Tetrahedron Letters,Vol.23,No.52,pp 5575-5578,1982 0040-4039/82/525575-04$03.00/0
Printed in Creat Britain

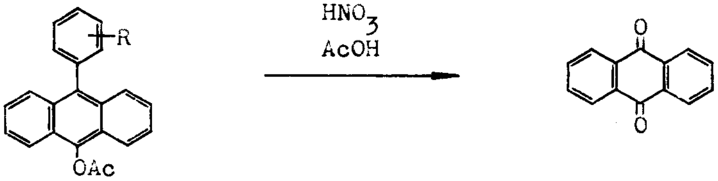
9-ACETOXYANTHRACENE DERIVATIVES. PART VIII[1]. THE MECHANISM OF DEGRADATION OF 9-ACETOXY-10-ARYLANTHRACENES TO ANTHRAQUINONE

Janina Gronowska, Adam Dzieleńdziak

Institute of Chemistry, N. Copernicus University, 87-100 Toruń, Poland

Abstract: The mechanism of degradation of 9-acetoxy-10-arylanthracenes to anthraquinone with the use of HNO_3 in AcOH has been reported. This was proved by way of example on 9-acetoxy-10-(4'-acetoxyphenyl)anthracene (1) by means of separation and identification of intermediate products 2, 3 and 4.

Previously[2] we have described the chemical method of confirming the structure of some 9-acetoxy-10-arylanthracenes:



The purpose of this paper was the investigation of the degradation mechanism of these compounds to anthraquinone. Our study was carried out on 9-acetoxy-10-(4'-acetoxyphenyl)anthracene(1), which was chosen as an example. Compound 1 heated for 5 minutes in oxidizing mixture (HNO_3 in AcOH) at 50-55°C yields 10-hydroxy-10-(4'-acetoxyphenyl)-anthrone-9 (2); at 70-75°C - compound 2 and small 10-hydroxy-10-(4'-hydroxyphenyl)anthrone-9 (3); at 90-95°C - compound 3, 10-hydroxy-10-(3',5'-dinitro-4'-hydroxyphenyl)anthrone-9 (4) nc, anthraquinone (5) and 2,4,6-trinitrophenol (6); at 105-110°C for 15 minutes - compounds 5 and 6 (see Table).

Acetylation of 2 and 3 with Ac_2O/AcONa give 10-acetoxy-10-(4'-acetoxyphenyl)anthrone-9 (7), m.p. 200-202°C (lit.[3] 205-206°C). All compounds were identified by IR and ^{1}H-NMR spectra.

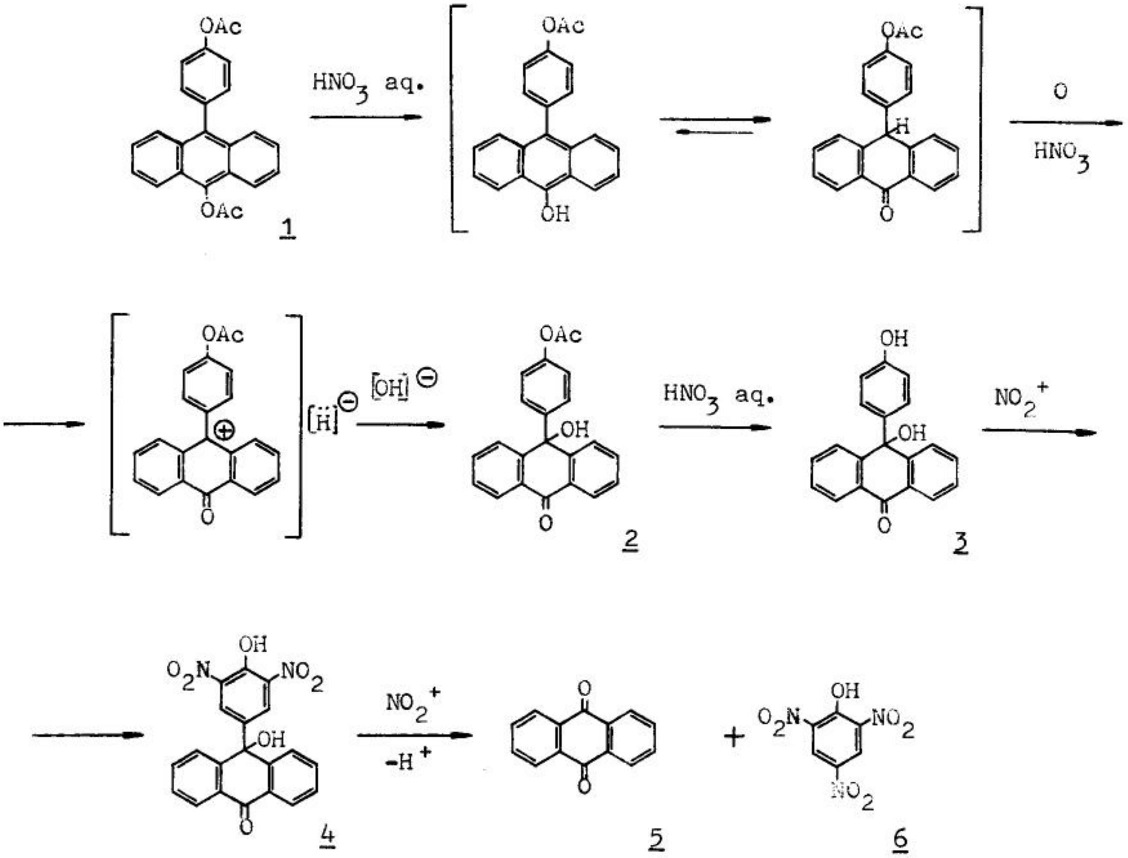
Table. The date (yield, m.p.) of the intermediate products of the 9-acetoxy-10-(4'-acetoxyphenyl)anthracene (1) degradation

Temp. of reaction [°C]	The yields of compounds [%]	Melting points [°C]
20 (8 min.)	2 - ca 85	283-284 (lit.[3] 282-283)
50-55 (5 min.)	2 - 90	as above
70-75 (5 min.)	2 - 80 3 - 10	as above 206-208 (lit.[3] 208-210)
90-95 (5 min.)	3 - 10 4 - 20 5 - 30 6 - 30	as above 239-240 284-286 (lit.[4] 284-285) 121-122 (lit.[5] 122)
105-110 (15 min.)	4 - 10 5 - 75 6 - 75	as above " "

4: m.p. 239-240°C (decomp.); IR (KBr-disk) 1640s, 1555s, 1540s, 1350s cm^{-1}; MS: m/e = 392; Analyses: Calcd. C 61.2%, H 3.1%, Found C 61.3%, H 3.1%.

Blicke and Warzynski[3] have obtained compound 2 by oxidation of compound 1 with CrO_3 in glacial AcOH; compound 3 through hydrolysis of 2 in alcohol solution 10% NaOH[3]; compound 7 as a result of reaction of AcOAg with 10-chloro-10-(4'-acetoxyphenyl)anthrone-9[3].

Our investigations showed that the mechanism of degradation of compound 1 to anthraquinone is like follows:



From authors[3] and our investigations it follows that in compound 1 the CAc group in position 9 hydrolyses very easily and as is known, the tautomeric anthranol form is not stable and easily changes into stable anthrone form[4].

Conc. HNO_3 in glacial AcOH has a hydrolyzing and oxidizing effect on 1, however in specific conditions 9-acetoxy-10-phenylanthracene is nitrated[7,8]. The OAc group in position 9 hydrolyses the most easily. It seems that the largeness of anthracene coplanar skeleton in comparison with benzene ring may by here of importance, and oxygen in position 9 demonstrates much inclination for forming the stable enthrone system, derivate of anthraquinone. In this reaction we could not separate the first product of hydrolysis, i.e. derivate of anthranol or anthrone. Probably, these products oxidize very quickly to compound 2.

It is posible that during oxidation of compound 1 in acetic acid at the presence of HNO_3, the $[\ddot{H}]^{\ominus}$ ion is separated from the central carbon atom similarly like in triarylmethane compounds. The conjugated system of anthrone-9, formed by hydrolysis of OAc group in position 9, may facilitate the $[\ddot{H}]^{\ominus}$ anion to splitt off. This ion may form hydroxyl ion by the reaction with an oxygen coming from the decomposition of HNO_3, and then hydroxylate a carbon atom in position 10.

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + 1/_2O_2$$

$$[\ddot{H}]^{\ominus} + O \longrightarrow OH^{\ominus}$$

The investigation of mechanism of degradation reaction is hindered by very rapid changes of the products of the succesive stages of reaction. According to papers[7,8] the possibility of nitration of some intermediate compounds of degradation of 9-acetoxy-10-arylanthracenes should also be taken into account.

REFERENCES

1. Part VII: J. Gronowska, K. Aleksandrzak, J. Heldt, Polish J. Chem., in the press.
2. J. Gronowska, A. Dzieleńdziak, Polish J. Chem., 53, 517 (1979).
3. F.F. Blicke, R.J. Warzynski, J. Am. Chem. Soc., 62, 3191 (1940).
4. G.M. Badger, J. Chem. Soc., 1947, 764.
5. L. Kofler, A. Kofler, Thermo-Mikro Methoden, 3 Aufl., Weinheim 1954.
6. H. Baba, T. Takemura, Tetrahedron, 24, 4779 (1968).
7. H.D. Christoffersen, M.P. Hartscorn, K.E. Richards, Austr. J. Chem., 30, 1865 (1977).
8. E.E. Barnett, J.W. Cook, J. Chem. Soc., 2631 (1923).

(Received in UK 21 October 1982)