COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 29 ANNÉE : 1983

Mercuration Of N,N'- Biisomaleimide And Its Diazido Derivative

by

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Ankara, Turquie

Communications de la Faculté des Sciences de l'Universite d'Ankara

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TURQUIE

Mercuration Of N,N'- Biisomaleimide And Its Diazido Derivative

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(Received April 29, 1984; accepted June 6, 1984)

SUMMARY

N, N'- Biisomaleimide reacts with mercuric acetate under different conditions to give various products via ring opening, addition and substitution reactions with the formation of monomercurated, and mercuri bis (mono-mercurated) producets.

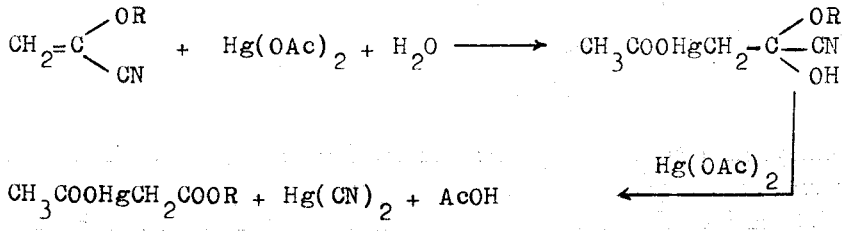
The reaction of mercuric acetate with the diazide compound (N,N'- bi -α- azidosuccinimide) gives mono and dimercurated azido products through N-N bond clavage.

INTRODUCTION

Ethylenic hydrocarbons had been mercurated by mercuric acetatate in aqueous solution where the entering groups were OH and $HgOCOCH_3$[1]. On carrying the reaction in alcohol, the groups adding to the double bond were RO and HgX. The addition follows Marckovnikov's rule.

α, β- Unsaturated oxocompounds were mercurated and the addition against Marckovnikov's rule[2].

The interaction of α- alkoxyacrylonitriles with aqueous $Hg(OAc)_2$ leads to the esters of monomercurated acetic acid.[3]



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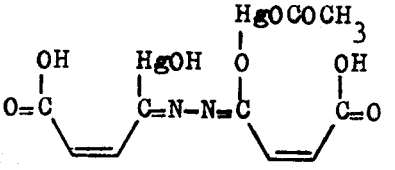
Recently, N,N'- biisomaleimide was allowed to react with organomagnesium halides (Grignard reagents) and the reaction took place via ring opening.[4]

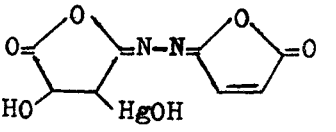
The present investigation deals with a comparative study for the behaviour of N,N'- biisomaleimide as an example of compounds containing both α, β- unsaturated ketonic and α, β- unsaturated iminosystems and its diazide (N, N'- bi -α- azidosuccinimide) towards mercuration reactions.

RESULTS AND DISCUSSION

N, N'- Biisomaleimide (0.1 mole) reacts with mercuric acetate (0.1 mole) in toluene and in presence of few ml acetic acid under reflux for 4 hours to give mainly three products via addition to the double bond with the formation of monomercurated acetoxy additive compound, monomercurated hydroxy additive compound and mercuri-bis (mercurated hydroxy) compound.



(I)



(II)

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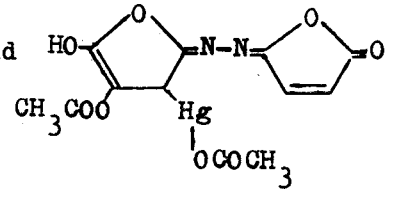
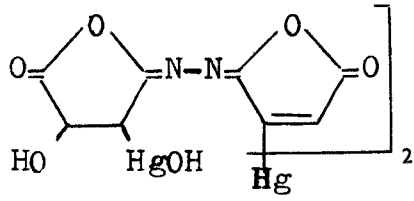


Analytical data and IR spectra confirmed their structures. The IR spectrum for compound (I) shows absorption bands at 3650-2700 cm^{-1}, 1720 cm^{-1} attributed to ν_{OH}, $\nu_{C=O}$. The absorption bands at 1880, 1810, 1830 cm^{-1}, attributed to the lactone ring completely disappeared, which indicate ring opening.

For compound (II) the IR spectrum shows ν_{OH} at 3650-2900 cm^{-1} $\nu_{C=O}$ at 1720 cm^{-1} (w), and the absorption band for the lactone ring at 1800, 1810, 1830 cm^{-1}.

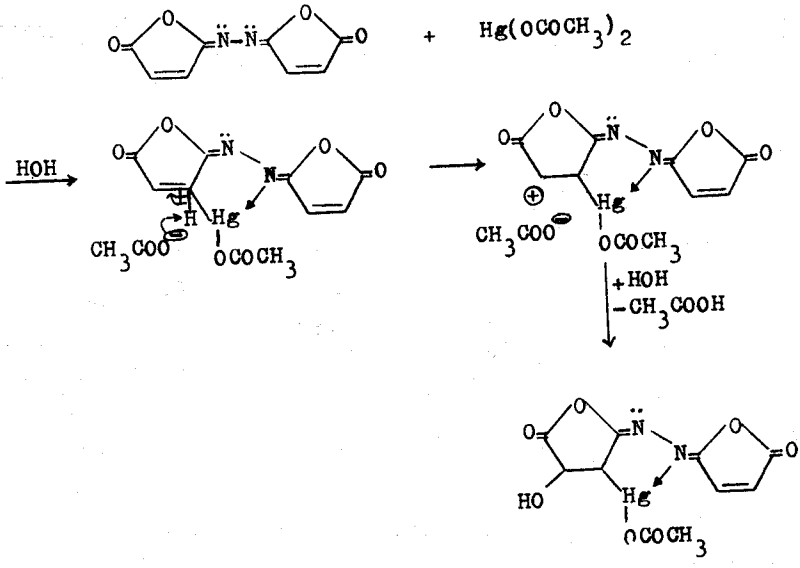
The IR spectrum for compound (III) shows ν_{OH} at 3650-2800 cm^{-1} and $\nu_{C=O}$ at 1720 cm^{-1}. It seems that the ν_{OH} group is due to the enol form.

Upon carrying the reaction for one hour, it gives rise to (II) and (IV).



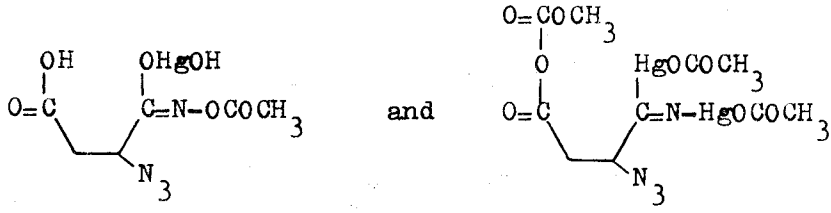
IV

In aqueous acetic acid the reaction of (1/1 molar ratio) mercuric acetate and N,N'- biisomaleimide at room temperature gives rise to one product (V). The reaction took place through addition reaction with the formation of acetoxymercuri- hydroxy additive product. The proposed mechanism can be as follows:



The reaction may be accelerated via coordination of mercuric acetate with the nitrogen atom together with addition to the double bond and then hydrolysis with water.

The reaction of equimolar (mercuric acetate and N,N'- bi- α- azidosuccinimide in boiling toluene and acetic acid gives two products (VI) and (VII) due to N-N bond cleavage:



IR spectra and microanalysis agreed with the suggested structures.

For compound (VI) the IR spectrum shows the absence of the absorption bands due to lactone ring, and the presence of the absorption bands at 3650-3100 cm^{-1}, 2105 cm^{-1} and 1705 cm^{-1} and 1640 cm^{-1} attributed to ν_{OH}, ν_{N3}, $\nu_{CO=}$ and $\nu_{C=N}$ respectively.

The IR spectrum for the other product (VII) shows the presence of absorption bands at 2100 cm^{-1} and 1720 cm^{-1}, attributed to ν_{N3} and $\nu_{C=O}$, also the absence of the absorption bands due to lactone ring.

EXPERIMENTAL

Reaction of N.N'- *Biisomaleimide with mercuric acetate*:

Mercuric acetate 3.18 gm (0.01 mole) dissolved in 10 ml acetic acid was added to the solution of N,N'- Biisomaleimide 1.92 gm (0.01 mole) in toluene. The reaction mixture was boiled for 4 hours under reflux, whereby crystalline yellowish-green product was precipitated out, filtered off, dried and recrystallised from acetic acid to give (I) in 25 % yield, m.p. 270 °C (dec.).

Analysis Calcd. for $C_{10}H_{10}N_2O_9$ Hg: N: 3.98; Hg: 57.05 %

Found: N: 4.20; Hg: 57.00 %.

The filtrate was left overnight to give a yellow crystalline product, filtered, dried and recrystallised from toluene to give (II) in 30 % yield, m.p. > 300 °C. Analysis Calcd. for $C_8H_6N_2O_2Hg$: C: 22.50; H: 1.40; N: 5.56, Hg: 47.02;

Found: C: 22.02; H: 1.49; N: 6.10; Hg: 46.90 %.

On evaporating the filterate to 1/3 its volume followed by addition of drops of ether, pale brown crystals were precipitated, recrystallised from toluene-water (III) in 30 % yield, m.p. 135-6 °C. Analysis Calcs. for $C_{12}H_{10}N_2O_8Hg$:
C: 28.20; H: 1.95; N: 5.48; Hg: 39.28 %. Found: C: 28.91; H: 1.72; N: 5.69; Hg: 39.19 %.

The reaction of (1/1 molar ratio) of the reactants in the same solvent and under reflux for 1 hour, gave clear solution, on cooling pale yellow crystalline product was deposited, filtered, dried, and recrystallised from acetic acid to give yellowish-white flakes (IV) in 40 % yield, m.p. decomposed at 270 °C. Analysis Calcd: for $(C_8H_5N_2O_6Hg)_2Hg$ C: 18.25; H: 0.95; N: 5.32; Hg: 57.21 %; Found: C: 18.07; H: 1.23; N: 5.23; Hg: 57.10 %.

The filtrate was left overnight to give compound (II) in 45 % yield.

Mercuration of N,N'- *biisomaleimide with mercuric acetate in equeous acetic acid*:

Mercuric acetate 3.18 gm (0.01 mole) in 10 ml acetic acid was added was added to 1.92 gm (0.01 mole) N,N'- biisomaleimide in 1: 1 aqueous acetic acid. After one hour, yellow crystals were precipitated out, filtered and dried. Recrystallisation of the product from toluene gave yellow crystals (V) in 80 % yield, m.p. decomposed at 222 °C. Analysis Calcd for $C_{10}H_8N_2O_7Hg$. 3/4 C_7H_8: C: 34.2; H: 2.62; Hg: 37.45; Found: C: 34.30; H: 2.4; Hg: 37.12 %.

Reaction of N,N'- *Bi-* α- *azidosuccinimide with mercuric acetate*:

The reaction was carried out as above. An equimolar quantities was reacted under reflux in toluene and acetic acid to give on cooling a crystalline monomercurated product (VI), recrystallised from toluene in 40 % yield, m.p. above 305 °C.

Analysis Calcd. for $C_6H_8N_4O_6Hg$: C: 16.60; H: 1.85; N: 12.92; Hg: 46.37 %; Found: C: 15.90; H: 1.9; N: 12.8; Hg: 46.20 %.

On adding petroleum ether 40-60 °C to the filtrate product (VII) was precipitated, recrystallised from toluene-petroleum ether in 25 % yield, m.p. decomposed at 245 °C. Analysis Calcd. for $C_{10}H_{12}N_4O_8Hg_2C_7H_8$ N: 7.06; Hg: 50.57 % Found: N: 6.90; Hg: 50.46 %.

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