STEREOSPECIFIC CYCLOADDITIONS OF *CIS*– AND *TRANS* - *N*-BENZYL-1,2-DIPHENYLAZIRIDINES WITH C_{60}

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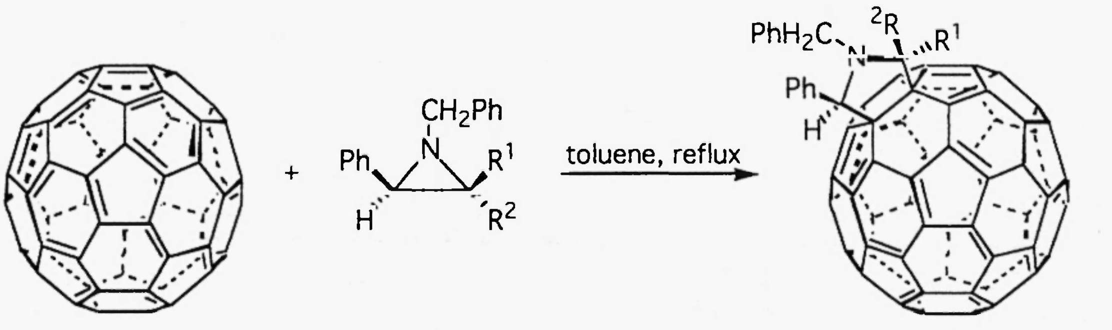
Abstract: The thermal cycloaddition of C_{60} with *cis*- and *trans*-*N*-benzyl-1,2-diphenylaziridines afforded the corresponding fullereno[1,2-*c*]pyrrolidines *via* a stereospecific process of 1,3-dipolar cycloaddition.

The extraordinary structure of fullerenes, particularly that of C_{60}, and their fascinating physical and chemical properties have attracted considerable attention in many scientific disciplines. Thus, in a very short time they became the subject of numerous publications (1). Due to the electron-withdrawing nature of each pyracyclene unit in fullerenes, these molecules appear to undergo the reactions characteristic to poorly-conjugated and electron-deficient alkenes showing a high tendency to behave as a reactive 2π component in cycloadditions. The cycloaddition reactions of C_{60} represent a useful strategy to modify fullerenes because easily separable, well-defined monoaddition adducts, which retained many of the fullerene's physical and chemical properties, are obtained in most cases. Thus, Diels-Alder (2), [2 + 2] (3), and [8 + 2] (4) cycloadditions of C_{60} have produced new fullerene derivatives resulting from the addition of one equivalent of reagent to the fullerene. The1,3-dipolar cycloadditions with diazoalkanes (the most studied) (5), alkyl or aryl azides (6), sulfinimines (7), nitrile ylides (8), disiliranes (9), and nitrile oxides (10) gave similar monoadducts. The functionalization of fullerene by 1,3-dipolar cycloadditions of C_{60} with azomethine ylides, generated *in situ* in different ways, was also reported (11). Due to their considerable theoretical and synthetic interest the [2 + 3] cycloadditions of azomethine ylides have been extensively explored (12). They represent one of the most reactive and versatile classes of 1,3-dipoles and can be generated from a



1

2
a: R^1 = Ph, R^2 = H
b: R^1 = H, R^2 = Ph

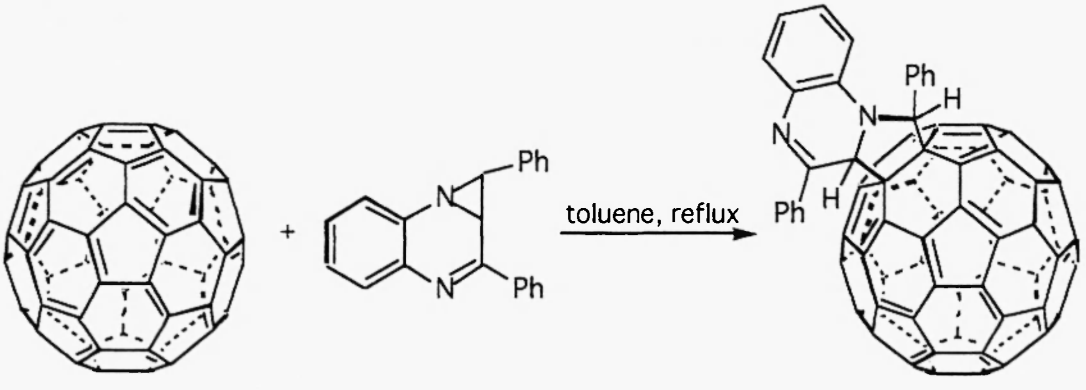
3
a: R^1 = Ph, R^2 = H (83%)
b: R^1 = H, R^2 = Ph (82%)

Scheme 1

wide variety of easily accessible starting materials. Specifically, we have studied the dipolar cycloadditions of the azomethine ylides generated by thermal electrocyclic ring opening of aziridines (13). In this context we now report the stereospecific cyloaddition of *cis-* and *trans*-1-benzyl-1,2-diphenylaziridines 2 onto C_{60} 1 (Scheme 1).

The reactions of *cis-* and *trans*-1-benzyl-1,2-diphenylaziridines 2a and 2b with C_{60} 1 took place smoothly when heated at reflux in toluene for 14 and 20 hours, to give the stable monoadducts 3a and 3b in good yields (14), respectively. The cycloaddition was completely stereospecific, with respect to the configuration of the aziridines being inverted in the fullerene derivatives. The cycloadducts 3 were separated by column chromatography (silica gel, hexane/benzene=10/1, v/v) and characterized by TOFMS (M^+, 1005), ^{1}H- and ^{13}C-NMR (15). The ^{1}H-NMR data allowed us to assign the structures of the two cycloadducts as *trans-N*-benzyl-2,5-diphenylfullereno[1,2-*c*]pyrrolidine 3a and *cis-N*-benzyl-2,5-diphenylfullereno[1,2-*c*]pyrrolidine 3b. Thus, the *cis* adduct 3b shows one singlet signal at δ 4.36, integrating for the two equivalent benzylic protons, whereas the *trans* adduct 3a shows for the homologue protons an AB quartet (J = 14.3 Hz) at δ 3.47 and 4.33, each integrating for one proton. These have been indeed the case for the analogous *N*-benzyl-2,5-diphenylpyrrolidines (13c,d). An inspection of the molecular models of 3a and 3b shows that the *cis* isomer 3b is sterically more congested around the 2,5-phenyl groups, thus perhaps leading to a less symmetric conformation. This fact is supported by the ^{13}C-NMR spectra which show a reduced number of signals for the *trans* isomer 3a, *i.e.* 31 as compared with 42 for the *cis* isomer 3b (15). The stereochemistry observed in these reactions is the one predicted for the cycloadditions involving thermal conrotatory ring-opening of aziridines (16).

Similarly, when refluxed for 20 hours in toluene with 1, 1,1a-dihydro-1,2-diphenylaziridino[1,2-*a*]quinoxaline 4 gave 1,4-diphenylfullereno[1,2-*c*]pyrrolidino[1,2-*a*]quinoxaline 5, (Scheme 2). This new quinoxaline fused fullereno[1,2-*c*]-pyrrolidine derivative 5 was also separated by column chromatography (silica gel, hexane/benzene=1/2, v/v) and characterized by TOFMS (M^+, 1016), ^{1}H- and ^{13}C-NMR (17).



1

4

5
(78%)

Scheme 2

Similar 1,3-dipolar cycloadditions of C_{60} with azomethine ylides generated by thermal ring-opening of aziridines have been reported by Maggini *et al.* (11b,c). However, to the best of our knowledge, this is the first example of thermal cycloaddition reactions of aziridines that afford completely stereospecifically the corresponding fullereno[1,2-*c*]pyrrolidine derivatives. Since the newly obtained fullerene derivatives 3 and 5 are well suited for further functionalization, the present [3 + 2] cycloaddition of C_{60} might offer potential use in the fields of compounds with biological activity and material chemistry (11b, 18).

Further studies and applications of this type of reactions are currently underway.

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(14) The yields, shown on Scheme 1 and Scheme 2, are based on C$_{60}$ conversion.

(15) (a) The NMR data for *trans*-1-*N*-benzyl-2,5-diphenylfullereno[1,2-*c*]pyrrolidine are 3a: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 3.47, 4.33 (ABq, *J* = 14.3 Hz, 2H, Ph-CH$_2$-), 6.22 (s, 2H, 2,5-H), 7.06-7.61 (m, 15H, 3 x Ph); ^{13}C-NMR (67.8 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 50.29 (N-CH$_2$), 74.40 (C$_{60}$: Csp^3), 76.42 (N-CH), 127.15, 128.11,128.46, 128.56, 128.61, 136.68, 137.91, 139.96, 141.55, 141.60, 141.95, 142.40, 142.54, 143.02, 144.42, 145.14,145.18, 145.39, 145.40, 145.86, 145.90, 146.01 146.06, 146.09, 146.14, 147.24, 153.81, 155.60.
(b) The NMR data for *cis*-1-*N*-benzyl-2,5-diphenylfullereno[1,2-*c*]pyrrolidine are 3b: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 4.36 (s, 2H, Ph-CH$_2$-), 5.28 (s, 2H, 2,5-H), 6.84-8.36 (m, 15H, 3 x Ph); ^{13}C-NMR (67.8 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 50.02 (N-CH$_2$), 74.33 (C$_{60}$: Csp^3), 76.14 (N-CH), 127.74, 128.09, 128.15, 128.37, 128.41, 129.19, 129.41, 130.19, 130.65, 130.81, 131.90, 135.55, 136.41, 136.47, 139.11, 139.64, 141.27, 141.64, 141.74, 141.79, 141.90, 141.92, 142.29, 142.39, 144.13, 144.42, 144.87, 145.00, 145.03, 145.27, 145.63, 145.70, 145.86, 145.96, 146.06, 146.49, 147.07, 153.28, 154.00.

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(17) The NMR data for 1,4-diphenylfullereno[1,2-*c*]pyrrolidino[1,2-*a*]quinoxaline 5 are: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 2.33 (s, 1H, 3a-H), 5.26 (s, 1H, 1-H), 6.84-8.21 (m, 14H); ^{13}C-NMR (67.8 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 67.53 (C-3a), 76.32 (C-3), 76.37 (C-2), 79.85 (C-1), 111.56 (C-9), 121.05 (C-7), 127.71, 127.82, 128.32, 128.43, 129.22, 129.78, 129.90, 131.03, 133.33, 133.98, 135.36, 135.66, 136.19, 136.87, 137.23, 137.66, 138.61, 139.22, 139.73, 140.10, 141.38, 141.47, 141.63, 141.68, 141.77, 141.84, 141.92, 141.95, 141.98, 142.03, 142.07, 142.35, 142.39, 142.48, 142.54, 142.57, 142.71, 142.90, 142.98, 143.64, 144.02, 144.07, 144.25, 144.68, 144.84, 144.96, 145.05, 145.12, 145.14, 145.17, 145.35, 145.68, 145.78, 145.82, 145.91, 145.96, 146.00, 146.09, 146.24, 146.69, 146.83, 147.81, 151.32, 152.40, 155.71, 157.13.

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