CCIX.—*Some Molecular Compounds of Styphnic and Picric Acids.*

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ALTHOUGH our knowledge of the molecular compounds formed by picric acid with other aromatic substances is fairly extensive, little work has so far been done on similar compounds which may be formed by the analogous trinitroresorcinol, styphnic acid. Noelting and Salis (*Ber.*, 1882, **15**, 1863) prepared naphthalene styphnate, and Summerer has recently described (*Diss.*, Zürich, 1907) cinnamaldehyde styphnate.

The styphnic acid used was successfully prepared according to Merz and Zetter's method (*Ber.*, 1879, **12**, 2037), and the following compounds have been prepared.

Acenaphthene Styphnate, $C_{12}H_{10}, C_6H(OH)_2(NO_2)_3$.

When 3.1 grams of acenaphthene and 5 grams of styphnic acid are each dissolved in alcohol and the solutions mixed while still warm,

acenaphthene styphnate crystallises out in long needles on cooling. It is obtained pure by recrystallisation from alcohol :

0.1510 gave 14.05 c.c. N_2 at 16.7° and 754.5 mm. : $N = 10.88$.

$C_{18}H_{13}O_8N_3$ requires $N = 10.53$ per cent.

Acenaphthene styphnate crystallises in long, orange-coloured, doubly-refracting prisms, which melt at $153-154^\circ$ to a red liquid. It is moderately soluble in cold alcohol, and is decomposed by a large excess of this solvent; after several crystallisations, pure acenaphthene (m. p. $= 95^\circ$) is obtained. In acetone and ethyl acetate it is readily soluble and stable, but in ether it is partly decomposed. The compound is decomposed by carbon disulphide, chloroform, carbon tetrachloride, light petroleum or benzene.

Phenanthrene Styphnate, $C_{14}H_{10}, C_6H(OH)_2(NO_2)_3$.

This compound is prepared by dissolving 3.6 grams of phenanthrene in alcohol, and adding the solution to 5 grams of styphnic acid, also dissolved in alcohol. On cooling, the substance separates out, and is easily purified by recrystallisation from alcohol :

0.1806 gave 15.10 c.c. N_2 at 18.5° and 763.3 mm. $N = 9.83$.

$C_{20}H_{13}O_8N_3$ requires $N = 9.93$ per cent.

Phenanthrene styphnate crystallises in yellowish-red, doubly-refracting needles melting at $125-126^\circ$. It is readily soluble and stable in alcohol, acetone or ethyl acetate. In benzene it is readily soluble, but the substance suffers decomposition. It is quickly decomposed by carbon disulphide, ether, chloroform or carbon tetrachloride in the cold, but more slowly by light petroleum.

α -Bromonaphthalene Styphnate, $C_{10}H_7Br, C_6H(OH)_2(NO_2)_3$.

On adding 4.2 grams of α -bromonaphthalene to a warm alcoholic solution of 5 grams of styphnic acid, bromonaphthalene styphnate is obtained. The compound is recrystallised from as little alcohol as possible; the pure substance possesses a distinct odour of bromonaphthalene :

0.1704 gave 13.6 c.c. N_2 at 20.0° and 757.5 mm. $N = 9.27$.

$C_{16}H_{10}O_8N_3Br$ requires $N = 9.30$ per cent.

α -Bromonaphthalene styphnate melts at $107-108^\circ$, and crystallises in small, bright yellow, doubly-refracting needles. It is soluble in ether, acetone or ethyl acetate, and is stable in these solvents. When light petroleum is added to the ethereal solution, styphnic acid is precipitated. The compound is soluble and fairly stable in alcohol, being decomposed by a large excess of the solvent. Bromonaphthalene styphnate is immediately decomposed by carbon

disulphide, chloroform, or carbon tetrachloride, styphnic acid being precipitated in all cases. In benzene the decomposition is not so rapid.

m-Nitroaniline Styphnate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2, \text{C}_6\text{H}(\text{OH})_2(\text{NO}_2)_3$.

This substance is formed when warm alcoholic solutions of equimolecular proportions of *m*-nitroaniline and styphnic acid are mixed and the solution allowed to evaporate spontaneously. The compound is very soluble in alcohol, and is best recrystallised from hot benzene:

0.1242 gave 19.6 c.c. N_2 at 16.0° and 757.0 mm. $\text{N} = 18.56$.

$\text{C}_{12}\text{H}_9\text{O}_{10}\text{N}_5$ requires $\text{N} = 18.28$ per cent.

m-Nitroaniline styphnate crystallises in pale yellow, doubly-refracting needles, which, like the corresponding picrate, tend to form in radiate masses. It melts at 137° , and is soluble and stable in alcohol, ethyl acetate or benzene. From its solutions in ether or acetone the compound does not crystallise well. It is decomposed by carbon disulphide, and to some extent by chloroform or carbon tetrachloride.

m-Nitroaniline Picrate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2, \text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$.

This compound has not been previously described. It is prepared in exactly the same way as *m*-nitroaniline styphnate, and may be purified by recrystallising from alcohol or benzene:

0.0728 gave 12.2 c.c. N_2 at 21.0° and 761.2 mm. $\text{N} = 19.48$.

$\text{C}_{12}\text{H}_9\text{O}_9\text{N}_5$ requires $\text{N} = 19.08$ per cent.

m-Nitroaniline picrate crystallises in doubly-refracting, radiating needles, which melt at 143° . The crystals are of a distinctly deeper yellow colour than those of the styphnate, but the properties generally of the two substances show a very close resemblance. The crystals deposited from a benzene solution lose benzene of crystallisation very rapidly and become opaque. The compound is also readily soluble and stable in alcohol, ethyl acetate, ether or acetone, but it does not crystallise well from the latter solvent. *m*-Nitroaniline picrate is almost insoluble, and not so stable in carbon disulphide or carbon tetrachloride; in chloroform it is rather more soluble. Even in hot water the compound suffers very little decomposition. It is interesting to note in this connexion that Vignon and Évieux, basing their evidence on the heat of solution in benzene of *o*-nitroaniline and of picric acid compared with that of a preparation made by mixing picric acid with fused *o*-nitroaniline, and also on a cryoscopic determination of the molecular

weight of the preparation, have quite recently (*Compt. rend.*, 1908, 147, 69) concluded that no combination between picric acid and *o*-nitroaniline takes place.

It is hoped to continue this investigation.

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