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Synthesis and characterization of 1-phenoxy-9,10-anthraquinones

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ABSTRACT

The photochromic compound of 1-phenoxy-9,10-anthraquinone was synthesized via different syntheses routes in this paper. 1-Phenoxy-9,10-anthraquinone has good photochromism. The Structure and the photochromism were characteristiced by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, MS, IR and UV-Vis spectrum. Mainwhile the photochromic influence for the Structure of the phenoxyanthraquinone was discussed.

KEYWORDS

Phenoxyanthraquinones;
Photochromic compounds;
Syntheses.

INTRODUCTION

Because the photochromic compounds are possible to use in the information storage and the optical memory devices, therefore it is paid attention in the high-tech research areas[1]. It has the enormous latent use in the modern times science and technology and the daily life, like development photography, each kind of radiation dosimeter and shielding materials, analytical reagent, camouflage and decoration material, computer storage element[2]. At present, the research about the photochromic material of the phenoxyquinones is less described. This materials are attractive due to their excellent properties such as low fatigue,as well as negligible thermal interconversion at room temperature[3]. For example, the "trans" quinine form undergoes a photochemical rearrangement to the "ana" quinone form upon irradiation with UV light. the reverse conversion of "ana" quinine form to "trans" quinine form readily occurs with visible light. Its photochemical rearrangement process could be repeated 500 times without decomposition of the materials.Based on the above characteristic, this kind of function material hopes to apply in the 3D optical memory devices[4]. The synthesis route was designed at first in this experiment(SCHEME 2). The yield of compound F is very low,because the phenol was not stable compare with the hydroquinone in the reaction. The phenol melting point was lower and the dehydration was difficult. So we designed the synthesis route as follows (SCHEME 1).

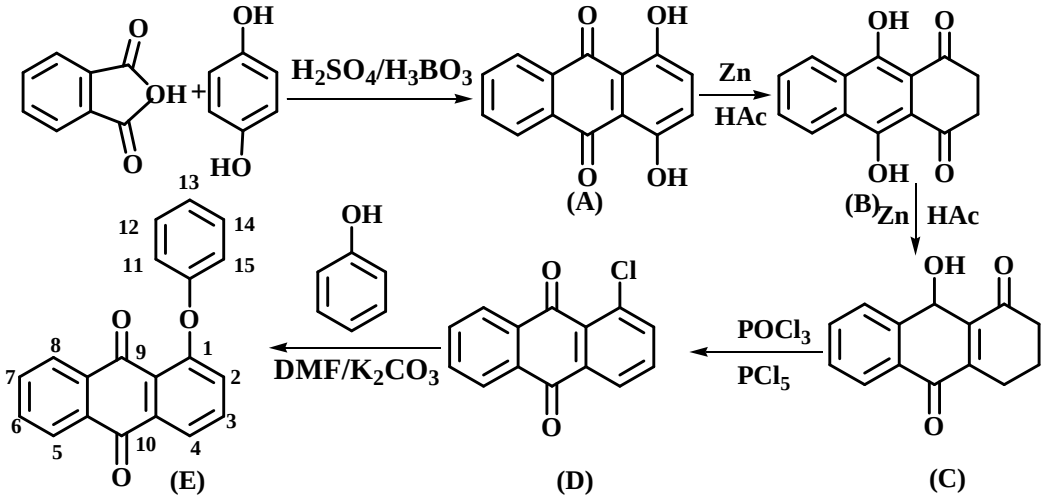
EXPERIMENTAL

Apparatus and reagents

The experimental reagents are all the analytic pure reagent which produced in Tianjin.The phthalic anhydride was sublimated before using; DMF was drid by the calcium hydride. The silica gel was bought from the Qingdao haiyang chemical company.an AV300 NMR spectrometer (Bruker company); a HP 1100 LC/MS (Agilent company); a FT-IR360 infrared Spectrophotometer (Nicolet company); a UV3010 UV-Vis spectrophotometer.

Synthetic method

1,4-Dihydroxy-9,10-anthraquinone(A)



SCHEME 1 : The syntheses route of 1-phenoxy-9,10-anthraquinone

44.4g(0.3mol)Phthalate anhydride, 0.93g (0.25mol)boric acid, 11g(0.1mol)hydroquinone and 98% 54ml (1mol) Sulfuric acid were thoroughly mixed and heated at 165,for 60 min in the oil bath. After that, the temperature was raised to 190, for 30min, and then poured the hot solution into 250ml water with stirring. The solution was cooled and filtered, than the residue dissolved in a sodium dicarbonate solution, filtered. The precipitate was recrystallizated from alcohol,than the orange crystals was abtained. Yield: 18.6g(77.5%).

2,3-Dihydro-9,10-dihydroxy -1,4-anthraquinone(B)

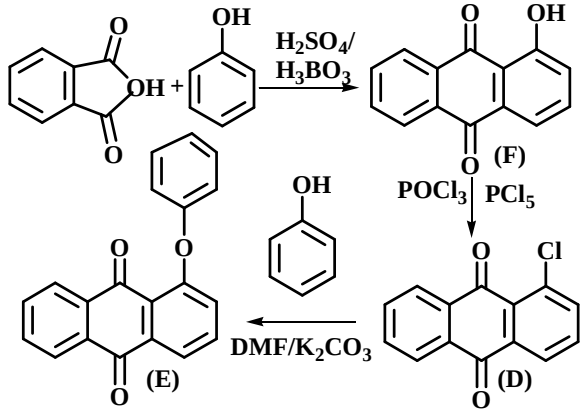
1.2g 1,4-Dihydroxy-9, 10-anthraquin-one, 10ml glacial acetic acid and 1g zinc powder were added into a 25ml flask, and the mixture was refluxed for 60 min, then poured it into water. The precipitate which had already been cooled and filtered was recrystallized from alcohol, Separated by the chromatogram,the yellow crystals was abtained. Yield:1.02g (86.7%).

9-hydroxy-2,3,4,9-tetrahydro-1,10-anthraquinone (C)

1g 2,3-Dihydro-9,10-dihydroxy-1,4-anthraquin one, 10ml glacial acetic acid and 1g zinc powder were added into a 25ml flask, and the mixture was refluxed for 24h, then poured it into water. The precipitate which had already been cooled and filtered was recrystallized in alcohol solution, The yellow crystals was abtained, yield :0.738g (78%).

1-chloro-9,10-anthraquinone(D)

0.1g (0.44mmol)9-hydroxy-2,3,4,9-tetrahydro-1,10-anthr-axquinone, 5ml phosphorus oxide trichloride and 0.092g(0.44mmol) phosphorus pentachloride were added into a 25ml flask and the mixture was refluxed for 24h. The reaction solution was Poured into the ice water, filtered.The precipitate was dissolved with chloroform and separated by the chromatogram,the yellow crystals was abtained, yield :0.041g(34.2%).



SCHEME 2 : The syntheses route of 1-phenoxy-9,10-anthraquinone

1-phenoxy-9,10-anthraquinone(E)

0.77g(0.81mmol)Phenol, 0.05g,0.2mmol,1-chloro-9,10-anthraquinone, 0.11g, 0.81mmol, anhydrous potassium carbonate and DMF 3ml were added into a 10ml flask, the mixture was heated at 110-120 , for 48 h. The reaction solution was Poured into the water, acidified with the diluted hydrochloric acid, and extracted with the CH_2Cl_2. Separated by TLC, the yelw crystals was abrained, yield :0.012g(43%).

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RESULT AND DISCUSSION

Structure characteristics

Compound (A): M.p. 200-201;^{1}H NMR,$CDCl_3$: δ12.93(s,2H, 1,4-OH), 8.35-8.38(m,2H, 5,8-H), 7.84-7.87 (m,2H, 6,7-H),7.33(s,2H, 2,3-H),IR,σ/cm^{-1}:3462(s,ν_{OH}),1623(vs,$\nu_{C=O}$),1577(m,$\nu_{C=C}$, Benzene bone), 1244 (s,ν_{C-O}),865, 784 (m,γ_{Ar-H});UV, (λmax/nm), 315, 334(Ar-C=O),478(Dione); MS,m/e., 241,M^{+}+1.,

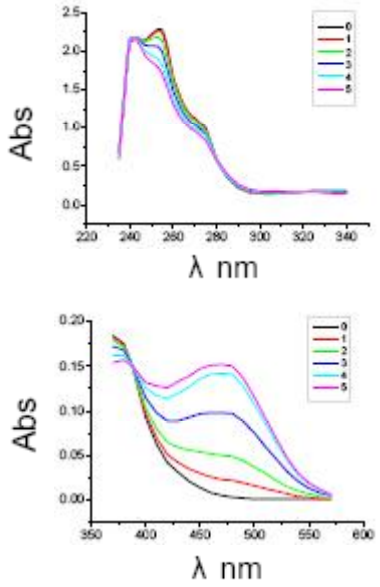
Compound (B): M.p.133-135,^{1}H NMR,$CDCl_3$: δ 13.65(s,2H, 9,10-OH),8.47-8.51(m,2H, 5,8-H), 7.78-7.82(m,2H, 6,7-H), 3.09(s,4H, 2,3-H), IR, σ/cm^{-1}, 3422(s,ν_{OH}), 2923(w,ν_{CH2}),1634(vs,$\nu_{C=O}$), 1581 (m,$\nu_{C=C}$, Benzene bone),1261(s,ν_{C-O}), 820,775(m, γ_{Ar-H}), MS,m/e, 243, M^{+}+1,

Compound (C): M.p.164-166,^{1}HNMR,$CDCl_3$: δ,13.90(s,1H,9-OH),8.44(d,1H,J=8.4Hz, 5-H), 8.06(d,1H,J=8.4Hz,8-H),7.65-7.71(m,1H,6-H),7.49-7.56(m,1H,7-H),4.67(s,1H,9-H),2.98(t,2H,J=6Hz,2-H),2.76(t,2H,J=6Hz,4-H),2.13-2.22(m,2H,3-H), IR,σ/cm^{-1}:3407 (s,ν_{OH}),2939 (w,ν_{CH2}), 1635,1611 (vs,$\nu_{C=O}$),1448(m,$\nu_{C=C}$, Benzene bone),1237(s,ν_{C-O}), 823,764(m,γ_{Ar-H}), MS:m/e 229,M^{+}+1.

Compound (D): ^{1}H NMR,$CDCl_3$: δ8.21 -8.26 (m,2H, 5,8-H),8.09 (d,1H,4-H),7.86 (d,1H,2-H), 7.78 -7.83 (m,2H,6,7-H), 7.69 (d,1H,3-H),IR, σ/cm^{-1}: 3084(w, ν_{Ar-H}), 1670, 1634(vs,$\nu_{C=O}$), 1588(m,$\nu_{C=C}$, Benzene bone), 1278, 1240(s,ν_{C-O}), 799, 723(m,γ_{Ar-H}), UV., (λmax/nm) 338,350(Ar-C=O),409(Dione) ; MS,m/e, 243,M^{+}+1.

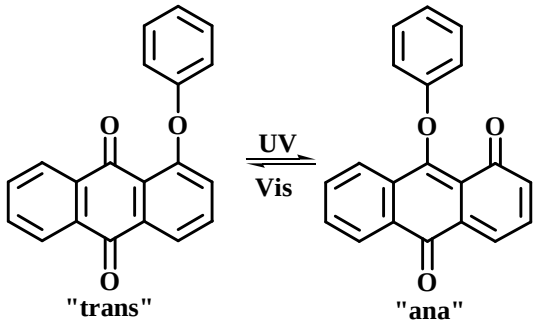
Compound (E): ^{1}HNMR,$CDCl_3$: δ8.27-8.29 (m,2H,5,8-H), 8.16(d,1H,J=7.5Hz,4-H),7.78- 7.81 (m,2H,6,7-H),7.67-7.73(t,1H,J=7.8Hz,3-H),7.37-7.40(t,2H,J=8.4Hz,12,14-H),7.27-7.32(m,1H,2-H),7.15-7.21(t,1H,J=9Hz,13-H),7.08 (d,2H,J=9Hz,11,15-H), ^{13}HNMR,$CDCl_3$, δ: 183,181, 157,156,135,134.7,134.3,133,132,129,127,126.7, 126.2,123,122,118, IR, σ/cm^{-1} 3050(w,ν_{Ar-H}),1675, 1632(vs,$\nu_{C=O}$),1572(m,$\nu_{C=C}$, Benzene bone), 1283 (s,ν_{C-O}), 832, 766, 712(m,γ_{Ar-H}),MS:m/e 301,M^{+}+1; Anal.calcd. for $C_{20}H_{12}O_3$: C,79.98; H,4.02.Found: C,79.83; H,4.06.

The photochromism



Peak 1 changing absorbency in 253.50nm; Peak 2 changing absorbency in 472.50nm; 1×10^{-5}M, in $CHCl_3$, time-gap respectively is 0, 1, 2, 4, 8, 12min

Figure 1: UV-Vis spectrum of 1-phenoxy-9,10-anthraquinone under 365nm ultraviolet light irradiation



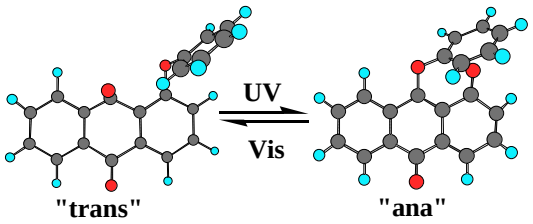
SCHEME 3: Photoisomerization of phenoxyanthraquinone

The spectrum of 1-phenoxy-9,10-anthraquinone was obtained by the UV3010 spectrophotometer.

The photochromic effect of 1-phenoxy-9,10-anthraquinone is better than that of other anthraquinones. it has three Isosbestic point in 387,319,281nm.The biggest absorbency of the "trans" quinine form appears in 253.50nm and the "ana" quinine form appears in 472.50nm (Figure 1). In general, the photochromism is the isomerization reaction from yellow "trans" quinine form to orange "ana" quinine form, which is caused by the group rearrangement in the light irradiation. The photochromic reaction from "trans" to "ana" can irradiate under ultraviolet light in λ≤450nm, the reverse achromatic reaction may occur under the visible

TABLE 1 : The change of absorbency in 253.50nm and 472.50 nm under the ultraviolet light irradiation, (n is the number of times under the 365nm ultraviolet light irradiation)

n	A(253.50nm)	A_{n+1}-A_n	A (472.50nm)	A_{n+1}-A_n
0	2.2712		0.0043	
1	2.2649	-0.0063	0.0232	0.0189
2	2.1952	-0.0697	0.0505	0.0273
3	2.0573	-0.1379	0.0985	0.0480
4	1.8874	-0.1699	0.1427	0.0442
5	1.7802	-0.1072	0.1527	0.0100



SCHEME 4: Photoisomerization of phenoxyanthraquinone, 3D

light[5](SCHEME 3).

The structure and the characteristics in the photoisomerization

TABLE 1 to show, absorbency in 253.50nm (benzene bone absorption peak) gradually turn to smaller from 2.2712 to 1.7802 (three isolating benzene rings turn to two benzene rings),and absorbency in 472.50nm (quinone bone absorption peak) gradually turn to bigger from 0.0043 to 0.1527("ana" quinone form to have six conjugated double bonds) after ultraviolet ray irradiation.SCHEME 3 to show, the phenoxy bonding in "trans" quinone form migrated to 9-site to be the "ana" quinone form, so the structure of conjugate system have been changed[6]. The quinone bone of the "trans" quinone form is not the planar structure, two carbonyl face to outside the rings, phenoxy face to inside the rings, but the quinone bone of the "ana"quinone form approaches in the planar structure (for example the 3D figure shows). The phenoxy bonding in the middle ring to the conjugate system contributing is bigger than that of bonding in the edge ring, therefore its absorbency increases among the visible light.

The small change of the absorbency in 273nm is the C=O n→π from the photoisomerized carbonyl. The absorbency of isosbestic point in 281nm is the C=O n→π from the unchangeable carbonyl, therefore the absorbency is invariable. The absorbency is not to change in isosbestic point of 319nm and 387nm, it should be the n→π of the C=C-C=O and the Ph-C=O. The results indicated that the photoisomerization is conformable the variety of the structure.

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