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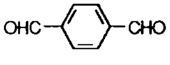
Synthesis of diaza [7,7] paracyclophanetetraene and diaza [7,2,7,2] paracyclophanehexaene.

Patrick Bauchat, André Foucaud*

Groupe de Chimie Structurale associé au C.N.R.S., Université de Rennes,
Campus de Beaulieu, 35042 Rennes, France.

Summary - The diazabicyclooctane - catalyzed reaction of terephthalaldehyde with methyl acrylate gave the diester **2** or the monoester **4**. The diester **2**, acetylated and treated with ammonia gave a diaza [7,7] paracyclophane **6** and the macrobicycle **7**. The diester **8**, obtained by the titanium induced reductive coupling reaction of the acetylated ester **5**, was treated by NH_3 to give a diaza [7,2 ,7,2] paracyclophane.

Cyclophanes are interesting compounds which have attracted considerable attention over the last two decades [1]. We report that the diazabicyclooctane (DABCO)-catalyzed reaction [2] of methyl acrylate with terephthalaldehyde **1** gave the esters **2** and **4** which are precursors of paracyclophanes. Ester **2** (92 % yield) was obtained by the reaction of aldehyde **1** with methyl acrylate (3 eq.) and DABCO (0.3 eq.) for 14 days. The reaction of **1** with methyl acrylate (2 eq.) and DABCO (0.6 eq.) for 1 h 30 gave **4** (86 % yield). The ester **2** was acetylated by AcCl-NEt_3 to yield **3** (97 %). Treated by an aqueous solution of NH_3 for 40 min, the acetate **3** in MeOH-THF gave the paracyclophane **6** (28 % yield, m.p. 262°) [3]. The ^1H NMR spectrum shows, for the vinyl proton, a singlet at δ 7.84, consistent with the configuration E of the double bond [4].



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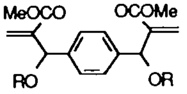

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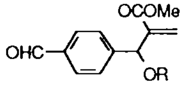
3 R = Ac



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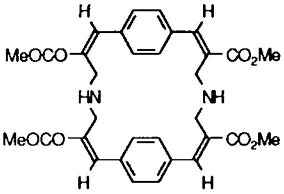

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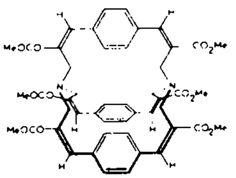

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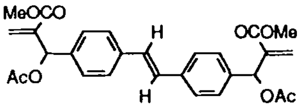
The reaction of **6** with acetate **3** in MeCN(reflux for 90 h) gave **7** [3] (95 % yield, m.p. 270°). The ^1H NMR spectra of **6** and **7** show that the aromatic protons and aromatic carbons are magnetically equivalent.

An upfield shift of the ^{1}H NMR signal of aromatic protons of **6** was observed in the presence of carboxylic acid (CF_3CO_2H : $\Delta\delta$ 0.8 ppm). The reason for this effect must be the ring currents of the aromatic rings facing each other.

The reaction of **4** with AcCl-NEt_3 gave the acetate **5**. The diacetate **8** (E isomer, 87 % yield) was obtained when a solution of **5** in THF was refluxed for 4 h in the presence of $TiCl_4$ and Zn [5] . Product **8** was purified by chromatography over silicagel (eluent ether-petroleum ether 1:1). The reaction of **8** in MeOH-THF with NH_3 gave a yellow precipitate of **9** (13 % yield, m.p. 270° déc.) [6], separated from by-products (mostly polymeric materials) by washing with THF.

The magnetic equivalences observed in the ^{1}H NMR and ^{13}C NMR spectra of **9** suggest that, at room temperature, the molecule turns inside out rapidly.



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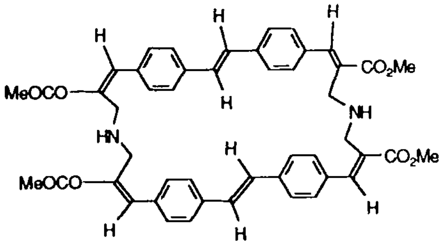

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References and notes

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3 Correct elemental analysis. ^{1}H NMR (300 MHz) : **6** ($CDCl_3$) δ 2.05 (s, 2H) ; 3.67 (s, 8H) ; 3 .87 (s, 12H) ; 7.81 (s, 8H) ; 7.84 (s, 4H). MS : M^+ calcd 574.2318 ; found 574.2315 ; **7** ($CDCl_3$) δ 2.91 (s, 12H) ; 3.77 (s, 18H) ; 6.97 (s, 12H) ; 7.76 (s, 6H). MS : M^+ calcd 844.3207 ; found 844.3182.

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6 Correct elemental analysis. ^{1}H NMR (300 MHz) ($CDCl_3$ + CF_3CO_2H), ; 3.95 (s, 12H) δ 4.21 (m, 8H); 7.02 (s, 4H) ; 7.12-7.41 (AA'BB', 16H) ; 8,06 (s, 4H).

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