[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY]

Absorption Spectra of Some Nitrostyrenes

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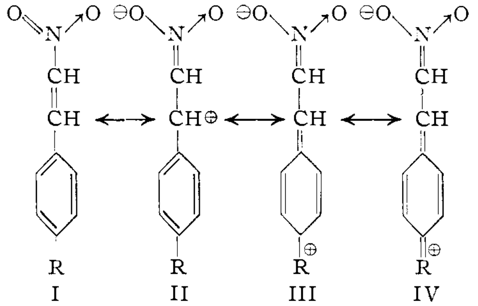
The absorption spectra of a series of substituted nitrostyrenes have been measured and the relative positions of the absorption maxima correlated with the "electrometric polarizability" of the various substituents. Secondary effects based on resonance structures not involving the nitrovinyl group and on inductive tendencies of the substituents are also discussed.

In a study of the kinetics of Michael-type additions to ring substituted β-nitrostyrenes,[1] it was found convenient to measure reaction rates by following the disappearance of the characteristic nitrostyrene absorption bands in the ultraviolet. Since such data for many of these compounds were not available, the absorption spectra of a series of nitrostyrenes in methanol were measured over the range 240 to 450 mμ.

The absorption by β-nitrostyrene at 310 mμ can be related to the primary benzene band at 204 mμ. Doub and Vandenbelt[2] have shown that substitution on benzene by a nitro group, as in nitrobenzene, shifts the primary band about 60 mμ toward the visible without appreciably changing the molar absorptivity. As shown in Table I, extension of the conjugated system by introduction of the vinyl group to give β-nitrostyrene extends the bathochromic shift an additional 50 mμ with an increase of 8500 in the molar absorptivity. This compares with a shift of 40 mμ and an increase in molar absorptivity of 9200 in going from benzene to styrene. Similarly, the ring-substituted β-nitrostyrenes show bathochromic shifts of 36 to 54 mμ and, with the exception of the *m*,β-dinitro compound, increases in molar absorptivity of 7200 to 9500 when compared with the correspondingly substituted nitrobenzenes.

Absorption by the nitrostyrenes in the ultraviolet probably arises from transitions involving the uncoupling of pairs of π-electrons to form essentially ionic excited states. These excited states bear a formal similarity to the hypothetical structures which explain stability and charge distribution in the ground state (II–IV) and are themselves subject to resonance stabilization to a more marked extent than the ground state.

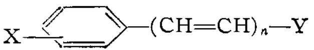


plus two ortho structures

If we may compare the excited state in electronic transitions with the transition state in chemical reactions, the stabilization of the excited state relative to the ground state due to the contribution of resonance structures such as IV is a measure of Ingold's "electromeric polarizability" of the various substituent groups.[3] This stabilization involving

TABLE I

ABSORPTION MAXIMA FOR VARIOUS NITROSTYRENES AND NITROBENZENES[a]



Compound X	Y	Primary absorption band, n = 1, λ, mμ	n = 1, ε × 10^{-4}	n = 0, λ, mμ	n = 0, ε × 10^{-4}	Shift due to vinyl group, Δλ, mμ	Shift due to vinyl group, Δε × 10^{-4}
H	H	244(AE)[b]	1.70	204(H)	0.78	40	0.92
H	NO_2	310(M)	1.65	260(E)[c]	.80	50	.85
		309(AE)[d]	1.65				
4-NO_2	NO_2	304(M)	2.19	258(M)	1.47	46	.72
3-NO_2	NO_2	271(M)	1.69	235(E)[c]	1.74	36	−0.05
4-Cl	NO_2	315(M)	1.91	270(AE)[e]	1.13	45	0.78
4-CH_3O	NO_2	350(M)	2.04	305(AE)[f]	1.30	45	.74
3,4-CH_2O_2	NO_2	363(M)[g]	1.60	....	..	..	..
4-$(CH_3)_2N$	NO_2	436(M)[h]	2.78	387(AE)[i]	1.83	49	.95
		435(AE)[j]	2.85				
4-$(CH_3)_2NH^+$	NO_2	294(M)[k]	1.75	240(HCl)[e]	0.80	54	.95
4-NO_2	H	300(M)[l]	1.39	260(E)[c]	0.80	40	.59
2,4,6-$(NO_2)_3$	H	No peak[m]	..	225(E)[c]	2.57	..	..

[a] Solvent in parentheses: M = methanol, AE = absolute ethanol, E = 95% ethanol, H = heptane, HCl = concentrated hydrochloric acid. [b] Ref. 6. [c] P. Fielding and R. J. W. LeFèvre, *J. Chem. Soc.*, 2812 (1950). [d] E. A. Braude, E. R. H. Jones and G. G. Rose, *ibid.*, 1104 (1947). [e] R. A. Morton and A. McGookin, *ibid.*, 901 (1934). [f] A. Burawoy and J. T. Chamberlain, *ibid.*, 2313 (1952). [g] Secondary band: ε (257) 8640; inflection: ε (310) 5600. [h] Secondary bands: ε (262) 10070; ε (312) 1970. [i] Ref. 7. [j] D. J. Drain and W. Wilson, *J. Chem. Soc.*, 767 (1949). [k] The solution was 0.1 *N* in HCl and the molar absorptivity was corrected for the concentration of free base as determined from the absorbance at 436 mμ. [l] M. Pestemer, T. Langer and F. Manchen, *Monatsh.*, **68**, 326 (1936), report λ_{max}, 303 mμ, ε 14,500. [m] No peaks were observed between 240 and 350 mμ; slight inflection ε (325) *ca.* 1000.

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(1) M. J. Kamlet and D. J. Glover, to be published.

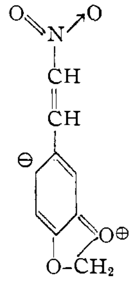
(2) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 73 ff.

π-bond formation by electrons initially on the substituent group would be expected to increase as R is varied from H to *p*-Cl to *p*-CH_3O to *p*-$(CH_3)_2N$. As shown in Table II this is the observed order of the bathochromic shift. By Ingold's definition, electromeric effects are strongly unidirectional, –M groups such as the *p*-nitro giving strong $-E$ effects in reactions (electronic transitions) in which the electrical needs of the reaction center (excited state) are of the right sign, but only weak $+E$ effects in reactions (transitions) in which the electrical needs are of the opposite sign. In the case of *p*,β-dinitrostyrene, therefore, the electromeric effect is probably nil, or at most only a slight factor in determining the stability of the excited state.

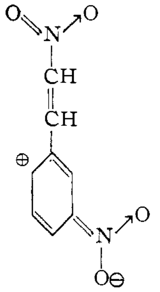
On the basis of electromeric polarizability alone, it is hard to account for the relative positions of the absorption maxima of *p*-methoxy-β-nitrostyrene (350 mμ) and the 3,4-methylenedioxy substituted compound (363 mμ). The 3,4-methylenedioxy group is more weakly electron-releasing than the *p*-methoxyl as evidenced by its less negative Hammett σ-constant,[4] and resonance structures like IV would be expected to contribute somewhat less to the stability of the excited state.

This situation may be rationalized, however, by considering the secondary effect of a resonance structure such as V in which the nitrovinyl group is not involved. Such resonance may, by increasing the electron density at the *ortho* and *para* positions, facilitate transition to the excited state by stabilizing resonance structures such as III in which these positions bear a positive charge. Thus, in comparing the methoxy with the methylenedioxy compounds, the additional contribution of structure V in the methylenedioxy may offset the slightly greater polarizability effect of the methoxyl group in structure IV.



V

plus two
ortho structures



VI

plus two
ortho structures

A similar secondary effect may account, at least partially, for the hypsochromic shift in the case of the *m*,β-dinitro compound. Here the effect of resonance structure VI is to decrease the electron density at the *ortho* and *para* carbons, thus labilizing structure III in both ground and excited states (but again to a greater extent in the excited state).[5]

Still a third factor which influences the positions of the various absorption maxima evolves from the electron-withdrawing inductive tendency of all the substituent groups in Table II. By withdrawing electrons from all positions in the ring this also tends toward the destabilization of structures like III with a corresponding relative increase in the energy of the excited state. Where strong electromeric effects obtain, this factor is easily overbalanced, but in the case of the *m*-nitro-, *p*-nitro- and *p*-dimethylammonium compounds it contributes significantly to the observed hypsochromic shift.

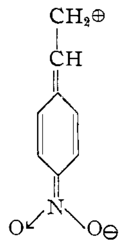
TABLE II

DISPLACEMENT OF THE ABSORPTION MAXIMUM OF β-NITROSTYRENE WITH RING SUBSTITUTION

$+$ = bathochromic shift

	Predicted effect of			
Substituent, X	Electromeric polarizability	Secondary resonance structures	Inductive tendency of X	Observed shift, mμ
m-NO_2	Nil	$(-)$	$(-)$	-39
p-$(CH_3)_2NH^+$	Nil	Nil	$(-)$	-16
p-NO_2	Nil	Nil	$(-)$	-6
H	Nil	Nil	Nil	0
p-Cl	$(+)$	Nil	$(-)$	$+5$
p-CH_3O	$(+)$	Nil	Slight $(-)$	$+40$
3,4-CH_2O_2	$(+)$	$(+)$	Slight $(-)$	$+53$
p-$(CH_3)_2N$	$(+)$	Nil	Slight $(-)$	$+126$

It is of interest to note that the spectrum of *p*-nitrostyrene very closely approximates that of the β-nitro isomer. The slightly lower λ_{max} and molar absorptivity may be due to a somewhat lesser stability of resonance structure VII involving a positive charge on the primary carbon atom as compared with the corresponding structure (II, R = H) in which a secondary benzyl carbon atom supports the positive charge.



The failure of 2,4,6-trinitrostyrene to show a peak above 240 mμ may result from steric inhibition of resonance. Similar phenomena with like compounds have been adequately discussed.[6,7]

Experimental[8]

Preparation and Purification of Materials.—2,4,6-Trinitrostyrene, kindly supplied to these laboratories by Dr. R. H. Wiley of the University of Louisville, was recrystallized from carbon tetrachloride and melted at 63.5–64.5°.[9] *p*-Nitrostyrene purchased from the Monomer-Polymer Chemical Co., Leominster, Mass., was recrystallized from carbon tetrachloride–hexane and melted at 28°. The preparation of the substituted β-nitrostyrenes is described in a previous paper.[10] Fisher Certified Reagent methyl alcohol was used without further purification.

Absorption Spectra.—Ultraviolet absorption spectra were

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(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

(5) The decrease in λ_{max} in going from nitrobenzene to *m*-dinitrobenzene to 2,4,6-trinitrobenzene may be attributable to a similar secondary effect. This problem is presently being investigated by Rip G. Rice of these laboratories.

(6) Y. Hirschberg, THIS JOURNAL, **71**, 3241 (1949).

(7) W. R. Remington, *ibid.*, **67**, 1838 (1945).

(8) All melting points are uncorrected.

(9) For the preparation of this compound, see R. H. Wiley and L. C. Behr, THIS JOURNAL, **72**, 1822 (1950).

(10) M. J. Kamlet, *ibid.*, **77**, 4896 (1955).

determined with a model DU Beckman spectrophotometer in 1-cm. quartz cells, point by point absorbance measurements being made at 2-mμ intervals or less. Concentrations were 1×10^{-3} to 1×10^{-5} mole per liter in methanol which was 0.1 *N* in hydrochloric acid except in the case of *p*-dimethylamino-β-nitrostyrene. In the latter case pure methanol was used in determining the spectrum of the free base. A methanolic solution 5 *N* in hydrochloric acid gave the spectrum of the conjugate acid, but the large amount of water in the methanol shifted the absorption maximum from 294 to 300 mμ (ε 18,000) presumably due to a solvent effect.[11] In the 0.1 *N* solution in methanol, peaks appeared for the free base at 436 mμ and for the conjugate acid at 294 mμ. The concentration of free base under these circumstances was calculated and a correction applied in calculating the molar absorptivity of the conjugate acid.

It was necessary to carry out all dilution operations in "low actinic" glassware and to avoid light wherever possible. Otherwise the nitrostyrenes in dilute solutions showed fading absorbancies at the $\lambda_{max.}$. This phenomenon, probably due to a light-catalyzed reaction,[12] led to absorbancy readings which differed by as much as 30% in the morning and afternoon or on a cloudy or sunny day, and depended to a great extent on the speed with which the operations were carried out. The use of protective "low actinic" glassware eliminated these difficulties and gave reproducible spectra.

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[11] D. J. Drain and W. Wilson, ref. *j*, Table I, report λ_{max} 305–308, ε 18,500 in 5 *N* aqueous HCl.

[12] Dr. Harold Shechter has pointed out that β-nitrostyrene undergoes a light-catalyzed dimerization [see B. Priebs, *Ann.*, **225**, 339 (1884); J. Meisenheimer and F. Heim, *ibid.*, **335**, 260 (1907)]. The structure of the dimer is presently being investigated at the Ohio State University by Dr. Shechter and D. Miller.

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[CONTRIBUTION FROM ROHM & HAAS CO.]

The Aminomethylation of Olefins. II. A New Synthesis of 1-Alkyl-4-aryl-4-piperidinols

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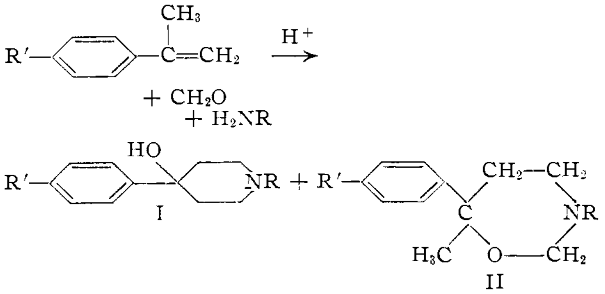
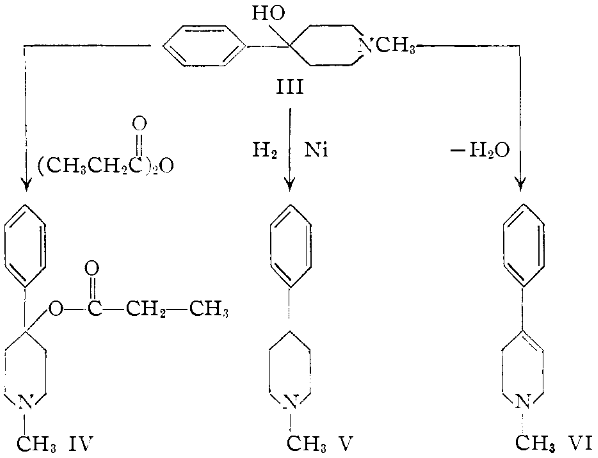
A new and relatively simple synthesis of 1-alkyl-4-aryl-4-piperidinols from α-methylstyrenes, formaldehyde and primary amine salts is reported.

It has been reported[1] that esters of 1-alkyl-4-aryl-4-piperidinols (I) are potent analgesics. Previously these piperidinols have been prepared[2-4] by the reaction of arylmagnesium halides or lithium aryls with 1-alkyl-4-piperidones. We have found that 1-alkyl-4-aryl-4-piperidinols (I) are formed along with 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (II) by the reaction of α-methylstyrenes, formaldehyde and primary amine salts.



While this work was in progress, Hartough, *et al.*,[5] reported that the reaction of α-methylstyrene, formaldehyde and methylamine hydrochloride gave 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine, but they did not identify 1-methyl-4-phenyl-4-piperidinol (III) as one of the products. The physical properties of the latter material III and those of its derivatives were found to agree with values reported in the literature.[2-4] Esterification with propionic anhydride gave 1-methyl-4-phenyl-4-propionoxypiperidine (IV), hydrogenolysis gave 1-methyl-4-phenylpiperidine (V) and dehydration gave 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (VI).



It therefore is the purpose of this paper to report on the 1-alkyl-4-aryl-4-piperidinols (I) which we have prepared by this new synthesis. These are summarized in Table I.

The reaction proceeds well in an aqueous medium thus making it possible to use aqueous formaldehyde, aqueous amine solutions and concentrated hydrochloric acid if desired. The formation of 1-methyl-4-phenyl-4-piperidinol (III) may be shown

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[1] R. H. K. Foster and A. J. Carman, *J. Pharmacol. Exptl. Therap.*, **91**, 195 (1947).

[2] K. A. Jensen and F. Lundquist, *Dansk. Tids. Farm.*, **17**, 173 (1943); *C. A.*, **39**, 2506 (1945).

[3] K. A. Jensen, U. S. Patent 2,589,943 (March 18, 1952); *C. A.*, **46**, 11249 (1952).

[4] A. Ziering, L. Berger, S. D. Heineman and J. Lee, *J. Org. Chem.*, **12**, 894 (1947).

[5] H. D. Hartough, J. J. Dickert and S. L. Meisel, U. S. Patent 2,647,117 (July 28, 1953); *C. A.*, **48**, 8265 (1954).