Synthesis of 1,2,3,4-Bisiminofullerene and 1,2,3,4-Bis(triazolino)fullerene—On the Mechanism of the Addition Reactions of Organic Azides to [60]Fullerene

Clifton K.-F. Shen, Hsiao-hua Yu, Chiun-Gung Juo, Kuo-Ming Chien, Guor-Rong Her, and Tien-Yau Luh*

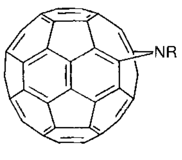
Dedicated to Professor Sunney I. Chan on the occasion of his 60th birthday

Abstract: The reactions of organic azides with [60]fullerene have paved the way for the synthesis of adducts with a variety of structures. Treatment of [60]fullerene with 2,2-dibenzyl-1,3-diazidopropane (**10**) in refluxing chlorobenzene afforded three products, namely, **8**, **9**, and **11** in 18, 25, and 11% yields, respectively. Thermolysis of **9a** in refluxing chlorobenzene gave a 40:54:6 mixture of **8**, **11**, and C_{60} in quantitative yield. No interconversion between **8** and **11** was observed. Whereas **11** was stable towards thermolysis, **8** decomposed to C_{60} (35% yield) on refluxing in chlorobenzene for 24 h, but it did not produce any **11**. This indicates that **9a** is an intermediate in the formation of **8** and **11**. A general mechanism for the addition of azides to C_{60} is proposed. A similar mechanistic pathway is suggested for the thermolysis of **9a**.

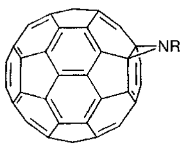
Keywords
azide adducts · fullerenes · reaction mechanisms · regioselectivity · thermolysis

Introduction

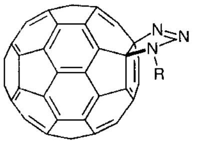
The reactions of organic azides with [60]fullerene have paved the way for the synthesis of adducts with a variety of structures.[1–9] Two types of monoadduct, **1**[1] and **2**,[2] have been obtained. The selectivity of this addition reaction appears to depend upon the reaction conditions. For example, a nitrene intermediate with an aryl or an acyl substituent, generated in situ by photolysis of the corresponding azides or by other means, yields **2** exclusively.[2f, j–l] Under thermolytic conditions, azides with an alkyl substituent add preferentially at the ring junction between five- and six-membered rings ([5,6] junction) to produce **1**, whereas azide reagents with an alkoxycarbonyl substituent lead predominantly to **2**. On the other hand, the thermal reaction of an aryl azide with C_{60} can yield either **1**[1a] or **2**.[2e] Interestingly, thermolysis of the triazoline adduct **3** gives **1** as the major, if not the exclusive, product.[2l, 3]



1

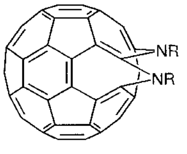


2

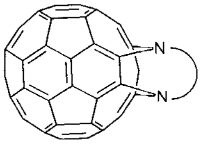


3

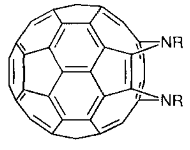
The situation is more complicated for bisadducts. Three distinct regioisomers of bisiminofullerenes have been obtained selectively, depending on the nature of the azide reagents.[3–9] Wudl and co-workers have elegantly synthesized bisiminofullerene **4** by treating C_{60} with alkyl azides.[3, 4] Reactions with bisazides tethered by a partial fragment of a crown ether behave



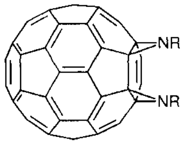
4



5



6



7

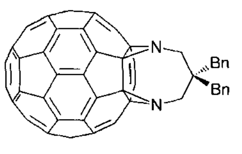
---

[*] Professor T.-Y. Luh, Professor G.-R. Her, C. K.-F. Shen, H.-h. Yu, C.-G. Juo, K.-M. Chien
Department of Chemistry, National Taiwan University
Taipei, Taiwan 106 (Republic of China)
Fax: Int. code +(2)363-6359
e-mail: tyluh@ccms.ntu.edu.tw

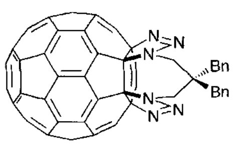
similarly.[5] The addition reaction occurs at the two [5,6] junctions of an acenaphthene moiety in C_{60}. In our preliminary communication, another type of bisiminofullerene, **5**, was obtained from the reaction of C_{60} with a bisazide tethered by an ethylene or a trimethylene bridge.[6] These azides add selectively at the two [5,6] junctions of a fluorene unit in C_{60}. Similar observations were made by Li and co-workers.[7] Hirsch and co-workers reported a third type of adduct, **6** ($R = CO_2R'$). Here the addition took place at the two ring junctions between six-membered rings ([6,6] junctions) of a phenanthrene unit in C_{60}; this was followed by a ring-opening process.[8, 9] It is interesting to note that none of these reactions lead directly to the formation of bisimino[60]fullerene **7**. It is believed that **7**, which may be formed initially, readily undergoes electrocyclic ring opening to produce **6**. Although AM 1 calculations suggest that the opened isomer **6** ($R = CO_2R'$) is more stable than **7**,[8, 9] addition at the diene moiety of a six-membered ring in C_{60} has been well documented.[10] More recently, Hirsch and co-workers examined the addition of alkoxycarbonylazides to C_{60}.[9] In addition to **6** ($R = CO_2Et$), six of seven other regioisomeric bisimino[60]fullerenes were isolated and characterized. Although **7** ($R = CO_2Et$) was not detected in this reaction, the corresponding parent bisimino[60]fullerene **7** (R = H) was obtained by treatment of **6** ($R = CO_2tBu$) with trifluoroacetic acid.[9] It was suggested that intermediate **7** (R = H) underwent an intramolecular Diels–Alder reaction. Apparently, the relative stability of **6** and **7** depends upon the substituent at nitrogen; this is also supported by theoretical calculations.[9] As part of our continuing interest in the addition of azides to fullerenes,[2d, 5] we now report our investigation of the first direct synthesis of 1,2,3,4-bisimino[60]fullerene **8** and 1,2,3,4-bis(triazolino)[60]fullerene **9** and discuss a plausible mechanism of addition of azides to fullerene.

Results and Discussion

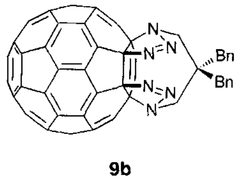
Our strategy is based on our previous work[6] in which tethered bisazide reagents were added to C_{60}. Since the trimethylene-bridged bisazide reacts with C_{60} to give the corresponding adduct **5** in satisfactory yield,[6] it was felt that introducing a geminal dialkyl group at the C2 position of the trimethylene bridge would induce a change in the reactivity, so that the intermediate product might be isolated. Thus, C_{60} was treated with 1.5 equiv 2,2-dibenzyl-1,3-diazidopropane (**10**) in refluxing chlorobenzene for 8 h; the standard workup procedure was then applied (see Experimental Section). Three products—**8**, **9**, and **11**—were obtained in 18, 25, and 11% yields, respectively. The structural assignments were based on ^1H and ^{13}C NMR spectra (Figure 1) as well as on the mass spectral data. The UV/Vis spectra for **8**, **9**, and **11** are shown in Figure 2.



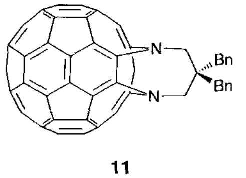
8



9a



9b



11

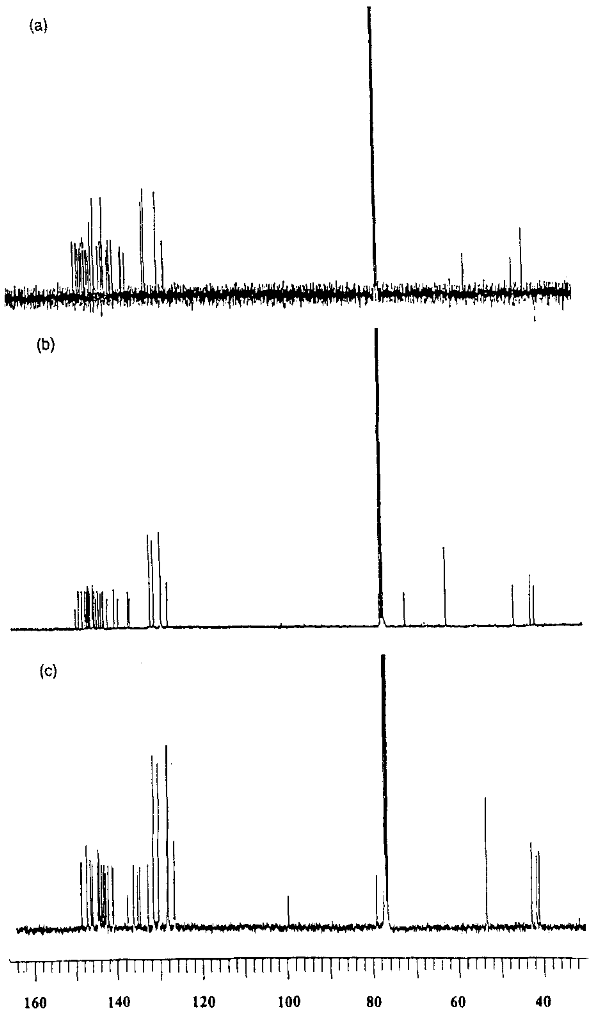


Figure 1. ^{13}C NMR spectra for a) **11**, b) **8**, and c) **9**.

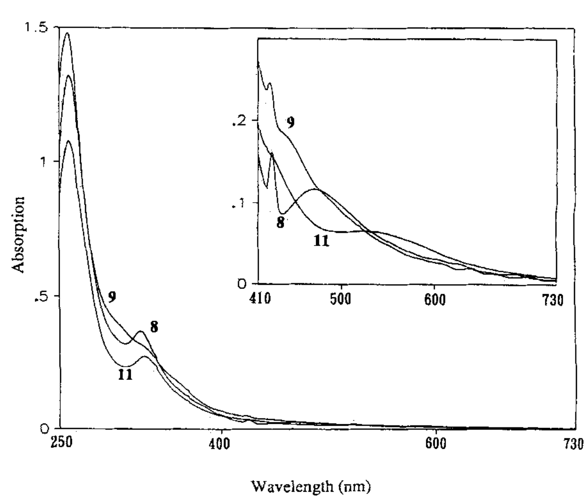


Figure 2. UV/Vis spectra for **11**, **8**, and **9** in $CHCl_3$ ($c = 1.0 \times 10^{-5}$ mol dm^{-3}; inset: $c = 5.0 \times 10^{-5}$ mol dm^{-3}).

The absorption spectrum and the ^{13}C NMR spectrum for **11** are consistent with the structure given above and similar to those reported previously for **5**.[6] Both **8** and **9** exhibit absorptions at a λ_{max} of about 425 nm, which is characteristic for adducts attached to a [6,6] junction. The broad band at a λ_{max} of 470 nm for **8** can also be found in the UV/Vis spectra of iminofullerene derivatives **2**.[2] In the ^{13}C NMR spectrum of **8**, the signals at $\delta = 71.74$ and 77.63, in addition to 30 peaks due to fullerene sp^2 carbons, clearly indicate the presence of a fused bisaziridine moiety. These results are also in agreement with those for **7** (R = H).[9]

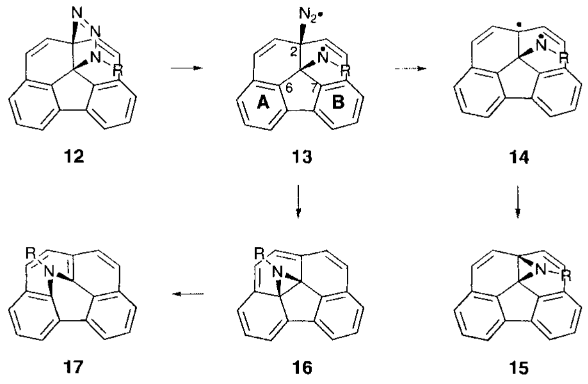
The isolation of the bistriazolino adduct **9** is not only interesting, but also significant. In the ^{13}C NMR spectrum, the 30 signals arising from the fullerene sp^2 carbons, in addition to the signals for the phenyl group and aliphatic carbons, are consistent with a C_s symmetry. The ^{13}C NMR absorptions for the two different fullerene sp^3 carbons in **9** appear at $\delta = 79.45$ and 99.82. In **3** the chemical shifts for sp^3 carbons of this type fall within the range $\delta \approx 80-110$, depending on the nature of the substituent on nitrogen.[2, 3, 11] Therefore, our results are in agreement with those already reported. Since the ^{13}C NMR data suggest that there is no ring opening in adduct **9**, we propose that addition has taken place at the [6,6] junction. Owing to the rigidity of the tether, **9a** or **9b** would be feasible structures.

Since **3** has been suggested to be an intermediate leading to **1** and **2**,[2, 3] it seems likely that **9** could also be an intermediate in the formation of **8** and **11**. Accordingly, thermolysis of **9** in refluxing chlorobenzene for 24 h afforded a 54:40:6 mixture of **8**, **11**, and C_{60} [Eq. (1)] in quantitative yield. It is noteworthy that there was no interconversion between **8** and **11**. When **8** was refluxed for 24 h in chlorobenzene, C_{60} was produced in 35% yield, but no **11** was detected. There was no decomposition of **11** under the same conditions. These results suggest that **9** may be an intermediate in the formation of **8** and **11**.

$$\mathbf{9} \xrightarrow{\Delta} \underbrace{\mathbf{8} + \mathbf{11}}_{\not\leftrightarrow} + C_{60} \qquad (1)$$

It is well documented that the C_{60} molecule behaves similarly to a [5]radialene in a number of addition reactions and that these double bonds are highly reactive. An enhancement in the reactivity would be expected for a bisazide **10**, which has a geminal dibenzyl group at C2. Stereochemically, the bisaddition reaction at two [6,6] junctions should occur preferentially to give **9**.

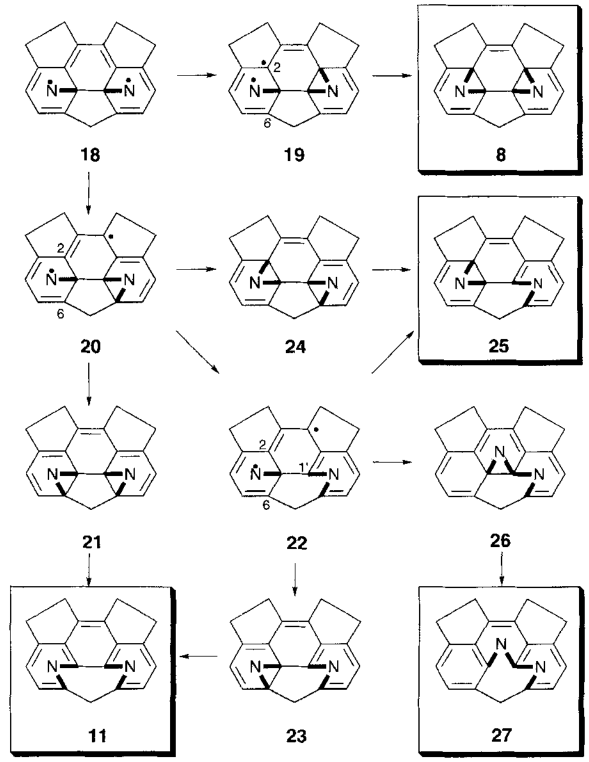
The mechanism for the thermolysis of triazolines has been investigated in detail.[12] Dipolar and biradical intermediates have both been suggested. Cleavage of the N–N single bond appears to precede cleavage of the C–N bond in both mechanisms. Nevertheless, before we discuss the conversion of **9** to **8** and **11**, we will present a possible mechanism for the thermolysis of triazoline **12** (Scheme 1).



Scheme 1. Possible mechanism for the thermolysis of triazoline **12** (only relevant section of the fullerene is shown).

A biradical intermediate **13** is expected from the thermal decomposition of **12**. Two possible routes will lead to **15** (**2**) or **17** (**1**), depending on the timing of the liberation of nitrogen molecule from **13**. If the cleavage of the C–N bond in **13** is fast, then biradical **14** will be formed, producing **15** on recombination at the C2 position. On the other hand, the nitrogen-centered radical in **13** may add to C6 or C7 (equivalent in the monoadduct) before the departure of the nitrogen molecule, leading to addition at the [5,6] junction to produce adduct **16**. At this point it is worth mentioning that **16** could be the kinetic product, because aromaticity of an additional six-membered ring moiety (ring A or B) will be lost with its formation. However, a rapid ring opening in **16** then yields stable **17**.

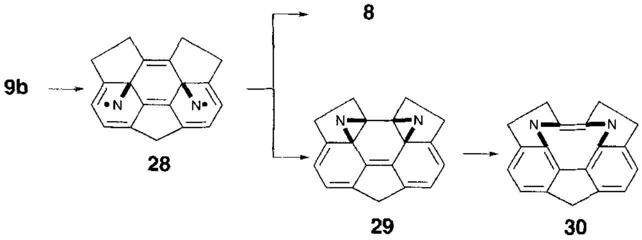
The possible route for the thermolysis of **9** is similar to that described in Scheme 1.[12] The two triazoline heterocycles may not decompose simultaneously. Since the three-carbon tether in **9** is quite rigid, the nitrogen-centered radical produced may not be as labile as that in **13**. Accordingly, there are several possibilities for the fate of the two nitrogen-centered radicals in **18**[13] generated stepwise from **9a** (Scheme 2). The formation of the first aziridine ring may lead to two delocalized biradicals, **19** and



Scheme 2. Possible reactions of the biradical species **18** (only relevant section of the fullerene is shown; substituents at nitrogen omitted for clarity).

20. Collapse of the biradical **19** by attack at C2 would yield **8**. In a similar manner, radical recombination at C6 in **20** would lead to **21**. Since the structure produced by ring closure at the [5,6] junction would be highly unstable,[2i] a simple ring opening of **21** would then yield **11**. Alternatively, there may be an initial ring opening of the aziridine moiety in **20** to give **22**. Further collapse of the biradical **22** by attack at C6 would give intermediate **23**, followed by another ring opening to produce **11**. It appears that the orientation of the aziridine ring that forms first might have a directing effect on the regioselectivity of the second aziridine ring. Recombination of biradicals **19** and **20** could also occur by different pathways and could eventually lead to the formation of further possible isomers **25** and **27** (Scheme 2). Since the two nitrogen atoms are tethered by a relatively rigid three-carbon chain, collapse of the biradical **20** or **22** by attack at C2 leading to **24** or **25**, respectively, might not be favorable. The absence of **27** from this reaction is striking. Presumably, in **20** or **22** the N_2 moiety may still be attached to C2, as in **13**, before collapse. A mechanism similar to the decomposition of **13** may occur here to produce **11**. Furthermore, the intermediate leading to **4** or **27** has been shown to be different from **9**.[3]

Decomposition of **9b** by a mechanism similar to that proposed in Scheme 2 would give **8** and **29** (Scheme 3). After ring opening, **29** would be converted into **30**, which was not detected. Accordingly, the most likely structure for **9** is **9a**.



Scheme 3. Possible decomposition reactions of **9b** (only relevant section of the fullerene is shown; substituents at nitrogen omitted for clarity)

Conclusion

We have described the first direct synthesis of bisimino[60]fullerene **8**, **11**, and bis(triazolino)[60]fullerene **9**, from the reaction of C_{60} and the corresponding bisazide. It has been established that **9** is an intermediate in the formation of **8** and **11**. These results serve as a useful clue to the understanding of the actual mode of the overall transformation in the addition of azides to C_{60}. A general mechanism has been proposed to explain the different regioselectivities for the addition of organic azides to [60]fullerene. Furthermore, the isolation of adduct **8** supports results from calculations performed by Hirsch, which indicate that the alkyl substituent on nitrogen would favor the bisring-closure product.[9]

Experimental Section

2,2-Dibenzyl-1,3-propanediyl dimesylate: To a solution of 2,2-dibenzyl-1,3-propanediol (2.56 g, 10.0 mmol) and Et_3N (4.0 g, 40 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added dropwise a solution of MsCl (4.0 g, 35 mmol) in CH_2Cl_2 (25 mL) over a period of 40 min. The mixture was allowed to warm to RT and stirred for 12 h. Aqueous HCl (10%, 50 mL) was added and the organic layer washed with NaOH (10%) and water. The organic layer was dried ($MgSO_4$) and evaporated in vacuo. The residue was recrystallized from methanol to give a white solid (2.68 g, 65%). M.p.: 124–125 °C; ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.81$ (s, 4H), 2.99 (s, 6H), 4.00 (s, 4H), 7.19–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 37.31$, 38.18, 42.15, 69.58, 127.20, 128.62, 130.59, 135.04; IR (KBr): $\tilde{\nu} = 1598$, 1494, 1461, 1413, 1387, 1360, 1333, 1328, 1281, 1267, 1172, 1051, 1030, 983, 948, 885, 865, 824, 775, 751, 733, 704 cm^{-1}; HRMS calcd for $C_{19}H_{24}O_6S_2$: 412.1014; found 412.1010.

2,2-Dibenzyl-1,3-diazidopropane (10): To a solution of the dimesylate prepared above (0.62 g, 1.5 mmol) in DMF (40 mL) and [15]crown-5 (one drop) was added NaN_3 (0.39 g, 6 mmol) and water (1 mL). The mixture was refluxed for one day then quenched with water (50 mL). The solution was extracted with ether and washed twice with water. The ether was evaporated in vacuo to afford **10** as a colorless viscous oil (0.25 g, 55%), which was used for the next reaction without further purification: ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 2.70$ (s, 4H), 3.06 (s, 4H), 7.26 (m); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 39.30$, 42.82, 54.06, 126.72, 128.41, 130.62. 136.43; IR (KBr): $\tilde{\nu} = 2100\ cm^{-1}$.

Reaction of 10 with C_{60}: To a refluxing solution of C_{60} (360 mg, 0.5 mmol) in chlorobenzene(360 mL) under N_2 was added dropwise bisazide **10** (0.75 mmol) in chlorobenzene (100 mL). The mixture was refluxed for 6–8 h and monitored by TLC. The solvent was removed in vacuo and the residue was repetitively chromatographed on silica gel to give three products **8** (85 mg, 18%), **9** (153 mg, 25%), and **11** (51 mg, 11%).

8: ^1H NMR ($CS_2/CDCl_3$, 300 MHz): $\delta = 2.86$ (s, 2H), 3.86 (d, $J = 12.5$ Hz, 2H), 3.91 (s, 2H), 4.48 (d, $J = 12.5$ Hz, 2H), 7.20–7.71 (m, 10H); ^{13}C NMR ($CS_2/CDCl_3$, 100 MHz): $\delta = 41.06$, 42.00, 45.88, 61.98, 71.74, 77.63, 126.90, 126.96, 128.43, 128.48, 130.15, 131.02, 135.71, 136.11, 138.47, 139.41, 139.43, 141.00, 141.88, 141.99, 142.17, 142.48, 142.59, 142.89, 143.02, 143.17, 143.55, 143.91, 143.95, 144.17, 144.31, 144.33, 144.44, 145.07, 145.32, 145.38, 145.49, 145.51, 145.73, 145.90, 146.21, 146.93, 147.78, 148.52; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-3}\ L\,mol^{-1}\,cm^{-1}$) = 689 (0.3), 652 (0.3), 625 (0.5), 470 (2.4), 425 (3.2), 325 (36.9), 259 (131.8) nm; IR (KBr): $\tilde{\nu} = 2366$, 2344, 1656, 1511, 1494, 1450, 1457, 1439, 1426, 1408, 1400, 1363, 1344, 1315, 1305, 1260, 1248, 1214, 1180, 1156, 1115, 1084, 1071, 1062, 1030, 760, 744, 729, 701, 648 cm^{-1}; FABMS: 970.8.

9: ^1H NMR ($CS_2/CDCl_3$, 300 MHz): $\delta = 2.78$ (s, 4H), 3.64 (s, 4H), 3.81 (d, $J = 15.0$ Hz, 4H), 4.62 (d, $J = 15.0$ Hz, 4H), 6.96–7.50 (m, 16H), 7.84–7.89 (m, 4H); ^{13}C NMR ($CS_2/CDCl_3$, 100 MHz): $\delta = 40.88$, 41.56, 42.67, 53.37, 79.45, 99.82, 126.86, 126.91, 128.24, 128.47, 130.65, 131.86, 133.08, 134.97, 135.42, 136.34, 136.52, 137.81, 141.12, 141.23, 141.31, 142.36, 142.83, 142.89, 143.10, 143.27, 143.49, 143.78, 144.01, 144.32, 144.50, 144.55, 144.60, 144.70, 144.76, 144.89, 146.04, 146.35, 146.47, 146.54, 147.36, 147.40, 148.63, 148.87; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-3}\ L\,mol^{-1}\,cm^{-1}$) = 699 (0.2), 658 (0.3), 637 (0.4), 607, 445, 422 (4.9), 331, 257 (147.9) nm; IR (KBr): $\tilde{\nu} = 1493$, 1467, 1438, 1427, 1378, 1355, 1331, 1305, 1275. 1191, 1167, 1154, 1112, 1072, 1032, 1011, 990, 961, 919, 856, 819, 762, 753, 729, 701 cm^{-1}; FABMS: 1026.2.

11: ^1H NMR ($CS_2/CDCl_3$, 300 MHz): $\delta = 3.17$ (s, 2H), 3.47 (s, 2H), 4.18 (d, $J = 22.6$ Hz, 2H), 4.33 (d, $J = 22.6$ Hz, 2H), 7.11–7.42 (m, 10H); ^{13}C NMR ($CS_2/CDCl_3$, 100 MHz): $\delta = 42.51$, 44.97, 45.19, 56.25, 126.74, 126.77, 128.35, 128.42, 131.18, 131.62, 135.71, 136.46, 136.52, 136.75, 138.59, 139.09, 139.37, 139.67, 139.85, 140.70, 140.92, 141.18, 141.24, 141.31, 141.88, 142.96, 142.98, 143.61, 143.68, 143.73, 144.11, 144.49, 144.77, 145.07, 145.08, 145.37, 145.76, 145.80, 146.17, 146.64, 147.05, 147.82.; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-3}\ L\,mol^{-1}\,cm^{-1}$) = 524 (1.3), 427, 329 (27.4), 258 (107.8) nm; IR (KBr): $\tilde{\nu} = 2096$, 1947, 1655, 1638, 1600, 1511, 1493, 1464, 1444, 1405, 1377, 1354, 1327, 1290, 1251, 1220, 1206, 1187, 1155, 1133, 1120, 1072, 1030, 1003, 917, 782, 749, 729, 701 cm^{-1}; FABMS: 970.8.

Thermolysis of 9: A solution of **9** (10 mg, 0.01 mmol) in chlorobenzene (10 mL) was refluxed for 24 h. The mixture was cooled to room temperature and then analyzed by HPLC [Buckyclutcher column, toluene:hexane = 2:1, flow rate = 3 $mL\,min^{-1}$, UV detector wavelength = 340 nm, retention time (min)]: C_{60} (1.6), **11** (1.9), **8** (2.0), and **9** (2.5)].

Compounds **8** and **11** were treated in the same way.

Acknowledgment: This work was supported by the National Science Council of the Republic of China.

Received: September 30, 1996 [F479]

---

[1] a) M. Prato, Q. C. Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, *115*, 1148; b) M. Takeshita, T. Suzuki, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1994**, 2587; c) C. J. Hawker, P. M. Saville, J. W. White, *J. Org. Chem.* **1994**, *59*, 3503; d) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Miller, A. T. Taylor, *J. Chem. Soc. Chem. Commun.* **1995**, 885; e) G. Schick, T. Grösser, A. Hirsch, *ibid.* **1995**, 2289; f) J. C. Hummelen, M. Prato, F. Wudl, *J. Am. Chem. Soc.* **1995**, *117*, 7003.

[2] a) T. Ishida, K. Tanaka, T. Nogami, *Chem. Lett.* **1994**, 561; b) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, D. W. H. Rankin, *J. Chem. Soc. Chem. Commun.* **1994**, 1365; c) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Miller, A. T. Taylor, *Tetrahedron Lett.* **1994**, *35*, 9067; d) L.-L. Shiu, K.-M. Chien, T.-Y. Liu, T.-I Lin, G.-R. Her, S.-L. Huang, T.-Y. Luh, *J. Chem. Soc. Perkin Trans. 1*, **1994**, *23*, 3355; e) M. Yan, S. X. Cai, J. F. W. Keana, *J. Org. Chem.* **1994**, *59*, 5951; f) J. Averdung, J. Mattay, D. Jacovi, W. Abraham, *Tetrahedron* **1995**, *51*, 2543; g) J. Averdung, H. Luftmann, J. Mattay, K.-U. Claus, W. Abraham, *Tetrahedron Lett.* **1995**, *36*, 2957; h) M. R. Banks, J. I. G. Cadogan, I. Gosney, A. J. Henderson, P. K. G. Hodgson, W. G. Kerr, A. Kerth, P. R. R. Langridge-Smith, J. R. A. Miller, A. R. Mount, J. A. Parkinson, A. T. Taylor, P. Thornburn, *J. Chem. Soc. Chem. Commun.* **1996**, 507; i) A. B. Smith III, H. Tokuyama, *Tetrahedron* **1996**, *52*, 5257; j) J. Averdung, H. Luftmann, I. Schlachter, J. Mattay, *ibid.* **1995**, *51*, 6977; k) J. Averdung, C. Wolff, J. Mattay, *Tetrahedron Lett.* **1996**, *37*, 4683; l) J. Averdung, J. Mattay, *Tetrahedron* **1996**, *52*, 5407.

[3] T. Grösser, M. Prato, V. Lucchini, A. Hirsch, F. Wudl, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1343.

[4] J. C. Hummelen, B. Knight, J. Pavlovich, R. González, F. Wudl, *Science* **1995**, *269*, 1554.

[5] L. Echegoyen, private communication.

[6] a) L.-L. Shiu, K.-M. Chien, T.-Y. Liu, T.-I Lin, G.-R. Her, T.-Y. Luh, *J. Chem. Soc. Chem. Commun.* **1995**, 1159; b) C. K.-F. Shen, K.-M. Chien, C.-G. Juo, G.-R. Her, T.-Y. Luh, *J. Org. Chem.* **1996**, *61*, 9242.

[7] G.-X. Dong, J.-S. Li, T.-H. Chan, *J. Chem. Soc. Chem. Commun.* **1995**, 1725.

[8] I. Lamparth, B. Nuber, G. Schick, A. Skiebe, T. Grösser, A. Hirsch, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2257.

[9] G. Schick, A. Hirsch, H. Mauser, T. Clark, *Chem. Eur. J.* **1996**, *2*, 935.

[10] a) M. Rasinkangas, T. T. Pakkanen, T. A. Pakkanen, M. Ahlgrén, J. Rouvinen, *J. Am. Chem. Soc.* **1993**, *115*, 4901; b) C. C. Henderson, C. M. Rohlfing, R. A. Assink, P. A. Cahill, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 786; c) I. J. Mavunkal, Y. Chi, S.-M. Peng, G. H. Lee, *Organometallic* **1995**, *14*, 4454; d) A. L. Balch, D. A. Costa, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1995**, *117*, 8926.

[11] B. Nuber, F. Hampel, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1996**, 1799.

[12] For a review, see: P. Scheiner in *Selective Organic Transformations, Vol 2* (Ed.: B. S. Thyagarajan), Wiley-Interscience, New York, **1970**, p 327.

[13] These two nitrogen-centered radicals may not exist at the same time. This intermediate is proposed for the sake of simplicity in order to explain the overall reaction.

0947-6539/97/0305-0748 $ 17.50+.50/0