6372 *J. Am. Chem. Soc.* **1984**, *106*, 6372–6375

and the tris(trideuteriomethyl)allylsilane distilled through a short vigreux column at 80 °C (bp 85–6 °C) to give 0.603 g (57.6%). For run 2, the above quantities were doubled and all else remained the same, furnishing 1.2158 g (58.0%) of tris(trideuteriomethyl)allylsilane: NMR (CCl$_4$) δ 4.56–6.11 (vinyl m, matches that of trimethylallylsilane). The deuterium incorporation was determined by the method of Biemann[8] and values of **6**-d_7 (1.6%), **6**-d_9 (98.4%) and **6**-d_6 (0.8%), **6**-d_8 (3.0%) and **6**-d_9 (96.2%) were obtained in run 1 and run 2, respectively. See Table I for the ion intensites used for these calculations.

Pyrolysis of Tris(trideuteriomethyl)allylsilane (6). Run 1. Compound **6** was slowly dripped into a vertical quartz tube packed with quartz chips and heated at 630 °C with use of nitrogen as a carrier gas with a flow rate of 30 mL/min. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 60% mass recovery. Analysis of recovered **6** and the trimethylvinylsilane was done by GCMS. See Table II and Table III for the percent deuterium incorporation and the actual mass spectral intensities. Isolation of deuterated **5** was attempted by preparative gas chromatography on a freshly packed 16 ft 20% SE 30 column: 300-MHz NMR (C$_6$D$_6$) δ 0.04–0.01 (m, 1 H), 0.40 (s, 1.25 H), 5.60–6.51 (m, 3.13 H, vinyl ABC pattern). The multiplet at δ 0.04–0.01 represents partial proton incorporation, while the singlet at δ 0.40 is an impurity, presumably from column bleed. The methyl protons in trimethylallylsilane absorb at δ 0.07.

Run 2. The flow pyrolysis in run 2 was conducted as in run 1. The pyrolyzate represented an 84.7% mass recovery. The GCMS analyses of both recovered **6** and **5** are presented in Table II and Table III, respectively. Isolation of **5** was accomplished on an aged 20 ft 20% SE 30 column: 300-MHz ^{1}H NMR (CCl$_4$) δ 0.04–0.10 (m, 1 H), 5.60–6.51 (m, 4.3 H, vinyl ABC pattern); 300-MHz ^{2}H NMR (CCl$_4$) δ 0.0 (s, 15 D) 5.53–5.84 (m, 1 D).

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Solvolysis of Ethenoanthracenyl Triflates. Novel Stabilized Cyclic Vinyl Cations

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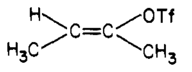
Abstract: The solvolytic behavior of ethenoanthracenyl (**3a**) and etheno-9,10-dimethylanthracenyl (**3b**) triflates was examined. Despite the strain inherent in these systems, **3a** reacts 10^5 times faster than cyclohexenyl triflate and 11 times faster than the unstrained *cis*-2-butenyl triflate. These results are explained by an unusual aryl stabilization of the incipient vinyl cations.

The solvolytic behavior of cyclic vinyl systems is of interest because of the question of the effect that ring strain has on the rate of reaction.[1] Vinyl cations in cyclic systems are rigidly held in bent geometries. If such bent structures are less favorable, then the rate of solvolysis of cycloalkenyl derivatives should be slower than that of similar acyclic precursors.[2]

The first attempt to generate cyclic vinyl cations by solvolysis of 1-cyclohexenyl tosylates and brosylates failed, resulting in addition–elimination in formic acid, and in 50% aqueous methanol at 130 °C after 18 days only starting material was observed.[3]

The solvolytic behavior of the cycloalkenyl triflates **2** has been extensively examined[2,4] and compared with that[5] of the acyclic model compound **1**. In the reactions of all cycloalkenyl triflates **2** except **2b**, first-order kinetics were observed. Cyclopentenyl triflate (**2b**) does not react via a vinyl cation intermediate[6] and it was recovered practically unchanged in a nonnucleophilic solvent such as CF$_3$CH$_2$OH (TFE) buffered with Et$_3$N after 10 days at 100 °C. For the reaction of the higher homologues, **2c**–**2e**, the kinetic data and relative reactivities[2,4] are in accord with a vinyl cation mechanism of solvolysis. Cyclohexenyl triflate (**2c**) reacts via a bent cation which has a high energy, resulting in 10^4 times slower solvolysis[2] than the acyclic triflate **1**. The vinyl cations resulting from triflates **2d** and **2e** have seven- and eight-membered rings which can reasonably accommodate the linear geometry of an sp-hybridized carbon coupled to a trigonal carbon, and hence the reactivities[2,4] of triflates **2d** and **2e** are comparable to that of the geometrically unrestricted acyclic analogue .



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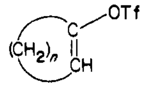
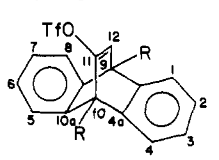


2a, $n = 2$
b, $n = 3$
c, $n = 4$
d, $n = 5$
e, $n = 6$

In this paper we report further aspects of the solvolytic behavior of cyclic vinyl triflates. In particular we investigated the solvolysis of triflates **3** with the bicyclo[2.2.2]octatrien-1-yl moiety which resembles the cyclohexenyl system in its strain and therefore would be expected to generate a vinyl cation with high energy due to ring strain. In fact, it is well-known that the strain in the bicy-



3a, R = H
b, R = CH$_3$

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[§] College of William and Mary.

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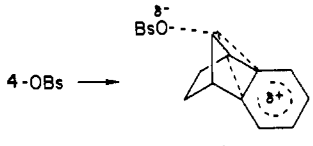
Table I. Rates of Solvolysis and Activation Parameters for Ethenoanthracenyl Triflates 3

compd	temp, °C	solvent[a]	10^4k, s^{-1}	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
3a	74.9 ± 0.2	70E	4.76 ± 0.04			
	64.7 ± 0.2	80E	1.79 ± 0.16	17.4	16.8	-26.5
	74.9 ± 0.2	80E	3.84 ± 0.09			
	74.9 ± 0.2	97T	7.65 ± 0.03			
3b	75[b]	70E	0.136			
	85.1 ± 0.2	70E	0.359 ± 0.005	23.8	23.1	-14.9
	94.8 ± 0.2	70E	0.867 ± 0.013			
	74.9 ± 0.2	97T	1.17 ± 0.009			

[a] 70E, 70% v/v EtOH; 80E, 80% v/v EtOH; 97T, 97% w/w TFE. [b] Extrapolated from other temperatures.

clo[2.2.2]octyl system is greater than in the cyclohexenyl ring. However, the presence of two aromatic rings in triflates **3** provides an opportunity to examine the stabilizing effect caused by possible π-participation of these unusual neighboring aryl groups.

Numerous similar cases are known where such participation of aryl groups and formation of novel carbocations were proposed. Tanida et al. studied the solvolysis of *anti*-7-benzonorbornenyl brosylate (**4**-OBs),[7] as well as *syn*- and *anti*-2-nitro-9,10-methanoanthracene-11-yl brosylates, **5**-OBs and **6**-OBs.[8] They concluded that the transition state **7** in the solvolysis of ester **4**-OBs must involve participation by the aromatic ring.



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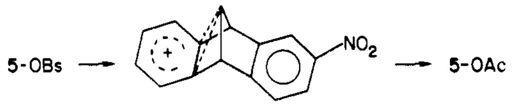
When esters **5**-OBs and **6**-OBs were solvolyzed in buffered acetic acid,[8] the only detectable product was the acetate with complete retention of configuration. These authors formulated the intermediate cations as bridged structures **8** and **9**, while the charge distribution of a symmetrical ion **10** was disproven.



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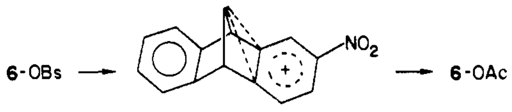

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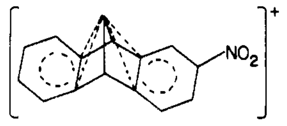
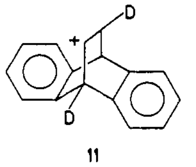


10

Cristol and Bopp[9] studied the isomerization of *cis*-1,3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate to the trans isomer and proposed that this reaction includes the cationic intermediate **11** or transition state **12**. However, they were unable to experimentally distinguish these structures.



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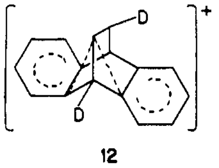
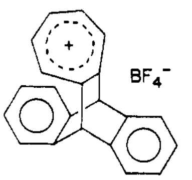


12

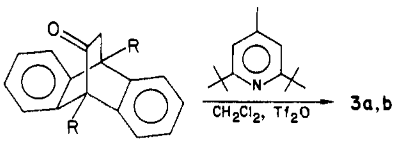
Nakazawa and Murata[10] examined the intramolecular remote $\pi-\pi$ interactions in salt **13**. These authors found that strong intramolecular charge-transfer interactions exist between the tropylium unit and the remote benzene rings, despite the minimized overlap of the orbital systems of both the donor and the acceptor.



13

Results and Discussion

Vinyl triflates **3a** and **3b** were prepared from the corresponding ketones **14a**[11] and **14b**[12] according to our standard procedure.[13]



14a, R = H
b, R = CH_3

Rates of solvolyses of triflates **3a,b** were measured conductometrically in unbuffered aqueous ethanol and trifluoroethanol. First-order rates of high precision were obtained in all instances to greater than 90% reaction. Activation parameters and first-order rate constants are summarized in Table I. These data are consistent with the direct unimolecular generation of the respective intermediate vinyl cation.

It is instructive to compare the reactivity of **3a** and **3b** with the monocyclic vinyl triflates **2** and the acyclic model **1**, as listed in Table II. It is evident from this comparison that despite the considerable strain inherent in the vinyl cations resulting from **3a** and **3b** they react significantly faster than comparably strained monocyclic analogues and even faster (in 70% TFE) than the unstrained acyclic model **1**. Specifically, compound **3a** reacts (1.5–2.0) × 10^5 *faster* than cyclohexenyl triflate and 11–14 times *faster* than unstrained **1**.

In fact, the reactivity of **3** is comparable to the unusually large reactivity of the highly strained cyclobutenyl triflate (**2a**) accounted for by the nonclassical nature of the intermediate cyclobutenyl cation.[14]

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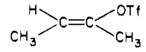
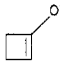
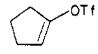
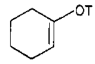
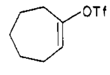
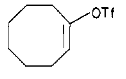
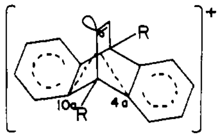
Table II. Relative[a] Reactivities of Cyclic Vinyl Triflates 2 and 3 at 75 °C

	triflate	k_{rel}	
		50% EtOH	70% TFE
1		1.0	1.0
2a		1.9	2.1
2b		5.9 × 10^{-6}	5.6 × 10^{-6}
2c		7.1 × 10^{-5}	6.1 × 10^{-5}
2d		0.25	0.18
2e		2.6	3.1
	3a	11.0	14.0
	3b	0.31	2.1

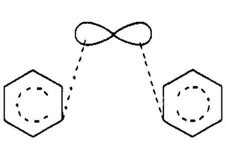
[a] Data for 1 and 2 from ref 4. The following average solvent ratios were used in calculating the relative rates: 50% EtOH/70% EtOH, 3.9; 70% TFE/97% TFE, 3.3.

This rate acceleration in the reactivity of 3 may be rationalized by π-participation of the aromatic groups resulting in the formation of the stabilized vinyl cation **15**.

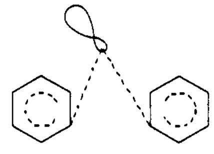


15a, R=H
b, R=CH_3

Similar π-participation was observed in the case of structures **7–9**, **12**, and **13**, which can all be classified as cations of type A with the orbitals of the electron-acceptor system (the empty p-orbital on the *saturated* carbon in **7–9** and **12** or the π-orbital of the tropylium moiety in cation **13**) being *perpendicular* (or almost perpendicular) to the plane of the methano, ethano, or etheno bridge of these structures. In contrast cation **15** belongs to type B which is characterized by interactions between the aromatic π-systems and the vacant sp-orbital on the *unsaturated* carbon, where this sp-orbital lies *in the plane* of the etheno bridge. These differences in the mode of charge delocalization in carbocations of types A or B are important because the interactions of the orbitals in type B are less pronounced than in the case of type A, and consequently the stabilization is less effective. However, we believe that the proposed mode of charge delocalization and stabilization in cation **15** is unique but viable due to the nature of vinyl cations.



A



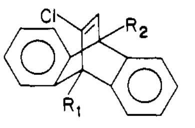
B

Vinyl cations are less stable than the corresponding secondary carbocations and, of course, even less stable than allylic and tropylium carbocations.[1] Therefore, vinyl cations (particularly cyclic vinyl cations) are very sensitive to any kind of stabilization. The demand for charge delocalization and stabilization is more pronounced in the solvolysis of cyclic vinyl substrates (such as **3a,b**) than in the case of the saturated substrates (which lead to cationic structures **7–9**, and **12**, as well as the hypothetical structure **10**) and systems which include highly stabilized allylic or tropylium cations (as salt **13**). Therefore the interaction of the empty p-orbital with the aromatic rings (particularly with the p-orbitals on the C_{4a} and C_{10a} centers) in structure **15** can significantly stabilize this cation and thereby enhance the reactivity of triflates **3a** and **3b** relative to cyclic triflates **2c–2e**.

The reactivity of the dimethyl-substituted triflate **3b** is reduced relative to the parent analogue **3a** (Table I). The two methyl substituents on the C_9 or C_{10} centers can sterically perturb the geometry of the cationic intermediate **15b** in such a manner that the interaction of vacant sp-orbital and the aromatic rings is diminished and the stabilization is less pronounced than in cation **15a**. Alternatively, differential solvation of the intermediate bridged ions, in highly polar aqeous media, from **3a** and **3b** due to the methyls in **3b**, may account for the slower reactivity of **3b** compared to **3a**. However, even this diminished stabilization is still effective enough to overcome the destabilizing factor of ring strain, resulting in the higher reactivity of triflate **3b** than of the cyclic vinyl triflates **2c–2e**. This π-participation and stabilization of cation **15b** are more effective in TFE (the solvent of low nucleophilicity and high ionization power[15]) than in aqueous EtOH. As a consequence **3b** is only slightly more reactive than cycloheptenyl triflate (**2d**) in aqueous EtOH whereas in aqueous TFE the reactivity of triflate **3b** is 10 times higher than that of **2d** and twice that of acyclic triflate **1**.

The observed activation parameters for triflates **3a** and **3b** (Table I) are fully consistent with the proposed explanation of their unusual reactivity. The $\Delta S^{\ddagger}$ values for the solvolysis of these triflates are highly negative, indicative of the charge delocalization in the transition states of these reactions.

Finally, we studied the products of solvolysis of triflate **3b** in 70% EtOH at 85 °C. Gas chromatography established that only one product was formed in this reaction. The IR spectrum and GC co-injection show it to be identical with precursor ketone **14b**. This result is consistent with the product study in the solvolysis of 11-chloro-9,10-ethenoanthracene (**16a**) (the chloro analogue of triflate **3a**) and its chlorinated derivatives **16b** and **16c**.[16] Acetolysis of the parent compound **16a** gave only the unrearranged ketone **14a**, whereas rearranged products were obtained when the bridgehead carbon atom (C_{10}) next to the positive charge was chloro substituted (compounds **16b** and **16c**).



16a, $R_1=R_2=H$
b, $R_1=Cl$, $R_2=H$
c, $R_1=R_2=Cl$

Experimental Section

Gas chromatography was performed on a Hewlett-Packard 5709 A instrument, on a 25 m × 0.31 mm (split ratio 100:1) column.

All melting points are uncorrected. Solvents and reagents were purified and dried by standard procedures immediately prior to use.

9,10-Dihydro-9,10-ethanoanthracen-11-one (**14a**)[11] and 9,10-dimethyl-9,10-ethanoanthracen-11-one (**14b**)[12] were prepared according to literature procedure.[17] Ketone **14b**: mass spectrum (chemical ionization), *m/z* 249 (M^+ + 1, 100%).

9,10-Dihydro-9,10-ethenoanthracen-11-yl Triflate (3a). This triflate was prepared according to our standard procedure.[13] Into a 50-mL round-bottom flask maintained under argon and equipped with a stirrer a solution of 2,6-di-*tert*-butyl-4-methylpyridine (1.03 g, 5.02 mmol) in dichloromethane (20 mL), ketone **14a** (550 mg, 2.50 mmol), and triflic anhydride (2.47 g; 8.75 mmol) are added sequentially. The mixture is stirred at room temperature for 3 days. The dichloromethane is rotary evaporated, and pentane (20 mL) is added to the residue. The pyridinium triflate is filtered off, and the pentane solution is washed with cold aqueous 10% HCl, saturated $NaHCO_3$, and saturated NaCl, and dried with $MgSO_4$. The pentane is removed and the residual product filtered through silica gel (2 g), using pentane–CH_2Cl_2 (1:1) as eluent. Evapo-

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ration of solvent gave pale-yellow crystals (661 mg, 75.1%): mp 45–56 °C; IR ($CDCl_3$, NaCl) 1636 ($C{=}C$), 1424, 1214, and 1141 (OSO_2CF_3), 765 and 748 cm^{-1} (aryl); ^1H NMR ($CDCl_3$, internal Me_4Si) δ 5.16 (d, 1 H, $C_9{-}H$), 5.22 (s, 1 H, $C_{10}{-}H$), 6.81–6.97 (m, 1 H, $C{=}C{-}H$), 7.08–7.30 (m, 4 H, ArH), 7.36–7.63 (m, 4 H, ArH). Mass spectrum: electron impact, *m/z* 352 (12%, M^+), 220 (17%, $C_{16}H_{12}O$), 204 (35%, $C_{16}H_{12}$), 203 (22%, $C_{16}H_{11}$), 192 (58%, $C_{15}H_{12}$), 179 (100%, $C_{14}H_{11}$); chemical ionization, *m/z* 353 (29%, $M^+ + 1$), 352 (16%, M^+), 222 (100%, $C_{16}H_{14}O$), 221 (31%, $C_{16}H_{13}O$), 179 (44%, $C_{14}H_{11}$).

9,10-Dimethyl-9,10-ethenoanthracen-11-yl Triflate (3b). This ester was prepared from ketone **14b** (570 mg, 2.30 mmol) by following the same procedure as described for the preparation of triflate **3a**. It was obtained (669 mg, 76.6%) as light-yellow crystals: mp 118 °C, dec; IR ($CDCl_3$, NaCl) 1630 ($C{=}C$) 1408, 1220 and 1150 (OSO_2CF_3), 775 and 750 cm^{-1} (aryl); ^1H NMR ($CDCl_3$, internal Me_4Si) δ 1.96 (3 H, s, $C_9{-}CH_3$), 3.15 (3 H, s, $C_{10}{-}CH_3$), 5.97 (1 H, s, $C{=}C{-}H$), 7.22–8.09 (8 H, m, ArH). Mass spectrum: electron impact, *m/z* 380 (100% M^+), 232 (27% $C_{18}H_{16}$), 231 (88%, $C_{18}H_{15}$); chemical ionization, *m/z* 381 (23%, $M^+ + 1$), 380 (25% M^+), 232 (100%, $C_{18}H_{16}$).

Kinetic Studies. Ethanol was purified according to Wiberg.[18] Trifluoroethanol was purified according to Shiner et al.[19] or Rappoport.[20] Solvents were prepared by weight from conductivity water (Millipore Systems) and appropriate organic solvents. Conductivity measurements were performed in sealed, paired cells by using a Hewlett-Packard Model 4274 A LCR bridge, with 5.5 digit precision, interfaced with a Hewlett-Packard Model 3497 A multiplexer and a Hewlett-Packard Model 9826 BASIC microcomputer. From 1 to 10 μL (depending on concentration) of a pentane solution of the triflate was utilized (in-cell concentration of triflate was ca. 2×10^{-4} M) for each run. Approximately 200 points at equal changes in perecent reaction was collected over a range 5–95% reaction. Rate constants were calculated by using a BASIC version nonlinear least-squares program written for the HP 9826 in our laboratories. Temperature control and measurement were accomplished by using a PRT-regulated proportional temperature controller and Hewlett-Packard quartz thermometer.

Product Study. Triflate **3b** was solvolyzed in 70% v/v EtOH at 85 °C for at least 10 half-lives. The capillary GLC analysis of the crude mixture showed only one product which was identical in IR with the authentic sample of ketone **14b**.

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Registry No. **3a**, 91759-14-7; **3b**, 91759-15-8; **14a**, 6372-63-0; **14b**, 73164-06-4.

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Thermochemistry of *trans*-Di-*tert*-butyl Hyponitrite

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Abstract: The heat of combustion of *trans*-di-*tert*-butyl hyponitrite, ΔH_{comb} = 1304.5 ± 1.8 kcal/mol, and its heat of vaporization, ΔH_v = 17.7 ± 0.3 kcal/mol, determined by an effusion technique, were used to calculate ΔH_f° = −41.3 ± 2.9 kcal/mol. This represents the first experimental determination of a heat of formation of a hyponitrite. From additivity relationships we estimate ΔH_f°(*trans*-$HON{=}NOH$) = 3.1 ± 3.1 kcal/mol, in good agreement with two reported values obtained by MO methods. The activation energies for homolysis of a number of *trans*-hyponitrites were estimated from additivity relationships, but did not agree well with experimental values. This result is associated with a compensating, linear relation between E_a and log A in the hyponitrite series.

The use of azo compounds for generation of radicals and biradicals has received an enormous amount of attention for theoretical[1a] and practical[1b] reasons, the bulk of which has focused on azoalkanes.[1a] We have elsewhere described the spectroscopy,[2a] kinetics,[2b] and excited-state yields[2c] from a number of *trans*-hyponitrites. In this paper we present the first experimental data on the heat of formation of an alkyl hyponitrite and derive relations between the thermochemistry and activation parameters of a series of these compounds.

Experimental Section

A sample of *trans*-di-*tert*-butyl hyponitrite was prepared[3] and recrystallized from CH_2Cl_2–CH_3OH at low temperature. The same batch of crystals was used for combustion and effusion measurements. The purity of the material was established from the melting point (84.5 °C dec; lit.[4] 84–84.5 °C dec) and UV spectrum (λ_{max} 223.4 nm (ϵ 7140 M^{-1} cm^{-1}) in pentane; lit.[5] λ_{max} 223.4 nm (ϵ 7130 M^{-1} cm^{-1})). **Caution:** The substance can detonate if struck.

Table I. Combustion Data for Di-*tert*-butyl Hyponitrite

wt, g	ΔT, °C	HNO_3 correction, cal	fuse correction, cal	$\Delta H_{combustion}^{298}$ cal/g	$\Delta H_{combustion}^{298}$ kcal/mol
0.28942	0.980	9.55	11.5	7510.01	1306.74
0.36789	1.152	14.00	17.6	7482.49	1301.95
0.28620	0.892	10.80	0	7492.58	1303.71
0.38140	1.190	14.20	0.5	7502.70	1305.47
0.30811	0.960	10.30	0	7497.39	1304.55

p-Bromochlorobenzene (Aldrich) was recrystallized from dichloromethane: mp 66.5–67 °C (lit.[6] 68 °C); λ_{max} 224.2 nm in isooctane (ϵ 1.26 × 10^4 M^{-1} cm^{-1}).

The heat of combustion of solid DBH was determined with a constant volume Parr Model 1241 adiabatic bomb calorimeter, standardized with

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