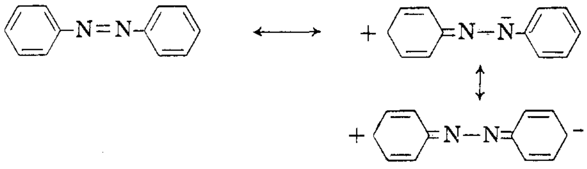
Ten new azo dyes have been prepared.

In previous papers of the series[3] the relation of the basicity of the various basic centers of an aminoazobenzene dye to tautomerism, resonance, inductive and steric effects, and inter- and intramolecular hydrogen bonding was discussed. In this paper the ultraviolet-visible absorption spectra of some 4-dimethylaminoazobenzene, DAB, derivatives is investigated.

The spectra of aromatic azo compounds show at least three regions of absorption in alcoholic solution. In the absence of a 2- or 4-amino group a weak absorption band is usually found at about 440–470 mμ. This band is believed to be derived from a transition involving the free non-bonding electrons of the $-N{=}N-$ group. This type of transition has been symbolized variously as n—V,[4] $n \rightarrow \pi^{*}$[5] and N→A.[6] The band has been thoroughly investigated by Burawoy, who believes it is due to a radical transition in the azo group and consequently has named it the R- band.[7]

The bands of moderate intensity at 210–290 mμ are believed to arise from electronic transitions in the aromatic rings.[8,9] As these bands are believed to arise from the E band of benzene at 205 mμ, they have been called E- bands.[10,11]

In azobenzene an intense band is found at 318 mμ which has been ascribed to the conjugation between the azo group and the aromatic ring system.[7] Some of the structures which contribute to the electronic transition involved in this band system are of a varying degree of importance depending upon the type of substituent and the environment. Substitution of electron-acceptor and/or electron-donor groups in positions of conjugation on the benzene rings decreases the energy of the zwitterionic structures. With such substitutions the change in energy involved in the transition from ground to excited state is decreased and the wave length maximum of this band system shows the expected bathochromic shift, Table I. This type of band structure where zwitterionic resonance structures



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[1] This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

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[3] E. Sawicki and F. Ray, *J. Org. Chem.*, **19**, 1686 (1954); E. Sawicki and D. Gerber, *J. Org. Chem.*, **21**, 410 (1956); E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

[4] P. Birnbaum, J. Linford, and D. Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

[5] M. Kasha, *Discussions Faraday Soc.*, **No. 9**, 14, 72, 74, 75 (1950).

[6] G. Wheland, *Resonance in Organic Chemistry*, p. 307, John Wiley and Sons, Inc., New York, 1955.

[7] A. Burawoy, *J. Chem. Soc.*, 1177 (1939); and previous work.

[8] G. Badger and R. Buttery, *J. Chem. Soc.*, 2156 (1953).

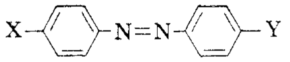
[9] A. Burawoy, *J. Chem. Soc.*, 1865 (1937).

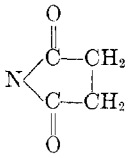
[10] P. Gore and O. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956).

[11] K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

TABLE I

ABSORPTION SPECTRAL DATA OF Z BAND IN 95% ETHANOL[a]



X	Y	λ_{max} (log ϵ)	X	Y	λ_{max} (log ϵ)
H	NO_2	332^{12} (4.38)	NHEt	H	405 (4.42)
H	COOMe	330^{4} (4.47)	NMe_2	H	408 (4.44)
H	H	318 (4.33)	NMeEt	H	411 (4.45)
	H	323^{13} (4.34)	NEt_2	H	415 (4.47)
Me	H	333 (4.37)	NMe_2	SCN	433 (4.51)
NMeCHO	H	338 (4.39)	$N(CH_2CH_2Cl)_2$	Ac	435^{14} (4.53)
NHTos[b]	H	346 (4.41)	NMe_2	$CH{=}CH_2$	435^{15} (4.33)
NHCHO	H	347 (4.44)	$N(CH_2CH_2Cl)_2$	NO_2	446^{14} (4.33)
NHAc	H	347^{13} (4.37)	NMe_2	Ac	447 (4.50)
OH	H	349 (4.42)	NMeEt	Ac	454 (4.52)
NHCOOEt	H	352 (4.42)	NEt_2	Ac	462 (4.54)
SMe	H	362 (4.38)	NMe_2	$—N{=}N—C_6H_5$	473 (4.55)
NH_2	H	385 (4.39)	NHC_6H_5	NO_2	475 (4.52)
OH	NO_2	386^{16} (4.47)	NMe_2	NO_2	478 (4.52)
$N(CH_2CH_2Cl)_2$	H	397^{14} (4.41)	NMeEt	NO_2	485 (4.52)
NHMe	H	402 (4.41)	NEt_2	NO_2	490 (4.56)

[a] An R-band at 430–450 mμ, log ε 2.9–3.2 is found for all compounds in the table from 4-nitroazobenzene to 4-hydroxy-4′-nitroazobenzene, except for 4-aminoazobenzene. In this compound and the *N*-alkylated aminoazo compounds, the R-band is hidden, but a fairly intense shoulder is found at the long wavelength slope of the main band which has been attributed to hydration of the azo dye.[17] [b] Tos is *p*-toluenesulfonyl.

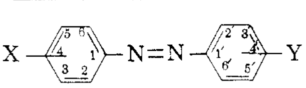
are involved has been called a zwitterionic resonance, or Z, band.[18]

In the 4-substituted azo dyes in Table I there is an increasing shift toward the visible with the following substituents $H < Me < NHAc < OH < SMe < NH_2 < N(CH_2CH_2Cl)_2 < NHMe < NHEt < NMe_2 < NMeEt < NEt_2$. Essentially with an increase in the electron-donor properties of the substituent there is a definite bathochromic shift in the absorption spectra. This same order has been found for 5-substituted 2,1,3-benzoselenadiazoles,[19] *para*-substituted nitrobenzene derivatives,[19] and *para*-substituted triphenylmethane dyes.[20] In the 4-aminoazobenzene dyes, substitution of electron-acceptor groups in the 4′-position causes an increasing shift toward the visible in the order $-H < C_6H_5 < SCN < CH{=}CH_2 < COCH_3 < N{=}N{-}C_6H_5 < NO_2$.

For some fifteen 4-dialkylaminoazobenzene dyes containing either a nitro or acetyl group at the negative end of the molecule the position of substitution affected the λ_{max} values in that the λ_{max} increased in the order 3′ < 2′ << 4′, Table II. This has also been shown for the nitro-4-di(2-

TABLE II

Z BAND OF MISCELLANEOUS AZO DYES IN 95% ETHANOL



X	Y	λ_{max} (log ϵ)
4-EtS-2-Me	H	367 (4.18)
4-MeS	4′-MeS	380 (4.39)
$4\text{-}Me_2N$	$4'\text{-}C_6H_5$	422 (4.53)[21]
$4\text{-}Me_2N$	$3'\text{-}CF_3$	423 (4.47)
4-MeEtN	$3'\text{-}CF_3$	426 (4.47)
$4\text{-}Me_2N\text{-}2\text{-}Me$	$2'\text{-}COOCH_3$	420 (4.41)
$4\text{-}Me_2N$	3′-Ac	420 (4.45)
$4\text{-}Me_2N\text{-}2\text{-}Me$	3′-Ac	424 (4.45)
$4\text{-}Me_2N\text{-}2\text{-}Me$	4′-Ac	452 (4.50)
$4\text{-}Me_2N$	$2'\text{-}NO_2$	440 (4.43)
$4\text{-}Me_2N$	$3'\text{-}NO_2$	431 (4.46)
$4\text{-}Me_2N\text{-}2\text{-}Me$	$2'\text{-}NO_2$	447 (4.43)
$4\text{-}Me_2N\text{-}2\text{-}Me$	$3'\text{-}NO_2$	441 (4.46)
$4\text{-}Me_2N\text{-}2\text{-}Me$	$4'\text{-}NO_2$	489 (4.49)
4-MeEtN	$2'\text{-}NO_2$	449 (4.43)
4-MeEtN	$3'\text{-}NO_2$	445 (4.47)
$4\text{-}Et_2N$	$3'\text{-}NO_2$	450 (4.50)

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(12) H. Dahn and H. Castelmur, *Helv. Chim. Acta*, **36**, 638 (1953).

(13) H. Henbest and T. Owen, *J. Chem. Soc.*, 2968 (1955).

(14) W. Ross and G. Warwick, *J. Chem. Soc.*, 1719 (1956).

(15) M. Martynoff, *Bull. soc. chim. France*, 374 (1955).

(16) A. Pongratz, G. Markgraf, and E. Mayer-Pitsch, *Ber.*, **71**, 1287 (1938).

(17) W. Brode, I. Seldin, P. Spoerri, and G. Wyman, *J. Am. Chem. Soc.*, **77**, 2762 (1955).

(18) E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956).

(19) E. Sawicki and A. Carr, *J. Org. Chem.*, **22**, 503 (1957).

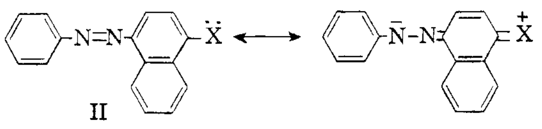
(20) N. Deno, J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

chloroethyl)aminoazobenzenes where the 2′, 3′-, and 4′-nitro derivatives have λ_{max} 420, 416, and 446 mμ, respectively.[14] Apparently the conjugation of the electronegative group with the amino group is of importance in bringing about the bathochromic shift.

A phenyl group can act as an electron donor or an electron acceptor. Substitution of the electron acceptor 4′-phenyl group in 4-dimethylaminoazobenzene causes a shift to 422 mμ.[21] The same phenomenon is seen in 2-4′-dimethylaminophenylazofluorene where a wave length maximum is found at 423 mμ. In 2-4′-dimethylaminophenylazo-7-nitrofluorene the electron acceptor properties of the fluorene group is materially increased. This causes a wave length shift to 460 mμ.

In both 4-phenylazo-1-naphthol (II, X = OH), λ_{max} 409 mμ, as compared to 4-hydroxyazobenzene (I, X = OH), λ_{max} 349 mμ, and 4-phenylazo-1-naphthylamine (II, X = NH_2), λ_{max} 430 mμ, as compared to 4-aminoazobenzene (I, X = NH_2), λ_{max} 385 mμ, there is a strong spectral shift. An important excited state structure of I involves a

I



II

p-benzoquinone ring. The analogous structure in II involves an α-naphthoquinone ring system. The relatively lower energy of the α-naphthoquinone structures would help to account for the strong bathochromic shift shown in II as compared to I. The presence of alkoxy, methylthio, or amino groups at the negative end of the molecule has very little effect on the wave length maximum in 95% ethanol.

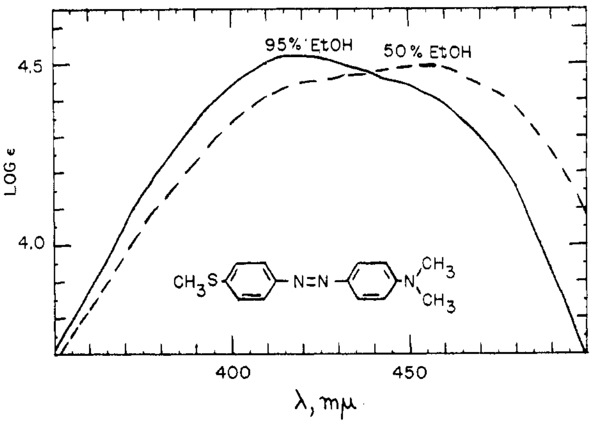


Fig. 1. Absorption spectra: 4′-Methylthio-4-dimethylaminoazobenzene; in 95% ethanol (——), in 50% ethanol (- - -).

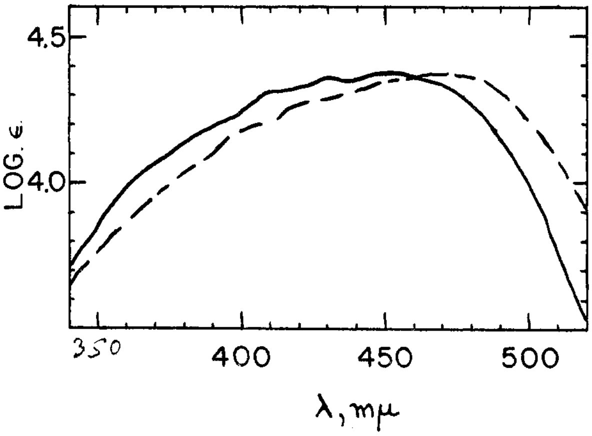
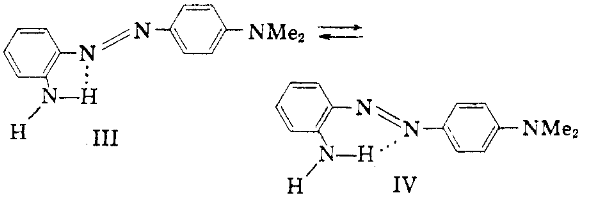


Fig. 2. Absorption spectra: 2′-Amino-4-dimethylaminoazobenzene; in 95% ethanol (——), in 25% ethanol (- - -)

On the other hand the addition of water to alcoholic solutions of 4-amino-, 4-dimethylamino-, 4-hydroxy and 4-methoxy substituted azobenzene gives rise to a new absorption band in the visible region. This new band is attributed to the formation of a hydrogen bond between the β azo nitrogen and water.[17] Examination of the visible absorption spectrum in 95% ethanol of a large number of chloro, methyl, methoxy, methylthio, and amino derivatives of 4-aminoazobenzene dyes indicates the presence of a strong unsymmetrical band sloping more gradually at the long wave-length side. This band system appears to consist of two bands. Increasing the amount of water in the solvent increases the intensity of the longer wave-length band while decreasing the intensity of the shorter wave length band, Table III, Fig. 1. An exception to this rule appears to be 2′-amino-4-dimethylaminoazobenzene which absorbs most strongly at 450 to 470 mμ in 95% and 25% alcohol, Table III, Fig. 2. In the visible spectrum this compound shows fine structure that appears to be absent in the other compounds. It is suggested that intermolecular hydrogen bonding between both alcohol and water with the azo nitrogens and intramolecular hydrogen bonding between the α- and β-azo nitrogens with the amino hydrogen probably account for the fine structure. The intramolecular hydrogen bond between the amino hydrogen and the β-azo nitrogen (see III) could account for the long wave length absorption even in 95% ethanol; the intramolecular hydrogen bond between the amino hydrogen and the α-azo nitrogen (see IV) could account for the absorption at approximately 360 mμ. III is stabilized by the attraction of the



III

IV

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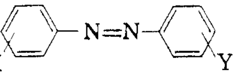
[21] W. Brode, J. Gould, and G. Wyman, *J. Am. Chem. Soc.*, 75, 1856 (1953).

TABLE III

Visible Spectral Data in Aqueous Alcohol



X	Y	λ_{max} (log ϵ) 95% EtOH	λ_{max} (log ϵ) 50% EtOH	X	Y	λ_{max} (log ϵ) 95% EtOH	λ_{max} (log ϵ) 50% EtOH
4-NMe_2	2′-OMe	413 (4.42) ~450s (4.29)[a]	425 (4.38) ~450s (4.36)	4-NHC_6H_5	4′-SMe	423 (4.56) ~445s (4.52)	425 (4.49) 442 (4.52)
4-NMe_2	3′-OEt	410 (4.45) ~440s (4.33)	425 (4.40) ~440s (4.39)	4-NMe_2	2′-NH_2	[b] 452 (4.36)	[b] 468 (4.37)[c]
4-NMe_2	4′-OMe	405 (4.46) ~440s (4.34)	420s (4.40) 440 (4.41)	4-NMe_2	3′-NH_2	410 (4.39) ~445s (4.20)	~410s (4.26)[c] 455 (4.36)[c]
4-NMe_2	4′-OEt	405 (4.47) ~440s (4.36)	420s (4.41) 440 (4.42)	2-Me-4-NMe_2	4′-NH_2	413 (4.48) ~460s (4.39)	420s (4.36)[c] 460 (4.43)[c]
4-NMe_2	4′-SMe	419 (4.52) ~455s (4.41)	422s (4.45) 455 (4.49)	4-NMe_2	4′-NH_2	410 (4.48) 440 (4.46)	~418s (4.36)[c] 458 (4.48)[c]
2-Me-4-NMe_2	4′-SMe	422 (4.54) ~460s (4.43)	432 (4.48) ~460s (4.48)				

[a] s = shoulder. [b] Fine structure is found at the short wave length side of the main band. [c] In 25% ethanol.

amino hydrogen for the β-nitrogen because of the high electron density at the β-nitrogen. On the other hand the five membered ring involved in the hydrogen bond of III is more strained than is the comparable six membered ring in IV.

EXPERIMENTAL[22]

Preparations. Most of the dyes were available from other investigations[3] in this laboratory and had been purified by crystallization to a constant melting point. 4′-Phenylazo-4-dimethylaminoazobenzene,[23] m.p. 198–199°, 4′-nitro-4-phenylaminoazobenzene,[24] m.p. 158–159°, 4,4′-bismethylthioazobenzene,[25] m.p. 170–171°, 4′-amino-4-dimethylaminoazobenzene,[26] m.p. 186–187°, 3′-amino-4-dimethylaminoazobenzene,[27] m.p. 168–169°, and 2′-amino-4-dimethylaminoazobenzene,[28] m.p. 105–106°, were prepared and purified by the procedures in the literature.

4′-Acetylamino-2-methyl-4-dimethylaminoazobenzene. Coupling of diazotized *N*-acetyl-*p*-phenylenediamine with *N,N*-dimethyl-*m*-toluidine by a standard procedure, followed by crystallization from benzene, gave orange crystals, m.p. 189–190°.

Anal. Calcd. for $C_{17}H_{20}N_4O$: N, 18.9. Found: N, 18.7.

4′-Amino-2-methyl-4-dimethylaminoazobenzene. Hydrolysis of the *N*-acetyl derivative was accomplished by refluxing for 0.5 hr. in Methyl Cellosolve[29]–25% aqueous sulfuric acid solution. Neutralization followed by several crystallizations from heptane gave red-gold plates, m.p. 128–129°.

Anal. Calcd. for $C_{15}H_{18}N_4$: N, 22.0. Found: N, 22.1.

2-4′-Dimethylaminophenylazo-7-nitrofluorene. Coupling of diazotized 2-amino-7-nitrofluorene with dimethylaniline followed by two crystallizations of the precipitate from nitrobenzene gave glistening black-brown plates, m.p. 270–271°.

Anal. Calcd. for $C_{21}H_{18}N_4O_2$: N, 15.6. Found: N, 15.2.

2-Methyl-4-thiocyanoazobenzene. To a solution of 1.07 g. of nitrosobenzene in 2 ml. of acetic acid and 6 ml. of alcohol was added 1.64 g. of 2-methyl-4-thiocyanoaniline,[30] m.p. 69–70°, in 2 ml. acetic acid and 4 ml. alcohol. The mixture was kept at 0–10° over 12 hr. The solid was collected and crystallized from hexane to give a 70–80% yield of gleaming orange needles, m.p. 88–89°.

Anal. Calcd. for $C_{14}H_{11}N_3S$: C, 66.4; H, 4.35; N, 16.6. Found: C, 66.3; H, 4.28; N, 16.5.

2-Methyl-4-methylthioazobenzene. A solution of 0.25 g. of 2-methyl-4-thiocyanoazobenzene and 0.11 g. of potassium hydroxide in 10 ml. of methanol was refluxed for 20 min., cooled, and then 0.1 ml. of methyl iodide was added. An hour later 15 ml. of water was added. Crystallization from hexane gave an 80% yield of orange rods, m.p. 76–77°.

Anal. Calcd. for $C_{14}H_{14}N_2S$: C, 69.4; H, 5.78; N, 11.6. Found: C, 69.6; H, 5.84; N, 11.4.

4′-Methylthio-4-dimethylaminoazobenzene. To a solution of 2.82 g. of 4′-thiocyano-4-dimethylaminoazobenzene,[31] m.p. 154°, in 40 ml. of methanol was added 1.23 g. of potassium hydroxide in 10 ml. of methanol. The mixture was refluxed 15 min., cooled to 0° and treated with 0.8 ml. of methyl iodide. After standing overnight at 0–10° excess water was added. The precipitate was crystallized from hexane to give a 70% yield of yellow crystals, m.p. 177–178°.

Anal. Calcd. for $C_{15}H_{17}N_3S$: N, 15.5. Found: N, 15.2.

4′-Methylthio-2-methyl-4-dimethylaminoazobenzene. The coupling of diazotized *p*-thiocyanoaniline[32] with *N,N*-dimethyl-*m*-toluidine by standard procedure gave the crude 4′-thiocyano-2-methyl-4-dimethylaminoazobenzene.

A solution of this crude product in methanol was treated with a solution of 12.3 g. of potassium hydroxide in 20 ml. of methanol. The mixture was refluxed 15 min., cooled to 0°, and filtered. The residue was crystallized from Methyl Cellosolve to give red crystals of 4,4′-bis(*p*-dimethylamino-*o*-tolylazo)diphenyl disulfide, m.p. 200°.

Anal. Calcd. for $C_{30}H_{32}N_6S_2$: N, 15.6. Found: N, 15.7.

The cold filtrate was treated with 8 ml. of methyl iodide. After several hours standing at 0–10°, excess water was added. Two crystallizations from heptane gave bulky red crystals, m.p. 120–122°.

Anal. Calcd. for $C_{16}H_{19}N_3S$: N, 14.7. Found: N, 14.6.

4′-Thiocyano-4-phenylaminoazobenzene. Coupling of diazotized *p*-thiocyano aniline with diphenylamine gave brown-yellow plates, m.p. 151–152°, after several crystallizations from alcohol.

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(22) All melting points are uncorrected.

(23) J. Hewitt and F. Thole, *J. Chem. Soc.*, **95**, 1393 (1909).

(24) R. Meldola, *J. Chem. Soc.*, **43**, 425 (1883).

(25) K. Brand and A. Wirsing, *Ber.*, **45**, 1757 (1912).

(26) R. Meldola, *J. Chem. Soc.*, **45**, 106 (1884).

(27) O. Wallach, *Ann.*, **234**, 350 (1886).

(28) W. Ross and G. Warwick, *J. Chem. Soc.*, 1724 (1956).

(29) Trade name for β-methoxyethanol.

(30) M. Likhosherstov and A. Petrov, *J. Gen. Chem. U.S.S.R.*, **3**, 759 (1933); *Chem. Abstr.*, **28**, 2690 (1934).

(31) T. Campbell, D. Young, and M. Rogers, *J. Am. Chem. Soc.*, **73**, 5789 (1951).

(32) H. Kaufmann, *Ber.*, **62**, 390 (1929).

Anal. Calcd. for $C_{19}H_{14}N_4S$: N, 17.0. Found: N, 16.7.

4'-Methylthio-4-phenylaminoazobenzene. This was prepared by the standard procedure. Crystallization from aqueous alcohol and heptane gave glistening orange crystals, m.p. 126–127°.

Anal. Calcd. for $C_{19}H_{17}N_3S$: N, 13.2. Found: N, 13.0.

Absorption spectral data. The intense long wavelength band of all compounds was measured with a Beckman Model DU Spectrophotometer in commercial 95% ethanol. The spectra of some of the compounds was determined in 50% and 25% aqueous alcohol. By 50% aqueous alcohol is meant a solution containing 50 ml. of water diluted to 100 ml. with 95% ethanol; by 25% aqueous alcohol is meant a solution containing 75 ml. of water diluted to 100 ml. with 95% ethanol.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Reaction of Sodium Methoxide with 2-Alkyl-2,3-dichloroaldehydes[1]

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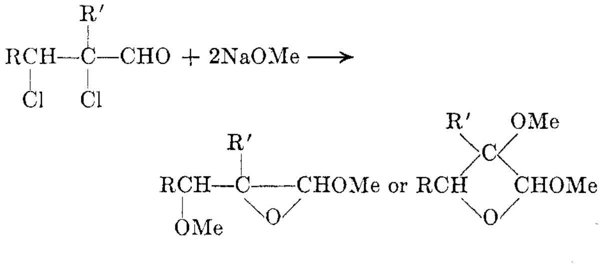
The reactions of sodium methoxide with 2-methyl-2,3-dichlorovaleraldehyde and 2-ethyl-2,3-dichlorohexanal in dry methanol and in dry ether have been investigated. The previous report that 4-membered cyclic acetals were formed in methanol solution was found to be incorrect, the products actually being α,β-epoxy dimethyl acetals. In ether, the products are 2-methoxy-3-chloroaldehydes. The effect of solvent differs from that observed for the reactions of various α-chlorocarbonyl compounds with sodium methoxide, apparently due to the large electrical effect of chlorine in the β-position.

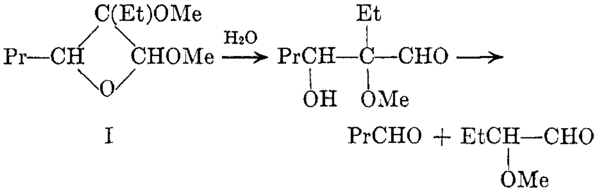
2-Alkyl-2,3-dichloroaldehydes undergo smooth substitution of both chlorine atoms when treated with alcoholic sodium methoxide (2 moles), whereas 2,3-dichloroaldehydes possessing α-hydrogen undergo dehydrohalogenation to unsaturated aldehydes.[2] The products from the former, however, are not the corresponding dimethoxyaldehydes, as they possess neither the chemical properties of aldehydes[2] nor the bond characteristic of the carbonyl group in the Raman spectrum.[3]

Since these compounds give the usual aldehyde reactions after they have been treated with aqueous acids, Lichtenberger and his coworkers considered them to be cyclic acetals possessing either the oxirane or the oxetane ring. More recently these products have been reinvestigated by Krausz,[4] who believed that he had definitely established the oxetane structure.



Negatively substituted oxetanes of this type appeared to be completely unknown[5–7] and would be of great interest in connection with current studies on substituted oxetanes.[8]

Krausz's argument for the presence of the oxetane ring in these compounds is based on his study of their hydrolysis products. After dilute sulfuric acid hydrolysis of the dimethoxy compound (I) obtained from 2-ethyl-2,3-dichlorohexanal (II), butyraldehyde was identified. This might have formed by a retrograde-aldol cleavage of a β-hydroxyaldehyde, formed as follows:



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This would not be possible if (I) were a cyclic acetal with the oxirane structure and cleaved to a hydroxymethoxyaldehyde.

For additional evidence on the structure of these compounds, Krausz subjected the dimethoxy compound (III) from 2-methyl-2,3-dichloropentanal (IV) to mild acid hydrolysis, obtained the prod-

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[1] Abstracted in part from the Ph.D. thesis of Edwin K. Ives, Kansas State College, 1957.

[2] J. Lichtenberger and M. Naftali, *Bull. soc. chim. France*, [5], 4, 325 (1937).

[3] R. Kirmann and J. Lichtenberger, *Compt. rend.*, **206**, 1259 (1939).

[4] F. Krausz, *Ann. chim.*, [12], **4**, 811 (1949).

[5] The report of 2-acetoxyoxetane from the reaction of 3-hydroxypropionaldehyde with acetic anhydride (M. Bergmann, A. Mickley, and E. O. Lippmann, *Ber.*, **62**, 1467 (1929)) has been shown to be incorrect by E. Spath and L. Pallam-Raschik (*Monatsh.*, **79**, 447 (1948)).

[6] "3-Chlorooxetane," reported by H. Bigot [*Ann. Chim. phys.*, [6], **22**, 433 (1891)], has been shown by W. E. Noland and B. N. Bastian [*J. Am. Chem. Soc.*, **77**, 3395 (1955)] to be actually 2-chloroallyl alcohol.

[7] Recently 2-phenyloxetane [S. Searles, K. A. Pollart, and E. F. Lutz, *J. Am. Chem. Soc.*, **79**, 948 (1957)] and a steroid derivative having a 3,3-ethylenedioxyoxetane structure [W. S. Allen, S. Bernstein, M. Heller, and R. Littell, *J. Am. Chem. Soc.*, **77**, 4784 (1955)] have been reported.

[8] S. Searles, K. A. Pollart, and F. Block, *J. Am. Chem. Soc.*, **79**, 952 (1957) and preceding papers.