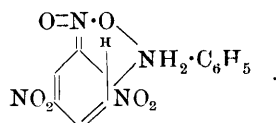


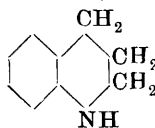
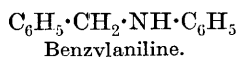
XXIX.—Additive Compounds of s-Trinitrobenzene with Heterocyclic Compounds Containing Nitrogen in the Ring.

By SOSALE GARALAPURY SASTRY.

IN various communications on the subject Sudborough and his co-workers have shown that various aromatic amines, phenols, phenolic ethers, and some heterocyclic compounds containing nitrogen in the ring, form additive compounds with s-trinitrobenzene and some other aromatic polynitro-compounds (T., 1899, **75**, 588; 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773; 1911, **99**, 209; see also Hepp, *Annalen*, 1882, **215**, 344; Sommerhoff, Dissertation Zurich, 1904; Noeltling and Sommerhoff, *Ber.*, 1906, **39**, 76). These compounds are relatively stable, crystalline substances, which can easily be alkylated, acetylated, and benzoylated. The influence, on the formation of the additive compounds, of introducing various alkyl, aryl, and negative groups into the ring has also been studied. The formation of the additive compound is to be provisionally attributed to the tendency of nitrogen and other multivalent atoms (as in phenols and thiophenols) to pass into a higher and saturated state of valency. Of the various formulæ that suggest themselves, the most probable one, according to Sudborough, is to be represented in conformity with the following scheme:

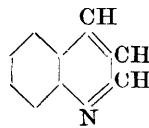


In the case of heterocyclic compounds and also some others, the formation of colourless or very pale-coloured compounds with s-trinitrobenzene seems to be in some manner due to the linking between carbon and nitrogen. The important point that was in view in the present investigation was whether in an additive compound of trinitrobenzene with an aromatic amine the presence of the linking N:C always produced a nearly complete removal of colour, as had been shown in the following pairs of compounds:



Tetrahydroquinoline

and



Quinoline.

In the above pairs the substances on the left gave highly coloured additive compounds, but those on the right nearly colourless ones. In the present work this has been confirmed, the linking $\cdot\text{CH}_2\cdot\text{NH}\cdot$ always producing compounds which are almost black.

Two other interesting additive compounds are those from phenazine and from azoxyanisole. Both have two nitrogen atoms directly linked with each other, and both the additive compounds are deep yellow.

EXPERIMENTAL.

Tetrahydro-p-toluquinoline-s-trinitrobenzene,
 $\text{C}_{10}\text{H}_{13}\text{N}, \text{C}_6\text{H}_3(\text{NO}_2)_3.$

This crystallises from alcohol in brownish-black needles melting at 113° . The pure additive compound can be obtained only in the presence of excess of the base:

0.1549 gave 23.8 c.c. N_2 at 22° and 690 mm. $\text{N}=15.77$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{N}=15.56$ per cent.

Tetrahydro-p-toluquinoline-s-trinitrobenzene,
 $\text{C}_{10}\text{H}_{13}\text{N}, \text{C}_6\text{H}_3(\text{NO}_2)_3.$

This crystallises from alcohol in dark plates melting at 102° :

0.3132 gave 0.1830 $\text{C}_6\text{H}_3\text{O}_6\text{N}_3$, on being treated with dilute hydrochloric acid (compare Sudborough and Beard, T., 1910, **97**, 795). $\text{C}_6\text{H}_3\text{O}_6\text{N}_3=58.43$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{C}_6\text{H}_3\text{O}_6\text{N}_3=59.16$ per cent.

Tetrahydro- α -naphthaquinoline-s-trinitrobenzene,
 $\text{C}_{13}\text{H}_{13}\text{N}, \text{C}_6\text{H}_3(\text{NO}_2)_3.$

α -Naphthaquinoline was reduced with tin and hydrochloric acid (*Ber.*, 1891, **24**, 2475). The additive compound crystallises from alcohol in dark needles melting at 129 — 130° :

0.2534 gave 34.50 c.c. N_2 at 22.5° and 692 mm. $\text{N}=13.97$.

$\text{C}_{19}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{N}=14.15$ per cent.

α -Naphthaquinoline-s-trinitrobenzene forms yellow needles melting at 133.5° (T., 1910, **97**, 773).

Tetrahydro- β -naphthaquinoline-s-trinitrobenzene,
 $\text{C}_{13}\text{H}_{13}\text{N}, \text{C}_6\text{H}_3(\text{NO}_2)_3.$

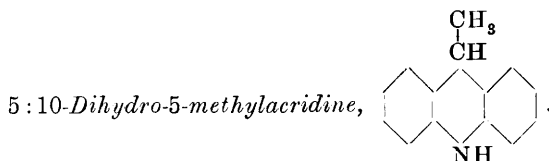
β -Naphthaquinoline was reduced by means of tin and hydrochloric acid (*Ber.*, 1891, **24**, 2643). The additive compound crystallises from alcohol in black needles melting at 138 — 139° :

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0.2262 gave 31.7 c.c. N_2 at 23° and 689 mm. $N=14.28$.

$C_{19}H_{16}O_6N_4$ requires $N=14.15$ per cent.

β -Naphthaquinoline-s-trinitrobenzene forms pale buff-coloured needles melting at 112° (T., 1910, **97**, 773).



Three grams of methylacridine (m. p. 114°) were dissolved in 150 c.c. of alcohol in a flask provided with a reflux condenser. The solution was heated to boiling, and 120 grams of sodium amalgam were added gradually through the condenser tube during about an hour and a half. The contents of the flask were kept boiling for about two hours more. After cooling, any unchanged amalgam and the mercury were separated from the alcoholic solution, which was afterwards acidified with moderately concentrated hydrochloric acid and then filtered. The residue on being crystallised from alcohol melted at $125-126^\circ$.

This dihydro-compound was converted into its *acetyl* derivative by heating it with acetic anhydride and pouring the product into water. The acetyl derivative, when crystallised from ethyl acetate, melted at 162° . On recrystallisation there was no alteration in the melting point:

0.3347 gave 21.4 c.c. N_2 at 27° and 685 mm. $N=6.30$.

$C_{16}H_{15}ON$ requires $N=6.27$ per cent.

5:10-Dihydro-5-methylacridine-s-trinitrobenzene,

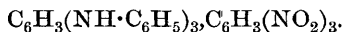


This crystallises from alcohol in black needles melting at $117-118^\circ$:

0.2560 gave 33.9 c.c. N_2 at 23.5° and 688 mm. $N=13.58$.

$C_{20}H_{16}O_6N_4$ requires $N=13.73$ per cent.

1:3:5-Trianilinobenzene-s-trinitrobenzene,



Trianilinobenzene was prepared from aniline and phloroglucinol (Minunni, *Gazzetta*, 1890, **20**, 337). The additive compound crystallises from a mixture of alcohol and ethyl acetate in black

needles and from chloroform in prisms. In either case the product melts at 160° :

0.2140 gave 31.7 c.c. N_2 at 27° and 688 mm. $N=14.91$.

$C_{30}H_{24}O_6N_6$ requires $N=14.89$ per cent.

Phenazine-s-trinitrobenzene, $C_{12}H_8N_2, C_6H_3(NO_2)_3$.

Phenazine was prepared from aniline and nitrobenzene by heating them together with powdered sodium hydroxide (*Ber.*, 1901, **34**, 2447). The additive compound crystallises from alcohol in yellow needles melting at $151-153^{\circ}$:

0.2084 gave 36.8 c.c. N_2 at 25° and 689 mm. $N=17.80$.

$C_{18}H_{11}O_6N_3$ requires $N=17.82$ per cent.

Azoxyanisole-s-trinitrobenzene, $C_{14}H_{14}O_3N_2, C_6H_3(NO_2)_3$.

This crystallises from alcohol in golden-yellow plates melting at $92-93^{\circ}$:

0.3050 gave 49.4 c.c. N_2 at 25.5° and 688 mm. $N=16.44$.

$C_{20}H_{17}O_9N_5$ requires $N=16.37$ per cent.

Benzylidene-1-phenyl-3-methyl-5-pyrazolone-s-trinitrobenzene.

The benzylidene derivative was prepared by heating together molecular proportions of benzaldehyde and 1-phenyl-3-methyl-5-pyrazolone, and crystallising the crude product (a red mass) from alcohol, from which it separates in red needles melting at $106-107^{\circ}$.

The additive compound with *s*-trinitrobenzene,

$C_{17}H_{14}ON_2, C_6H_3(NO_2)_3$,

forms scarlet plates melting at $113-114^{\circ}$:

0.1430 gave 22.2 c.c. N_2 at 31° and 678.5 mm. $N=14.92$.

$C_{23}H_{17}O_7N_5$ requires $N=14.73$ per cent.

With *s*-trinitrobenzene, dihydrophenylacridine gives a black additive compound and *s*-diphenylcarbazine gives orange needles. Tetrahydroisoquinoline gives only a resin.

I desire to thank Prof. J. J. Sudborough, under whose direction the present work was done, for all his kindnesses during the progress of the work.

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