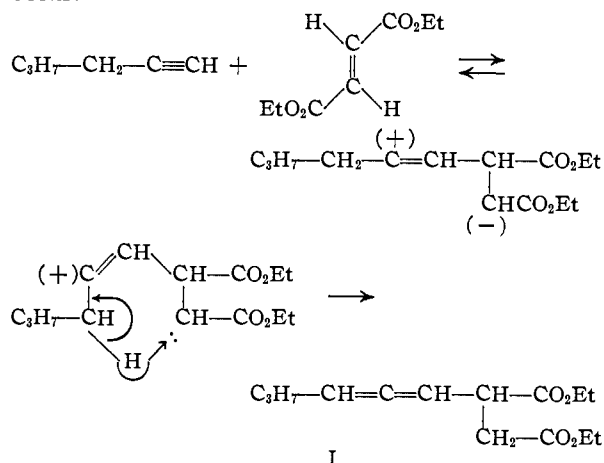


acid identified as *n*-hexylsuccinic acid. The monoadduct appears to have structure I.

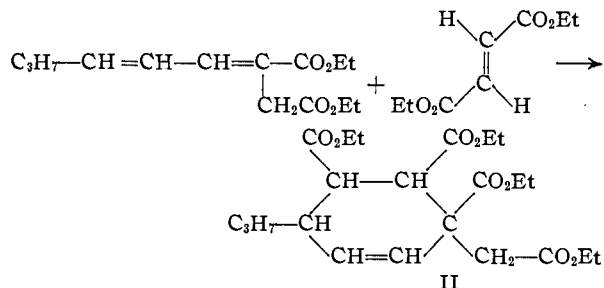
Discussion

Arnold and Dowdell³ have proposed that the reaction of monoolefins with dienophiles proceeds *via* a transient cyclic complex. The possibility of a short-lived ionic intermediate was not excluded. It also has been proposed¹ that when vinyl acetylenes react with dienophiles, the first product may be an allenic adduct. A combination of these two proposals satisfactorily explains our experimental results.

In the reaction of 1-hexyne and diethyl fumarate, a short-lived ionic intermediate appears to be necessary. Since the system C—C≡C is linear, addition and hydrogen transfer cannot be simultaneous; however, the formation of an ionic intermediate would allow the alkyl group to swing into position and the hydrogen transfer could then occur.



A probable mode of formation of the major product, the diadduct, then becomes apparent. Under the conditions of the reaction, rearrangement of the allene to a diene is likely,⁴ especially since an $\alpha,\beta,\gamma,\delta$ -di-unsaturated ester would be formed. The resulting diene could react with another molecule of diethyl fumarate to yield the diadduct II.



Experimental Details

Reaction of 1-Hexyne and Diethyl Fumarate.—A mixture of 30 g. of 1-hexyne (Farchan Research Labs.) and 200 g. of diethyl fumarate was heated in a stainless steel autoclave at

(3) R. T. Arnold and J. F. Dowdell, *THIS JOURNAL*, **70**, 2590 (1948).

(4) B. K. Mereshkowski, *J. Russ. Phys. Chem. Soc.*, **45**, 1940 (1913); G. Egloff, G. Hulla and V. I. Komarevsky, "Isomerization of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1942, p. 73.

230° for 4 hr. On distillation, 10.5 g. of 1-hexyne and 116 g. of diethyl fumarate were recovered. The minor product, 4 g., b.p. 140–150° (6 mm.), and the major product, 50.5 g., b.p. 195–199° (1 mm.), n_D^{25} 1.4641, were isolated by distillation. The major product was found by analysis to correspond to a 2:1 diethyl fumarate/1-hexyne adduct.

Anal. Calcd. for C₂₂H₃₄O₈: C, 62.0; H, 8.0. Found: C, 61.9; H, 8.2.

Infrared absorption at 6.0 and 10.3 μ indicated internal unsaturation; the spectrogram showed no allenic band at 5.1 μ . No further characterization of this adduct was undertaken.

Structure of the Monoadduct.—The infrared absorption spectrogram of this adduct showed a strong band at 5.1 μ characteristic of allenes.⁵ For identification, the adduct was hydrogenated in methanol at 2–3 atmospheres hydrogen pressure with a 10% palladium-on-charcoal catalyst, and the hydrogenated product was saponified with alcoholic potassium hydroxide by standard procedures. The acid obtained was identified as *n*-hexylsuccinic acid by conversion to *n*-hexylsuccinamic acid, m.p. 119–121° (lit.⁶ 122°). The melting point was undepressed on admixture with the anilic acid prepared from an authentic sample of *n*-hexylsuccinic acid made essentially by the method of Alder, Söll and Söll.⁷

As a further check, the unknown acid was converted to its *p*-toluidide, m.p. 78–80°. The melting point was unchanged on mixing with a sample of *N-p*-tolyl-*n*-hexylsuccinimide prepared from the authentic sample of *n*-hexylsuccinic acid.

Anal. Calcd. for C₁₇H₂₃O₂N: C, 74.7; H, 8.5; N, 5.1. Found: C, 74.1; H, 8.4; N, 5.2.

(5) J. H. Wotiz and W. D. Celmer, *THIS JOURNAL*, **74**, 1860 (1952); R. B. Barnes, R. C. Gore and R. W. Stafford, *Anal. Chem.*, **20**, 402 (1948).

(6) A. Higson and J. F. Thorpe, *J. Chem. Soc.*, **89**, 1471 (1906).

(7) K. Alder, H. Söll and H. Söll, *Ann.*, **565**, 75 (1949).

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The Indicator and Dye Properties of Some Aromatic Phosphonic Acids and their Arsenic Analogs

BY GENNADY M. KOSOLAPOFF AND GERALD G. PRIEST

RECEIVED JUNE 1, 1953

It is not uncommon to find in reviews and treatises dealing with dyestuffs a mention of the possibilities of the utilization of acidic groups other than the commonly employed sulfonic acids in synthesis of materials that have dyeing properties. Yet, one is unable to find concrete information about the fundamental properties of such dye analogs in the chemical literature. It was in order to supply such data that the present study was made. The model substances selected for analog variations were methyl orange, ethyl orange and congo red. This choice, for the present investigation, was made for two reasons. The synthesis of analogs of these dyes containing either the phosphonic or the arsenic acid residues can be accomplished quite readily from easily obtainable intermediates. At the same time, the relatively small molecules of these analogs should be expected to display any property differences more readily than more complex dye molecules. Finally, since the sulfonate model compounds are rather well known indicators, the present choice of the analogs permits, as well, a comparison of the indicator properties of these substances.

Generally, the dyeing properties of the compounds under present consideration can be summa-

TABLE I

Compound	pH range	Color change
I, <i>p</i> -Me ₂ NC ₆ H ₄ N ₂ C ₆ H ₄ PO ₃ H ₂ - <i>p</i>	3.0-4.7-5.9	Red-red orange-orange
II, <i>p</i> -Me ₂ NC ₆ H ₄ N ₂ C ₆ H ₄ AsO ₃ H ₂ - <i>p</i>	1.6-4.7-5.5	Red-orange-yellow
III, <i>p</i> -Et ₂ NC ₆ H ₄ N ₂ C ₆ H ₄ SO ₃ H- <i>p</i>	3.3-5.0	Red-orange red
IV, <i>p</i> -Et ₂ NC ₆ H ₄ N ₂ C ₆ H ₄ PO ₃ H ₂ - <i>p</i>	3.5-5.8	Red-orange red
V, <i>p</i> -Et ₂ NC ₆ H ₄ N ₂ C ₆ H ₄ AsO ₃ H ₂ - <i>p</i>	2.1-4.9-5.5	Orange red-orange-yellow orange
VI, [<i>p</i> -(1-NH ₂ -2-N ₂ -4-PO ₃ H ₂ -C ₁₀ H ₈)C ₆ H ₄] ₂	2.2-5.3-6.4	Blue-brown-orange red
VII, [<i>p</i> -(1-NH ₂ -2-N ₂ -4-AsO ₃ H ₂ -C ₁₀ H ₈)C ₆ H ₄] ₂	0-2.6-5.8	Purple-brown-yellow orange

rized as follows. The phosphonic and the arsonic acid analogs of methyl orange and ethyl orange showed almost no affinity for cotton fabrics, as expected. They were, however, very readily applied, with good leveling properties, to specimens of silk and wool fabrics. The phosphonic and the arsonic acid analogs of congo red were found to be excellent direct dyes for cotton, as well as silk and wool. The dyed fabric specimens were tested for wash-fastness by laundering with a commercial type of a sodium alkyl sulfate detergent. All the dyes that showed affinity for the various fabrics, as listed above, showed excellent fastness and no evidence of fading or running. The detergent employed contained an alkaline builder which did cause some color changes that were expected from the indicator nature of the dyes used. The colors deposited on the various fabrics corresponded to the colors displayed normally by the various substances at the pH values employed.

The indicator properties of the dyes are summarized in the data of Table I.

The positions of the first absorption maxima exhibited by these substances on both the acid and the base side of the indicator color changes were determined

Compound	Abs. max., m μ	pH	Compound	Abs. max., m μ	pH
Methyl orange	562	2.1	IV	594	2.5
	554	6.0		605	6.8
I	554	2.0	V	570	1.1
	542	7.0		565	6.5
II	549	1.1	VI	620	0.5
	544	6.0		575	8.0
III	574	2.0	VII	612	Ca. 0
	557	6.0		552	8.0

Experimental Part

Preparation of the Compounds

Preparation of the Phosphonic Analog of Methyl Orange (I).—*p*-Bromobenzenephosphonic acid was prepared from the corresponding fluoborate of diazotized *p*-bromoaniline¹ in 60% yield; m.p. 202°. The bromo derivative was aminated under pressure at 100°,^{2,3} with cuprous oxide catalyst. The following yields of phosphanilic acid were obtained after amination for various intervals: 23.6% after 2 hours, 57% after 5 hours, 80% after 6 hours, 63.5% after 9 hours and 52.5% after 10 hours.

Phosphanilic acid (3.36 g.) was dissolved in 200 ml. of water containing 5.3 g. of sodium carbonate and the solution was cooled to 0°. After addition of 3.34 g. of sodium nitrite to the above solution, it was treated with stirring with precooled (0°) 6 *N* hydrochloric acid (19 ml.). After ten minutes' standing this solution was treated with 6.15 ml. of dimethylaniline dissolved in 45.6 ml. of *N* hydrochloric acid. The solution was adjusted to pH 5 by means of 20% sodium hydroxide and stirred slowly for four hours.

An excess of sodium acetate was added and the precipitated product was collected on a filter and washed with water until free of the chloride ion. The product was reprecipitated from sodium hydroxide solution with 3 *N* hydrochloric acid, washed as above and dried *in vacuo*, yielding 87% of I as a dark red microcrystalline powder.

Anal. Calcd. for C₁₄H₁₆O₃N₃P: P, 10.2. Found: P, 10.22.

Preparation of the Arsonic Analog of Methyl Orange (II).—*p*-Nitrobenzenearsonic acid was prepared in 79% yield from the corresponding diazonium fluoborate.⁴ The *p*-nitro acid was reduced to arsanilic acid, by ferrous hydroxide in 10% sodium hydroxide, in 79% yield. Arsanilic acid was coupled with dimethylaniline, as described under I and the mono-sodium salt of II was isolated in the usual manner.⁵

Preparation of Ethyl Orange (III).—This substance was prepared by the usual coupling of sulfanilic acid with diethylaniline, instead of dimethylaniline.⁶

Preparation of the Phosphonic Analog of Ethyl Orange (IV).—The preparation of I was duplicated with diethylaniline, instead of dimethylaniline, as the coupling agent. The product was obtained as a scarlet powder, which was secured in 71% yield.

Anal. Calcd. for C₁₆H₂₀O₃N₃P: P, 9.3. Found: P, 9.36.

Preparation of the Arsonic Analog of Ethyl Orange (V).—The preparation of II was duplicated with diethylaniline as the coupling agent. The product isolated as a red powder, was obtained in 37.6% yield.

Anal. Calcd. for C₁₆H₂₀O₃N₃As: As, 19.9. Found: As, 19.73.

Preparation of the Phosphonic Analog of Congo Red (VI).—4-Nitro-1-aminonaphthalene was prepared by acetylation and nitration of 1-naphthylamine.⁷ This was converted to the corresponding diazonium fluoborate by treatment of the diazotized material with sodium fluoborate solution; the fluoborate was obtained in 71.5% yield and decomposed at 137°. It was converted to 4-nitronaphthalenephosphonic acid by the usual method¹ in ethyl acetate solution with cuprous chloride catalyst. The acid, after crystallization from hot water, was obtained in 45.5% yield in the form of light yellow needles, which decomposed about 220°.

Anal. Calcd. for C₁₀H₈O₃NP: P, 12.25. Found: P, 12.29.

The nitro acid was reduced with ferrous hydroxide in aqueous sodium hydroxide at pH 10 and the resulting 4-aminonaphthalenephosphonic acid was recrystallized from a large volume of hot water, after initial precipitation at pH 5. The compound forms tiny light yellow needles, which decompose to a purple liquid at about 170°. The yield of the amino acid was 83%.

Anal. Calcd. for C₁₀H₁₀O₃NP: P, 13.9. Found: P, 13.82.

Benidine (3.68 g.) was dissolved in 9.6 ml. of concentrated hydrochloric acid and 60 ml. of water, and the resulting solution, after cooling to 0°, was treated with 2.76 g. of sodium nitrite in 20 ml. of water. After stirring for 15 minutes, the diazo solution was treated with 9.2 g. of the above amino acid in the form of its mono-sodium salt in the presence of 16.7 g. of sodium acetate in 200 ml. of water. The mixture was adjusted to pH 6 with 10% hydrochloric

(4) *Org. Syntheses*, **19**, 40 (1939); **26**, 60 (1946).

(5) M. Barrowcliff, F. L. Pyman and F. G. Remfry, *J. Chem. Soc.* **92**, 1898 (1908).

(6) H. Lucas and D. Pressman, "Principles and Practice of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 283.

(7) C. R. Saunders and C. S. Hamilton, *THIS JOURNAL*, **54**, 686 (1932).

(1) G. O. Doak and L. D. Freedman, *THIS JOURNAL*, **75**, 683 (1953).

(2) H. Bauer, *ibid.*, **63**, 2137 (1941).

(3) G. M. Kosolapoff, *ibid.*, **69**, 2112 (1947).

acid and stirred for two hours at 0°, after which it was saturated with sodium chloride. The precipitated product was dried *in vacuo* after washing until free of the chloride ion. The mono-sodium salt was obtained as a dark-red powder, soluble in cold alkali, sparingly soluble in hot concentrated hydrochloric acid, and very little soluble in cold or hot dilute hydrochloric acid. The yield was 93.5%.

Anal. Calcd. for $C_{32}H_{28}O_6N_6P_2Na$: P, 9.2. Found: P, 9.31.

Preparation of the Arsonic Analog of Congo Red (VII).—4-Nitronaphthalenearsonic acid was prepared according to Saunders and Hamilton⁷ in 80% yield and the product was reduced with ferrous hydroxide as described above. The product, purified by reprecipitation from 10% sodium hydroxide with 3 *N* hydrochloric acid, formed light yellow plates, which decomposed at 215°; yield 69.5%. Coupling of the amino acid with benzidine was carried out as described under VI and the product was isolated in 69% yield as a dark-red mono-sodium salt, whose properties were similar to those of VI.

Anal. Calcd. for $C_{32}H_{25}O_6N_6As_2Na$: As, 19.65. Found: As, 19.7.

Determination of Indicator Properties.—The various substances were dissolved in 0.01 *N* hydrochloric acid and the colors of the solutions were observed while either 0.1 *N* sodium hydroxide or 0.1 *N* hydrochloric acid was added to the system. Upon establishment of color the *pH* of the system was determined with a *pH* meter. An average of four determinations was made on each compound, with reproducibility of 0.1 *pH* unit. It must be noted that VII failed to develop its full purple color until the solution was very strongly acid.

Dyeing Experiments.—The Indian Head cotton cloth used for the tests was desized by boiling with sodium alkyl sulfonate detergent and the thoroughly washed strips were treated with the various dyes (I–VII) in saturated solutions which were adjusted to *pH* 8 with stirring for 30 minutes at 80–90°. The specimens were then removed, immersed in 1% hydrochloric acid, thoroughly rinsed and air-dried. The dyeing of silk and wool fabrics was done directly by immersion into a saturated solution of each dye for five minutes at 95°, followed by stirring at this temperature for 25 minutes. A drop of hydrochloric acid was placed into the dye solution (100 ml. of water) to facilitate solution. After washing, the specimens were air-dried.

Absorption Measurements.—Saturated solutions of the dyes in water at the various *pH* levels were examined by means of a Beckman DU model quartz spectrophotometer. The congo red analogs were examined in absolute alcohol solution owing to their low solubility in aqueous medium within *pH* ranges employed. Readings of optical density were taken at 2- μ intervals from the low-frequency side until the first maximum was passed.

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Reduction of 3-(2-Pyridyl)-propionaldehyde

BY F. M. MILLER

RECEIVED JUNE 3, 1953

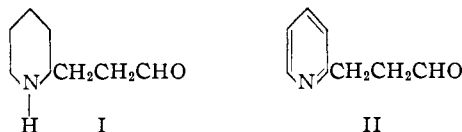
Previous attempts at preparation of the highly unstable pomegranate alkaloid pelletierine (I) have been made by hydrolysis of its acetal,^{1,2} available from the corresponding pyridine compound by hydrogenation, and by lithium aluminum hydride reduction of 3-keto-octahydropyrrocoline.³ These methods failed, presumably due to aldolization catalyzed by the basic piperidine nitrogen atom.

(1) J. P. Wibaut and M. G. J. Beets, *Rec. trav. chim.*, **60**, 905 (1941); M. G. J. Beets, *ibid.*, **62**, 553 (1943).

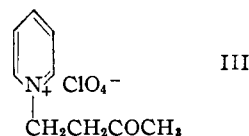
(2) M. A. Spielman, S. Swadesh and C. W. Mortensen, *J. Org. Chem.*, **6**, 780 (1941).

(3) J. A. King, V. Hofman and F. H. McMillan, *ibid.*, **16**, 1100 (1951); F. Galinovsky, O. Vogel and R. Weiser, *Monatsh.*, **83**, 114 (1952).

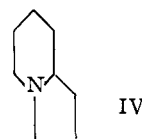
It was reasoned that if the sequence of the two reactions of the first method be reversed, *i.e.*, hydrolysis of the acetal of the pyridylpropionaldehyde (II, dehydropelletierine) followed by reduction of the pyridine ring, that the lower basicity of the nitrogen function of II, particularly in the form of a salt, such as the hydrochloride, might permit the direct formation of I.



Dehydropelletierine has been reported as an unstable base,¹ but in this work it has been found to be quite stable as the hydrochloride. Hope for reduction of the pyridine ring of II without affecting the carbonyl group was based on the previously observed⁴ selective reduction of the pyridine ring of the quaternary ketone III.



Reduction of dehydropelletierine hydrochloride in alcohol⁵ gave only octahydropyrrocoline (IV). Similar behavior has been observed in reduction of the acetal of II in both hydrochloric and acetic



acids, although it was found that increasing the concentration of the acetic acid solution of the acetal gave pelletierine acetal as the major product rather than IV.¹

Attempts to control the reduction of II hydrochloride by increasing its concentration in alcohol were without effect. When reduction was carried out in glacial acetic acid at high concentrations the solution became dark, even during the reaction, and from the tarry product the only crystalline derivatives obtainable were those of small amounts of octahydropyrrocoline. Although crystalline derivatives of I could not be isolated, the occurrence of tars in the manner observed indicates the probable formation and subsequent polymerization of pelletierine during the course of the reduction.

Acknowledgment.—The author wishes to acknowledge the technical assistance of Mr. Frank Vasington.

Experimental⁶

Dehydropelletierine (II).—A solution of 10 g. of 3-(2-pyridyl)-propionaldehyde diethyl acetal² in 10 ml. of 10% hydrochloric acid and 15 ml. of alcohol was refluxed for three hours. The alcohol was removed under vacuum and the solution was made basic with 10% sodium carbonate and extracted with ether. The ether extracts were dried over sodium sulfate, evaporated and the residue distilled. The fraction boiling at 106–108° at 9 mm. was collected as a

(4) F. M. Miller, unpublished results.

(5) T. S. Hamilton and R. Adams, *THIS JOURNAL*, **50**, 2260 (1928).

(6) Melting points observed on a Fisher-Johns melting point block. Analyses by Oakwold Laboratories, Alexandria, Virginia.