Action of Diazomethane Derivatives on 1,2-Naphthoquinone-4-Sulphonic Acid

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(Received 5th November, 1995, revised 5th June, 1996)

Summary: 1,2-Naphthoquinone-4-sulphonic acid reacts with 9-diazofluorene, diphenyldiazomethane, phenylbenzoyl diazomethane and 2-diazo-1,3-hydrindenedione in benzene to give α-ketoepoxides, cyclopropane and methylene dioxy derivatives accompanied with desulphonation reaction. The products are confirmed by analytical data, IR, UV, NMR,. MS spectra as well as some chemical tests.

Introduction

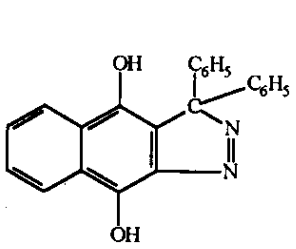
It was found [1], that diphenyldiazomethane reacts with 1,4-naphthoquinone to give product (I) which decomposed with the loss of nitrogen. It had been reported by Eistert *et al.* [2] that the reaction of 2-halogeno or 2,3-dihalogeno derivatives of 1,4-naphthoquinone with diazomethane leads to unstable adducts which are converted to the halogen free pyrazoles.

Jones *et al* [3] stated that 1,4-benzoquinone reacts with 9-diazofluorene with the loss of nitrogen to give cyclopropane and bis-cyclopropane, also the reaction of 1,4-naphthoquinone gives cyclopropane derivative.

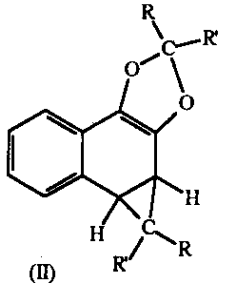
No work on 1,2-naphthoquinone-4-sulphonic acid with diazo-alkanes has so far, been reported.

The present work deals with the reactions of diazolalkane derivatives with 1,2-naphthoquinone-4-sulphonic acid in order to study the effect of sulphonic group on the reaction product 1,2-naphthoquinone-4-sulphonic acid reacts with diphenyl-diazomethane and phenylbenzoyl diazomethane to produce the methylene dioxy derivatives (II) (a) and (b) respectively accompanied with desulphonation reaction.

The structures of the products (IIa) and (IIb) were established from their analytical data and their infra red spectra which showed the presence of an aliphatic carbon-hydrogen stretching frequency in the range of 2950-2850 cm^{-1} and aliphatic carbon-hydrogen bending frequency at 1470 cm^{-1}. The spectrum of compound (IIb) shows



(I)



(II)

(a) R = R' = Ph
(b) R = Ph, R' = C(=O)—Ph

the presence of a carbonyl stretching frequency at 1675 cm^{-1} which was not present in (IIa). The NMR spectrum of (IIa) shows signals at δ=7.3 - 7.8 ppm for aromatic protons (24 H) and δ=1.3 ppm for aliphatic protons (2 H).

The mass spectra (Table-1) for compounds (IIa) and IIb) shows the molecular ion peak for compound (IIa) at m/e 490 (0.16%) and did not show the molecular ion peak for compound (IIb). The base peak for the former is at 283 (100%) while the base peak for the latter is at m/e 18 (100%).

The reaction of 1,2-naphthoquinone-4-sulphonic acid with diazofluorene and 2-diazo-1,3-hydrindenedione leads to the formation of the corresponding α-ketoepoxides to which structures (III) and (IV) are suggested respectively.

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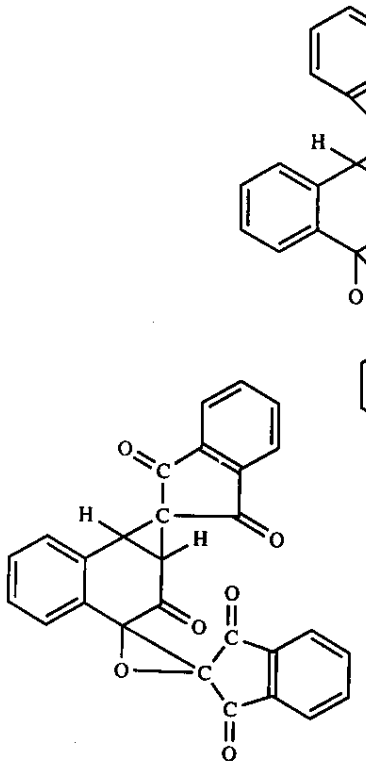
Besides analytical data, structure (III) is inferred from the infra red spectrum which shows carbon-hydrogen stretching frequency at 3050-3040 cm^{-1} due to the presence of the cyclopropane ring, a carbonyl stretching frequency at 1715 cm^{-1} and oxirane stretching frequencies [4] at 1240, 870 and 815 cm^{-1}. Its NMR spectrum shows signals at δ=7.16 - 7.7 ppm characteristic for atomatic protons (2 H) and signals at δ=1.89 - 1.91 ppm for aliphatic protons (2 H).

It also gives positive epoxide test [5], forms 2,4-dinitrophenyl-hydrazone derivative and gives a negative sulphur test.

Structure (IV) is established, from the analytical data and the infrared spectrum which shows aliphatic carbon hydrogen stretching frequency at 2950-2850 cm^{-1}, aliphatic carbon hydrogen bending frequency at 1470 cm^{-1}, carbonyl stretching frequencies at 1725, 1710, 1650 cm^{-1} and oxirane stretching frequencies at 1225, 830, 810 cm^{-1} also a negative sulphur test. The mass spectral data of compound (III) (Table-1) confirms the suggested structure.



The mass spectrum of IV shows the molecular ion peak at 486 (0.02%) and the base peak is at m/e 180 (100%).

Experimental

The analyses were carried out in the Microanalytical Center, Cairo University.

Infra red spectra were measured on Perkin-Elmer 1430 infrared spectrophotometer using KBr wafer technique. The mass spectra were recorded at 70 ev on Finnigan MAT, LR=2000, Karlsruhe

Mass spectra for compound IIa, IIb and IV.

For compound IIa at 120°C		For compound IIb at 300°C		For compound IVa at 50°C	
m/z	% Rel. Int.	m/z	% Rel. Int.	m/z	% Rel. Int.
490	0.16	546	0.18	486	0.16
472	1.99	221	3.97	468	0.16
326	5.41	220	0.77	319	0.05
309	0.04	219	0.33	283	1.43
293	0.89	211	0.2	266	0.07
292	0.40	210	0.1	198	2.43
283	1.00	145	0.12	197	0.44
282	1.7	144	0.14	182	8.59
181	20.15	118	0.42	181	30.46
180	39.71	105	19.38	180	100
145	9.23	103	13.32	165	10.22
142	4.30	91	3.22	140	0.28
127	2.02	77	8.45	126	7.61
118	25.83	51	2.38	119	2.1
113	1.6	41	0.76	118	4.63
101	0.94	28	56.82	100	2.29
91	3.16				
77	71.77	26	0.42	77	4.71
75	2.39			76	20.16
64	1.33			51	3.39
51	14.3				
38	2.39				
28	6.59				
25	0.42				

University. UV spectra were recorded on Perkin Elmer-Lambada 48 UV/Vis spectrophotometer. ^{1}H-NMR specta were recorded on Bruker WH-300 spectrophotometer, Karlsruhe University, Germany.

Action of diphenyl diazomethane and 2-diazo-1,3-hydrindene-dione on 1,2-naphthoquinone-4-sulphonic acid

A mixture of 1,2-naphthoquinone-4-sulphonic acid (0.005 mole), diazomethane derivative (0.015 mole) and copper bronze (0.005

Table-2

No.	M.P. °C	% Yield	Shape of Crystals	Solvent of Crystallisation	%C	%H	λ_{max} nm	ε
IIa	157	69.38	Prismatic Crystals	Benzene/ Pet. ether (40-60)	found 88.12 calcd. 88.16	5.39 5.30	3043	$17x10^3$
IIb	202	57.69	Plates	Benzene/ Pet. ether (40-60)	found 88.83 calcd. 83.51	4.78 4.76	246.4 275.7	$11.6x10^3$ $0.74x10^3$
III	164-5	80.65	Needles	Pet. ether (40-60)	found 89.01 calcd. 88.88	4.32 4.53	281.7 454.7	$4.8x10^3$ $9.8x10^3$
IV	117	72.72	Powder	Benzene/ pet.ether (40-60)	found 75.12 calcd. 75.33	2.95 3.13	291	$9.8 x10^3$

mole) was boiled under reflux in 100 ml benzene for five (5) hours. Copper bronze was filtered off and the product obtained crystallized from the proper solvent (Table-2).

Action of phenylbenzoyl diazomethane and 9-diazofluorene on 1,2-naphthoquinone-4-sulphonic acid

A mixture of 1,2-naphthoquinone-4-sulphonic acid (0.005 mole) diazomethane derivative (0.0459 mole) and copper bronze (0.05 mole) was ground together in a mortar for a few minutes, then boiled in chlorobenzene under reflux for five hours. Copper bronze was removed by filtration and copper oxide (0.05 mole) added to the mixture and refluxed for about 6 hours. Copper oxide was removed by decantation and the product obtained crystallised from the proper solvent (Table-2).

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