

**Figure 2.** Part of the crystal structure of **8a** (asymmetric unit); selected distances (pm): N1-C1 146.2 (3), N1-C8 145.8 (3), N1-C9 145.2 (3), O1-C3 121.5 (3), O2-C7 121.1 (3), C1-C2 159.0 (3), C1-C15 152.0 (3), C2-C7 153.8 (3), C2-C16 151.5 (4), C3-C4 150.1 (3), C4-C5 153.6 (3), C4-C9 154.4 (3), C4-C17 151.9 (4), C5-C6 153.0 (3), C6-C7 150.0 (4), C6-C8 154.4 (3), C6-C18 152.7 (3), C10-C11 137.9 (4), C10-C15 138.2 (3), C11-C12 137.4 (4), C12-C13 136.4 (4), C13-C14 138.8 (4), C14-C15 139.5 (3). The values for the second molecule do not significantly deviate from these data.

These facts support the conclusion that the unstable aza bicycle **6** is partly degraded in the complex reaction system, generating formaldehyde equivalents, which enable the reorganization toward the thermodynamically more stable heterotricyclic adamantane system.

We used this result for preparative purposes. Adding formaldehyde analogues (in excess) to the reaction mixture stops the degradation and establishes a simple route to  $\alpha$ -substituted 1-azaadamantanes **8** (Figure 1).<sup>8</sup> We consider compounds **8** to be valuable products for further investigations. The overall reaction sequence cuts off a one-carbon unit from the tricycle and replaces this by variable CHR groups. This results in a remarkable arylation of a saturated tertiary amine within three steps.

Figure 2 shows the result of the X-ray analysis of **8a** and confirms the interpretations of the spectroscopic data.<sup>9</sup> Furthermore, it is obvious that one or two more  $\alpha$ -substituents are necessary for the development of good model systems for concave bases.<sup>3</sup>

The azaadamantane **8a** crystallizes in the monoclinic space group  $P2_1/c$  [ $a = 1490.0$  (5) pm,  $b = 1478.1$  (6) pm,  $c = 1360.9$  (8) pm,  $\beta = 91.12$  (4)°,  $V = 2999$  (2)  $\times 10^6$  pm<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 1.255$  g/cm<sup>3</sup>]. The structure was refined to  $R > 0.048$  and  $R_w = 0.050$  for 3394 independent reflections [ $F > 4\sigma(F)$ ]. Figure 2 shows the two enantiomeric molecules of **8a**, which are found in the asymmetric unit of the monoclinic cell. The bonding parameters of **8a** are in good agreement with literature data: The C4-C9 bond distance, for example, is well comparable to the distance of a normal single bond [154.1 (3) pm]<sup>10</sup> and the value found in adamantane [153.6 (5) pm].<sup>11</sup> N-C and C-C (phenyl) distances are also normal. The C-C bonds, which are neighbors of one C-O bond [e.g., C6-C7 = 150.0 (4) pm], do not deviate from literature data [150.0 (2) pm].<sup>10</sup> The carbon atom in the neighborhood of two C-O bonds, however, shows two elongated C-C(CO) bonds [C2-C3 = 151.3 (3) pm, C2-C7 = 153.8 (3) pm], a strongly elongated C-C (ring) bond [C2-C1 = 159.0 (3) pm], and a slightly shortened C-C(Me) bond [C2-C16 = 151.5 (4) pm]. The deformation of the tricyclic system induced by the

incorporation of the phenyl ring is quite small.

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**Registry No.** 1, 136947-01-8; 2, 136947-02-9; 3, 136911-70-1; 4, 136911-71-2; 5, 136911-72-3; **8a**, 136911-73-4; **8b**, 136911-74-5; **8c**, 136911-75-6; **8d**, 136911-76-7; **8e**, 136911-77-8; benzaldehyde, 100-52-7; 4-nitrobenzaldehyde, 555-16-8; 2-nitrobenzaldehyde, 552-89-6; 4-(dimethylamino)benzaldehyde, 100-10-7; 2-furaldehyde, 98-01-1.

**Supplementary Material Available:** Tables of positional parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen positions of **8a** (9 pages). Ordering information is given on any current masthead page.

## 2,3-Dioxa-5,7-bicyclo[2.2.2]octadiene (Benzene 1,4-endo-Peroxide)

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Energy-rich endoperoxides of aromatic hydrocarbons are of both synthetic and theoretical interest.<sup>1-9</sup> Benzene 1,4-endo-peroxide (2,3-dioxa-5,7-bicyclo[2.2.2]octadiene **1**), the simplest and most energetic member of this series, is not yet known. We have developed a convenient synthesis of *cis,anti*-dibenzene **2**,<sup>10</sup> which is a reactive substrate in Diels-Alder addition,<sup>11,12</sup> and its adducts

<sup>†</sup> Dedicated to Professor George H. Büchi on the occasion of his 70th birthday.

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(7) The yields and the analysis of the products show that three parts of **5** reorganize to two parts of the diketone **1** and one part of the cyclohexanedione **7**.

(8) Preparation of **8a**: 4 mL of concentrated hydrochloric acid is added dropwise to a mixture of 0.48 g (2.25 mmol) of **5** and 1.1 g (10.5 mmol) of benzaldehyde. The mixture is stirred at room temperature for 12 h. With ice cooling, ammonia (25% aqueous solution) is slowly added until an alkaline pH is obtained. Elution with dichloromethane is followed by washing of the organic layer with dilute ammonia. The organic layers are dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Unreacted benzaldehyde and **8a** are separated by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/acetone, 10:1). **8a** is isolated as colorless crystals (0.45 g, 1.6 mmol, 72%, mp 131 °C).

(9) The X-ray data will be helpful in future investigations to get information about the interactions between the 1,3-dicarbonyl system and the nitrogen lone pair. The pK<sub>a</sub> values of compounds of type **1** are in the region of 3.5-4, which is remarkably low.

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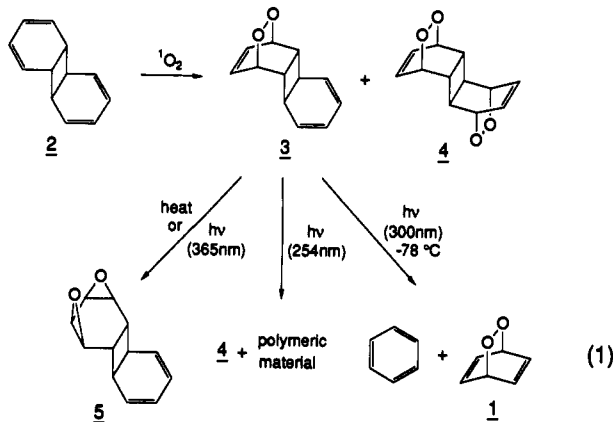
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**Table I.** Results and Activation Parameters of Thermolyses of Arene Endoperoxides

endoperoxides	solvent	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$^1\text{O}_2$ yield, %
9,10-diphenyl-1,4-dimethylanthracene 9,10- <i>endo</i> -peroxide <sup>a,b</sup>	dioxane	31.8 ± 0.3	7.4 ± 0.8	50
9,10-diphenyl-1,4-dimethylanthracene 1,4- <i>endo</i> -peroxide <sup>a</sup>	dioxane	29.8 ± 0.3	-1.8 ± 0.8	95
naphthalene 1,4- <i>endo</i> -peroxide <sup>c</sup>		23.2 ± 0.9	-0.2 ± 1.1	≈100
benzene 1,4- <i>endo</i> -peroxide <sup>d</sup>	THF- <i>d</i> <sub>8</sub>	17.8 ± 0.5	-0.4 ± 1.9	>90 ± 3

<sup>a</sup> Reference 6. <sup>b</sup> Anthracene 9,10-*endo*-peroxide does not undergo thermal dissociation to yield singlet oxygen, ref 8. <sup>c</sup> Reference 4. <sup>d</sup> This work.

are potential intermediates in the synthesis of formal cycloadducts of benzene via retrophotocycloaddition (reaction 1). This communication deals with the synthesis and chemistry of **1**.

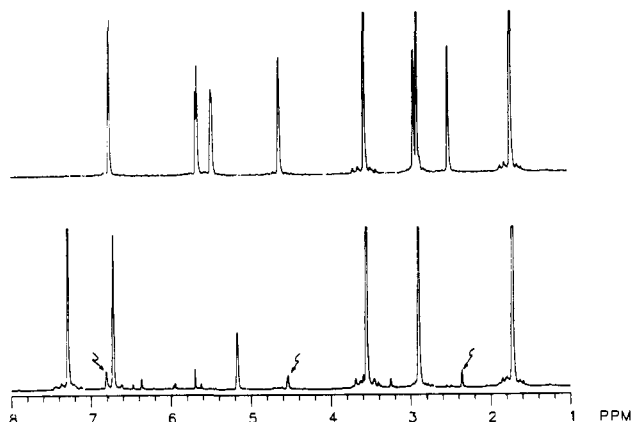


Singlet oxygenation of **2** yields a mixture of monoperoxide **3** and diperoxide **4**.<sup>13</sup> Under carefully controlled conditions, **3** may be obtained in 35–40% yield, mp (dichloromethane–hexane) 114–6 °C dec; NMR (CDCl<sub>3</sub>)  $\delta$  6.79 (2 H, m,  $J = 3.9$  Hz, OCCH=CHCO), 5.71 (2 H, dd,  $J = 7.8$  and 2.7 Hz, C=CHCH=C), 5.47 (2 H, m, CCH=C), 4.68 (2 H, m, C=CCHO), 3.11 (2 H, br s, cyclobutyl CH), and 2.56 ppm (2 H, br s, cyclobutyl CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  131.27, 125.63, 121.34, 72.20, 44.70, 32.67 ppm; IR (CHCl<sub>3</sub>) 3033, 2956, 1618, 1604, and 1587 cm<sup>-1</sup>; UV (cyclohexane)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 275 nm (3000); MS (EI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub> 188.0837, obsd 188.0852. Compound **3** undergoes thermolysis to give diepoxide **5** (78%) and fragmentation products.<sup>14</sup> The products obtained from low-temperature photolysis of **3** were monitored by <sup>1</sup>H NMR spectroscopy and were found to be dependent on the wavelength of the exciting light. Wavelength dependence of peroxide photolysis is known and has been analyzed by Kearns.<sup>1,2</sup> Excitation into each of the three accessible excited states of **3**, the  $n, \sigma_{\text{O-O}}^*$  and  $n, \sigma_{\text{C-O}}^*$  of the peroxide group and the  $\pi, \pi^*$  state of the 1,3-cyclohexadiene moiety, may thus lead to a selective photochemical pathway. We found that irradiation of **3** with 365-nm light leads mainly to the O–O cleavage and the formation of the diepoxide **5** via the  $n, \sigma_{\text{O-O}}^*$  excitation, and irradiation with 254-nm light leads mainly to the C–O cleavage and the formation of **4** and polymeric material via the  $n, \sigma_{\text{C-O}}^*$  excitation. These observations are in agreement with the analysis formulated by Kearns.<sup>2</sup> However, the 1,3-cyclohexadiene moiety of **3** may still undergo the desired retrophotocycloaddition to **1** and benzene, since the more intense  $\pi, \pi^*$  transition of the 1,3-diene is known to protect an endoperoxide from photodecomposition in the region of the diene absorption.<sup>3</sup> Compound **3** (0.02 M) was thus irradiated in THF-*d*<sub>8</sub> with a Hanovia Hg arc through a

(12) Noh, T., unpublished results.

(13) Diperoxide **4** exhibits the following features: mp 147 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.53 (4 H, br s, cyclobutyl H), 4.63 (4 H, m, C=CCHO), and 6.87 ppm (4 H, m, C=CH); IR (KBr) 3065, 2970, 2944, 1374, 1242, 1040, 942, and 899 cm<sup>-1</sup>; MS (EI<sup>+</sup>), 220, 188 (M – 32), 104, 91, 81 (100), and 78.

(14) Diepoxide **5** exhibits the following features: mp (CH<sub>2</sub>Cl<sub>2</sub>–hexane) 136–138 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.81 (2 H, d,  $J = 2.2$  Hz, cyclobutyl H), 2.93–2.95 (4 H, m, 2 oxiranyl H and 2 cyclobutyl H), 3.49 (2 H, d,  $J = 2.6$  Hz, oxiranyl H), 5.62 (2 H, m, C=CH), and 5.78 ppm (2 H, dd,  $J = 7.7$  and 2.7 Hz, C=CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  32.85, 40.05, 48.01, 50.36, 122.35, and 125.78 ppm; IR (CHCl<sub>3</sub>) 3025, 3018, 2938, 1603 (w), 1584, 1418, 1372, 1268, 1058, 944, and 875 cm<sup>-1</sup>; UV (cyclohexane)  $\lambda_{\text{max}}$  ( $\epsilon$ ), 274 nm (3200); MS (EI<sup>+</sup>) 188, 115, 110, 91, 81 (100), and 78.



**Figure 1.** (a) Upper curve: <sup>1</sup>H NMR (500 MHz) spectrum of **3** in THF-*d*<sub>8</sub> at –45 °C; the peaks at 1.72 and 3.55 ppm are due to THF, and the peak at 2.89 ppm is due to H<sub>2</sub>O. (b) Lower curve: <sup>1</sup>H NMR spectrum of **3** in THF-*d*<sub>8</sub> at –45 °C after irradiation; the peaks at 5.17 and 6.72 ppm are due to **1**, the peak at 7.30 ppm is due to benzene, and those at 2.39, 4.58, and 6.80 ppm (marked by arrows) are due to **4**.

300-nm interference filter ( $\pm 5$  nm) at –78 °C (dry ice–ether in a quartz Dewar). The reaction was complete after 5 h, and the <sup>1</sup>H NMR spectrum of the reaction mixture at –45 °C is given in Figure 1. The result indicates that a major product of  $\approx 90\%$  purity is formed in 40–60% yield which exhibits two peaks at  $\delta$  5.17 and 6.72 ppm at a ratio of 1:2 in addition to that of benzene at 7.30 ppm. The major byproduct is **4**, most of which precipitated from the solution at that temperature, and its <sup>1</sup>H NMR peaks in solution are marked in Figure 1b. The structural assignment of **1** is supported by its <sup>1</sup>H NMR spectrum, which exhibits signals in the expected region,<sup>4</sup> and its thermal and chemical behavior presented below.

The thermolysis of arene endoperoxides has been studied extensively by many chemists, and some of the results are summarized in Table I. Wasserman and Scheffer reported the first instance of singlet oxygen formation from meso-substituted anthracene and rubrene peroxides.<sup>5</sup> Turro and co-workers showed that the yield of singlet oxygen is higher from anthracene 1,4-*endo*-peroxides than from the 9,10-*endo*-peroxides and that singlet oxygen formation from arene endoperoxide, which has a low activation entropy, is thus a concerted retrocycloaddition.<sup>6</sup> A similar observation was noted by Vogel in the thermal dissociation of naphthalene 1,4-*endo*-peroxide.<sup>4</sup> When the solution of **1** was warmed up to 21 °C, its NMR peaks disappeared while the benzene peak intensified. The rate of decomposition was determined at five different temperatures between –30 to –47 °C. The calculated values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are  $17.8 \pm 0.5$  kcal·mol<sup>-1</sup> and  $-0.4 \pm 1.9$  eu, respectively. When either 9,10-dimethylanthracene or excess **3** was used as a trapping agent for singlet oxygen, the corresponding endoperoxides, identified by comparison with authentic samples, were obtained in  $90 \pm 3\%$  yield.<sup>7,13</sup> Our results are in agreement with a mechanism by which the thermolysis of **1** to benzene and singlet oxygen is a concerted process and the rate of arene endoperoxide thermolysis to the corresponding arene and singlet oxygen is related to delocalization energy of the arene product.

**CAUTION.** Due to its thermal instability and high energy content derived from the strain energy and the delocalization energy of its product, no attempt was made to prepare **1** in a purer or more concentrated form. Peroxides **3** and **4** are also potentially hazardous compounds.

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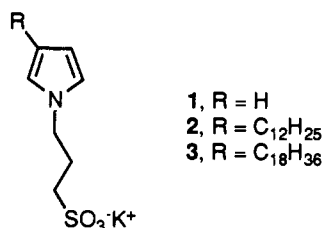
## A Lamellar Conducting Polymer by Self-Assembly of an Electropolymerizable Monomer

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Despite the number of studies of electronically conductive polymers,<sup>1</sup> material intractability<sup>2</sup> and the design of anisotropic conductors have only recently been addressed. Attempts to impart directional asymmetry to the structure of conducting polyheterocycles include polymerization in restricted geometries<sup>3</sup> and with bulky counterions,<sup>4</sup> stretch orientation of the polymers,<sup>5</sup> dissolution of the polymers in multilayered films,<sup>6</sup> and polymerization of heterocyclic monomers with high molecular anisotropy.<sup>7</sup> The latter two approaches include studies directed toward the preparation of Langmuir-Blodgett multilayers of conductive polymers. Here we demonstrate that by further increasing the molecular anisotropy (amphiphilicity) of a monomer (**2**) we can rely on molecular self-assembly to afford a highly ordered lamellar polymer which is soluble in chloroform and water.



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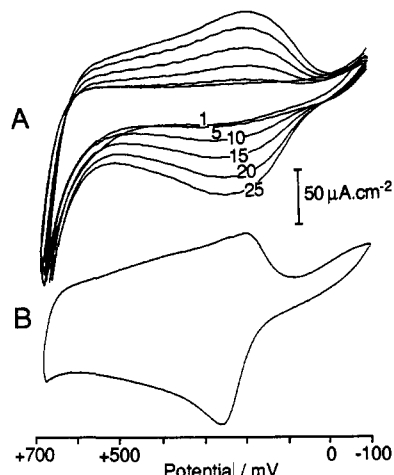
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**Figure 1.** Formation and electrochemical cycling of poly(potassium 3-(3-dodecylpyrrol-1-yl)propanesulfonate): (A) cyclic voltammetry (25 cycles at 100 mV s<sup>-1</sup>) of 5 mM **2** in 0.1 M aqueous KNO<sub>3</sub> at a gold electrode, versus Ag/AgCl (saturated KCl) reference electrode; (B) cyclic voltammetry (100 mV s<sup>-1</sup>) of poly(**2**) prepared in part A in 1 M HClO<sub>4</sub>.

Potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates **1-3** were prepared by the reaction between the potassium salt of 3-alkylpyrrole<sup>8</sup> and 1,3-propanesultone.<sup>9</sup> The critical micellar concentrations (cmc) of these surfactants were determined by the method of Corrin et al., whereby the color of a solution containing pinacyanol chloride turns from pink to blue upon increasing the concentration through the cmc.<sup>10</sup> In deionized water the cmc of **2**<sup>11</sup> is 5 × 10<sup>-5</sup> M. Upon addition of potassium nitrate (0.1 M), the value is reduced to 2 × 10<sup>-5</sup> M. The higher homologue **3** is not sufficiently soluble to exhibit a cmc. The unsubstituted analogue **1**<sup>9</sup> is freely soluble in water. These potassium sulfonates are soluble in DMSO, only slightly soluble (<1 mM) in acetonitrile and benzonitrile, and insoluble in dichloromethane and THF.

The monomers described here undergo an irreversible electrochemical oxidation to form a nonconductive film on a gold electrode surface if the potential is swept to greater than ca. 1 V (vs Ag/AgCl (saturated KCl)).<sup>9</sup> If the positive potential is limited to +800 mV, polymerization takes place to afford a conducting film. When a 5 mM micellar solution of **2** in 0.1 M KNO<sub>3</sub> is repeatedly cycled between 0 and +700 mV, a smooth red polymer, poly(**2**), is deposited on a gold electrode. The current at the upper potential limit increases during the first 10 cycles, Figure 1A. A reversible wave develops at ca. +200 mV corresponding to redox cycling of poly(**2**), which persists upon transfer to monomer-free electrolyte solution (Figure 1B). The charge beneath the polymer redox wave corresponds to approximately 5% of the charge passed during deposition although this is difficult to determine with certainty because of the change in capacitive charging. Assuming a two-electron oxidative mechanism for the addition of one pyrrole unit to the growing chain, this implies a doping level of ca. 10% (i.e., there is 1 cationic charge/10 repeat units in the oxidized polymer).

In contrast, cyclic voltammetry of 5 mM solutions of pyrrole or *N*-methylpyrrole in 0.1 M KNO<sub>3</sub> failed to deposit a polymer layer, with a conductive polymer being deposited only at higher concentrations (60 mM).<sup>12</sup> The observation of polymer formation

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