Novel Heteroatom-Linked Analogues of Trityl Radicals: Diaryl(benzotriazol-1-yl)methyl Radical Dimers

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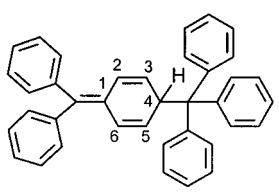
The lithiation of diaryl(benzotriazol-1-yl)methanes followed by addition of iodine generates phenanthridines and dimers of hitherto unknown trityl analogues in which the radical center is directly attached to a heteroatom. These dimers differ from those of triarylmethyl radicals by not dissociating in solution, but variable temperature ESR measurements provided direct evidence for the formation of the corresponding diaryl(benzotriazol-1-yl)methyl radicals as intermediates in solution.

Introduction

Free radicals are highly important and extensively used synthetic intermediates. The triphenylmethyl or trityl radical and its substituted derivatives are important as the prototype class of C-centered persistent radicals, the properties and reactivities of which have been extensively studied.[1−6] Diaryl(heteroaryl)methyl radicals are far less well-known. Although Mangini and co-workers et al. reported the formation and ESR spectra of trithienylmethyl,[7] thienyldiphenylmethyl, and dithienylphenylmethyl[8] radicals, in all of these the radical center is still connected to three carbon atoms. No trityl analogue, in which the radical center is connected directly with a heteroatom of a heteroaryl ring, has previously been reported. We were interested in such radicals and specifically in replacing one of the three phenyl groups in the trityl radical by a benzotriazol-1-yl substituent. Benzotriazolyl groups possess large conjugated systems and, like phenyl, can delocalize electrons: thus, a benzotriazol-1-yl substituent stabilizes an α-carbanion center which can then react with electrophiles to give the expected α-substituted products.[9,10] By contrast, α-deprotonation of *N*-2-alkylbenzotriazoles (Bt^2CH_2R) gives carbanions which rapidly form the corresponding symmetrical dimers ($Bt^2CHRCHRBt^2$), together with "tetramers" ($Bt^2CHRCHRCHRCHRBt^2$), derived from four molecules of the substrate, and olefins (RCH=CHR), all via radical intermediates.[11−13] We recently reported that the lithiation of diaryl(benzotriazol-1-yl)methane followed by the addition of copper(I) iodide yielded phenanthridine derivatives.[14] We now report the results of our study of a new class of radicals, $Bt^1C^{\bullet}Ar_2$, including the elucidation of their dimeric structures and a comparison of their properties with those of the analogous trityl radicals.

As is well-known,[15] the class of triarylmethyl radicals is stable because the unpaired electron can be delocalized onto the ortho and para positions of the phenyl rings. Dimerizations of these radicals take place at the para ring position due to steric hindrance at the ortho position. Lankamp et al.[3] demonstrated by UV and NMR spectroscopic evidence in 1968 that the structure of the triphenylmethyl radical dimer was 1-(diphenylmethylene)-4-trityl-2,5-cyclohexadiene (**1**), and not hexaphenylethane, as had long been assumed. Tokura et al. found that the



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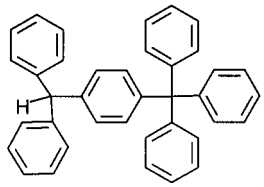

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dimer **1** was converted into isomeric *p*-benzhydryltetraphenylmethane (**2**) in good yield (80%) in the presence of protic acids, and they also undertook mechanistic investigations using deuterated phenol.[16] Interestingly,

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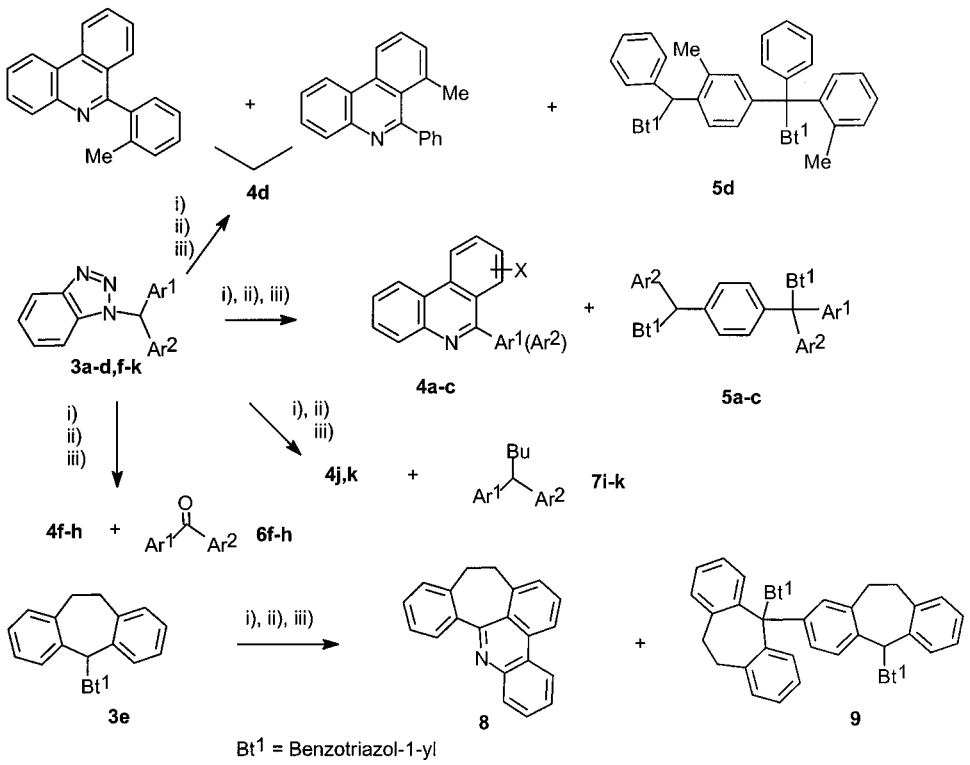
Scheme 1



a: $Ar^1 = Ar^2 = Ph$; **b**: $Ar^1 = Ph$, $Ar^2 = p\text{-}MeC_6H_4$; **c**: $Ar^1 = Ph$, $Ar^2 = p\text{-}ClC_6H_4$; **d**: $Ar^1 = Ph$, $Ar^2 = o\text{-}MeC_6H_4$; **e**: Ar^1, Ar^2 = dibenzosuberanyl; **f**: $Ar^1 = Ar^2 = p\text{-}MeC_6H_4$; **g**: $Ar^1 = Ar^2 = p\text{-}ClC_6H_4$; **h**: $Ar^1 = Ar^2 = p\text{-}FC_6H_4$; **i**: $Ar^1 = Ar^2 = p$-dimethylaminophenyl; **j**: $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$; **k**: $Ar^1 = p$-dimethylaminophenyl, $Ar^2 = Ph$

i) *n*-BuLi (1.1 equiv), THF/-78 °C; ii) I_2 (1 equiv), -78 °C; iii) H_2O, -78 °C.

Staab et al. found that the dimer **1** also undergoes a [1,5]-proton shift to form isomer **2** under basic conditions.[17] These rearrangements provide further evidence of the structure 1-(diphenylmethylene)-4-trityl-2,5-cyclohexadiene (**1**) for the dimer of Gomberg's trityl radical. In diaryl(benzotriazol-1-yl)methyl radicals, the unpaired electron can also be delocalized onto the ortho or para positions of the phenyl rings and such radicals could be expected to dimerize in a fashion similar to that of the trityl radical. However, such a dimer should undergo a [1,5]-proton shift to give dimer **5** quite readily due to the electron-withdrawing character of the benzotriazolyl group. The unpaired electron could also go to the benzotriazole ring and induce the ring opening by loss of nitrogen, followed by cyclization to form phenathridines **4**.

Results and Discussion

Preparation of Diaryl(benzotriazol-1-yl)methyl Radicals, Their Dimers, and Phenanthridine Ring Closure Products. Triarylmethyl radicals are usually prepared by the reaction of a triarylmethyl halide with a metal.[18] The starting diaryl(benzotriazol-1-yl)methanes **3a**−**k** were prepared by the reactions of benzotriazole with diarylmethyl halides or diarylmethanols as previously described.[14] Diaryl(benzotriazol-1-yl)methanes **3a**−**k** were lithiated by *n*-BuLi at −78 °C for 10 min, and this was followed by the addition of an iodine solution in THF at this temperature. After the solutions were stirred for 15 min at −78 °C, the reactions were quenched with water. Instead of the expected diaryl(benzotriazol-1-yl)-methyl iodides, phenanthridine derivatives **4a**−**c** and **8** and dimers **5a**−**c** and **9** of the desired radicals were obtained directly (Scheme 1, Table 1). The formation of trityl radicals by reactions of carbanions with iodine has previously been reported by Rajca.[19,20]

When Ar^1 and Ar^2 are not identical, but are of similar electronic character as in **3c** and **3d**, two isomers of phenanthridine **4** are formed which are difficult to separate by column chromatography. For example, when α-(*p*-methylphenyl)-α-(benzotriazol-1-yl)toluene (**3c**) was treated with *n*-butyllithium followed by I_2 at −78 °C, a mixture of 6-(*p*-methylphenyl)phenanthridine (**4c**) and 9-methyl-6-phenylphenanthridine (**4c′**) was obtained along with dimer **5c**. However, when Ar^1 and Ar^2 differ significantly in electronic character, as in compound **3k**, the ring closure reaction occurs only at the ring with the lower electron density to form a single phenanthridine (**4k**). However, only one isomer of dimers **5a**−**d** was obtained, although Ar^1 and Ar^2 are different in the starting materials **3a**−**d**, and there should be the possibility of formation of other isomers. In every case, the dimers **5a**−**d**, **9** were formed, as shown in Scheme 2, via α,para dimerization. No α,α or α,ortho dimerizations were observed, even for the cases where there are

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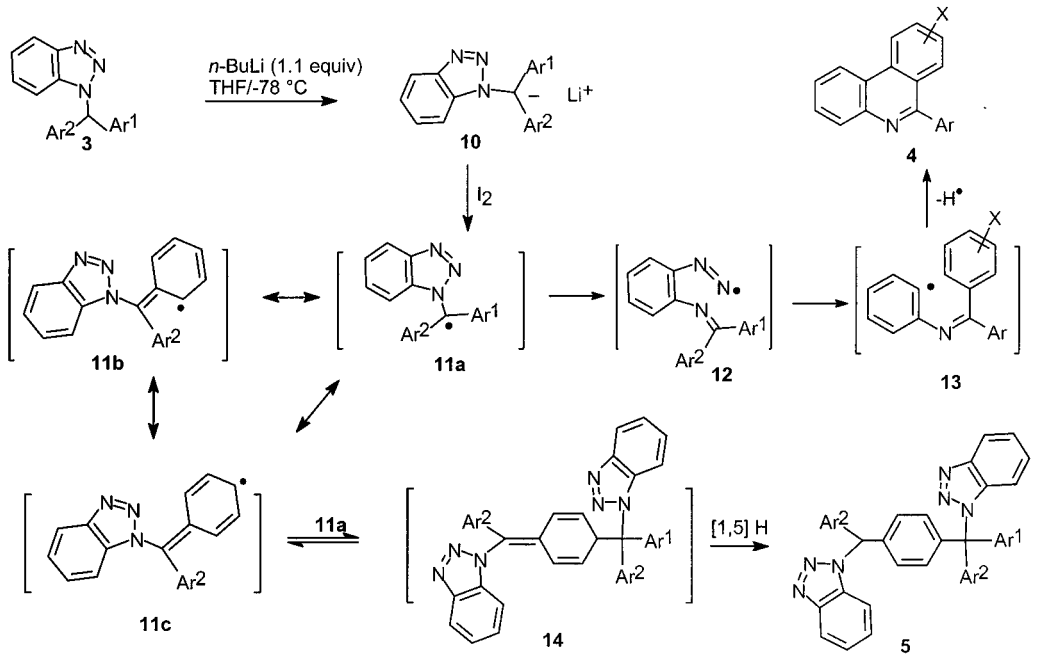
Table 1. Preparation of Phenathridines 4 and 8 and Dimers 5 and 9

	3 and **5**		**4** (or **8**)			**5** (or **9**)
starting material	Ar^1	Ar^2	Ar^1	X	yield (%)	yield (%)
3a	Ph	Ph	Ph	H	25	44
3b	Ph	*p*-ClC_6H_4			0	80
3c	Ph	4-MeC_6H_4	Ph	9-Me	27[a]	59
			4-MeC_6H_4	H		
3d	Ph	2-MeC_6H_4	Ph	7-Me	56[a]	22
			2-MeC_6H_4	H		
3e	dibenzosuberan-5-yl[b]		**8**[b]		20	15 (**9**)
3f	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	9-Me	60	0
3g	4-ClC_6H_4	4-ClC_6H_4	4-ClC_6H_4	9-Cl	28	0
3h	4-FC_6H_4	4-FC_6H_4	4-FC_6H_4	9-F	39	0
3i	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$			0	0
3j	4-$MeOC_6H_4$	4-$MeOC_6H_4$	4-$MeOC_6H_4$	9-MeO	7	0
3k	4-$Me_2NC_6H_4$	Ph	4-$Me_2NC_6H_4$	H	35	0

[a] Mixture of two isomers. [b] See Scheme 1.

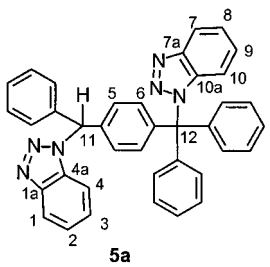
Scheme 2



substituents in the para position. Similar behavior was previously noted for the trityl class of radicals.[3]

There are several noteworthy features of these reactions. (i) When both aryl groups in the starting material are substituted at the para position, the reaction gave only the phenanthridine as product and no dimer was obtained. The reason is probably steric hindrance by the para substituents. However, a single para substituent in the starting material did not inhibit dimerization. (ii) When (2-methylphenyl)phenyl(benzotriazol-1-yl)methane was reacted under these conditions, (2-methylphenyl)-phenyl(benzotriazol-1-yl)methyl radical dimerized at the 2-methylphenyl group to give dimer **5d** as well as the phenanthridine **4d**. (iii) Reaction of bis(4-(dimethylamino)phenyl)(benzotriazol-1-yl)methane (**3i**) under the same conditions gave 1,1-bis(4-(dimethylamino)phenyl)pentane and BtH, and no corresponding compound **4** was generated. Treatment of bis(4-dimethoxyphenyl)(benzotriazol-1-yl)methane (**3j**) under these conditions gave **4j** in only 7% yield together with a large amount of 1,1-bis(4-methoxyphenyl)pentane and free benzotriazole. Strong electron-donating groups (dimethylamino and methoxy) allow the benzotriazolyl group to be displaced easily in *N*-(*p*-substituted benzyl)benzotriazoles.[9]

Proof of Structure of Dimers. Compounds **5a**−**d** and **9** were characterized by NMR and by HRMS. The spectra showed their structures to be different from those of the trityl radical dimers. From the NMR spectra, it is clear that they possess two different benzotriazol-1-yl groups. Thus, in the ^{13}C NMR spectra, every dimer gives two sets of benzotriazol-1-yl signals (Table 2), e.g., in dimer **5a**, (i) 146.2, 133.0, 127.4, 123.7, 120.0, 110.5 ppm



and (ii) 146.4, 134.2, 127.7, 123.9, 120.2, 113.5 ppm (Table 2). In dimer **5d**, the two methyl groups display different chemical shifts (2.18 and 1.50 ppm). The methyl at the higher field is shielded by a benzotriazol-1-yl or a phenyl group. In the ^1H NMR spectrum of **9**, protons at the

Table 2. NMR Data of Dimers 5a−d and 9

	^{1}H NMR		^{13}C NMR		
compd	H-1, H-7, H-10	others	C-11	C-12	others
5a	8.02−8.10 (m, 2H), 6.39 (d, J = 8.4 Hz, 1H)	7.00−7.42 (m, 25H)	66.6	78.7	110.5, 113.5, 120.0, 123.7, 123.9, 126.7, 127.4, 127.6, 128.0, 128.2, 128.6, 128.8, 129.9, 130.8, 133.0, 134.2, 137.2, 137.3, 140.9, 142.0, 146.2, 146.4
5b	8.02−8.10 (m, 2H), 6.40 (d, J = 8.4 Hz, 1H)	7.05−7.40 (m, 23H)	65.7	78.1	110.0, 113.2, 120.1, 120.2, 123.8, 124.0, 127.0, 127.6, 127.7, 128.0, 128.1, 128.3, 129.0, 129.6, 130.5, 131.4, 132.8, 133.9, 134.1, 134.5, 135.7, 137.2, 139.6, 139.7, 140.2, 141.7, 146.1, 146.4
5c	8.04−8.10 (m, 2H), 6.41 (d, J = 8.4 Hz, 1H)	7.00−7.33 (m, 22H), 7.35 (s, 1H), 2.33 (s, 6H)	66.5	78.5	21.0, 21.1, 110.6, 113.6, 120.0, 120.1, 123.6, 123.8, 126.7, 127.3, 127.5, 127.9, 238.0, 128.2, 128.6, 129.5, 129.9, 130.6, 132.9, 134.2, 134.3, 137.5, 137.9, 138.0, 138.1, 138.4, 141.1, 142.0, 146.2, 146.4
5d	8.04−8.08 (m, 2H), 6.26 (d, J = 8.5 Hz, 1H)	6.89−7.35 (m, 22H), 7.55 (s, 1H), 2.17 (s, 3H), 1.47 (d, J = 3.9 Hz, 3H)	64.2	79.0	19.3, 21.7, 110.4, 113.0, 119.9, 120.1, 123.6, 123.8, 125.7, 126.3, 126.8, 127.3, 127.4, 127.8, 127.9, 128.1, 128.2, 128.7, 128.8, 129.4, 130.2, 131.0, 131.1, 132.8, 133.1, 134.5, 135.5, 136.6, 136.9, 139.1, 139.4, 139.5, 141.0, 141.7, 146.2, 146.3
9	8.00−8.03 (m, 1H), 8.10 (d, J = 8.4 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H)	7.52 (d, J = 7.1 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.06−7.36 (m, 10H), 6.89−6.95 (m, 3H), 6.85 (s, 1H), 6.72−6.77 (m, 2H), 6.15 (d, J = 8.4 Hz, 2H), 2.60−3.18 (m, 8H)	70.7	78.5	31.6, 32.3, 34.4, 111.3, 114.2, 119.9, 120.0, 123.7, 123.8, 125.8, 126.6, 126.8, 127.1, 128.4, 128.6, 129.5, 130.1, 130.9, 131.1, 131.2, 133.1, 133.2, 134.1, 134.2, 134.8, 139.0, 140.1, 140.6, 141.3, 143.2, 146.3, 146.5

Table 3. Melting Points and HRMS of Dimers 5a−d and 9

compd	mol formula	mp (°C)	HRMS found (calcd) (M^+)
5a	$C_{38}H_{28}N_6$	225−227	450.2014 (450.1970) (M^+ − Bt)
5b	$C_{38}H_{26}Cl_2N_6$	136−139	518.1019 (518.1190) (M^+ − Bt)
5c	$C_{40}H_{32}N_6$	139−141	596.2727 (596.2688)
5d	$C_{40}H_{32}N_6$	143−145	596.2713 (596.2688)
9	$C_{42}H_{32}N_6$	180−183	620.2694 (620.2688)

4-position of the two benzotriazol-1-yl groups produce signals at 8.10 and 8.00−8.03 ppm, respectively. In the ^{13}C NMR spectrum of **9**, there are two groups of benzotriazol-1-yl signals, 146.3, 133.1, 126.6, 123.7, 119.9, 113.3 and 146.5, 133.2, 126.8, 123.8, 120.0, 114.2 ppm. At the high field, the signals at 78.5 and 70.7 ppm belong to the quaternary carbon and the tertiary carbon, respectively. These assignments were confirmed by 2D and APT spectra. In comparison to the structure of the trityl radical dimer **1**, which has a large conjugated system, the protons on the central phenyl group (protons 2, 3, 5, and 6) are in the range of 6.01−6.40 ppm and the proton at position 4 is at 5.09 ppm in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, the carbon at position 4 is at about 42 ppm.[21] It is clear that the structures of our dimers **5** and **9** are different from the structures of trityl radical dimers.

In the MS spectra of compounds **5** and **9**, the molecular ion and molecular fragments are observed. The base peak at $M^+ - 118$ reflects the ease of loss of a benzotriazolyl group from the crowded molecule (Table 3).

As is well-known, the dimers of trityl radicals undergo reversible dissociation to the corresponding radicals in solution.[3] A crossover experiment was conducted to investigate possible dissociation of the present dimers in solution. Dimers **5a** and **5b** were mixed and dissolved in THF, but refluxing for 10 h led to the recovery of starting materials, **5a** and **5b**, and no new dimers were generated. This also indicates that the structures of dimers **5** are different from those of the trityl radical dimer.

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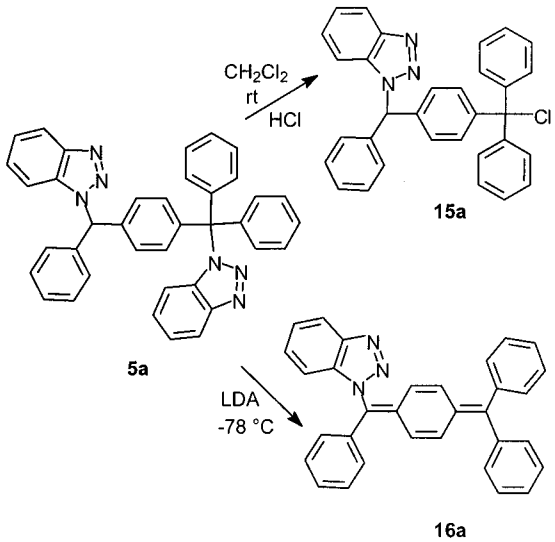
Scheme 3



Reaction Mechanism. The proposed mechanism for formation of phenanthridines **4** and **8** and dimers **5** and **9** is given in Scheme 2. Carbanion **10** (formed by lithiation of diaryl(benzotriazol-1-yl)methane) reacts with iodine to generate radical **11**. The unpaired electron in radical **11** is delocalized as indicated by the canonical forms to the ortho (cf. **11b**) or para positions (cf. **11c**). Dimerization involving forms **11a** and **11c** gives, after a [1,5]-proton shift, a dimer of type **5**. The unpaired electron of radical **11** can also reside on the triazole ring which opens to form **12** and looses nitrogen to give **13** which undergoes intramolecular cyclization to generate phenanthridine. Whether **4** or **5** is formed is probably controlled by the relative rates of the irreversible steps **12** → **13** and **14** → **5**.

Reactivity of the Dimers 5. Treatment of dimer **5a** with hydrochloric acid in methylene chloride at room temperature for 4 h gave the chloride derivative **15a** with the loss of one benzotriazol-1-yl group (Scheme 3). In the ^{1}H NMR spectrum of **15a**, the low-field signal (8.02−8.08 ppm) integrated for one proton only existing instead

Figure 1. ESR spectrum of 5-(benzotriazol-1-yl)dibenzosuberane radical.

of for two protons as for **5a**. The ^{13}C NMR spectrum of **15a** confirmed that only a single benzotriazol-1-yl group remained.

Treatment of **5a** with LDA at −78 °C gave product **16a** (98%) in which one of the benzotriazole groups had been eliminated (Scheme 3). Compound **16a** is red due to a highly conjugated system. In the ^1H NMR spectrum of **16a**, four protons, 6.18, 6.82, 6.96, 7.10 ppm, have moved to a higher field when compared with the ^1H NMR spectrum of **5a**; the low-field signal at 8.12 ppm, integrated for only one proton, which belonged to a single benzotriazol-1-yl group. The ^{13}C NMR spectrum of **16a** displayed only one set of benzotriazol-1-yl signals (111.0, 120.1, 124.1, 127.9, 131.9, 145.9 ppm). The structure of **16a** was also further supported by HRMS. Heating dimer **5a** with methanolic sodium hydroxide at 60 °C for 12 h or treatment with MeMgBr also gave **16a**.

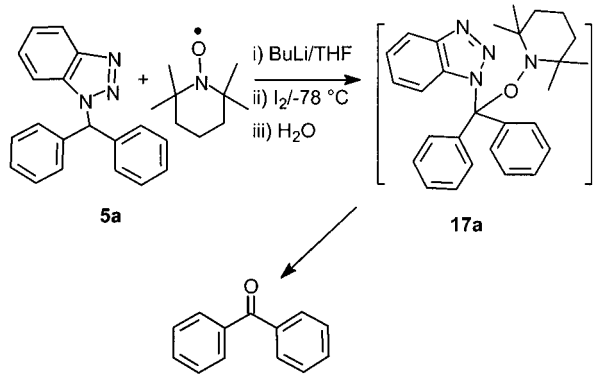
ESR Results. An important aspect of this study was to establish definitive evidence for the formation of the radical intermediates as postulated in Scheme 2. From the fast formation and disappearance of coloration in the reaction mixture, it was clear that the radicals were too reactive to be detected from any reaction mixture above −78 °C. However, below −78 °C, they are stable as evidenced by strong ESR signals detected from the reaction mixture.

Figure 1 shows a typical ESR spectrum obtained from reaction of 5-(benzotriazol-1-yl)dibenzosuberane **3e** with *n*-BuLi and iodine. The spectrum is centered at a *g* value of 2.0029 ± 0.0005, with a complex, only partially resolved multiline hyperfine structure. This *g* value is characteristic of a C-centered free radical with an extensive delocalization of the unpaired spin density; for example, *g* is 2.0026 for the triphenylmethyl radical.[4] Further evidence for the delocalization is the presence of the complex hyperfine structure. Several attempts were made to enhance the spectral resolution by optimizing the radical concentration, microwave power, magnetic field modulation amplitude, solvent polarity, sample temperature, and oxygen removal, but even the best results (shown in Figure 1) were not good enough for any quantitative assignment of the radical structure. However, the spectra obtained do allow the following conclusions:

(i) A C-centered radical is formed as an initial step in the reaction. This radical is highly reactive, with a lifetime of only a few minutes at −78 °C, but more stable at lower temperatures.

(ii) Full resolution of the hyperfine structure must await measurements of the hyperfine couplings by the electron−nuclear double resonance (ENDOR) technique, as was needed for triphenylmethyl radicals.[4]

Scheme 4



(iii) The radical's unpaired electron is delocalized from its central C-atom over a multitude of atomic sites. Qualitatively, the observed spectrum is consistent with the electron having dominant hyperfine interaction with one strongly coupled nitrogen and two protons, which should give rise to a roughly 1:2:1 triplet, split by a 1:1:1 triplet. The nitrogen splitting is evident from the fact that the central peak in Figure 1 has an approximate 1:1:1 triplet structure in the model. However, the (smaller) couplings with the remaining nitrogens and the ring protons blur the main peaks. Computer simulation was not possible because of the lack of resolution leading to a large degree of redundancy in the number as well as magnitude of the hyperfine couplings. Nevertheless, the spectra indicate the formation of a C-centered radical extensively delocalized with at least two nitrogen and two or more proton couplings and is consistent with the postulated dimerization pathway (Scheme 2).

Radical Trapping Reaction. TEMPO is widely used as an efficient radical trap. However, adding TEMPO to our reaction gave only diphenyl ketone which probably originated by decomposition of the hindered radical intermediate **17a** (Scheme 4).

In summary, the diaryl(benzotriazol-1-yl)methyl dimers **5** and **9** and the phenanthridine derivatives **4** and **8** were obtained by lithiation of diaryl(benzotrizol-1-yl)methanes followed by adding I_2. The structure of dimers **5** and **9** is different than those of the analogous trityl dimer. Intermediate, diphenyl(benzotriazol-1-yl)methyl radicals of the trityl type but with the radical center directly connected with a heteroatom have been demonstrated by ESR and radical trapping experiments.

Experimental Section

General. Melting points were determined with a Kofler hot stage apparatus without correction. ^1H and ^{13}C NMR spectra were recorded on a 300 and 75 MHz spectrometer in $CDCl_3$ with TMS or $CDCl_3$ as the internal reference. High-resolution mass spectra were measured on a Kratos/AE1-MS 30 mass spectrometer. THF was distilled from sodium/benzophenone prior to use. Lithiation reactions were carried out under the protection of dry nitrogen. All glassware was oven-dried. All moisture-sensitive reagents were transferred by means of predried syringes. Preparation of diaryl(benzotriazol-1-yl)methane was reported in our previous work.[14]

ESR Measurements. ESR measurements were made using a Varian E112 spectrometer operating at the X-band (9.50 G Hz) frequencies. The *g*-values were measured relative to the ESR standard 1,1-diphenyl-2-picrylhydrazyl (DPPH). Sample temperature was varied from about 90−350 K by using a Varian variable temperature (VT) accessory. All the reagents were well degassed and stored under nitrogen prior to

ESR measurements. It was necessary to make the ESR measurements at low temperatures, because the radical reactivity was high in the fluid media. No radicals could be detected at temperature above −50 °C, but they were quite stable below −78 °C. The radical concentration was estimated around a few mmol from signal intensities as compared with DPPH. Unfortunately, despite our efforts at sample degassing, temperature variation, and optimization of microwave power saturation and modulation amplitude, the ESR spectra did not exhibit well-resolved hyperfine splitting.

Preparation of Phenanthridines 4 and 8 and Dimers 5 and 9 (General Procedure). To a solution of diaryl-(benzotriazol-1-yl)methane (2 mmol) in dried THF (20 mL) was added *n*-BuLi (1.1 mL, 2 M, 2.2 mmol) at −78 °C under nitrogen, and the solution was stirred at this temperature for 10 min. Then, an I_2 (254 mg, 1 mmol) solution of THF (5 mL) was transferred into the reaction mixture. After the solution was stirred for 20 min at −78 °C, water (5 mL) was added to quench the reaction. The mixture was warmed to room temperature, washed with sodium bisulfate solution (2 × 20 mL), and then extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane) to obtain phenanthridines **4** (or **8**) and dimers **5** (or **9**) (Tables 1, 2, 3). The NMR data of phenanthridines **4** and **8** are identical with that obtained in our previous report.[14]

Preparation of α-[4-(Diphenylchloromethyl)phenyl]-α-(benzotriazol-1-yl)toluene (15a). A mixture of dimer **5a** (568 mg, 1 mmol), methylene chloride (10 mL), and concentrated hydrochloric acid (2 mL) was stirred at room temperature for 4 h. The mixture was neutralized by NaOH aq (2 N, 2 × 10 mL) and washed with water, before being extracted with ethyl acetate (3 × 10 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane 1:9) to give **15a** in 60% yield (290 mg): mp 80−82 °C; ^{1}H NMR ($CDCl_3$) δ 8.02−8.07 (m, 1 H), 7.37 (s, 1 H), 7.05−7.35 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 147.2, 146.5, 145.9, 137.4, 136.3, 132.9, 128.7, 128.3, 128.2, 127.8, 127.7, 127.3, 127.2, 123.9, 119.9, 110.5, 81.7, 66.8. HRMS calcd for $C_{32}H_{24}ClN_3$ 485.1659 (M^+), found 485.1743.

Preparation of 1-(Diphenylmethylene)-4-[phenyl(benzotriazol-1-yl)methylene]-2,5-cyclohexadiene (16a). To a solution of **5a** (568 mg, 1 mmol) in dried THF (30 mL) was added LDA (0.72 mL, 1.5 N in hexane, 1.1 mmol) at −78 °C under N_2 and the solution was stirred for 10 min. The reaction solution changed to red. After the reaction mixture was warmed to 0 °C, water (2 mL) was added to quench the reaction. The mixture was then extracted with ethyl acetate (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated to give the product **16a** as a red solid in 98% yield (440 mg): mp 220−223 °C; ^{1}H NMR ($CDCl_3$) δ 8.08−8.14 (m, 1 H), 7.18−7.39 (m, 17 H), 7.05−7.10 (m, 2 H), 6.96 (dd, J = 10.0, 1.9 Hz, 1 H), 6.82 (dd, J = 10.0, 1.9 Hz, 1 H), 6.18 (dd, J = 10.0, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 145.9, 144.7, 141.4, 141.2, 135.5, 134.2, 131.9, 131.6, 131.4, 131.3, 131.0, 129.4, 128.9, 128.7, 128.1, 128.0, 127.9, 127.5, 125.5, 125.0, 124.1, 120.1, 111.0. HRMS calcd for $C_{32}H_{23}N_3$ 450.1970 ($M^+ + 1$), found 450.2018.

Radical Trapping. To a solution of **5a** (283 mg, 1 mmol) were added TEMPO (156 mg, 1 mmol) in dried THF (20 mL) and *n*-BuLi (0.55 mL, 2M, 1.1 mmol) at −78 °C under nitrogen, and the solution was stirred at this temperature for 20 min. Then, an I_2 (127 mg, 0.5 mmol) solution of THF (5 mL) was transferred into the reaction mixture by syringe. After the solution was stirred for 20 min at −78 °C, water (5 mL) was added to quench the reaction. The reaction mixture was then allowed to warm to ambient temperature before washing with sodium bisulfite (2 × 10 mL) solution. The mixture was then extracted with ethyl acetate (3 × 20 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography to give diphenyl ketone in 70% yield, mp 48 °C.

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