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Improved Synthesis of Dibenzo[*a,j*]perylene-8,16-dione

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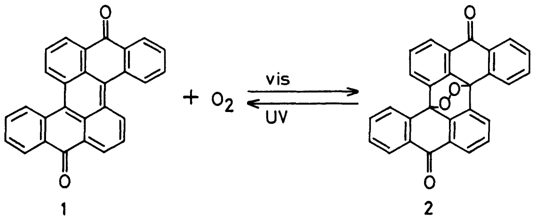
Synopsis. An improved method for the synthesis of the title compound **1** has been achieved through an application of the Scholl reaction. The key to the new approach is to use the dimeric compounds of 10-methyleneanthrone as the precursors of **1**.

Photochromic systems which are based on photoreversible addition of O_2 to arene derivatives have recently received much attention in connection with their potential use as photoresponsive materials.[1-12] The photochromic conversion of dibenzo[*a,j*]perylene-8,16-dione (heterocoerdianthrone) (**1**) into 4b,12b-epidioxy-4b,12b-dihydrodibenzo[*a,j*]perylene-8,16-dione (*endo*-peroxide) (**2**) is among the most extensively investigated reactions.[1-8,11] The self-sensitizing photooxidation of reddish violet **1** by visible light irradiation in air-saturated solution leads to the formation of colorless **2**, which reproduces the parent compound **1** and O_2 in a singlet state by ultraviolet light. The photochromic system consisting of **1** and **2** is highly reversible and thermally stable.[4,6,11]

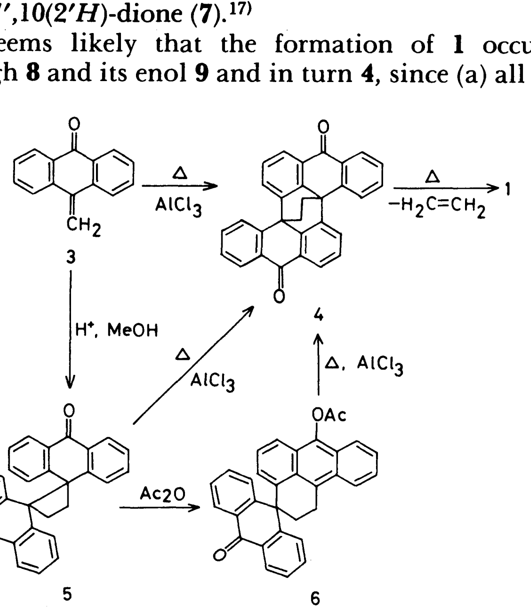


The methods reported to date for the synthesis of **1** are as follows: (a) Dehydration of 9,10-diphenyl-1,5-anthracenedicarboxylic acid which is prepared in four steps from the readily available starting material, 9,10-anthraquinone-1,5-dicarboxylic acid,[13] (b) thermolysis of 4-chloroanthrone whose preparation is difficult,[14] (c) reaction of 4-chloroanthrone with zinc chloride in pyridine,[15] and (d) the Scholl reaction of readily available 10-methyleneanthrone (**3**) with aluminium chloride.[16] The overall yield of **1** from the anthraquinonedicarboxylic acid by method (a), which is often employed, is low (ca. 23—25%). In method (d), **1** is prepared in one step from **3**. However, its detailed direction and yield have not been published. We have, therefore, examined the convenient synthesis of **1** using the Scholl reaction of **3** and its dimeric compounds.

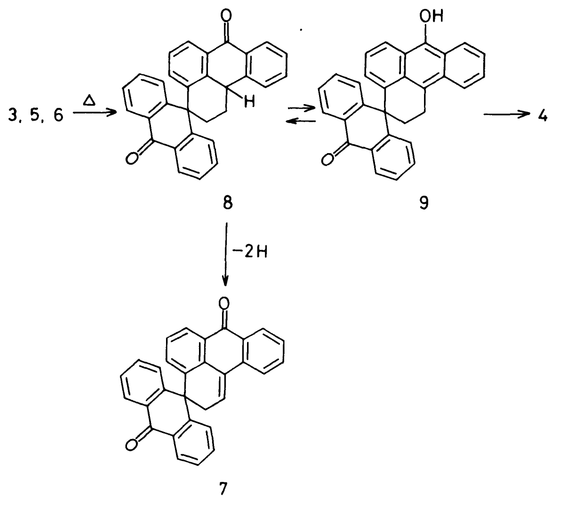
Treatment of **3** with aluminium chloride-sodium chloride at 200 °C, in a modification of literature method,[16] gave very low yield of **1** (16%), together with anthraquinone (4%). The addition of a proper amount of the hydrogen acceptor, manganese dioxide, resulted in an increase in the yield of **1**. Similar treatment of **3** in the presence of manganese dioxide, 2—3 wt%/aluminium chloride, led to **1** in a 22% yield. However, addition of an organic base, e.g., pyridine, was without effect. The similar reaction of **3** at the reaction temperature of 150—170 °C afforded the intermediate, 4b,12b-dihydro-4b,12b-ethanodibenzo[*a,j*]perylene-8,16-dione (**4**), the structure of which followed from spectral data and thermolysis to **1**. Its IR spectrum indicates absorption for the carbonyl group at 1650 cm^{-1} and its ^1H NMR spectrum reveals an A_2B_2 multiplet due to the ethylene group at δ 1.92—2.26 and 2.40—2.74. Heating of **4** at its melting point gave **1** in a high yield, together with evolution of ethylene.

It seemed to us, based on the formation of **4**, that the dimeric compounds of **3**, dispiro[anthracene-9(10*H*), 1′-cyclobutane-2′,9″(10″*H*)-anthracene]-10,10″-dione (**5**) and 7′-acetoxy-1′,2′-dihydrospiro[anthracene-9(10*H*), 3′-[3*H*]benz[*de*]anthracene]-10-one (**6**),[17] would be favorable precursors for conversion to **1** via the Scholl reaction. The dimer **5** and its acetylated compound **6** were prepared from **3** in high yields according to the previously studied method (**5**: 97%; **6**: 89%), as shown in the scheme. The dimeric compounds **5** and **6** gave the expected dye **1** or its intermediate **4** under the Scholl reaction conditions (Table 1). The yields of **1** or **4** from **5** and **6** were much higher than those from **3**; under the optimum conditions, the reactions of **5** and **6** led to **1** in 33 and 26% yields, respectively. In addition, the Scholl reactions of **5** and **6** did not yield anthraquinone whose separation from **1** using the means of vatting process is troublesome, whereas **3** led to a significant amount of anthraquinone. Thus, the method involving the Scholl reaction of the dimer **5**, prepared from **3**, to **1** (**3**→**5**→**1**) is preferable to the other two (**3**→**1** and **3**→**5**→**6**→**1**) in terms both of convenience and yield. A similar treatment of **5** with zinc chloride as a Friedel-Crafts reagent did not give **1**, but, instead, gave spiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene]-7′,10(2′*H*)-dione (**7**).[17]

It seems likely that the formation of **1** occurs through **8** and its enol **9** and in turn **4**, since (a) all of



the reaction of **8**, **5**, and **6** with aluminium chloride at low temperature (150—170 °C) gave the intermediate **4** which yielded **1** by thermolysis, and (b) similar reactions at 135—140 °C led to **7** which probably arises from the dehydrogenation of **8** or **9**,[17] (c) the acid-catalyzed reaction of **3** in organic solvents readily gave **5**, which thermally rearranged with a synchronous ring expansion to give unstable **8** and/or **9**.[17] These peri-condensation reactions effected by aluminium chloride occured in the presence of a trace of water or hydrogen chloride.[18,19] In addition, hydrogen acceptors such as air, supplied by vigorous stirring of the reaction mixture, and manganese dioxide resulted in an increase in the yield of **1**. A conceivable mechanism for the formation of **1** from **3**, **5**, and **6** may be as follows: First, the formation of the enol **9** from **3**, **5**, and **6**, second, the protonation on the anthracene moiety of **9** by moist aluminium chloride to give σ complexes[20] which undergo the electrophilic substitution (cyclization) involving the C-11′b and C-4 atoms, third, the dehydrogenation promoted by air or manganese dioxide to lead to **4**, and finally, the retro Diels-Alder reaction of **4** to give **1** and ethylene. The low yields of these Scholl reactions might result from the deactivation at the 4-position by the inductive effect of the carbonyl group and the steric hindrance in the intramolecular electrophilic substitution of the σ complex. However, the synthetic method of **1** via the Scholl reaction of the dimer **5** can compete in terms of convenience and yield with those through 9,10-diphenyl-1,5-anthracenedicarboxylic acid.



8

9

7

Experimental

The following compounds were prepared according to previously known procedures: **3**,[21] **5**,[17] and **6**.[17]

Dibenzo[*a,j*]perylene-8,16-dione (1). To a finely ground mixture of aluminium chloride (50 g), sodium chloride (15 g), and manganese dioxide (1.00 g), 5 (5.00 g) was added. The mixture was vigorously stirred and heated until TLC showed the absence of the intermediate **4**. The reaction temperature was kept at 160 °C during the first 10 min and then raised to 200 °C in 5—10 min, where it was kept for ca. 2 h. The resulting mixture was poured into ice-water (500 g) followed by addition of hydrochloric acid (100 ml). After boiling, the precipitate was filtered off and washed with water. The product mixture was extracted repeatedly with a hot alkaline sodium dithionite solution (NaOH, 10 g; $Na_2S_2O_4$, 10 g; H_2O, 500 ml). The alkali-soluble leuco product (deep green) was oxidized to the crude dye by contact with air. The dye was washed with water, dried, and recrystallized from chlorobenzene or pyridine to give pure **1** (33%) as reddish violet microcrystals, identical with an authentic specimen:[13] mp 363—365 °C (lit,[4] 361 °C); IR (KBr) 1643 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=7.55—7.95 (6H, m), 8.15—8.30 (2H, m), 8.50—8.65 (2H, m), 8.83 (2H, dd), and 9.00 (2H, d), MS *m/z* 382 (M^+); Anal. ($C_{28}H_{14}O_2$) C, H.

Results of the reactions of **3**, **5**, and **6** under the different conditions are summarized in Table 1.

4b,12b-Dihydro-4b,12b-ethanodibenzo[*a,j*]perylene-8,16-dione (4). The procedure for the Scholl reaction was similar to that for **1** except that the reaction was carried out without manganese dioxide at 160 °C for 1 h until TLC showed the absence of the starting material. The product mixture from **5** was chromatographed on silica (benzene as

Table 1. Scholl Reactions of **3**, **5**, and **6**

Reactant	Reaction Condition					Product/%	
	Reagent : Reactant/wt ratio			Temp	Time		
	$AlCl_3$	NaCl	MnO_2	°C	h	**1**	**4**
3	10	3	0	200	2	16[a)]	0
3	10	3	0.2	200	2	22[a)]	0
3	10	3	0	160[b)]	1	Trace	16[a)]
5	10	0	0	200	2	18	0
5	7	2.1	0	200	2	16	0
5	10	3	0	200	2	25	0
5	10	3	0.2	200	2	33	0
5	10	3	0.5	200	2	29	0
5	10	3	0.2	220	2	28	0
5	10	3	0.2	200	3	24	0
5	10	3	0	160[b)]	1	Trace	24
6	10	3	0	210	2	21	0
6	10	3	0.2	210	2	26	0
6	10	3	0	160[b)]	1	Trace	22

a) The reaction gave anthraquinone (ca. 4—5%) as by-product. b) At this reaction temperature, the addition of manganese dioxide resulted in an inadequate melting of aluminium chloride-sodium chloride medium. Consequently, it led to a decrease in the yield of **4**.

eluant). Recrystallization of the appropriate fraction from benzene-hexane gave **4** (24%) as nearly colorless microcrystals: TLC (Merck, silica gel 60 F_{254}, precoated plastic sheet, 0.2 mm, benzene) R_f 0.35; mp 319—321 °C; IR (KBr) 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.92—2.26 (2H, m), 2.40—2.74 (2H, m), 7.15—7.40 (4H, m), 7.50—7.95 (6H, m), 8.15 (2H, dd), and 8.50—8.70 (2H, m); MS m/z 410 (M^+); Anal. ($C_{30}H_{18}O_2$) C, H.

Results for the similar reactions of **3** and **6** are shown in Table 1.

Thermolysis of 4. Compound **4** (2.05 g, 50 mmol) was heated at its melting point in a test tube for 5 min during which time gas was evolved. The violet product was recrystallized from chlorobenzene to give **1** (1.74 g, 89%). GLC analysis of the gas evolved in the thermolysis showed the presence of ethylene.

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