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A convenient preparation of octafluoro[2,2]paracyclophane and dodecafluoro[2,2]paracyclophane

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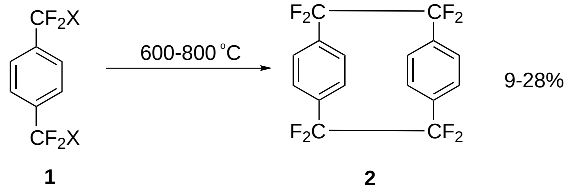
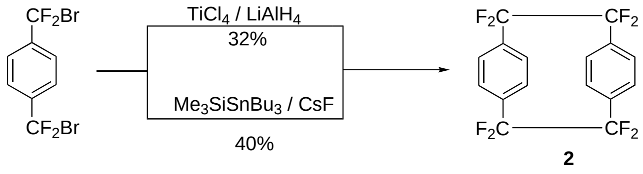
Abstract—A new and convenient synthesis of octafluoro[2,2]paracyclophane and dodeca-fluoro[2,2]paracyclophane is reported. It is accomplished by treatment of 1,4-bis(halodifluoromethyl)benzene with $PbBr_2$/Al in DMF at room temperature via the cyclocoupling of the reactive intermediate $\alpha,\alpha,\alpha'\alpha'$-tetrafluoro-*p*-xylylene. © 2002 Elsevier Science Ltd. All rights reserved.

Poly($\alpha,\alpha,\alpha',\alpha'$-tetrafluoro)-*p*-xylylene (parylene AF4) is an interesting and a commercially valuable material which combines a low dielectric constant, high thermal stability and low moisture absorption.[1–3] The precursor of this polymer is per-α-fluoro-[2,2]paracyclophane (AF4 **2**) which was first prepared by Union Carbide chemists in 1970.[4,5]



In 1993, Dolbier's research group reported a reductive method for the synthesis of **2** in which a low valent Ti complex was used to effect the dehalogenation of 1,4-bis(bromodifluoromethyl)benzene. This procedure allowed relatively easy preparation of gram quantities of **2** in 32% yield.[2] Recently they found that by using an active species generated (in situ) from the reaction of (trimethylsilyl)tributyltin with cesium fluoride, the yield of **2** was improved to 40% and this method can be carried out on a larger scale.

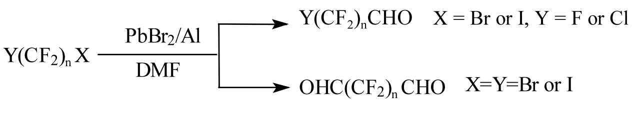


Nevertheless, these two methods required high dilution technology. In a typical experimental 2.7 L of anhydrous THF was used for the preparation of 1.4 g of **2**[1] or 8 L of absolute THF and 2 L of DMSO were used to prepare 22.7 g of **2**.[2]

In our laboratory, a new redox system $PbBr_2$/Al has been successfully used in the dehaloformylation reaction of perfluoroalkyl halides or α,ω-dihaloperfluoroalkanes (Scheme 1).[6]

It was interesting to note that under the same reaction conditions 1,4-bis(bromodifluoromethyl)benzene did not give the expected products $OHCCF_2$-C_6H_4-CF_2CHO or $BrCF_2$-C_6H_4-CF_2CHO. The product has been characterized as a mixture of **2** and **3**. Here we report these results.

In a typical reaction, a solution of 1,4-bis(halodifluoromethyl)benzene **1a** (50 mmol, 12.35 g) in DMF (10 ml) was added over a period of 2 h to a flask containing



Scheme 1.

Keywords: poly($\alpha,\alpha,\alpha'\alpha'$-tetrafluoro)-*p*-xylylene (parylene AF4); per-α-fluoro-[2,2]paracyclophane; AF4; dodecafluoro[2,2]paracyclophane.

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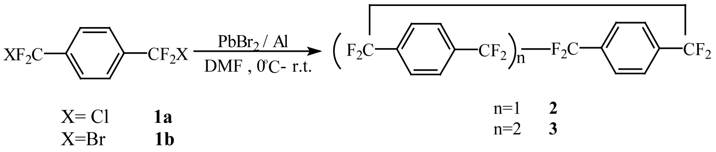
Table 1. Preparation of **2** under different reaction conditions

Entry	Reactant p-R-C_6H_4-R	Reagents	Solvents	Temperature (°C)	Time (h)	Products and yield (%)[a]
1	**1a**	CuI/Zn	DMF	80	6	**2** (8)
2	**1b**	$TiCl_2Cp_2$/Zn	DMF	90	6	**2** (12)
3	**1b**	InI_3/Al	DMF	80	8	**2** (10)
4	**1a**	InI_3/Al	DMF	80	8	**2** (8)
5	**1a**	$PbBr_2$/Al	DMF	80	20	**2** (10), **3** (7)
6	**1a**	$PbBr_2$/Al	DMF	0-Rt	24	**2** (19), **3** (18)
7	**1a**	$PbBr_2$/Al	DMF	0-Rt	50	**2** (22), **3** (20)
8	**1b**	$PbBr_2$/Al	DMF	0-Rt	30	**2** (22), **3** (19)
9	**1b**	$PbBr_2$/Al	THF	0-Rt	30	**2** (9), **3** (4)

[a] Isolated yields based on **1**.



$PbBr_2$ (2 mmol, 0.734 g), aluminum powder (66 mmol, 1.78 g) and DMF (90 ml) at 0°C under a nitrogen atmosphere. After the addition, the reaction mixture was stirred for 24 h at room temperature. General work-up gave a mixture of the dimer **2** and trimer **3** in a combined yield of 37%.[7]

The above described reaction conditions have been optimized with respect to choice of redox system, solvent and reaction temperature. Several other redox systems such as CuI/Zn, $TiCl_2Cp_2$/Zn and InI_3/Al were tried. They were all workable and gave the dimer **2** as the only product but in low yield (8–11%). These reactions could also be carried out in dioxane or THF, however, DMF was the most suitable solvent. These results are summarized in Table 1.

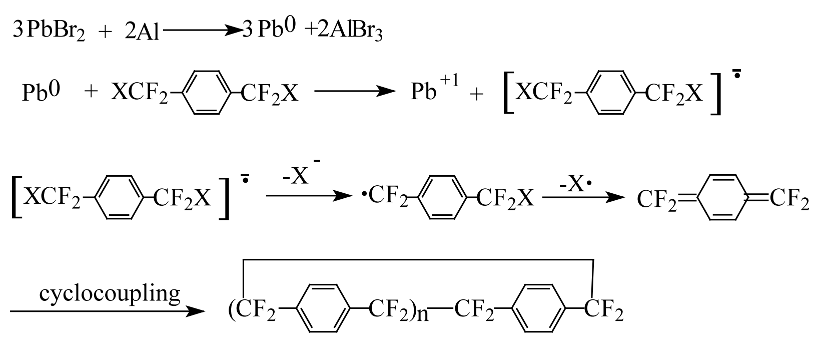
It is believed that a single electron transfer (SET) process could be involved in the dehalocyclocoupling reaction of **1**, using the redox $PbBr_2$/Al system. A possible reaction mechanism is proposed as shown below.

In our previous work, we also found that 1,2-dihalotetrafluoroethane XCF_2CF_2Y reacted with $PbBr_2$/Al in DMF not to give the dehaloformylation product XCF_2CF_2CHO,[8] but in fact decomposed to CF_2=CF_2 which was formed from the intermediates of radical [CF_2CF_2Y].

Elemental analysis of the inorganic salt which was filtered out from the reaction mixture indicated a high concentration of fluoride. It might be formed by the decomposition of the intermediate α,α,α′,α′-tetrafluoro-*p*-xylylene and results in a decrease in the yield of cyclocoupled products.

The mixture of dimer and trimer can be separated by recrystallization from benzene or $CHCl_3$. The solubility of the trimer in $CHCl_3$ is very low. It was noticed that there was one peak in the ^{19}F NMR spectrum of **2** or **3**, which indicated that all the fluorine atoms were chemically equivalent in these two compounds. The ^{19}F and ^1H NMR spectra of **3** [$\delta_F(CF_2) = -112.8$ $\delta_H(C_6H_4) = 7.35$] are at a lower field compared with compound **2** [$\delta_F(CF_2) = -118.8$ ppm $\delta_H(C_6H_4) = 7.17$]. Recrystallization of **3** from benzene gave fine crystals,[9] the molecular structure of which is shown in Fig. 1.

In conclusion, octafluoro[2,2]paracyclophane and dodecafluoro[2,2]paracyclophane have been prepared by dehalocyclocoupling of 1,4-bis(halodifluoromethyl)-benzene using several redox systems, among which the $PbBr_2$/Al system gave the best result.



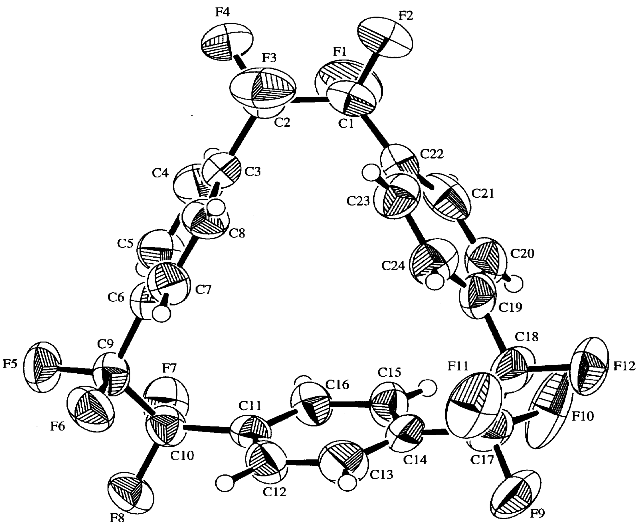


Figure 1. X-Ray structure of compound **3**.

Acknowledgements

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7. Compound **3**: ^{1}H NMR $\delta_H = 7.35$ ppm; ^{19}F NMR ($CDCl_3$) $\delta_F = -112.8$ ppm; MS (*m*/*z*, %): 528 (M^+, 0.44), 352 ($M^+ - CF_2C_6H_4CF_2$, 5.92), 176 ($M^+ - CF_2C_6H_4CF_2$, 100.00); IR (ν_{max}, cm^{-1}): 3100 (w, C–H), 1402 (s, C=C), 1002–1264 (s, C–F). Anal. calcd for **3** C, 36.36; H, 1.52; F, 28.79%. Found: C, 36.60; H, 1.57; F, 28.51%. Compound **2**: ^{1}H NMR δ_H (C_6H_4) = 7.17 ppm, ^{19}F NMR ($CDCl_3$) $\delta_F = -118.8$ ppm; MS (*m*/*z*, %): 352 (M^+, 6.32), 176 ($M^+ - CF_2C_6H_4CF_2$, 100.00).
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9. X-Ray diffraction analysis data for compound **3**. $C_{24}H_{12}F_{12}$, $M = 528.34$, $a = 15.340(2)$, $b = 10.339(2)$, $c = 17.173(2)$ Å, $\beta = 94.69$ (1)°, $V = 2708.1(6)$ Å^3, $Z = 4$, $D_c = 1.487$ g/cm^3, $F(000) = 1224.00$ μ(Mo Kα) = 1.44 cm^{-1}, $R_w = 0.065$, $R_f = 0.073$. Crystal dimensions: 0.20×0.20×0.30 mm. Data were measured at 293 K on a Rigaku AFC7 R diffractometer with graphite-monochromated Mo Kα radiation and a 12 kW rotating anode generator.