Thermolysis and photolysis of 1-substituted triptycenes. Divergent fragmentation pathways of the triptycyl skeleton

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While thermolysis of 1-benzyltriptycene 1a in the gas phase at 600 °C/10^{-4} mmHg did not result in any appreciable decomposition, similar pyrolysis of compounds 1 bearing various substituents (X) at the benzyl methylene (1b–d) underwent smooth decomposition to give 8-benzylbenz[*a*]aceanthrylene 2. The reaction is explained in terms of homolysis of the C–X bond followed by triptycyl ring cleavage in the resulting benzyl radical 7. Generation of radical 7 in solution, however, did not result in a similar ring-opening reaction. Irradiation of compounds 1, on the other hand, afforded norcaradienes 3 almost exclusively, obviously as a result of di-π-methane rearrangement. No products resulting from a carbene species proposed to be involved in the di-π-methane reaction of triptycenes were detected. Thermolysis of compounds 3 gave not only compound 2 but also benz[*a*]aceanthrylene 4 and benz[*a*]indeno[1,2,3-*cd*]azulene 5 whose compositions were found to be sensitive to both the substituent (X) and the thermolysis temperature.

Mechanisms of the reactions are discussed in terms of the relationship between the thermal and photochemical fragmentations.

Introduction

Thermolysis and photolysis of cyclic compounds often result in reactions triggered by ring cleavage upon excitation.[1,2] Curiosity about the relationship between the thermal and photochemical fragmentations has been an important stimulus to research in this area since the eventual reactions upon excitation sometimes reflect the difference in energies and environments. Investigations along this line also provide insight in order to gain comprehensive understanding of the relationship between reactivity and structure. Triptycene is an especially interesting group in this connection due to its potential reactivities arising from ring strain and its unique alignment of 'triptyc' benzene rings. While skeletal reorganization of triptycenes upon photoexcitation has been relatively well studied [3,4] and attracted much attention in connection with its rigid and unique cyclic structure, almost no information is currently available concerning its thermal reactivity. Thus, we carried out thermolysis of triptycenes bearing substituents at one of the bridged positions and found that while the triptycene ring system itself was thermally stable, it was easily cleaved once a radical centre was generated on the substituent α carbon.

Results

Preparation of 1-benzyltriptycenes 1

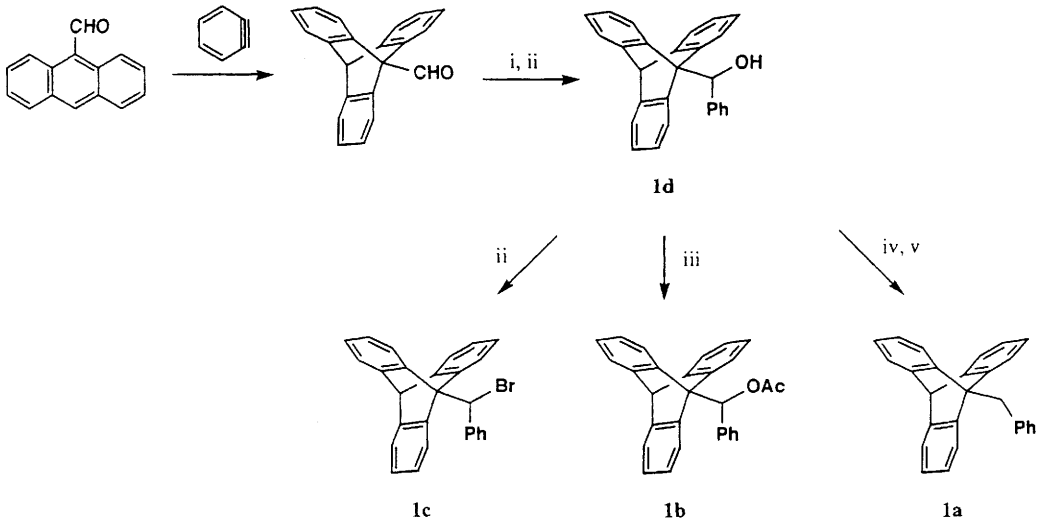
Triptycenes bearing a series of leaving groups were prepared according to the procedures outlined in Scheme 1. Thus, 1-formyltriptycene, obtained by Diels–Alder addition of benzene to 9-formylanthracene, was treated with phenyllithium to give compound **1d**, which was then converted into the corresponding acetate **1b** and bromide **1c** by the conventional method. These compounds **1** were obtained as stable solids or oils which could be handled without any special precautions.

Flash vacuum pyrolysis (FVP) of compounds 1

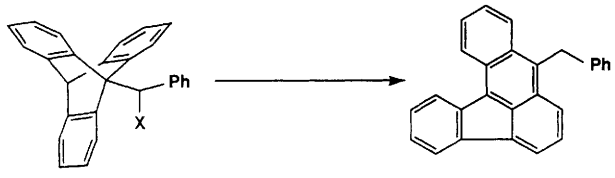
A series of FVP experiments of compounds **1** were conducted from 300 to 600 °C at 10^{-4} mmHg in the reaction zone and the pyrolysate was collected at −196 °C. FVP of compound **1a** did not result in any appreciable decomposition of the starting compound even at 600 °C. In marked contrast, benzyltriptycenes bearing leaving groups at the benzyl methylene underwent smooth decomposition upon FVP. Thus pyrolysis of compound **1b** at 600 °C afforded 8-benzylbenz[*a*]aceanthylene (**2**, 49%) as the sole isolable volatile product. Similar FVP of the bromide **1c** also gave compound **2** (47%) as a major product along with a small amount (< 1%) of debrominated substrate **1a** in this case, while the alcohol **1d** was found to be very much less reactive (Scheme 2). The identity of compound **2** was established by comparison of its spectra (^{1}H NMR, MS) with those of an authentic specimen prepared by the $LiAlH_4$–$AlCl_3$ reduction of 8-benzoylbenz[*a*]aceanthrylene. The observations suggest that, while the triptycene skeleton is thermally fairly stable, the cyclic structure is easily cleaved once a leaving group is introduced at the position adjacent to the bridging carbon.

Photolysis of compounds 1

Irradiations of a solution of a benzyltriptycene **1** either in methanol or in cyclohexane were carried out in a quartz tube with a low-pressure Hg lamp at room temperature. Photolysis of compounds **1** proceeded smoothly under these conditions regardless of the nature of the substituent X to give norcaradienes **3** as the sole isolable product, except for compound **1c** which was essentially recovered unchanged (Scheme 3). The reluctance of compound **1c** to undergo photolysis to the hexacycle **3c** is obviously due to the inner-filter effect of an intense yellow colour developed immediately after commencement of the irradiation. The norcardiene structure for products **3** was assigned not only on the basis of ^{1}H NMR spectra showing a doublet at δ 2.80 assignable to the cyclopropane ring protons but also by the characteristic UV–VIS absorption band at around 350 nm.[4] The isolation of norcaradienes **3** as stable solids after chromatographic separation on silica gel is rather surprising in the light of preceding observations that many norcaradienes are unstable and undergo rearrangement, especially upon chromatography even on neutral alumina as well as on treatment with dilute acid or on heating, to give benz[*a*]aceanthrylene **4**.[3,4] More interestingly, by-products often reported[4] to be formed in the photolysis of triptycenes, presumably from carbenic intermediate, *i.e.*, 2-(fluoren-9-yl)phenylcarbenes **6**, were not detected at least under these irradiation conditions.



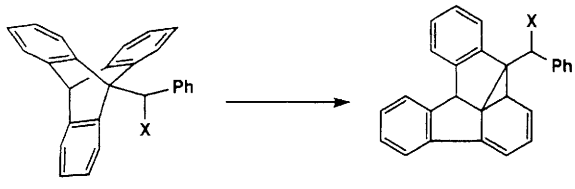
Scheme 1 *Reagents and conditions:* i, PhLi, PhH; ii, aq. NH_4Cl; iii, PBr_3, 1,4-dioxane; iv, Ac_2O, H^+; v, CrO_3, H_2SO_4; vi, KOH, N_2H_4, EtOH, 130 °C



1 2

	Yield (%)
a; X = H	0
b; X = OAc	49
c; X = Br	47
d; X = OH	4

Scheme 2 *Conditions:* FVP, 600 °C



1 3

	Yield (%)
a; X = H	33
b; X = OAc	62
c; X = Br	0
d; X = OH	38

Scheme 3 *Conditions: hv*

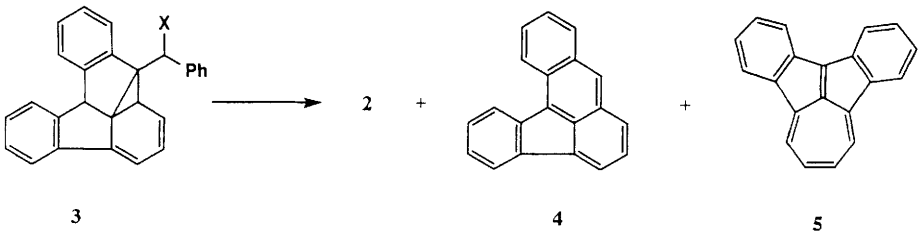
FVP of norcaradienes 3

In order to obtain more insight into the thermal properties of the norcaradiene structure, compounds **3** (**a**, **b** and **d**) obtained in the photolysis compounds **1** were subjected to thermolysis. Heating of norcaradienes **3** in refluxing xylenes for 1 h resulted in the recovery of the starting compounds without showing any products, thus confirming the thermally stable nature of norcaradienes **3**. FVP at 300 °C of compounds **1**, on the other hand, resulted in appreciable decomposition to produce three products depending on the reaction temperatures and substituent X. Thus, FVP of compound **3a** gave pentacycle **4** as the sole isolable product, while FVP of **3b** at 300 °C gave compound **2** in 90% yield, no parent pentacycles **4** and **5** being detected. FVP of compound **3b** at much higher temperature, however, afforded benz[*a*]aceanthrylene **4** at the expense of compound **2**. FVP of compound **3d** at 300 °C, finally, gave benz[*a*]indeno[1,2,3-*cd*]azulene **5**[4f] at the complete expense of compound **4** which appeared as a minor product in higher temperature (600 °C) thermolytic runs, no compound **2** being formed under either set of conditions (Scheme 4).

Discussion

There are several *a priori* possible pathways for the formation of compound **2** in FVP of triptycenes **1b–d**. Formation of compound **2** in the FVP of the norcaradiene **3b**, for example, may indicate that, upon heating, compound **1b** was first converted into compound **3b** which then undergoes subsequent reorganization leading to compound **2** in a hot-tube. Formation of compound **3b** can be explained in terms of expulsion of the bridgehead carbon followed by intramolecular addition of the resulting carbene **6b** to the aromatic ring and a 1,5-sigmatropic shift. However, this possibility is eliminated in the light of the fact that FVP of compound **3b** at 600 °C, where the triptycene **1b** produced only compound **2**, afforded benzaceanthrylene **4** as main product at the expense of compound **2**. This is further supported by the completely different results observed for FVP of compound **1d** and photolysis of the norcaradiene **3d** not only in terms of reactivity but also in the product structures. Furthermore, the putative carbene **6** should undergo 1,2-H migration [5] at least faster than the addition to the aromatic ring to give alkenes (*i.e.*, **13**, *vide infra*).

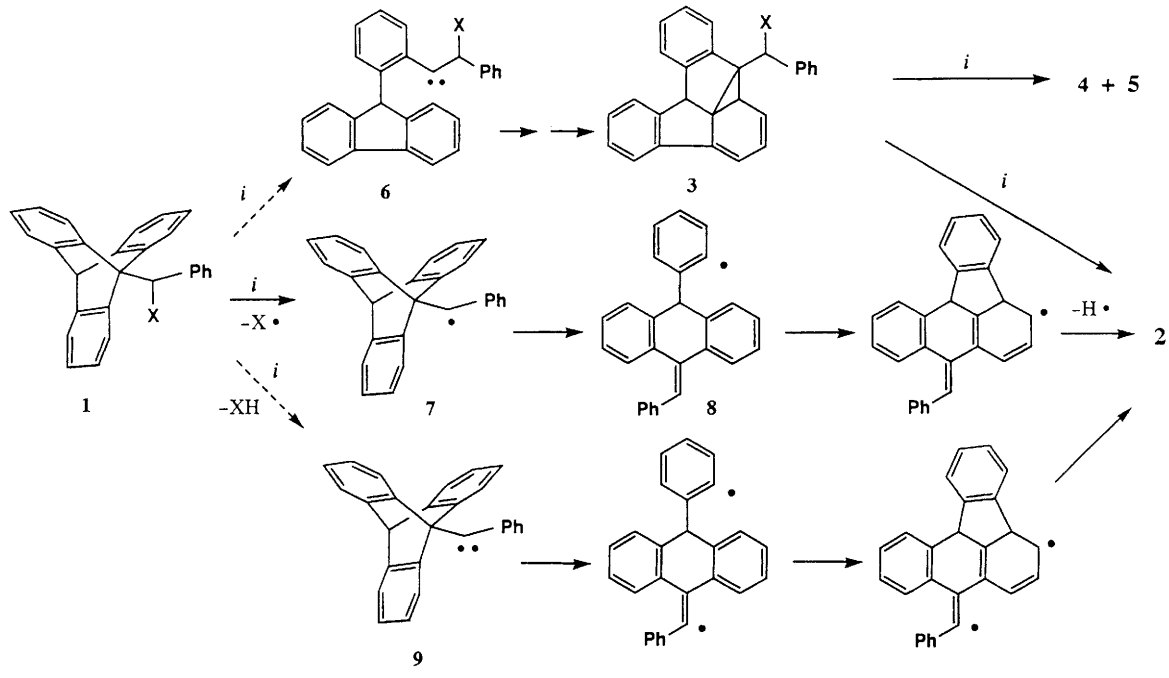
A more likely possibility is that the reaction is initiated by cleavage of α-substituents (X) upon heating to leave the benzyl radical **7**. Apparent dependence of the reactivities of triptycenes **1** on the leaving ability of X and, more convincingly, almost complete inertness of compound **1a** to the thermolysis support this assumption. The radical then undergoes cleavage of a bridgehead C–C bond to generate a phenyl radical **8**, which is trapped intramolecularly by the proximate aromatic ring to lead to the final product as a result of extrusion of HX. It may be that triptycenes **1** undergo α-elimination either directly or by way of the radical **7** to generate a carbene **9** since it is well known [1] that α-elimination of a carboxylic acid from an ester in which normal β-elimination is not structurally possible occurs with formation of an intermediate carbene. An essentially similar rearrangement as outlined for radical **7** can be applied for the carbene **9** to explain the formation of compound **2**. However, preferential formation of a species with higher energy, *i.e.*, carbene, is less likely especially when the other pathway involving a lower energy species is available. Moreover, it is well documented [1,5b,6] that phenylcarbenes generated in the gas phase undergo carbene–carbene rearrangement where a divalent centre is transmitted from one site to another through a benzene ring. We were not able to detect any product other than compound **2**



3 4 5

	T/°C		Yield (%)	
a; X = H	300	<1	56	0
b; X = OAc	600	<1	0	31
c; X = OH	300	90	0	0
	600	21	41	<1
	300	0	<1	34
	600	0	13	25

Scheme 4 *Conditions:* FVP

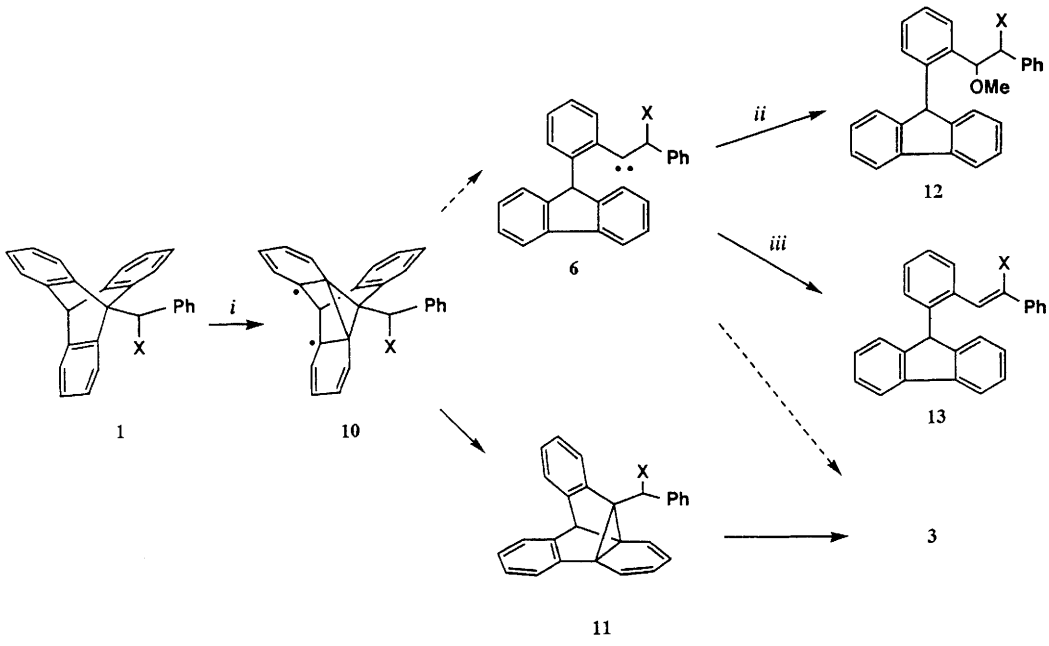


Scheme 5 *Conditions:* i, reflux

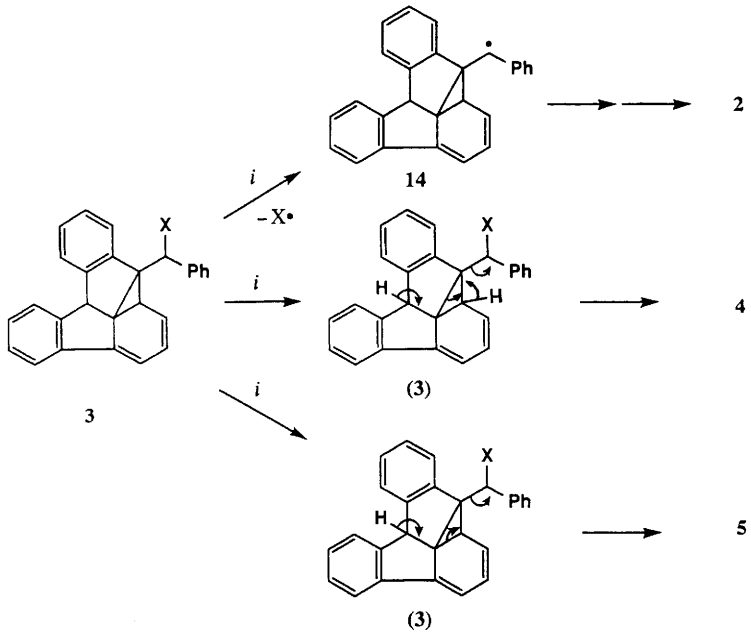
in the pyrolytic mixture. See Scheme 5 for routes from the triptycenes **1** to compound **2**.

Formation of norcaradienes **3** in the irradiation of triptycenes **1** is, on the other hand, not unusual in terms of the product structure since similar photochemical reorganization of triptycene derivatives has been well documented.[3,4] A reaction pathway has been proposed[3] with a 'normal' di-π-methane rearrangement[7] in which the semibullvalene **11** is formed as an initial product which then undergoes a thermal sigmatropic rearrangement to give the final norcaradiene product. However, based upon examination of the rearrangement using trapping experiments either intermolecularly or intramolecularly, the intervention of a carbene which is generated from the initial cyclopropyldicarbinyl diradical **10** presumably due to the driving force of rearomatization is proposed.[4] In the present photomixtures from triptycenes **1**, however, no products expected from carbene **6** were detected. Thus, no methyl ethers **12** expected to be formed as a result of O–H insertion into carbene† were detected in the photomixture in methanol and no trace of alkenes **13** presumed to be produced by a 1,2-H migration were formed (see Scheme 6). ^{1}H NMR analysis of the photomixture obtained in the early stage of the reaction also showed that only a norcaradiene **3** was present as a product, suggesting that products **3** were not formed from initial carbenic products during work-up procedures. In the light of preceding observations that triptycenes bearing a 1-substituent such as H,[4a] Ph,[4i] Ac,[4a] RO,[4d,e] RS[4f] and ROCO[4f] are all shown to generate carbene upon photoexcitation, it is rather surprising to note that the intermediacy of carbene is not attained simply upon such a small change in the substituent structure. Recently, however, a more detailed study of photochemistry of 1-benzyloxytriptycenes has been carried out,[4h] which reveals that the norcaradiene is formed in a one-photon process as an initial product while the products from α-alkoxycarbene are produced by a two-photon pathway probably by secondary photolysis of the initially formed norcaradiene. A notable difference in the photochemistry between those triptycenes thus far reported and the present system is that, while the final norcaradiene products are detected but not stable enough to be isolated from the photomixture in the previous examples, the dienes **3** are rather inert not only to the work-up procedure but also to the irradiation, and are isolated without any precautions being necessary. It is quite reasonable then to propose that photochemical rearrangement of triptycenes must proceed by way of the 'normal' di-π-methane rearrangement followed by 1,5-sigmatropic shift, as was originally suggested by Walsh,[3a] and that the carbenic products are formed in the previous example simply because the final norcaradienes happened to be

† For a review of O–H insertion into carbenes, see ref. 4*i*.



Scheme 6 *Reagents and conditions:* i, *hν*; ii, MeOH; iii, ~H



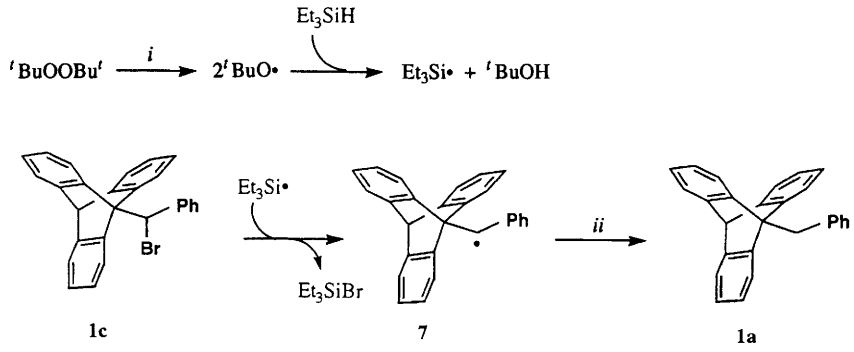
Scheme 7 *Conditions:* i, reflux

very sensitive to irradiation. It should be noted here that the other aspects of the present rearrangement of triptycenes **1** are essentially similar to that observed for the other triptycenes. Thus, no products originating from the bridging of the di-π-methane moiety to the opposite site of the phenyl rings are formed.

Thermolytic reactions of the photoproduct **3** are rather divergent and sensitive to the substituent X. Thus, compound **2** is formed only when the substituent (X) is a good leaving group. This suggests that the reaction leading to compound **2** is initiated by cleavage of C–X bond to generate a radical **14** which then undergoes opening of the bridging C–C bond (Scheme 7). Elimination of the bridgehead H followed by 1,3-H shift will form compound **2**. When X is not a good leaving group, two reactions involving ring cleavage of the norcaradiene cyclopropane and elimination of the substituent on the ring, already observed[3,4] in the other more unstable norcaradienes at much lower temperatures, take place. Among these reactions, formation of the aceanthrylene **4** is more common than that of the azulene **5**, which is known[4f] only in the case where the norcaradiene cyclopropane has a very good leaving group such as OCOR. In the present FVP reaction, formation of the azulene is also observed only for compound **3d**. The exact mechanism which controls these two competing pathways is not clear at this time.

Conclusions

The present investigation reveals that, while the triptycene skeleton is thermally fairly stable in contrast to its photolability, ring-opening is induced by the generation of a radical centre on the α-position of the 1-substituent. One would naturally wonder whether analogous reactions are feasible for this radical in a fluid solution at much lower temperature. In order to check this possibility we irradiated a benzene solution containing the bromide **1c**, di-*tert*-butyl peroxide and triethylsilane since the Et_3Si radical generated in this system has been shown to abstract bromine from alkyl bromides, leaving the correspond-



Scheme 8 *Reagents and conditions:* i, *hν*/reflux; ii, Et_3SiH

ing alkyl radical in many cases.[8] Product analysis of the photomixture showed the presence of the reduction product **1a**, no trace of compound **2** being detected (Scheme 8). Essentially the same results were obtained when the system was pyrolysed at 170 °C in a sealed tube. The use of tributylstannane instead of triethylsilane also gave the same result. These control experiments demonstrate that the ring-opening in the radical is not an energetically favourable pathway. In the solution, the radical **7** is presumably readily quenched by hydrogen donors, *e.g.*, the silane, before it undergoes ring cleavage. This is reasonable since the ring cleavage requires C–aromatic bond cleavage generating a phenyl radical. In the gas phase, in other words, the radical undergoes ring-opening not only because other low-energy processes are not available but also because it is generated in a vibrationally excited state due to lack of the vibrational cooling of the excessive energy under those highly unimolecular environments.

Experimental

General methods

IR spectra were measured on a JASCO A-100 recording spectrometer, and mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ^1H and ^{13}C NMR spectra were determined with a JEOL JNM-EX 270 spectrometer, and *J* values are given in Hz. UV/VIS spectra were determined with a JASCO V-560 spectrometer. Preparative TLC (PLC) was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral). HPLC and GPC were undertaken with a JASCO 800 chromatograph equipped with a UVIDEC-100II UV/VIS detector using a Fine pack C18-T5 column (4.6 × 25 cm) and a Shodex GPC H-2001 (20 mm × 50 cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using an OV-17 on Diazolid L (5.0 mm × 50 cm).

Preparation of 1-(α-hydroxybenzyl)triptycene 1d

To Grignard reagent prepared from bromobenzene (0.23 cm^3, 2.2 mmol, 2.0 mol equiv.) and Mg (58 mg, 2.4 g-atoms, 2.2 mol equiv.) in dry Et_2O (4 cm^3) under N_2 was added a solution of 1-formyltriptycene[9] (300 mg, 1.1 mmol, 1.0 mol equiv.) in dry benzene (10 cm^3) dropwise over a period of 30 min and the mixture was stirred for 2 h. The reaction was quenched with saturated aq. NH_4Cl (50 cm^3). The combined organic layer was separated, and the aqueous phase was extracted with Et_2O (50 cm^3). The combined organic layers were dried over anhydrous Na_2SO_4. After evaporation off of the solvent, the crude viscous residue (470 mg) was chromatographed on silica gel with hexane–CH_2Cl_2 (1 : 1) to give 1-(α-hydroxybenzyl)triptycene **1d** (290 mg, 73%) as a viscous liquid; $\delta_H(CDCl_3)$ 1.62 (1 H, d, *J* 4.62), 5.42 (1 H, s), 6.51 (1 H, d, *J* 4.62), 6.89–7.04 (3 H, m), 7.07–7.24 (2 H, m), 7.30–7.40 (5 H, m), 7.47–7.56 (3 H, m), 7.72 (1 H, d, *J* 7.59) and 7.91 (1 H, d, *J* 7.59); $\delta_C(CDCl_3)$ 55.4, 58.4, 73.7, 123.4, 123.7, 124.0, 124.2, 124.6, 125.4, 125.5, 125.6, 125.8, 128.2, 128.3, 128.4, 130.8, 140.6, 141.9, 144.3, 146.9, 147.0, 147.5 and 147.8; *m/z* (rel. int.) 361 (M + 1, 100%), 360 (M^+, 94.2), 358 (27.4), 343 (23.5), 342 (23.5), 254 (23.9), 253 (65.4) and 78 (23.3).

Preparation of 1-(α-acetoxybenzyl)triptycene 1b

To a solution of alcohol **1d** (240 mg, 0.67 mmol, 1.0 mol equiv.) in Ac_2O (1 cm^3) was added a catalytic amount of conc. H_2SO_4 (~ 0.05 cm^3) with stirring at room temperature. After 5 min, the reaction mixture was poured into ice–water and extracted with Et_2O. The organic layer was successively washed with 5% $NaHCO_3$ and brine, and was dried over anhydrous Na_2SO_4. Evaporation off of the solvent afforded 256 mg of a yellow oil which was purified by PLC using CH_2Cl_2–hexane (1 : 2). 1-(α-Acetoxybenzyl)triptycene **1b** (228 mg, 85%) was obtained as a yellowish viscous liquid; $\delta_H(CDCl_3)$ 2.12 (3 H, s), 5.40 (1 H, s), 6.65–6.70 (2 H, m), 6.87–7.03 (4 H, m), 7.11 (1 H, dd, *J* 6.93 and 7.26), 7.23–7.37 (6 H, m), 7.49 (1 H, d, *J* 6.93), 7.67 (2 H, d, *J* 7.25), 7.80 (1 H, s) and 7.94 (1 H, d, *J* 7.92); $\delta_C(CDCl_3)$ 21.9, 55.0, 57.7, 73.7, 121.0, 123.3, 123.4, 123.6, 124.0, 124.2, 124.9, 125.0, 125.1, 125.4, 128.0, 128.5, 131.2, 137.7, 142.2, 143.3, 145.8, 146.3, 146.7, 147.0 and 171.8; ν_{max}(NaCl)/cm^{-1} 1728s, 1448s, 1368m and 1232s; *m/z* (rel. int.) 403 (M + 1, 100%), 402 (M^+, 88.0), 361 (23.9), 360 (23.9), 342 (33.5), 269 (61.8) and 253 (40.2).

Preparation of 1-(α-bromobenzyl)triptycene 1c

A dioxane (10 cm^3) solution of compound **1d** (240 mg, 0.67 mmol, 1.0 mol equiv.) and PBr_3 (0.19 cm^3, 2.0 mmol, 3.0 mol equiv.) was heated at reflux for 3 h. The reaction mixture was poured into crushed ice and the aqueous phase was extracted with Et_2O. The organic layers were successively washed with water and brine, and dried over anhydrous Na_2SO_4. After evaporation of the solution under reduced pressure, a yellowish residue (300 mg) was purified by PLC with CH_2Cl_2–hexane (1 : 2) to afford 1-(α-bromobenzyl)triptycene **1c** (245 mg, 86%) as a yellowish solid, mp 251.9–256.0 °C (from CH_2Cl_2); $\delta_H(CDCl_3)$ 5.38 (1 H, s), 6.50–6.70 (2 H, m), 6.80–6.96 (2 H, m), 6.96–7.17 (6 H, m), 7.22–7.40 (5 H, m), 7.52 (1 H, d, *J* 7.26), 8.05 (1 H, d, *J* 7.59) and 8.21 (d, *J* 6.93); $\delta_C(CDCl_3)$ 53.3, 54.9, 57.5, 123.3, 123.4, 123.5, 123.7, 123.8, 124.0, 124.5, 124.8, 124.9, 125.0, 125.6, 128.1, 128.5, 139.4, 140.7, 143.1, 145.6, 145.7, 146.8 and 148.0; *m/z* (rel. int.) 424 (M + 2, 8.1%), 422 (M^+, 8.1), 361 (45.9), 360 (49.1), 345 (20), 344 (42.5), 343 (36.8), 266 (32.3), 265 (36.5), 254 (85.5), 253 (100) and 252 (69.0).

Preparation of 1-benzyltriptycene 1a

A mixture of CrO_3 (111 mg, 1.1 mmol, 1.5 mol equiv.), water (0.72 cm^3), conc. H_2SO_4 (0.06 cm^3) was added dropwise to a stirred solution of **1d** (260 mg, 2.2 mmol, 1.0 mol equiv.) in acetone (10 cm^3). The mixture was stirred for 2 h at room temp. The solution was poured into water. The aqueous phase was extracted with CH_2Cl_2, and the organic layer was washed with 5% aq. $NaHCO_3$ and dried over Na_2SO_4. Evaporation off of

the solvent afforded almost pure 1-benzoyltriptycene (260 mg, ~100%) as a solid, which was used for reduction without further purification, mp 235.1–238.6 °C; $\delta_H(CDCl_3)$ 5.40 (1 H, s), 6.89 (3 H, dd, *J* 7.26 and 7.59), 7.00 (3 H, dd, *J* 7.26 and 7.59), 7.29–7.34 (3 H, m), 7.42 (2 H, d, *J* 7.26), 7.52 (3 H, d, *J* 7.58) and 7.81 (2 H, d, *J* 6.93); $\delta_C(CDCl_3)$ 54.8, 63.1, 123.4, 124.6, 125.4, 125.7, 127.8, 131.1, 132.8, 137.9, 144.5, 145.8 and 199.5; ν_{max}(KBr)/cm^{-1} 1672s, 1592m, 1440s, 1240s and 744s; *m*/*z* (rel. int.) 358 (M^+, 69.3%), 339 (23.6), 254 (23.6), 253 (100), 252 (67.9), 105 (56.9) and 77 (33.1).

A mixture of the ketone (250 mg, 0.7 mol, 1.0 mol equiv.), KOH (200 mg, 3.5 mmol, 5.0 mol equiv.) and dry hydrazine (1/7 cm^3, 53 mmol, 75 mol equiv.) in dry EtOH (2 cm^3) was placed in an autoclave. The autoclave was gradually heated to 130 °C and kept for 24 h. After cooling, the mixture was poured into crushed ice and the aqueous phase was extracted with Et_2O. The organic layer was dried over anhydrous $MgSO_4$. After evaporation off of the solvent, the residual yellowish oil (240 mg) was purified by PLC on silica gel with CH_2Cl_2–hexane (1:3) to afford 1-benzyltriptycene **1a** (218 mg, 90%) as crystals; mp 136.1–142.2 °C; $\delta_H(CDCl_3)$ 4.48 (2 H, s), 5.45 (1 H, s), 6.90 (3 H, dd, *J* 7.25 and 7.59), 6.98 (3 H, dd, *J* 7.26 and 7.59), 7.20–7.39 (9 H, m) and 7.69 (2 H, d, *J* 7.26); $\delta_C(CDCl_3)$ 33.1, 51.8, 54.1, 122.9, 123.0, 124.0, 124.5, 125.2, 127.2, 130.1, 136.7, 145.2 and 146.1; *m*/*z* (rel. int.) 344 (M^+, 35.7%), 254 (22.6), 253 (100) and 252 (58.6).

Preparation of 8-benzylbenz[*a*]aceanthrylene 2[10]

To a solution of benz[*a*]aceanthrylene **4** (126 mg, 0.50 mmol, 1.0 mol equiv.), prepared by using procedure of Cho and Harvey,[11] in dry CS_2 (20 cm^3) was added $AlCl_3$ (760 mg, 5.7 mmol, 12.4 mol equiv.) under argon. To this stirred mixture was added dropwise a solution of benzoyl chloride (77.3 mg, 0.55 mmol, 1.1 mol equiv.) in CS_2 (5 cm^3) over a period of 45 min. The resulting mixture was stirred for an additional 30 min and quenched with ice. The aqueous phase was extracted with Et_2O and the combined organic layers were dried over anhydrous Na_2SO_4. The crude mixture (150 mg) obtained after evaporation of the solution was subjected to PLC on silica gel with CH_2Cl_2–hexane (1:2) to afford benzoylbenz[*a*]aceanthrylene (132 mg, 77%) as a yellow liquid; $\delta_H(CDCl_3)$ 7.42–7.64 (7 H, m), 7.67 (1 H, d, *J* 8.85), 7.70 (1 H, d, *J* 8.55), 7.85 (2 H, d, *J* 7.02), 7.91 (1 H, d, *J* 8.85), 8.00 (1 H, d, *J* 6.41), 8.02 (1 H, d, *J* 7.63), 8.45 (1 H, d, *J* 7.63) and 8.85 (1 H, d, *J* 8.85); ν_{max}(KBr)/cm^{-1} 1664s, 1592m and 1448s.

To a suspension of $LiAlH_4$ (91 mg, 2.4 mmol, 10.0 mol equiv.) in dry tetrahydrofuran (30 cm^3) was added the ketone (100 mg, 0.28 mmol, 1.0 mol equiv.) under Ar. The mixture was heated at reflux for 4 h, then was cooled to 0 °C and $AlCl_3$ (160 mg, 1.4 mmol, 5.0 mol equiv.) was added in small portions. The mixture was heated at reflux for 2 h and the excess of $LiAlH_4$ was hydrolysed with water (3 cm^3). The organic layer was decanted, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (~40 cm^3) and the solution was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was subjected to PLC with hexane to afford compound **2** (78 mg, 86%) as orange crystals, mp 177.9–179.5 °C; $\delta_H(CDCl_3)$ 5.08 (2 H, s), 7.12–7.20 (5 H, m), 7.40 (1 H, dd, *J* 7.26 and 7.58), 7.46–7.52 (2 H, m), 7.62–7.69 (2 H, m), 8.01–8.04 (2 H, m, ArH), 8.22 (1 H, d, *J* 8.91, ArH), 8.33 (1 H, d, *J* 8.58, ArH), 8.40 (1 H, d, *J* 7.26) and 8.83 (1 H, d, *J* 8.58); $\delta_C(CDCl_3)$ 28.0, 114.4, 116.1, 118.1, 119.3, 119.4, 119.7, 120.5, 120.8, 121.2, 121.4, 122.0, 122.3, 122.4, 122.7, 123.0, 124.0, 124.8, 125.2, 127.1, 129.3, 131.9, 133.3, 134.8 and 135.6; λ_{max}(cyclohexane) (log ε)/nm 431.5 (3.48), 367.5 (3.20), 275.0 (4.25), 259.5 (4.29) and 242.5 (4.12) (Found: M^+, 342.1363. Calc. for $C_{27}H_{18}$: M, 342.1407).

Flash vacuum pyrolysis

The apparatus used for the FVP consisted of a quartz tube (30 mm i.d. × 35 cm long) maintained at the desired temperature by resistance wire. The tube was fitted with a loose plug of quartz wool 10 cm below the top of the heated zone. At the top of the tube, provision was made for the introduction of solid reactants *via* a solid addition tube. The lower end of the tube was fitted with consecutive U-tubes that were immersed in liquid nitrogen. The pyrolysis tube was bent near the bottom such that the pyrolysis zone was angled about 35° from the vertical.

In a typical experiment, the sample (~15 mg) coated on an inert support such as powdered quartz was placed in the top tubes and added gradually from the top tube at an operating pressure of 10^{-4} mmHg.‡[,12] The volatile products were collected in a trap cooled with liquid nitrogen, and individual components were isolated either by PLC or GPC and identified by NMR and MS. For analytical runs, the sample was washed out of the trap with CH_2Cl_2; the wash was diluted to 5.0 cm^3 and an internal standard was added for NMR analysis.

FVP of compound 3a. Pyrolysis of compound **3a** (15 mg, 0.043 mmol) at 300 °C afforded compound **4** (56%) along with a trace amount of compound **2**. Similar FVP of compound **3a** at 600 °C gave compound **5** (31%) as a main component.

FVP of compound 3b. Pyrolysis of compound **3b** (15 mg, 0.042 mmol) at 300 °C afforded compound **2** almost exclusively (90%). FVP at 600 °C gave compound **4** (41%) in addition to compound **2** (21%).

FVP of compound 3d. Pyrolysis of compound **3d** (15 mg, 0.042 mmol) at 300 °C afforded compound **5** (34%), along with trace amounts of compound **4**. The yield of the mixture was changed [**4** (13%), **5** (25%)] when FVP was carried out at 600 °C.

Irradiation for product identification. In a typical run, a solution of compound **1** (~100 mg) in a solvent was placed in a quartz tube and degassed by bubbling dry argon immediately prior to irradiation. Irradiation was carried out with a low-pressure, 30 W mercury lamp at room temperature unless otherwise noted. The mixture was then concentrated on a rotary evaporator below 10 °C. Individual components were isolated by PLC and/or gel permeation chromatography (GPC) and identified by NMR and MS.

Photolysis of compound 1a. Irradiation of compound **1a** (100 mg, 0.29 mmol) in MeOH (60 cm^3) in a quartz tube for 2 h gave the norcaradiene **3a** [42 mg, 0.12 mmol, 42% (52% conversion)] as a yellowish liquid after GPC purification; $\delta_H(CDCl_3)$ 2.60 (1 H, d, *J* 16.52), 2.79 (1 H, d, *J* 16.52), 2.80 (1 H, d, *J* 4.95), 4.60 (1 H, s), 6.02 (1 H, dd, *J* 4.94 and 9.24), 6.27 (1 H, dd, *J* 5.94 and 9.57), 6.46 (1 H, d, *J* 5.94), 6.96–7.10 (m), 7.16–7.18 (5 H, m), 7.26–7.29 (2 H, m) and 7.52–7.56 (3 H, m); λ_{max}(cyclohexane)/nm (log ε) 251.0 (4.04) and 348.5 (3.61).

Photolysis of compound 1b. Irradiation of compound **1b** (100 mg, 0.25 mmol) in MeOH (60 cm^3) in a quartz tube for 2 h afforded compound **3b** [62 mg, 0.16 mmol, 62% (75% conversion)] as a yellowish oil after PLC with CH_2Cl_2–hexane (1:2) as eluent. The major isomer was isolated by re-crystallization (EtOH) as crystals, compound **3b** (major isomer) (20 mg, 0.05 mmol, 20%), crystals; mp 202.3–205.7 °C; $\delta_H(CDCl_3)$ 1.36 (3 H, s), 2.92 (1 H, d, *J* 5.28), 4.60 (1 H, s), 5.83 (1 H, s), 6.20 (1 H, dd, *J* 5.28 and 9.24), 6.33 (1 H, d, *J* 7.59), 6.44–6.52 (2 H, m), 6.96 (1 H, dd, *J* 7.26 and 7.92), 7.18–7.39 (8 H, m) and 7.54–7.59 (3 H, m); $\delta_C(CDCl_3)$ 20.1, 28.5, 40.3, 51.4, 55.2, 70.1, 111.1, 120.8, 121.0, 124.2, 124.7, 125.2, 126.7, 126.8, 126.9, 127.0, 127.1, 127.8, 128.3, 128.4, 139.4, 139.7, 140.0,

‡ All attempts to introduce the sample by sublimation through the hot zone resulted in the decomposition of the sample within the zone even at very low pressure to afford rather complex product mixtures. This is due to the fact that most samples were highly involatile and thermally unstable. We have checked that the samples were stable on powdered quartz supports and hence suppose that the reaction is not catalysed by the support.

144.1, 144.9, 145.3 and 170.4; ν_{max}(KBr)/cm^{-1} 1720s, 1456m, 1368s, 1240s, 1024s, 744s and 704s; λ_{max}(cyclohexane) (log ε)/nm 248.0 (3.88) and 338.5 (3.25).

Photolysis of compound 1d. Irradiation of compound **1d** (100 mg, 0.28 mmol) in MeOH (60 cm^3) in a quartz tube for 2 h afforded compound **3d** [12 mg, 26% (56% conversion)] as a yellowish liquid by PLC with CH_2Cl_2–hexane (1:2) as an eluent; δ_H($CDCl_3$) 2.03 (1 H, br s), 2.80 (1 H, d, *J* 4.62), 4.57 (1 H, s), 4.75 (1 H, s), 6.26 (1 H, dd, *J* 4.62 and 8.91), 6.48 (1 H, dd, *J* 8.91 and 6.26), 6.53 (1 H, d, *J* 5.61), 6.72–6.88 (5 H, m), 7.06–7.14 (2 H, m), 7.27–7.32 (2 H, m), 7.40–7.47 (2 H, m), 7.59 (2 H, d, *J* 5.94); λ_{max}(cyclohexane) (log ε)/nm 248.5 (4.07) and 338.0 (3.25).

Irradiation of compound 1c in solution. The bromide **1c** (50 mg, 0.12 mmol, 1.0 mol equiv.), Et_3SiH (40 mm^3, 0.25 mmol, 2.01 mol equiv.) and di-*tert*-butyl peroxide (60 mm^3, 0.41 mmol, 3.4 mol equiv.) were dissolved in dry benzene (1 cm^3) and placed in a Pyrex tube. The mixture was degassed by repeated freeze–degas–thaw cycles at 10^{-5} mmHg and irradiated with a 300 W high-pressure Hg lamp for 2 h. The irradiation mixture was then concentrated on a rotary evaporator. ^{1}H NMR analysis of the resultant mixture showed the presence of benzyltriptycene **1a**.

Pyrolysis of compound 1c in solution. A solution of the bromide **1c** (50 mg, 0.12 mmol, 1.0 mol equiv.), Et_3SiH (40 mm^3, 0.25 mmol, 2.01 mol equiv.) and di-*tert*-butyl peroxide (60 mm^3, 0.41 mmol, 3.4 mol equiv.) in dry benzene (1 cm^3) was placed in a Pyrex tube, degassed by repeated freeze–degas–thaw cycles at 10^{-5} mmHg and the Pyrex tube was heated in an oil-bath at 170 °C for 2 h. ^{1}H NMR analysis of the pyrolysate showed almost exclusive formation of compound **1a**.

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Paper 5/04135J
Received 27*th June* 1995
Accepted 19*th September* 1995