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9,9'-ANTHRIL
(DI-9-ANTHRYLETHANEDIONE)

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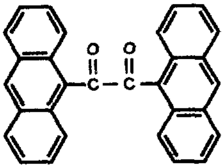
Abstract. 9,9'-Anthril has been synthesized both from 9-anthryllithium/oxalyl chloride at -78 °C, and from methyl 9-anthrilate by a reverse benzilic acid rearrangement. Anthril isomerizes by Diels-Alder reaction. Reduction gives 9,9'-anthroin and hydro-9,9'-anthroin.

In connection with current photochemical studies on bichromophoric anthracenes we realized that neither 9,9'-anthril (1) nor 9,9'-anthroin (2) had been prepared previously, and that classical organic reactions, by which benzil and benzoin are accessible, are not applicable to the synthesis of 1 and 2. Thus, Friedel-Crafts reaction of anthracene with oxalyl chloride leads to aceanthrene quinone.[1] Cyanide ion catalyzed benzoin condensation proceeeds smoothly both with 1-naphthaldehyde and 9-phenanthraldehyde, but 9-anthraldehyde undergoes nucleophilic substitution by cyanide ion to give 9,10-dicyanoanthracene.[2-4]



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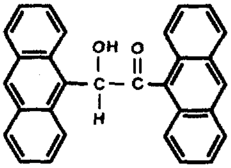

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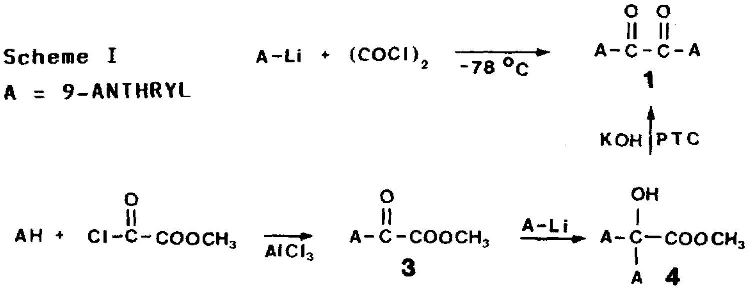
We have now found that 9,9'-anthril can be prepared in about 50% yield when oxalyl chloride (3 mmol) is added to a solution of 9-anthryllithium (6 mmol) in ether (50 mL) at -78 °C. The solution must be kept at -78 °C for about 4 h, as anthril in the presence of 9-anthryllithium at higher temperature is rapidly consumed by nucleophilic addition reactions to the carbonyl double bond.[5] A second route to 9,9'-anthril circumventing this difficulty involves the reverse benzilic acid rearrangement of methyl 9-anthrilate (4; pale yellow crystals; mp 190-193 °C). The latter was synthesized from anthracene via methyl 9-anthrylglyoxalate (3; yellow crystals, mp 103-105 °C) as outlined in Scheme I. When a solution of 4 (1 g) in dichloromethane (100 mL) containing solid KOH (1 g) and 18-crown-6 (50 mg) is stirred at 20 °C for 1 h, 9,9'-anthril is formed in 33% yield.[6]

9,9'-Anthril forms deep red crystals which melt at 254-258 °C (dec, crystal phase transition > 225 °C).[7] Its electron spectrum in solution exhibits the structured anthracene absorption around 375 nm, indicating that the carbonyl groups are twisted

Scheme I
A = 9-ANTHRYL



$$\text{A-Li} + (\text{COCl})_2 \xrightarrow{-78\ ^{\circ}\text{C}} \text{A}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{A}\ \ \mathbf{1}$$

$$\text{AH} + \text{Cl}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{COOCH}_3 \xrightarrow[\text{AlCl}_3]{} \underset{\mathbf{3}}{\text{A}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{COOCH}_3} \xrightarrow{\text{A-Li}} \text{A}-\underset{\text{A}}{\overset{\text{OH}}{\text{C}}}-\text{COOCH}_3\ \ \mathbf{4} \xrightarrow{\text{KOH}\ |\ \text{PTC}} \mathbf{1}$$

out of the planes of the anthracenes.[8] The presence of the 1,2-diketo chromophore is borne out by the extended end absorption with an onset at about 570 nm (Fig. 1).

Anthril isomerizes upon melting, or at room temperature in dichloromethane in the presence of aluminum chloride, to give 5 (yellow crystals, mp 219-224 °C) by a Diels-Alder reaction in which the central ring of one anthracene participates as diene, and the 1,2-bond of the other anthracene functions as dienophile. The dehydrogenation product of 5, i.e. triptycene derivative 6 (purple crystals, mp > 350 °C) is obtained in 73% yield by keeping a solution of anthril in benzene (sealed tube) at 220 °C for 90 min in the presence of an equimolar amount 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[9,10] The necessarily coplanar arrangement of the 1,2-dicarbonyl chromophore with the anthracene π-system in 6 accounts for the absorption around 500 nm (see Fig. 1).

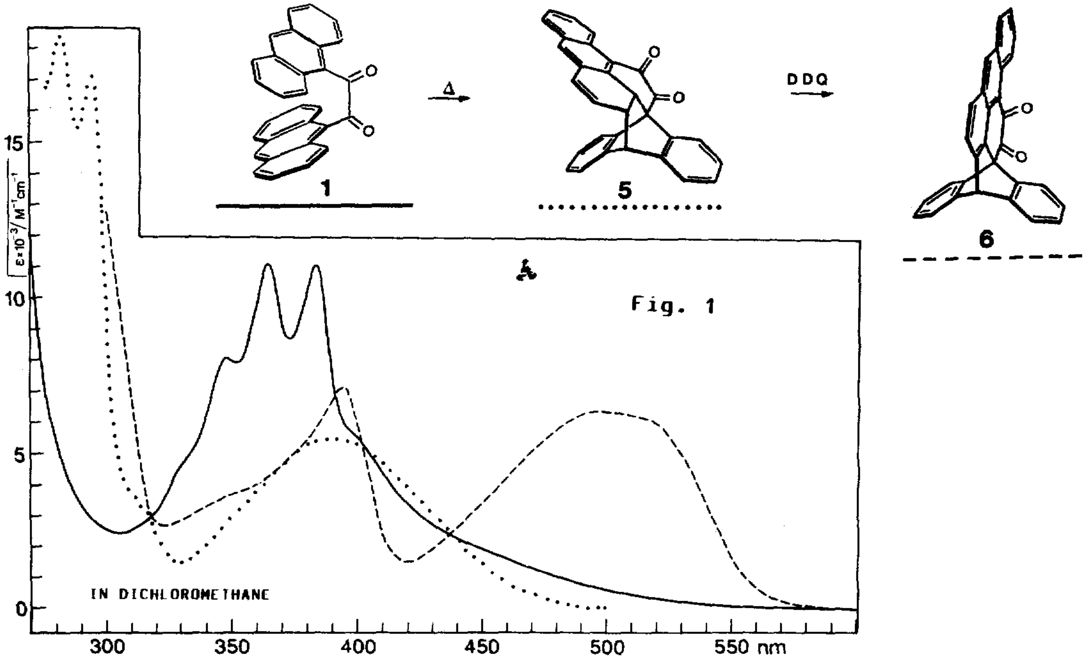
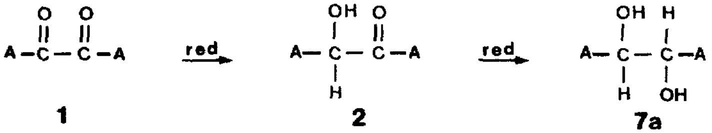


Fig. 1

Reduction of anthril with sodium borohydride in tetrahydrofuran (THF)/methanol gives 9,9'-anthroin (2; yellow crystals, mp 186-187 °C) in 90% yield. meso-Hydro-9,9'-anthroin (7a; yellow crystals, mp 255-256 °C) can be obtained in 61% yield by reduction of anthril with lithium aluminum hydride in THF.[11] The electron spectrum of 7a exhibits well-resolved vibrational bands of high molar extinction coefficients, suggesting a staggered anti conformation of the 1,2-di-9-anthrylethane moiety. The noticeably broadened absorption of 9,9'-anthroin (Fig. 2) indicates intramolecular overlap of the two anthracene moieties.

Upon irradiation in dichloromethane ($\lambda>420$ nm)[12] anthril isomerizes with extremely low quantum efficiency to give the $4\pi+2\pi$ cyclomer 5 whose electronic absorption (Fig. 1) largely overlaps with that of 1. By contrast, the photochemical isomerization of anthroin in dichloromethane proceeds smoothly to give the $4\pi+4\pi$ cyclomer 8 (colorless crystals, mp 190-220 °C; dec) with a quantum yield of 0.21. Oxidation of 8 with Dess-Martin periodinane[13] in dichloromethane then gave in 90% yield the formal $4\pi+4\pi$ cyclomer of anthril, i. e. 1,2-cyclobutanedione derivative 9 (deep red crystals, mp 219-244 °C; dec). By comparison with the electron spectrum of the unsubstituted 1,2-cyclobutanedione (λ_{max} 500 nm, ε 28),[14] the carbonyl $n-\pi^*$ absorption of 9 is bathochromically shifted and markedly enhanced, due to 3,3,4,4-tetraphenyl substitution (see Fig. 3).



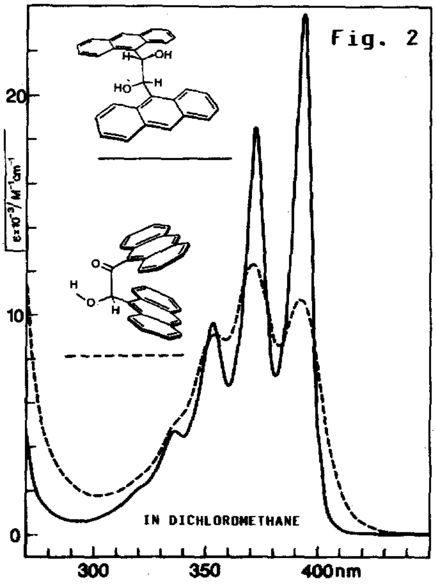
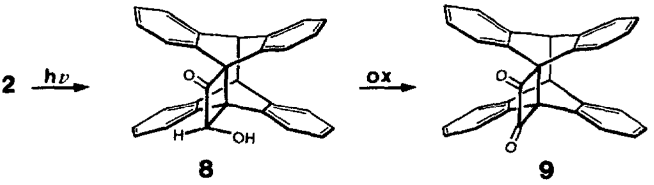


Fig. 2



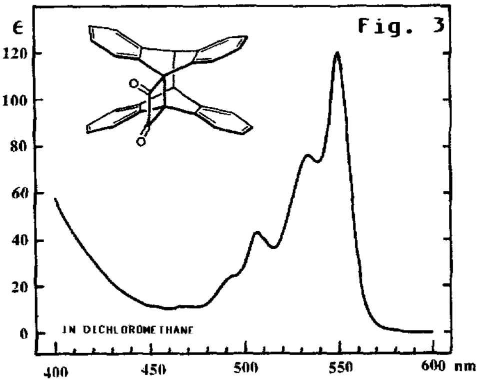
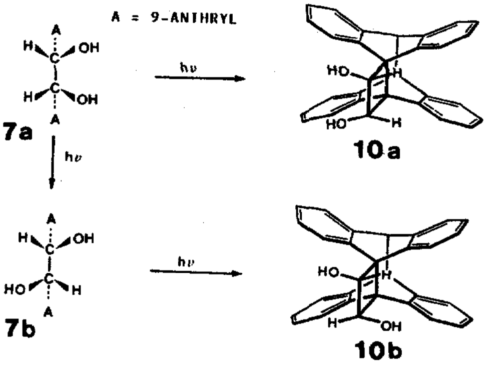


Fig. 3

Hydro-9,9'-anthroin 7a disappears upon irradiation in toluene with a quantum yield of 0.15.[15] To our surprise, however, we find that the expected cis-1,2-cyclobutanediol 10a (mp 188-192 °C) is only a minor product. The major photo-isomer of 7a turned out to be the sterically less congested trans-cyclobutanediol 10b (mp 220-227 °C).[16]

Scheme II



We assume the cyclomer 10a to be stable under the photochemical conditions, and we rationalize the formation of the trans-diol 10b by a reversible cleavage of the central single bond in photo-excited 7a to give racemic 7b (see Scheme II). Since irradiation of the diacetate of 7a[11] smoothly leads to the diacetate of the cis-1,2-cyclobutanediol 10a, the photolytic cleavage of the ethane bond in 7a apparently is associated with the presence of hydroxyl groups.

References and Notes

1. C. Liebermann and M. Zsuffa, Ber. Dtsch. Chem. Ges., 23, 907 (1911).
2. M. Gomberg and F. J. Van Natta, J. Am. Chem. Soc., 51, 2238 (1929).
3. B. Eistert, H. Schneider, and R. Wollheim, Chem. Ber., 92, 2061 (1959).
4. N. A. Goeckner and H. R. Snyder, J. Org. Chem., 38, 481 (1973).
5. The product formed by addition of 9-anthryllithium to 9,9'-anthril spontaneously undergoes a formal reverse Wittig ether-carbinol rearrangement. To be published.
6. In a competing reaction, methyl 9-anthrilate undergoes base-catalyzed isomerization which involves migration of a 9-anthryl moiety from carbon to oxygen. Cf. Ref. 5.
7. Anthril crystallizes in two modifications in which the dihedral angle between the two carbonyl groups is 44 and 180 degrees, respectively. Details will be presented in a forthcoming comprehensive paper with A. H. White of the University of Western Australia on the molecular structures of anthril and its isomerization products.
8. Other spectroscopic data for anthril: IR (KBr): 1670 cm^{-1}. 270 MHz H NMR (CDCl): 8.53 (s, H-10/H-10'), 8.0 ("d", J =8 Hz; 4 H), 7.86 ("d", J = 8 Hz, 4 H), 7.44 (m, 8 H).
9. The parent aromatic hydrocarbon of 6 has been synthesized from 1,2-di-9-anthrylethane; see H.-D. Becker and K. Andersson, Tetrahedron, 42, 1555 (1986).
10. The anthril isomer 5 may also undergo acid-catalyzed rearrangement. To be published.
11. The meso-structure of 7a was established by X-ray diffraction of its diacetate: H.-D. Becker, L. Hansen, B. W. Skelton, H. Sörensen, A. H. White, Aust. J. Chem., in press.
12. Photochemical isomerizations were carried out at 12 °C under argon with a 125 watt high-pressure mercury lamp in an immersion well apparatus equipped with liquid-filter set-up.
13. D. B. Dess and J. C. Martin, J. Org. Chem., 48, 4155 (1983).
14. J. M. Conia and J. M. Denis, Tetrahedron Lett., 2845 (1971).
15. Measurements are complicated due to the concomitant formation 9-anthraldehyde.
16. The stereochemical assignments of the cis- and trans-diols 10a/10b are deduced from their H NMR spectra. For the H NMR spectra of cis- and trans-1,2-cyclobutanediol, cf. J. P. Barnier, J. Champion, and J. M. Conia, Org. Synth., 60, 25 (1981).

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