Stereoselective Isomerization of Tetrakistrifluoromethyl Tetraaryl [4]Radialenes to the Type II (All-Z) Isomers

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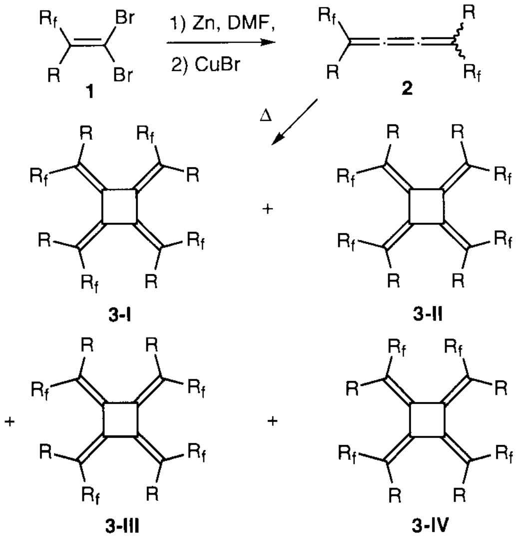
(Received September 24, 1997; CL-970738)

Coupling reaction of 2-aryl-1,1-dibromo-3,3,3-trifluoropropenes using zinc and copper(I) bromide gave [4]radialenes in almost statistic ratios in addition to [3]cumulenes. Thermal dimerization of the cumulenes in neat gave mixtures of four isomeric [4]radialenes in moderate yields. When the isomers were heated in solid at appropriate temperatures, thermal isomerization occurred to afford type II (all-Z) isomers of [4]radialenes in high selectivity.

Radialenes attract increasing attention because of their properties arising from the unique π-electron system, including ferromagnetism and multi-redox property.[1] Although many synthetic methods accessing these compounds have been reported so far, most of successful examples are preparation of these compounds with high symmetry.[1] Selective formation of the type II (all-*Z*) isomer[2] of [4]radialenes in the thermal dimerization of dimethyl 2,5-diphenylhexa-2,3,4-trienedioate in solid was reported by Nader et al.[3] The mechanistic details giving the type II (all-*Z*) isomer,[2] however, still remain unclear probably due to the difficulty to monitor the progress of the dimerization reaction. Thus, we started to investigate this phenomenon by using [3]cumulenes with trifluoromethyl group and found the stereoselective isomerization to the type II [4]radialenes[2] in solid.

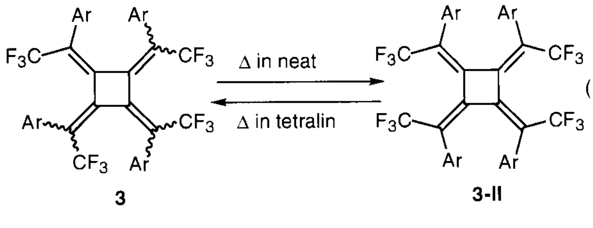


	R_f	R		R_f	R
a	CF_3	Ph	**e**	CF_3	4-PhC_6H_4
b	CF_3	4-MeC_6H_4	**f**	CF_3	4-$MeO_2CC_6H_4$
c	CF_3	4-$MeOC_6H_4$	**g**	C_6F_{13}	Ph
d	CF_3	4-ClC_6H_4	**h**	CF_3	*c*-C_6H_{11}

Scheme 1.

The aryl [3]cumulenes **2a-g** were prepared from the coupling reaction of dibromides **1a-g** according to the method reported by Burton *et al.* (Scheme 1).[4] The coupling reaction of *c*-hexyl derivative **1h** afforded a complex mixture, from which the [3]cumulenes **2h** and [4]radialenes **3h** were isolated by repeated column chromatography and GPC in low yields. In this coupling reaction, formation of [3]radialenes was also detected.

When the [3]cumulenes **2a-d** were heated at 150 °C in neat,[5] the [4]radialenes **3a-d** were gradually formed from about 2 h and all cumulenes disappeared within 24-48 h. Although the isomeric ratios of [4]radialenes gradually changed during the thermal reaction, they became finally *ca.* I:II:III:IV[2] = 1:12:6:2, in all cases. The yields of **3a-d** calculated by the integration of trifluoromethyl signals in ^{19}F NMR were *ca.* 40-60% and the type II isomers[2] were isolated by column chromatography on silica gel in 20-35% yields. On the other hand, the dimerization of cumulenes **2e** and **2f** required the higher temperature (200 °C, 2 h). In the case of tridecafluorohexyl cumulene **2g**, no dimerization was observed even at 200 °C for 8 h. Stereochemistry of four [4]radialene isomers was unambiguously assigned by ^{19}F and ^1H NMR. Thus, type III and IV isomers[2] were easily identified due to the low symmetry (C_s and C_{2v}, respectively)[6] and the type I (C_{4h})[6] and II (D_{2h})[6] isomers[2] could be distinguished by the ^1H NMR analysis based on the up-field shift of aromatic protons of the type II (D_{2h})[6] isomer[2] due to an anisotropic effect of stacking aromatic rings. Aromatic protons of the type II isomer of tetramethyl 1,2,3,4-tetraphenyl[4]radialene-1,2,3,4-tetracarboxylate whose structure was confiemed by X-ray analysis[3] were also reported to show the similar up-field shift.[7] All protons of four phenyl groups in **3a-II** and protons of two phenyl groups in **3a-III** and **3a-IV** appeared in the higher fields than chloroform, whereas all aromatic protons of **3a-I** resonanced in the lower fields.[8]



(1)

Next, the thermal isomerization of [4]radialenes was examined in a solution or in solid (Eq 1). A *ca.* 10% solution of **3a-II** (I:II:III:IV = 0:97:3:0) in tetralin was heated at 170 °C in a NMR tube and the progress was monitored by ^{19}F NMR. The ratio reached to 6:57:32:5 in 30 min and did not change any more. This ratio is almost the same as that obtained in the thermal dimerization of **2a**. When this resulting isomeric mixture was heated at the same temperature in solid after removal of the solvent, the ratio became 2:87:9:2 for 24 h. The predominant formation of **3-II** was also realized in the thermal isomerization of other tetraaryl [4]radialenes in solid (Table 1). The thermal stability of radialenes is quite good and no formation of by-products at the examined temperatures was observed except for **3f** at 170 °C and **3h** at 240 °C. In the case of the *c*-hexyl derivative **3h**, however, the isomerization in neat was slow even at 200 °C and no distinct preference to the formation of any isomer was observed at 240 °C.

Table 1. Thermal isomerization of [4]radialenes **3**

En-		Starting 3	Conditions			Final
try		**I:II:III:IV**	Solv.	Temp/°C	Time	**I:II:III:IV**
1	**3a**	0:97:3:0	tetralin[a]	170	5 min	3:70:24:3
2	**3a**	0:97:3:0	tetralin[a]	170	30 min	6:57:32:5
3	**3a**	0:97:3:0	tetralin[a]	170	20 h	7:56:32:5
4	**3a**	7:56:32:5	neat	170	24 h	2:87:9:2
5	**3a**	79:2:14:5	neat	150	24 h	2:95:3:trace
6	**3a**	0:0:0:>99	neat	150	2 h	1:64:2:33
7	**3a**	0:0:0:>99	neat	150	70 h	1:97:1:1
8	**3a**	2:2:85:11	neat	150	24 h	2:2:85:11
9	**3a**	2:2:85:11	neat	200	2 h	2:83:12:3
10	**3b**	0:>99:0:0	tetralin[a]	170	23 h	5:61:28:6
11	**3b**	5:61:28:6	neat	170	6 h	1:96:2:1
12	**3c**	0:98:2:0	$C_6D_5CD_3$[a]	100	112 h	4:70:22:4
13	**3c**	4:56:33:7	neat	150	24 h	1:96:2:1
14	**3c**	4:56:33:7	neat	170	24 h	1:93:5:1
15	**3c**	4:56:33:7	neat	200	2 h	5:77:9:9
16	**3d**	1:67:23:9	neat	170	24 h	7:91:1:1
17	**3e**	0:>99:0:0	tetralin[a]	200	3 h	3:63:26:8
18	**3e**	3:63:26:8	neat	200	4 h	trace:97:3:trace
19	**3f**	0:>99:0:0	tetralin[a]	170	17.5 h	5:59:29:7[b]
20	**3f**	5:59:29:7[b]	neat	170	9 h	trace:97:3:trace[c]
21	**3h**	6[d]:1[d]:75:18	neat	200	2 h	6[d]:1[d]:75:18
22	**3h**	6[d]:1[d]:75:18	neat	240	13.5 h	—[e]
23	**3h**	0[d]:>99[d]:0:0	tetralin[a]	200	2 h	trace[d]:88[d]:12:trace
24	**3h**	0[d]:>99[d]:0:0	tetralin[a]	200	142 h	10[d]:47[d]:36:7[f]

[a] The concentration was *ca.* 10%. [b] The purity of [4]radialenes was *ca.* 90%. [c] The purity of [4]radialenes was *ca.* 72%. [d] The assignment of **3h-I** and **3h-II** could not be done. [e] Considerable decomposition was observed and the ratio could not be estimated. [f] The purity of [4]radialenes was *ca.* 63%.

Effective radii of trifluoromethyl and aryl groups are reported to be 2.2 ± 0.13 and 1.62 ± 0.02 Å, respectively.[9] One of the reason why the type II isomers are favorably formed both in solution and in solid is the stacking effects which could overwhelm the unfavorable steric interaction of large trifluoromethyl groups. This is supported by the following facts: any preference to forming the type II isomer was not seen in the *c*-hexyl derivative **3h** (entries 21-24) and all type II isomers except **3h** have very strong fluorescence even in solid probably due to the intramolecular excimer formation. Efficiency for the predominant formation of the type II isomers in neat definitely depended on the purity of radialenes. Although determination of the critical purity was difficult, this phenonenon was always observed whenever solidification occurred during heating in neat. Turn our attention to the mechanism of this isomerization. Cycloreversion of radialenes to cumulenes followed by recombination seems not to work in this case, because no formation of cumulenes was observed and no crossover radialene was detected when radialenes **3a** and **3c** were heated at 170 °C in tetralin. Thus, rotation of the exomethylene double bonds must occur during the isomerization. If only one exomethylene double bond rotates, type I and IV isomers must isomerize first to type III and then to type II. However, the type I and IV isomers of **3a** easily isomerized to **3a-II** at 150 °C for 24 h, whereas the sample containing **3a-III** as the major component did not isomerize under the same conditions (entries 4-9). Although some concerted processes might concern the isomerization, the reason is not clear at this moment.

In conclusion, we found the novel isomerization of [4]radialenes leading to the type II (D_{2h})[6] isomers[2] which had two sets of stacking aryl groups.

References and Notes

1 H. Hopf and G. Maas, *Angew. Chem., Int. Ed. Engl.*, **31**, 931 (1992), and references cited therein.

2 Analogously to the porphyrin chemistry, we prefer to use I, II, III, and IV as the types of four isomers instead of 1E,2E,3E,4E, 1Z,2Z,3Z,4Z, 1Z,2Z,3E,4E, and 1Z,2E,3Z,4E[3] for brevity.

3 F. W. Nader, C. -D. Wacker, H. Irngartinger, U. Huber-Patz, R. Jahn, and H. Rodewald, *Angew. Chem., Int. Ed. Engl.* **24**, 852 (1985).

4 P. A. Morken, P. C. Bachand, D. C. Swenson, and D. J. Burton, *J. Am. Chem. Soc.*, **115**, 5430 (1993).

5 Crystals of cumulenes gradually melted as the dimerization reaction proceeded.

6 Strictly, symmetry of the isomers is lower than that indicated due to torsion of the central cyclobutane ring.

7 The reported value for the aromatic protons of the all-*Z* tetramethyl 1,2,3,4-tetraphenyl[4]radialene-1,2,3,4-tetracarboxylate is δ = 6.84—7.26.

8 The NMR data are as follows: **3a-I**: ^{1}H NMR δ 7.28 (8H, m) and 7.38—7.48 (12H, m); ^{13}C NMR δ 122.2 (q, J = 275 Hz), 122.8 (q, J = 33 Hz), 128.1, 128.7, 129.6, 132.3 (ipso), and 137.1 (br, ring); ^{19}F NMR δ -62.56 (s). **3a-II**: ^{1}H NMR δ 6.82 (8H, m), 7.06 (8H, m), and 7.16 (4H, m); ^{13}C NMR δ 122.6 (q, J = 275 Hz), 122.6 (q, J = 37 Hz), 127.8, 128.5, 128.7, 131.7 (ipso), and 137.5 (br, ring); ^{19}F NMR δ -63.01 (s). **3a-III**: ^{1}H NMR δ 6.70 (2H, br m), 6.87 (2H, m), 6.95—7.2 (6H, m), 7.34 (2H, m), and 7.4—7.55 (8H, m); ^{13}C NMR δ 121.7 (q, J = 275 Hz), 122.0 (q, J = 275 Hz), 122.2 (q, J = 33 Hz), 122.6 (q, J = 274 Hz), 122.6 (q, J = 33 Hz), 122.9 (q, J = 274 Hz,), 123.2 (q, J = 33 Hz), 124.5 (q, J = 34 Hz), 127.7, 127.8, 128.1, 128.4, 128.4, 128.5, 128.6, 128.6, 128.8, 128.8, 129.5, 129.6, 131.7 (ipso), 131.8 (ipso), 132.5 (ipso), 132.7 (ipso), 136.8 (br, ring), 137.6 (br, ring x 2), and 137.9 (br, ring); ^{19}F NMR δ -63.40 (3F, q, J = 10 Hz), -62.89 (3F, s), -62.54 (3F, q, J = 10 Hz), and -62.48 (3F, s). **3a-IV**: ^{1}H NMR δ 6.72 (4H, m), 6.99 (4H, m), 7.09 (2H, m), and 7.49 (10H, m); ^{13}C NMR δ 121.6 (q, J = 275 Hz), 122.3 (q, J = 33 Hz), 122.8 (q, J = 276 Hz), 124.6 (q, J = 34 Hz), 127.7, 128.4, 128.5, 128.7, 128.7, 129.6, 131.9, 132.7, 137.2 (br, ring), and 137.9 (br, ring); ^{19}F NMR δ -62.68 (6F, s) and -63.09 (6F, s).

9 G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980).