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SYNTHESIS OF SOME DERIVATIVES 9-ARYL-1,8-DIOXOOCTAHYDROXANTHENE AND 2,2'-ARYL-METHYLENE BIS(3-HYDROXY-2-CYCLOHEXENE-1-ONE) IN AQUEOUS MEDIA

MARWAN M. F. AL-HEETY

DEPT. OF CHEMSRTY- COLLEGE OF EDUCATION- UNIVERSITY OF AL- ANBAR

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ABSTRACT

This research concerned with the reaction of Aryl- benzoylchloride with 1,3-cyclohexanedione in aqueous media (which has been catalyzed by p-dodecylbenezenesulfonic acid (DBSA) or sodiumdodecylsulfate (SDS)). The product include two types derivatives: seven compounds from 9-aryl-1, 8-dioxooctahydroxanthene derivatives and seven compounds from 2,2'-arylmethylene Bis-(3- hydroxy- 2-cyclohexene-1-one) derivatives. The Products were diagnosed by the spectral methods (I.R.) and the elements quantities analyses (C.H.N.). Add-on products compound's, This method provides several advantages such as good yield, simple work-up procedure and environment friendly.

Introduction

In recent years, polyfunctionalized benzopyrans and their derivatives have attracted strong interest due to their useful biological and pharmacological properties, such as anticoagulant, spasmolytic, diuretic, antianaphylactin, anticancer.(1) In addition, they also constitute a structural unit of a series of natural products (2) and because of the inherent reactivity of the inbuilt pyran ring are versatile synthesis. (3) Furthermore, these compounds can be employed as cosmetics, pigments (4) and utilized as potential biodegradable agrochemicals. (5) Thus, synthesis of the heterocyclic nucleus is of such current importance. Octahydroxanthene derivatives containing a structural unit of benzopyrans can be used as antispasm (6) and fluorescent fuel (7). The tetraketones and their enol forms are the precursors of synthesis of. acridines, xanthenes and thiaxanthenes which contain structures such as dihydropyridine, pyran and thia pyran. (8).

———* Corresponding author at: DEPT. OF CHEMSRTY- COLLEGE OF EDUCATION- UNIVERSITY OF AL- ANBAR, Iraq.

The reaction of Aryl-benzalchloride and 1,3-cyclohexanedione can yield 9-aryl-1,8-dioxo-octahydroxanthene and their derivatives and 2,2'-arylmethyl-ene bis (3-hydroxy-2-cyclo- hexene-1-one) by many methods. However, the use of p-dodecylbenezenesulfonic acid (DBSA) or sodium dodecyl ulfate (SDS) as the catalyst in aqueous media for the synthesis of 9-aryl-1,8-dioxo-octahydroxanthene nd their derivatives and 2,2'-arylmethylene bis(3-hydroxy-2-cyclohexene-1-one) has not been reported. Herein, we wish to synthesize 9-aryl-1,8-dioxooctahydroxanthene derivatives and 2,2'- arylmethylene bis (3-hydroxy-2-cyclohexene-1-one) using p-dodecyl-benezenesulfonic acid (DBSA) or sodium dodecyl sulfate (SDS) as the catalyst in aqueous media.

At the beginning of the new century a shift in emphasis in chemistry is apparent with the desire to develop environmentally benign routes to a myriad of materials using non-toxic reagents, solvents and catalysts (10) Recently "ideal synthesis" was defined as one in which the target compound is generated in

one step, in quantitative yield from readily available and inexpensive starting materials in a resource-effective and environmentally acceptable process. (9) Recently organic reactions in water without use of harmful organic solvents have attracted much attention, because water is a cheap, safe, and environmentally benign solvent. 10 DBSA and SDS have been used in a number of organic reactions as good catalysts. In the course of our investigations to develop new synthetic methods in water using DBSA and SDS as catalysts, we exa-mined the synthesis of 9-aryl-1,8-dioxo-octahydroxanthenederivatives and 2,2'-arylmethylene bis(3-hydroxy-2- cyclohexene-1-one) in water, as a green solvent. (See Scheme 1)

Experimental PROCEDURE

A mixture of an Benzoylchloride (10 gm, 0.077 mol), 1, 3-cyclohexane -dione (17.36 gm, 0.155 mol) and DBSA (20 mL) or SDS (10 mL) in water (20 mL) was stirred with refluxing for four hours. After comple-tion of the reactions, the mixture was cooled to room temperature and solid was filtered off and washed with H2O (40 mL) and the crude products were got. The crude products a and b were purified by recrystallization by ethanol 95%. (See Table(2)), and The spectra I.R. and the elements quantities analyses (C.H.N.). for compounds yields , (See ,Table (1), fig.(1),(2) and (3)).

Results and Discussion

In a typical general experimental procedure, a solution of an Aryl-Benzoylchloride and 1,3-cyclohexane -dione in water was heated under reflux water in the presence of a catalytic amount of DBSA (20 mL) or SDS (10 mL) for a certain period of time required to complete the reaction, the corresponding 9-aryl-1,8-dioxooct -ahydroxanthene derivatives and 2,2'-arylmethylene bis(3- hydroxy-2-cyclo-hexene-1-one) were obtained in good yields. The results are summarized in Table 2. As shown in Scheme 1, the different products were obtained using different catalyst in this reaction. In a typical general experimental procedure

Aryl-Benzoylchloride and 1,3-cycl-ohexanedione reacted in the presence of a catalytic amount of DBSA or SDS, the corresponding products a and b were obtained in good to excellent yields. The catalyst effect shows that acid is needed during the cyclization.

To study the generality of this process, several examples illustrating this method for the synthesis a and b were studied. As shown in Table 2. The effect of electron and the nature of substituents on the aromatic ring did not show strongly obvious effects in terms of yields under this reaction conditions. The reaction proceeded smoothly under refluxing water to give the corresponding products a and b in good yields. Benzoylchloride and other Aryl-Benzoylchloride containing elect-ron-withdrawing groups such as nitro group, halide) or electron donating groups (such as hydroxy group, alkoxyl group) were employed and reacted well to give the corresponding a and b in good to excellent yields.

The catalyst plays a crucial role in the success of the reaction in terms of the rate and the yields. For example, 3-Bromobenzalchloride reacted with 1, 3-cyclohexanedione in the presence of 20mL DBSA to give the product 2a in good yield (80.7%) at refluxing water after four hours of reaction time. Increasing of the catalyst to 20 and 30mL results in accelerating the reaction yields to 79% and 75.4% respectively. Use of just 20mL DBSA in refluxing water is sufficient to push the reaction forward. Higher amounts of the catalyst did not improve the results to a greater extent. Thus, 20mL DBSA was chosen as a quantitative catalyst for these reactions. In addition, it must be

pointed out that all of these reactions were carried out in water and those products were characterized by melting point and IR.

Recommendation: Future reaction Bis-aryl- benzoylchloride with 1,3-cyc-

lohexanedione in aqueous media yields two products : Bis-(9-aryl-1,8-dioxo -

octahydroxanthene derivatives)and Bis (2,2'-arylmethylene Bis(3-hydroxy-2-cyclohexene-1-one))in water. Scheme (2). No further work has been done on the point since it is beyond our present work.

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Table (1) Same Characterization I.R. absorption bonds

Comp. No.	Cm^{-1}							
	C = O	C-H	C-O-C	C-C	C = C	O-H	Other	
1a	1870	2830	1050	950	1500	----	---	---
2a	1875	3010	1240	890	1590	----	C-Br	670
3a	1800	2900	1090	950	1630	----	C-Br	675
4a	1890	2890	1220	890	1580	----	C-Br	710
5a	1850	2900	1210	920	1610	----	C-C	960
6a	1865	3010	1055	980	1650	----	C-C	875

7b	6b	5b	4b	3b	2b	1b	7a
1820	1790	1795	1795	1790	1750	1820	1772
2980	3020	3020	3010	2890	3010	2885	2980
----	----	----	----	----	----	----	1220
880	970	910	930	890	875	870	950
1588	1690	1700	1650	1585	1590	1598	1670
3490	3680	3710	3550	3610	3550	3650	----
C-O	C-C	C-C	C-Br	C-Br	C-Br	---	C-O
1120	955	860	690	610	590	---	1085

*** as KBr disc**

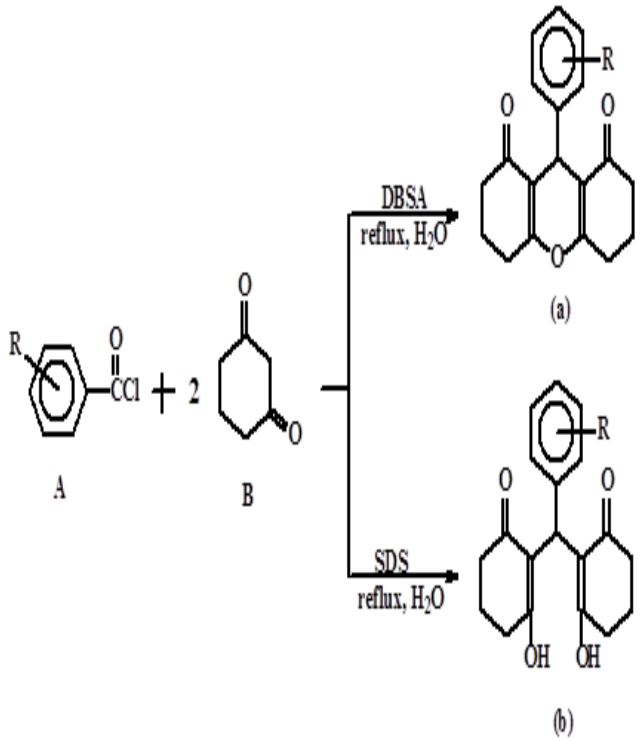
Table (2) Synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives and 2,2'-aryl-methylene Bis(3-hydroxy-2-cyclohexene-1-one) in aqueous media

R	Comp.No.	Yield(%)	M.P./ C^0	
			Found	Reported
H	1a	95	273-274	272-273 [8,9]
4-CH3	5b	84	202-203	----
4-Br	4b	80.1	199-198	----
2-Br	3b	77.5	225-224	----
3-Br	2b	65.9	198-197	----
H	1b	88	220-221	210-211 [9]
4-CH_3O	7a	76.5	203-204	196-197 [8, 9]
3-C_2H_5	6a	77	270-271	----
4-CH_3	5a	74	264-265	262-263 [9]
4-Br	4a	75.4	220-221	----
2-Br	3a	79	210-209	----
3-Br	2a	80.7	212-213	----
3-C_2H_5	6b	91.4	275-276	----

4-CH3O	7b	89	200-201	----

Table (3) Characterization data for the synthesized compounds

Comp.	Formula (M.Wt.)	Analysis calc./Found		
		C	H	
1a	$C_{19}H_{17}O_3$ (294)	6.46 6.40	6.12 6.09	----
2a	$C_{19}H_{17}O_3Br$ (373)	5.09 5.00	4.56 4.50	0.27 0.25
3a	$C_{19}H_{17}O_3$ Br (373))	5.09 5.05	4.56 4.52	0.27 0.23
4a	$C_{19}H_{17}O_3$ Br (373)	5.09 5.02	4.56 4.49	0.27 0.26
5a	$C_{20}H_{20}O_3$ (308)	5.49 5.33	6.49 6.44	----
6a	$C_{21}H_{23}O_3$ (323)	6.50 6.20	7.12 7.10	----
7a	$C_{20}H_{20}O_4$ (324)	6.17 6.11	6.17 6.08	----
1b	$C_{19}H_{20}O_4$ (312)	6.09 6.01	6.41 6.37	----
2b	$C_{19}H_{19}O_4Br$ (391)	4.86 4.80	4.86 4.80	0.26 0.20
3b	$C_{19}H_{19}O_4Br$ (391)	4.86 4.45	4.86 4.78	0.26 0.22
4b	$C_{19}H_{19}O_4Br$ (391)	4.86 4.68	4.86 4.82	0.26 0.21
5b	$C_{20}H_{22}O_4$ (326)	6.13 6.10	6.75 6.70	----
6b	$C_{21}H_{24}O_4$ (340)	6.18 6.02	7.06 7.00	----
7b	$C_{20}H_{22}O_5$ (342)	5.85 5.79	6.43 6.38	----



R = H, 3-Br, 2-Br, 4-Br, 4-CH_3, 3C_2H_5, 4-CH_3O,

Scheme(1) Synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives and 2,2'-arylmethylene bis(3-hydroxy-2-cyclohexene-1-one) in water

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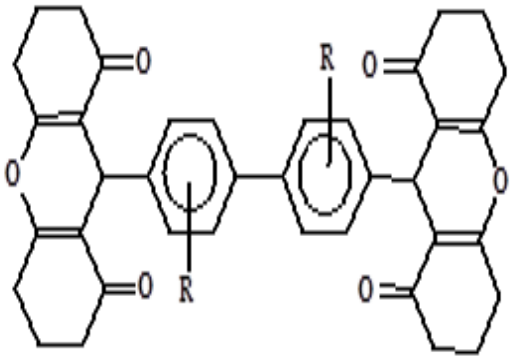
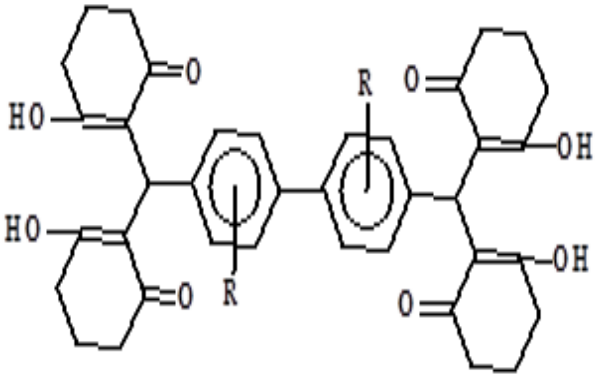
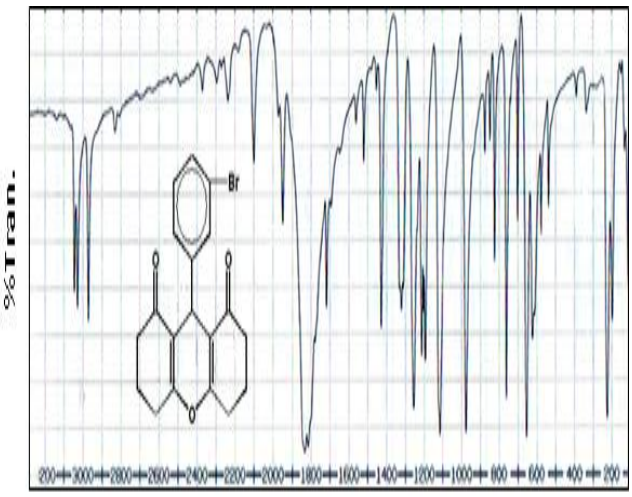


(C)



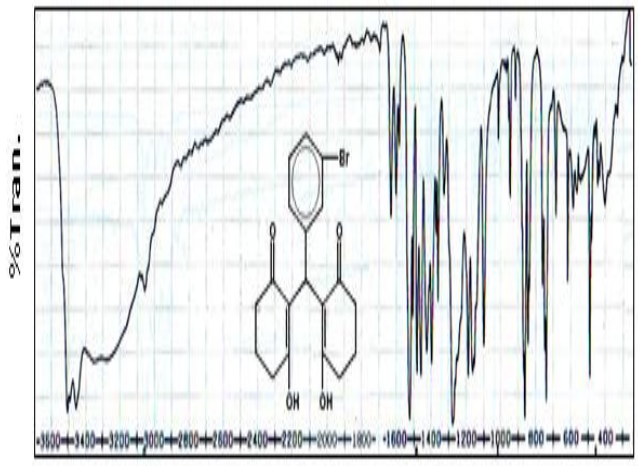
(D)

Scheme(2) Bis-(9-aryl-1,8-dioxooctahydroxanthene derivatives)and Bis (2,2'-arylmethylene bis(3-hydroxy-2-cyclohexene-1-one))in water



ύ cm^{-1}

Fig.(1) Spectra. IR. to (1a)



ύ cm^{-1}

Fig.(2) Spectra IR. to (2b)

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تحضير بعض مشتقات ٩-أريل-٨,١ – دايأوكسوأوكتاهيدروزانثين و ٢,٢'-أريل – مثليين بيس(٣-هيدروكسي-٢- سايكلوهكسين-١- أون) في أوساط مائية

مروان محمد فرحان الهيتي

قسم الكيمياء- كلية التربية – جامعة الانبار

الخلاصة

تضمنت هذه الدراسة تفاعل Aryl-benzoylchloride مع 1,3-cyclohexanedione في أوساط مائية وباستخدام عوامل مساعدة من *p*-dodecylbenezenesulfonic acid (DBSA) وsodium dodecyl sulfate (SDS) وباستخدام هذه العوامل أنتج نوعين من المشتقات سبع مركبات مشتقة من 9-aryl-1, 8-dioxooctahydroxanthene وسبع مركبات أخرى مشتقة من 2,2'-arylmethylene Bis-(3- hydroxy- 2-cyclohexene-1-one) وشخصت هذه النواتج باستخدام طيف الأشعة تحت الحمراء والتحليل الكمي للعناصر. وإضافة إلى تحضير هذه المركبات اذ تُزوّدُ هذه الطريقةِ عِدّة فوائد مثل نسب المنتوج الجيدِ، وطريقة عمل بسيطة في ظروف مناسبة.