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20

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Reaction Of Methyl Red And Methyl Orange With Mercuric Salts

By

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SUMMARY

The mercuration of methyl red and methyl orange with mercuric acetate, mercuric chloride, mercuric oxide, and mercuric iodide gave different mercurated products. Mercuration was found to occur predominantly in the orthoposition. The structure of these componuds were confirmed by IR, NMR, Mass spectra and micro chemical analysis. The regiospecifity of these reactions suggest that the mercury atom is directed into an ortho position by the coordination to the azo nitrogen .

INTRODUCTION

Methyl red and methyl orange (substituted azobenzene) have been used in analytical chemistry as acid-base indicators. The introduction of mercury atom may affect their properties.

Many publications have been described the direct metallations of azobenzene[2–6]. In all cases metallation occurs in the ortho position, presumably by coordination of the metal to an azonitrogen and subsequent substution.[2] There have been two indirect ortho-reactions of azobenzene reported in literature.[5,6] The mercurials react readily with halogens to produce haloazobenzenes, and these can be converted to numerous other derivatives.[7] Recently, a direct mercuration of azo benzene and the effect of various other substituents on this mercuration reaction was discussed[8].

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The present work deals with the mercuriation of methyl red and methyl orange (ortho-and para substituted azobenzene) with different mercurating agents, mercuric acetate, chloride, oxide, and iodide. The method of preparation is by fusion of the reaction mixture. All mercurated compounds were determined to be pure by thin layer chromatography, melting point, and elemental chemical analysis.

EXPERIMENTAL

All NMR spectra were recorded on a varian T-60 spectrometer in $CDCl_3$ solutions with TMS as the internal standart, UV spectra were recorded on a Beckman, Acta MVII spectrophotometer in methanol. All IR spectra were recorded on a Beckman IR 4240 spectrophotometer. The mass spectra were determined on a Varian MATSM IB with data system SS 100 mass spectrometer operating at 70 ev, mass resolution approximately 1000 and ion source temperature of 190°C. The direct inlet system was used, the sample temperature is 45°C. Two mass spectra were carried out, one with correct peak height ratios and the other was registered at higher sensitivity to show small peaks. Melting points were taken on a melting temperature apparatus and are uncorrected. Microanalyses were carried out by the Micro Analytical Centre, Cairo University and Analytische Laboratorien vorm. Alfred Bernhardt West Germany.

Mercuration of methyl red

In a round bottomed flask equipped with a reflux condenser surmounded with calcium chloride drying tube, mercuric salt (0.1 mole) was gradually added with stirring to (0.1 mole) methyl red. This was heated gradually on hot plate until the mixture melted. The reaction mixture was allowed to cool to room temperature and then the unreacted material (methyl red) was extracted with methanol at room temperature when the methyl alcohol was evaporated to one third its orinal volume. It gave the same m.p., mixed m.p. and the infrared spectra of methyl red. The insoluble part in methyl alcohol was crystallized from toluene-petroleum ether 40-60°C.

4- N, N- dimethyl amino, 3- hydroxy mercuri, 6′-hydroxy mercuricarboxylate azo benzene. (methyl red dimercuri-hydroxide) It was crystallized from toluene-petroleum ether 40-60°C to give deep violet needles, 48 % yield, m.p. 188-189°C.

Analysis: Found: % C 26.00; % H 2.4; % Hg 56.91

$C_{15}H_{15}N_3O_4Hg_2$ calcd.: % C 25.63: % H 2.14; % Hg 57.13

3- acetoxymercuri, 4-N, N- dimethylamino ,6- acetoxymercuri-carboxylate azobenzene. (methyl red dimercuri-acetete). It was prepared by the previous method using (0.1 mole) methyl red and (0.2 mole) mercuric acetate. It was recrystallized from toluene-petroleum ether 40-60°C to give red crystalline product, 90 % yield, m.p. 171-172°C.
Analysis: Found : % C 32.3; % H 2.8; % N 5.09; % Hg 48.01

$C_{19}H_{19}N_3O_6Hg_2 \cdot \frac{1}{2}\ C_7H_8$ Calcd; % C 32.44; % H 2.76; % N 5.05; % Hg 48.26

4 -N, N- Dimethylamino, 5- hydroxymercuri, 2 -mercuri -2- carboxylate, azobenzene. It was prepared by the reaction of (0.1 mole) methyl red with (0.1 mole) mercuric iodide. The product recrystallized from toluene-petroleum ether 40-60°C to give a deep violet crystals, 42 % yield, m.p. 195-196°C.

Analysis: Found : % C 26.00; % H 2.03; % N 5.91; % Hg 58.56
$C_{15}H_{14}N_3O_3Hg_2$ Calcd : % C 26.2; % H 2.04; % N 6.12; % Hg 58.55

The reaction of (0.1 mole methyl red with (0.1 mole) mercuric chloride gave rise to unidentified product, recrystallised from toluene-petroleum ether to give violet needles, m.p. 169-170°C.

Analysis: Found: % C 61.20; % H 5.0; % N 12.4; % Hg 26.55

However (0.1 mole) methyl red reacted with (0.1 mole) mercuric oxide to give also uncharacterized product. Recrystallization from toluene-petroleum ether gave violet crystals; m.p. 174-175°C.

Analysis: Found: % C 63.9; % H 5.3; % Hg 25.29

Mercuration of methyl orange

Reaction of methyl orange with mercuric salts took place as in the previous experiments. The insoluble product in methanol was treated with acetic acid and then boiled for 10 minutes followed by filtration. Some products crytallised from acetic acid and the other insoluble in it even in other solvents of crystallization. Reaction of methyl orange (0.1 mole) with (0.1 mole) mercuric acetate gave rise to two products which were separated by crystallisation from acetic acid.

4– N, N- Dimethyl amino, 4′ sulphonic, 6′ hydroxymercuri, azobenzene. Recrystallized from acetic acid to give deep red crystals, 46 % yield, m.p. 260°C (Decomposed).

Analysis: Found % C 33.1; % H 2.54; % N 7.74; % Hg 38.19

$C_{14}H_{15}N_3O_4SHg$ Calcd. : % C 32.2; % H 2.87; % N 8.05; % Hg 38.45

3- Acetoxymercuri, 4-N, N-dimethylamino, 4- sulphonic, 6- hydroxymercuri, azobenzene. It was the insoluble part in acetic acid. Trials for crystallisation were unsuccessful. But it gave one spot with TLC. The brownish red crystals, 35 % yield, m.p. 250°C (Decompose).

Analysis: Found : % C 24.0; % H 2.1; % Hg 51.09

$C_{16}H_{17}N_3SHg_2$ Calcd. : % C 24.6; % H 2.1; % Hg 51.42.

3- Hydroxymercuri, 4- N, N- dimethylamino, oxo 6, 6′- bis- mercuri, azobenzene. Methyl orange (0.1 mole) reacted with (0.2 mole) mercuric acetate gave rise to one product. Trials for crystallization of this compound were unsuccessful. The brown crystals, 30 % yield. m.p. 308°C (Dec).

Analysis: Found : % C 18.62; % H 1.26; % N 3.88; % S 3.04; % Hg 61.81

$C_{16}H_{15}N_3O_6SHg_3$ Calcd. : % C 19.61; % 1.50 % N 4.29; % S 3.26; % Hg 61.48

Mercuration of (0.1 mole) methyl orange with (0.1 mole) mercuric chloride gave rise to two products; seperated by fractianal crystallization from acetic acid.

4- N, N- Dimethylamino, 2′- chloromercuri, 4′- sulphonic, azobenzene hydrochloride. Recrystallized from acetic acid to give brown crystals, 40 % yield, m.p. 260°C (Dec.).

Analysis: Found : % C 27.7; % H 2.8; % N 6.8; % S 5.7; % Hg % 34.71

$C_{14}H_{15}N_3O_3SHgCI_2$Calcd.: % C 29.1; % H 2.6; % N 7.2; % S 5.55; % Hg34.4

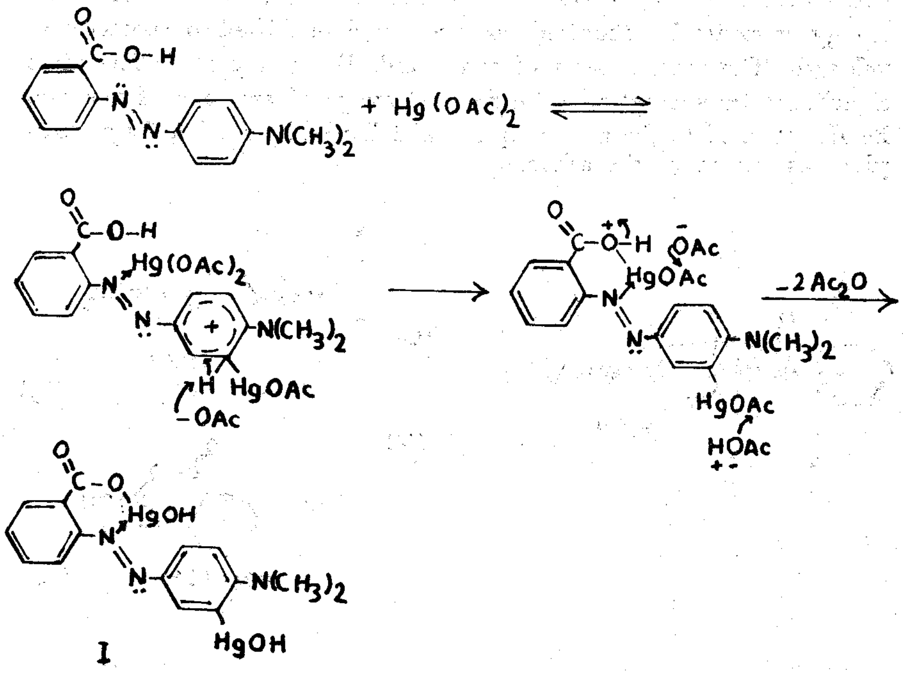
Mercuri, bis- (methyl orange), mono-mercuri-chloride. Trials for crystallization had failed. The reddish-violet crystals, 30 % yield, m.p. 230 °C (Dec.).

Analysis: Found : % C 34.8; % H 3.1; % N 9.5; % S 6.6; % Cl 4.7; Hg 42.16

$C_{28}H_{27}N_6O_3S_2Hg_2CI$ Calcd: % C 35.4; % H 2.95: % N 8.85; % S 6.7; % Cl 13.8; Hg 42.28

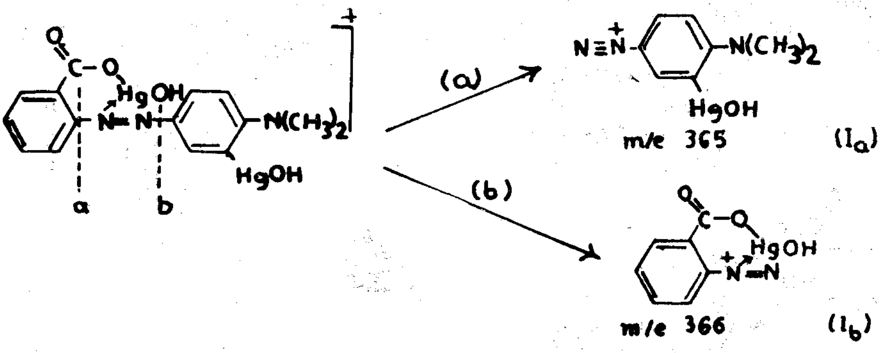
RESULTS AND DISCUSSION

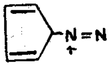
Mercuric acetate (0.1 mole) reacted with (0.1 mole) methyl red to give compound (1). The mechanism of the reaction is as follows:

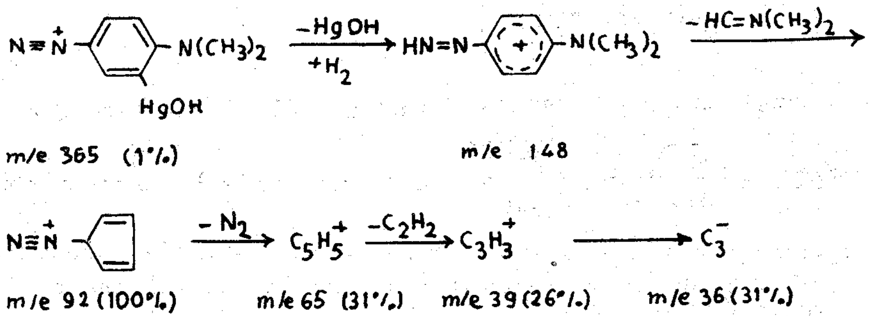


The structure was confirmed by elemental chemical analysis, IR, NMR, UV, and mass spectroscopy. The bands due to isolated hydrogen, two adjecent and four adjacent hydrogen in the aromatic rings at 900-700 cm^{-1} had appeared in the infrared spectra. The bands at 3400, 2810, and 1525 were attributed to the - OH, -N- $(CH_3)_2$ and N=N respectively.

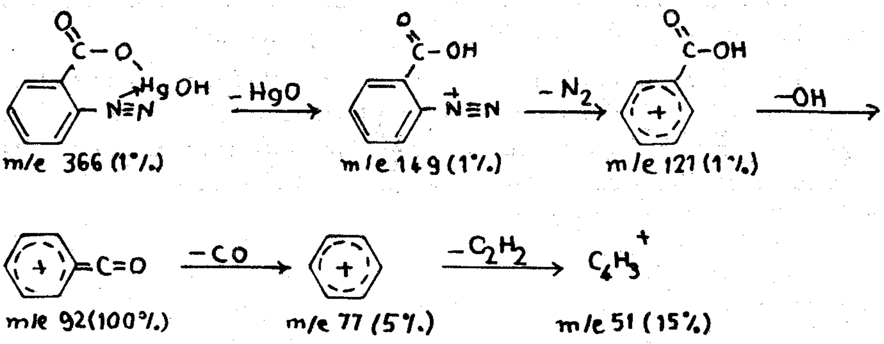
The NMR spectra showed signals for aromatic protons at δ 7.3 ppm. It revealed also signals at δ 3.2, 0.6 ppm due to -N- CH_3 and -OH protons. The UV K-band shifts helped to further confirm the assignment of the structure to this product. The K-band absorption shifted to longer wavelengths, and this was due to coordination of the mercury with an azo nitrogen.[8] It was noticed that the absorption maxima due $\Pi \rightarrow \Pi^*$ for methyl red is 412.5 nm, while $\Pi \rightarrow \Pi^*$ transition for compound (1) showed shifted absorption at 450 nm and appeared as a shoulder. The shoulder at 500 nm for methyl red became intense peak at. 487 nm. This indicated that the coordination of mercury with an azo nitrogen had an effect on the energy of exictation of $n \rightarrow \Pi^*$, i.e. it increased the energy of excitation required for $n \rightarrow \Pi^*$ and so shifted to shorter wavelength. The mass spectra of compound (I) was reported. The most significant fragmentation arise from cleavage of any one of the two bonds attached to the azo group N=N followed by further fragmentayions as shown in the scheme:



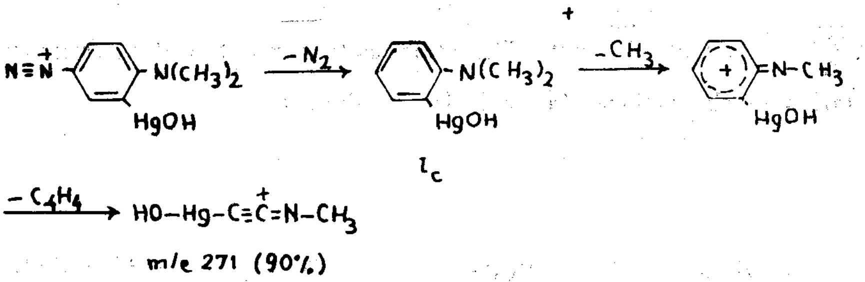
The base peak of this spectrum at m/e 92 (100 %) was due to  , and  These fragments were obtained via fragmentation of the cations (Ia) and (Ib) as shown;

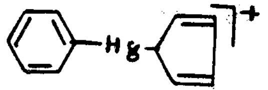


However, cation (Ib) fragmented as follows:



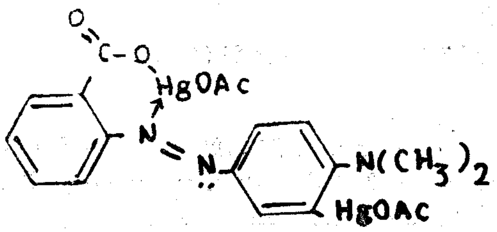
The intense peak at m/e 202 (92 %) and m/e 271 (90 %) were due to mercurous ion and HO-Hg -C $\equiv C^{+}{=}N{-}CH_3$ cation respectively. The latter cation obtained due to the fragmentation of (Ic).



The peaks at m/e 237 (15 %) and m/e 316 (7 %) were due to $C_3\overset{+}{Hg}$ and  The former may be due to the combination of mercury ion with the negative fragment C^{-}_{3}[9] and the latter may be also due to the combination of mercury ion with the cation $C_6H_5^+$ and $C_5H_5^+$ which were produced via previous fragmentation of cations (Ia) and (Ib).

The reaction of (0.2 mole) mercurac acetate with (0.1 mole) methyl red gave ride to compound (II). The mechanism of the reaction is the same as in compound (1) but with the elimination of acetic acid instead of acetic anhydride in the case of compound (I). The mercuration was found to occur predominately in an ortho-position.[10]

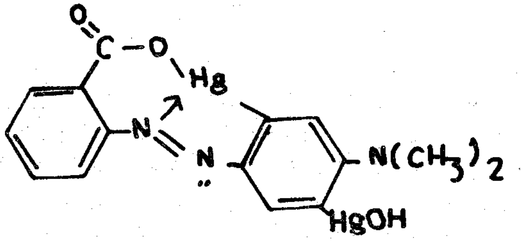
The regiospecifity of these reactions suggest that the mercury atom is directed to an ortho-position by coordination of the mercury to an azo nitrogen and the subsequent electrophilic substitution. The results are in agreement with the following proposed structure.



(II)

These results are further supported by IR and NMR spectroscopy. The IR spectra of compound (II) show an absorption bands at 825 and 770-735 Cm^{-1}, indicating 2 and 4 adjacent hydrogen atoms respectively, in the aromatic rings. The band at 1525 Cm^{-1} is due to trans-N=N with little shift attributed to the coordination of the mercury atom to the azo nitrogen. The absorpsion bands at 2810, 1730, and 1385-1865 Cm^{-1} are due to -N- $(CH_3)_2$ carbonyl and the acetate groups respectively. The NMR spectrum shows signals for aromatic protons at δ 7.3 ppm, δ 3.1 and δ 2.2 ppm for -N- $(CH_3)_2$ and ($-OCOCH_3$) protons respectively, which is in good agreement with the suggested structure,

The reaction of (0.1 mole) mercuric iodide with (0.1 mole) methyl red gave compound (III).

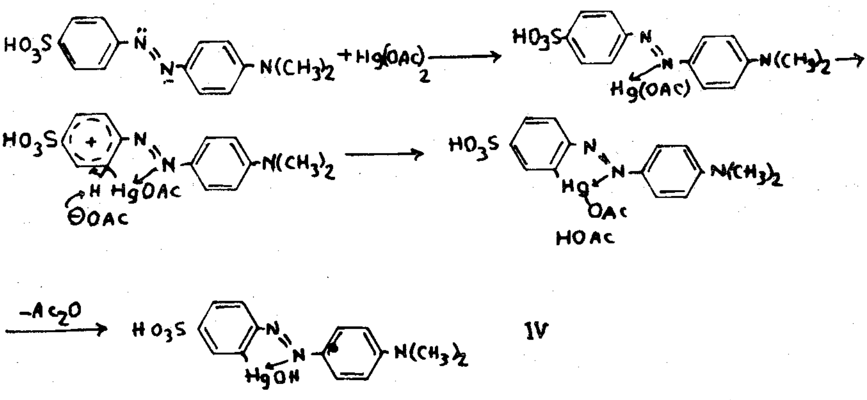


(III)

The reaction leads us to suggest that the mercury is directed into an ortho-position by coordination of the mercury to an azo nitrogen and followed by the subsequent electrophilic substitution. Electrophilic substitution reaction took place also in the aromatic ring containing -N-$(CH_3)_2$ with the elimination of hydrogen iodide and replacement of the iodine by the -OR group.

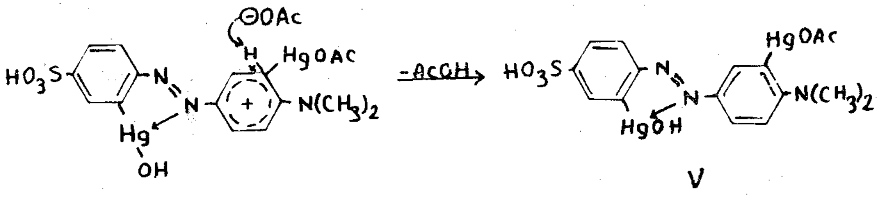
The structure was confirmed by elemental analysis, IR, and NMR spectra. The IR spectra showed a shift of -OR stretching vibration combined to mercury and C=O from 1730 in the case of methyl red to 1695 Cm^{-1} for product (III). The NMR spectra show signals for aromatic protons at δ 7.3 ppm. The -N- $(CH_3)_3$ protons and OH proton have bands at δ 3.3 and δ 2.2 ppm respectively.

Methyl orange (0.1 mole) reacted with mercuric acetate (0.1 mole) by fusion to give mono-and di-mercurials product IV and V. The two products were isolated by fractional crystallisation from acetic acid. The proposed mechanism depends on coordination of mercury to an azo nitrogen followed by electrohphelic substitution with the liberation of acetic anhydride as follows:



IV

The infrared spectra of compound (IV) show the characteristic-OH stretching broad band at 3600-2800 Cm^{-1}, which is attributed to hydrogen bonding. The stretching band at 2825 Cm^{-3} is due to $-N-(CH_3)_2$. The absorption of the hydrogens of the ortho and para disubstituted benzene rings are at 845 and 820 Cm^{-1}. Product (V) was formed due to further mercuration of the mercurated compound (IV) in the ortho position respect to -N $(CH_3)_2$[10].

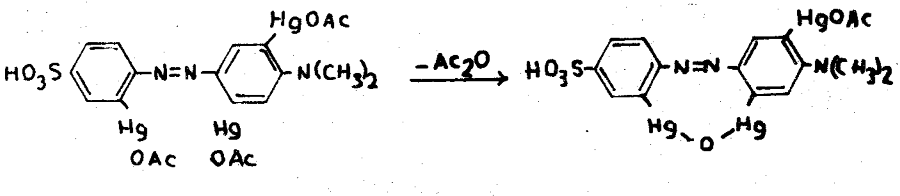


V

The IR spectra of compound (V) agree with the proposed structure as well as with its elemental analysis.

The reaction of (0.1 mole) methyl orange with (0.2 mole) mercuric acetate produced a compound containing 3 atoms of mercury. The suggested structure was confirmed to be that of (VI). The proposed mechanism is based on the coordination of mercury to an azo nitrogen followed by electrophilic substitution. The third mercury entered in the ortho position of the -N $(CH_3)_2$[10] group.

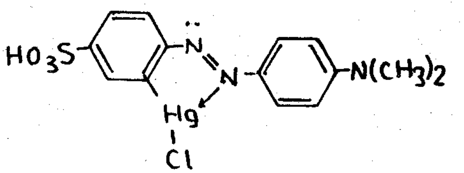
Elimination of acetic anhydride took place with the formation of product (VI) as follows:



VI

The structure was confirmed by chemical analysis. IR and NMR spectra. The IR spectra showed bands at 3030, 1600, 890, 830 and 800 Cm^{-1} indicating ortho-, para-substituted aromatic rings. The stretching band at 1712 Cm^{-1} indicated the carbonyl of the acetate group, with the absorption bands at 1400, 1335, 1200 and 1145 Cm^{-1} showing the presence of $-SO_2$ -O. The band at 2805 and very weesk band at 1575Cm^{-1} are due to -N $(CH_3)_2$ and -N=N- respectively. The NMR spectra show the signals of the aromatic protons at δ 7.3 ppm. The signal at δ 1.58 ppm is due to CH_3COO- protons.

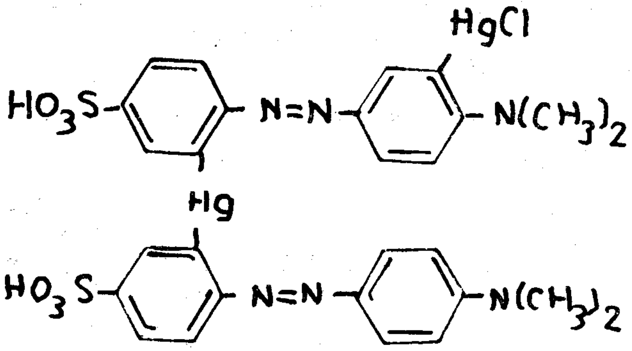
Reaction between (0.1 mole) methyl orange and (0.1 mole) mercuric chloride gave products (VII) and (VIII). The suggested structure for compound (VII) is the following:



VII

Electrophilic substitution reactions took place in the ortho-position to the azo group of the sulphonic ring with the elimination of hydrochloric acid, it was crystallised from acetic acid.

However, for compound (VIII) the proposed structure is the following:



VIII

The reaction took place through electrophilic substitution followed by elimination of hydrochloric acid. It was noticed that one of the mercurated methyl orange acted as mercurating agent for the other. The structures were further supported by the results of elementel chemical analysis and IR spectra.

Mercuration of (0.1 mole) methyl red with (0.1 mole) mercuric chride, and (0.1 mole) methyl red with (0.1 mole) mercuric oxide gave rise to undetectable products (IX), and (X) respectively.

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