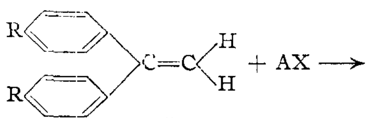
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

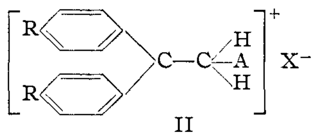
Color Reactions of Some Unsymmetrical Diarylethylenes[1]

BY D. S. TARBELL AND E. G. LINDSTROM

It has been shown, mainly by Pfeiffer and Wizinger and their collaborators,[2] that unsymmetrical diarylethylenes, containing electron-donating groups in the aromatic rings, form colored addition products with a variety of substances. The process may be represented as follows, where R may be OCH_3, $N(CH_3)_2$ or similar group, and AX may be an acid (mineral acid, or organic acid, in some cases), halogen, benzoyl chloride, cyanogen chloride, alkyl halide, diazonium salt or other substance. The colored salts II frequently eliminate HX to give the β-substitution products $Ar_2C{=}CHA$, and many of the typical "aromatic" substitution reactions can be carried out on the diarylethylenes.[2] The stability of the colored salts clearly depends on the ability of the cation to exist as a hybrid of a number of resonance structures, as well as on the anionic stability of X. The easily polarizable character of the ethylenic double bond and the electron density on the β-carbon in type I compounds are emphasized by the observation that they add to naphthoquinone in the same manner as other nucleophilic compounds.[3]



I



II

The wide variety of compounds which give colored salts with the diarylethylenes led us to study their usefulness as detecting agents for a number of toxic substances. We have investigated a series of diarylethylenes, some of them new compounds, as detectors for arsenicals and other toxics. Although some of the ethylenes were sensitive to low concentrations of toxic, they lacked sufficient stability to be useful.

The ethylenes prepared and tested as detectors are listed in Table I, which also gives some information about the preparation of compounds which had been previously reported in the literature. The colors produced with liquid lewisite or ethyldichloroarsine were determined by adding a drop of arsenical to the solid ethylene. The colors faded appreciably in a few minutes. Dianisylpropylene, when mixed with about twenty times its weight of silica gel, gave a detectable pink color with less than a gamma of lewisite, when air containing only a few gamma of the arsenical/liter was drawn through the silica gel. The color was not produced in air of high humidity, however.

The series of compounds 1,1-*bis*-(4-dimethylaminophenyl)-ethylene, -propene and -isobutene, when adsorbed on silica gel from benzene solution, gave colors on the gels, which were about the same as the color formed from the compounds and liquid arsenical.[4]

The formation of colored salts from the diarylethylenes must require a high electron density on the β-carbon. It was apparent that in some cases one β-methyl tended to lower, and two β-methyls greatly decreased the stability of the colored products from liquid arsenicals. This may be due to steric hindrance, or to the inductive effect of the alkyl groups in decreasing the electron density on the β-carbon. The inactivity of the β-phenyl compound is probably due to the same causes. These β-substituted compounds were prepared in the hope of increasing the stability of the ethylenes (by decreasing their tendency to oxidize or polymerize) without destroying their ability to form colored salts.

Although Wizinger[2] reports that diveratrylethylene (1,1-*bis*-(3,4-dimethoxyphenyl)-ethylene) forms more stable colored salts than dianisylethylene (1,1-*bis*-(4-methoxyphenyl)-ethylene), we found that this was not the case in the reaction with arsenicals. Since a methoxyl group in the meta position to the ethylenic side-chain cannot readily increase the reasonance possibilities of the cation, its effect on the stability of the colored salts would be expected to be slight.

It should be possible, by a study of the absorption curves of a series of colored salts of type II, in which R is varied while AX is held constant, to get more precise evidence as to the effectiveness of different electron-donating groups in stabilizing the positively-charged ion. Furthermore, with ortho substituted ethylenes, such as III, the steric inhibition of resonance structures with double bonds between the α-carbon and the aromatic rings should greatly diminish the tendency to form stable colored salts. Adams[5] and

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[1] The work described in this paper was done under Contract OEM-sr-319, recommended by the National Defense Research Committee, between the Office of Scientific Research and Development and the University of Rochester.

[2] (a) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928); (b) Wizinger, *J. prakt. Chem.*, **154**, 1 (1939). The latter paper gives a summary of a large amount of work on these compounds.

[3] Gates, THIS JOURNAL, **66**, 124 (1944).

[4] For other observations on the effect of adsorption on producing color, see Weitz and co-workers, *Z. Elektrochem.*, **47**, 65 (1941), and earlier papers, and Buu-Hoi and Cagniant, *Bull. soc. chim.*, **11**, 410 (1944); *C. A.*, **40**, 2134 (1946).

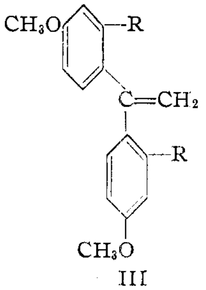
[5] Adams and Mecorney, THIS JOURNAL, **67**, 798 (1945), is the latest paper in this field.

TABLE I

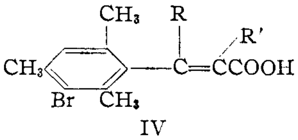
Compound	Color with liq. arsenical	Preparation yield,[a] %	Appearance and recrystallization solvent	M. p., °C.	Reported m. p.
1,1-*bis*-(4-Methoxyphenyl)-ethylene	Dark red	84	White platelets (benzene–alcohol)	142–144	142–143[b]
1,1-*bis*-(4-Methoxyphenyl)-propene	Dark red	80	White crystals (alcohol)	100–101	100–101[c]
1,1-*bis*-(4-Methoxyphenyl)-isobutene	No color	18[d]	White platelets (dilute alcohol)	65–66	64[c]
1,1-*bis*-(4-Methoxyphenyl)-2-phenylethylene	No color	59[e]	White platelets (alcohol)	61–65	59–64[f]
1,1-*bis*-(3,4-Dimethoxyphenyl)-ethylene	Transient purple	[g]	....	....	....
1,1-*bis*-(4-Dimethylaminophenyl)-ethylene	Intense blue-green	14	Pale yellow crystals (alcohol–benzene)	123–125	124[h]
1,1-*bis*-(4-Dimethylaminophenyl)-propene	Intense blue-green	65	Pale yellow needles (alcohol)	100.5–101.5	99–100[i]
1,1-*bis*-(4-Dimethylaminophenyl)-isobutene	Green	Low	Pale yellow-green crystals (dilute alcohol)	92–92.3	89[j]
1,1-*bis*-(4-Phenoxyphenyl)-ethylene	Orange red	[g]	....	....	....
1,1-*bis*-(4-Phenoxyphenyl)-propene	Faint transient pink	[g]	....	....	....
1,1-*bis*-(4-Methylthiolphenyl)-ethylene	Transient light green	[g]	....	....	....
1,1-*bis*-(4-Methylthiolphenyl)-propene	No color	[g]	....	....	....

[a] These compounds were made by the action of the appropriate Grignard reagent on the diaryl ketone, followed by dehydration. The yield given is that of purified product based on the amount of ketone used. [b] Coenen, Dissertation, Bonn (1935); borrowed from the Harvard University Library. [c] Ref. 2a, p. 145. [d] This compound was purified by distillation at 186–190° (3 mm.). [e] Difficulty was experienced in obtaining this compound in crystalline form. It was distilled twice, b. p. 230–235° (4 mm.) and only the middle portion of the distillate was collected the second time. The oil obtained crystallized after standing several days; it recrystallized slowly from alcohol. [f] Ley and Kirchner, *Z. anorg. Chem.*, **173**, 395 (1928). [g] See Experimental part. [h] Fecht, *Ber.*, **40**, 3902 (1907). [i] Freund and Mayer, *ibid.*, **39**, 1118 (1906). [j] Genioult, *Compt. rend.*, **152**, 963 (1911); **154**, 1623 (1912).

his students have shown that compounds of type IV, where R is methyl, chlorine or bromine, and R′ is methyl or hydrogen, can be resolved, indicating the hindrance to assumption of a coplanar structure. The ethylenes of type III would also be expected to have great hindrance to formation of a coplanar structure.



III



IV

The ultraviolet absorption curves for the ortho-substituted ethylenes III should be markedly different from those of the unsubstituted compounds I,[6] due to steric inhibition of some of the resonance structures.

Experimental

1,1-bis-(3,4-Dimethoxyphenyl)-ethylene.—This compound was prepared in low yield from *bis*-(3,4-dimethoxyphenyl) ketone[7] and methylmagnesium iodide. After several crystallizations from methanol, platelets with a very slight yellow tinge were obtained, of m. p. 98–99.5°. Since the literature[8] gives no m. p. or analysis, and the observed m. p. is close to that (95–96°) reported[7] for the intermediate carbinol, the compound was analyzed.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.71. Found: C, 71.98; H, 6.65.

The colored salts of the compound are mentioned in ref. 2b, p. 6, but no details are given.

1,1-bis-(4-Phenoxyphenyl)-ethylene.—To the Grignard reagent from 20 g. of 4-bromodiphenyl ether and 1.9 g. of magnesium in 100 cc. of ether and 50 cc. of benzene was added 3.5 cc. of ethyl acetate. After refluxing for twelve hours, the mixture was acidified and steam distilled for four hours. The non-volatile residue was taken up in benzene; after removal of the solvent, the product was recrystallized from ethanol four times to give a white powder, m. p. 103–105°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.69; H, 5.53. Found: C, 85.22; H, 5.47.

1,1-bis-(4-Phenoxyphenyl)-propene was prepared by the action of 4-phenoxyphenylmagnesium bromide on ethyl propionate. The product of this reaction was heated at 300° (35 mm.) to remove lower-boiling material. The residue was taken up in benzene and alcohol was added; crystals were obtained by permitting the solvent to evaporate partially. Two crystallizations from methanol gave white needles, m. p. 78–80°.

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(6) O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940), found a marked difference between the absorption curves for acetophenone or benzophenone, and their ortho-substitution products. The analogous case of the effect of ortho-substitution on the absorption of biphenyls has been studied by several workers (O'Shaughnessy and Rodebush, cited above; Williamson and Rodebush, *ibid.*, **63**, 3018 (1941); Remington, *ibid.*, **67**, 1838 (1945)).

(7) Kostanecki and Tambor, *Ber.*, **39**, 4022 (1906); Robinson, *J. Chem. Soc.*, **107**, 273 (1915).

(8) Vanzetti, *Gazz. chim. ital.*, **57**, 162 (1927); *C. A.*, **21**, 1974 (1927).

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 86.01; H, 5.76.

1,1-bis-(4-Methylthiolphenyl)-propene.—The Grignard reagent was prepared from 10 g. of 4-bromothioanisole[9] and 1.2 g. of magnesium in 130 cc. of ether and 50 cc. of benzene. Ethyl propionate (2 cc.) was added, the mixture refluxed gently for four hours, acidified, and steam distilled for three hours. The residue was extracted with benzene, and after the benzene was evaporated, 4 g. of crystals was obtained. After four crystallizations from alcohol, the compound was obtained as pale yellowish crystals, of m. p. 85.5–87.5°

Anal. Calcd. for $C_{17}H_{18}S_2$: C, 71.28; H, 6.33. Found: C, 71.34; H, 6.23.

1,1-bis-(4-Methylthiolphenyl)-ethylene was prepared in the same manner as the corresponding propene. After seven crystallizations from alcohol, it was a white amorphous material, m. p. 123–126° with preliminary sintering. The analysis indicated that it was still impure.

Anal. Calcd. for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 67.41; H, 7.25.

Summary

A number of unsymmetrical diarylethylenes, some of them new compounds, have been prepared, and their color reactions with various toxic agents studied. Lewisite and ethyldichlorarsine give colors with most of the compounds tested.

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[9] This was prepared in 95% yield by bromination of thioanisole and distilled at 138–143° (8 mm.); *cf.* Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 407 (1911).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1071]

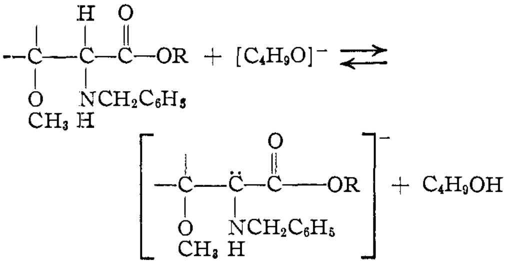
The Reduction of Ethyl α-Benzylamino-β-methoxy-n-caproate with Sodium and Butyl Alcohol

BY CARL NIEMANN AND CARL T. REDEMANN

Ethyl α-benzylamino-β-methoxy-n-caproate when subjected to the action of sodium and butyl alcohol is converted into 2-benzylamino-1-hexanol. The loss of a methoxy group from the former compound under the conditions of the Bouveault–Blanc reduction was not anticipated. However, with the experimental observation at hand an explanation of the observed phenomena may be offered.

It is reasonably certain that under the conditions of the reaction the following equilibrium (I) is established

(I)

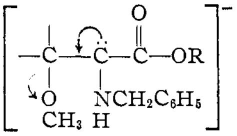


$$-\underset{\substack{|\\ O\\ CH_3}}{\overset{|}{C}}-\underset{\substack{|\\ NCH_2C_6H_5\\ H}}{\overset{\substack{H\\ |}}{C}}-\overset{\substack{O\\ \|}}{C}-OR + [C_4H_9O]^- \rightleftarrows \left[-\underset{\substack{|\\ O\\ CH_3}}{\overset{|}{C}}-\underset{\substack{|\\ NCH_2C_6H_5\\ H}}{\ddot{C}}-\overset{\substack{O\\ \|}}{C}-OR\right]^- + C_4H_9OH$$

The anion formed by the reaction of butoxide ion with the ester is a resonance hybrid and the structure indicated above is but one of the contributing structures but certainly an important one. Structures in which a proton is added to the nitrogen atom cannot be significant in the presence of a base such as butoxide ion though it is true that both the benzylamino group and the carbethoxy group contribute to the activation of the hydrogen on the α-carbon atom and thereby facilitate its removal as a proton.

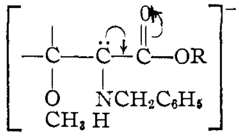
By analogy with the mechanism proposed for the base catalyzed dehydrohalogenation of alkyl halides[1] and the base catalyzed dehydration of β-hydroxy esters[2] one would expect that the unshared electron pair on the α carbon atom of the anion would tend to swing into the bond between the α and β carbon atoms and to thereby increase the ionic character of the carbon–oxygen bond of the β carbon atom (II). In the case at hand the

(II)



$$\left[-\underset{\substack{|\\ O\\ CH_3}}{\overset{|}{C}}-\underset{\substack{|\\ NCH_2C_6H_5\\ H}}{\ddot{C}}-\overset{\substack{O\\ \|}}{C}-OR\right]^-$$

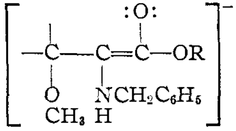
(III)



$$\left[-\underset{\substack{|\\ O\\ CH_3}}{\overset{|}{C}}-\underset{\substack{|\\ NCH_2C_6H_5\\ H}}{\ddot{C}}-\overset{\substack{O\\ \|}}{C}-OR\right]^-$$

tendency also exists for the unshared electron pair on the α carbon atom to swing into the bond between the α carbon atom and the carbonyl carbon atom and thereby augment the polarization of the carbonyl carbon–oxygen bond (III). This latter tendency gives rise to another important contributing structure, of the anion resonance hybrid, in which the unshared electron pair is on the carbonyl oxygen atom (IV).

(IV)



$$\left[-\underset{\substack{|\\ O\\ CH_3}}{\overset{|}{C}}-\underset{\substack{|\\ NCH_2C_6H_5\\ H}}{C}=\overset{\substack{:\ddot{O}:\\ |}}{C}-OR\right]^-$$

Thus while one of the contributing structures of the resonance hybrid of the anion tends to increase the ionic character of the carbon–oxygen bond of the β carbon atom and the other contributing

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[1] Hauser, THIS JOURNAL, **62**, 933 (1940).

[2] Hauser and Breslow, *ibid.*, **62**, 3344 (1940).