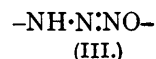
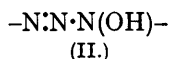
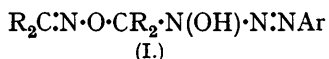


120. *The Azo-group as a Chelating Group. Part IV. The Constitution of the Arylazo-bis-oximes.*

By MARJORIE ELKINS and LOUIS HUNTER.

Strong support for Bamberger's structure for the arylazo-bis-oximes is provided by the preparation of a series of co-ordinated cupric, ferric, nickel and cobalt derivatives whose properties point to the hydroxytriazene structure in the original azo-compounds.

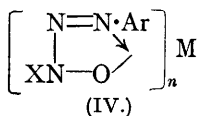
By coupling diazonium salts (1 mol.) with ald- or ket-oximes (2 mols.), Mai (*Ber.*, 1891, **24**, 3418; 1892, **25**, 1685) discovered a group of substances, conveniently known as the arylazo-bis-oximes, which are listed in Beilstein's "Organische Chemie" (4th edn., vol. XVI, p. 459) as being "of uncertain constitution." The formulæ suggested by Mai for these compounds did not accord well with their properties, but the subsequent discovery of the hydroxytriazene (Bamberger, *Ber.*, 1896, **29**, 104) revealed the similarity of the two groups of compounds, and led Bamberger (*Ber.*, 1899, **32**, 1546) to propose a formula (I) for the arylazo-bis-oximes embodying the hydroxytriazene skeleton (II).



Bamberger's evidence rested mainly on the decomposition of the arylazo-bis-oximes by mineral acids into azoimides, and the development, by the addition of ferric chloride, of deep blue colours characteristic of all hydroxytriazenes. In a recent review of the reactions of the arylazo-bis-oximes Mangini (*Atti R. Accad. Lincei*, 1935, vi, **22**, 452) submits exhaustive evidence for rejecting Mai's structures and for adopting that of Bamberger. Certain reactions necessitated, however, the postulation of a tautomeric equilibrium II \rightleftharpoons III.

Independent support for Bamberger's hydroxytriazene structure is now provided in the preparation of a series of co-ordinated cupric, ferric, nickel and cobaltous complexes, the properties of which are extraordinarily similar to those of the metallic derivatives of the simple hydroxytriazene described in Part III (J., 1938, 1346). They are deeply coloured, crystalline substances, although the parent azo-compounds are white or cream-coloured; they are insoluble in water, but readily soluble in most organic solvents. They are easily decomposed by mineral acids, but are stable to aqueous or alcoholic alkali even on boiling. They melt at remarkably low temperatures, some even below the melting points of the parent azo-compounds; this would seem to indicate a considerable degree of co-ordinative saturation, for few of the compounds described have molecular weights below 600. No stable cobaltic complexes were obtained; but by using hydrogen peroxide in the course of the preparation as in the case of the cobaltic derivatives of the simple hydroxytriazene (Part III, *loc. cit.*) transient purple-brown colorations or precipitates were obtained which rapidly gave place to tarry deposits. This may be taken as evidence of the momentary formation of cobaltic complexes similar to those previously described. When crystallised from pyridine, some of the nickel derivatives form pyridine addition compounds.

These properties so strongly resemble those of the metallic derivatives of the simple hydroxytriazens as to make it highly probable that their structure is similar, and the formula assigned to the metallic derivatives of the arylazo-bis-oximes is therefore (IV; M = n -valent metal, X = $R_2C:N\cdot O\cdot CR_2$). Bamberger's structure for the arylazo-bis-oximes therefore receives very strong support, and Mangini's requirement of prototropic change within the hydroxytriazen group is adequately met by the resonance formula proposed in Part III (*loc. cit.*, p. 1347).



EXPERIMENTAL.

The arylazo-bis-oximes were prepared in good yield by Mai's method (*loc. cit.*; *ibid.*, 1906, 39, 876). Metals were estimated as described in Part III, and nitrogen analyses were performed by Drs. Weiler and Strauss, Oxford.

Phenylazo-bis-acetoxime, washed repeatedly with cold light petroleum (b. p. 40—60°) to remove coloured impurities, formed pale cream-coloured crystals from alcohol, m. p. 135—137°. The *cupric* compound was prepared by the dropwise addition of saturated aqueous copper acetate to a warm 2% solution of the azo-compound in alcohol. It formed grey-brown platelets with a silver reflex from acetone, m. p. 175—178° (Found: Cu, 11.2. $C_{24}H_{34}O_4N_8Cu$ requires Cu, 11.3%). The *nickel* compound, prepared similarly, formed small yellowish-green needles from alcohol, m. p. 166° (Found: Ni, 10.4. $C_{24}H_{34}O_4N_8Ni$ requires Ni, 10.5%). By the careful addition of water to a pyridine solution, a *dipyridinonickel* compound was precipitated as pink-buff platelets, m. p. about 108° after losing pyridine at about 80°. It was dried for analysis in an atmosphere of pyridine vapour (Found: Ni, 7.4; loss on heating to 90°, 24.5. $C_{24}H_{34}O_4N_8Ni\cdot 2C_5H_5N$ requires Ni, 7.9; loss for $2C_5H_5N$, 24.6%); by standing in the air it lost pyridine and reverted to the original green nickel compound, m. p. 167°. The *ferric* compound, obtained similarly by the addition of ferric acetate to the azo-compound, formed black micro-needles from pyridine, m. p. 138° (Found: Fe, 7.7; N, 19.7. $C_{36}H_{51}O_6N_{12}Fe$ requires Fe, 7.1; N, 20.9%); its solutions in organic solvents were purple. The *cobaltous* compound formed short orange-brown needles from acetone, m. p. 148° (Found: Co, 10.5. $C_{24}H_{34}O_4N_8Co$ requires Co, 10.4%).

o-Tolylazo-bis-acetoxime is somewhat unstable in solution (cf. Mai, *Ber.*, 1906, 39, 880), and the crude product (cream platelets, m. p. 78—82°) was used in the preparation of metallic derivatives. The *cupric* compound formed rust-red micro-crystals from acetone, m. p. 131° (Found: Cu, 10.9. $C_{26}H_{38}O_4N_8Cu$ requires Cu, 10.8%). The *nickel* compound formed a bright green, crystalline powder from pyridine, m. p. 143° (Found: Ni, 10.0. $C_{26}H_{38}O_4N_8Ni$ requires Ni, 10.0%). It formed no pyridine addition compound. The *ferric* compound, prepared from ice-cold solutions in the presence of sodium acetate, formed jet-black platelets with a golden lustre from acetone, m. p. 125° (Found: Fe, 5.4; N, 19.9. $C_{36}H_{57}O_6N_{12}Fe$ requires Fe, 6.6; N, 19.9%). The *cobaltous* compound formed a dark olive-green powder from pyridine, m. p. 128° (Found: Co, 10.1. $C_{26}H_{38}O_4N_8Co$ requires Co, 10.1%).

p-Tolylazo-bis-acetoxime was obtained as cream needles from alcohol, m. p. 143°, though when crystallised in bulk it gave a less pure product of m. p. 136—138°. The latter can be used in the preparation of metallic derivatives. The *cupric* derivative was obtained in two forms, one being probably a hydrated compound. The *anhydrous* compound formed small rust-red prisms from acetone, m. p. 181° (Found: Cu, 10.8; N, 18.8. $C_{26}H_{38}O_4N_8Cu$ requires Cu, 10.8; N, 19.0%). By precipitating the solution in alcohol, acetone, or pyridine with water, the *monohydrate* was formed as silver-brown platelets, m. p. 180° (Found: Cu, 10.4; N, 18.2. $C_{26}H_{38}O_4N_8Cu\cdot H_2O$ requires Cu, 10.5; N, 18.4%), which reverted to the rust-red anhydrous form on heating above 100°. The *nickel* compound formed fine greenish-yellow needles from alcohol, but was best recrystallised from pyridine; the brown pyridine addition complex first formed lost pyridine on standing in air to give yellow platelets, m. p. 174° (Found: Ni, 10.0. $C_{26}H_{38}O_4N_8Ni$ requires Ni, 10.0%). The *dipyridinonickel* compound was precipitated by the addition of water to a pyridine solution of the nickel complex as light brown platelets (Found: Ni, 7.2; loss on heating, 22.7. $C_{26}H_{38}O_4N_8Ni\cdot 2C_5H_5N$ requires Ni, 7.6; loss for $2C_5H_5N$, 23.7%); it lost pyridine on heating to about 110° and reverted to the yellow nickel compound. The *ferric* compound formed very fine blue-black needles from acetone, m. p. 136—137° (Found: Fe, 6.6. $C_{36}H_{57}O_6N_{12}Fe$ requires Fe, 6.6%). Its solutions in acetone and pyridine were violet-black.

Phenylazo-bis-methylethylketoxime was obtained as fine cream-coloured needles from light

petroleum (b. p. 40—60°), m. p. 92—93°. The *cupric* compound formed dark brown platelets with a silver lustre from acetone or pyridine, m. p. 106° (Found: Cu, 10.5. $C_{28}H_{42}O_4N_8Cu$ requires Cu, 10.3%). The *nickel* compound formed greenish-golden platelets from alcohol, m. p. 97°, but was best purified by precipitating the dark brown pyridine addition compound from the pyridine solution by the addition of water; this lost pyridine in air, leaving mustard-yellow clusters of needles, m. p. 101° (Found: Ni, 9.5. $C_{28}H_{42}O_4N_8Ni$ requires Ni, 9.6%). The addition of water to a pyridine solution precipitated the *dipyridinonickel* compound as a dark green oil which solidified on cooling. Repetition at lower temperature produced light brown platelets, m. p. 80° (Found: Ni, 8.0; loss on warming, 22.5. $C_{28}H_{42}O_4N_8Ni, 2C_5H_5N$ requires Ni, 7.4; loss for $2C_5H_5N$, 22.9%), which slowly lost pyridine on exposure and reverted to the yellow nickel compound. The *ferric* compound formed slate-blue platelets from alcohol, m. p. 88—90° (Found: Fe, 7.2; N, 19.8. $C_{42}H_{63}O_6N_{12}Fe$ requires Fe, 6.3; N, 18.9%). The *cobaltous* compound was isolated as a *dihydrate* by precipitating a pyridine solution with water as orange-gold platelets, m. p. 115—118° (Found: Co, 9.0; N, 17.5. $C_{28}H_{42}O_4N_8Co, 2H_2O$ requires Co, 9.1; N, 17.3%).

m-Tolylazo-bis-methylethylketoxime was prepared by coupling *m*-toluenediazonium chloride (1 mol.) with an alkaline solution of methylethylketoxime (2 mols.). The oily product first formed slowly solidified to orange crystals, which were dissolved in alcohol and reprecipitated by the addition of small lumps of ice. It formed pale cream platelets, m. p. 50—51° (Found: C, 61.6; H, 8.1; N, 18.9. $C_{15}H_{24}O_2N_4$ requires C, 61.6; H, 8.2; N, 19.2%). It was very soluble in all organic solvents, and slowly decomposed in alcoholic solution at the ordinary temperature. The *cupric* compound was isolated in the form of a *monohydrate* by precipitation from ice-cold alcoholic solution by the addition of water, as light brown plates with a silver reflex, m. p. 86—88° (Found: Cu, 9.6; N, 17.2. $C_{30}H_{46}O_4N_8Cu, H_2O$ requires Cu, 9.6; N, 16.9%). By crystallising the monohydrate from hot alcohol by the addition of a small amount of hot water, the *anhydrous* form was deposited, on cooling, as long, fine, red-brown needles with a bronze lustre, m. p. 103—105° (Found: Cu, 9.8; N, 17.4. $C_{70}H_{46}O_4N_8Cu$ requires Cu, 9.8; N, 17.4%). The *nickel* compound formed first a green oil, which subsequently solidified; recrystallisation from alcohol yielded greenish-yellow platelets, m. p. 80—82° (Found: Ni, 9.2. $C_{30}H_{46}O_4N_8Ni$ requires Ni, 9.2%). Although it was very soluble in pyridine, no addition compound could be isolated. The *ferric* compound was obtained as somewhat oily, slate-blue crystals melting indefinitely at about 50°. It dissolved readily in alcohol to form a violet solution, but could only be isolated therefrom as an oil. The *cobaltous* compound formed bronze needles from alcohol, m. p. 80—85° (Found: Co, 9.0. $C_{30}H_{46}O_4N_8Co$ requires Co, 9.2%).

Phenylazo-bis-benzaldoxime was obtained from ether as a cream-coloured crystalline powder, m. p. 132—134° (lit., 125°). It is somewhat unstable, a week-old specimen having m. p. 100°. The *cupric* compound formed fine pink-buff needles from a chloroform solution on addition of light petroleum (b. p. 40—60°), m. p. 187° (Found: Cu, 8.4. $C_{40}H_{34}O_4N_8Cu$ requires Cu, 8.4%). It was far less soluble in organic solvents than the previously described copper derivatives of azo-bis-ketoximes. The *nickel* compound formed a dull yellow, crystalline powder from acetone, m. p. 168° (Found: Ni, 7.7. $C_{40}H_{34}O_4N_8Ni$ requires Ni, 7.8%). Precipitation of a pyridine solution by the slow addition of water produced an unstable *dipyridinonickel* compound as a buff powder, m. p. 150—155°, losing pyridine on standing (Found: Ni, 6.2; loss on heating to 75°, 12.8. $C_{40}H_{34}O_4N_8Ni, 2C_5H_5N$ requires Ni, 6.4; loss for $2C_5H_5N$, 19.5%). The *ferric* compound was obtained in an impure condition as a blue-black powder, m. p. 110° after softening at 80° (Found: Fe, 10.7; N, 12.7. $C_{60}H_{51}O_6N_{12}Fe$ requires Fe, 5.1; N, 15.3%). The substance dissolved in organic solvents to give purple solutions, from which the original compound could not be recovered undecomposed. The *cobaltous* compound formed a dull brown powder which could not be recrystallised without decomposition, m. p. 80—85° (Found: Co, 7.8. $C_{40}H_{34}O_4N_8Co$ requires Co, 7.8%).

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