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Action of Mercuric Acetate on N-Aminophthalimide and Its Alkylidene and Arylidene Derivatives

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SUMMARY

N-Aminophthalimide and some of its alkylidene and arylidene derivatives react with mercuric acetate in toluene (1/1 molar ratio) to give compounds containing N-Hg and N-NH-Hg bonds. In one of the products aromatic substitution as well as N=C bond cleavage takes place. IR and mass spectra confirm the proposed structures.

INTRODUCTION

2-Arylamino-4-methyl-5-carbethoxy thiazoles react with mercuric acetate in a mixture of alcohol and dilute acetic acid to give the corresponding monomercurated product via substitution of the aromatic ring[1].

Mercuration of 1-phenyl-2,3-dimethyl-5-pyrazolone[2] with mercuric acetate leads to the polymercurated product.

Organomagnesium halides react with N-alkylidene and N-arylmethyleneaminophthalimides to give (a) or (b) or (c). Product (c) was obtained through addition and cleavage[3].

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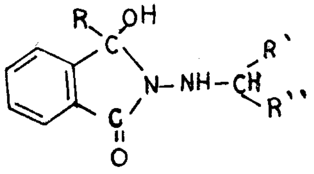
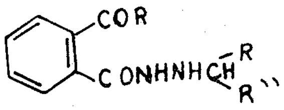


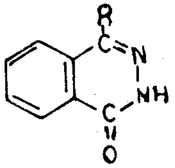
(a)

or



(b)

or



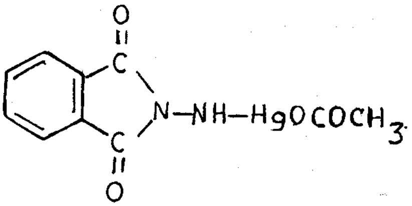
(c)

The present investigation deals with the interaction of mercuric acetate with N-alkylidene and N-arylidene-aminophthalimides.

RESULTS AND DISCUSSION

N-Aminophthalimide and N-cyclohexylidene, isopropylidene, and benzylidene-aminophthalimides are mercurated with mercuric acetate in an equimolar ratios in boiling toluene and acetic acid for 3 hours.

The reaction of N-aminophthalimide with mercuric acetate leads to the formation of a compound to which structure (I) is assigned. It seems that the reaction took place via coordination and rearrangement.

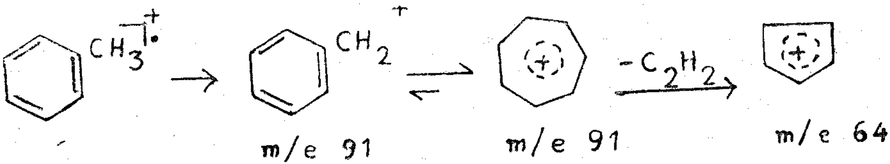


(I)

The infrared spectrum shows absorption bands at 3400 cm^{-1}, 1780 cm^{-1} and 1750 cm^{-1} attributed to ν_{N-H}, $\nu_{C=O}$ of CO-N-CO cyclic five membered ring, and $\nu_{C=O}$ of the acetate group respectively.

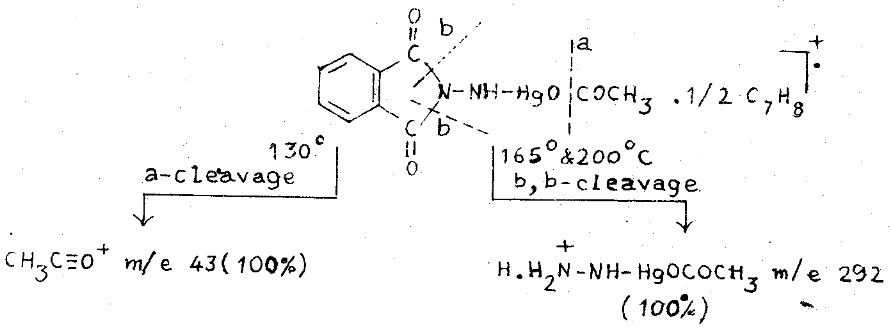
The spectrum shows also absorption bands at 640, 920 & 1400 cm^{-1} attributed to ν_{N-Hg} and at 770–735 cm^{-1} due to 4 adjacent hydrogen. The structure of (I) is infered also from its mass spectrum.

The fragmentation is carried out at different temparatures. When the sample temperature is 130 °C the base peak is at m/e 43 which attributed to acetylonium ion $CH_3 C{\equiv}O^+$, while at 165 °C and 200 °C the base peak is m/e 292. This fragment may be due to $H.H_2{}^+N\text{-}NH\text{-}Hg\text{-}OCOCH_3$ (or) and $C_7H_7Hg^+$. The later one is attributed to the fragment obtained via interaction of mercury ion with toluene (solvent of crystallisation), where analytical data confirm the presence of half mole toluene, this is confirmed by m/e 91 for $C_7H_7{}^+$, where the relative intensity is 32 % at 130 °C, while 12 % & 21 % at 165 ° and 200 °C (cf. Fig. 1). The low relative intensity may be due to further fragmentation as follows:

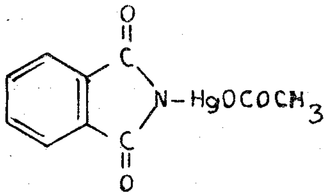


also may be due to the reaction of mercury ion with the tropylium ion to form $C_7H_7Hg^+$ ion.

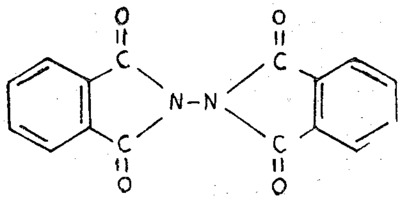
The mode of fragmentation relative to the sample temperature can be clarified as follows:



N-Cyclohexylidene-aminophthalimide is mercurated under the same condition as the parent (N-aminophthalimide) and lead to two products (II) and (III).



(II)

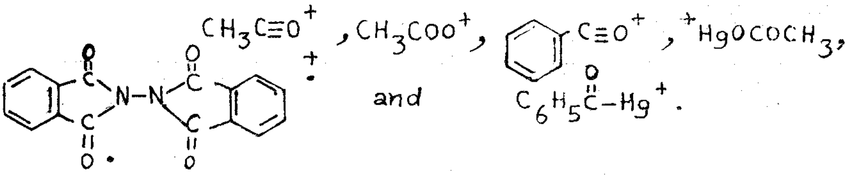


(III)

These suggested structures are based on N-N bond cleavage where N-acetoxymercuri-phthalimide (II) can be obtained via mercuration. The later N, N'-biphthalimide (III) is identical with an authentic sample[4].

The IR spectrum for (II) shows $\nu_{C=O}$ stretching frequency at 1740 cm^{-1}, it also shows absorption bands at 640, 920, 1400 cm^{-1} attributed to ν_{N-Hg}.

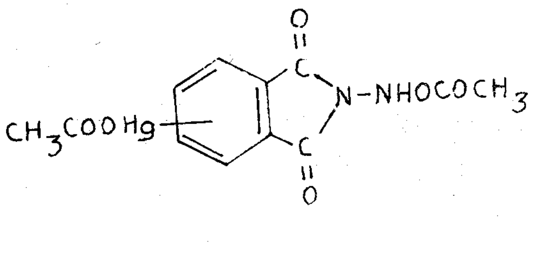
The mass spectrum of (II) (Fig. 2) shows the base peak at m/e 202 attributed to 202_{Hg}^{+} ion (100%). The intense peaks at m/e 43 (70%), 59 (43%), 104 (17%), 261 (38%), 292 (21%), and 305 (18%) are attributed to:



The small peaks at m/e 77 (12%), 215 (10%) and m/e 320 (2%) attributed to $C_6H_5^+$, CH_3Hg^+ and $202_{Hg}\ (OCOCH_3)_2^{\cdot +}$ respectively.

The mass spectrum of compound (III) is represented in Fig. 3. The base peak at m/e 292 is attributed to the molecular ion. Other fragments are shown in the figure.

The action of mercuric acetate on N-isopropylidene gives rise to product (IV).



(IV)

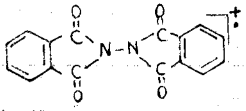
The suggested structure is based on $N{=}C$ bond cleavage with electrophilic substitution on the aromatic ring.

Analytical data, IR spectrum and mass spectrum are in good agreement with the proposed structure.

The IR spectrum of (IV) shows ν_{N-H} at 3400 cm^{-1}, and absorption bands at 1780, 1750 & 1720 cm^{-1} attributed to carbonyl streching frequencies for CO-N-CO cyclic five membered ring, $HgOCOCH_3$ and and $NHOCOCH_3$ respectively. A noticable change in the absorption bands for aromatic substitution between 900–700 cm^{-1}, indicating substitution in the aromatic nucleus.

In its mass spectrum the base peak is m/e 202 (100%) due to 202 Hg^+, while the intense peaks are m/e 43 (81%), 60 (50%), 77 (22%), 261 (27%), 292 (51%) and m/e 305 (8%) are due to $CH_3C{\equiv}O^+$, $CH_3COOH^{\cdot +}$,

$C_6H_5^+$, Hg^+OCOCH_3,



and $C_6H_5CO\text{-}Hg^+$.

The reaction of (0.1 mole) mercuric acetate with (0.1 mole) N-phenylmethylene aminophthalimide gives mercurous acetate (V), N, N′-biphthalimide (III), and benzoic acid (VI).

The proposed mechanism may be N-N bond cleavage, and dimerization to form N, N′-biphthalimide followed by oxidation with the formation of benzoic acid and mercurous acetate.

IR spectra, analytical data, and mass spectra confirm their structures.

EXPERIMENTAL

Action of Mercuric Acetate on N-Alkylidene, N-Arylidene and N-Aminophthalimide.

GENERAL PROCEDURE

1/1 Molar ratio of the reactants in toluene was boiled under reflux for 3 hours. Acetic acid (10 ml) was added at the begining of the reaction whereby it became clear. The reaction mixture was left to cool at room temperature to allow for the precipitaion of a solid product which is filtered off, dried, and recrystallised from the suitable solvent.

The filterate was concentrated to give N, N′-biphthalimide (in the case of cyclohexylidene) and N-phenylmethylene derivatives as crystalline product (III), filtered off, dried and recrysallised.

The filterate was evaporated to give benzoic acid (in the case of N-phenylmethylene derivative).

The mass spectra were determined on a (Varian MAT) SM 1B with data system SS 100 mass spectrometer, operating at 70 eV, mass resolution approximately 1000 and ion source temperature of 200 °C. For each sample two mass spectra are performed. One mass spectrum with correct peak heights ratios (percent base peak).

Compound (No.)	Solvent of crys.	m.p °C	Yield	Analysis				
					%C	%H	%N	%Hg
$C_{10}H_8N_2Hg$.	Toluene	d.270	70%	Calc.	34.72	2.57	6.00	42.99
1/2 C_7H_8(I)				Found	34.88	2.42	6.12	43.50
$C_{10}H_7N0_4Hg$ (II)	Toluene	above	30%	Calc.	29.58	1.72	3.45	49.45
	or Acetic	300		found	28.98	1.67	3.27	49.12
$C_{16}H_8N_20_4$(III)	Toluene	312–3°	15%	Calc.	65.75	2.74	9.59	
	or Acetic			found	65.76	2.85	9.53	
$C_{12}H_{10}N_20_6Hg$	Acetic	d.230	65%	calc.	30.08	2.08		41.91
(IV)	acid			found	30.49	2.07		41.41

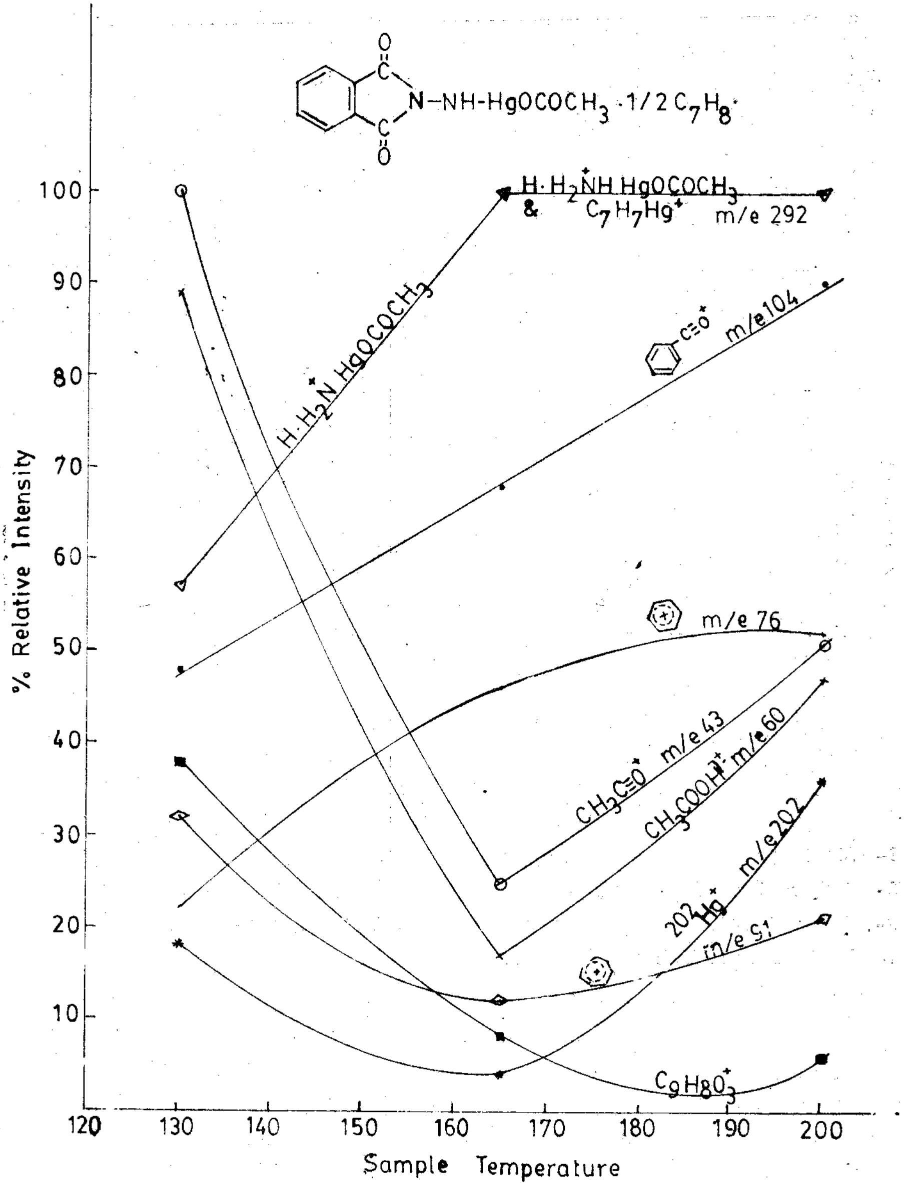


Figure 1 . Effect of sample temperature on relative intensity of the fragments

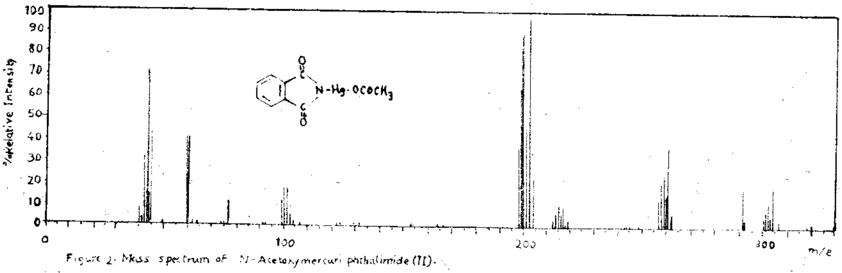


Figure 2- Mass spectrum of N-Acetoxymercuri phthalimide (II).

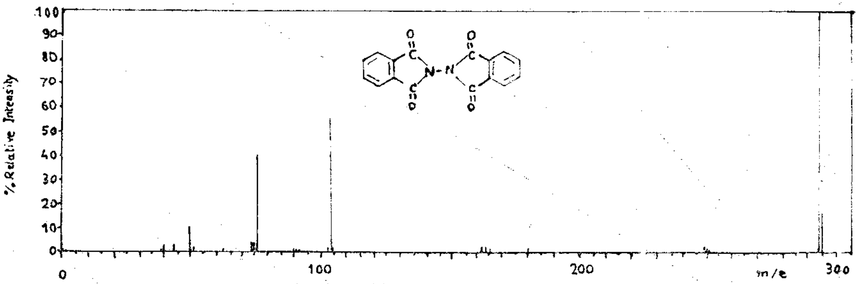


Figure 3- Mass spectrum of N,N'-Biphthalimide (III)

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