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Reaction of 2-Azidobenzothiazole and 1-Azido-4-(3',5'-dimethyl-1'-pyrazolyl)tetrafluorobenzene with [60]Fullerene and Characterization of the Adducts by Fast-atom Bombardment Mass Spectrometry

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Abstract.— By FAB-MS and ^{13}C NMR spectroscopy the structures of three new imino[60]fullerenes have been established: two monoadducts **5** (σ-azaridinefullerene) and **7** (π-azafullaroid) and one bisadduct (π-bisazafullaroid) **8**. Copyright © 1996 Elsevier Science Ltd

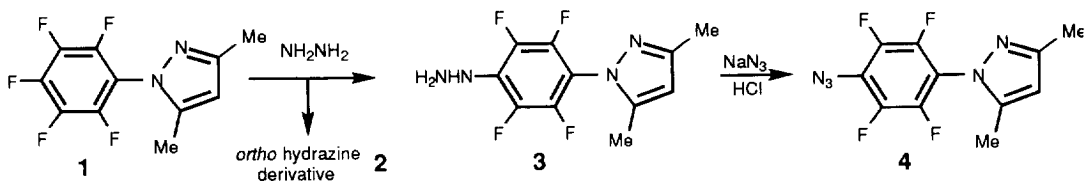
INTRODUCTION

Imino[60]fullerenes have been reported as products of photochemical or thermal reactions between [60]fullerene and organic azides.[1-11] These [60]fullerene derivatives are either σ-azaridinefullerenes,[1-4] [6-6]-closed transannular bond-bridged compounds, or π-azafullaroids,[5-8] [5-6]-open transannular bond-bridged compounds. The question that arises is: can the azafulleroid ([5-6]-π bonding type) or aziridinefullerene ([6-6]-σ bonding type) formation be explained by the duality of azide decomposition mechanisms?. The reaction of organic azides can take place by two pathways. In one, the azide is converted to a nitrene which adds to the [60]fullerene. This pathway is most common for the carbonyl azides and recently[1-3] the direct addition of acylnitrenes has been reported leading to ([6-6]-σ)[60]fullerene adducts. In the other pathway, a [6-6]-σ-triazoline[60]fullerene intermediate is formed by 1,3-dipolar cycloaddition of the azide on the [60]fullerene which yields a [5-6]-π-azafullaroid by nitrogen extrusion. Evidence for the 1,3-dipolar cycloaddition was brought out[8] by the isolation of a triazoline [60]fullerene intermediate which was, under heating, converted to a ([5-6]-π)[60]fullerene derivative as the major product. A [5,6]-σ-iminofullerene structural determination has been reported[10] but it was denied by A. Hirsch *et al.*.[11] Recently, some imino[60]fullerene compounds have been reported[12-14] to be precursors of the azafulleronium $C_{59}N^+$. This ion was formed in the gas-phase and its existence was based on mass spectrometric studies. We now report our results of the thermal addition of 2-azidobenzothiazole and 1-azido-4-(3',5'-dimethylpyrazol-1'-yl)tetrafluorobenzene to [60]fullerene. The adducts were characterized by mass spectrometry and their structural assignments were realized by ^{13}C NMR spectroscopy. The formation of the ion $C_{59}N^+$ from the bis-2-azabenzothiazol-adduct **8** was studied by FAB-mass spectrometry.

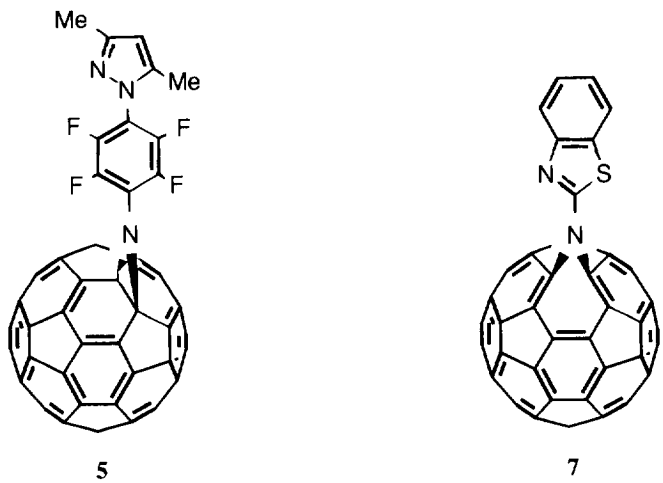
RESULTS AND DISCUSSION

Synthesis. For our purpose we synthesized 1-azido-4-(3',5'-dimethylpyrazol-1'-yl)tetrafluorobenzene (**4**) according to the sequence of reactions described in the following scheme. The preparation of hydrazines **2** and **3** has been previously described in the literature.[15] Azide **4** was obtained from hydrazine **3** by action of sodium nitrite in presence of hydrochloric acid. The fullerene derivative **5** was formed by refluxing [60]fullerene and azide **4** in toluene for 48 hours. Compound **5** was isolated by chromatography on silica gel as the unique reaction

product in 70% yield based on recovered [60]fullerene. 2-Azidobenzothiazole (**6**) has been previously prepared and described.[16] Its addition to [60]fullerene in refluxing chlorobenzene yielded a mixture of mono and polyadducts. Chromatography of the mixture on a chromatotron allowed the isolatation of the fullerene monoadduct **7** in 25% and the bisadduct **8** in 11% yield based on unreacted [60]fullerene.



Mass Spectrometry. The [60]fullerene derivatives **5**, **7** and **8** have been characterized and analyzed by mass spectrometry. Most of [60]fullerene related compounds degrade under direct electron impact ionization conditions, therefore, the analyses have been done by fast-atom bombardment ionization using the *m*-nitrobenzyl alcohol (NBA) matrix.



The FAB-MS spectra of **5**, **7** and **8** are consistent with the proposed structure. A typical characteristic of the FAB technique is the presence of a protonated molecular ion MH^+.[17] A result of most MS techniques for the [60]fullerene derivatives is the presence of the ion C_{60}^+ at m/z = 720 in their MS spectrum. It is never clear whether this ion corresponds to the loss of the organic adduct part or to the presence of [60]fullerene in the sample. By using the CAD-MS technique we found an evidence for the retro-addition phenomenon. For instance, the FAB-MS of compound **5** displays both ions at m/z = 720 and 978, and in the negative mode presents the ions m/z = -720, -977 and -978, as reported in figure 1. The analysis of the CAD-MS of the ion MH^+ at m/z = +978 showed a prominent molecular ion at m/z = 720 (figure 2). Therefore this ion proceeds from the fragmentation of the ion m/z = +978. This result supports and confirms the hypothesis of a retroaddition reaction occurring while recording a FAB-MS spectrum. Moreover, it has been described[18-23] that the use of *m*-nitrobenzyl alcohol, as matrix to record the FAB-MS spectrum, leads to the formation of oxidized ions MO^+ and MOH^+ (M = C_{60}). These oxidative properties have to be taken into account while interpreting a FAB-MS spectrum. In our case, we observed the oxygen fixation on [60]fullerene derivative **5**. Its FAB-MS spectrum (negatives ions) shows two ions at m/z = -736 and -994 corresponding to $[C_{60} + OH]^+$ and $[M + OH]^+$ respectively. A similar phenomenon

was observed in the case of the 2-azidobenzothiazole bisadducts **8**. The double addition would yield a compound having a molecular weight of 1016 Da. However, the spectrum of **8** showed two abundant ions at m/z = +1033 (1016 + OH) and m/z = +1181 (1164 + OH) characteristic of the oxygenated ions of the bis- and trisadduct fullerenes. ^{13}C NMR revealed the very small amount of the derivative of triple addition compared to the abundance of bisadduct **8**. The FAB-MS spectrum of bisadduct **8** revealed the presence of a peak at m/z = 722 the intensity of which is half of the abundance of the peak at m/z = 720 (C_{60}^+). Using the "Isotope Pattern Calculator" (version 1.6.5) the relative abundance of C_{60} peaks appears to be: 720 (100%), 721 (67.35%), 722 (22.30%), and 723 (4.84%). A relative abundance of 50% shows that the peak at m/z = 722 includes the ion $C_{59}N^+$ which is formed by fragmentation of **8**.

^{13}C NMR Spectroscopy. The structure of the compounds **5** and **7** have been determined by ^{13}C NMR spectroscopy based on symmetry considerations. The adduct part of compound **5** was characterized by the signals of the pyrazole C-5 at 149.96 ppm, C-3 at 139.74 ppm, C-4 at 106.18 ppm, and the signals of the two methyl groups at 13.21 and 10.17 ppm. The signals of the tetrafluorophenyl carbons did not appear on the spectrum due to their complicated coupling pattern with the fluorine atoms. The C_{2v}-symmetry of **5** was deduced from the number of sp^2-C signals, sixteen in the range of 145-140 ppm. The presence of one signal at 79.68 ppm, characteristic of an sp^3-carbon of the fullerene core, confirmed an ([6-6]-σ) aziridine structure. The stability of the aziridine structure has been tested by refluxing compound **5** in chlorobenzene. We observed no evolution to an ([5-6]-π) azafulleroidal structure. The ^{13}C NMR spectrum of the azidobenzothiazole **7** exhibits 4 phenyl-C signals between 109 and 127 ppm and thirty peaks in the fullerene sp^2-C area (134-149 ppm), the latter being consistent with a C_s symmetry. Due to the absence of a signal characteristic of a fullerene sp^3-C and the presence of a sp^2-C signal at 145.37 ppm having a higher intensity (3 sp^2-carbons), compound **7** was assigned to an ([5-6]π) open annulene with an azafulleroid structure. Azidobenzothiazole bisadduct **8** showed characteristic fullerene peaks in the range 150-135 ppm and eight signals corresponding to the sp^2 carbons of the two benzothiazole units.

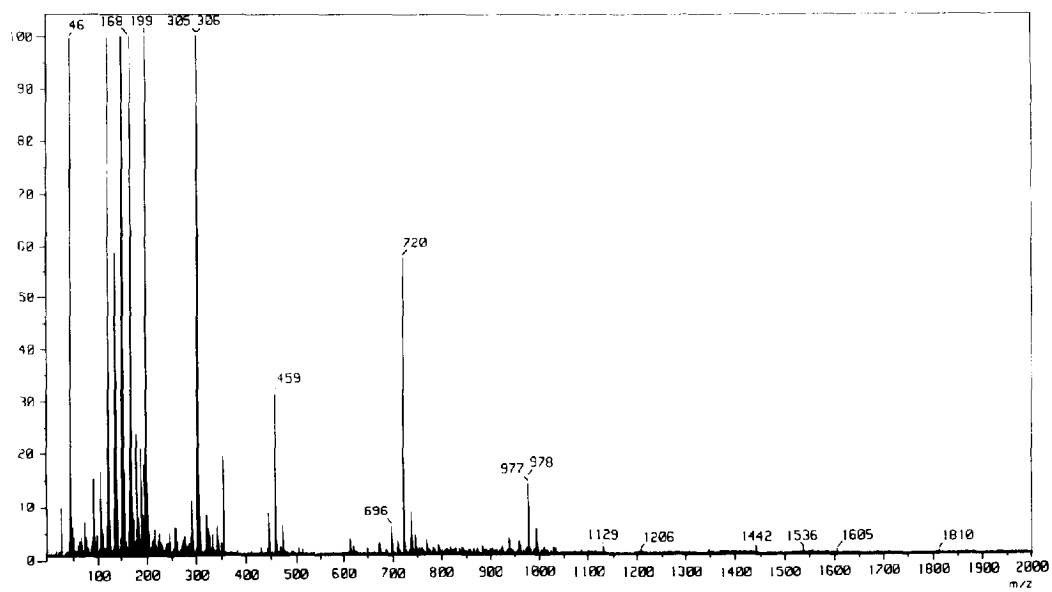


Figure 1

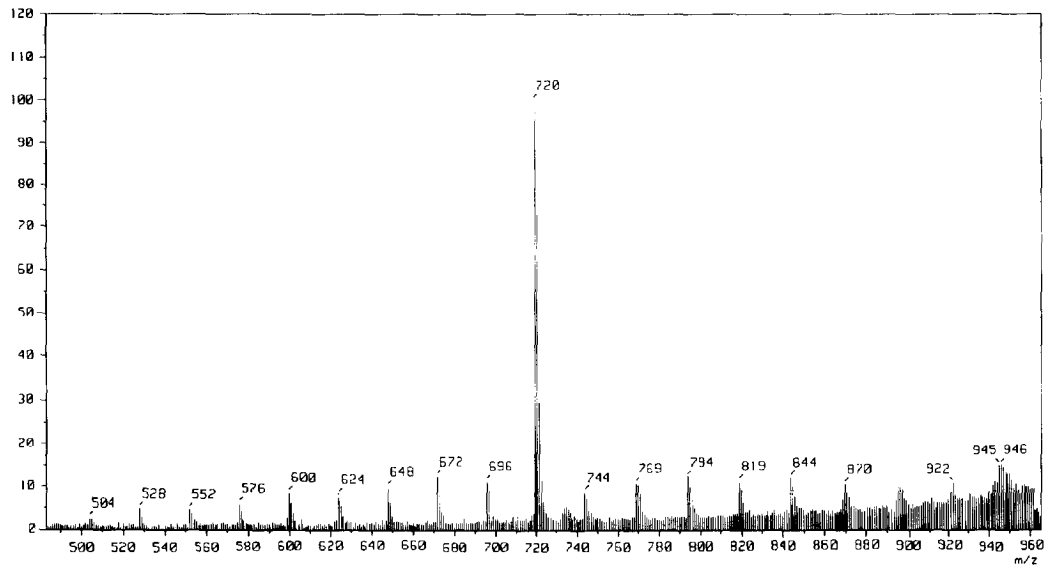


Figure 2

EXPERIMENTAL

General remarks and materials. The preparation of 2-azidobenzothiazole (**6**) has already been reported in the literature.[15] The fullerene C_{60} (>99.5%) was purchased from MER Corporation. The FAB mass spectra were recorded by using SX102 spectrometer (Jeol, Tokyo, Japan). Xenon was used in the FAB experiments. The beam energy of neutral atoms was set to 3 KeV (emission currents 20 mA). Instrument callibration was accomplished using Ultramark 1621 as a reference. Samples were placed on the target by dissolving them directly in the matrix. Collisionally activated dissociation (CAD) was performed in the first field-free region of the spectrometer and product ion spectra were obtained by B/E scanning. The collision gas (helium) pressure was adjusted to 50% attenuation of the precursor in beam. The matrix, *m*-nitrobenzyl alcohol (NBA), was purchased from Aldrich. ^{1}H NMR spectra were obtained from a 200 MHz Varian-Gemini spectrophotometer and ^{13}C NMR spectra were recorded on a Varian-Unity spectrophotometer at 500 MHz. Chemical shifts are given in ppm downfield of tetramethylsilane (TMS). NMR solvents were $CDCl_3$ or CS_2. While using CS_2 a capillary tube filled with DMSO-d_6 was added to the NMR sample for internal lock. IR spectra were performed on Perkin Elmer 681 IR spectrophotometer.

Pentafluoro(3,5-dimethylpyrazol-1-yl)benzene (**1**)

500 mg (2.50 mmol) of pentafluorophenylhydrazine, 245 mg (2.45 mmol) of 2,4-pentadione in 10 mL ethanol were heated to reflux for 1.5 h. Then the reaction mixture was kept stirring at room temperature overnight. Evaporation of the solvent followed by chromatography on silica gel of the residue eluting with CH_2Cl_2 then with MeOH/CH_2Cl_2 (1:19) yielded 528 mg (81%) of the orange oil **1**.

1. EI-MS (m/z): 262. ^{1}H NMR (200 MHz; $CDCl_3$): δ = 6.02 (s, 1H, pyrazol-H), 2.24 (s, 3H, CH_3), 2.12 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz; $CDCl_3$): δ = 151.56 (pyrazol C-3), 144.18 (*o*-phenyl-C, ddt, $^1J_{C\text{-}F}$ = 254 Hz, $^2J_{C\text{-}F}$ = 12 Hz, $^3J_{C\text{-}F}$ = 4 Hz), 142.06 (pyrazol C-5), 141.56 (*p*-phenyl-C, dtt, $^1J_{C\text{-}F}$ = 254 Hz, $^2J_{C\text{-}F}$ = 13 Hz, $^3J_{C\text{-}F}$ = 4 Hz), 137.75 (*m*-phenyl-C, dddd, $^1J_{C\text{-}F}$ = 254 Hz, $^2J_{C\text{-}F}$ = 12 and 13 Hz, $^3J_{C\text{-}F}$ = 4 Hz), 115 (1-

phenyl-C, tt, $^2J_{C-F}$ = 12 Hz, $^3J_{C-F}$ = 4 Hz), 106.69 (pyrazol C-4), 13.24 (3-CH_3), 10.36 (5-CH_3) ppm.

2- and 4-(3',5'-Dimethylpyrazol-1'-yl)tetrafluorophenyl hydrazines (**2**) and (**3**).
2.0 g (7.60 mmol) of pentafluoro(3,5-dimethylpyrazol-1-yl)benzene (**1**) were diluted in 20 mL ethanol. 0.52 mL (16.80 mmol) of anhydrous hydrazine was added dropwise. The reaction mixture was stirred at room temperature for 48 h. The solution was then filtrated and evaporated. The residue was carefully chromatographied on silica gel eluting with MeOH/CH_2Cl_2 (1:19) to yield 116 mg (5%) of **2** and 804 mg (37%) of **3**.
2. EI-MS (m/z): 274. ^{1}H NMR (200 MHz; $CDCl_3$): δ = 5.99 (s, 1H, pyrazol-H), 5.25 (s, 1H, NH), 2.20 (s, 3H, CH_3), 2.06 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz; $CDCl_3$): δ = 151.64 (pyrazol 3-C), 142.13 (pyrazol 5-C), 106.77 (pyrazol 4-C), 14.06 (3-CH_3), 11.22 (5-CH_3) ppm.
3. EI-MS (m/z): 274. ^{1}H NMR (200 MHz; $CDCl_3$): δ = 5.97 (s, 1H, pyrazol-H), 5.64 (s, 1H, NH), 4.07 (s, 2H, NH_2), 2.23 (s, 3H, CH_3), 2.07 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz; $CDCl_3$): δ = 151.52 (pyrazol C-3), 145.00 (*o*-phenyl-C), 142.90 (pyrazol C-5), 138.00 (*m*-phenyl-C), 132.00 (*p*-phenyl-C), 106.77 (pyrazol C-4), 14.06 (3-CH_3), 11.22 (5-CH_3) ppm, 1-phenyl-C not observed.

4-(3',5'-Dimethylpyrazol-1'-yl)tetrafluorophenyl azide (**4**).
To 0.32 mL of HCl (35%) in 30 mL H_2O, 500 mg (1.82 mmol) of 4-(3,5-dimethylpyrazol-1-yl)tetrafluorophenyl hydrazine (**3**) dissolved in 30 mL diethylether were added at 0°C. At the same temperature a solution of 145 mg (2.10 mmol) of sodium nitrate dissolved in 2 mL H_2O were added dropwise. The reaction mixture was then stirred at 0°C for 15 minutes. The ethereal layer was separated and the aqueous layer was extracted with diethylether. The combined ethereal solutions were dried over Na_2SO_4 and evaporated. Chromatography on silica gel of the crude product eluting with ethylacetate/hexanes (1:9) yielded 220 mg (42%) of **4**.
4. IR (KBr): ν_{N_3} = 2117 cm^{-1}. EI-MS (m/z): 285. ^{1}H NMR (200 MHz; $CDCl_3$): δ = 6.00 (s, 1H, pyrazol-H), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz; $CDCl_3$): δ = 151.07 (pyrazol C-3), 144.30 (*o*-phenyl-C), 142.70 (pyrazol C-5), 141.00 (*m*-phenyl-C), 130.50 (*p*-phenyl-C), 126.50 (1-phenyl-C), 107.26 (pyrazol C-4), 13.96 (3-CH_3), 11.09 (5-CH_3) ppm.

4-(3',5'-Dimethylpyrazol-1'-yl)tetrafluorophenyl azafullerene (**5**).
A solution of 60 mg (0.08 mmol) C_{60} and 38 mg (0.13 mmol) of 4-(3,5-dimethylpyrazol-1-yl)tetrafluorophenyl azide (**4**) in 100 mL of distilled toluene was heated to reflux under nitrogen for 48 h. The solution turned from purple to red-brown. The solvent was evaporated under reduced pressure. The black crude residue was chromatographed on silica gel eluting with toluene allowing to recover unreacted C_{60} (36 mg), then eluting with toluene/ethylacetate (49:1) 10 mg (70% yield based on recovered C_{60}) of **5** has been isolated.
5. FAB-MS (NBA; m/z): 978 (MH^+). ^{1}H NMR (200 MHz; CS_2): δ = 5.75 (s, 1H, pyrazol-H), 2.02 (s, 3H, CH_3), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (500 MHz; CS_2): δ = 149.96 (pyrazol C-5), 144.76, 144.67, 144.60, 144.44, 143.92, 143.68, 143.31, 143.23, 142.54, 142.46, 142.38, 142.08, 141.52, 141.45, 140.48, 140.39, 139.74 (pyrazol C-3 and 16 fullerene-sp^2C), 106.18 (pyrazol C-4), 79.68 (fullerene-sp^3C), 13.21 (3-CH_3), 10.17 (5-CH_3) ppm.

(2-Benzothiazol)azafullerene (**7**) *and bis(2-benzothiazol)azafullerene* (**8**).
To 300 mg (0.41 mmol) C_{60} dissolved in 50 mL distilled chlorobenzene were added 90 mg (0.51 mmol) of 2-azidobenzothiazole (**6**). The reaction mixture was heated to 180°C for a week. The solution was then evaporated and the residue was chromatographed on silica gel eluting with toluene to recover 223 mg of C_{60} and a brown-red fraction which was chromatographed on a chromatotron eluting toluene/MeOH (49:1) yielding 23 mg (24.8%) of compound **7** and 12 mg (11%) of compound **8**.
7. FAB-MS (NBA; m/z): 869 (MH^+). ^{1}H NMR (200 MHz; CS_2): δ = 7.40 (d, 1H, J=7.7 Hz), 7.28 (d, 1H, J=7.9 Hz), 7.03 (dd, 1H), 6.88 (dd, 1H) ppm. ^{13}C NMR (500 MHz; CS_2): δ = 148.67, 147.28, 147.09, 145.70, 145.59, 145.47, 145.37, 144.94, 144.91, 144.77, 144.62, 144.37, 144.13, 143.90, 143.34, 142.26,

142.18, 141.99, 141.77, 141.63, 141.52, 141.49, 141.45, 141.13, 140.07, 139.87, 138.85, 137.42, 135.00, 134.51 (fullerene-sp^2C), 126.47, 123.14, 121.77, 109.52 (phenyl-C) ppm.

8. FAB-MS (NBA; m/z): 1018 (MH^+). ^1H NMR (200 MHz; CS_2): δ = 7.70-6.80 (m)ppm. ^{13}C NMR (500 MHz; CS_2): δ = 147.80-135.16 (fullerene-sp^2C), 132.85, 126.81, 126.35, 125.34, 124.13, 123.58, 120.86, 120.08 (phenyl-C) ppm.

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References

1. Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Millar, J. R. A.; Taylor, A. T. *J. Chem. Soc. Chem. Commun.* **1995**, 885.
2. Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Millar, J. R. A.; Parkinson, J. A.; Rankin, D. W. H.; Taylor, A. T. *J. Chem. Soc. Chem. Commun.* **1995**, 887.
3. Averdung, J.; Mattay, J.; Jacobi, D.; Abraham, W. *Tetrahedron* **1995**, *51*, 2543.
4. Yan, M.; Xiaong Cai S.; Keana, J. F. W. *J. Org. Chem.* **1994**, *59*, 5951.
5. Prato, M.; Chan Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
6. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc. Chem. Commun.* **1994**, 925.
7. Hawker, C. J.; Saville, P. M.; White, J. W. *J. Org. Chem.* **1994**, *59*, 3503.
8. Grösser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1343.
9. Dong, G.-X.; Li, J.-S.; Chan, T.-H. *J. Chem. Soc. Chem. Commun.* **1995**, 1725.
10. Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Millar, J. R. A.; Taylor, A. T. *Tetrahedron Lett.* **1994**, *35*, 9067.
11. Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc. Chem. Commun.* **1995**, 2289.
12. Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grösser, T.; Hirsch, A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2257.
13. Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554.
14. Mattay, J. *Tetrahedron* **1995**, *51*, 6977.
15. Henrie II, R. N.; Yeager, W. H. *Heterocycles* **1993**, *35*, 415.
16. Faure, R.; Galy, J.-P.; Vincent, E.-J.; Fayet, J.-P.; Mauret, P.; Vertut, M.-C.; Elguero, J. *Can. J. Chem.* **1977**, *55*, 1728.
17. Miller, J. M.; Chen, L. Z. *Rapid Commun. Mass Spectrom.* **1992**, 6, 184.
18. Wood, J. M.; Kahr, B.; Hoke II, S. H.; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.
19. Kowalski, M. H.; Sharp, T. R.; Stang, P. J. *Org. Mass Spectrom.* **1987**, *22*, 642.
20. Fachin, G.; Zanotto, L.; Sertaglia, R.; Traldi. P. *Org. Mass Spectrom.* **1992**, *27*, 1181.
21. Reynolds, J. D.; Cook, K. D.; Burn, J. L. E.; Woods, C. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 113.
22. Davey, S. N.; Tetler, L. W.; Laigh, D. A.; Moody, A. E. *Org. Mass Spectrom.* **1993**, *28*, 559.
23. Hoke II, S. H.; Molstad, J.; Kahr, B.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 209.

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