Thermal Dimerization of 10-Methyleneanthrone

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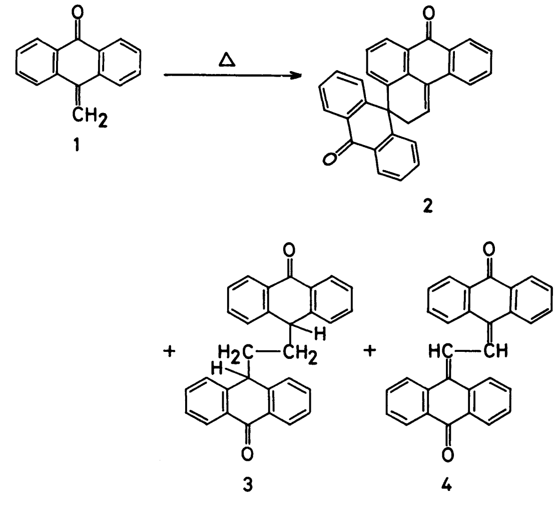
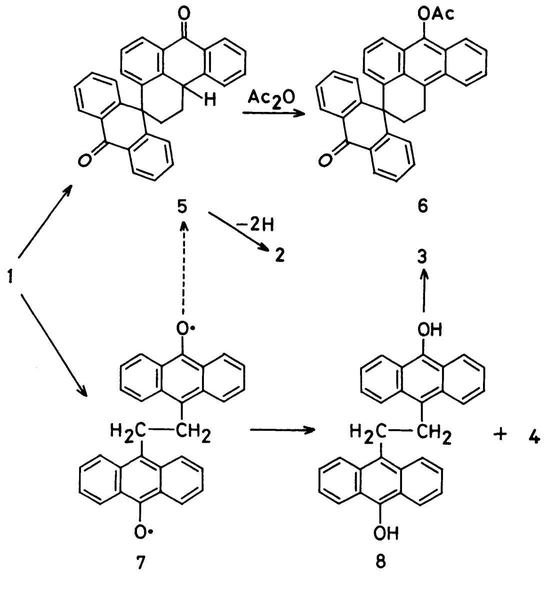
Synopsis. The thermal reaction of the title compound (**1**) gave three dimeric products which were formed via a path involving two competitive reactions, Diels-Alder and radical dimerization.

10-Methyleneanthrone (**1**) is a certain member of a class of compounds which are called "quinone methides." This system is, as a rule, unstable and is subject to reactions which form dimers, trimers, and polymers, because of the possibility that the aromatization of the cyclohexadienone portion of the molecule might supply a strong driving force for reactions.[1] However, **1** is stable and shows no tendency toward spontaneous aromatization under ordinary conditions. Such a low probability of the central ring's becoming aromatic makes its quinone methide character weak. For that reason, its chemistry has received much attention. It has been known that the base-[2] and phosphite-induced,[3,4] autoxidative,[3,5] and ketone-sensitized photochemical reactions[6] of **1** give Diels-Alder dimeric products, a dimeric peroxide, and a reductive dimeric product, respectively. Also, we previously reported that the acid-induced reaction of **1** leads to a dimeric dispiro compound, which thermally rearranged with a synchronous ring expansion.[7,8] We investigated the previously unnoticed thermal reaction of **1** and found that it undergoes thermal dimerization.

Heating compound **1** without solvent at 150 °C led to dimeric products, spiro[anthrone-10,3′(2′*H*)-benz[*de*]anthrone] (**2**), 10,10′-(1,2-ethanediyl)bisanthrone (**3**), and 10,10′-(1,2-ethanediylidene)bisanthrone (**4**) in 27, 12, and 4% yields, respectively. In a similar treatment at 180 °C, red and violet products (formulas $C_{46}H_{26}O_3$ and $C_{62}H_{34}O_4$) were obtained bisides the dimeric products, but have not yet been identified. Compounds **2** and **4** were identified by a comparison with authentic samples.[6,7] **3** was isolated as the keto rather than the enol-tautomer, the structure of which was confirmed by comparison with a sample prepared independently by the acid-induced hydrolysis of 10,10′-(1,2-ethanediyl)bis[9-anthracenol] diacetate, the reductive acetylation product of **1** with zinc and acetic anhydride. The IR spectrum of **3** indicates absorption for the carbonyl group (1665 cm^{-1}) and no hydroxy function. Its ^1H NMR spectrum reveals a triplet of H-10 and −10′ (δ 1.48). A heat treatment of **1** in refluxing xylene gave only **2**; **1** in refluxing *o*-dichlorobenzene yielded **2** along with minor products **3** and **4**. Anthraquinone was isolated in all runs and resulted from the autoxidation of **1**.



A conceivable mechanism for the thermal reaction of **1** is shown in the scheme. There would be two competing reactions in which **1** could be consumed. One is a Diels-Alder dimerization in which **1** behaves both as a dienophile and as a diene, followed by an isomerization to **5**. Compound **5** is unstable and leads to **2** by autoxidation.[7] The other is dimerization involving the formation of biradical **7** whose disproportionation leads to **8** and **4**. Compound **8** isomerizes to a more stable keto-tautomer **3**.[9] The Diels-Alder dimerization was predominant to the radical one. The former path is supported by the following facts. The reaction of **1** in a low-boiling-point solvent such as xylene gave only **2** and in acetic anhydride afforded only **6**, acetate of **5**. Thus, at a reaction temperature below



ca. 140 °C, **1** undergoes the Diels-Alder dimerization (exclusively). No ESR signal was detected in the reaction mixture of **1** while refluxing xylene and acetic anhydride under nitrogen. Also, **3** was not detected in any reaction products at 140 °C even in a solvent labile on hydrogen abstraction, such as decalin. Therefore, it seems unlikely that the formation of **2** involves an alternative path via the intramolecular cyclization of **7** to **5**. The latter would readily be rationalized both by the formation of **3** and **4** and by the concomitant appearance of a multiline ESR signal which might be attributable to **7** in the thermal reaction of **1** without solvent under nitrogen.

10-Methyleneanthrone (**1**) behaves as a quinone methide as well as an olefin (diene or dienophile). Such a fact shows the comparative isolation of the ethylenic bond from the carbonyl group in the molecule.

Experimental

Thermal Reaction of 10-Methyleneanthrone (1). (a) Without solvent. Finely ground **1**[3] (2.06 g,10 mmol) was heated at its melting point (148 °C) in a sealed test tube for 15 min. The reaction mixture was chromatographed on silica with benzene and then with chloroform. The first fraction (benzene) contained anthraquinone (0.04 g, 2%). The second (benzene) consisted of spiro[anthrone-10,3′(2′*H*)-benz[*de*]anthrone] (**2**) (0.55 g, 27%), light yellow microcrystals (from benzene–hexane), mp 298—300 °C, identical with an authentic specimen.[7] The third (benzene) afforded 10,10′-(1,2-ethanediyl)bisanthrone (**3**) (0.24 g, 12%), colorless microcrystals (from chloroform–hexane), mp 249—251 °C (lit,[6] 245—246 °C), identical with an authentic specimen prepared independently by the method described below. The fourth eluate (chloroform) gave 10,10′-(1,2-ethanediylidene)bisanthrone (**4**) (0.08 g, 4%), orange-red microcrystals (from chloroform), mp 290—292 °C, identical with an authentic specimen.[10]

(b) In an inert solvent. A solution of **1** (1.03 g, 5 mmol) in xylene, *o*-dichlorobenzene, or decalin (30 ml) was heated under nitrogen for 30 h. The solvent was distilled off under reduced pressure, and the residue was chromatographed on silica. The results of analyses of the isolated products are as follows. The product mixture from the reaction of **1** in xylene (bp of the solution: 141 °C) gave **1** (70%) and **2** (7%). *o*-Dichlorobenzene (at 181 °C): **1** (42%), **2** (10%), **3** (1%), and **4** (trace). Decalin (at 140 °C): **1** (68%) and **2** (6%). Decalin (at 191 °C): **1** (47%), **2** (9%), **3** (1%), and **4** (trace).

(c) In acetic anhydride. A solution of 1 (1.03 g, 5 mmol) in acetic anhydride (30 ml) was heated under reflux for 1 d (bp of the solution: 139 °C). After cooling, the resulting mixture was poured into water. The crystals were collected, washed with water, and chromatographed (benzene as eluant). The first fraction gave unchanged **1** (0.85 g, 82%), and the second afforded 7′-acetoxy-1′,2′-dihydrospiro[anthrone-10,3′-[3*H*]benz[*de*]anthracene] (**6**) (0.11 g, 11%) as yellow microcrystals, mp 282—283 °C, identical with an authentic specimen.[7]

Preparation of 3. A mixture of **1** (2.06 g, 10 mmol) and zinc dust (6 g) in acetic anhydride (40 ml) was stirred and heated under reflux for 5 h. The hot mixture was filtered, and the filtrate was poured into water; the precipitate was chromatographed on silica (benzene as eluant). The first eluate afforded 9-acetoxy-10-methylanthracene (0.03 g, 1%) as light yellow needles, mp 167—169 °C (lit, 167 °C), identical with an authentic specimen.[11] The second gave 10,10′-(1,2-ethanediyl)bis[9-anthracenol] diacetate (2.17 g, 87%), light yellow needles, mp 300—302 °C (lit,[6] 295—297 °C).

A solution of the diacetate (1.00 g, 2 mmol) in sulfuric acid (20 ml) was allowed to stand at room temperature for 30 min. The mixture was poured into ice water (200 g), and the precipitate was collected and washed with water. Recrystallization from chloroform–hexane gave **3** (0.67 g, 81%) as colorless microcrystals, mp 261—262 °C. Its spectral data were identical to those of a specimen of **3** obtained from the ketone-sensitized photochemical dimerization of **1**.[6]

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