

Acceleration of the Retro-Diels-Alder Reactions of Anthracene Cycloadducts by Distal Siloxy Substituents

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Received January 31, 1997

The retro-Diels-Alder reaction can be used to synthesize strained and otherwise interesting olefins.¹⁻⁵ Such reactions typically are carried out under flash vapor pyrolysis conditions, although the use of oxyanionic⁶⁻⁹ and carbanionic¹⁰ substitution sometimes results in cycloreversion at much lower temperatures. Our interest in the design of Diels-Alder catalytic cycles¹¹ has induced a related interest in learning how to facilitate retro-Diels-Alder reactions of neutral cycloadducts.¹² Acceleration of the retro-Diels-Alder reaction via siloxy substitution has been described previously, in which the siloxy group resided at the reaction center.⁶ This substitution pattern is not ideal for our purposes because: 1) steric hindrance is expected to slow the cycloaddition leading to the adduct's synthesis; and, 2) for our catalysis work, it would be optimal to place a catalytic group near the site of reaction instead. Consequently, we have examined the potential of siloxy groups distal to the reaction center as accelerating substituents, and found that a substantial rate acceleration is obtained even when the substituent is three bonds away from the reaction site.

Experimental

Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. All the commercial chemicals were used as obtained without further purification. Microanalysis were carried out at Canadian Microanalytical Service, New Westminster, B.C. Mass spectra were obtained by use of a Kratos-30 mass spectrometer. IR-NMR spectra were obtained at 7.0T (300 MHz).

Cycloadduct of bis[(di-*tert*-butylsilylene)dioxy]-9,10-dimethylantracene (1). Bis[(di-*tert*-butylsilylene)dioxy]-9,10-dimethylantracene (231 mg, 0.42 mmol), prepared by the literature procedure,¹³ was added to a pressure tube with acrylonitrile (10 mL) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (2 crystals). The pressure tube was sealed, wrapped in aluminum foil, and placed in an oil bath at 85 °C for 44 h. The resulting orange solution was evaporated under reduced pressure to an orange oil that was taken up in a minimal amount of hot CCl₄. Upon cooling, impurities precipitated. The orange mixture was eluted through a Celite plug with CCl₄ and the filtrate was evaporated to yield cycloadduct **1** (213 mg, 84%): ¹H NMR (CDCl₃) δ 1.10 (s, 36, t-Bu), 1.80 (s, 3, CH₃), 1.81 (dd, 1, CH *trans* to CN), 2.05 (s, 3, CH₃), 2.06 (dd, 1, CH *cis* to CN), 2.65 (dd, 1, CH), 6.90 (s, 4, Ar H); mass spectrum, m/e 603 (M⁺), 550 (M⁺-acrylonitrile).

Cycloadduct of 9,10-dimethylantracene (4). In a pressure tube 9,10-dimethylantracene (182 mg, 88 mmol) was placed with acrylonitrile (10 mL) and BHT (2 crystals).

The pressure tube was sealed, wrapped in aluminum foil, and warmed in an oil bath at 50 °C for 21 h. The resulting solution was evaporated under reduced pressure to dryness and recrystallized from ethanol to afford cycloadduct **4** (206 mg, 98%): mp 101-103 °C; ¹H NMR (CDCl₃) δ 1.46 (dd, 1, CH *trans* to CN), 1.98 (s, 3, NCCCCCH₃), 2.11 (dd, 1, CH (*cis* to CN), 2.17 (s, 3, NCCCCCH₃), 2.75 (dd, 1, CH), 7.30 (m, 8, Ar H).

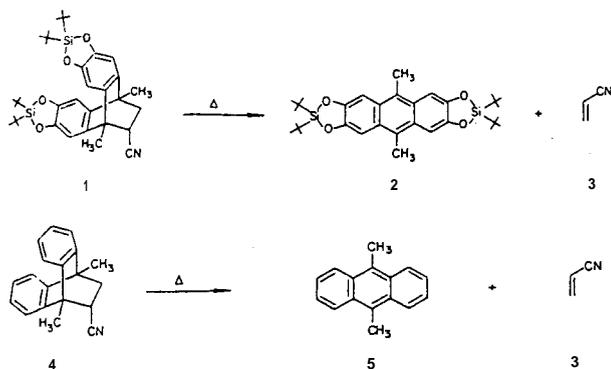
Cycloadduct of 9,10-bis(trimethylsilyloxy)anthracene (6a). In a pressure tube 9,10-bis-(trimethylsilyloxy)anthracene was placed with ethyl acrylate (5 mL) and BHT (2 crystals). The pressure tube was sealed, wrapped in aluminum foil, and placed in an oil bath at 120 °C for 72 h. The resulting solution was evaporated to dryness and recrystallized from methanol to afford cycloadduct **6a** (32 mg, 25%): mp 79-80 °C; ¹H NMR (CDCl₃) δ 0.48 (d, 18, SiMe₃), 1.11 (t, 3, CH₃), 2.09-2.51 (m, 2, CH₂), 3.19 (dd, 1, CH), 4.05 (q, 2, OCH₂), 7.24-7.64 (m, 8, Ar H); mass Spectrum, m/e 354 (M⁺-100).

Kinetic measurements. For each of the cycloreversion reactions we ran, a 1.1-1.2 × 10⁻⁴ M solution of the adduct in dry diphenyl ether was prepared. The formation of an anthracene product was assayed by monitoring the absorbance at that anthracene's long wavelength λ_{max}. At the start of the run, the absorbance at the monitored wavelength was always ≤ 0.05 inasmuch as neither the adduct nor diphenyl ether absorb in this region. Cycloadducts were added to preheated diphenyl ether (200 °C) in a three-neck flask and the temperature of the solution was monitored by an internal thermometer. The determination of first-order rate constants and of kinetic activation parameters was accomplished by using the computer program LSTSQ, available from Serena Software, 489 Screna Lane, Bloomington, IN 47401.

Results and Discussion

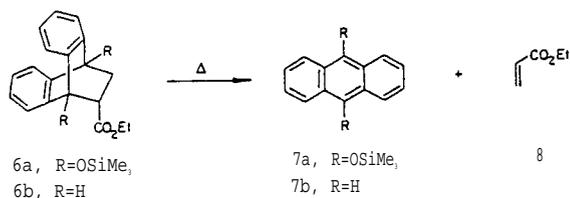
Cycloreversion reactions were carried out in dry diphenyl ether at 200 °C and were followed by the increase in absorption at 378 nm, which is the diagnostic of anthracene formation. The reaction of **1** followed demonstrated clean first-order kinetic behavior for only one half-life, owing to a concurrent decomposition of product **2** (likely oxidative and confirmed using **2** itself under identical conditions). The rate constants obtained by linear least-squares analysis were 4.5 × 10⁻⁴ s⁻¹ for **1** and 2.4 × 10⁻⁵ s⁻¹ for **4**, and reveal a 19-fold rate increase for the siloxy-substituted compound (**1**) as compared to the reference (**4**).

Details concerning the cycloaddition steric requirements of anthracene **2** were obtained by measuring the rates of the



reaction of **2** and **5** with substituted maleimides. In chloroform at 25 °C, the ratio ($k^{\text{Me}}/k^{\text{H}}$) of second-order rate constants using maleimide (H) and N-methylmaleimide (Me) is 3.01 for **2** and 3.43 for **5**; this indicates that, in the absence of a major steric perturbation, electronic changes of the dienophile affect the reactions with dienes **2** and **5** about equally. However, $k^{\text{Ph}}/k^{\text{H}}$ is 0.84 for **2** and 2.51 for **5**; clearly, the perpendicular phenyl group of N-phenylmaleimide is finally large enough to interact with one of the siladioxy *t*-butyl groups in **2**. An examination of CPK molecular models corroborates this conclusion.

For comparison, we have measured the rates of cycloreversion for adducts **6a** and **6b**. Bissiloxy adduct **6a** was prepared from the corresponding anthracene (**7a**)¹⁴ by heating in neat ethyl acrylate at 120 °C for 72 h; the yield is only 25%, owing to the ready reversibility of this reaction. Adduct **6b** was prepared from anthracene by the same procedure in 85% yield. Cycloreversion reactions were carried out described above and were monitored at the anthracene's long wavelength λ_{max} (378 nm for **6a** in diphenyl ether). The rate constants obtained were $4.5 \times 10^{-3} \text{ s}^{-1}$ for **6a** and $1.7 \times 10^{-5} \text{ s}^{-1}$ for **6b**, and show a 263-fold rate increase for the siloxy-substituted compound (**6a**) as compared to the reference (**6b**). This result is in accord with the work of Grimme,⁶ which showed an approximately 150-fold acceleration in the cycloreversion of a monosiloxy adduct similarly substituted at the bridgehead position.



It is of interest to consider what effect siloxy substitution has on the polar character of these pericyclic transition structures. We have shown previously that substitution by a strongly electron-donating substituent can result in large (*ca.* 6-fold) solvent effects on cycloreversion reaction rates, which are ordinarily very insensitive to solvent polarity.^{12b} However, in the siloxyanthracenes we have examined, no such large solvent effects were observed. At 200 °C, the cycloreversion of adduct **6a** is only 16% slower when conducted in pentadecane instead of diphenyl ether. Furthermore, when the cycloaddition reaction of anthracene **2** with N-methylmaleimide was conducted in heptane instead of chloroform, the rate actually increases by 25%. It therefore does not seem likely that siloxy substitution dramatically changes the polar character of Diels-Alder reactions.

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