

COMMUNICATIONS

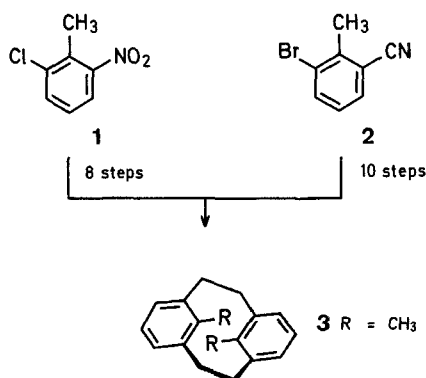
Studies on Selective Preparation of Aromatic Compounds; 19. A Convenient Synthesis of 8,16-Dimethyl[2,2]metacyclophane¹

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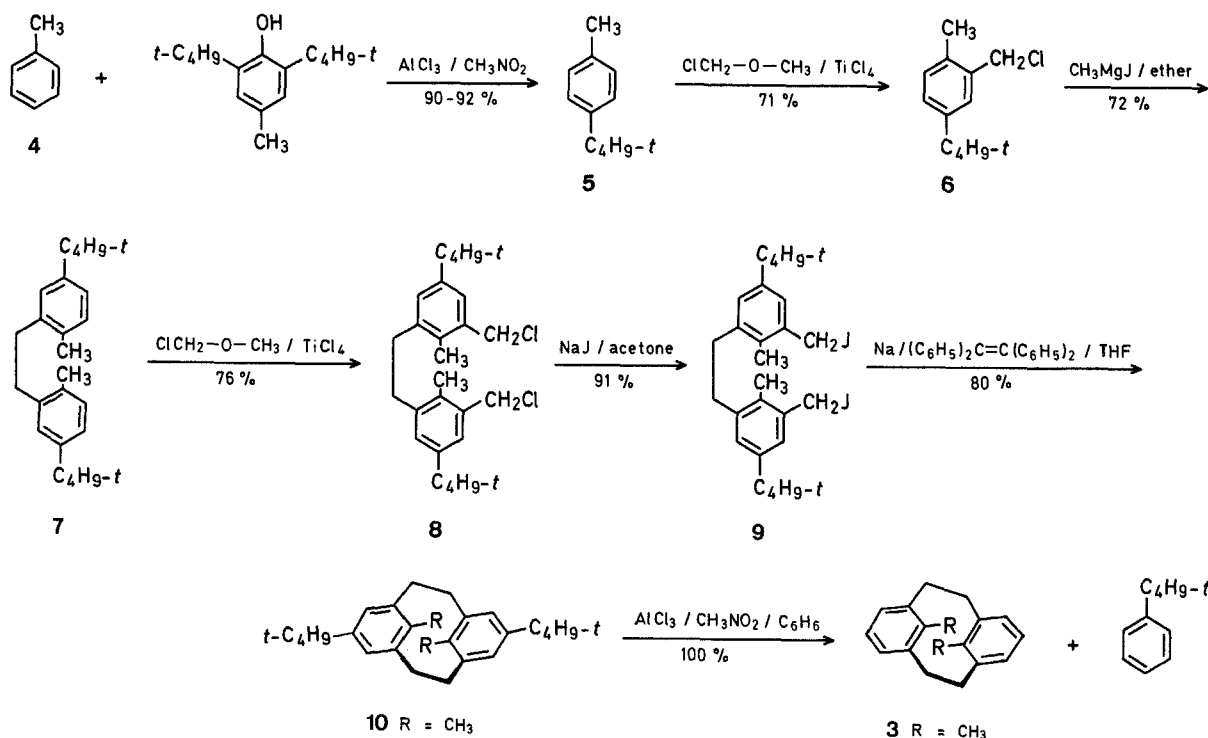
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It has been reported that the *t*-butyl group can be used as a positional protective group for the preparation of some phenolic compounds²⁻⁵, diarylalkanes⁶, 1,2-di- and 1,2,3-tri-substituted benzenes⁷, and 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene⁸.

Although Boekelheide and coworkers⁹ reported two syntheses of 8,16-dimethyl[2,2]metacyclophane (**3**) in low total yield from 2-chloro-6-nitro- (**1**) and 2-bromo-6-cyanotoluene (**2**) by a sequence including several steps, the starting compounds such as **1** and **2** are not readily available.



We now wish to report a convenient preparation of **3** in seven steps from toluene (**4**) involving use of the *t*-butyl



group as a positional protective group. The preparation of 4-*t*-butyltoluene (**5**)¹⁰, and 5,5'-di-*t*-butyl-2,2'-dimethyldiphenylethane (**7**)⁶ from **5** were described in the previous reports. The titanium(IV) chloride-catalyzed chloromethylation of **7** with chloromethyl methyl ether afforded the dichloride **8** in 76 % yield, which was converted to the corresponding diiodide **9** in 91 % yield. When the diiodide **9** was added to a mixture of finely divided sodium and tetraphenylethylene in dry tetrahydrofuran, ring closure occurred smoothly in 80 % yield to give the expected 5,13-di-*t*-butyl-8,10-dimethyl[2,2]metacyclophane (**10**). The aluminum chloride/nitromethane-catalyzed transalkylation of **10** in benzene afforded the desired **3** in almost quantitative yield.

Preparation of 5,5'-Di-*t*-butyl-3,3'-bis[chloromethyl]-2,2'-dimethyldiphenylethane (**8**):

To a solution of 5,5'-di-*t*-butyl-2,2'-dimethyldiphenylethane⁶ (16.1 g, 50 mmol), chloromethyl methyl ether (12 g, 150 mmol), and carbon disulfide (30 ml) is added at 5° titanium(IV) chloride (6.4 ml). After the reaction mixture has been stirred at 30° for 30 min, it is quenched with ice/water (100 ml) and extracted with ether. The ethereal solution is dried over sodium sulfate and evaporated in vacuo to afford the crude product, which on recrystallization from hexane gives **8** as colorless needles; yield: 16 g (76%); m.p. 133–135°.

C ₂₆ H ₃₆ Cl ₂	calc.	C 74.45	H 8.65
(419.5)	found	74.89	8.84

I.R. (KBr): ν_{\max} = 2960, 1480, 1360, 1260, 890, 750 cm⁻¹.

¹H-N.M.R. (CCl₄): δ = 1.21 (s, 18H); 2.21 (s, 6H); 2.87 (s, 4H); 4.50 (s, 4H); 6.89–7.19 ppm (q, 4H).

Preparation of 5,5'-Di-*t*-butyl-3,3'-bis[iodomethyl]-2,2'-dimethyldiphenylethane (**9**):

To a solution of **8** (8.4 g, 20 mmol) in acetone (340 ml) is added sodium iodide (33.6 g). After the reaction mixture has been heated under reflux for 2 h, it is evaporated in vacuo to leave a residue

which on recrystallization from hexane gives **9** as colorless needles; yield: 11 g (91 %); m.p. 117–118°.

$C_{26}H_{36}J_2$	calc.	C 51.84	H 6.02
(602.4)	found	52.17	6.07

I.R. (KBr): ν_{\max} = 2960, 1470, 1155, 880, 735 cm^{-1} .

1H -N.M.R. (CCl_4): δ = 1.15 (s, 4H); 2.08 (s, 6H); 2.83 (s, 4H); 4.35 (s, 4H); 6.75–7.10 ppm (q, 4H).

Preparation of 5,13-Di-*t*-butyl-8,16-dimethyl[2,2]metacyclopheane (10):

To a suspension of sodium (5.5 g) and tetraphenylethylene (400 mg) in tetrahydrofuran (100 ml) is added at -80° under a stream of nitrogen a solution of **9** (5.03 g, 8.4 mmol) in tetrahydrofuran (500 ml) over a period of 36 h. After filtration of unchanged sodium from the reaction mixture, the filtrate is evaporated in vacuo to leave a residue which is dissolved in chloroform (500 ml). The chloroform solution is washed with dilute hydrochloric acid (200 ml) and evaporated to leave a residue which on column chromatography (active Al_2O_3) with benzene as an eluent affords **10** as colorless needles from hexane; yield: 2.34 g (80%); m.p. 254–255°.

$C_{26}H_{36}$	calc.	C 89.59	H 10.41
(348.6)	found	89.68	10.44

I.R. (KBr): ν_{\max} = 2960, 1470, 1450, 1350, 1280, 1180 cm^{-1} .

1H -N.M.R. (CCl_4): δ = 0.55 (s, 6H); 1.27 (s, 18H); 2.83 (d, 8H); 7.10 ppm (s, 4H).

Preparation of 8,16-Dimethyl[2,2]metacyclopheane (3):

The aluminum chloride/nitromethane-catalyzed transalkylation of **10** in benzene solution is carried out as previously reported⁸ to afford the desired **3** in almost quantitative yield together with *t*-butylbenzene (**11**). Compound **3**: colorless needles; m.p. 205–206° (hexane), Lit.⁹, m.p. 204–205°.

Received: January 30, 1978

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