[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Aromatic Nitration. III. The *ortho* to *para* Ratio in Nitration of Benzonitrile

BY GEORGE S. HAMMOND[1] AND KATHARINE J. DOUGLAS[2]

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The nitration of benzonitrile by nitric acid in 72% perchloric acid gives approximately 80% *m*-nitrobenzonitrile. The *o*- and *p*-isomers are also produced in the ratio 3.3 to 1. Since the linear cyano group can provide no steric assistance to *o*-nitration, it is concluded that the high value of the *ortho*/*para* ratio reflects the tendency of the unsaturated substituent to continue a weak electron withdrawal from the ring even in the transition states involved in electrophilic substitution reactions. This is in accord with the earlier suggestions of other authors[3,10,11] and casts doubt on the significance of special steric effects.[5]

The study of the *ortho* to *para* ratio obtained on nitration of various substituted benzenes has led to the conclusion by Dewar[3] that the high values of the *ortho*/*para* ratio found among the by-products in the nitration of monosubstituted benzenes bearing the so-called *m*-directing groups could be explained by the "naive" LCAO molecular orbital approximation if the selection of the parameters were sufficiently judicious. His results indicated that only in cases where the substituent is very electronegative would the *p*-position be electronically less deactivated than the *o*-position. His results are in qualitative agreement with experiment, but the appropriate electronegativity parameters for the various substituents are very uncertain. Brown[4] has shown that when the substituent is a conjugated hydrocarbon system, the uncertainty about the electronegativity parameter disappears and the molecular orbital approximation provides an unequivocal prediction of the relative reactivities at the various nuclear positions. He, as well as Dewar, attributes the observed superior reactivity of the *p*-position in biphenyl to steric effects rather than to failure in the MO theory.

Hammond, Modic and Hedges[5] from their study of the *ortho* to *para* ratios obtained in the nitration of 2,5-dibromo- and 2,5-dichloronitrobenzene have suggested a mechanism by which *ortho* direction by non-linear, unsaturated substituents could be facilitated. According to this mechanism, the negative end of the dipole in a group such as NO_2, COOH, CHO, etc., attracts the *o*-hydrogen and facilitates the approach of the electrophilic attacking group so that the proton is displaced in one concerted process and appears first on the neighboring group. The picture was similar to that suggested earlier by Lapworth and Robinson[6] to account for *ortho* activation.

In order to determine if this steric influence is real, we have undertaken the study of the isomer ratio obtained on nitration of benzonitrile. Previous work[7] showed that the *m*-isomer was the main product and that the chief by-product was *o*-nitrobenzonitrile. However, the analytical method employed could not give an estimate of the *p*-isomer formed except by difference, and no accurate value of the *ortho* to *para* ratio could be determined.

Experimental

Nitrobenzonitriles.—Separate pure samples of the three nitrobenzonitriles were prepared by means of Sandmeyer reactions from purified samples of the three nitroanilines according to the method of Hodgson and Heyworth.[8] The pure compounds were separated from the reaction mixtures by steam distillation. The melting points were; *ortho*, 110°; *meta*, 116.5°; and *para*, 147°, in agreement with the literature.

Nitration of benzonitrile was carried out in 70% perchloric acid. In a typical experiment 10 ml. of 70% perchloric acid and 1 ml. of fuming nitric acid were mixed in a tube fitted with a cold-finger condenser and cooled in an ice-bath. One gram, or 1 ml. (d. 1.01 g./ml.) of redistilled (b.p. 189.7–189.9°) benzonitrile was dissolved in the cold acid mixture, and the tube was removed to a water-bath which was maintained at the desired temperature where it was kept for the stated time interval. Table I gives the data for the quantitative nitration experiments.

TABLE I

QUANTITATIVE NITRATION EXPERIMENTS

Medium: 10 ml. of 70% $HClO_4$ and 1 ml. of fuming HNO_3

Run	Amount of benzonitrile[a]	Temperature, °C.	Time, hours
1	0.972 g.	25	8
2	1 ml.	35	1
3	1 ml.	35	2
4	0.810 g.	35	4
5	1.008 g.	35	6
6	1 ml.	35	6
7	1.033 g.	35	8
8	1 ml.	43	1
9	1 ml.	43	1

[a] From syringe; 1 ml. = 0.997 g. ± 0.003 g.

Infrared analysis of the nitration mixtures was carried out by means of a Perkin–Elmer model 13 infrared spectrophotometer equipped with sodium chloride optics. The spectra of benzonitrile and the three nitrobenzonitriles were studied in carbon disulfide solution and the absorption maxima for each compound in the range 11 to 14 μ are shown in Table II.

TABLE II

INFRARED ABSORPTION MAXIMA

Compound	Wave lengths in microns					
Benzonitrile	..	...	...	13.22	...	...
o-Nitrobenzonitrile	..	11.78	12.78	...	13.42	...
m-Nitrobenzonitrile[a]	11.2	...	12.72	...	...	13.63
p-Nitrobenzonitrile	..	11.75	...	...	13.38	...

[a] In addition *m*-nitrobenzonitrile shows a maximum at 12.4 μ.

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(1) Division of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) Department of Chemistry, Newcomb College, New Orleans, La.

(3) M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949).

(4) R. D. Brown, THIS JOURNAL, **75**, 4077 (1953).

(5) G. S. Hammond, F. J. Modic and R. M. Hedges, *ibid.*, **75**, 1388 (1953).

(6) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. and Phil. Soc.*, **72**, 43 (1928).

(7) J. W. Baker, K. E. Cooper and C. K. Ingold, *J. Chem. Soc.*, 430 (1928).

(8) H. H. Hodgson and F. Heyworth, *ibid.*, 1131 (1949).

As indicated, *p*-nitrobenzonitrile shows only two significant absorption maxima, and these are common to the spectrum of *o*-nitrobenzonitrile. Although slight differences in wave length are noted for separate samples of the pure compounds, there is only one maximum at each wave length in the spectrum of a mixture of the two compounds. The *m*- isomer shows two distinct absorption maxima at 11.2 and 13.63 μ. Calibration curves showing a linear relationship between concentration of *m*-nitrobenzonitrile and log I_0/I were drawn up for these two wave lengths. Figure 1 shows these curves and includes points obtained from synthetic mixtures of the three nitrobenzonitriles, as well as from solutions of *m*-nitrobenzonitrile alone.

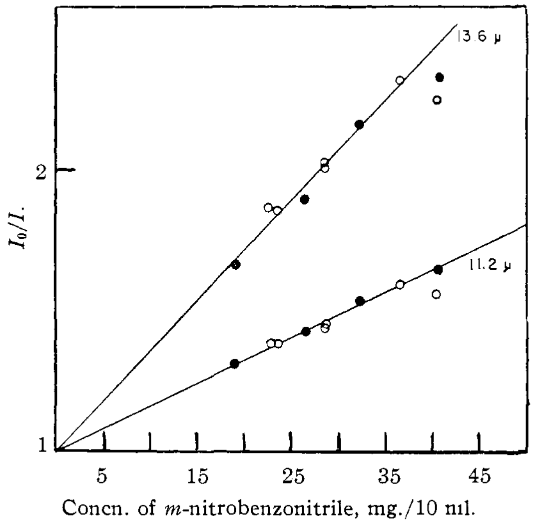

Fig. 1.—Calibration curves for *m*-nitrobenzonitrile: ●, pure *m*-dinitrobenzonitrile; ○, synthetic mixtures.

Attempts to prepare similar calibration curves for the *o*- and *p*-nitrobenzonitriles failed because Beer's law does not hold closely for these two compounds. It was observed, however, that at 11.7 μ the slope of the curve obtained for *p*-nitrobenzonitrile was considerably higher than that for *o*-nitrobenzonitrile—the two being of the order of 1.7×10^{-2} and 0.6×10^{-2}, respectively. The curves obtained at 13.4 μ showed the opposite tendency; and although good straight lines were not obtained, the slopes were of the order of 1.6×10^{-2} for *o*-nitrobenzonitrile and 0.3×10^{-2} for *p*-nitrobenzonitrile. Thus, in a mixture of nitrobenzonitriles, absorption at 11.7 μ was due more to the *p*-isomer, while absorption at 13.4 μ was due more to the *o*-isomer. A series of synthetic mixtures of the three nitrobenzonitriles were prepared as shown in Table III, and a curve showing the relationship of the *ortho* to *para* ratio to the ratio of the absorption at the two wave lengths was drawn up. Figure 2 gives this curve and includes points showing the estimated values of the *ortho* to *para* ratios obtained for the nitration products.

TABLE III

SYNTHETIC MIXTURES OF NITROBENZONITRILES

Wt. of isomers, mg. *ortho*	*meta*	*para*	% *meta*	*o/p*	D^a 13.4 μ	11.7 μ	13.6 μ	11.2 μ	$D_{13.4}/D_{11.7}$
10.4	60.5	2.9	82.0	3.59	1.51	1.31	..[b]	..[b]	1.153
8.0	28.6	2.4	73.4	3.33	1.39	1.28	2.04	1.37	1.085
7.9	22.8	2.9	67.9	2.72	1.40	1.34	1.82	1.31	1.045
7.9	40.5	3.0	78.9	2.62	1.39	1.34	2.38	1.47	1.037
7.3	36.5	2.1	79.6	3.48	1.33	1.25	2.50	1.51	1.064
11.5	23.5	2.9	62.0	3.97	1.52	1.33	1.82	1.30	1.143
9.7	28.5	8.5	61.0	1.14	1.46	1.61	2.01	1.36	0.906

[a] $D = I_0/I$ at the wave length given. [b] All of the *m*-isomer was not in solution.

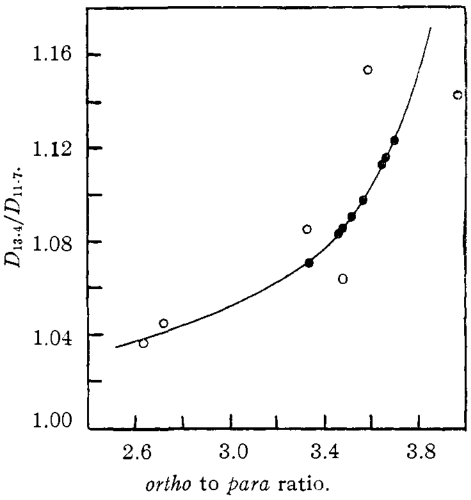

Fig. 2.—Calibration curve for estimating *ortho* to *para* ratio: ○, synthetic mixtures; ●, nitration products.

In reading the infrared spectra, the base line technique[9] was found less satisfactory than a simpler method of compensation for the differences in the various spectra due to displacement of the spectral curves on the recording paper and the noise level of the instrument. The point at 12.05 μ showed minimum absorption on all curves. This point was therefore taken to represent 100% transmittancy, and a correction was applied to the entire curve. The same correction was applied to all wave lengths, whereas, in the base line technique, a different correction is applied at each absorption maximum. Since the data obtained using the two widely separated maxima for *m*-nitrobenzonitrile give close agreement, this method of unifying the spectra seems justified.

Results

Table IV gives the data and results obtained from the quantitative nitration of benzonitrile. It was not possible to get accurate estimates of the percentages of the three nitrobenzonitriles obtained in the nitration experiments, but the percentage *m*-nitrobenzonitrile and the *ortho* to *para* ratio obtained as indicated above are given. It was clear from preliminary experiments that no dinitration occurred and that mononitration was quantitative. Attempts to analyze completely the nitration products by the infrared methods showed that the sum of the estimated *o*-, *m*- and *p*-isomers agreed very well with the theoretical yield for mononitration. The methods which might have given percentages of the various isomers failed because they could not clearly differentiate between the *o*- and *p*-isomers. Thus, the sum of these two isomers could be estimated accurately, but the ratio could not. Since the value of the *ortho* to *para* ratio was of chief concern in this work, these methods of analysis had to be abandoned, even though they

TABLE IV

ANALYSIS OF NITRATION PRODUCTS

Run	Sample wt., mg.	*D* 11.7 μ	13.4 μ	13.6 μ	11.2 μ	$D_{13.4}/D_{11.7}$	Estimate of *o/p*	% *m*
1	43.9	1.16	1.29	2.45	1.50	1.112	3.65	82.0
2	47.5	1.22	1.36	2.58	1.53	1.115	3.66	80.2
3	47.2	1.26	1.35	2.55	1.52	1.071	3.32	79.9
4	39.1	1.19	1.29	2.20	1.43	1.084	3.48	81.6
5	47.7	1.22	1.33	2.40	1.48	1.090	3.52	73.6
6	47.5	1.24	1.36	2.47	1.50	1.097	3.56	76.6
7	46.4	1.20	1.30	2.25	1.46	1.083	3.46	72.0
8	47.5	1.22	1.37	2.53	1.52	1.123	3.70	78.7
9	48.0	1.22	1.37	2.48	1.51	1.123	3.70	76.9

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[9] J. J. Heigel, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

did establish that quantitative yields of mononitrobenzonitriles were obtained and that dinitration was negligibly small.

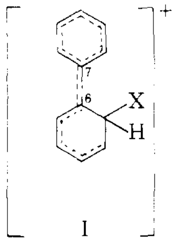
The *ortho* to *para* ratio was determined from the ratio of I_0/I at 13.4 μ to I_0/I at 11.7 μ as shown in Fig. 2 where D represents I_0/I. The isomer ratio was clearly greater than two, and in no experiment did it fall below 3.3. This shows that there is a definite *ortho*-directing influence present in the molecule. The infrared analytical method gave estimates of 72 to 82% *m*-nitrobenzonitrile in the nitration product in agreement with values reported earlier.[7] The low values occurred from nitration runs which were allowed long reaction times, and neither the percentage *m*-nitrobenzonitrile nor the *ortho* to *para* ratio appears to be dependent on the reaction temperature. All data for synthetic mixtures having compositions close to those produced in nitration were used in the construction of Fig. 2 so there is no independent measure of the accuracy of the analysis. The best judgment of the error limits are obtained from the graph itself. Calculations from distances of the known points from the line indicate an expected error of ±6% in the value of the *ortho/para* ratio. The distances in Fig. 2 appear deceptively large since mixtures were made up to match the experimental compositions as closely as possible and the results were plotted on an expanded scale. Compositions lying outside the limits of Fig. 2 were studied and gave results consistent with those shown but are not included in the figure as a matter of convenience in plotting.

Discussion

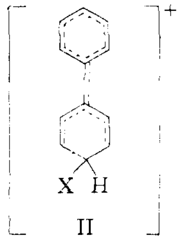
Baker, *et al.*,[7] have pointed out that the conditions of nitration must be carefully chosen to prevent hydrolysis of the cyano group, but they did not indicate how hydrolysis was detected. If even 10% hydrolysis occurred before nitration, the observed high yield of *o*-nitro isomer may be due to the nitration of the benzamide or benzoic acid present. In the present work, many preliminary nitration experiments were run and the infrared spectra of unpurified products were also run. If in any case the product spectrum showed any absorption near 6 μ (characteristic of the amide carbonyl group), the product was discarded and the nitration was repeated under different conditions. The nitration solvent of choice was 70% perchloric acid. Not only were there no detectable hydrolysis products in the nitration mixtures, but separate experiments showed that neither benzonitrile nor the three nitrobenzonitriles hydrolyzed when treated with 70% perchloric acid at 25° for three hours.

The suggested explanation of Hammond, Modic and Hedges[5] of the enhanced *ortho* reactivity does not apply in this case. Since the cyano group is linear, it could not exert an attraction for the *o*-hydrogen or the entering electrophile in the same way proposed for the nitro group. The fact that the *ortho* to *para* ratio obtained for nitration of benzonitrile is high casts doubt on this explanation of the high *ortho* to *para* ratio obtained in nitration of the dichloronitrobenzene. These experiments show that the influence of the nitro and cyano groups is substantially the same and that the *ortho* effect observed in both benzonitrile and nitrobenzene must be due more to electronic than to special steric influences.

The significance of these observations is to provide orientation as to the quantitative significance of electronic influences which have been indicated qualitatively by semi-theoretical treatments. The conclusions of Brown[4] that there should, in the absence of steric effects, be a preference for *ortho* substitution in completely conjugated, all-carbon systems such as biphenyl is easily understood on a semi-intuitive basis. In a transition state, such as I, the positive charge is less concentrated in the first ring than it is in the corresponding *para* transition state, II. In the molecular orbital calculations, this appears as a consequence of the relatively heavy weight which the term H_{67} carries in solutions for the lowest roots from the secular determinant. Looking at the problem from the point of view of the free electron theory, we would say, qualitatively, that the conjugated system in I represents a longer electron box than does that in II.[10]

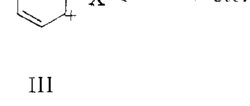


I

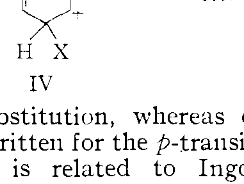


II

It is not immediately obvious that the same consequences are predictable for substitution *ortho* and *para* to unsaturated, electron-withdrawing groups since it is very doubtful that groups such as cyano and nitro supply electrons to the ring undergoing substitution, as does the second ring in biphenyl. Electron migration in the opposite sense, that is, from the ring to the substituent, is of major importance in the ground states of the aromatic molecules, and the question arises as to whether or not it is the tendency to preserve this type of interaction which determines the orientation behavior. An explanation of this type was given many years ago by Branch and Calvin[11] who pointed out that three resonance structures such as III could be written for the



III



IV

transition state for *o*-substitution, whereas only two such as IV could be written for the *p*-transition state. The explanation is related to Ingold's proposal of specific *p*-deactivation.[12] The Ingold

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[10] This is borne out by unpublished calculations by Dr. L. S. Bartell of this department.

[11] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 477.

[12] C. K. Ingold, *Ann. Repts. on Progress Chem.*, **23**, 740 (1926); "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 262.

description is somewhat less specific as to origin of the effect. This is more or less the equivalent of Dewar's conclusion that if the conjugated interaction between the substituent and the ring (as measured by the magnitude of the size of the resonance and overlap integrals) is large enough, the compounds in question will show preferential *ortho* orientation despite the differential increase in the electron affinity of the *o*-carbon atom. One is reluctant to assign significant weight to structures such as III and IV because of the obvious electrostatic complications. Similarly, the significance of the naive MO picture may be questioned since the theory does not attempt to correlate the π-electrons in the many electron system.

It is our view that the experimental evidence points clearly to the conclusion that there is some measurable gain derived from maintaining the conjugate interaction between the substituent and the ring in the transition states involved in electrophilic substitution reactions. Since this is true in benzonitrile, it must also be true of related nitro- and carboxyl-substituted compounds. The steric effect which was suggested previously[5] may play a significant role, but there is no direct evidence to support such a view. The separation of steric and electronic effects in these systems appears to be a rather formidable problem.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Cross-linking of Polymers with Dimaleimides[1]

BY PETER KOVACIC AND RICHARD W. HEIN

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From gelation and compounding studies, dimaleimides were found to cross-link a wide variety of polymers including unsaturated hydrocarbon types, polyethylene, polymers containing amino groups and a urethan polymer. Except for the amino-containing polymers, the presence of catalytic amounts of peroxide was necessary for effective cross-linking. The chemistry of the cross-linking processes is discussed.

Introduction

Dimaleimides represent a recent addition[2] to the group of compounds which cross-link polymers. This report is concerned with the versatility of dimaleimides as cross-linking agents for various types of polymers and with the chemistry of the reactions involved.

Results and Discussion

The dimaleimides were synthesized according to the method[3] of Searle. In general, a diamine was condensed with maleic anhydride to give the corresponding dimaleamic acid which upon elimination of water yielded the dimaleimide (I).

$$\begin{matrix} \text{CHCO} & & \text{COCH} \\ \| & \rangle\text{NRN}\langle & \| \\ \text{CHCO} & & \text{COCH} \end{matrix} \qquad \text{(I)}$$

From gelation and compounding studies, dimaleimides were found to cross-link a wide variety of polymers including unsaturated hydrocarbon types, polyethylene, polymers containing amino groups and a urethan polymer.

Unsaturated Hydrocarbon Polymers.—In the literature many types of compounds are reported as cross-linking agents for unsaturated polymers, particularly natural rubber. Of these reagents, sulfur–accelerator combinations and peroxides are the best known and most useful.

TABLE I

NATURAL RUBBER, N,N'-*m*-PHENYLENEDIMALEIMIDE AND PEROXIDES: GELATION STUDIES[a]

MPD, g.[b]	Dicumyl peroxide, g.	Benzoyl peroxide, g.	Extent of gelation	Temp., °C. Gelation	Temp., °C. Maximum
5	0.5	..	Good	125–128	131
5	.25	..	Fair	142–144	144
5	.1	..	None	.....	177
2	.5	..	Good	141–150	173
2	.25	..	Fair	148	152
2	.1	..	None	.....	179
1	.5	..	None	.....	160
5	..	..	None	.....	176
..	.5	..	None	.....	177
..	..	..	None	.....	173
5[c]	.5	..	None	.....	175
5	..	0.5	Good	108–109	113
5	..	.25	Good	109	109
5	..	.1	None	.....	150
..	..	.5	Slight	100–110	178
..	..	.25	None	.....	150

[a] Weights are based on 100 g. of pale crepe as a 3% solution in *o*-dichlorobenzene. [b] MPD = N,N'-*m*-phenylenedimaleimide. [c] No natural rubber present.

Gelation studies (Table I) in *o*-dichlorobenzene showed that N,N'-*m*-phenylenedimaleimide (5% by weight based on the polymer) readily cross-linked natural rubber at 108-150° in the presence of catalytic amounts of dicumyl peroxide or benzoyl peroxide. When either the dimaleimide or dicumyl peroxide was decreased in amount by 80%, no

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(1) Paper 1 in the series "New Cross-linking Agents for Polymers." This paper was presented at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958, and is in part an abstract of a portion of the M.S. thesis of R. W. Hein, Case Institute of Technology, 1958.

(2) P. Kovacic, U. S. Patent 2,818,405 (1957); *C. A.*, **52**, 5018 (1958).

(3) N. E. Searle, U. S. Patent 2,444,536 (1948); *C. A.*, **42**, 7340 (1948); H. W. Arnold and N. E. Searle, U. S. Patent 2,462,835 (1949); *C. A.*, **43**, 4421 (1949).