Reductions with Diphenylhydroxymethyl Radicals. Synthesis of Dianthrylethanes and Dianthrylethylenes

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Received May 15, 1979

The reductive dimerization of 10-methyleneanthrone by diphenylhydroxymethyl radicals, generated by thermal dissociation of benzpinacol, gives 1,2-bis(10-hydroxy-9-anthryl)ethane. Its utilization in the synthesis of anthronylethyl-substituted anthracenes, dianthrylethanes, and dianthrylethylenes is described. The compound reported in the literature to be the cis isomer of 1,2-bis(9-anthryl)ethylene apparently is 9-cyanoanthracene.

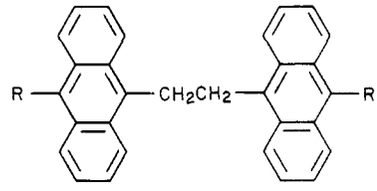
The conceivable involvement of ketyl radicals in ketone-sensitized photochemical reductions of quinonoid compounds had prompted us several years ago to mimic the photochemical hydrogen transfer with thermally generated diphenylhydroxymethyl radicals (**2a**).[1] Thermal dissociation of benzpinacol (**1a**) in the presence of equimolar amounts of quinonoid compounds Q is known to lead smoothly to benzophenone and the reduction product QH_2.[2] However, when applied to quinone methides whose methylidene carbon does not carry sterically demanding substituents, the reaction was found to give diarylethanes by reductive dimerization, obviously involving intermediate 4-hydroxybenzyl radicals.[3]

From a preparative point of view, the diphenylhydroxymethyl radical complements the list of conventional reducing agents for quinonoid compounds by virtue of its selectivity and its applicability under neutral conditions. The potential synthetic superiority of hydrogen atom transfer to quinone methides from ketyl radicals was utilized in the reductive dimerization of 10-methyleneanthrone (**3**) described in this paper.

Results and Discussion

10-Methyleneanthrone (**3**) represents the rare example of an isolable quinone methide unsubstituted in the α position, and for that reason, its chemistry has long been of interest.[4] Reduction of **3** by zinc in the presence of acetic acid did not give any identifiable products,[5] while treatment with zinc in the presence of ammonia afforded 1,2-bis(9-anthryl)ethane, obviously derived from some unstable primary reduction product.[6,7] We have found during the course of the present investigation that catalytic hydrogenation of 10-methyleneanthrone, followed by acetylation of the oxygen-sensitive[8] reduction product assumed to be 9-hydroxy-10-methylanthracene in equilibrium with its keto tautomer, gave 9-acetoxy-10-methylanthracene.

In contrast to the reductions mentioned above, the reaction of 10-methyleneanthrone with thermally generated diphenylhydroxymethyl radicals (**2a**) gives, in 75% yield, the previously inaccessible 1,2-bis(10-hydroxy-9-anthryl)ethane (**5a**). Its structural assignment rests on its spectroscopic and chemical properties discussed below. The experimental conditions for the reductive dimerization of **3** are strikingly simple, as pure **5a** precipitates upon refluxing a solution of stoichiometric amounts of 10-methyleneanthrone and benzpinacol in xylene under nitrogen for 25 min.



5a, R = OH
b, R = $OCOCH_3$
c, R = OCH_3
d, R = $OSiMe_3$
e, R = H
f, R = CH_3
g, R = C_6H_5

We rationalize the formation of dimer **5a** in terms of hydrogen atom transfer from radical **2a** to the carbonyl oxygen of methyleneanthrone to give "benzyl" radical **4** (R = H) which dimerizes. Support for this mechanism can be deduced from the formation of the mixed coupling product **6** (R = trimethylsilyl) which we obtained by thermal dissociation of benzpinacol–bis(trimethylsilyl) ether (**2b**) in the presence of an equimolar amount of methyleneanthrone (see Scheme I).

In solution, dimer **5a** was found to be labile. In the presence of air, it was readily autoxidized to give a bis(hydroperoxide) (**8b**) which was converted into the bis(trimethylsilyl) ether **8c** and, by catalytic reduction, into the dihydroxy compound **8d**. When dissolved in dimethyl sulfoxide or dimethylformamide in the absence of oxygen, dimer **5a** readily tautomerizes to the anthronylethyl-substituted 9-hydroxyanthracene **7a** which was isolable only because of its low solubility. It was characterized by its derivatives **7b** and **7c** and was converted into the parent anthronylethyl-substituted anthracene **7d** by partial reduction with sodium borohydride.

In dimethylformamide solution, 9-hydroxyanthracene **7a** isomerizes further to give the dianthronylethane **8a**

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(1) Becker, H.-D. *J. Org. Chem.* **1969**, *34*, 2472. For a review, see Becker, H.-D. In "The Chemistry of the Hydroxy Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1969; pp 835–936.
(2) (a) Schenck, G. O.; Mathias, G.; Pape, M.; Cziesla, M.; v. Bünau, G. *Justus Liebigs Ann. Chem.* **1968**, *719*, 80. (b) Rubin, M.; Ben-Bassat, J. M. *Tetrahedron Lett.* **1971**, 3403.
(3) Becker, H.-D.; Sanchez, D. *Tetrahedron Lett.* **1975**, 3745. Part of the present results were reported in this communication.
(4) Becker, H.-D.; Sanchez, D. *J. Org. Chem.* **1979**, *44*, 1787.
(5) Meyer, K. H. *Justus Liebigs Ann. Chem.* **1920**, *420*, 134.
(6) de B. Barnett, E.; Mathews, M. A. *Chem. Ber.* **1926**, *59*, 769.
(7) Akiyama, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 351.
(8) Franck, B.; Zeidler, U. *Angew. Chem.* **1967**, *79*, 935.

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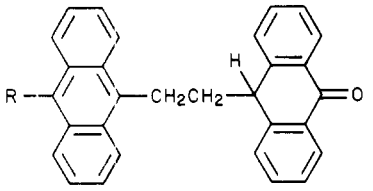
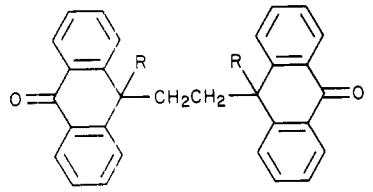


7a, R = OH
b, R = $OSiMe_3$
c, R = OCH_3
d, R = H

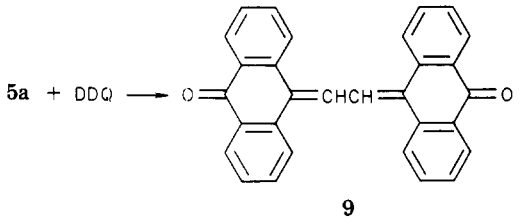


8a, R = H
b, R = OOH
c, R = $OOSiMe_3$
d, R = OH
e, R = OC_2H_5

(which can be obtained directly by reductive dimerization of **3** with thermally generated **2a** in DMF). UV-spectroscopic monitoring of the isomerization of **5a** and **7a** in DMF by following the disappearance of the typical anthracene absorption above 300 nm reveals that the equilibrium of the keto–enol tautomerism **5a** ⇄ **7a** ⇄ **8a** strongly favors the diketo form, and the exhibition of isosbestic points (at 322 and 335 nm) suggests that the conversions proceed cleanly.

Stable derivatives of dimer **5a**, such as **5b–d**, were obtainable from either **5a** or its diketo tautomer **8a**. Likewise, dianthrylethanes, such as **5e–g**, are readily accessible by nucleophilic addition reactions to the carbonyl groups in **8a** and subsequent aromatization by acid-catalyzed elimination of water. The UV spectra of **5**, as well as those of **7** and **8**, are in agreement with the proposed structures (see Experimental Section).

Toward the dehydrogenating agent 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ), dimers **5a** and **8a** behaved differently. Thus, oxidation of the diketo tautomer **8a** in chloroform containing ethanol gave the diethoxy compound **8e**, suggesting the involvement of cationic intermediates in the hydrogen transfer reaction to DDQ.[9] By contrast, dehydrogenation of dimer **5a** by DDQ in dioxane solution proceeded smoothly, as expected[9] for a 4,4′-dihydroxy-substituted bibenzyl, to give dianthronylideneethane (**9**). The molecular geometry and photophysical properties of dianthronylideneethane prepared in this fashion have been reported elsewhere.[10]



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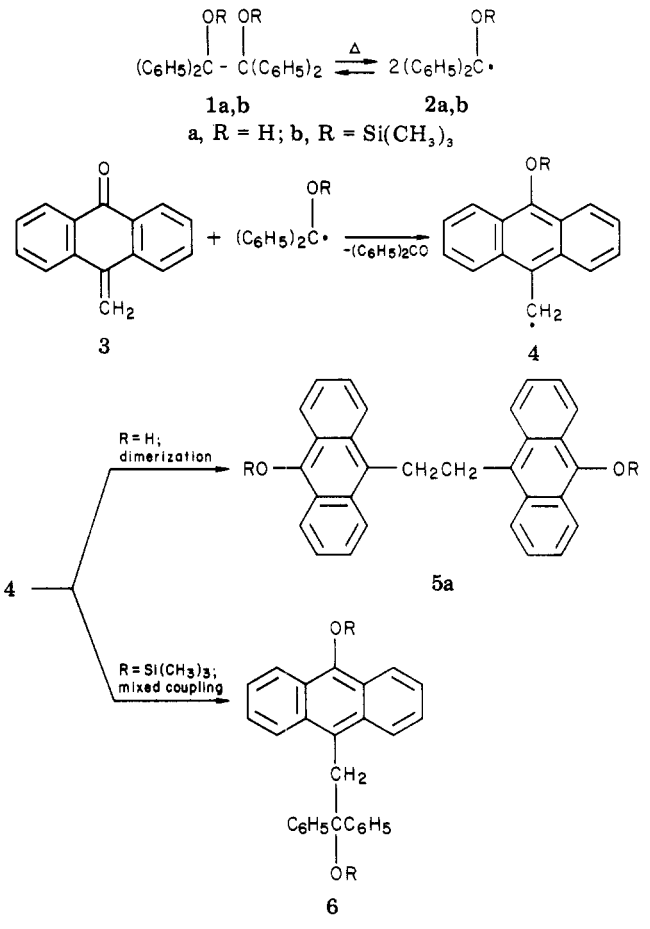
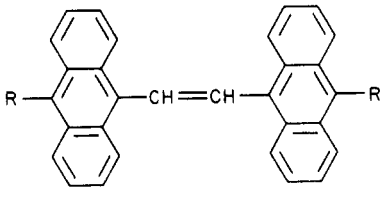
In agreement with its quinonoid structure, dianthronylideneethane was found to undergo reduction with

Scheme I



thermally generated diphenylhydroxymethyl radicals to give the previously unknown 1,2-bis(10-hydroxy-9-anthryl)ethylene (**10a**). In solution, dianthrylethylene **10a**



10a, R = OH
b, R = $OCOCH_3$
c, R = OCH_3
d, R = $OSiMe_3$
e, R = H

was found to be highly sensitive toward molecular oxygen, undergoing smooth dehydrogenation to give dianthronylideneethane. However, blocking the hydroxyl function of **10a** by esterification or etherification afforded stable derivatives such as **10b–d**.

As far as the geometry of the dianthrylethylenes **10** is concerned, the similarities of their electronic absorption spectra with that of the known[11] *trans*-1,2-bis(9-anthryl)-ethylene (**10e**) leave no doubt that we are dealing with trans isomers (see Figure 1). The bathochromic shift of the longest-wavelength absorption induced by the substituents OAc, OMe, and $OSiMe_3$ follows the same order observed recently[4] for substituted benzanthracenes.

(9) For a review, see Becker, H.-D. In "The Chemistry of Quinonoid Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1974; pp 335–423.

(10) Becker, H.-D.; Karlsson, B.; Pilotti, A.-M. *Chem. Phys. Lett.* **1976**, *44*, 589. Becker, H.-D.; Sandros, K.; Karlsson, B.; Pilotti, A.-M. *Chem. Phys. Lett.* **1978**, *53*, 232.

(11) (a) Wood, J. H.; Bacon, J. A.; Meibohm, A. W.; Throckmorton, W. H.; Turner, G. P. *J. Am. Chem. Soc.* **1941**, *63*, 1334. (b) Horner, L.; Beck, P.; Toscano, G.; *Chem. Ber.* **1961**, *94*, 1323. (c) Nagornaya, L. L.; Nurmukhametov, R. N.; Malkes, L. Y.; Shubina, L. V. *Izv. Akad. Nauk. SSSR, Ser. Fiz.* **1963**, *27*, 748.

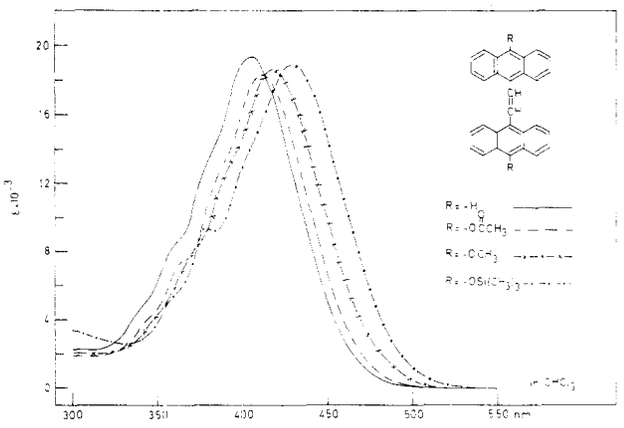


Figure 1. Electronic absorption spectra of dianthrylethylenes **10** in chloroform solution.

We are currently engaged in correlating the photophysical properties of anthracenes with their molecular geometry, and for that reason, it appeared desirable to compare the absorption spectra of *trans*-dianthrylethylenes **10** with those of their cis isomers.[12] According to the literature, *cis*-1,2-bis(9-anthryl)ethylene can be prepared by thermal decomposition of 9-anthralazine.[13] It has been described to be a yellow crystalline substance melting at 176 °C, and the structural assignment rests mainly on absorption and emission spectroscopic data which are typical of the anthracene chromophore, these features being quite different from the more or less structureless absorption and emission of the *trans*-dianthrylethylene.[14]

By following the literature procedure in every respect, we have synthesized the yellow compound which had been claimed to be *cis*-dianthrylethylene. Its physical properties, such as melting point (176 °C), ultraviolet absorption, and emission spectra (typical of the anthracene chromophore), and the infrared spectrum ("definite similarities" with that of anthracene)[14] were found to be in perfect agreement with the previously published data. However, all of these data are also in exact agreement with those of 9-cyanoanthracene, and so are the 270-MHz ^1H NMR and mass spectra of the so-called *cis*-1,2-bis(9-anthryl)ethylene. The presence of the CN stretching vibration at about 2210 cm^{-1} has obviously earlier escaped attention because the reported[14] analysis of the infrared spectrum only covered the wavenumber range of 700–1700 cm^{-1}. Consequently, we feel compelled to conclude that the compound believed to be the cis isomer of dianthrylethylene **10e** is, in fact, 9-cyanoanthracene, whose formation by thermal decomposition of 9-anthralazine is rather plausible.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark. Infrared spectra, in KBr pellets, were recorded on a Beckman IR 9 instrument. Electronic absorption spectra were taken on a Beckman DK 2 spectrophotometer. NMR spectra were recorded on a Varian A-60 or a Bruker 270 spectrometer. Chemical shifts are given in ppm downfield from Me_4Si. Mass spectra were obtained on an AEI MS 902 instrument.

Catalytic Hydrogenation of 10-Methyleneanthrone. 9-Acetoxy-10-methylanthracene. 10-Methyleneanthrone[15] (1.03 g; 5 mmol) in ethyl acetate (100 mL) was hydrogenated over $Pd–CaCO_3$ catalyst (250 mg). After hydrogen uptake had ceased, perchloric acid (1 mL) and acetic anhydride (6 mL) were added to the reaction mixture. After 1 h, the mixture was diluted with ethanol (100 mL) and filtered. Evaporation of solvents from the filtrate gave a yellow crystalline product which was recrystallized from ethanol to give 880 mg (70%) of pale yellow crystals: mp 168 °C (lit.[6] mp 167 °C); NMR (60 MHz) ($CDCl_3$) δ 8.4–7.2 (m, 8), 2.95 (s, 3), 2.55 (s, 3).

1,2-Bis(10-hydroxy-9-anthryl)ethane (5a). A stirred suspension of 10-methyleneanthrone (20.6 g; 0.1 mol) and benzpinacol (18.3 g; 0.05 mol) under nitrogen in xylene (300 mL) was rapidly warmed to reflux to give a deep yellow solution after about 10 min. During 15 min of refluxing, a green-yellow crystalline precipitate was formed. It was removed from the warm reaction mixture by vacuum filtration, washed with xylene, and dried [25 °C, (5×10^{-3} torr)]: yield, 15.5 g (75%) of greenish-yellow needles. When heated, the material starts decomposing at about 150 °C and is completely molten at 215 °C: IR 3340 cm^{-1} (OH); MS, m/e 414 (M^+), 193 (base peak). Anal. Calcd for $C_{30}H_{22}O_2$ (414.50): C, 86.93; H, 5.35. Found: C, 86.81; H, 5.31.

1,2-Bis(10-acetoxy-9-anthryl)ethane (5b). A stirred suspension of **5a** or **8a** (621 mg, 1.5 mmol) in acetic anhydride (10 mL) and pyridine (10 drops) under nitrogen was heated to reflux. After 15 min, a yellow crystalline compound precipitated from the yellow solution. Ethanol (70 mL) was then added to the reaction mixture, and the solvents were evaporated in vacuo to give a yellow crystalline residue which was recrystallized from a chloroform–ethanol mixture: yield, 690 mg (92%); mp 295–297 °C; IR 1753 cm^{-1} (OAc); UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 253 (187), 261 (187), 340 (4.8), 357 (10.6), 379 (21.5), 403 (24.3); NMR (270 MHz) ($CDCl_3$) δ 8.60–7.20 (m, 16), 4.08 (s, 4), 2.65 (s, 6). Anal. Calcd for $C_{34}H_{26}O_4$ (498.57): C, 81.90; H, 5.25. Found: C, 81.67; H, 5.18.

1,2-Bis(10-methoxy-9-anthryl)ethane (5c). Sodium methoxide (10 g) was added to a stirred solution of **5a** (1.65 g; 4 mmol) in dimethylformamide (85 mL) under nitrogen. Dimethyl sulfate (3 mL) was added dropwise to the deep-red-colored solution. After the yellow reaction mixture was stirred for 15 min, water (100 mL) was added. Extraction with methylene chloride followed by the usual workup gave a yellow crystalline precipitate which was recrystallized from a methylene chloride–ethanol mixture: yield, 1.6 g (90%); mp 232–34 °C; UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 253 (185), 262 (200), 350 (5.5), 366 (10.5), 387 (18.5), 410 (20.2); NMR (60 MHz) ($CDCl_3$) δ 8.53 (m, 8), 7.50 (m, 8), 4.18 (s, 6), 4.09 (s, 4); MS, m/e 442 (M^+). Anal. Calcd for $C_{32}H_{26}O_2$ (442.56): C, 86.85; H, 5.92. Found: C, 86.87; H, 5.94.

1,2-Bis(10-(trimethylsiloxy)-9-anthryl)ethane (5d).[16] Bis(trimethylsilyl)acetamide (BSA, 1 mL) was added to a stirred suspension of **5a** or **8a** (414 mg; 1 mmol) in dioxane (5 mL) under nitrogen. The yellow solution obtained upon warming was refluxed for 4 h. Dioxane, excess BSA, and (trimethylsilyl)acetamide were removed by vacuum distillation and sublimation, respectively. The solid residue was recrystallized from a methylene chloride–ethanol mixture to give yellow plates: mp 190 °C; yield, 510 mg (92%); IR 1112 cm^{-1} ($OSi(CH_3)_3$); UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 254 (178), 260 (171), 353 (5.3), 369 (10.6), 392 (16.3), 418 (17.3); NMR (60 MHz) ($CDCl_3$) δ 8.23 (m, 8), 7.41 (m, 8), 4.03 (s, 4), 0.30 (s, 18); MS, m/e 558 (M^+). Anal. Calcd for $C_{36}H_{38}O_2Si_2$ (558.84): C, 77.37; H, 6.85. Found: C, 77.20; H, 6.87.

1,2-Bis(9-anthryl)ethane (5e). This compound was prepared from **8a** (1.03 g; 2.5 mmol) by reduction with zinc (10 g) in dioxane (20 mL) in the presence of aqueous ammonia (30 mL) in the same fashion as was described in the literature[7] for the preparation of **5e** from methyleneanthrone: yield, 600 mg (63%); mp 328–30 °C; UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 248 (202.8), 256 (225.3), 320 (2.4), 335 (5.1), 352 (10.4), 370 (21.1), 391 (28.2); MS, m/e 382 (M^+).

1,2-Bis(10-methyl-9-anthryl)ethane (5f). Commercially available methyllithium solution (3 mL; 2 M) was added to a solution of **8a** (414 mg; 1 mmol) in benzene (100 mL) under

(12) Becker, H.-D.; Sandros, K. *Chem. Phys. Lett.* **1978**, *53*, 228. *Ibid.* **1978**, *55*, 498.

(13) Malkes, L. Y.; Shubina, L. V.; Nagornaya, L. L. *Zh. Org. Khim.* **1965**, *1*, 587. Cf. Beilsteins Handbuch der Organischen Chemie, Vol. 5, E III, p 2704.

(14) Nurmakhametov, R. N.; Timofeyuk, G. N.; Chaplina, I. M.; Nagornaya, L. L. *Russ. J. Phys. Chem. (Engl. Transl.)* **1964**, *38*, 1331. See also ref 11c.

(15) Methyleneanthrone was prepared according to Starnes, Jr., W. H. *J. Org. Chem.* **1970**, *35*, 1974.

(16) Cf. also Bouas-Laurent, H.; Lapouyade, R.; Brigand, C.; Desvergne, J. P. *C. R. Hebd. Seances Acad. Sci.* **1970**, *270*, 2167.

nitrogen. The reaction mixture was refluxed for 1 h and then acidified with concentrated hydrochloric acid (5 mL). Usual workup and recrystallization from benzene gave 200 mg (49%) of a yellow crystalline compound: mp 281–82 °C (lit.[17] mp 272 °C); NMR (270 MHz) ($CDCl_3$) δ 8.6–7.2 (m, 16), 4.05 (s, 4), 3.16 (s, 6).

1,2-Bis(10-phenyl-9-anthryl)ethane (5g) was prepared from **8a** (414 mg; 1 mmol) and phenyllithium (2 mL; 2 mol) analogous to the method used for **5f**: yield, 440 mg (82%); mp 323–26 °C (lit.[18] mp 322–23 °C); NMR (270 MHz) ($CDCl_3$) δ 8.5–7.2 (m, 26), 4.2 (s, 4).

9-(Trimethylsiloxy)-10-[(trimethylsiloxy)methyl]-anthracene (6). A stirred suspension of 10-methyleneanthrone (1.03 g; 5 mmol) and bis(trimethylsilyl) benzpinacolate[19] (2.55 g; 5 mmol) in xylene (25 mL) under nitrogen was refluxed for 1.5 h. Vacuum evaporation of xylene followed by vacuum sublimation (5×10^{-2} torr, 80 °C) of benzophenone (900 mg) gave a residue which was recrystallized from a chloroform–ethanol mixture: yield, 2.2 g (85%) of yellow crystals; mp 121–22 °C: NMR (60 MHz) ($CDCl_3$) δ 8.42–7.87 (m, 4), 7.53–6.95 (m, 14), 4.58 (s, 2), 0.30 (s, 9), −0.47 (s, 9); MS, *m/e* 534 (M^+). Anal. Calcd for $C_{34}H_{38}O_2Si_2$ (534.85): C, 76.35; H, 7.16. Found: C, 76.56; H, 7.12.

1-(9,10-Dihydro-10-oxo-9-anthryl)-2-(10-hydroxy-9-anthryl)ethane (7a). **5a** (2.0 g) was dissolved in dimethylformamide or dimethyl sulfoxide (5 mL). After 5 min, yellow-orange crystals began to precipitate. After 30 min, they were removed by filtration and dried [80 °C (5×10^{-3} torr)] for 2 h to give 1.6 g (80%) of yellow-orange crystals: mp 285 °C (rods changing to needles at 175 °C); IR 3340 (OH), 1645 cm^{-1} (CO); MS, *m/e* 414 (M^+), 193 (base peak). Anal. Calcd for $C_{30}H_{22}O_2$ (414.50): C, 86.93; H, 5.35. Found: C, 87.07; H, 5.43.

1-(9,10-Dihydro-10-oxo-9-anthryl)-2-(10-(trimethylsiloxy)-9-anthryl)ethane (7b). Bis(trimethylsilyl)acetamide (0.25 mL) was added to a stirred suspension of **7a** (414 mg; 1 mmol) in dioxane (5 mL) under nitrogen. The reaction mixture was refluxed for 3 h to give a yellow solution. Vacuum evaporation of dioxane and excess BSA followed by vacuum sublimation of (trimethylsilyl)acetamide [85 °C (2×10^{-2} torr)] gave a solid yellow residue which was recrystallized from a methylene chloride–ethanol mixture to give 430 mg (89%) of yellow crystals: mp 169–71 °C; IR 1660 c (CO), 1112 cm^{-1} ($OSi(CH_3)_3$); UV (in cyclohexane) λ (ε × 10^{-3}) 256 (90.7), 265 (172), 355 (4.1), 372 (7.3), 392 (10.1), 417 (8.3); NMR (270 MHz) ($CDCl_3$) δ 7.85 (m, 16), 4.50 (t, *J* = 4.4 Hz, 1), 2.81 (m, 2), 2.43 (m, 2), 0.27 (s, 9); MS, *m/e* 486 (M^+). Anal. Calcd for $C_{33}H_{30}O_2Si$ (486.66): C, 81.44, H, 6.21. Found: C, 81.58, H, 6.26.

1-(9,10-Dihydro-10-oxo-9-anthryl)-2-(10-methoxy-9-anthryl)ethane (7c). Methyl iodide (17 g) was added dropwise to a stirred suspension of **7a** (414 mg, 1 mmol) and potassium *tert*-butoxide (124 mg) in boiling methanol (40 mL) under nitrogen. The reaction mixture was refluxed for 1 h to give a yellow precipitate which was removed by filtration, recrystallized from methylene chloride–ethanol, and chromatographed on SiO_2, using CH_2Cl_2 as eluant: yield, 115 mg (27%) of yellow needles; mp 213–215 °C; IR 1665 cm^1 (CO); UV (in cyclohexane) λ (ε × 10^{-3}) 254 (110.2), 262 (196), 346 (3.5), 362 (7.0), 381 (11.8), 403 (11.6); NMR (270 MHz) ($CDCl_3$) δ 8.6–7.2 (m, 16), 4.6 (t, *J* = 4.4 Hz, 1), 4.05 (s, 3), 2.85 (m, 2), 245 (m, 2); MS, *m/e* 428 (M^+). Anal. Calcd for $C_{31}H_{24}O_2$ (428.53): C, 86.89; H, 5.65. Found: C, 86.81; H, 5.59.

1-(9,10-Dihydro-10-oxo-9-anthryl)-2-(9-anthryl)ethane (7d). Sodium borohydride (270 mg) was added to a stirred suspension of dimer **5a** (2.08 g; 5 mmol) in a mixture of dioxane (50 mL) and methanol (25 mL) under nitrogen. After 5 min, the reaction mixture was diluted with water (50 mL) and acidified with concentrated HCl (10 mL). The solid precipitate obtained was subjected to column chromatography on SiO_2, using CH_2Cl_2 as eluant: yield, 120 mg (6%) of pale green crystals; mp 255–260 °C (from CH_2Cl_2–C_2H_5OH); UV (in cyclohexane) λ (ε × 10^{-3}) 250 (103), 257 (181), 318 (1.8), 333 (3.5), 350 (7.1), 368 (12.1), 388 (12.4); NMR (270 MHz) ($CDCl_3$) δ 8.5–7.2 (m, 17), 4.6 (t, *J* = 4.6 Hz, 1), 2.9 (m, 2), 2.5 (m, 2). Anal. Calcd for $C_{30}H_{22}O$ (398.51): C, 90.42; H, 5.56. Found: C, 90.40; H, 5.60.

1,2-Bis(9,10-dihydro-10-oxo-9-anthryl)ethane (8a). (a) By Isomerization of 5a. Sodium methoxide (10 mg) was added to a suspension of **5a** (5 g) in ethanol (150 mL) under nitrogen; and the reaction mixture was stirred in a stoppered flask for 20 h. After addition of acetic acid (1 mL) and partial removal of solvent by vacuum evaporation, the yellow crystalline precipitate was filtered off. Recrystallization from a methylene chloride–ethanol mixture gave 4.6 g (96%) of colorless crystals: mp 245–46 °C; IR 1660 cm^{-1} (CO); NMR (270 MHz) ($CDCl_3$) δ 8.25 (m, 4), 7.36 (m, 8), 6.93 (m, 4), 4.00 (br s, 2), 1.41 (t, *J* = 3 Hz, 4); MS, *m/e* 414 (M^+). Anal. Calcd for $C_{30}H_{22}O_2$ (414.50): C, 86.93; H, 5.35. Found: C, 86.62; H, 5.45.

(b) From 10-Methyleneanthrone with Benzpinacol in DMF. A stirred suspension of 10-methyleneanthrone (4.94 g; 0.024 mol) and benzpinacol (4.39 g; 0.012 mol), in dimethylformamide (40 mL) under nitrogen, was refluxed for 15 min. Dimethylformamide and benzophenone were removed by vacuum distillation and sublimation, respectively. The solid residue was recrystallized from methylene chloride–ethanol: yield, 3.1 g (63%); mp 245–46 °C.

1,2-Bis(9-hydroperoxy-10-hydro-10-oxo-9-anthryl)ethane (8b). A stream of oxygen was passed into a stirred suspension of **5a** (500 mg) in dry methylene chloride (50 mL). After 3.5 h, an essentially colorless precipitate was filtered off and recrystallized from an ethyl acetate–petroleum ether mixture to give 530 mg (90%) of colorless crystals: mp 295 °C (rods changing to needles at 220 °C); IR 3300 (OH), 1657 cm^{-1} (CO); NMR (60 MHz) (pyridine-d_5) δ 8.45 (m, 4), 7.50 (m, 12), 4.76 (br s, 2), 1.85 (s, 4). Anal. Calcd for $C_{30}H_{22}O_6$ (478.48): C, 75.30; H, 4.63. Found: C, 75.31; H, 4.94.

1,2-Bis(9-[(trimethylsilyl)peroxy]-10-hydro-10-oxo-9-anthryl)ethane (8c). A stirred suspension of **8b** (478 mg; 1 mmol) in dioxane (40 mL) and bis(trimethylsilyl)acetamide (1 mL) was refluxed for 1.5 h to give a yellow solution. The colorless crystalline precipitate obtained on cooling the reaction mixture to room temperature was filtered off and recrystallized from methylene chloride by addition of ether: yield, 600 mg (96%); mp 245 °C; IR 1668 cm^{-1} (CO); NMR (60 MHz) ($CDCl_3$) 8.32 (m, 4), 7.33 (m, 12), 1.28 (s, 4), −0.83 (s, 18); MS, *m/e* 622 (M^+). Anal. Calcd for $C_{36}H_{38}O_6Si_2$ (622.84): C, 69.42; H, 6.15. Found: C, 69.53; H, 6.09.

1,2-Bis(9-hydroxy-10-hydro-10-oxo-9-anthryl)ethane (8d). A solution of **8b** (956 mg; 2 mmol) in ethyl acetate (300 mL) was catalytically hydrogenated over Pd–$CaCO_3$ (250 mg), whereby 4 mmol of hydrogen were consumed. The residue obtained on vacuum evaporation of solvent was treated with pyridine (50 mL). The catalyst was then removed by filtration, and part of the solvent was evaporated in vacuo. Upon addition of ethanol (150 mL) to the filtrate, a colorless crystalline compound precipitated: yield, 640 mg (73%); mp 350–52 °C (lit.[20] mp 288 °C); IR 3440 (OH), 1650 cm^{-1} (CO); NMR (60 MHz) (pyridine-d_5) δ 8.32 (m, 4), 7.82 (m, 4), 7.39 (m, 8), 4.10 (br s, 2), 1.96 (s, 4); MS, *m/e* 446 (M^+). Anal. Calcd for $C_{30}H_{22}O_4$ (446.51): C, 80.70; H, 4.97. Found: C, 80.65; H, 4.89.

1,2-Bis(9-ethoxy-10-hydro-10-oxo-9-anthryl)ethane (8e). A stirred suspension of **8a** (414 mg, 1 mmol) and DDQ (454 mg; 2 mmol) in chloroform (50 mL) containing ethanol was refluxed for 2.5 h. The residue obtained on vacuum distillation of solvents was treated with methylene chloride (10 mL) to precipitate $DDQH_2$ (380 mg). The residue obtained after vacuum evaporation of solvent from the filtrate was recrystallized from a methylene chloride–ethanol mixture to give 310 mg (62%) of colorless crystals: mp 325 °C; IR 1674 cm^{-1} (CO); NMR (60 MHz) ($CDCl_3$) δ 8.29 (m, 4), 7.30 (m, 12), 2.69 (q, *J* = 7 Hz, 4), 1.34 (s, 4), 0.84 (t, *J* = 7 Hz, 6). Anal. Calcd for $C_{34}H_{30}O_4$ (502.61): C, 81.25; H, 6.01. Found: C, 80.98; H, 5.87.

Dianthronylideneethane (9). A stirred suspension of **5a** (1.24 g; 3 mmol) and DDQ (1.36 g; 6 mmol) in dioxane (50 mL) was refluxed for 10 min. As **5a** dissolved and reacted, $DDQH_2$ precipitated. Vacuum evaporation of solvent, followed by addition

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of methylene chloride (50 mL), gave a red-colored suspension from which $DDQH_2$ was removed by filtration. The residue obtained after evaporation of solvent from the filtrate was recrystallized from methylene chloride by addition of ethanol: yield, 815 mg (65%) of orange-red crystals; mp 292–94 °C (lit.[21] mp 292 °C); IR 1650 cm^{-1} (CO). Anal. Calcd for $C_{30}H_{18}O_2$ (410.44): C, 87.78; H, 4.42. Found: C, 87.86; H, 4.59.

1,2-Bis(10-hydroxy-9-anthryl)ethylene (10a). A stirred suspension of **9** (410 mg; 1 mmol) and benzpinacol (366 mg; 1 mmol) in xylene (10 mL) under nitrogen was heated to reflux to give a red-colored solution from which a yellow-brown crystalline substance started precipitating after 5 min. Refluxing was continued for 10 min, and the yellow-brown crystalline precipitate was then filtered off, washed with methylene chloride, and dried [50 °C (5×10^{-3} torr)]; yield 390 mg (96%). Upon heating, the crystals turn red at about 200 °C, probably due to autoxidation. The observed mp of 295 °C is that of **9**: IR 3300 cm^{-1} (OH); MS, m/e 412 (M^+). Anal. Calcd for $C_{30}H_{20}O_2$ (412.49): C, 87.35; H, 4.89. Found: C, 87.53; H, 4.94.

1,2-Bis(10-acetoxy-9-anthryl)ethylene (10b). A suspension of **10a** (206 mg; 0.5 mmol) in acetic anhydride (5 mL) and pyridine (5 drops) under nitrogen was refluxed for 10 min to give a reddish solution from which yellow crystals precipitated. Addition of ethanol (30 mL) followed by vacuum evaporation of solvents gave a solid residue which was recrystallized from chloroform by addition of ethanol: yield, 235 mg (95%) of yellow crystals; mp 282–84 °C; IR 1760 cm^{-1} (OAC); NMR (270 MHz) ($CDCl_3$) δ 8.80–7.90 (m, 8), 7.82 (s, 2), 7.55 (m, 8), 2.67 (s, 6); MS, m/e 496 (M^+). Anal. Calcd for $C_{34}H_{24}O_4$ (496.56): C, 82.24; H, 4.87. Found: C, 82.50; H, 5.02.

1,2-Bis(10-methoxy-9-anthryl)ethylene (10c). Dimethyl sulfate (3 mL) was added dropwise to a solution of **10a** (412 mg; 1 mmol) and sodium methoxide (5 g) in dimethyl sulfoxide (35 mL) under nitrogen. Addition of water after 10 min gave a yellow precipitate which was extracted with methylene chloride. Usual workup gave a yellow crystalline product which was recrystallized from methylene chloride by addition of ethanol: yield, 360 mg (82%); mp 223–24 °C; NMR (270 MHz) ($CDCl_3$) δ 8.55 (m, 8), 7.52 (m, 8), 7.80 (s, 2), 4.21 (s, 6); MS, m/e 440 (M^+). Anal. Calcd for $C_{32}H_{24}O_2$ (440.54): C, 87.24; H, 5.49 Found: C, 86.96; H, 5.23.

1,2-Bis(10-(trimethylsiloxy)-9-anthryl)ethylene (10d). Bis(trimethylsilyl)acetamide (BSA, 2 mL) was added to a stirred suspension of **10a** (1.02 g; 2.5 mmol) in dioxane (10 mL) under nitrogen to give an orange-colored solution which was refluxed for 1 h. Vacuum evaporation of solvent and excess BSA, followed by vacuum sublimation [80 °C (5×10^{-3} torr)] of (trimethylsilyl)acetamide, gave an orange-colored residue that was recrystallized from methylene chloride by addition of ethanol to give 1.17 g (83%) of yellow crystals: mp 185 °C; IR 1123 cm^{-1} O-$Si(CH_3)_3$; NMR (270 MHz) ($CDCl_3$) δ 8.55 (m, 8), 7.88 (s, 2), 7.52 (m, 8), 0.40 (s, 18); MS, m/e 556 (M^+). Anal. Calcd for $C_{36}H_{36}O_2Si_2$ (556.82): C, 77.66; H, 6.52. Found: C, 77.50; H, 6.67.

Acknowledgment. We are indebted to Dr. Kjell Sandros for spectroscopic data and to Mr. Gunnar Svensson for technical assistance. Part of this work was supported by the Swedish Natural Science Research Council.

Registry No. **3**, 4159-04-0; **5a**, 58382-08-4; **5b**, 58382-04-0; **5c**, 71582-25-7; **5d**, 28871-55-8; **5e**, 4709-79-9; **5f**, 53545-70-3; **5g**, 71582-26-8; **6**, 71582-27-9; **7a**, 58382-09-5; **7b**, 58448-60-5; **7c**, 21859-40-5; **7d**, 71582-28-0; **8a**, 58382-11-9; **8b**, 58382-10-8; **8c**, 58399-42-1; **8d**, 58382-05-1; **8e**, 58382-06-2; **9**, 5816-02-4; **10a**, 58382-12-0; **10b**, 71582-29-1; **10c**, 71582-30-4; **10d**, 58382-07-3; 9-acetoxy-10-methylanthracene, 31688-72-9; ethyl acetate, 141-78-6; acetic anhydride, 108-24-7; bis(trimethylsilyl)acetamide, 10416-58-7; methyllithium, 917-54-4; phenyllithium, 591-51-5; bis(trimethylsilyl) benzpinacolate, 22341-08-8; methyl iodide, 74-88-4; DDQ, 84-58-2; dimethyl sulfate, 77-78-1.

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Insertion Reaction of Triphenylarsine and Triphenylantimony with Tetramethyl-1,2-dioxetane: Preparation of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane and -dioxastibolane

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Received June 12, 1979

The reaction of tetramethyl-1,2-dioxetane (1) with several group 5A compounds was investigated. The reaction of 1 with Ph_3N and Ph_3Bi resulted in catalytic decomposition of 1 to acetone. The reaction of 1 with Ph_3As produced the stable arsenic(V) adduct 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane (2). The reaction of 1 with Ph_3Sb resulted in the formation of a stable antimony(V) adduct, 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxastibolane (3), as well as formation of acetone via catalytic decomposition. The relative yield of adduct 3 to acetone increased upon changing the reaction solvent from C_6D_6 to $CDCl_3$. The kinetics was investigated. Ph_3Sb was found to be slightly less reactive than Ph_3P while Ph_3As was found to be least reactive. The results were consistent with a concerted (biphilic) insertion of the group 5A compounds into the peroxy bond of 1. The reaction of 1 with arsines and stibines represents a new, convenient method for the synthesis of cyclic arsenic(V) and antimony(V) compounds.

1,2-Dioxetanes have been extensively studied because of their unique chemiluminescent thermal decomposition to two carbonyl fragments.[1] Under controlled conditions, dioxetanes undergo a number of interesting ground-state reactions. Tetramethyl-1,2-dioxetane has been shown to undergo rearrangement to a carbonyl oxide upon treatment with boron trifluoride.[2] Metal ions have been shown to catalytically decompose dioxetanes to carbonyls via a nonluminescent pathway.[3] Trivalent phosphorus compounds

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