

yield a mixture of fatty acids having a specific activity of 1695 d./sec./mg. Bromination of a 98.7-mg. sample of the fatty acid mixture in 3.5 ml. of *n*-pentane according to White and Brown¹⁹ gave 83.85 mg. of crude *threo,threo*-9,10,12,13-tetrabromooctadecanoic acid (TBS) and showed the mixture to contain 89% linoleic acid. (Preliminary experiments with corn oil fatty acids and with linoleic acid¹⁸ gave 65 and 95% linoleic acid, respectively, in good agreement with the expected values.) The crude TBS and successive recrystallized (from acetone) samples had specific activities of 92.1, 23.0, 18.3, and 17.0 d./sec./mg., the last corresponding to a linoleic acid content in the oleic-1-C¹⁴ acid of 1.90%.

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(19) M. F. White and J. B. Brown, *J. Am. Oil Chem. Soc.*, **26**, 385 (1949).

Diels-Alder Reactions of *o*-, *m*-, and *p*-Nitrostyrene¹

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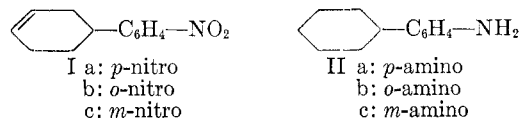
The electrophilic properties of 2- and 4-vinylpyridine and of the electronically similar *o*- and *p*-nitrostyrene have been amply verified in recent years. Thus, it has been shown that these compounds readily undergo Michael-type addition at the double bond with a wide variety of nucleophiles.² That this behavior may be traced directly to the conjugation of the ethylenic linkage with the electronegative imino or nitro group is indicated by the lack of reactivity of 3-vinylpyridine and of *m*-nitrostyrene under the same conditions.^{2a-c}

Although a detailed description of the mechanism of the Diels-Alder reaction is still lacking, it is generally assumed that the activity of the dienophile may be correlated with the degree of activation of the olefinic bond by electronegative groups acting through conjugation.³ In view of these facts, it seemed reasonable to expect enhanced dienophilic properties in those vinyl aromatics for which electrophilic properties had been demonstrated.² Doering and Rhoads explored this possibility with 2- and 3-vinylpyridine⁴; their results, while confirming the activity of 2-vinylpyridine, also revealed 3-vinylpyridine as an equally effective

dienophile. In order to test the generality of this lack of differentiation among position isomers, the study has now been extended to the nitrostyrene series.⁵

So that a direct comparison might be made in this series, a standard set of reaction conditions was used. Butadiene served as the reference diene in all cases. Preliminary runs indicated that a reaction temperature of 125° and a mole ratio of diene to dienophile of *ca.* 2.5 to 1 brought about appreciable reaction over a period of 20 to 40 hr. while minimizing the concurrent polymerization. Even so, the latter was appreciable and necessitated the development of isolation procedures which would assure the best yields of adducts. The thermal stability of the adducts under the reaction conditions was examined by heating them alone at 125° or higher for 40 hr.

The reaction of *p*-nitrostyrene and butadiene proceeded readily under the reaction conditions to yield the adduct, 4-(*p*-nitrophenyl)cyclohexene (Ia). The structural assignment is based on analysis and on reduction of the adduct to the known *p*-aminophenylcyclohexane (IIa). In Ia, as in the other adducts, the position of the double bond is assigned by analogy to the usual Diels-Alder result.



Under the same conditions, *o*-nitrostyrene added butadiene to form 4-(*o*-nitrophenyl)cyclohexene (Ib). The latter, a low melting solid, was characterized as its dibromide, III. Catalytic reduction of Ib gave the known *o*-aminophenylcyclohexane (IIb).

m-Nitrostyrene has been prepared from the corresponding nitrocinnamic acid by a modification of the method of Wiley and Smith.^{6a} By using a flash distillation technique^{6b} to remove the styrene from the reaction flask, yields of 88% have been realized. The reaction of *m*-nitrostyrene and butadiene yielded the expected addition product, 4-(*m*-nitrophenyl)cyclohexene (Ic). On reduction, Ic absorbed four mole equivalents of hydrogen producing *m*-aminophenylcyclohexane (IIc), characterized as the benzenesulfonamide.

Under the standard reaction conditions of 40 hr. at 125°, the yields of purified, stable adducts, Ia, Ib, and Ic, were 60, 48, and 44%, respectively. Although such data are admittedly crude, it seems

(1) Abstracted from the M. S. theses of C. B. H. and V. M. H.

(2) (a) W. von E. Doering and R. A. N. Weil, *J. Am. Chem. Soc.*, **69**, 2461 (1947); (b) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 3482 (1949); (c) W. J. Dale and C. W. Strobel, *J. Am. Chem. Soc.*, **76**, 6172 (1954); (d) W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).

(3) K. Alder, C. V. Wilson, and J. A. VanAllan in *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers, Inc., New York, N. Y., 1948, p. 399.

(4) W. von E. Doering and S. J. Rhoads, *J. Am. Chem. Soc.*, **75**, 4738 (1953).

(5) N. C. Deno and J. D. Johnston [*J. Am. Chem. Soc.*, **74**, 3233 (1952)] have reported the reactions of *o*-, *m*-, and *p*-nitrostyrene with sorbic acid, but under reaction conditions which make assessment of relative reactivity difficult.

(6) (a) R. H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **70**, 2295 (1948); (b) cf. R. H. Wiley and M. H. Hobson, *ibid.*, **71**, 2429 (1949) who developed this technique for the preparation of the thermally sensitive *p*-formylstyrene.

clear that the reactivities of the isomeric nitrostyrenes in the Diels-Alder reaction do not show the *pronounced* difference which has been observed in the reactions of addition to the double bond proceeding by a simple ionic mechanism.^{2c} As with the vinylpyridines,⁴ there appears to be little parallelism between dienophilic and electrophilic reactivity in this series.

It is, tentatively, suggested that ionic forces, directly transmitted through a conjugated system to the reacting olefinic bond, are not of prime importance in determining the reactivity of the dienophile, and, by inference, the stability of the intermediate or activated complex. In harmony with Alder's empirical rule of "maximum accumulation of unsaturation,"⁷ a more significant factor may be the mere presence of unsaturated centers and nonbonded electrons, which can, by orbital interaction, stabilize the reacting aggregate.^{8,9}

EXPERIMENTAL¹⁰

Nitrostyrenes. The *o*- and *p*-nitrostyrenes were prepared by dehydrohalogenation of the corresponding nitrophenylethylbromides¹¹ according to the method of Strassburg, Gregg, and Walling.¹² Properties: *p*-nitrostyrene: yellow crystals, m.p. 20–21°, n_D^{20} 1.6074; *o*-nitrostyrene: heavy yellow oil, b.p. 60–62° at 0.1 mm., m.p. 11.5–12.0°, n_D^{20} 1.5783.

m-Nitrostyrene was prepared by the decarboxylation of *m*-nitrocinnamic acid in a modification of the Wiley-Smith method.^{6a} By adapting the flash distillation technique^{6b} to this preparation a considerable improvement in yield has been realized. *m*-Nitrocinnamic acid (5.0 g.) and cupric acetate (0.1 g.) were dissolved in 45 g. of warm quinoline. The resulting solution was added dropwise to a 125-ml. distillation flask containing copper powder and maintained at 300–310° in a metal bath. The rate of addition was regulated so that the flask remained fairly dry. Fresh copper powder was added as the original copper became coated with polymer. The entire distillate was transferred to a flask containing one and one-half times the quantity of 2.5*N* sulfuric acid required to neutralize the quinoline. Direct steam distillation into a Dean-Stark tube gave *m*-nitrostyrene as a heavy oil which was washed with successive portions of cold 6*N* sulfuric acid, water and sodium carbonate solution. Distillation of the dried, neutral material gave 3.0 to 3.4 g. (78–88%) of *m*-nitrostyrene, b.p. 75–76° at 0.35 mm., n_D^{20} 1.5845; reported, b.p. 90–96° at 3.5 mm., n_D^{20} 1.5836.^{6a}

General procedure for Diels-Alder reactions. Five grams (0.034 m.) of the nitrostyrene, 7 ml. (0.08 m.) of butadiene (Matheson, c.p. grade) and 0.1 g. of hydroquinone were sealed in a Pyrex bomb tube. The tube was placed in a furnace maintained at 125 ± 2° for a period of 40 hr., after

which it was cooled in a dry ice bath and opened.¹³ Excess butadiene was present in all cases. The tube contents were leached out with ether (or benzene) and the ether soluble portion was transferred to a distillation apparatus. Fractionation of the reaction products gave the dimer of butadiene (4-vinylcyclohexene), the unreacted dienophile, and the *ortho*- and *meta*- adducts. The *para*- adduct was more easily separated from the polymeric residue by extraction with ethanol or by vacuum sublimation.

4-(p-Nitrophenyl)cyclohexene (Ia). In the reactions with *p*-nitrostyrene, the reaction tube at the end of the heating period always contained a considerable quantity of sticky, yellow polymer which required extensive leaching with ether or benzene. Recovery of the unreacted styrene was prevented by its instability. The adduct could be sublimed from the solid residue remaining after removal of solvent and butadiene dimer. At a bath temperature of 93° and a pressure of 10 mm. the sublimate consisted of feathery, white flakes, m.p. 87.0–87.2°. Recrystallization of the crude adduct from ethanol afforded pure white plates, m.p. 87.2–87.5°.

Anal. Calcd. for C₁₂H₁₃NO₂: C, 70.9; H, 6.5; N, 6.9. Found: C, 70.7; H, 6.1; N, 6.4.

Under the standard conditions, the best yield of Ia obtained was 60% of the theoretical.

4-(o-Nitrophenyl)cyclohexene (Ib). The reaction mixture from the reaction of *o*-nitrostyrene and butadiene was ether-soluble but after removal of the butadiene dimer and unreacted nitrostyrene, a tarry polymer remained with the adduct. Molecular distillation at 0.2 mm. and a bath temperature of 90° permitted the separation of Ib as a heavy oil which solidified on cooling, m.p. (crude) 18–19°. Recrystallization of the crude adduct from ethanol in a dry ice bath gave fine, white crystals, m.p. 24–25°, after vacuum drying at 0°. For analysis, Ib was converted to the higher melting dibromo derivative, III. (*Vide infra.*) The best yield of Ib obtained under the standard conditions was 48% with a recovery of unreacted *o*-nitrostyrene of 13%.

4-(m-Nitrophenyl)cyclohexene (Ic). In the case of the *m*-nitrostyrene the reaction mixture was soluble in ether but still contained a dark, glassy polymer. The adduct was separated from the polymer by distillation at 125° and 0.6 mm. to give, after recrystallization from ethanol and vacuum drying at room temperature, colorless plates, m.p. 47.0–47.5°. The analytically pure sample melted at 47.4–47.6°.

Anal. Calcd. for C₁₂H₁₃NO₂: C, 70.9; H, 6.5; N, 6.9. Found: C, 71.0; H, 6.5; N, 7.4.

The best yield of Ic obtained under the standard conditions was 44% with a 43% recovery of unreacted *m*-nitrostyrene.

1,2-Dibromo-4-(o-nitrophenyl)cyclohexane (III). To a solution of 0.515 g. of Ib in 10 ml. of carbon tetrachloride was added dropwise and with cooling in an ice-salt bath, a solution of an equivalent quantity of bromine in carbon tetrachloride. Removal of the solvent left an oil which was triturated under hexane at dry-ice temperature to yield a crystalline dibromide, m.p. 88–91° (50% yield). Recrystallized from hexane as pale, yellow needles, it melted at 90.4–91.0°.

Anal. Calcd. for C₁₂H₁₃Br₂NO₂: C, 39.7; H, 3.6; N, 3.9; Br, 44.0. Found: C, 39.8; H, 3.7; N, 3.4; Br, 44.0.

4-Aminophenylcyclohexane (IIa). Reduction of 0.487 g. of Ia dissolved in ethanol was accomplished over Adams catalyst in a microhydrogenation unit. Hydrogen absorption amounted to 94% of the theoretical four mole equivalents. The amine was isolated as an oil in 86% yield and crys-

(13) These conditions were selected as standard for the comparison of yields of adducts. Exploratory runs were made at other temperatures and for shorter times in order to determine the best set of conditions and to develop the most efficient method of working the reaction mixtures. The yields obtained in these preliminary runs are not considered reliable indications of relative reactivity and are not included here.

(7) K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

(8) Cf. H. Henecka, *Z. Naturforsch.*, **4b**, 15 (1949); *C. A.*, **44**, 1909 (1950).

(9) The inadequacy of the "ionic" mechanism for many Diels-Alder reactions has been pointed out by others in a different connection. See refs. 5 and 7.

(10) All melting points are corrected. The analyses were performed by the Clark Microanalytical Laboratory, Urbana, Ill.

(11) E. L. Foreman and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1435 (1940).

(12) R. W. Strassburg, R. A. Gregg, and C. Walling, *J. Am. Chem. Soc.*, **69**, 2141 (1947).

tallized from ethanol-water as colorless plates, m.p. 50.8–52.4°, reported m.p. 57°,¹⁴ 54–55°.¹⁵ IIa was converted to the acetyl derivative, m.p. 131.4–131.9°, reported, m.p. 130–131°¹⁵; and to the phenylthiourea derivative, m.p. from ethanol, 157.8–158.1°, reported, m.p. 163–164°,¹⁵ 157–158°.¹⁶

2-Aminophenylcyclohexane (IIb). An ethanolic solution of 0.475 g. of Ib was catalytically reduced with Adams catalyst and absorbed four mole equivalents of hydrogen to furnish 0.39 g. (95%) of the crude amine, IIb. The amine was characterized as the acetyl derivative, colorless needles, m.p. 101.2–102°, reported, m.p. 101°,¹⁴ 102–103°¹⁵; and as the benzoyl derivative, felted needles from hexane, m.p. 153.8–154.4°, reported, m.p. 154°.¹⁴

3-Aminophenylcyclohexane (IIc). Reduction of 3.0 g. of the *meta*- adduct Ic proceeded rapidly and quantitatively over Adams catalyst to furnish 75% of the purified amine, IIc, b.p. 123–125° at 1.5 mm. IIc was converted to the benzenesulfonamide in the usual way. Recrystallization from ethanol afforded colorless crystals, m.p. 128.0–128.2°.

Anal. Calcd. for C₁₈H₂₁NO₂S: C, 68.5; H, 6.7; N, 4.4. Found: C, 68.6; H, 6.6; N, 4.3.

Stability of the adducts. The thermal stability of the adducts, Ia, Ib, and Ic was established by heating them alone at 125° or higher for 40 hr. in sealed tubes. In each case, the adduct could be recovered essentially unchanged.

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(14) O. Neuhoeffer, *J. Prakt. Chem.*, **135**, 95 (1932); *Chem. Abstr.*, **26**, 2435 (1932).

(15) W. J. Hickinbottom, *J. Chem. Soc.*, 2646 (1932).

(16) N. Kursanoff, *Ann.*, **318**, 309 (1901); *J. Chem. Soc. (Abstr.)*, **82**, 20 (1902).

Ultraviolet Spectra of 2-Substituted Furans and 5-Substituted Methyl Furoates

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The recent synthesis of many furan compounds containing furan to heteroatom bonds² together with the few compounds for which spectra have been recorded has permitted a fairly complete compilation of ultraviolet spectral data for simple furan derivatives. The wave length maxima, log ϵ , and $\Delta\lambda$ ³ values are recorded in Table I for the 2-substituted furans and in Table II for the methyl 5-substituted-2-furoates. In each table the

(1) Taken from the Ph.D. thesis of Donald G. Manly, Quaker Oats Fellow in Organic Chemistry 1954–56. Present address, Research Laboratories, The Quaker Oats Company, Barrington, Ill.

(2) D. G. Manly and E. D. Amstutz, *J. Org. Chem.*, **21**, 516 (1956).

(3) The concept of $\Delta\lambda$ was introduced and applied to a few benzene derivatives by L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **69**, 2714 (1947). See also J. M. Vandenberg, "Correlation of Ultraviolet Absorption and Chemical Structure of Benzenoid Compounds" A.D.M.A. Research and Development Section Meeting, Cleveland, 1950 and Hot Springs, 1955.

corresponding benzene or methyl *p*-substituted benzoate $\Delta\lambda$ values are included and are designated as $\Delta\lambda_{Ph}$.

TABLE I

$x(C_4H_5O)$

x	$\lambda_{max}(m\mu)$	$\log \epsilon$	$\Delta\lambda^a$	$\Delta\lambda_{Ph}^b$
H—	(208)	(3.9)	0	0
Br—	215.5	3.99	7.5	6.5 ^c
MeO—	221.0	3.82	13.0	13.5 ^c
C ₆ H ₅ O—	222.0	4.06	14.0	23.2
C ₆ H ₅ S—	241.5	4.21	33.5	28.3
C ₆ H ₅ SO ₂ —	249.5	4.13	41.5	32.8
MeOOC—	252.1	4.13	44.1	26.3

^a $\lambda_{max} - \lambda$ where $\lambda = 208$. ^b $\lambda_{max} - \lambda$ where $\lambda = 203.5$.

TABLE II

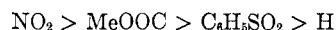
$x(C_4H_5O)COOMe$

x	$\lambda_{max}(m\mu)$	$\log \epsilon$	$\Delta\lambda^a$	$\Delta\lambda_{Ph}^b$
H—	252.1	4.13	44.1	26.3
Cl—	260.5	4.23	52.5	37.5 ^c
C ₆ H ₅ SO ₂ —	261.7	4.33	53.7	39.0
Br—	264.1	4.23	56.1	41.5
MeOOC—	264.6 ^d	4.19	56.6	38.5
C ₆ H ₅ O—	275.0	4.25	67.0	54.5
MeO—	279.0	4.10	71.5	53.0
C ₆ H ₅ S—	291.8	4.33	83.8	89.7
O ₂ N—	295.4	4.08	87.4	55.0

^a $\lambda_{max} - \lambda$ where $\lambda = 208$. ^b $\lambda_{max} - \lambda$ where $\lambda = 203.5$. ^c Taken from Doub and Vandenberg, ref. 3. ^d Taken from ref. 4.

To calculate $\Delta\lambda$ values it was necessary to assume a wave length maximum for furan of 208 which was obtained by extrapolation of the experimental curve. The extrapolation of the solvent spectrum appears to be valid since a vapor spectrum (max = 222) was obtained of almost identical shape.

The $\Delta\lambda$ value is a measure of the electronic interaction of the group with the aromatic system to which it is attached and may provide information of a sort not obtainable from a study of reaction rates, for example, since it does not involve polarization by a reagent. By first separating the substituents into those which are "*ortho-para*" directing and those which are "*meta*" directing and then arranging each group in order of increasing $\Delta\lambda$ the following series are obtained:



These results agree qualitatively with the degree of directing power observed in various aromatic electrophilic substitution reactions.

In Table I the most significant differences in $\Delta\lambda$ and $\Delta\lambda_{Ph}$ are to be found in cases where the substituents are of the markedly electrophilic type (ϕ -SO₂— and MeO—CO—). These differences require the furan ring to be a stronger nucleophile than the benzene ring. The same conclusion is required by the fact that for the phenoxy group