Additive Compounds of Arylamines with Nitro-derivatives of Naphthalene.

By J. J. Sudborough, Norman Picton and D. D. Karvé.

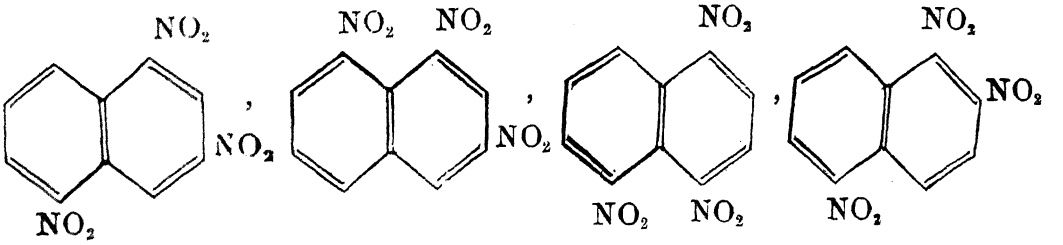
—:o:—

In previous communications (J. Chem. Soc., 1901, *79*, 522; 1903, *83*, 1344; 1906, *89*, 583; 1910, *97*, 773; 1911, *99*, 209; this Journal, *1*, 149, 159, 167. Compare also Hepp, Annalen, 1882, *215*, 344; Van Romburgh, Rec. trav. chim., 1895, *14*, 67; Bamberger, Ber., 1900, *33*, 109; Wedekind, *ibid*, 426; Loring Jackson and Clarke, Ber., 1904, *37*, 176; Chem. Soc. Proc., 1906, *22*, 83; Noelting and Sommerhoff, Ber., 1906, *39*, 76; Sommerhoff, Diss. Zurich, 1904; Kremann, Monatsh., 1911, *32*, 609; Bugnet, Compt. rend., 1909, *149*, 857) attention has been drawn to the characteristic colored compounds, which are formed by the union of *s*-trinitrobenzene and similar compounds with aromatic hydrocarbons, arylamines, phenols and phenolic ethers, phenyl-hydrozones and unsaturated compounds.

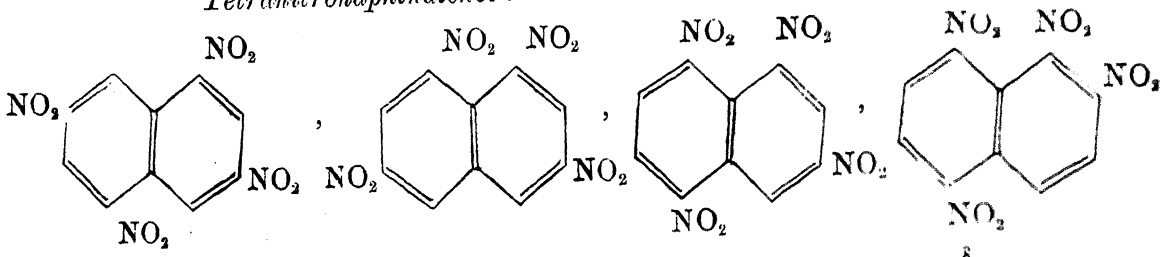
The present paper contains an account of experiments which were undertaken with the object of ascertaining whether poly-nitro-derivatives of naphthalene can form similar additive compounds, and, if so, to determine the influence of the positions of the nitro-groups on the formation of the colored compounds.

We have attempted to include all the known tri- and tetranitro-naphthalenes in the scope of the investigation. The following are described in the literature .—

Trinitronaphthalenes :—



Tetranitronaphthalenes :—



α 1:3:5:7 , *β* 1:3:6:8 , *γ* 1.3:5:8 , *δ* 1:2:5:8

We have succeeded in preparing all the compounds with the exception of the δ-tri-compound. We have examined the product stated by Will (Ber., 1895, *28*, 377) to be a mixture of the *α*- and δ-trinitronaphthalenes in almost equal quantities. We have been able to isolate from this mixture a small amount of γ-trinitronaphthalene, together with a trinitronaphthalene (m. p. 119°) which yields extremely well-defined crystalline compounds with *α*-naphthylamine and other arylamines. The trinitronaphthalene recovered from the additive compounds crystallises well from glacial acetic acid, melts at 119° and is the *α*-compound described by Aguiar (Ber., 1872, *5*, 372, 897).

Experimental.

I. Additive Cmpounds of *α*-Trinitronaphthalene.

α-Trinitronaphthalene-α-naphthylamine. $2C_{10}H_5(NO_2)_3, C_{10}H_7NH_2$, may readily be obtained from benzene, chloroform or alcoholic solutions of the components, provided a slight excess of base is used. It crystallises from chloroform or benzene in deep purple-black prisms or from alcohol, in which it is only sparingly soluble, in needles melting at 135·5°. When boiled with alcohol, an almost colorless solution is obtained and as the solution cools, colorless crystals of *α*-trinitronaphthalene are deposited together with colored needles of the additive compound.

The compound was analysed by decomposing it with warm dilute hydrochloric acid and weighing the *α*-trinitronaphthalene. 0·3018 gave 0·2330 gram (after allowing for solubility) =77·2. $C_{10}H_5(NO_2)_3, C_{10}H_7NH_2$ requires 64·8 and $2C_{10}H_5(NO_2)_3, C_{10}H_7NH_2$ requires 78·6 per cent. 0·1476 gave 18·8 cc. of moist N at 15° and 751 mm. N=14·74. $C_{30}H_{19}O_{12}N_7$ requires N=14·65 per cent.

Molecular weight determination. 0·2032 gram dissolved in 17·54 grams of pure benzene lowered the freezing point 0·271°.

M=214. After addition of a further 0·2020 gram the freezing point was lowered 0·532°. M=217. These numbers show conclusively that this additive compound, like those derived from trinitrobenzene, is almost completely resolved into its components in dilute benzene solution. One third the molecular weight of $2C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$ is 223.

α - Trinitronaphthalene - β-Naphthylamine is obtained in the form of dark, purple-red, flat needles when benzene solutions of the components are mixed. It melts at 145·5-146°, and is not so soluble as the *α* - naphthylamine derivative in the majority of solvents, and is partially decomposed when warmed with most organic liquids.

0·1604 gave 20·2 c.c. of moist N. at 15·5° and 763 mm.= 14·77. $C_{30}H_{19}O_{12}N_7$ requires N=14·65 per cent.

0·3672 when decomposed with hot dilute hydrochloric acid gave 0·2852 of *α* - trinitronaphthalene=77·7. $2C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$ requires 78·6 per cent.

α - Trinitronaphthalene - benzidine, 2 $C_{10}H_5(NO_2)_3$, $NH_2C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, crystallises from benzene in black prisms melting at 138°. 0·0788 gave 0·1554 CO_2* and 0·0245 H_2O. C=53 8 and H=3·43. $C_{32}H_{22}O_{12}N_8$ requires C=54·1 and H=3·10 per cent.

α - Trinitronaphthalene - anisidine, $C_{10}H_5(NO_2)_3$, 2 $C_6H_4(OCH_3)(NH_2)$, forms minute black crystals from acetone and melts at 128°. 0·200 gave 22·4 c.c. nitrogen at 13° and 759 mm. N= 13·23. $C_{24}H_{23}O_8N_5$ requires N=13·80 per cent.

α - Trinitronaphthalene-psuedo - cumidine, $C_{10}H_5(NO_2)_3$, $C_6H_2(CH_3)_3NH_2$, crystallises from benzene in black needles melting at 101°. 0·200 gave 25·2 c.c. of nitrogen at 16° and 733 mm. N=14·15. $C_{19}H_{18}O_6N_4$ requires N = 14·07 per cent. 0·200 in 15 grams of pure benzene lowered the freezing point 0·32°. M=208·3.

α-Trinitronaphthalene-m-penylenediamine, $C_{10}H_5(NO_2)_3$, $C_6H_4(NH_2)_2$, crystallises from a mixture of alcohol and benzene in thin deep chocolate needles melting at 170°. 0·204 gave 0·1452 of *α* - trinitronaphthalene = 71·2. $C_{10}H_5(NO_2)_3$, $C_6H_4(NH_2)_2$ requires 72·5 per cent.

α - Trinitronaphthalene-1 : 5 - naphthylenediamine, $C_{10}H_5(NO_2)_3$, $C_{10}H_6(NH_2)_2$, crystallises from a mixture of alcohol and

* Carbon and hydrogen were determined, as nitrogen would give no indication of the composition, since the nitrocompound and the base contain practically the same percentage of nitrogen.

benzene in thin black needles melting and decomposing at 243°. 0·1116 gave 18·58 c. c. of nitrogen at 29° and 675 mm. N=16·72. $C_{20}H_{17}O_6N_5$ requires N=16·63 per cent.

α-Trinitronaphthalene-ethyl-α-naphthylamine, $C_{10}H_5(NO_2)_3$, $C_{10}H_7NHC_2H_5$, is obtained in the form of small reddish black needles when the nitrocompound and an excess of base are dissolved in benzene and alcohol added. It melts at 109° and is readily decomposed by dilute hydrochloric acid. 0·3016 gave 0·1800 of trinitronaphthalene = 59·7. $C_{10}H_5(NO_2)_3$, $C_{10}H_7NHC_2H_5$ requires 60·6 per cent.

α-Trinitronaphthalene-diphenylamine, $2C_{10}H_5(NO_2)_3$, $(C_6H_5)_2NH$, crystallises from a mixture of alcohol and benzene in dark red needles, or from toluene in deep brown, shining plates melting at 101°. 0·1050 gave 14·75 c.c. of nitrogen at 28·8° and 678·5 mm. N=14·19. $C_{32}H_{21}O_{12}N_7$ requires N=14·1 per cent. Using the method of Gadre and Sudborough, (This Journal, 1916, *1*, 161) 0·2276 gram gave 0·0655 gram diphenylamine hydrochloride = 23·66, and 0·1761 gram α-trinitronaphthalene = 77·3. $2C_{10}H_5(NO_2)_3$, $(C_6H_5)_2NH$ requires 24·31 and 75·7 per cent. respectively.

α-Trinitronaphthalene-dimethylanline, $2C_{10}H_5(NO_2)_3$, $C_6H_5N(CH_3)_2$, is only formed when a large excess of the base is employed. It crystallises from benzene, in which it readily dissolves, in black lustrous prisms melting at 102°. It readily loses dimethylanilime when heated at 100°. 0·4980 when heated in this manner gave 0·4024 of α-trinitronaphthalene melting at 120° = 80·8. $2C_{10}H_5(NO_2)_3$, $C_6H_5N(CH_3)_2$ requires 81·3 per cent.

It is readily decomposed into its components when warmed with ether, alcohol or dilute acids.

α-Trinitronaphthalene-diethyl-β-naphthylamine, $C_{10}H_2(NO_2)_3$, $C_{10}H_7N(C_2H_5)_2$, crystallises in long black needles with a metallic lustre and melts at 57-58°. 0·3016 gave 0·1792 of trinitronaphthalene=59·4. $C_{10}H_5(NO_2)_3$, $C_{10}H_7N(C_2H_5)_2$ requires 57·0 per cent.

α-Trinitronaphthalene-carbazole, $C_{10}H_5(NO_2)_3$, $(C_6H_4)_2NH$, crystallises from chloroform in red needles melting at 166°. 0·120 gave 14·0 c.c. of nitrogen at 18° and 739 mm. N=13·1. $C_{22}H_{14}O_6N_4$ requires N=13·0 per cent.

II. Additive Compounds of β-Trinitronaphthalene.

These compounds are somewhat more difficult to obtain than those derived from the α-trinitro-compound. They are less

stable and are only formed in the presence of an excess of the base. When warmed with organic solvents in the absence of an excess of base they are readily resolved into their components. The compounds which have been obtained, crystallise remarkably well and are less soluble in benzene or toluene than the *a* - trinitro-compounds.

β-Trinitronaphthalene - a - naphthylamine. In the preparation of the compound, we noticed that the product differed in appearance according to the relative amounts of the nitro-compound and base and also that the products had no sharp melting points. The following experiments were made with benzene solution (*a*) 1 gram of nitro-compound with 2 grams of base, (*b*) 1 with 3, (*c*) 1 with 4 and (*d*) 1 with 5, approximately the same amount of benzene being used in each case, namely 150 c.c. In each experiment crystals of the same type were deposited as the solution cooled, namely large, deep crimson red needles melting at 145-151°. An analysis of the compound from experiment (*a*) gave the following numbers :—0·3342 gave 0·2616 of β-trinitronaphthalene melting at 215° when decomposed with warm dilute hydrochloric acid=78·3. $2C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$ requires 78·6 per cent.

0·343 of the compound from experiment (*d*) when decomposed in a similar manner gave 0·2728 of the trinitro-compound=79·5 per cent.

A different product was obtained when 1 gram of the nitro-compound and 8 grams of the base were dissolved in the smallest possible amount of hot benzene and the solution allowed to cool. Small dark brown prisms melting at 125-140°, and quite different in appearance from the red prismatic needles already described, were deposited 0·288 gave 0·1892 of β-trinitronaphthalene=65·7. $C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$ requires 68·8 per cent.

A compound melting at the same temperature and having the same composition was obtained when a mixture of 1 gram of nitro-compound and 4 grams of base was crystallised from toluene. It forms characteristic deep violet black plates. 0·4084 gave 0·2650 of trinitronaphthalene=64·9 per cent. When crystallised from benzene containing a small amount of *a* - naphthylamine, this compound yields red needles melting at 145-151° and the red needles when crystallised from toluene containing an excess of base yield the purple-black plates.

β - Trinitronaphthalene and β-naphthylamine yield an additive compound $2C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$, which crystallises from benzene, in which an excess of the base is present, in

deep red prisms melting at 132-133°. 0·3566 gave 0·2808 of β-trinitronaphthalene= 78·7. 2 $C_{10}H_5(NO_2)_3$, $C_{10}H_7NH_2$ requires 78·6 per cent.

A compound formed by the union of one molecule of nitro-compound with one of base could not be isolated, as when a large excess of base is used, this crystallises out with the additive compound described above.

No additive compound could be obtained from the β-trinitro-derivative and dimethylaniline or diethyl β-naphthylamine even in the absence of a solvent.

III. Additive Compounds of γ-Trinitronaphthalene.

An additive compound of γ-trinitronaphthalene and α-naphthylamine is obtained when a mixture of the nitro-compound with three times its weight of base is crystallised from a mixture of benzene and alcohol. It forms slender dark red needles melting at about 67-68° and is readily decomposed when washed with relatively large amounts of solvent. 0·1456 gave 0·0640 gram of trinitronaphthalene=44·0. $C_{10}H_5(NO_2)_3$, 2 $C_{10}H_7NH_2$ requires 47·9 per cent. Another specimen prepared from a mixture of ether and alcohol gave 46·5 per cent of trinitronaphthalene.

β-naphthylamine also forms an additive compound with γ-trinitronaphthalene, but so far it has not been obtained in a pure form, as it is usually accompanied by crystals of the trinitronaphthalene or of the base, and is also readily decomposed when washed with solvents.

No additive compound of the γ-trinitro-derivative and diethyl-β-naphthylamine has been isolated.

IV. Additive Compounds of α-Tetranitronaphthalene.

The additive compound of α-tetranitronaphthalene and α-naphthylamine is readily obtained in the form of glistening black needles when a mixture of the components is crystallised from glacial acetic acid. It melts and decomposes with rapid evolution of gas at about 220° when slowly heated, and is not readily soluble in the majority of organic solvents. When mixed with a small amount of α-naphthylamine and crystallised from toluene it forms glistening black plates. It is decomposed when gently warmed with acetic anhydride.

0·2012 gave 26·6 cc. of moist N. at 14° and 775 mm. N=15·86. 0·2048 gave 27·1 cc. of moist N at 15° and 770 mm.

=15·71. 0·3022 when decomposed with hot dilute hydrochloric acid gave 0·2032 of tetranitronaphthalene = 67·2. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires 15·52 per cent. of nitrogen and 68·3 per cent. tetranitronaphthalene.

β-naphthylamine yields a very similar additive compound with α-tetranitronaphthalene. It crystallises from toluene in glistening black needles and melts at 220-221°. 0·3004 gave 0·2048 of tetranitronaphthalene = 68·1. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires 68·3 per cent.

An additive compound of α-tetranitronaphthalene and diethyl-β-naphthylamine is formed when a mixture of the nitro-compound with four times its weight of base is crystallised from a mixture of benzene and alcohol. It forms slender dark green needles, melts not very sharply at 134-136° and is immediately decolorised by cold dilute hydrochloric acid. 0·3280 gave 0·2030 of α-tetranitronaphthalene=61·9. $C_{10}H_4(NO_2)_4$, $C_{10}H_7N(C_2H_5)_2$ requires 60·8 per cent. No additive compound could be obtained from the α-tetranitro-compound and dimethylaniline.

V. Additive Compounds of β-Tetranitronaphthalene.

β-Tetranitronaphthalene crystallises from benzene in flat glistening yellow needles melting at 207°. and containing benzene of crystallisation. The crystals gradually lose this benzene on exposure to air and become opaque. 1·0016 lost 0·2014 when heated at 100° = 20·1. $C_{10}H_4(NO_2)_4$, C_6H_6 requires 20·2 per cent.

β-Tetranitronaphthalene-naphthalene, $C_{10}H_4(NO_2)_4$,$C_{10}H_8$, crystallises from benzene in slender, lemon yellow needles melting at 191-192°. 0·0994 gave 12·79 c.c. nitrogen at 28° and 677 mm. N=13·00. $C_{20}H_{12}O_8N_4$ requires N=12·84 per cent.

β-Tetranitronaphthalene-anthracene, $C_{10}H_4(NO_2)_4$, $C_{14}H_{10}$, crystallises from acetone in deep red shining needles melting at 212-214°. 0·1872 gave 21·39 c.c. nitrogen at 26° and 678·6 mm. N=11·67. $C_{24}H_{14}O_8N_4$ requires N=11·52 per cent.

β-Tetranitronaphthalene-phenanthrene, $C_{10}H_4(NO_2)_4$, $C_{14}H_{10}$, crystallises from benzene in orange yellow needles melting at 243°. 0·0987 gave 11·48 c. c. nitrogen at 28·0° and 677 mm. N=11·75. $C_{24}H_{14}O_8N_4$ requires N=11·52 per cent.

β-Tetranitronaphthalene-acenaphthene, $C_{10}H_4(NO_2)_4$ $C_{12}H_{10}$, crystallises from benzene in shining deep red prisms, or from acetone in slender orange needles, melting at 125°. 0·1492

gave 18·1 c.c. nitrogen at 25·5° and 676·7 mm. N=12·35. $C_{22}H_{14}O_8N_4$ requires N=12·14 per cent.

β - Tetranitronaphthalene - aniline, $C_{10}H_4(NO_2)_4$, $C_6H_5NH_2$, is formed when equimolecular quantities of the two components are heated together in the absence of a solvent. It is in the form of a dark brown solid, smelling of aniline and melting fairly sharply at 154°. 0·1231 gave 0·0946 β - tetranitronaphthalene on washing with hot dilute hydrochloric acid=76·9. $C_{10}H_4(NO_2)_4$, $C_6H_5NH_2$ requires 76·8 per cent.

β - Tetranitronaphthalene - α - naphthylamine, $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$, is readily obtained, when equal weights of the components are crystallised from hot benzene, in the form of deep purple needles with a metallic lustre. It melts at 204-205° and is sparingly soluble in the majority of organic solvents, with the exception of cold acetone, hot benzene, toluene or acetic acid. It is resolved into its components when dissolved in chloroform and the solution allowed to cool. 0·220 gave 28·76 c.c. of moist nitrogen at 17° and 775 mm. N=15·48. 0·3730 gave 0·2523 of β - tetranitronaphthalene when decomposed with hot dilute hydrochloric acid = 67·6. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires N = 15·52 per cent. and tetranitronaphthalene= 68·3 per cent.

The additive compound with β - naphthylamine may be prepared in a similar manner; it crystallises in deep brown flat plates melting at 211-212°. A mixture of the α and β compounds melts at about 207° but softens at a lower temperature. This compound is less soluble than its isomeride in the majority of solvents. 0·3018 gave 0·2024 of tetranitronaphthalene=67·1. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires 68·3 per cent.

As these derivatives of the β - tetranitro-compound appear to be among the most stable of the additive compounds of nitro-derivatives of naphthalene and arylamines we have attempted to prepare their acetyl derivatives (compare J. Chem. Soc., 1901, *79*, 529.)

1 gram of α - naphthylamine - β - tetranitronaphthalene was gently warmed with 5 cc. of acetic anhydride until a clear deep yellow solution was obtained; as this cooled, slender yellow needles separated. After recrystallisation from acetic anhydride these melted at 184-185°. An acetyl derivative is also formed when a mixture of β - tetranitronaphthalene (0·5 gram) and acet - α - naphthalide (2 grams) is crystallised from ethyl alcohol. It forms slender, canary yellow needles and contains alcohol of crystallisation. 0·5008 when heated at 100° lost 0·0426=8·5

and turned a somewhat deeper yellow colour. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH{\cdot}COCH_3$, C_2H_5OH requires 8·53 per cent. loss. The product thus obtained was boiled with dilute hydrochloric acid until the yellow colour had completely disappeared and the tetranitronaphthalene estimated. 0·4168 gave 0·2606 tetranitronaphthalene=62·5. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH{\cdot}COCH_3$ requires 62·5 per cent. 0·4102 of the canary yellow crystals obtained from the alcoholic solution gave 0·2341 tetranitronaphthalene=57·1 per cent. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH{\cdot}COCH_3$, C_2H_5OH requires 57·1 per cent.

An acetyl derivative of β-naphthylamine-β-tetranitronaphthalene can be obtained in a similar manner. It crystallises from the acetic anhydride in slender golden yellow needles melting at 200-201°. 0·3472 gave 0·2104 of tetranitronaphthalene= 60·6. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH{\cdot}COCH_3$ requires 62·5 per cent.

When boiled with ethyl alcohol the acetyl derivative is largely decomposed into its components, but it may be synthesised from these in alcoholic solution, provided a large excess of acet-β-naphthalide is used. The yellow crystals thus obtained melt at 201-202° and do not contain alcohol of crystallisation.

β - Tetranitronaphthalene - benzidine, $C_{10}H_4(NO_2)_4$, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, crystallises from benzene in black prisms or from xylene in glistening black needles melting at 194°. 0·1692 gave 0·3318 of CO_2 and 0·062 H_2O. C=53·5 and H=4·1. $C_{22}H_{16}O_8N_6$ requires C=53·7 and H=3·25 per cent.

β - Tetranitronaphthalene - psuedo - cumidine, $C_{10}H_4(NO_2)_4$, $C_6H_2(CH_3)_3{\cdot}NH_2$, crystallises from benzene in black needles when an excess of base is used. It melts at 155°. 0·092 gave 12·8 c.c. nitrogen at 17° and 741 mm. N=15·74. $C_{19}H_{17}O_8N_5$ requires N=15·80 per cent.

β - Tetranitronaphthalene - dianisidine, forms a black crystalline powder melting at 205°.

β - Tetranitronaphthalene - methyl - α - naphthylamine, $C_{10}H_4(NO_2)_4$, $C_{10}H_7{\cdot}NH{\cdot}CH_3$, crystallises in purple-black needles which soften at 160° and melt at 165°. They are moderately soluble in benzene or alcohol and are decomposed by acetic anhydride. 0·5366 gave 0·3741 of β-tetranitronaphthalene = 69·7. $C_{10}H_4(NO_2)_4$, $C_{10}H_7{\cdot}NH{\cdot}CH_3$ requires 66·2 per cent.

β - Tetranitronaphthalene-ethyl - α - naphthylamine, $C_{10}H_4(NO_2)_4$, $C_{10}H_7{\cdot}NH{\cdot}C_2H_5$, is obtained from a mixture of alcohol and a small amount of benzene, in the presence of a large excess

of the base in the form of slender black needles melting at 134°. It is readily decomposed by most organic solvents except when an excess of the base is present. 0·3040 gave 0·1940 of tetranitronaphthalene=63·8. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH{\cdot}C_2H_5$ requires 64·3 per cent.

β-Tetranitronaphthalene-diphenylamine, $2C_{10}H_4(NO_2)_4$, $NH(C_6H_5)_2$, crystallises from benzene when an excess of the base is present, in black needles melting at 185°. 0·180 gave 26·4 c.c. nitrogen at 20° and 732·5 mm. N=16·15. $C_{32}H_{19}O_{16}N_9$ requires N=16·05 per cent.

β-Tetranitronaphthalene-phenyl-β-naphthylamine, $C_{10}H_4(NO_2)_4$, $C_6H_5{\cdot}NH{\cdot}C_{10}H_7$, crystallises from a mixture of alcohol and acetone when a large excess of the base is present in deep violet-brown needles melting at 173-174°. 0·1168 gave 15·05 c.c. nitrogen at 24·7° and 677·6 mm. N=13·17 $C_{26}H_{17}O_8N_5$ requires N=13·28 per cent.

β-Tetranitronaphthalene-benzyl-α-naphthylamine, $C_{10}H_4(NO_2)_4$, $CH_2{\cdot}C_6H_5{\cdot}NH{\cdot}C_{10}H_7$, crystallises from benzene, when a slight excess of the base is present in deep black, microscopic needles melting at 160°. 0·1220 gave 15·51 c.c. nitrogen at 24·0° and 679·5 mm. N=13·06. $C_{27}H_{19}O_8N_5$ requires N=12·94 per cent.

β-Tetranitronaphthalene-p-tolyl-β-naphthylamine, $C_{10}H_4(NO_2)_4$, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_7$, crystallises from a mixture of alcohol and acetone in the presence of a large excess of the base in slender deep black, shining needles melting at 150°. 0·0994 gave 14·00 c.c. nitrogen at 27° and 675 mm. N=14·24. $C_{27}H_{19}O_8N_5$ requires N=12·94 per cent.

β-Tetranitronaphthalene-dimethylaniline, $C_{10}H_4(NO_2)_4$, $C_6H_5{\cdot}N(CH_3)_2$, crystallises from benzene containing a large excess of the base in black prisms, which have no sharp melting point. 0·500 gave 0·3595 of nitro-compound when heated at 100°= 71·9. $C_{10}H_4(NO_2)_4$, $C_6H_5N{\cdot}(CH_3)_2$ requires 71·8 per cent. It is extremely readily decomposed into its components.

β-Tetranitronaphthalene-diethyl-β-naphthylamine, is obtained in the form of black, lustrous, rectangular plates when a mixture of the nitro-compound and a large excess of the base is crystallised from alcohol. It melts at 122-123°, and is slowly decomposed by cold dilute hydrochloric acid. 0·3064 gave 0·1872 of tetranitronaphthalene = 61·1. $C_{10}H_4(NO_2)_4$, $C_{10}H_7N(C_2H_5)_2$ requires 60·7 per cent. It is decomposed when warmed with different organic solvents.

The compounds of β-tetranitronaphthalene with quinoline, *iso*quinoline and the two corresponding tetrahydro-derivatives are obtained when equimolecular quantities of the two components are heated together in the absence of a solvent. These were analysed by washing with warm dilute hydrochloric acid.

The quinoline compound is a dark brown solid melting at 123-124°. 0·1320 gave 0·0930 β-tetranitronaphthalene=70·45. $C_{10}H_4(NO_2)_4$, C_9H_7N requires 70·5 per cent.

The isoquinoline compound is also a dark brown solid melting at 137°. 0·1328 gave 0·0936 tetranitronaphthalene= 70·45. $C_{10}H_4(NO_2)_4$, C_9H_7N requires 70 5 per cent.

The tetrahydroquinoline compound is a shining black substance melting at 112°. 0·2132 gave 0·1486 tetranitronaphthalene=69·7. $C_{10}H_4(NO_2)_4$, $C_9H_{11}N$ requires 69·9 per cent.

The tetrahydroisoquinoline compound is a deep black substance melting at 85-87°. 0·1839 gave 0·1289 β-tetranitronaphthalene=70·1. $C_{10}H_4(NO_2)_4$, $C_9H_{11}N$ requires 69·9 per cent.

β-Tetranitronaphthalene-β-napthol-ethyl ether, $C_{10}H_4(NO_2)_4$, $C_{10}H_7OC_2H_5$, crystallises from acetone in the presence of an excess of the ether in bright scarlet leaflets melting at 140-140·5°. 0·2026 gave 23·33 c.c. nitrogen at 27·5° and 677 mm. N=11·65. $C_{22}H_{16}O_9N_4$ requires N=11·67 per cent.

β-Tetranitronaphthalene-benzaldehyde-phenylhydrazone, $C_{10}H_4(NO_2)_4$, 2 $C_6H_5{\cdot}HC{:}N{\cdot}NH{\cdot}C_6H_5$ crystallises from a mixture of alcohol and acetone, in the presence of a slight excess of the hydrazone, in violet-brown powdery needles melting at 200°. 0·1368 gave 22·01 c.c. nitrogen at 29° and 676·3 mm. N=16·18. $C_{38}H_{28}O_8N_8$ requires N=16·00 per cent.

β-Tetranitronaphthalene-acetophenone-phenylhydrazone, $C_{10}H_4(NO_2)_4$, 2 $CH_3{\cdot}C(C_6H_5){:}N{\cdot}NH{\cdot}C_6H_5$, crystallises from a mixture of acetone and alcohol, in the presence of an excess of the phenylhydrazone in small, shining black flat crystals melting at 171°. 0·1448 gave 21·92 c.c. nitrogen at 24·5° and 678 mm. N=15·49. $C_{38}H_{32}O_8N_8$ requires N=15·39 per cent.

β-Tetranitronaphthalene-cinnamylidene-acetophenone, $2C_{10}H_4(NO_2)_4$, $C_6H_5{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5$, crystallises from a mixture of alcohol and acetone in thin bright yellow needles melting at 192°. 0·1272 gave 16·64 c.c. nitrogen at 27° and 676 mm. N=13·26. $C_{37}H_{22}O_{17}N_8$ requires N=13·18 per cent.

β - Tetranitronaphthalene - dibenzylidene - acetone, $2C_{10}H_4(NO_2)_4$, $CO(CH{:}CH{\cdot}C_6H_5)_2$, crystallises from a mixture of alcohol and acetone in thin lemon yellow needles melting at 234°. 0·1208 gave 15·60 c.c. nitrogen at 25·0° and 679·5 mm. N=13·23. $C_{37}H_{22}O_{17}N_8$ requires N=13·18 per cent.

Compounds could not be obtained from the β-tetranitro-derivative and diphenyl, triphenylmethane and phenylacridine.

VI. Additive Compounds of γ-Tetranitronaphthalene.

γ - Tetranitronaphthalene - α - naphthylamine crystallises from benzene in slender black needles melting and decomposing at 162°. It is only sparingly soluble in alcohol and is decomposed by even small amounts of acetic anhydride, so that no acetyl derivative could be isolated. 0·2682 gave 0·1830 of tetranitronaphthalene=68·2. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires 68·3 per cent.

The isomeric β - compound, crystallises in slender, bronze-green needles melting at 163-164° and is immediately decolorised by dilute hydrochloric acid. 0·317 gave 0·2100 of γ - tetranitronaphthalene=66·2. $C_{10}H_4(NO_2)_4$, $C_{10}H_7NH_2$ requires 68·3 per cent. It dissolves readily in acetic acid, benzene or acetone and moderately in chloroform or alcohol. When mixed with a slight excess of acetic anhydride, it yields an acetyl derivative which crystallises from the anhydride in bright scarlet needles. These melt at 158° and are decomposed when warmed with ethyl alcohol.

γ - Tetranitronaphthalene-dimethylaniline, $C_{10}H_4(NO_2)_4$, $C_6H_5N(CH_3)_2$ crystallises in slender black needles melting at about 113°. It is readily decolorised when washed with alcohol but may be recrystallised from this solvent provided an excess of the base is used. 0·500 when heated gave 0·3623 of γ - tetranitronaphthalene = 72·5. $C_{10}H_4(NO_2)_4$, $C_6H_5N(CH_3)_2$ requires 71·8 per cent.

The additive compound of diethyl β - naphthylamine and γ - tetranitronaphthalene forms slender black needles melting at 118-119°; it is moderately soluble in alcohol but decomposes at the same time into its components 0·3056 gave 0·1760 of γ - tetranitronaphthalene = 57·6. $C_{10}H_4(NO_2)_4$, $C_{10}H_7N(C_2H_5)_2$ requires 60·7 per cent.

VII. Conclusion.

The following is a list of additive compounds prepared with their compositions and melting points.

1. α-Trinitronaphthalene.

Addendum.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.
1. α-Naphthylamine ...	2 : 1	Deep purple-black prisms.	135·5°
2. β-Naphthylamine ...	2 : 1	Purple red flat needles	145·5-146°
3. Benzidene ...	2 : 1	Black prisms	138°
4. Anisidine ...	1 : 2	Minute black crystals	128°
5. Psuedo-cumidine ...	1 : 1	Black needles	101°
6. *m*-Phenylenediamine ...	1 : 1	Deep chocolate needles	170°
7. 1:5-Naphthylenediamine ...	1 : 1	Thin black needles	243°
8. Ethyl-α-naphthylamine...	1 : 1	Reddish black needles	109°
9. Diphenylamine ...	2 : 1	Dark red needles	101°
10. Dimethylaniline ...	2 : 1	Black prisms	102°
11. Diethyl-β-naphthylamine.	1 : 1	Long black needles	57-58°
12. Carbazole ...	1 : 1	Red needles	166°

2. β-Trinitronaphthalene.

Addendum.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.
1. α-Naphthylamine ...	? : 1	Deep crimson-red needles.	145-151°
2. „ „ ...	1 : 1	Dark brown prisms	125-140°
3. β-Naphthylamine ...	2 : 1	Deep red prisms	132-133°

3. γ-Trinitronaphthalene.

Addendum.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.
1. α-Naphthylamine ...	1 : 2	Slender dark red needles.	67-68°
2. β-Naphthylamine ...		Could not be obtained pure.	

4. α-Tetranitronaphthalene.

Addendum.	Mols. of nitro-compound : mols. of addendum.	Appearance	M. P.
1. α-Naphthylamine ...	1 : 1	Glistening black plates	220°
2. β-Naphthylamine ...	1 : 1	Glistening black needles	220-221°
3. Diethyl-β-naphthylamine	1 : 1	Dark green needles	134-136°

5. β - Tetranitronaphthalene.

Addendum.	Mols. of nitro compound : mols. of addendum.	Appearance.	M. P.
1. Naphthalene ...	1 : 1	Lemon-yellow needles ...	191-192°
2. Anthracene ...	1 : 1	Deep-red shining needles ...	212-214°
3. Phenanthrene ...	1 : 1	Orange yellow needles ...	243°
4. Acenaphthene ...	1 : 1	Shining deep-red prisms ...	125°
5. Aniline ...	1 : 1	Dark-brown solid ...	154°
6. α - Naphthylamine ...	1 : 1	Deep purple needles ...	204-205°
7. β - Naphthylamine ...	1 : 1	Deep-brown plates ...	211-212°
8. Acet- α - naphthalide ...	1 : 1	Slender yellow needles ...	184-185°
9. Acet-β - naphthalide ...	1 : 1	Slender golden yellow needles ...	200-201°
10. Benzidene ...	1 : 1	Black prisms ...	194°
11. Psuedo-cumidine ...	1 : 1	Black needles ...	155°
12. Dianisidine ...	—	Black crystalline powder ...	205°
13. Methyl- α - naphthylamine ...	1 : 1	Purple-black needles ...	165°
14. Ethyl - α - naphthylamine ...	1 : 1	Slender black needles ...	134°
15. Phenyl- β - naphthylamine ...	1 : 1	Deep violet-brown needles ...	173-174°
16. Benzyl- α - naphthylamine ...	1 : 1	Minute deep black needles ...	160°
17. *p*-Tolyl-β - naphthylamine ...	1 : 1	Deep black shining needles ...	150°
18. Diphenylamine ...	2 : 1	Black needles ...	185°
19. Dimethylaniline ...	1 : 1	Black prisms ...	—
20. Diethyl β - naphthylamine ...	1 : 1	Black plates ...	122-123°
21. Quinoline ...	1 : 1	Deep brown solid ..	123-124°
22. *Iso*quinoline ...	1 : 1	Dark brown solid ...	137°
23. Tetrahydroquinoline ...	1 : 1	Deep black solid ...	112°
24. Tetrahydro*iso*quinoline ...	1 : 1	Deep black solid ...	85-87°
25. β - Naphthol-ethyl ether ...	1 : 1	Bright scarlet leaflets ...	140-140·5°
26. Benzaldehyde-phenylhydrazone .	1 : 2	Violet-brown needles ...	200°
27. Acetophenone-phenylhydrazone .	1 : 2	Small black flat crystals ...	171°
28. Cinnamylidene-acetophenone ...	2 : 1	Bright yellow needles ...	192°
29. Dibenzylidene-acetone ...	2 : 1	Thin lemon-yellow needles ...	234°

6. γ - TETRANITRONAPHTHALENE.

Addendum.	Mols. of nitro compound : mols. of addendum.	Appearance.	M.P.
1. α - Naphthylamine ...	1 : 1	Slender black needles	162°
2. β - Naphthylamine ...	1 : 1	Bronzy-green needles	163-164°
3. Dimethylaniline ...	1 : 1	Slender black needles	113°
4. Diethyl- β -naphthylamine.	1 : 1	Slender black needles	118-119°

These results show that the tri- and tetra-nitronaphthalenes studied, with the exception of 1 : 2 : 5 : 8-tetranitronaphthalene, yield additive compounds with many arylamines.

The trinitronaphthalenes do not yield additive compounds as readily as *s*-trinitrobenzene does. In order to obtain additive compounds with α - and β - naphthylamines, an excess of the base is usually necessary. On the whole, the α - or 1 : 3 : 5-trinitro-compound yields additive cempounds most readily.

The tetranitronaphthalenes yield additive compounds more readily and in fact resemble *s*-trinitrobenzene. But even in the case of these, an excess of the base is frequently, though not always, necessary, and the additive compounds can be recrystallised from different solvents which contain a slight excess of the base ; otherwise a separation of the crystals of the tetranitronaphthalene is brought about. Of the three tetranitro-derivatives, the capacity for forming additive compounds is greatest in the β- or 1 : 3 : 6 : 8-derivative and diminishes in the order β-, α - , and γ -. The δ-compound does not combine with arylamines.

It is clear that the number and position of the nitro-groups have an appreciable effect upon the capacity of the nitro-compound to yield stable additive compounds and a maximum number of nitro-groups in the *meta* position with respect to each other is a strengthening factor.

DEPARTMENT OF GENERAL AND ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

I. I. S. No. 70—R. P. B.—8-1921.—500.