Electrophilic Chemistry (Protonation, Nitration, Bromination) of Crowded (*Z*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene; Formation of Phenanthrenium Ions by Facial Ring Protonation/Transannular Cyclization in Superacid Media; *p,p*-Dinitration and *p,p*-Dibromination with $NO_2^+BF_4^-$ and Br_2–SO_2

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Sterically congested (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene **1** is ring protonated in $FSO_3H{\cdot}SbF_5$(1 : 1)–SO_2ClF or in $FSO_3H{\cdot}SbF_5$(4 : 1)–SO_2ClF superacid media and undergoes a rapid transannular cyclization eventually leading to mixtures of persistent phenanthrenium mono- and dications. The cofacial relationship of the phenyl groups is required for phenanthrenium ion formation. Low-temperature protonation of the corresponding (*E*)-stilbene **2** gives Bu^{t+} as the main product and a complex mixture of aromatic products.

Low-temperature nitration of **1** with $NO_2^+BF_4^-$–SO_2 and bromination with Br_2–SO_2 led to disubstitution at the *para* positions in both cases. The arenium ion precursors could not be observed. The (*Z*)-dinitro- and (*Z*)-dibromo-stilbenes are stable compounds.

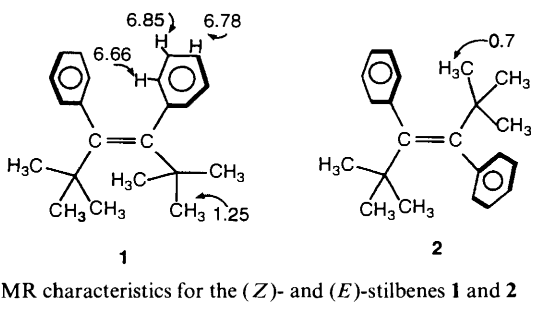
The cofacial or face-to-face relationship of the phenyl rings in the sterically crowded stilbene (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene, **1**, has recently been established by X-ray analysis.[1,2] Structural studies reveal that the 'sterically inaccessible' central double bond is orthogonal to the arene π-systems and remains untwisted. The 2.65 Å C(*ipso*)–C(*ipso*) distance is well below the normal van der Waals distance (3.4 Å). Although the molecule lacks a rigid framework, the *Z* stereochemistry is maintained.

There is no evidence in solution (variable-temperature NMR) for restricted *tert*-butyl rotation,[3] but restricted phenyl rotation has been shown.[4a] Photoelectron spectroscopy demonstrated substantial mixing of the arene MOs.[4b] The PES spectrum of **1** reveals that the cofacial interaction at the *ipso* positions substantially reduces the ionization potential, compared with benzene, by raising the energy of the b_2 MO, the HOMO, to activate electrophilic attack at the *para* positions.[4a] AM1 calculations indicate this position should be greatly activated even when the opposing ring is *para*-nitro substituted.[4b]

The *Z*- and *E*-isomers can be interconverted photochemically and (*E*)-stilbene **2** can be thermally converted back into **1** (Scheme 1).[3] No side products are observed in either case.

In accord with the X-ray analysis, the cofacially disposed arene protons are anisotropically shielded in the ^1H NMR spectrum and appear between 6.85–6.66 ppm with the doublet due to the *ortho* hydrogen being most upfield (6.66 ppm). In **2**, the *Bu^t methyls* are anisotropically shielded (0.7 ppm) and the aromatic protons are normal.

In view of its unusual cofacial rings, short *ipso–ipso* distance, and inaccessible double bond, the electrophilic chemistry of **1** is of particular interest. Attempted room-temperature bromination of **1** in deuteriochloroform failed to produce a *p,p*-disubstituted (*Z*)-dibromostilbene or a product of addition to the central double bond.[4b] Instead, the presence of bromine led **1** to isomerize to **2**. The mechanism of this bromine-catalysed isomerization is unknown.



1 **2**

^1H NMR characteristics for the (*Z*)- and (*E*)-stilbenes **1** and **2**

The **1**·AgOTf complex has been prepared and found to be exceptionally stable.[5] Its X-ray analysis confirms that Ag^+ is in the cleft and situated near the *para* position.[5]

In relation to our previous studies of cations derived from face-to-face aromatic rings,[6–9] we now report on the low-temperature protonation, nitration and bromination of **1**.

Results and Discussion

(*a*) *Low-temperature Protonation in Superacid Media*.—Careful addition of a clear, homogeneous, solution of $FSO_3H{\cdot}SbF_5$(1 : 1) 'magic acid^R'–SO_2ClF to a cold slurry of **1** in SO_2ClF at dry ice–acetone temperature under dry nitrogen initially produces a green solution on contact, which, upon further mixing and a slight increase in temperature (*ca.* −70 °C), turns irreversibly red, suggesting arenium ion formation.†

The aliphatic region of the ^1H NMR spectrum of the sample exhibits two deshielded Bu^t singlets at 1.30 and 1.40 ppm with unequal populations (1 : 0.7), with a more deshielded (minor) broad Bu^t at 1.98 ppm. A distinct sharp singlet at 3.90 ppm for Bu^{t+} (see later), and a broad featureless arenium CH_2^+ at *ca.* 4.60 ppm are also present.

The highly deshielded aromatic region exhibits a singlet at 9.05 ppm and doublets at 9.10, 8.72, 7.70 and 7.35 ppm, together with other overlapping resonances. The presence of free Bu^{t+} in the sample was confirmed by the ^{13}C NMR spectrum, showing resonances at 333 [$Bu^t(C^+)$] and 48 ppm Bu^t(Me). In addition,

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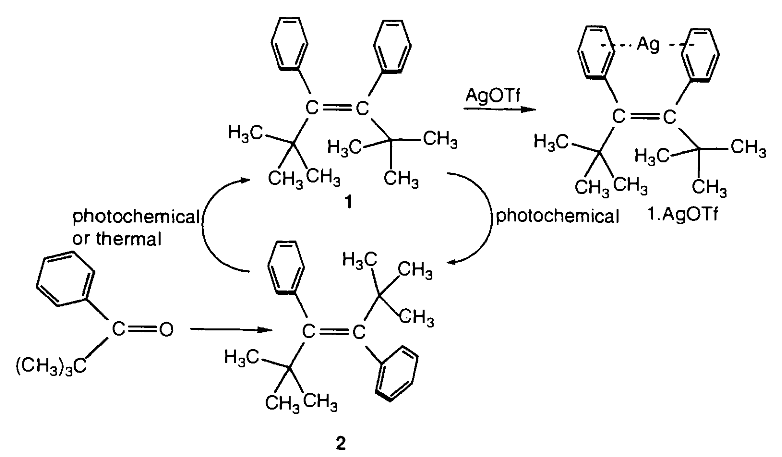
† It is conceivable that the initially formed green sample is a π-complex formed between the superacidic proton and the hindered central bond which is rapidly converted into an arenium ion. The alkene π-complex ⟶ arenium ion conversion can, in principle, occur either intramolecularly or *via* rapid deprotonation/reprotonation equilibria. Due to rapid green ⟶ red conversion, we have not been able to study directly the initially formed green solution.



Scheme 1 Synthesis, isomerization and AgOTf complexation of 1

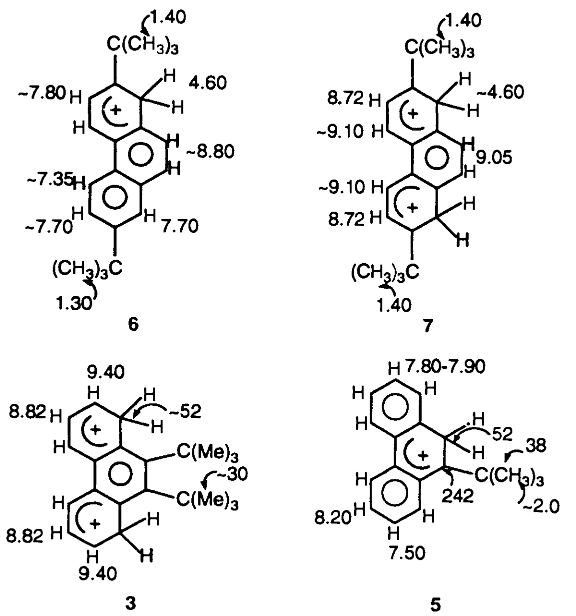


Fig. 1 Characteristic NMR chemical shifts for the phenanthrenium ions 3, 5, 6 and 7

two Bu^t(Me) signals are seen at 32 and 33 ppm with their Bu^t(C) resonances at 37 and 38 ppm. There are two sp^3 (C^+) signals between 46–47 ppm. The aromatic region contains at least 18 resonances between 198–125 ppm, corroborating a mixture of arenium ions.

The NMR data (Fig. 1) are best interpreted in terms of a mixture of phenanthrenium ions 6 and 7, with the latter being the minor component, together with Bu^{t+}. The positions of the assigned resonances are in close agreement with those of the structurally related persistent methylphenanthrenium mono- and di-cations we reported over a decade ago.[10] Other possibilities, namely facial ring protonation without subsequent aryl participation/ring closure, and central double-bond protonation to form a tertiary carbenium ion are incompatible with the NMR data.

In an independent experiment, 1 was treated with the less acidic superacid FSO_3·SbF_5(4 : 1)–SO_2ClF at dry ice–acetone temperature, as before. A green solution was obtained on contact; the subsequent change to red occurred relatively more slowly as compared with the 'magic acid' reaction and was complete within minutes at dry ice–acetone temperature, and definitely prior to NMR data acquisition. The ^1H and ^{13}C data showed that Bu^{t+} was again present, and that a mixture of phenanthrenium ions was formed, the constitutions of which were different from those formed in 'magic acid'.

Thus, the aliphatic region of the ^1H NMR spectrum exhibited a broad envelope of deshielded Bu^t methyls (between 1.50–1.0 ppm) indicative of restricted Bu^t rotation. In addition, a separate sharp Bu^t methyl was seen further downfield at *ca.* 2.0 ppm. The Bu^{t+} (Me) and the arenium CH_2^+ absorptions are also observable. The aromatic region exhibited five doublets, three triplets and one singlet, all between 9.40–7.50 ppm, in addition to other broad, overlapping, absorptions.

In the ^{13}C NMR spectrum, broad Bu^t (Me) resonances (at 30, 33 and 38 ppm), the Bu^{t+} (at 48, and 333 ppm), and an arenium CH_2^+ absorption (at 51.5 ppm) were observed. The aromatic region exhibited 14 signals in the range 243–126.6 ppm.

The NMR data (Fig. 1) are most compatible with the phenanthrenium ion mixture 3, 5 (with dication 3 being more prominent), and Bu^{t+}. The most deshielded carbon resonance at 242 ppm assigned to C-10 of 5 correlates well with the C-10 resonance for 8 observed at 227.2 ppm by Shubin *et al.*[11] Similarly, the key proton resonances ascribed to 3 and 5 are in good agreement with those of 7 as well as other structurally related methylphenanthrenium ions[10,11] (see Fig. 2).

Quenching of the ion solution (ice–bicarbonate) and extraction gave a light brown residue. Its identity as a mixture of *tert*-butylphenanthrenes was implied from the ^1H NMR spectrum showing three major Bu^t singlets between 1.7–1.6 ppm and an aromatic envelope centred around 7.40 ppm. The ^{13}C NMR spectrum of the crude organics similarly indicated two Bu^t(Me) signals between 31 and 32 ppm, and an aromatic envelope between 125 and 135 ppm (the carbon resonances of the authentic phenanthrene are between 122 and 132 pm).[12]

GC–MS analysis of the crude organic residue obtained by quenching of the superacid solutions of 1 corroborated the presence of di-*tert*-butylphenanthrene (*m*/*z* 290).

Formation of isomeric *tert*-butyl-substituted phenanthrene by protonation of 1 was also examined in CF_3SO_3H ('TfOH'). Addition of cold TfOH to 1 at *ca.* – 30 °C gave a yellow solution on contact, which upon vortex mixing and a rise in temperature, slowly turned red. The sample was allowed to stand at room temperature for 1 h before quenching. The ^1H NMR spectrum of the crude organics was similar to that of the low-temperature superacid protonation, exhibiting two major Bu^t signals (1 : 1 ratio) and an aromatic envelope centred at 7.35 ppm.

For comparison, we also studied the protonation of 2 in FSO_3H·SbF_5(4 : 1)–SO_2ClF. A light red solution was formed on contact at dry ice–acetone temperature. The ^1H NMR spectrum of the solution indicated extensive formation of Bu^{t+}, but no phenanthrenium ion. A broad, deshielded, aromatic envelope in the range 9.60–7.40 ppm, and a broad aliphatic envelope

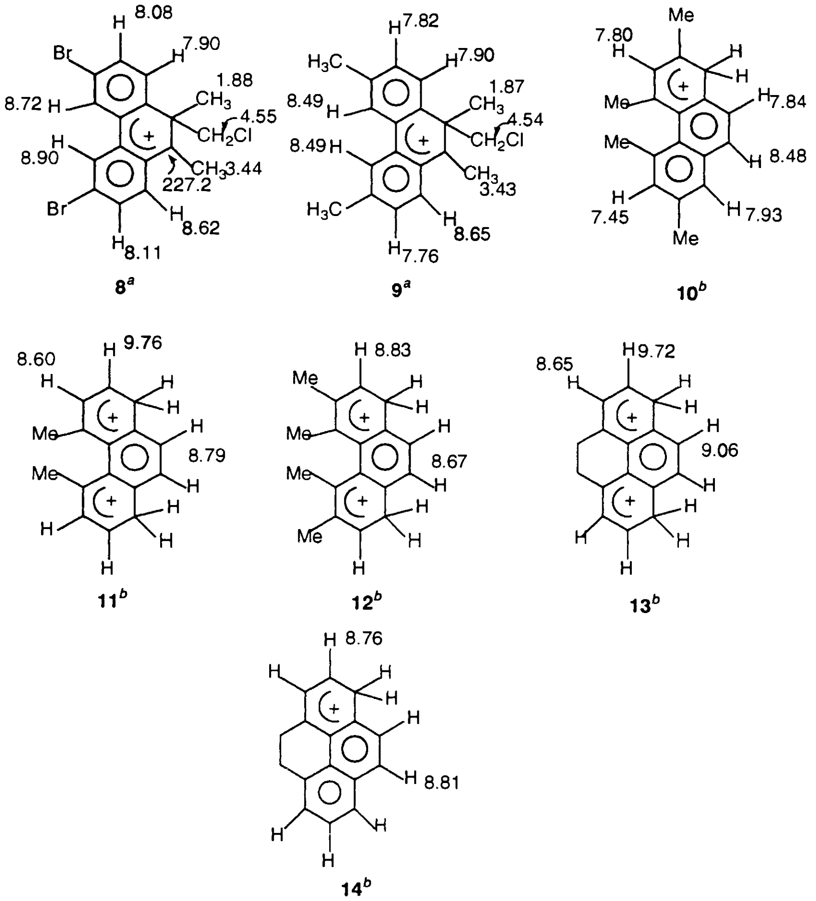


Fig. 2 Characteristic NMR data for structurally related phenanthrenium mono- and di-cations **8**–**14**. [a] Ref. 10. [b] Ref. 11.

between 2.0 and 0.6 ppm were observed with no other resonances appearing between these two regions. The deshielded nature of the aromatic resonances and the absence of sp^3 (CH) suggest that polycondensation and subsequent oxidation had taken place. The $Bu^{t\,+}$ signal and the superacid peak remained sharp.

It is apparent that phenanthrenium ions are formed only when the cofacial *Z*-isomer is protonated.

(*b*) *Nitration and Bromination of* **1**.—Careful addition of $NO_2^+\ BF_4^-$ in SO_2 solvent to **1** (3 : 1 molar ratio) gave a yellow-brown solution the ^1H NMR spectrum of which (recorded at −65 °C) consisted of a Bu^t singlet resonance at 1.24 ppm and two aromatic doublets at 7.54 and 6.80 ppm with 8.0 Hz coupling; the triplet resonance for the *para* protons of **1** had disappeared. The data clearly indicate clean conversion into the *para*-dinitrated product **15** (Scheme 3). Neither a persistent NO_2^+·**1** complex nor a benzenium ion of nitration were detected under these conditions. Deprotonation of nitration σ-complexes is known to be extremely rapid even under 'stable ion conditions'.[13] A broad resonance at 8.55 ppm was also present and assigned to HBF_4.

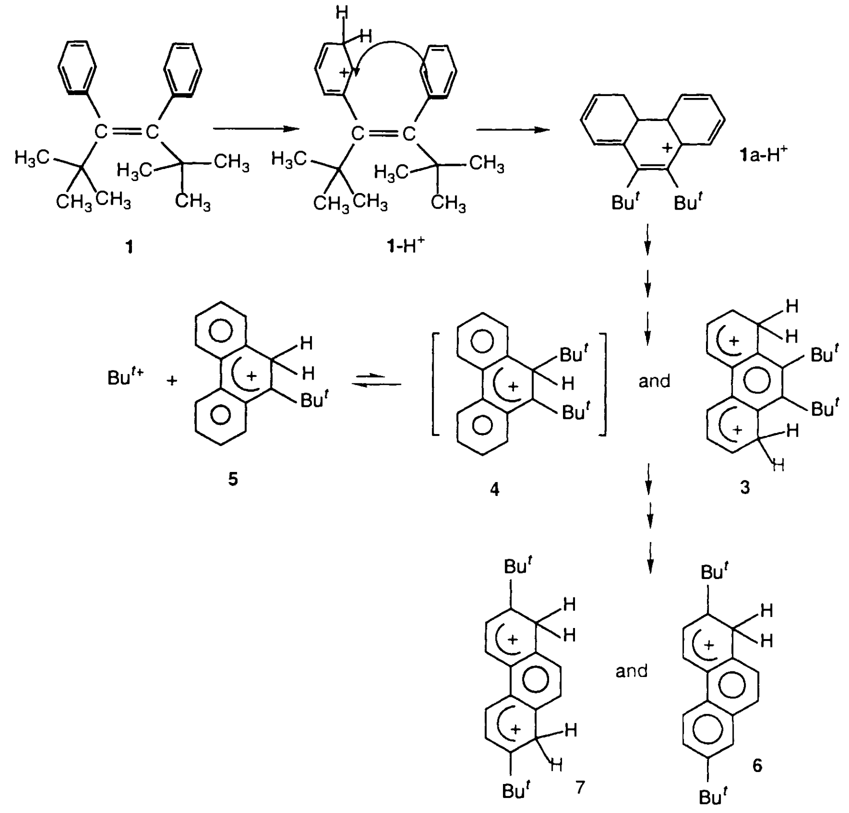
In addition to the dinitro *Z*-isomer, exothermic quenching of the sample provided *ca.* 20% of the dinitro *E*-isomer **16** (two 1 : 1 doublets at 8.17 and 7.35 ppm with 8.5 Hz coupling; the anisotropically shielded Bu^t of **16** gives rise to a high-field singlet at 0.67 ppm). The broad peak at 8.55 ppm disappeared on quenching.

The ^{13}C NMR spectrum of the nitration reaction mixture before quenching exhibited one Bu^t group (33.3 and 33.6 ppm) and two H-bearing ring carbons (131.4 and 121.0 ppm); the *ipso* carbons were not detected.

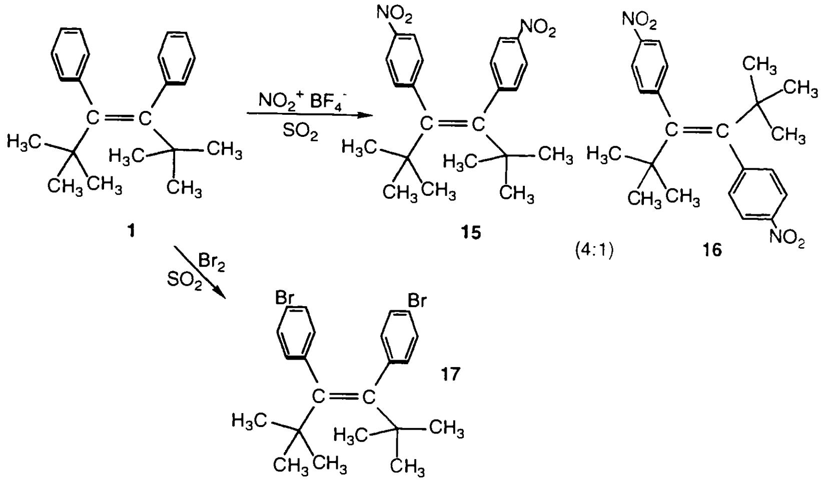
The Br_2–SO_2 system is known to be more effective for aromatic bromination than Br_2 itself.[14] Bromination of **1** with an excess of Br_2–SO_2 gave a yellow solution the ^1H NMR spectrum of which (at −45 °C) no longer contained *para* protons. The spectrum consisted of two aromatic doublets (1 : 1) at 7.01 and 6.67 ppm and a singlet Bu^t(Me) at 1.59 ppm. The data correspond to *para* dibromination (**1** $\longrightarrow$ **17**). In addition, two broad humps at *ca.* 7.30 and 4.60 ppm were present. These disappeared on quenching of the sample and are assigned to HBr and H_2O showing slow exchange on the NMR timescale in the low-temperature spectrum.

The Mechanistic Aspects; A Comparative Discussion.—Our suggested mechanism for the formation of phenanthrenium ion from **1** is outlined in Scheme 2. Among possible sites of facial ring protonation, the σ-complex of *meta* attack (**1**-H^+) is most likely to bring about π-participation by the *vis-à-vis* ring and transannular bond formation to give a six-membered ring (**1a**-H^+), leading eventually to the observed phenanthrenium ions **3** and **5**. In analogy with nitration, bromination and activation of the *para* position by cofacial interaction,[4b] it is possible that the initial site of protonation in superacid media is the *para* position; the arenium ion of protonation undergoes a facile 1,2-H shift and subsequently cyclizes. Formation of **5** (*via* **4**) generates the observed $Bu^{t\,+}$ which does not realkylate **5** to give an unsymmetrical dication.

Both DEWAR-PI and Hückel calculations[15] show that for phenanthrene the tetrahedral intermediates formed by attack at C-9/C-10 (meso positions) and those of attack at C-1/C-8 are very close in energy and are the most stable.[10,15] The presence of two Bu^t groups at C-9/C-10 must induce an observable rotational barrier in dication **3**. Analogous processes are



Scheme 2 Low-temperature protonation of **1** in superacid media



Scheme 3 Nitration and bromination of **1**

envisaged in the more acidic (H_0) 'magic acid', except that the phenanthrenium ions are subject to further dealkylation/realkylation steps, ultimately leading to the observed least congested, most stabilized, 2,7-substituted phenanthrenium cations **6** and **7**.

In nitration and bromination reactions, *para* disubstitution occurs. The σ-complex intermediates were not observed. The absence of cyclization may be due to a very rapid deprotonation of the nitration σ-complexes. In addition, unlike 1,2-hydride shifts, 1,2-NO_2 shifts are uncommon, although they have been observed in specific cases.[13]

The *Z* ⟶ *E* isomerization to form a 4:1 mixture of **15** and **16** is catalytic or photochemical. Thermal isomerization during quenching is ruled out by the slow isomerization observed. In a control experiment, the **15**:**16** ratio changed from 4:1 to 1:1 after hours in refluxing hexane. Since the **1** ⟶ **2** isomerization would not occur thermally at these temperatures and since complete rearrangement occurs in the presence of bromine in chloroform within 30 min at room temperature, a catalysed isomerization of **15** is not surprising.[4a]

Experimental

The syntheses of **1** and **2** were based on previously published procedures.[3,16] FSO_3H (Allied) and SbF_5 (Aldrich) were distilled twice under dry nitrogen in an all-glass distillation unit prior to use. SO_2ClF (Aldrich) and anhydrous SO_2 (Linde) were used without further purification. $NO_2^+BF_4^-$ (Aldrich) was used as received. The preparation of the super acid solutions and the procedures for stable ion generation were analogous to those already described.[8]

NMR Spectra.—Spectra were recorded on a GE GN-300 instrument using CD_2Cl_2 as lock and reference for low-temperature studies.

$NO_2^+BF_4^-$ *Nitration.*—A solution of the nitronium salt (0.2 mmol) in SO_2 (1 cm^3) was added slowly under nitrogen to a slurry of **1** (20 mg, 0.067 mmol) in SO_2 (*ca.* 1 cm^3) at dry ice–acetone temperature. In order to mix the sample efficiently it was necessary to allow the temperature to rise to *ca.* −65 °C. Vigorous mixing (vortex) gave a yellow-brown solution; a cold aliquot (50% of the sample) was transferred into a 5 mm NMR tube. Subsequent quenching of the entire sample was accomplished by pouring the contents of the NMR tube into ice–bicarbonate and extraction with CH_2Cl_2. GC–MS showed a single peak at long retention time: *m/z* 382 (M^+), 326, 309, 279, 270 and 57 (base peak). Preparative TLC gave a single major band the ^1H NMR spectrum of which showed it to be a 1 : 1 mixture of **15** and **16**. The NMR data for **16** were identical with those of a sample prepared by nitration of **2** using HNO_3–H_2SO_4 in nitrobenzene.[4a]

Br_2–SO_2 *Bromination.*—Liquid SO_2 (*ca.* 1 cm^3) and Br_2 (*ca.* 0.4 mmol) were mixed to give a homogeneous solution. This was added under dry nitrogen at dry ice–acetone temperature to a slurry of **1** (28 mg, 0.095 mmol) in SO_2 (*ca.* 1 cm^3). Vigorous mixing while allowing the temperature to increase in order to reduce viscosity, gave a homogeneous yellow sample which was liquid above −50 °C. The NMR spectra recorded at −45 °C exhibited sharp signals. Quenching of the solution was similar to that used in the nitration experiment. GC–MS showed a single peak at long retention time: *m/z* 452 (2.1), 450 (5.0), 448 (M^+, 2.3), 314 (32.7), 312 (30.7) and 57 (100). Preparative TLC gave a single major product with a ^1H NMR spectrum identical with that observed at low temperature in SO_2.

Acknowledgements

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