vs 1- and 2-adamantyl tosylates ($Y_{OTs}$),[16a] and $Y_{OTs}$ has also been shown to be a satisfactory solvent parameter for correlating rates of solvolyses of *p*-nitrobenzoates.[3a,16b,c]

There may be differences in strain energy released on ionization of *p*-nitrobenzoates and sulfonates, similar to those noted in comparisons of tertiary chlorides and *p*-nitrobenzoates.[7b] Tosylate/halide rate ratios for secondary and tertiary substrates are strongly influenced by steric factors.[17] The lower estimated tosylate/*p*-nitrobenzoate ratios (ca. $10^7$) are based on an intermediate calculation of rate data for chlorides,[3a] in which data for both secondary and tertiary substrates are included. Tosylate/chloride rate ratios from secondary systems give ratios that are too small for direct comparisons with *p*-nitrobenzoate/chloride rate ratios from tertiary systems, and hence low tosylate/*p*-nitrobenzoate ratios were obtained.[3a]

Trifluoroacetates would be more suitable than chlorides as "bridges" between reactive sulfonates and unreactive *p*-nitrobenzoates because they are similar sterically. Also, trifluoroacetates are about as reactive as chlorides,[16a,18] and they can be prepared directly from alcohols without the possibility of carbocationic rearrangements. A minor disadvantage of trifluoroacetates is their low solubility.[16a,18b]

A rate ratio of 490 ± 20 for solvolyses of tosylates in acetic acid at 25 °C and 3,5-dinitrobenzoates in 60% acetone/water at 100 °C has previously been established for three cyclopropylcarbinyl substrates.[19] At 25 °C, 3,5-dinitrobenzoates solvolyze six times faster than *p*-nitrobenzoates,[11,20] which are 20–25 times more reactive than benzoates.[2c] Relative rates of solvolyses of sulfonate esters can be obtained from a compilation of data for tosylates and mesylates (see Table 5 of ref 9b) or from $\rho$ values for solvolyses of arenesulfonates.[2a,2b]

The sulfonate/*p*-nitrobenzoate rate ratios discussed here are ratios of "titrimetric" rate constants. Benzhydryl *p*-nitrobenzoate (1, X = $OCOC_6H_4NO_2$) is known to undergo $^{18}O$ exchange about three times faster than solvolytic release of acid,[21] and similar observations have been made for sulfonates.[22] A note of caution[23a] about a previous assumption of constant tosylate/bromide rate ratios was based on $\rho^+$ values for solvolyses of 1-aryl-1-(trifluoromethyl)ethyl substrates; $\rho^+$ was −6.85 for tosylates[23b] and −10.3 for bromides.[23a] However, only one substituent (Me) was common to these two plots. Also, bromides are structurally less similar to tosylates than are *p*-nitrobenzoates.

## Conclusion

Tosylate/*p*-nitrobenzoate solvolysis rate ratios ($3 \times 10^9$ in 80% ethanol/water at 25 °C) are relatively insensitive to solvent and structural effects (steric and perhaps also electronic effects). The ratio varies almost 100-fold over a 100 °C range of temperatures and, allowing for this effect, consistent results (Table IV) have been obtained for four substrates (1–3 and 5). Previous estimates of tosylate/*p*-nitrobenzoate rate ratios (spanning nearly 3 orders of magnitude at 25 °C) are unreliable because of the indirect comparisons required. The corresponding tosylate/3,5-dinitrobenzoate rate ratio is $5 \times 10^8$ at 25 °C.

## Experimental Section

**Chemicals.** 1-Adamantyl *p*-nitrobenzoate (2, X = $OCOC_6H_4NO_2$) was recrystallized from ethanol, mp 188–189 °C (lit.[24] mp 185.8–186.1 °C, 1-adamantyl mesylate (2, X = OMs) was prepared as described previously,[4c,25] benzhydryl *p*-nitrobenzoate (1, X = $OCOC_6H_4NO_2$) was recrystallized from 50/50 hexane/acetone, mp 134–135.5 °C (lit.[26] mp 131–133 °C), and benzhydryl mesylate (1, X = OMs) was prepared in situ.[6]

**Kinetics.** Conductimetric procedures for fast reactions were as described previously,[4c,d,6] except that LSKIN calculations[27] were performed in a few seconds on an Amstrad PC1512 (approximately equivalent to an IBM XT). Because 1-adamantyl *p*-nitrobenzoate is relatively insoluble, the following procedure was adopted: the substrate (7.5 mg)[28] was mixed with dry acetonitrile (1 mL), warmed, sonicated for 10 min, and then filtered. 2,6-Dimethylpyridine (1 μL) was added to the solvolysis medium (50 mL), this solution ($1.7 \times 10^{-4}$ M) was dispensed into 5-mL ampules, and the acetonitrile solution (25.0 μL) was then added ($<10^{-4}$ M *p*-nitrobenzoate). HPLC analyses required only 25.0 μL of solution, eluted with 95% methanol/water, with detection at 260 nm ($A$ = 0.05).

**Acknowledgment.** We are grateful to the SERC (UK) for a studentship (S.J.N.) and for two HPLC equipment grants, to the British Council for support via the Anglo–German Academic Research Collaboration, and to M. S. Garley for further modifications to the LSKIN computer program allowing convenient operation on a PC.

**Registry No.** 1 (X = OMs), 135513-20-1; 1 (X = $OCOC_6H_4$-*p*-$NO_2$), 25115-94-0; 2 (X = OMs), 25236-60-6; 2 (X = $OCOC_6H_4$-*p*-$NO_2$), 968-84-3.

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(28) Four-fold less sample could conveniently have used if the sample had been less plentiful.

# Acyclic 1,4-Radical Cations. Direct Observation and Stability

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## Introduction

One of the most characteristic reactions of radical ions is the unimolecular or biomolecular formation of "distonic radical ion" in which charge and radical sites are separated from each other.[1] An introduction of an electron-donating group such as a methoxyl group which stabilizes the cationic site of the distonic radical ion enhances the efficiency and the selectivity of the reaction of radical cations.[2] A typical example of the distonic radical ions is an acyclic

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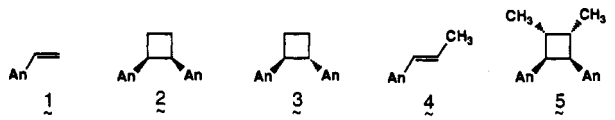
0022-3263/91/1956-6240$02.50/0 

1,4-diyl radical cation which has been proposed as a common intermediate for both cyclodimerization of electron-rich terminal olefins and cycloreversion of the corresponding cyclodimers induced by one-electron oxidation.[3] However, the intermediacy of the acyclic 1,4-radical cation was eliminated for the dimerization of anethole for which a quasi-concerted [2 + 1] cyclodimerization mechanism was proposed.[4] Such a distinguished difference in the reactivity of terminal and internal olefins suggests that the position of equilibrium between acyclic and cyclic 1,4-radical cations is determined by steric as well as electronic effects of the substituents.

Here, we report direct observation of cyclic and acyclic 1,4-bis(4-methoxyphenyl)-1,4-radical cations and the remarkable effects of methyl substituents on the stability of the 1,4-radical cation by use of pulse radiolysis and 77 K matrix γ-irradiation of the following substrates (1–5).




1 2 3 4 5

An - : 4-Methoxyphenyl

## Experimental Section

**Pulse Radiolysis.** The L-band linear accelerator at Osaka University was used as the source of electron pulse. The energy was 28 MeV and the pulse width was 8 ns. The peak current was 8 A and the dose was 0.7 kGy per pulse. The diameter of the electron beam spot on the surface of a cell was ca. 4 mm. A 450-W xenon lamp (Osram, OPG-450) was used as the analyzing light source. The light passing through a sample solution was monitored by a photomultiplier (Hamamatsu Photonics, R-928) after a monochrometer (Nikon, G-250). The light signal was developed on a transient digitizer (Tektronix, 7912AD). A spectral grade of 1,2-dichloroethane was used as a solvent. The sample solutions were filled in a Suprasil quartz cell (10 × 10 mm²) and deareted by argon saturation.

**77 K Matrix γ-Irradiation.** Butyl chloride was repeatedly shaken with concentrated sulfuric acid and washed with water and also with a solution of sodium bicarbonate. Then, butyl chloride was dried with calcium chloride and fractionally distilled. The sample solutions were filled in a Suprasil quartz cell (optical path, 2 mm) and degassed under high vacuum. The sample solutions were irradiated at 77 K with γ-rays from a 370 TBq $^{60}$Co source. The transient absorption spectra were measured at 77 K and also during annealing by a multichannel-photodetector (Otsuka Electronics).

**Materials.** 4-Methoxystyrene (1) and *trans*-anethole (4) purchased from Wako Pure Chemical Industry were distilled before use. Cyclodimers were synthesized by the following procedures.

***trans*-1,2-Bis(4-methoxyphenyl)cyclobutane (3).** A solution of 1 (3 g, 22 mmol) and 1,4-dicyanobenzene (0.3 g, 2.3 mmol) in acetonitrile (100 mL) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter under argon atmosphere for 5 h. After evaporation of solvent from the reaction mixture, dimer 3 was isolated by column chromatography on silica gel: $^1$H NMR ($CDCl_3$): δ 1.87–2.37 (4 H, m), 3.20–3.31 (2 H, m), 3.63 (6 H, s), 6.66 (4 H, d, $J$ = 8.0 Hz), and 7.00 (4 H, d, $J$ = 8.0 Hz).

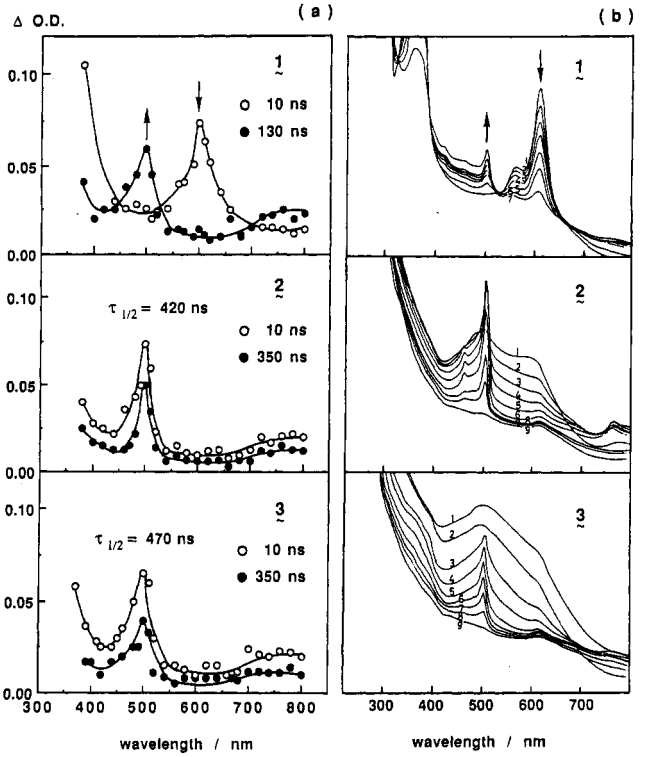



**Figure 1.** (a) Transient absorption spectra obtained at various times after an 8-ns pulse irradiation of 1,2-dichloroethane solutions of 1–3 (20 mM) at room temperature. (b) Absorption spectra of γ-irradiated *n*-butyl chloride solutions (5 mM) of 1–3 at 77 K: 1, 77 K; 2–7 or 9, warming.

***cis*-1,2-Bis(4-methoxyphenyl)cyclobutane (2).** A solution of 1 (3 g, 22 mmol) in benzene (100 mL) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter under argon atmosphere for 10 h. After evaporation of the reaction mixture, dimer 2 was isolated by column chromatography on silica gel: $^1$H NMR ($CDCl_3$) δ 2.33–2.40 (4 H, m), 3.66 (6 H, s), 3.67–3.97 (2 H, m), 6.50 (4 H, d, $J$ = 9.0 Hz), and 6.73 (4 H, d, $J$ = 9.0 Hz).

**(1α,2α,3β,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (5).** A solution of 4 (10 g, 68 mmol) in cyclohexane (150 mL) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter under argon atmosphere for 10 h. After evaporation of the solvent, dimer 5 was recrystallized from methanol, mp 53–54 °C.

## Results and Discussion

**4-Methoxystyrene (1) and the Cyclodimers 2 and 3.** The transient absorption spectra recorded at various times after an 8-ns electron-pulse irradiation to 1,2-dichloroethane solutions of 1–3 at room temperature are shown in Figure 1a. The absorption spectra of γ-irradiated butyl chloride solutions of 1–3 at 77 K are also presented in Figure 1b. In these halogenated solvents, it is well-known that radical cations of the solute molecule which possesses a lower ionization potential than that of the solvent used are mainly produced by the irradiation.[5] In the case of 1, a sharp absorption band with $\lambda_{max}$ at 600 nm was obtained at 10 ns after the pulse. This band was assigned to a monomer radical cation of 1 on the basis of the results obtained by 77 K matrix γ-irradiation. The 600-nm band decayed according to the pseudo-first-order kinetics with

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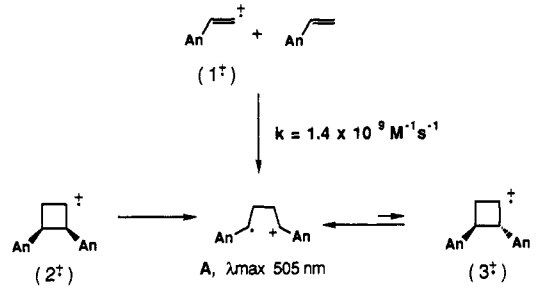
**Scheme I**




a simultaneous formation of a 505-nm band (the decay rate, $1.4 \times 10^7$ s$^{-1}$; the formation rate, $2.6 \times 10^7$ s$^{-1}$). The rate of the 600-nm band decay increased with increasing the concentration of 1, which suggests the newly formed species to be a dimer cation A of 1. A plot of the decay rate constant vs the concentration of 1 was linear, and the slope yielded the dimerization rate constant to be $1.4 \times 10^9$ M$^{-1}$ s$^{-1}$.

On the other hand, pulse radiolysis of both cyclodimers 2 and 3 demonstrated very rapid formation of the 505-nm band, which is very similar to that of A. However, the absorption spectra of the radical cations of cyclodimers ($2^{\bullet+}$, $3^{\bullet+}$) obtained by 77 K matrix $\gamma$-irradiation exhibit very broad bands around 400–650 nm and are quite different from that of the dimer cation A obtained above. When the matrix temperature was increased, the latter 505-nm band appeared to grow (Figure 1b). The efficiency of the 505-nm band formation was higher in more strained cis isomer 2 than the trans isomer 3, which indicates the latter species A to be of an open structure, i.e., an acyclic 1,4-radical cation. These results are summarized in Scheme I.

It has been previously reported that the photoelectron-transfer-sensitized dimerization of 1 results in the formation of trans cyclodimer 3.[3e] In the present study, the formation of 3 was also confirmed by the $\gamma$-irradiation of a deaerated 1,2-dichloroethane solution of 1. Thus, the 1,4-radical cation A may be interconvertible to the trans cyclodimer radical cation $3^{\bullet+}$. On the other hand, the evidence that shows that A undergoes cleavage to $1^{\bullet+}$ and 1 or one-electron reduction to give the corresponding biradical intermediate could not be obtained. Thus, the 1,4-radical cation A seems to be the most stable species among the various radical cations produced under the reaction conditions and the main decay process of the 1,4-radical cation might be a bimolecular neutralization with chloride ions, which are the counter anion in the present system.

***trans*-Anethole (4) and the Cyclodimer 5.** Figures 2a and 2b show the results obtained for *trans*-anethole (4) and the cis cyclodimer 5. In the case of 4, a sharp absorption band with $\lambda_{max}$ at 610 nm was assigned to the monomer radical cation of 4 ($4^{\bullet+}$). In contrast to 1, the decay rate of $4^{\bullet+}$ was independent of the concentration of 4 up to 0.1 M, and the formation of a new dimer cation could not be detected around the 500-nm wavelength region. These results demonstrate that the dimerization of 4 via the radical cation, reported by several groups,[4] proceeds with a rather slow rate constant, probably less than $10^7$ M$^{-1}$ s$^{-1}$. This is consistent with the estimation of the rate constant for the photoelectron-transfer dimerization of 4 obtained from the quenching data by 1,2,4-trimethoxybenzene in acetonitrile, $2 \times 10^6$ M$^{-1}$ s$^{-1}$.[4b]

On the other hand, pulse radiolysis of 5 provided a quite similar transient absorption spectra to that of 4. This shows that a very rapid cycloreversion of $5^{\bullet+}$ to the monomer radical cation $4^{\bullet+}$ took place at room temperature. The intermediate acyclic 1,4-radical cation B could not be detected in this system.

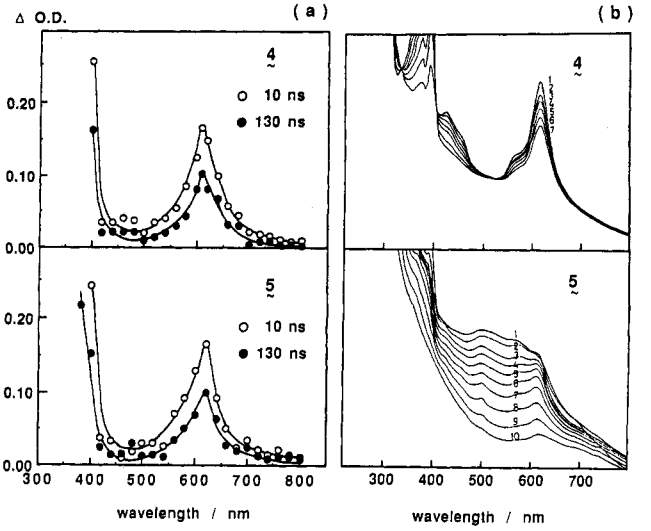
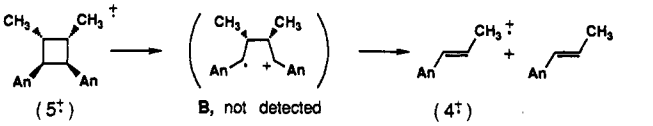



**Figure 2.** (a) Transient absorption spectra obtained at various times after an 8-ns pulse irradiation of 1,2-dichloroethane solutions of 4 and 5 at room temperature. (b) Absorption spectra of $\gamma$-irradiated *n*-butyl chloride solutions (5 mM) of 4 and 5 at 77 K: 1, 77 K; 2–7 or 10, warming.

Consistent with these results obtained by pulse radiolysis, 77 K matrix $\gamma$-irradiation of 4 and 5 indicated that the dimerization of $4^{\bullet+}$ is also very slow, although an unidentified transient species formed around 400–450 nm. The latter species might be an associated dimer cation of 4 since it is very unstable and could not be detected by pulse radiolysis at room temperature. Cycloreversion of $5^{\bullet+}$ did not proceed efficiently under low temperature (Figure 2b), which suggests the presence of a higher energy barrier for the cycloreversion of $5^{\bullet+}$ than those of $2^{\bullet+}$ and $3^{\bullet+}$. In the photoelectron-transfer cycloreversion of 5 in acetonitrile, it has been reported that the cycloreversion of $5^{\bullet+}$ proceeds via a chain mechanism involving the free-radical cation of 5, which undergoes ring cleavage at a relatively slow rate.[3h]

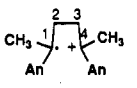



The present results are compatible with the conclusion that a long-lived acyclic 1,4-radical cation is eliminated as an intermediate for the dimerization of *trans*- and *cis*-anethole and the cycloreversion of the cyclodimer via the radical cation.[4] In contrast to A, B seems to be a less stable species than $5^{\bullet+}$ and $4^{\bullet+}$ and immediately undergoes cyclization or monomerization, even if formed.

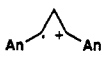
**Stabilities of Acyclic Radical Cations.** It has been clarified by a series of experiments with 4-methoxyphenyl derivatives that the stabilities of cyclic and acyclic radical cations are affected by the introduction of methyl substituents at $\beta$ positions of the methylene chain, although the substitution at the $\alpha$ position did not affect so much as observed in the case of an acyclic 1,4-radical C.[6] The stability was also affected by the chain length of the acyclic 1,*n*-radical cation. Previously, we have reported the formation of an acyclic 1,3-radical cation D by the pulse radiolysis of *cis*- and *trans*-bis(4-methoxyphenyl)cyclo-

(6) Takamuku, S. et al. Unpublished results.

propane in 1,3-dichloroethane.[2a]



C, λmax 520 nm



D, λmax 580 nm

The absorption maximum of D was 580 nm and was quite different from that of the corresponding 1,4-analogue A, $\lambda_{max}$ 505 nm. This means that both terminal sites of the acyclic radical cation are electronically interacting with each other and the degree of the interaction seems to depend on the chain length.

Introduction of two methyl substituents at C2 and C3 positions of A induces the destabilization, and the 1,4-radical cation B is no longer detectable. This also indicates that the mutual interaction of the terminal sites is reduced by the methyl substituents probably due to the electronic and steric effects. The effects induce the destabilization of the species. On the contrary, the two methyl substituents enhance the stability of the corresponding cyclic structure by reducing an electron deficiency of the C1–C4 bond of $5^{\bullet+}$, and the monomer radical cation $4^{\bullet+}$ is also stabilized by the methyl substituent. Thus, the lifetime of B becomes very short, if formed, which supports the previous observation that the cyclodimerization and cycloreversion of this series may proceed by a quasi-concerted mechanism.

**Acknowledgment.** This work was supported in part by a grant from the research program on "Creation of New Materials through Intelligient Design" of ISIR, Osaka University. We are grateful to the members of the Radiation Laboratory of ISIR for running the linear accelerator.

**Registry No.** 1, 637-69-4; $1^{\bullet+}$, 135639-41-7; 1 dimer cation, 135658-80-9; 2, 52498-14-3; $2^{\bullet+}$, 135684-17-2; 3, 52498-15-4; $3^{\bullet+}$, 135684-18-3; 4, 4180-23-8; $4^{\bullet+}$, 117467-10-4; 5, 19043-23-3; $5^{\bullet+}$, 112246-69-2.

## Synthesis of Naphtho[*f*]ninhydrin

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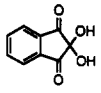
*Received May 13, 1991*

In 1910, Ruhemann discovered ninhydrin (1) and recognized its reaction with α-amino acids to form a purple-blue product known as Ruhemann's Purple.[1] Ninhydrin soon became widely used as a universal reagent for the analysis of α-amino acids in biochemical studies. In 1954, Oden and von Hofsten reported the use of ninhydrin for the development of latent fingerprints via reaction with the α-amino acids of palmar sweat residue, which comprises latent prints.[2] Since the 1960s, ninhydrin has become the most widely used reagent for the development of latent prints on porous surfaces (mainly paper). However, contrast and visualization of weak fingerprints, particularly on some surfaces such as paper and cardboard, are often unsatisfactory. More recently it was found that treatment of ninhydrin-developed prints with zinc chloride forms a coordination compound that is highly fluorescent under blue-green excitation, typically from an argon-ion laser.[3-5]

Since the early 1980s, ninhydrin analogues have been investigated as alternatives to ninhydrin, both in the conventional fingerprint detection mode and for laser detection after zinc chloride treatment.[7-9] Benzo[*f*]ninhydrin (2) was found to offer several advantages over ninhydrin for the fluorescence detection of latent fingerprints[8] and a convenient synthesis of benzo[*f*]ninhydrin has appeared.[10]

Another ninhydrin analogue with excellent potential as a fingerprint reagent[11] is the unknown compound naphtho[*f*]ninhydrin (3). Previous attempts to prepare 3 have been unsuccessful.[12,13] We now report the synthesis of this elusive compound.



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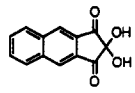
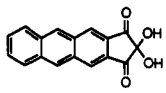
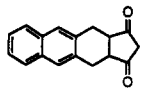


2



3



4

5

### Results and Discussion

Our initial attempt to prepare naphtho[*f*]ninhydrin (3) involved an adaptation of the method published by Heffner, Sarafyn, and Joullié[10] for the synthesis of benzo[*f*]ninhydrin (2). In their method, the three-ring skeleton of 2 was conveniently constructed by ultrasonication of 1,2-bis(bromomethyl)benzene with activated zinc metal and 1,4-cyclopentadiene in dioxane.[10] Although we were able to repeat the reported cyclization, even extended ultrasonication of 2,3-bis(bromomethyl)naphthalene[14] under the same conditions failed to produce the desired tetracyclic Diels–Alder adduct 4. For another Diels–Alder cyclization, a much lower adduct yield was reported when an *o*-xylylene intermediate was replaced with the annulated analogue 5.[15]

Attention was then shifted to the preparation of unknown 2,3-trimethyleneanthracene (8), a potential precursor to 3 by oxidation. Friedel–Crafts acylation of indan with phthalic anhydride gave 75–90% yields of 6 (Scheme I), which was cyclized with fuming sulfuric acid to provide 55–60% yields of the substituted anthraquinone 7. Reduction of 7 to substituted anthracene 8 was accomplished in 72% yield with aluminum cyclohexoxide in cyclohexanol. Unfortunately, hydrocarbon 8 was unaffected by selenium dioxide in refluxing dioxane[16] and was transformed back into the substituted anthraquinone precursor

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