Reactions of C_{2v}-symmetrical C_{60} pentakis-adducts with diazomethane: regioselective formation of hexakis- to octakis-adducts and mechanism of methanofullerene formation by addition of diazomethane followed by dinitrogen extrusion

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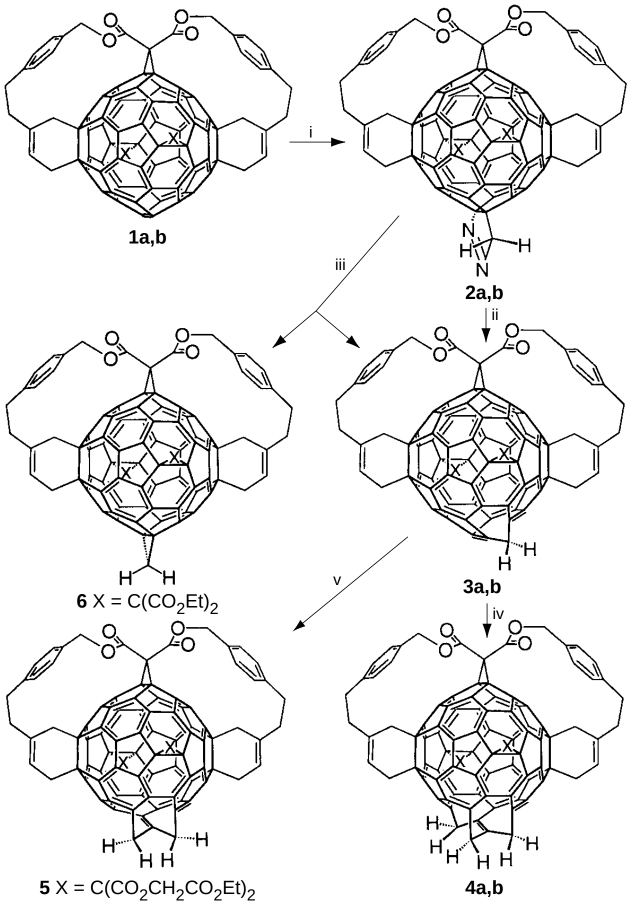
Repeated treatment of the C_{2v}-symmetrical C_{60} pentakis-adducts 1a,b with diazomethane provided with high regioselectively the novel heptakis- 5 and octakis-adducts 4a,b *via* hexakis-adducts 3a,b; an orbital symmetry-controlled reaction mechanism for the thermal dinitrogen extrusion from the pyrazoline intermediates in the addition of diazomethane to fullerenes is proposed.

The 1,3-dipolar cycloaddition of diazomethane to C_{60} or C_{70} occurs at 6-6-bonds (bonds at the junction between two 6-membered rings) under formation of isolable pyrazoline derivatives.[1,2] Photolysis of these intermediates under N_2-extrusion provides an isomeric mixture of methanofullerenes, namely 6-6-closed ones, in which the 6-6-bond is bridged in a cyclopropane-type fashion, and 6-5-open ones, in which the methano group bridges the open junction between a 6- and 5-membered ring,[2] similar to the bonding in 1,6-methano-[10]annulene.[3] In contrast, thermolysis of the pyrazolines proceeds with high regioselectivity and yields 6-5-open adducts almost exclusively.[1,2a,c] As part of our research on higher adducts of C_{60},[4] we became interested in exploring whether diazomethane would still add to highly functionalised carbon spheres of considerably reduced electrophilicity[4c] and dienophile character and whether the product distribution obtained by N_2-extrusion from the intermediate pyrazolines would be similar to that observed for the parent fullerenes. The C_{2v}-symmetrical pentakis-adducts **1a** and **1b**[4b] (Scheme 1) were chosen as starting materials in these investigations since their reactivity is limited to a single 6-6-bond in pseudo-octahedral position.[5] Addition to this bond is particularly favourable since it generates a residual fullerene π-chromophore consisting of eight stable benzenoid ring sub-structures.[6] Here, we report the stepwise addition of diazomethane to **1a**,**b** under formation of novel hexakis- to octakis-adducts of C_{60} and propose a mechanism for the N_2-extrusion from the intermediate pyrazolines to give methanofullerenes.

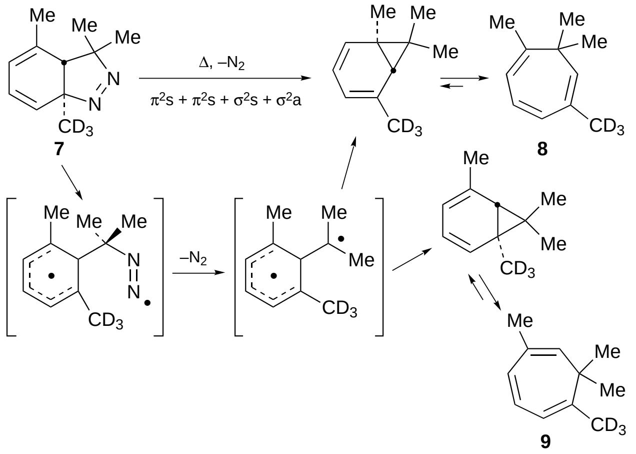
Reaction of **1a**,**b** with CH_2N_2 (*ca.* 60-fold excess) in $CHCl_3$ at 0 °C afforded the corresponding yellow, C_s-symmetrical pyrazolines **2a**,**b** in high yields (Scheme 1).† Upon heating to reflux in CCl_4, N_2-extrusion led to the orange-coloured, C_1-symmetrical 6-5-open methanofullerenes **3a**,**b** in nearly quantitative yield. Treatment of **3a**,**b** with CH_2N_2 (*ca.* 40-fold excess) in $CHCl_3$ at 0 °C gave within 15 min the yellow–orange, C_1-symmetrical octakis-adducts **4a**,**b** in an astonishing 90% yield. A further reaction of **4a**,**b** with additional diazomethane was not observed. When **3b** was reacted with CH_2N_2 (*ca.* 20-fold excess) for 10 min in CH_2Cl_2 at −80 to −60 °C, followed by quenching of the excess reagent with AcOH at −60 °C and workup at room temperature, heptakis-adduct **5** was directly obtained. Neither in the formation of **4a**,**b** nor in the preparation of **5** were pyrazoline intermediates observed. When pyrazoline **2a** was photolysed, the C_{2v}-symmetrical hexakis-adduct **6** and the C_1-symmetrical regioisomer **3a** were obtained in *ca.* 1 : 1 ratio and a combined yield of 15%. The isomeric mixture could not be separated by column chromatography. Therefore, **6** was purified by adding CH_2N_2 at 0 °C to the mixture in CH_2Cl_2 which transformed **3a** into octakis-adduct **4a** while leaving **6** unchanged. Chromatographic purification (SiO_2, CH_2Cl_2) was subsequently feasible, yielding **6** as a bright yellow solid. Thus, the reaction of diazomethane with pentakis-adducts **1a** ultimately yielded similar products to those observed in the addition to C_{60}: diazomethane added to the 6-6-bond and



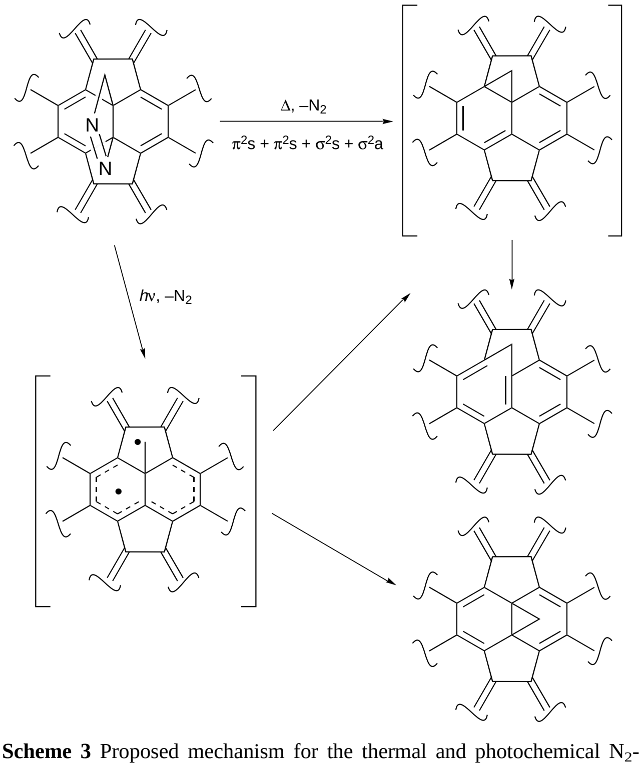
Scheme 1 *Reagents and conditions*: i, CH_2N_2 (*ca.* 60 equiv.), $CHCl_3$, 0 °C, 1.5 h; 71% (**2a**), 93% (**2b**); ii, CCl_4, reflux, 15 min; 93% (**3a**, **b**); iii, *h*ν (Hg medium pressure lamp, 250 W), C_6D_6, c = 9.6 mmol dm^{-3}, T = 5–10 °C, 8 min, 15% (**6** and **5a** in *ca.* 1 : 1 ratio); iv, excess CH_2N_2 (*ca.* 40 equiv.), $CHCl_3$, 0 °C, 15 min; 90% (**4a, b**); v, CH_2N_2 (*ca.* 20 equiv.), CH_2Cl_2, −80 to −60 °C, 10 min, then excess HOAc, −60 °C, and workup at 20 °C; 79% (**3**)

photolysis of **2a** gave a mixture of 6-6-closed **6** and 6-5-open **3a** methanofullerenes, whereas thermolysis exclusively provided the 6-5-open derivative **3a**. None of the isomeric 6-6-closed methanofullerene **6** was detected in the ^{1}H NMR spectrum of the crude thermolysis product.

According to semiempirical PM3 calculations,[4a,7] the 6-6-closed methanofullerene **6** is 2.1 kcal mol^{-1} (1 cal = 4.184 J) more stable than the 6-5-open isomer **3a**. The preferred formation of the thermodynamically less stable product suggested that thermolysis proceeded under kinetic control, and one of us (F. G. K.) recognised the close analogy of the N$_2$-elimination of diazomethane–fullerene adducts to 6-5-open methanofullerenes to the previously reported N$_2$-elimination from diazoalkane–toluene adducts (Scheme 2).[8] Starting from **7**, thermolysis provides in an orbital symmetry controlled $[\pi^2s + \pi^2s + \sigma^2s + \sigma^2a]$ rearrangement with high regioselectivity cycloheptatriene **8**, resulting from ring-opening of the intermediate norcaradiene. In contrast, photolysis of **7** presumably proceeds *via* a diradical mechanism, leading to a mixture of **8** and isomeric **9**. We propose a similar mechanism (Scheme 3) to explain the product distribution obtained during thermolysis and photolysis of diazomethane–fullerene adducts. Even the surprising formation of **5** and **4a**,**b** can be rationalized by this mechanism. A 1,3-dipolar cycloaddition of diazomethane to **3a**,**b** or **5** is followed by rapid, regioselective, concerted N$_2$-elimination and valence bond isomerisation. It might also be responsible for the analogous preference of azide adducts of C$_{60}$ to thermally form 6-5-open azafullerenes.[9]



Scheme 2 Proposed mechanism for the thermal and photochemical N$_2$-extrusion from diazoalkane adducts of toluene



Scheme 3 Proposed mechanism for the thermal and photochemical N$_2$-extrusion from diazalkane adducts of fullerenes (shown only in part)

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Footnote

† All compounds were fully characterised by ^{1}H and ^{13}C NMR (CDCl$_3$), IR, UV–VIS, and FABMS (3-nitrobenzyl alcohol). *Selected data* for **2a**: IR (CHCl$_3$): 1569 cm^{-1} (N=N); ^{1}H NMR: δ 5.73 (s, pyrazoline CH$_2$); ^{13}C NMR: 23 of the 24 expected resonances expected for the fullerene sp^2-C-atoms; FABMS: *m/z* 1522.6 (22, M$^+$), 1492.5 (100 [M − N$_2$]$^+$). For **3a**: ^{1}H NMR: δ 4.71 and 2.13 (2 × d, *J* 9.9 Hz, methano CH$_2$); ^{13}C NMR: 44 of the 50 resonances expected for fullerene sp^2-C-atoms; FABMS: *m/z* 1493.7 (100, M$^+$). For **6**: ^{1}H NMR: δ 2.57 (s, methano CH$_2$); ^{13}C NMR: all 12 resonances expected for fullerene sp^2-C-atoms; FABMS: *m/z* 1493.7 (100, M$^+$). For **5**: ^{1}H NMR: δ 4.48 (d, *J* 10.9, 2 H, methano CH), 2.75 (d, *J* 10.9, 2 H, methano CH); ^{13}C NMR: all 26 resonances expected for fullerene sp^2-C-atoms; FABMS: *m/z* 1739.1 (M$^+$). For **4b**: ^{1}H NMR: δ 4.53 (d, *J* 15.6, 1 H), 4.46 (d, *J* 15.2, 1 H), 4.10 (d, *J* 10.2, 1 H), 3.49 (d, *J* 15.6, 1 H), 3.38 (d, *J* 15.2, 1 H), 2.02 (d, *J* 10.2, 1 H) all methano CH; ^{13}C NMR: 48 of the 50 resonances expected for the fullerene sp^2-C-atoms; FABMS: *m/z* 1753.3 (M$^+$, 100).

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