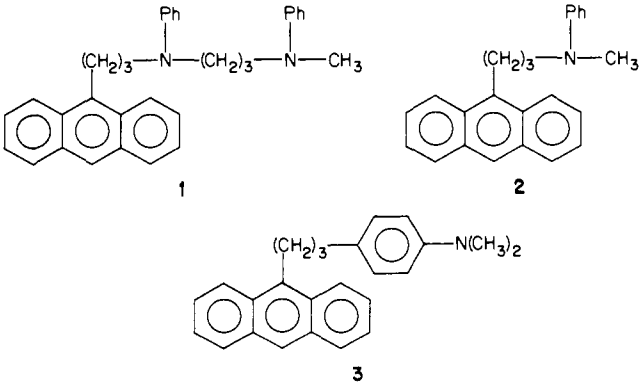
Table I. Excited State Behavior of 1-3

	1	2	3
	In Dichloromethane		
fluorescence			
λ_{max}	530 nm	530 nm	552 nm
ϕ_f[a]	<0.01	0.12	b
τ_f[a]	<2 ns[c]	28 ± 1 ns	b
absorption			
470 nm, τ_{decay}[d]	19 ± 3 ns	e	b
700 nm, τ_{decay}[a,d,f]	20 ± 1 ns	28 ± 2 ns	b
425 nm, τ_{rise}[a,f]	21 ± 2 ns	27 ± 2 ns	b
	In Acetonitrile		
absorption			
470 nm, τ_{decay}[g]	2.0 ± 0.2 ns	2.0 ± 0.3 ns	270 ± 30 ps
700 nm, τ_{decay}[f,g]	2.0 ± 0.3 ns	1.6 ± 0.4 ns	270 ± 30 ps
425 nm, τ_{rise}[f,g]	1.8 ± 0.3 ns	2.5 ± 0.4 ns	e

[a] In deaerated solution. [b] Not measured. [c] Calculated from the quantum yield and the radiative lifetime of **1**. [d] Rise time is <2 ns or instrument limiting. [e] No appreciable absorption detected with our instruments. [f] The values were the same within experimental error when they were measured over a 10-nm range. [g] Rise time is 10 ps or less, see also ref 19-21.

530 nm, $\phi_f < 0.01$) in dichloromethane but yields the absorptions of both the dialkylanilino radical cation and the anthryl radical anion. Furthermore, in contrast to radical ions generated from photoexcited **1-3** in acetonitrile, the radical ions generated from **1** in dichloromethane exhibit a lifetime of 20 ± 3 ns, 10-75 times longer than those generated from **1-3** in acetonitrile, and annihilate to give anthryl triplet among the products (risetime, 21 ± 1 ns). All these times are about an order of magnitude longer than the estimated lifetime of the intramolecular exciplex form **1**.

[Arene*-dialkylaniline] exciplexes are highly polar systems which exhibit a dipole moment of approximately 10-13 D;[16,26] therefore, the exciplex exhibits a high effective polarity in its vicinity even in a nonpolar solvent. Since a photoexcited molecule is known to react with a donor to generate an ion pair in a polar environment, it is not surprising that a donor molecule will react with an exciplex in a nonpolar medium in view of this high effective polarity, while an excited "nonpolar" uncomplexed aromatic hydrocarbon cannot. The ion pair generated from **1** in this interaction differs from the intimate ion pairs generated from **2** and **3** in that the average distance between the donor and the acceptor is increased which may retard the back electron transfer (reaction 4). A similar suggestion has been made by Mataga and his



co-workers independently on a linked polychromophoric system containing one porphyrin group as the photoexcited donor and two quinoid groups as the acceptor.[8,27] Since amine dimer cation radicals have been implicated as intermediates in the exciplex quenching processes,[6,28] the anilino intermediate detected in our study may be such a species. The longer lifetime of ion pairs formed from excited **1** in dichloromethane may also be caused by the delocalization of the charge between the two anilino groups.

In conclusion, our investigation of the photochemical behavior of polychromophoric systems containing an anthryl group and one or two dialkylanilino groups demonstrates that the presence of the second anilino group promotes the electron transfer of arene-amine exciplexes to generate radical ion pairs in dichloromethane. These ion pairs exhibit an appreciably longer lifetime than the ion pairs generated from the electron transfer of photoexcited bichromophoric analogue in polar media. The results will assist us in the construction of other sytems which may yield radical ions of even longer lifetimes. Such an investigation may lead to a better understanding of the conversion of light energy into chemical energy via electron transfer among organic compounds.

Acknowledgment. The work at the University of Chicago was supported by the National Science Foundation, and the work at the Argonne National Laboratory was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38. We thank Professor Graham Fleming for many valuable discussions and Dr. James R. Larson for the preparation of **1** used in this investigation.

Registry No. **1**, 82665-24-5; **2**, 55789-86-1; **3**, 38474-11-2.

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(27) The porphyrin-quinone systems differ from our arene-amine systems in that they form ground-state complexes and undergo light-induced electron transfer in nonpolar media,[5] while arene-amine systems do not.[8] However, the lifetime of ion pairs generated from the trichromophoric porphyrin-quinone system was increased over the bichromophoric one in dioxane from 140 to 300 ps.[5]
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Thermal Behavior of C_8H_8 Hydrocarbons.[1] 2. Semibullvalene:[2] Kinetic and Thermodynamic Stability

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Received March 29, 1985

Semibullvalene SBV, (**1**) is a hydrocarbon, discovered by Zimmerman and Grunewald,[3a] remarkable for undergoing a rapid degenerate Cope rearrangement at −150 °C.[3b,c] We were led to investigate its higher temperature thermal behavior in connection with separate studies of the isomeric molecules, cyclooctatetraene (COT, **2**)[4] and cubane.[5] There are conflicting reports of the product of SBV (**1**) decomposition. Two studies[6,7] claim COT (**2**) as the product while a third states that it reacts reversibly to

(1) Part 1: Martin, H.-D.; Urbanek, T.; Braun, R.; Walsh, R. *Int. J. Chem. Kinet.* **1984**, *16*, 117. This is also part 51 of "Small and Medium Rings" (Part 50: Honegger, E.; Heilbronner, E.; Urbanek, T.; Martin, H.-D. *Helv. Chim. Acta* **1985**, *68*, 23).
(2) Systematic name: tricyclo[3.3.0.0^{2,8}]octa-3,6-diene.
(3) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (b) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887. (c) For a general review of the thermal behavior of SBV (**1**), see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; p 232.
(4) Martin, H.-D.; Urbanek, T.; Walsh, R., unpublished results.
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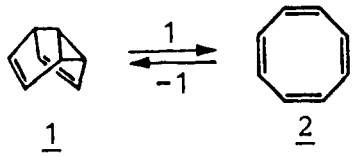
Scheme I



form 1,5-dihydropentalene.[8] Its heat of formation has been given values ranging from 53[9] to 91 kcal mol^{-1}.[10] One of us has previously estimated[11] an approximate value of 71 kcal mol^{-1}, which, if correct, would make it of similar stability to COT.[13] Thus in this case the possibility exists of establishing an equilibrium between SBV (**1**) and COT (**2**) (Scheme I). We wish to report results demonstrating that this does in fact occur and also to describe the kinetics of approach to equilibrium.

Until now one of the practical problems with analysis for SBV (**1**) has been the difficulty of finding a stable gas chromatographic column that resolves it from COT (**2**).[14] We have found that a fluorosilicone oil column (3 m, 20% w/w on Chromosorb W, HMDS treated and with 1% ATPET) operated at 40 °C with N_2 carrier gas will accomplish this separation. Retention times (in minutes) were COT (**2**) (20.5), SBV (**1**) (26.0). SBV (**1**) was prepared by long-wavelength photolysis of COT (**2**)[15] to a purity of 99% after removal of benzene by low-pressure distillation. Pyrolyses were carried out by admission of the vapor (ca. 1 torr) into a heated Pyrex reaction vessel (volume 100 cm^3). After the desired reaction time, the vessel contents were shared with a sample bulb (reaction being thereby quenched) and analysed by gas chromatography. Prior to use, the vacuum line and gas chromatograph were treated with ammonia to reduce the risk of SBV (**1**) losses through acid catalysis. The reactor was further treated with HMDS to prevent surface-catalyzed reaction.

SBV (**1**) pyrolysis was investigated as a function of time, pressure, and temperature. The only observed product was COT (**2**) (dihydropentalenes, if formed, would have been readily detected). At temperatures >270 °C and reactant pressures of ca. 1 torr, an equilibrium with COT (**2**) was established in less than 30 min with equilibrium quantities of SBV (**1**) between 2% and 4% of total C_8H_8. This was established by approach *from both sides*. Samples of COT (**2**) (>99.9% pure) were heated for equal times at the same temperatures and produced, within experimental error,[16] equal yields of SBV (**1**). There was a small temperature dependence of the equilibrium constant in the experimental range 270–360 °C (the yield of **1** increased slightly at higher temperatures). For the process (Scheme I) an analysis of the data gave $\Delta\bar{H}° = -2.37 \pm 0.11$ kcal mol^{-1} and $\Delta\bar{S}° = 3.02 \pm 0.19$ cal K^{-1} mol^{-1}. From the known data for COT (**2**)[13] these lead[17] to $\Delta H_f°$(**1**, 298 K) = 73.6 ± 1.0 kcal mol^{-1} and $S°$(**1**, 298 K) = 75.1 ± 0.3 cal K^{-1} mol^{-1}. The experimental heat of formation is in good agreement with our earlier estimate[11] but not with those of MINDO/3 calculations.[10] There is no previous published value for the entropy. Kinetic studies in the temperature range 200–240 °C showed a good fit, at each temperature, to reversible first-order behavior. Starting from SBV (**1**) (initial pressures ca. 1 torr) the data at each of five temperatures fitted the Arrhenius equations

$$\log (k_1/\mathrm{s}^{-1}) = (13.81 \pm 0.08) - (39.82 \pm 0.19 \text{ kcal mol}^{-1})/(RT \ln 10)$$

$$\log (k_{-1}/\mathrm{s}^{-1}) = (13.15 \pm 0.08) - (42.19 \pm 0.19 \text{ kcal mol}^{-1})/(RT \ln 10)$$

Separate tests showed that k_1 was independent of pressure (0.4–6.0 torr) and unaffected by change in vessel surface to volume ratio.

These results clarify considerably the confusion surrounding SBV (**1**) and illuminate further the thermal behavior of COT (**2**) viz.: (a) As suggested previously by the tetra-[18] and octamethyl[19] cases, SBV (**1**) and COT (**2**) lie close in energy. The four and eight methyl substituents merely alter the balance in favor of the SVB geometry. Until now the low proportion of SBV **1** in the parent case has escaped detection.

(b) COT (**2**) is now shown to be involved in two reversible valence isomerizations, one at temperatures of ca. 100 °C producing ca. 0.01% of bicyclo[4.2.0]octa-2,4,7-triene[20] and the other at 300 °C producing ca. 2.7% SBV (**1**), as described here. The mechanism of SBV (**1**) conversion to COT (**2**) probably involves the bicyclo[3.3.0]octa-2,6-dien-4,8-diyl biradical **3**[21] (Scheme II).

A thermochemical estimate[12] of $\Delta H_f°$ (**3**) is ca. 95 ± 4 kcal mol^{-1} making it easily energetically accessible. Since **3** is reasonably suggested as the intermediate in the rearrangement of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**4**) to SBV (**1**)[22] this implies that **3** reverts more readily to SBV (**1**) than to COT (**2**), thus making the second step rate determining in the **1** → **2** rearrangement. This information also tells us that formation of intermediate **3** is *not* rate determining in the higher temperature COT (**2**) rearrangement.[4,8,23] In this latter system it is a reluctant 1,2-H-shift from

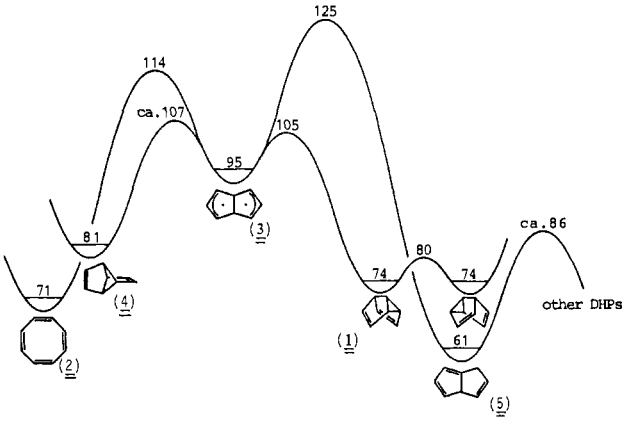
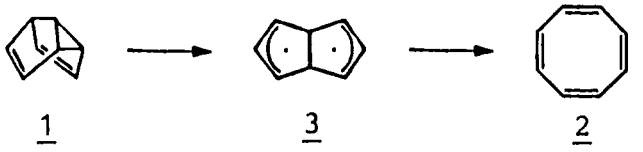


Figure 1. Potential energy hypersurface for bicyclo[3.3.0]octa-2,6-dien-4,8-diyl (**3**) formation and decay pathways ($\Delta H_f°$ values in kcal mol^{-1}).

Scheme II



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(16) A typical value was 2.67 ± 0.17% at 300 °C. Starting from SBV (**1**), the equilibrium was slightly less certain because an unknown impurity peak of ca. 0.7% eluted between COT (**2**) and SBV (**1**).
(17) This assumes negligible temperature dependence of $\Delta H°$ and $\Delta S°$. This is reasonable for an isomerization reaction but may not be exactly true. Error limits have been widened to allow for the extra uncertainty.
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3, giving 1,8-dihydropentalene **5** and thence other DHPs, that is the slow step.[4,7] A portion of the C_8H_8 energy hypersurface involving SBV (**1**), COT (**2**), and intermediate **3** is shown in Figure 1.

Acknowledgment. We thank the European Photochemistry Association, the British Council, the Fonds der Chemischen Industrie, the Dr. Jost-Henkel-Stiftung, and the BASF AG for financial support.

Registry No. 1, 6909-37-1; **2**, 629-20-9.

Stereospecific Total Synthesis of (±)-Gephyrotoxin 223AB

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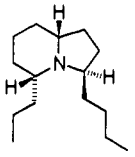
Received April 24, 1985

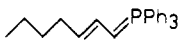
Gephyrotoxin (GTX) 223AB (**1**), one of the neurotoxin alka-



1

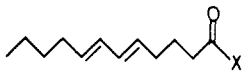
loids isolated in minute quantity from skin extracts of neotropical poison-dart frogs (family Dendrobatidae),[1,2] has attracted a vast amount of interest because of its unusual biological characteristics. Numerous groups have thus been involved in the development of methodology for the total synthesis of this molecule. These efforts have recently resulted in the syntheses of stereoisomers of **1**[3-5] and also (−)-**1**.[6] Herein, we report on the efficient preparation of (±)-GTX 223AB based upon an acyl nitroso Diels–Alder reaction[7] with *complete* stereochemical control. Our synthesis is distinguished from these previous efforts[3-6] by the fact that *the entire sequence provided single stereoisomers in the desired sense and thus met with no separation problems.*

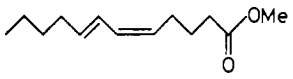
Reduction of ethyl (*E*)-2-heptenoate, prepared by the Wittig reaction of 4-pentanal with (ethoxycarbonyl)methylene triphenylphosphorane, with AlH_3 in ether afforded the alcohol **2** (80%), bp 78–80 °C (16 mmHg). Bromination of **2** with PBr_3 (petroleum ether, −10 °C) followed by treatment of the resultant bromide **3**, bp 64–65 °C (16 mmHg), with Ph_3P provided the phosphonium bromide **4**, mp 159–161 °C. The ylide **5** derived from **4** (*n*-BuLi, THF, −5 °C) was treated with methyl 5-oxopentanoate[8] in THF–HMPA (9:1) at −5 °C to produce methyl 5,7-dodecadienoate in 89% yield. Since the resulting material included 25% (by ^{1}H NMR) of the 5*Z*,7*E* isomer **7**, it was con-



2 X = OH
3 X = Br
4 X = $PPh_3^+Br^-$

5





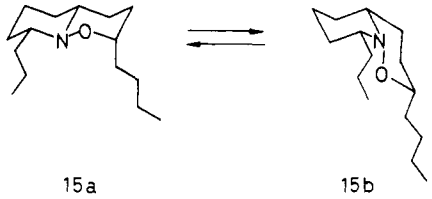
6 X = OMe
8 X = OH
9 X = Cl

7

verted to the isomerically pure (5*E*,7*E*)-ester **6** by irradiation (hexane, I_2). Saponification of **6** and chlorination (ClCOCOCl, benzene) of the resultant acid **8** gave the acid chloride **9**, which was allowed to react with hydroxylamine under aqueous alkaline conditions to form hydroxamic acid **10**, mp 78–80 °C, in 58% overall yield from the ester **6**. The yield of this construction was improved when the ester **6** was exposed to hydroxylamine in methanolic KOH at room temperature (15 h). In this manner the pure hydroxamic acid **10** was directly obtained from the ester **6** in 81% yield after collecting crystalline product followed by simple recrystallization (hexane).

Treatment of this hydroxamic acid with tetrapropylammonium (meta)periodate in chloroform (0–5 °C) generated in situ the acyl nitroso compound **11**. Under the reaction conditions, **11** underwent intramolecular [4 + 2] cycloaddition to give as the sole product the 1,2-oxazine derivative **12** in 82% yield after purification by silica gel chromatography (benzene/chloroform, 1:1). Hydrogenation (Pd/C, H_2, MeOH) of **12** provided **13** in 90% yield. Then **13** was treated with the Grignard reagent in ether at ambient temperature to give somewhat unstable enamine **14** (89%), which was subsequently subjected to reduction with $NaCNBH_3$ in methanol at pH 3.8–5.4 (10% HCl/MeOH, bromcresol green) resulting in the exclusive formation of **15** (70%).

The ^{13}C NMR spectrum[9] of **15** at 24 °C showed pairs of resonances for each of the carbons in the molecule. The relative intensity of each doublet was nearly unit independent of temperature and the doublet collapsed into a single line at high temperature depending on its peak separation. These observations strongly indicate that **15** exists in conformational equilibrium between **15a** and **15b** (eq 1) due to nitrogen inversion with nearly



(1)

15a 15b

equal population energy barrier ($\Delta G^{\ddagger}$), estimated to be about 8.0 kcal mol^{-1}.[10]

The ^{1}H NMR spectra (270 MHz) in pyridine-d_5 of **15** at 27.5 °C showed two sets of multiplets at δ 3.87 ($W_{1/4}$ = 23.9 Hz) and 3.72 ($W_{1/4}$ = 31.6 Hz) with an integration ratio of 10:9 for the C-2 proton, indicative of the equatorial hydrogen in **15a** and the axial hydrogen in **15b**, respectively. These C-2 proton signals converged to a single resonance centered at δ 3.88 at 100 °C.

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(10) The exchange rates (*R*) between **15a** and **15b** were calculated from temperature dependence of the peak separations for several sets of doublets in the spectrum using the exchanged Bloch equation.[11] Plots of ln *R* vs. $1/T$ exhibited a straight line, from which the $\Delta G^{\ddagger}$ was calculated.
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