Studies on the Organic Molecular Compounds. Part IV. The Relation between Compound-Formation and the Substituent in the Monosubstitution Products of Several Aromatic Hydrocarbons.

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According to the writer's studies, in the two series of binary systems of aromatic—nitroaromatic compound and of aromatic compound—antimony trihalide, the formation of crystalline molecular compounds is closely related not only to the nature of the aromatic ring, but also to the position, the number, and the variety of its substituents.⁽¹⁾ The influence of the substituent in the aromatic monosubstitution products on the formation of molecular compounds will now be discussed.

I. **Greater Tendency of Compound-Formation of the α-Naphthalene Monosubstitution Products.** It is supported by a number of facts that naphthalene α-monosubstitution products are generally more reactive than the β-isomers. Of the binary systems in previous reports, α-naphthol was generally proved to be more strongly additive than β-naphthol⁽²⁾ on compound-formation. Besides, as will be seen in Table 1, the foregoing relation holds also with naphthalene monosubstitution derivatives of simple substituent.⁽⁸⁾

Trinitrobenzene, picric acid, and tetranitrobenzene, arranged in the order of the tendency, were all used as a nitro component of greater tendency of compound-formation. Some irregularities were found in the systems of tetranitrobenzene (the system of α-methyl naphthalene having a lower $\imath$ than that of the β-isomer). At the same time in the systems of this nitrobenzene, the compound ratios other than 1:1, have been observed. A like ratio was found also in the systems of naphthoic acid.

In Table 1 a comparison of the compound-formation of two series of naphthalene monosubstitution products with each other and with that of naphthalene, brought out the interesting result that the α-compound had either a higher or lower "melting point elevation," while that of all the β-isomers were usually lower than that of naphthalene, from which it is concluded that substitution of any radical in the β-position of the naphthalene nucleus hindered compound-formation of this type.⁽³⁾ Similar results were noted in the anthracene and phenanthrene molecular compounds, with trinitrobenzene and picric acid, respectively, as the nitro component.⁽⁴⁾ The sequences are

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(1) This Bulletin, **15** (1940), 92, 137, 259.

(2) Parts, I, II of these studies, *ibid,* **15** (1940), 92, 137.

(3) This type of combination seems to be formed by the affinity of the aromatic ring—nitro radical or aromatic ring—antimony trihalide; the effects of substituents in the latter case were described in Part III.

(4) These compounds are distinctly halochromic (Beilstein, "Handbuch der organischen Chemie," 4 Aufl., B. VI, 704; Erstes ergänz. B, VI, 339.).

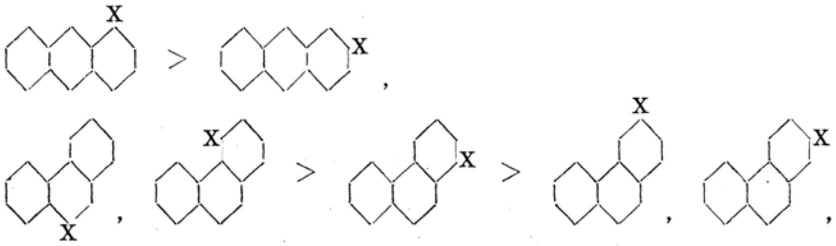
Table 1.

A [Melting point]	B [Melting point] Mol ratio A : B [Melting point]	Trinitrobenzene	Picric acid	Tetranitrobenzene
		[123.0]	[122.0]	[126.0]
α-Naphthylamine	[50.0]	1:1 (214)* 127.5	{1:1 (161)* 75}	Decomposed
β- ,,	[110.0]	1:1 [161]* 45.0	{1:1 (190)* 74}	Decomposed
α-Methylnaphthalene	[−22]*	1:1* [148.5] 98.0	1:1 (142)* 92	1:1 [U : Ca. 86]
β- ,,	[35.0]	1:1 (123)* 44	1:1 (117)* 38.5	1:1 [127.0] 46.5
α-Naphthol	[96.0]	1:1 [193.5] 84.0	1:1 [190.5]* 81.5	1:1 [137.0] 26.0
β- ,,	[122.0]	1:1 [158.5] 36.0	1:1 [156.3]* 34.3	1:1 [130.5] 6.5
α-Ethylnaphthalene	[<−14]*	—	1:1 (98)* > 44	—
β- ,,	[−19]*	—	1:1 (71)* 19.5	—
α-Methoxynaphthalene	[−10]*	1:1 (138)* 82	—	—
β- ,,	[73.0]	1:1* [94.0] −4.0	1:1* [115.0] 17.5	2:1 [100] 9.3
α-Chloronaphthalene	[−17]*	1:1 [132.5] 79.5	1:1 [125.7]* 73.2	1:1 [U:62.0] (1:1 [73.0] 18.5)
β- ,,	[58.5]	1:1 [94.0] 3.2	1:1 [81.5]* −8.8	3:2 [U:93.0]
α-Bromonaphthalene	[5]*	1:1* [134.0] 70.0	1:1* [129.6] 66.1	—
β- ,,	[59]*	—	1:1 [83.5]* −7.0	—
α-Ethoxynaphthalene	[54]*	1:1 (125.5)* 61.3	—	—
β- ,,	[37]*	1:1 (95)* 15.0	—	—
Naphthalene	[80.0]	1:1 [152.5]* 51.0	1:1 [151.5]* 50.5	3:2 [139.5] 41.1
α-Naphthoic acid	[160.0]	2:1* [191.5] 43.8	2:1 [193.5] 46.2	4:1 [165.0] 11.8
β- ,,	[182.5]	3:2 [U : 142.0]	3:2 [U : 143.0]	∨ or (4:1 [U : 156])
β-Naphthylacetate	[68.0]	1:1 [71.0] −24.5	1:1 [PM : 80.0]	1:1 [79.5] −17.5
β-Methylnaphthoate	[75.0]	1:1* [105.5] 5.5	1:1 [72.5] −26.0	∨ [E : 49.5]
α-Phenoxynaphthalene	[56]*	1:1 (112.5)* 23.0	—	—
β- ,,	[93]*	1:1 (105.5)* −2.5	—	—
α-Naphthonitril	[37.0]	1:1* [88.0] 8.0	1:1 [97.5] 18.5	2:1 [72.0] 5.3
β- ,,	[66.0]	1:1* [95.0] 0.5	1:1 [79.0] −15.0	2:1 [84.0] −2.0
α-Naphthophenone	[75.5]*	1:1 (89)* −10.3	—	—
β- ,,	[82]*	—	1:1 (113)* 11	—
α-Nitronaphthalene	[57.0]	{2:1 [PM : 70.0] 1:1* [71.0] −19.0	1:1* [U : 70.0]	∨ [E : 42.0]
β- ,,	[78.0]	∨ or 1:1 [75.5] −25.0	∨ [E : 52.0]	∨ [E : 57.0]

* Data from literature.

( ) Melting points in parentheses represent those of molecular compounds obtained from solution.

{ } Data in brackets are those of other types of molecular compounds.



where X is OH, OC_2H_5, or OCH_3.[4]

Since the real shape of these molecules are regarded as not to differ much from the above formula, i.e. each benzene ring being considered a regular hexagon, the "projection" of substituent X from the aromatic nucleus, which is more prominent in β-position, may interfere with the compound-formation of this type; and in the case of five phenanthrene derivatives, it will be easily understood that the substituent X should be in a freer state (consequently a more hindering state) in the 2- or 3-position than in the 4- or 9-position.

II. The Relation between Compound-Formation and the Substituent in the Monosubstituted Naphthalene Derivatives. From the results enumerated in the second column of Table 1, the effect of substituents on compound-formation in the systems of naphthalene α-derivatives with trinitrobenzene may be given in the following order;

$$\begin{gathered} NH_2 > CH_3 > OH > C_2H_5 > OCH_3 > Cl > Br > OC_2H_5 > (H) \\ > CO_2H > CO_2CH_3 > OC_6H_5 > CN > COC_6H_5 > NO_2 . \end{gathered}$$

This order, which is virtually the same as that in the case of the β-isomer, also holds in the systems of picric acid or tetranitrobenzene. The foregoing order is also related to that of the function groups in the substitution rule of benzene and in other cases.(5) Since the tendency of compound-formation runs parallel with that of the positivity of the substituents, α- and β-nitronaphthalene have the least affinity with three polynitro derivatives of benzene.(6) Such a weakening effect upon affinity seems to be in parallel with the magnitude of the substituents. This is marked in the substituents of analogaous constitution, for example, $CH_3 > C_2H_5$; $OH > OCH_3 > OC_2H_5 > OC_6H_5$; $CO_2H > CO_2CH_3$; $Cl > Br$; etc.(7)(8) These relations are observed in the case of the inorganic—organic molecular compound, of which by Menschutkin the data of some naphthalene derivatives were given in Table 2, together with those observed by the writer.(9)

In the systems dealt in this paper, halochromism appeared regularly. But in the case of crystalline molecular compounds of the naphthylamines with picric acid, it was less halochromic (greenish yellow or yellow) than with trinitrobenzene (dark red or red), from which the existence of another type of compound may be expected.(10)

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(5) This roughly agrees with the diminishing order of dipole moment of these substituents in the aromatic nucleus; and this order is reproduced in the serial measurements of oxidation-reduction potentials of phenanthraquinone derivatives whose 1- or 3-position is occupied by those substituents. (L.F. Fieser, *J. Am. Chem. Soc.* **51** (1929), 3101.).

(6) In the binary and ternary systems of polynitroaromatic compounds only, a few systems belong to a very feeble compound type, and the others to a simple eutectic type.

(7) The number could be increased, for example, $CHO > COCH_3 > COC_6H_5$; $Br > I$.

(8) It will be rather difficult to attribute a plane shape to a whole molecule of naphthalene derivatives of such a large group as $-CO_2H$, $-CO_2CH_3$, $-OCOCH_3$, $-COC_6H_5$.

(9) Details will be reported in a future paper.

(10) Naphthylamine—trinitrocresol and naphthylamine—styphnic acid were produced and they were confirmed to be of the same type of molecular compound.

Table 2.

Mol ratio A:B [Melting point] τ A B	$SbCl_3$	$SbBr_3$
Naphthalene	1:2 [86] 10.7	1:2 [66] −23.3
α-Naphthol(9)	1:2 [77.5] −3.2	—
β- ,, (9)	∨	—
α-Nitronaphthalene	1:1 [39] −26.0	(1:1 [38.2] −37.3) or ∨
β- ,, (9)	1:1 [44.0] −31.5	—
α-Chloronaphthalene	1:2 [46] 3.0	∨
β- ,,	1:1 [29.5] −35.0	∨
α-Bromonaphthalene	1:1 [34.5] −3.5	∨

Experimental.

(1) α-Nitronaphthalene—trinitrobenzene.

Trinitrobenzene: 6.6 mg.

Mol% trinitrobenzene	88.5	76.0	55.6	52.7	48.0	39.8	22.8	15.3	12.1
Melting point	113.0	102.0	—	70.0 (56.0)	71.0	70.0	68.0	65.0	62.5
Thawing point	70.0	69.0	69.0	69.0 (46.0)	69.0	68.0	52.0	52.0	52.0

Total nitronaphthalene: 22.7 mg.

Mol% nitronaphthalene	100.0	97.3	90.0	73.9	70.4	65.6	60.4	52.7	50.1	
Melting point	57.0	55.0	59.0	70.0	70.0	70.2	70.0	71.0	71.0	
Thawing point	56.0	52.5 ↓	51.5	59.0	66.5	69.0	68.3	69.0	(52.0),	70.0
						47.6	44.8	41.4	58.2	64.7
						71.0	78.0	82.0	70.2	70.0
						70.0 ↓	70.0	70.0	68.8	68.8

Eutectic point: 52.0°, 69.0°, 70.0°; 94.5 mol%, 56.0 mol%, 47.3 mol% α-nitronaphthalene.

Compound (1:1): yellowish powder, melting at 71.0°.

Compound (2:1): yellowish powder, melting at 70.0° into two mutually non-miscible liquids.

Range of partial miscibility on liquidus: 75.0 mol%~57.0 mol% α-nitronaphthalene.

(2) α-Nitronaphthalene—picric acid.

Nitronaphthalene: 7.8 mg.

Mol% nitronaphthalene	93.7	73.5	54.5	49.3	40.7	34.5	21.1
Melting point	53.0	61.0 (47.0)	72.0	(72.0)	(84.5)	(93.0)	108.0
Thawing point	49.0	48.0 (40.0)	66.0	69.0 ↓	69.0	69.0	69.0

Total picric acid: 26.5 mg.

Mol% picric acid	64.4	60.2	54.5	50.5	46.8	41.9	36.9	32.7	60.7
Melting point	(92.0)	88.0	83.0	78.0	72.5	71.5	70.0	67.0	90.8
Thawing point	69.8	70.0	70.0	70.0	69.0 ↓	—	50.0	48.0	70.0

Eutectic point: 48.0°, (70.0°); 85.0 mol%, (46.5 mol%) α-nitronaphthalene.

Pertectic point: 72.0°, 53.5 mol% α-nitronaphthalene.

Compound (1:1): pale yellow powder with an incongruent melting point (its unstable congruent melting point: 72.0°).

(3) α-Nitronaphthalene—tetranitrobenzene.

Tetranitrobenzene: 7.0 mg.

Mol% tetranitrobenzene	73.4	43.1	23.3	11.1
Melting point	112.5	81.0	48.0	50.0
Thawing point	45.0	—	43.0 ↓	—

Nitronaphthalene: 5.1 mg.

Mol% nitronaphthalene	96.4	88.3	70.4	38.4
Melting point	54.0	49.0	60.5	101.0
Thawing point	43.0	42.0	41.8	42.8

Eutectic point: 42.0°; 80.0 mol% α-nitronaphthalene.

(4) β-Nitronaphthalene—trinitrobenzene.

Total nitronaphthalene: 7.2 mg.

Mol% nitronaphthalene	100.0	83.4	74.8	47.1	54.8	41.2	26.6
Melting point	78.0	69.0, 65.5	59.0, 68.0	—, 75.5	—, 75.0	—, 80.0	101.0
Thawing point	77.0	45.0, —	46.0, 62.0	46.0 (11)→ 74.0	—, 66.0 ↓	—, 73.0	46.0→73.0

Trinitrobenzene: 10.8 mg.

Mol% trinitrobenzene	93.5	77.2	62.4	54.6	51.7	47.8	41.1	37.5	33.5	29.7	23.0	17.2
Melting point	117.0	103.5	87.0	77.0, —	73.0	66.5, —	—, 74.5	—, 74.0	51.0, 73.0	—, 71.0	61.0, 65.5	68.0, —
Thawing point	90.0	45.0	46.0, —	46.0, —	—	46.0, —	—, 62.0	46.0→62.0	46.0→62.0	46.0→62.0	—, 62.0 ↓	46.0→62.0

In the simple eutectic type,
Eutectic point: 46.0°, 63.0 mol% β-nitrinaphthalene.
In the congruent type,
Eutectic point: 62.0°, 73.5°; 80.5 mol%, 44.4 mol% β-nitronaphthalene.
Compound (1:1): slightly halochromic powdery crystals, melting at 75.5°.

(5) β-Nitronaphthalene—picric acid.

Nitronaphthalene: 4.8 mg.

Mol% nitronaphthalene	92.7	77.0	65.8	55.0	45.3	29.5	12.0
Melting point	73.5	—	—	—	79.0	100.0	114.0
Thawing point	53.5	52.0	52.0 ↓	52.0	51.5	51.5	52.0

Picric acid: 5.0 mg.

Mol% picric acid	80.8	57.4	44.0	34.4	28.9	22.1	13.8
Melting point	109.0	85.0	66.0	54.0	58.0	62.5	70.0
Thawing point	52.0	52.0	51.5 ↓	52.0	52.0	52.0	52.0

Eutectic point: 52.0°, 64.0 mol% β-nitronaphthalene.

(6) β-Nitronaphthalene—tetranitrobenzene.

Nitronaphthalene: 3.9 mg.

Mol% nitronaphthalene	90.7	81.8	66.7	49.0	22.7
Melting point	71.0	63.5	70.0	92.5	114.0
Thawing point	57.0	58.0 ↓	58.0	—	—

Tetranitrobenzene: 3.4 mg. ↓

Mol% tetranitrobenzene	60.3	32.3	25.7	18.8	9.4
Melting point	101.3	68.5	57.0	63.0	71.0
Thawing point	57.0	57.0	57.0	56.0	57.0

Eutectic point: 57.0°, 74.3 mol% β-nitronaphthalene.

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(11) Distinct transition was observed; it is indicated by a horizontal arrow.

In the foregoing six systems (Fig. 1), the hindering effect of substituent in the benzene and naphthalene nucleus was very marked. The presence of nitro radicals in the aromatic rings of both components in the binary system, does not increase the tendency of compound-formation; α- and β-nitronaphthalene showed very little affinity with trinitrobenzene, less with picric acid, and the least with tetranitrobenzene. With the same nitro component, β-nitronaphthalene had less affinity than the α-isomer, presumably the β-isomer has a more reactive nitro radical than the α-isomer.

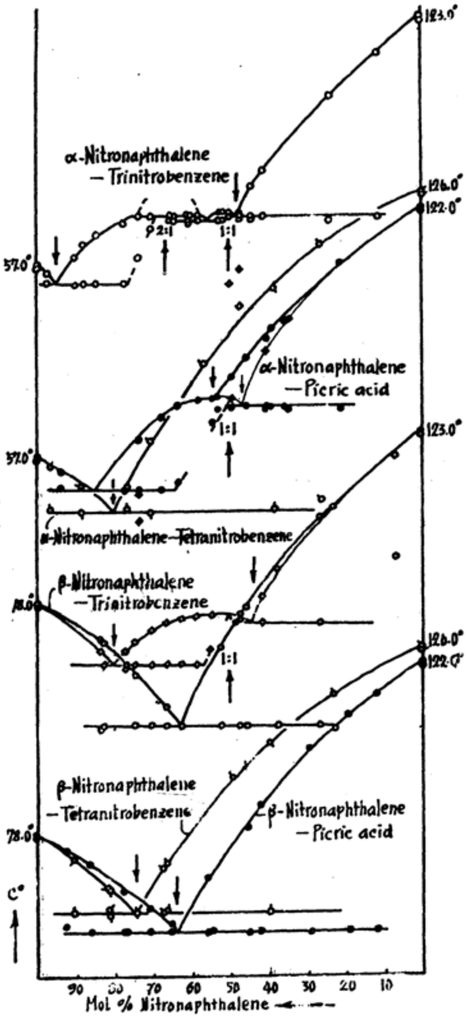

Fig. 1.

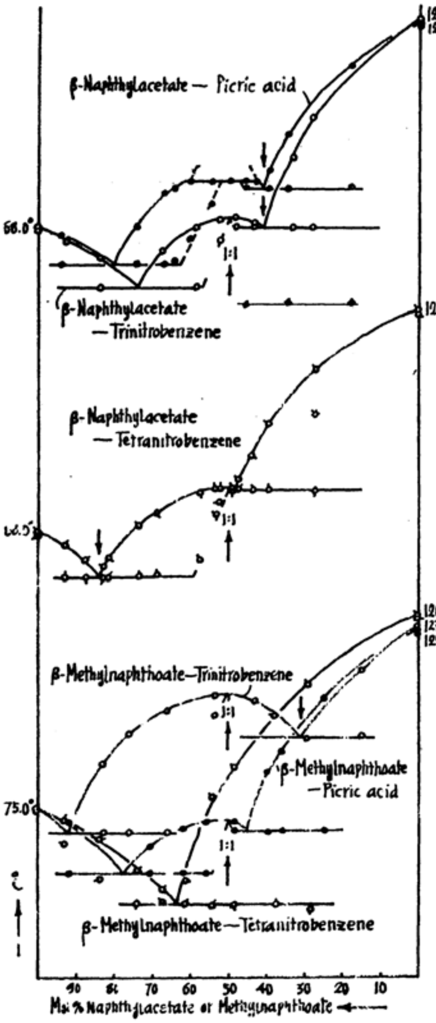

Fig. 2.

(7) β-Naphtylacetate—trinitrobenzene.

Naphtylacetate: 8.4 mg.

Mol% naphthylacetate ...	100.0	92.2	83.5	67.2	58.8	52.4	48.2	43.8	33.2	28.1
Melting point	68.0	64.0	60.0	62.0	68.0	70.0	70.8	69.0	86.8	97.0
Thawing point	67.5	58.5	52.0	viscous	52.0	64.5	68.0	68.0 ↓	68.0	68.0

Eutectic point: 52.0°, 68.0°; 73.7 mol%, 41.8 mol% β-naphthylacetate.

Compound (1:1): light yellow leafy or powdery crystals, melting at 71.0°.

(8) β-Naphthylacetate—picric acid.

Naphthylacetate: 8.8 mg.

Mol% naphthylacetate	93.8	74.0	66.3	54.3	45.3	42.5	34.5	27.6	17.9
Melting point	66.0	68.0	77.0	80.0	80.3	80.0	92.8	102.5	111.0
Thawing point	58.0	58.0	58.0	—	(47.0)→78.5	—	(48.0)→78.0	78.0	(48.0)→79.0

Picric acid: 6.5 mg.

Mol% picric acid	60.8		54.6	50.2	45.2	40.0	36.0
Melting point	83.0		80.0	80.0	80.0	80.0	78.0
Thawing point	78.0	↓	78.5	80.0	74.0	65.0	59.0

Eutectic point: 58.0°, 78.0°; 80.0 mol%, 41.0 mol% β-naphtylacetate.
Compound (1:1): yellow powder, melting at 80.0° into two mutually non-miscible liquids.
Range of partially miscibility on liquidus: 61.5～42.0 mol% β-naphthylacetate.

(9) β-Naphthylacetate—tetranitrobenzene.

Naphthylacetate: 5.6 mg.

Mol% naphthylacetate	92.9	82.9	73.4	68.3	57.7	53.3	47.4	39.3	27.1
Melting point	64.5	59.0	69.8	73.0	78.0	79.5	82.0	96.5	(99.0), 111.0
Thawing point	56.0	56.0	56.5	57.0	60.5	72.5	79.0	79.0	78.5

Total tetranitrobenzene: 6.2 mg.

Mol% tetranitrobenzene	51.0	47.5	56.1	18.1		12.6
Melting point	79.5	79.5	88.0	61.0		60.5
Thawing point	79.0	76.0	79.0	56.0	↓	56.0

Eutectic point: 56.0°, 79.0°; 84.0 mol%, 48.5 mol% β-naphthylacetate.
Compound (1:1): yellow powder, melting at 79.5°.

(10) β-Methylnaphthoate—trinitrobenzene.

Trinitrobenzene: 5.9 mg.

Mol% trinitrobenzene	85.2	71.0		57.6	47.0	34.5	24.6	17.6	0.0
Melting point	111.0	—		104.0	105.0	101.0	95.0	87.0	75.0
Thawing point	94.5	94.0	↓	101.0	100.0	69.0	69.0	69.0	74.0

Eutectic point: 69.0°, 94,3°; 91.5 mol%, 31.0 mol% β-methylnaphthoate.
Compound (1:1): fine light yellow needles, melting at 105.5°.

(11) β-Methylnaphthoate—picric acid.

Total methylnaphthoate: 16.5 mg.

Mol% methylnaphthoate	91.2	70.2	48.1	39.6	61.8	55.7	35.8	24.6
Melting point	72.0	65.0	72.0	85.0	70.0	72.0	90.0	104.0
Thawing point	58.0	58.0	69.5	69.0	58.0	58.0	69.5	69.5

Eutectic point: 58.0°, 69.5°; 77.5 mol%, 45.5 mol% β-methylnaphthoate.
Compound (1:1): yellow prisms, melting at 72.5°.

(12) β-Methylnaphthoate—tetranitrobenzene.

Methylnaphthoate: 5.6 mg.

Mol% methylnaphthoate	92.9	83.8	67.2	61.3	48.3	37.8
Melting point	71.8	66.5	53.0	56.0	86.0	99.8
Thawing point	65.5	56.0	50.0	49.5	49.5	49.5

Tetranitrobenzene: 6.2 mg.

Mol% tetranitrobenzene	71.2	45.7	26.0
Melting point	107.5	78.0	58.0
Thawing point	48.0	49.0	49.5

Eutectic point: 49.5°, 63.7 mol% β-methylnaphthoate.

In the behaviour of compound-formation of β-naphthylacetate and its isomer, namely, β-methylnaphthoate, the former resembles naphthol and the latter naphthoic acid, as will be seen from Table 1 and Fig. 2.

Summary.

The effect of the substituents in the aromatic (naphthalene) ring on compound-formation was studied in connexion with "aromatic—nitro-aromatic combination," the results of which were in good agreement with those previously reported.

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