

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

A STUDY OF MOLECULAR ORGANIC COMPOUNDS. III. THE MOLECULAR ORGANIC COMPOUNDS OF CERTAIN ORTHO, META AND PARA MONOSUBSTITUTED NITROBENZENES<sup>1</sup>

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In previous publications<sup>2</sup> the influence in the benzene ring of the hydroxy, chloro, bromo and methyl groups (in position 1) and two nitro groups (in positions 2,4) on molecular compound formation was discussed. The present paper deals with the same groups in the *o*-, *m*- and *p*-positions to one nitro group in the benzene ring.

Kremann<sup>3</sup> appears to be the only investigator who has studied the molecular compounds of monosubstituted nitrobenzenes to any great extent. His method consisted in the construction of freezing point curves which reveal, without any isolation, molecular compound formation.

In Tables I, II and III are shown the molecular compounds<sup>4</sup> isolated. It is significant that they contain with a single exception a nitrophenol and an amino compound. The presence of the hydroxy group in one and an amino group in the other component suggests, in the most common—the equimolecular—type, the electronic formula (A). The next most common type, among the phenylenediamines, in which the molecular ratio is 2:1 may be explained in a similar manner.

The inability of the *o*-nitrophenol to add has been discussed previously by Kremann.<sup>5</sup> Sidgwick's<sup>6</sup> representation of this compound (B) seems to offer the most satisfactory explanation for this inactivity. Diethylamine alone appears to be able to break the chelate ring and add on to the phenolic group.

With a decrease in the number of the nitro groups in the

<sup>1</sup> This paper is an abstract of the Masters' Theses presented by Chester R. Alexander and Garland Stratton at the University of Tennessee.

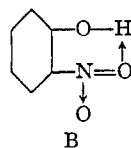
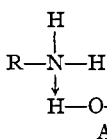
<sup>2</sup> Buehler, *et al.*, THIS JOURNAL, **48**, 3168 (1926); **52**, 1939 (1930).

<sup>3</sup> The references, which are of interest in connection with this investigation, to the work of Kremann and his co-workers on the nitrophenols, may be enumerated as follows: *Monatsh.*, **27**, 125 (1906) (with aniline and urea); **37**, 723 (1916) (with  $\alpha$ - and  $\beta$ -naphthylamines); **38**, 385 (1917) (with *p*-toluidine); **38**, 405 (1917) (with the three phenylenediamines); **39**, 441 (1918) (with acid amides); **42**, 196 (1921) (with anthracene).

<sup>4</sup> The original list of second components, Buehler and Heap, THIS JOURNAL, **48**, 3168 (1926), has been modified in that quinol, pyrogallol, resorcinol, catechol, phloroglucinol, *o*-cresol, triphenylmethane, carbazole, anisole, phthalimide, *p*-bromoacetanilide and diphenylamine have been omitted and urea, acetamide and *m*-toluidine have been added.

<sup>5</sup> Kremann, *Monatsh.*, **27**, 125 (1906).

<sup>6</sup> Sidgwick, *J. Chem. Soc.*, 2027 (1930).



benzene ring, the ability to form molecular compounds is generally lessened. However, in going from 2,4-dinitrophenol to *p*-nitrophenol, the opposite is true. The removal of the chelate ring in the former is apparently responsible for this increased activity.

Since phenol adds so readily it appears that one nitro group interferes in varying degrees with molecular compound formation. In the ortho position it practically prohibits, while in the meta and para its influence, though much less pronounced, is felt. In these latter cases where chelate ring formation is not likely, the nitro group probably offers some attraction for the phenolic hydrogen.

### Experimental Part

The high melting molecular compounds were prepared in absolute alcohol, benzene or chloroform solutions and for purification were recrystallized from the same solvent. The low melting compounds were prepared by fusing the components together and then heating for several minutes at a fairly high temperature,<sup>7</sup> after which the molecular compound was crystallized out by cooling with a mixture of salt and ice or solid carbon dioxide and ether. Purification in the latter case was accomplished by repeating the freezing out process. In doubtful cases<sup>8</sup> freezing point curves were

TABLE I  
MOLECULAR COMPOUNDS OF *p*-NITROPHENOL

Second component	M. p.,	F. p.,	Color	Mol. ratio	Nitrogen, %		
	°C. (corr.)	°C. (lit.) <sup>a</sup>			Calcd.	Found	
<i>o</i> -Toluidine	53.4	..	Gray	1:1	11.38	11.28	11.30
<i>p</i> -Toluidine	26.5 <sup>b</sup>	24.5	Red	1:2	11.90	11.78	11.80
$\alpha$ -Naphthylamine	68.5	68.2	Green-yellow	1:1	9.93	9.81	9.76
$\beta$ -Naphthylamine	82.1	81.5	Light tan	1:1	9.93	9.69	9.85
Benzidine	149.9	..	Yellow	1:1	13.00	12.81	12.85
<i>o</i> -Phenylenediamine	87.8	87.9	Tan	2:1	14.51	14.29	14.37
<i>m</i> -Phenylenediamine	120.8	119.9	Gray	2:1	14.51	14.28	14.45
<i>p</i> -Phenylenediamine	118.9	117.5	Dark red	1:1	17.01	16.99	17.06
<i>p</i> -Phenylenediamine	129.0	134.2	Light green	4:1	12.65	12.45	12.58
Urea	118.4	116.0	Light yellow	1:1	21.10	20.96	20.99
Acetamide	98.3	96.1	White	1:1	14.06	14.06	14.09
Benzamide	99.3	97.2	White	1:1	10.78	10.84	10.75
Diethylamine	109.6	..	Green-yellow	1:1	13.19	12.93	13.05
Pyridine	63.8	..	Light yellow	2:1	11.77 <sup>c</sup>	11.60	11.66

<sup>a</sup> Determined by Kremann. <sup>b</sup> Freezing point. <sup>c</sup> The Dumas method of analysis was employed here since pyridine is not decomposed in the Kjeldahl method.

<sup>7</sup> In some cases heat of activation seemed to be necessary to promote molecular compound formation.

<sup>8</sup> The method of cooling a solution of equimolecular parts of the two components may give an equimolecular solid in case the eutectic is reached at this concentration. *o*-Nitrophenol with *p*-toluidine [Philip, *J. Chem. Soc.*, **83**, 814 (1903)] and *p*-nitrotoluene with *p*-toluidine gave such solids which were shown by freezing point curves to be simply mixtures and not molecular compounds.

TABLE II  
 MOLECULAR COMPOUNDS OF *m*-NITROPHENOL

Second component	M. p., °C. (corr.)	F. p., °C. (lit.) <sup>a</sup>	Color	Mol. ratio	Nitrogen, %		
					Calcd.	Found	
<i>o</i> -Toluidine	40.6	..	Yellow	1:1	11.38	11.30	11.28
<i>p</i> -Toluidine	39.8	36.5	Cream	1:1	11.38	11.25	11.47
$\alpha$ -Naphthylamine	67.8	56.3	Yellow	1:1	9.93	9.93	9.89
$\beta$ -Naphthylamine	69.4	63.5	Gray	1:1	9.93	9.87	9.89
Benzidine	112.3	..	Brick-red	1:1	13.00	13.04	12.97
<i>o</i> -Phenylenediamine	76.8	73.9	Tan	2:1	14.51	14.42	14.47
<i>m</i> -Phenylenediamine	82.2	80.3	Yellow	1:1	16.99	16.78	16.76
<i>m</i> -Phenylenediamine	74.6	74.5	White	2:1	14.51	14.31	14.32
<i>p</i> -Phenylenediamine	140.6	137.8	Orange	2:1	14.51	14.44	14.47
Urea	81.8	80.5	White	1:1	21.10	21.05	21.17
Acetamide	52.9	51.5	White	1:1	14.06	14.07	14.15
Benzamide	44.2	38.7	White	1:1	10.78	10.60	10.63
Diethylamine	43.0	..	Orange	1:1	13.19	13.43	13.37

<sup>a</sup> Determined by Kremann.

 TABLE III  
 MOLECULAR COMPOUNDS OF *o*-NITROPHENOL AND *p*-NITROCHLOROBENZENE

Molecular compound	M. p., °C. (corr.)	Color	Mol. ratio	% Nitrogen		
				Calcd.	Found	
<i>o</i> -Nitrophenol·diethylamine	105.1	Yellow	1:1	N, 13.21	13.19	13.32
<i>p</i> -Nitrochlorobenzene· $\alpha$ -naphthol	65.2	Light yellow	1:1	Cl, 11.76	11.63	11.80

constructed. It was usually possible to isolate any compounds<sup>9</sup> indicated by the diagrams thus obtained.

Analyses for nitrogen were accomplished by the modified Kjeldahl<sup>10</sup> method. The determinations for chlorine and the melting points were made as reported previously.

### Summary

New molecular compounds of *o*-, *m*- and *p*-nitrophenol and *p*-nitrochlorobenzene have been isolated.

Differences in the ability to form molecular compounds among the *o*-, *m*- and *p*-nitrophenols are attributed to the chelate ring in the *o*-isomer.

The comparatively high additive power of the *m*- and *p*-nitrophenols together with the fact that they combine almost exclusively with amino compounds indicates that the union occurs, at least in the simpler types, between the phenolic and amino groups.

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<sup>9</sup> In spite of numerous attempts we were unable to isolate the following molecular compounds which were shown to exist by Kremann: *p*-nitrophenol·aniline, *m*-nitrophenol·anthracene and *m*-nitrophenol·aniline.

<sup>10</sup> Sisley and David, *Bull. soc. chim.*, **45**, 312 (1929), or Dyer, *J. Chem. Soc.*, **67**, 811 (1895).