



Cycloaddition Reaction of 1-(4-Nitrophenyl)-3-phenylnitrile Ylide to Buckminsterfullerene[60]

A.A.Ovcharenko, V.A.Chertkov, A.V.Karchava, M.A.Yurovskaya

Department of Chemistry, M.V.Lomonosov Moscow State University
Moscow, 119899, Russia

Abstract: Cycloaddition of 1-(4-nitrophenyl)-3-phenylnitrile ylide generated *in situ* from N-benzyl-4-nitrobenzimidoyl chloride to C₆₀ yields to 1,2-[3,4-dihydro-2-phenyl-5-(4-nitrophenyl)-2H-pyrrolo]-[60]fullerene and diastereomeric mixture of two 5,6-open isomers. Moreover, double carbon-nitrogen bond of 5,6-open of adduct is located in α position to unsubstituted phenyl ring.

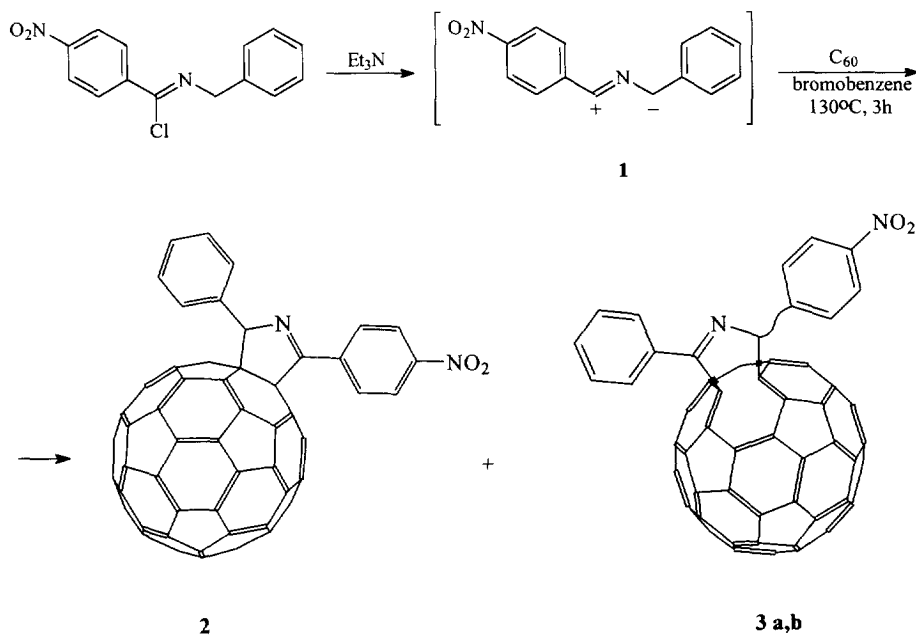
© 1997 Published by Elsevier Science Ltd.

The derivatives of fullerene attract much attention due to their interesting properties and possibilities of application. Functionalization by cycloaddition reactions represents a powerful route to fullerene derivatives.¹ The [3+2] cycloaddition reaction to buckminsterfullerene have been very frequently used for the synthesis of 1,2-dihydrofullerene adducts with annexed five-membered heterocyclic rings.² Commonly the addition leads to 6,6-ring bridged derivatives with a few exceptions.³ For instance, the 1,3-dipolar cycloaddition of nitrile oxides to 6-6 double bond of C₆₀ leads to isoxazoline derivatives. The cycloaddition reaction with these 1,3-dipoles was extensively studied.⁴ By contrast, the reactions of C₆₀ with carbon and nitrogen analogs of nitrile oxides (nitrile ylides⁵ and nitrile imines⁶) were much less examined. Averdung et al.^{5a} have reported that reaction of C₆₀ with 1,3-diphenyl nitrile ylide generated by irradiation of 2,3-diphenyl-2H-azirine affords exclusively one monoadduct identified as 1,2-(3,4-dihydro-2,5-diphenyl-2H-pyrrolo)-[60]fullerene.

We are now reporting the first example of cycloaddition of 1-(4-nitrophenyl)-3-phenylnitrile ylide **1** generated *in situ* from N-benzyl-4-nitrobenzimidoyl chloride⁷ to buckminsterfullerene C₆₀.

A solution of N-benzyl-4-nitrobenzimidoyl chloride (60 mg, 0.22 mmol) in dry bromobenzene (20 ml) was added dropwise to a stirred solution of C₆₀ (100 mg, 0.14 mmol) in bromobenzene (15 ml) containing triethylamine (25 mg, 0.25 mmol) at 130°C during 3 h under atmosphere of nitrogen. The colour of the reaction mixture changed from purple to dark brown. The solvent was distilled off and the residue was treated with ether. Column chromatography on silica gel (benzene) of the resulting dark brown powder afforded unreacted C₆₀ (12 mg) as the first fraction and *two* distinct cycloadducts in 38% and 30% yield (based on C₆₀ conversion) as black solid.

As it is obvious from mass spectra both **2**⁸ and **3**⁹ represent the isomeric monoadducts. The spectra exhibit peaks at *m/z* 958 (C₇₄H₁₀N₂O₂, monoadducts) and [MH-C₁₄H₁₀N₂O₂]⁺ at *m/z* 721. The analysis of mass spectra suggested that the molecules **2** and **3** consisted of a C₆₀ moiety and a substituent C₁₄H₁₀N₂O₂.



The IR spectra^{8,9} of both products showed the characteristic bands at 1690 (C=N), 1540 and 1355 (NO₂), 723 and 530 cm⁻¹ (C₆₀).

The UV/VIS^{8,9} spectra are similar to that of C₆₀.

The ¹H-NMR spectra^{8,9} as well as mass spectra suggested that the products **2** and **3** are constitution isomers. Moreover, as shown by ¹H-NMR the product **3** represents a mixture of two diastereomers in a 2:1 ratio¹⁰. We succeeded in the isolation of the major diastereomeric adduct **3a**.⁹

The position of double carbon-nitrogen bond in monoadducts **2** and **3a** was assigned on the basis of double resonance experiments.¹¹ Thus, the long range ¹H-¹H coupling constants between 2-H proton at 7.21 ppm and *ortho*-, *para*- and *meta*- protons of unsubstituted phenyl ring were observed for monoadduct **2**, while the protons of 4-nitrophenyl group did not display a coupling constants with same proton. For the other isomer **3a** the methine proton resonance at 7.36 ppm couples only with protons of 4-nitrophenyl group. On the basis of these data it may be concluded that the double carbon-nitrogen bond is located in the α position to 4-nitrophenyl substitute in monoadduct **2**, and α position to unsubstituted phenyl group in monoadduct **3a**. Probably double carbon-nitrogen bond in minor diastereomer **3b** is arranged in the same manner as for **3a**.

The ¹³C-NMR spectra of the fullerene derivatives **2**⁸ and **3**⁹ show the typical number of fullerene signals of C₁ symmetrical molecules. The spectrum of **2** exhibits 3 signals in *sp*³-area at 78.37, 88.87 and 89.10 ppm, 63 peaks in *sp*²-area in the range of 128-155 ppm (7 have a relative intensity of 2 carbons) including signals of aromatical substituents in dihydropyrrole ring and peak at 175.94 ppm (signal for C=N). Thus, the ¹³C-NMR spectrum confirms an 6,6-closed structure.

The second isomer **3** shows only one signal in *sp*³-area at 87.74 ppm. The signals of the two bridged *sp*²-hybridised carbon atoms appear at lower field in fullerene area and can not be assigned clearly. The 60 peaks (12 have a relative intensity of 2) were indicated in the range of 124-155 ppm (*sp*²-area). The signal of C=N subunit appeared at 172 ppm. Consequently, due to the absence of characteristic signals of 1,2-dihydrofullerene structure in *sp*³-area and the presence of *sp*³-C signal at 87.74 compounds **3** was assigned to 5,6-opened annulene structure.

Acknowledgements: V.A.Chertkov acknowledges the financial support of this work by the Russian Fundamental Investigation Foundation (Grant N 97-03-33794a).

References and Notes

1. Taylor, R.; Walton, D.R.M. *Nature*. **1993**, *363*, 685.
2. Resent reviews: a) Hirsh, A. *Synthesis*. **1995**, 895. b) Sliwa, W. *Fullerene Sci. Tech.* **1995**, *3*, 243
3. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wuld, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479. b) Banks, M.R.; Cadgan, J.I.C.; Gosney, I.; Hodgson, P.K.G.; Langridge-Smith, P.R.R.; Parkinson, J.A.; Rankin, D.W.H.; Taylor, A.T. *J. Chem. Soc., Chem. Commun.* **1995**, 887.
4. a) Meier, M.S.; Poplawska, M. *Tetrahedron*. **1996**, *52*, 5043, and ref. cited. b) Irgartinger, H.; Weber, A. *Tetrah. Lett.* **1966**, *37*, 4137. c) Irgartinger, H.; Weber, A.; Escher, T. *Liebigs Ann.* **1966**, 1845
5. Averdung, J.; Albrecht, E.; Lauterwein, J.; Luftmann, H.; Mattay, J.; Mohn, H.; Muller, W.H.; ter Meer, H.U. *Chem. Ber.* **1994**, *127*, 787. b) Averdung, J.; Mattay, J. *Tetrahedron*. **1996**, *52*, 5407
6. Muthu, S.; Maruthamuthu, P.; Ragunathan, R.; Vasudena Rao, P.R.; Mathews, C.K.; *Tetrah. Lett.* **1994**, *35*, 1763. b) Matsubara, Y.; Tada, H.; Nagase, S.; Yoshida, Z. *J. Org. Chem.* **1995**, *60*, 5372
7. Huisgen, R.; Stangl, H.; Strum, H.J.; Raab, R.; Bunge, K. *Chem. Ber.* **1972**, *105*, 1258.
8. MS (Chemical ionization, *i*-C₄H₁₀): *m/z* (%) 1016 (13) [MH⁺ C₄H₁₀]⁺, 1015 (51) [M⁺ C₄H₁₀]⁺, 959 (96) [MH⁺], 958 (2) [M⁺], 929 (4) [MH⁺-NO], 777 (100) [(M+C₄H₁₀)-C₁₄H₁₀N₂O₂]⁺, 721 (26) [MH⁺-C₁₄H₁₀N₂O₂], 720 (10) [M⁺-C₁₄H₁₀N₂O₂]. IR (C₂Cl₄), cm⁻¹: 1695 (C=N), 1538 (NO₂), 1390, 1355 (NO₂), 1285, 1210, 1090, 723 (C₆₀), 655, 550, 530 (C₆₀). UV/VIS, λ_{max} nm (lg ϵ): 330 (4.29), 430 (3.26), 630 sh. (2,43), 690 (2.27). ¹H-NMR (400 MHz, CS₂-acetone-D₆, 9:1) δ ppm : 7.21 (1H, s, N-CH), 7.33 [1H, t.t,

- $^3J=7.6$ Hz, $^4J=1.32$ Hz, *p*-H(Ph)], 7.44 [2H, t.t., $^3J=7.6$ Hz, $^4J=1.3$ Hz, *m*-H(Ph)], 7.69 [2H, d.t., $^3J=7.6$ Hz, $^4J=1.3$ Hz, *o*-H(Ph)], 8.33 [2H, d.d., $^3J=8.9$ Hz, $^5J=1.8$ Hz, *m*-H(NO₂Ph)], 8.46 [2H, d.d., $^3J=8.9$ Hz, $^5J=1.8$ Hz, *o*-H(NO₂Ph)]. ¹³C-NMR (100 MHz, CS₂-acetone-D₆, 9:1) δ ppm: 78.38, 88.87, 89.10 (*sp*³-C), 124.33 (2C), 128.54 (2C), 128.63, 128.94 (2C), 129.05, 129.15, 129.39, 129.49, 129.54, 129.59, 130.78 (2C), 131.05, 131.10, 134.34, 135.29, (2C), 140.15, 140.38, 140.43, 140.75 (2C), 141.07, 141.81, 142.17, 142.26, 142.37, 142.53, 142.59, 142.78, 142.96, 143.14, 143.20, 143.24, 143.29, 143.68, 144.46, 144.85, 144.92, 145.36, 145.43, 145.49, 145.60, 145.69, 145.79, 145.86, 145.89, 145.94, 145.99, 146.09, 146.30, 146.40, 146.47 (2C), 146.57, 146.84, 146.90, 147.24, 147.37, 147.45, 147.49, 148.42, 149.47, 149.55, 152.76, 155.32, 175.94 (C=N).
9. **3a**: MS (Chemical-ionization, *i*-C₄H₁₀): *m/z* (%) 1016 (7) [MH⁺ C₄H₁₀]⁺, 1015 (25) [M⁺ C₄H₁₀]⁺, 959 (45) [MH⁺], 958 (21) [M⁺], 777 (100) [(M+C₄H₁₀)-C₁₄H₁₀N₂O₂]⁺, 721 (48) [MH⁺-C₁₄H₁₀N₂O₂], 720 (57) [M⁺-C₁₄H₁₀N₂O₂]. IR (C₂Cl₄), cm⁻¹: 1693 (C=N), 1540 (NO₂), 1390, 1353 (NO₂), 1288, 1270, 1210, 1090, 725 (C₆₀), 655, 550, 530 (C₆₀). UV/VIS, λ_{max} nm (lg ε): 320 sh.(4.19), 440 (3.15), 645 sh. (2.40), 680 (2.37), 710 (2.29). ¹H-NMR (400 MHz, CS₂-acetone-D₆, 9:1) δ ppm: 7.36 (1H, s, N-CH), 7.53 [3H, m, 2*m*-, *p*-H(Ph)], 8.08 [2H, d, $^3J=8.0$ Hz, *m*-H(NO₂Ph)], 8.22 [2H, d.d., $^3J=7.8$ Hz, $^4J=1.25$ Hz, *o*-H(Ph)], 8.29 [2H, d, $^3J=8.0$ Hz, *o*-H(NO₂Ph)]. ¹³C-NMR (100 MHz, CS₂-acetone-D₆, 9:1) δ ppm: 87.74 (*sp*³-C), 124.58, 128.86 (2C), 129.33, 129.83, 129.93, 131.41, 131.42 (2C), 131.89 (2C), 134.73, 134.86, 135.70, 136.63 (2C), 136.88, 140.49 (2C), 140.72, 141.09, 142.26, 142.30, 142.50, 142.57, 142.61 (2C), 142.76, 142.79, 142.82 (2C), 142.99, 143.25, 143.30, 143.32, 143.35, 143.74, 143.77, 144.60 (2C), 144.65, 144.80, 144.98, 145.36, 145.61 (2C), 145.72 (2C), 145.83, 145.93, 145.95, 146.10, 146.25, 146.39, 146.48, 146.50, 146.57, 146.60 (2C), 146.89, 146.94, 147.05, 147.55, 147.56, 147.70, 147.76 (2C), 148.00, 148.37, 149.05, 152.20, 155.30, 172.16 (C=N).
10. The ratio of **3a**:**3b** was determined from ¹H-NMR spectrum of mixture in bromobenzene-D₅; **3a**: 7.69 [d, *o*-H(Ph)], 8.15 [d, *o*-H(NO₂Ph)]; **3b**: 7.82 [d, *o*-H(Ph)], 7.97 [d, *o*-H(NO₂Ph)], the other protons signals cannot be distinguished from signals **3a**.
11. The value of long range ¹H-¹H coupling constants between aromatic protons and α protons at *sp*³-C in ¹H-NMR spectra of **2** and **3a** are closely similar to that of toluene (see Hansen, M.; Jakobsen, H.J. *J. Magn. Reson.* **1975**, *20*, 520). The values of coupling constants for **2** and **3** will be reported.

(Received in UK 23 June 1997; accepted 8 August 1997)