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THE PREPARATION OF NEW[2.2]METACYCLOPHANEQUINONES[1)]

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The convenient preparative method of anti-[2.2]metacyclophanequinone (4) and 5-t-butyl-8-methoxy[2](2,6)-p-benzoquinono[2]metacyclophane (5) is described.

Although many [2.2]paracyclophanequinones[2-6)] and [3.3]metacyclophanequinone[7)] have been reported, [2.2]metacyclophanequinones were not yet prepared.

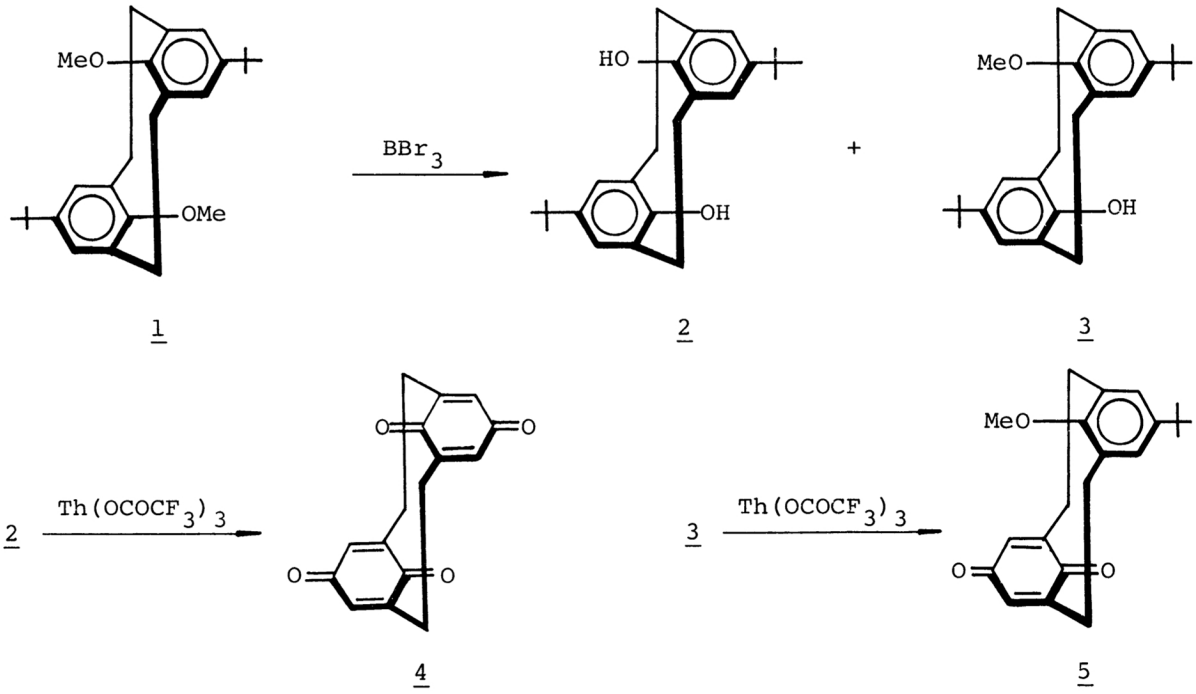
We have previously reported[8)] on the formation of 5,13-di-t-butyl-8,16-dimethyl[2.2]metacyclophane which easily afforded 8,16-dimethyl[2.2]metacyclophane by the $AlCl_3$-CH_3NO_2 catalyzed trans-t-butylation. It was also found that 5,13-di-t-butyl-8,16-dimethoxy[2.2]metacyclophane (1), which seems to be a good starting compound for the preparation of the titled compound, could be easily prepared by similar way.[9)]

We wish to report preliminary results on the preparation of 5,8,13,16-tetraoxo (4)[10)] and 5,8-dioxo-13-t-butyl-16-methoxy[2.2]metacyclophane (5).[10)]

Treatment of 1 with BBr_3 in benzene at room temperature affords in about 70% yield a mixture of 5,13-di-butyl-8,16-dihydroxy[2.2]metacyclophane[(2), colorless prisms (hexane), mp 267-268°. H^1-nmr ($CDCl_3$); δ 1.28 (18H, s), 2.14 (2H, s, exchanged with D_2O), 2.76 (8H, s), 7.08 (4H, s). ν_{OH} 3525 cm^{-1}]10) and 5,13-di-t-butyl-8-hydroxy-16-methoxy[2.2]metacyclophane[(3), colorless prisms (hexane), mp 182-183°. H^1-nmr ($CDCl_3$); δ 1.30 (9H, s), 1.32 (9H, s), 1.94 (1H, s, exchanged with H_2O), 2.69 (8H, m), 2.95 (3H, s), 7.10 (4H, s). ν_{OH} 3550 cm^{-1}].[10)] The separation of 2 and 3 can be carried out fractional recrystallization from hexane.

The oxidation of 2 with $Th(OCOCF_3)_3$[11-13)] at room temperature for 2 hr gives in 53% yield the desired [2.2]metacyclophanequinone[(4), yellow prisms (acetone), mp 285-289° (decomp.). H^1-nmr ($CDCl_3$); δ 2.78 (8H, A_2B_2 pattern, J=8Hz), 6.44 (4H, s). $\nu_{C=O}$ 1660 cm^{-1}. $\lambda_{max}^{CH_3CN}$ = 258 nm (ε = 37150). Mass spectrum: m/e = 268 (M^+)].

Similarly the oxidation of 3 affords in 70% yield 5-t-butyl-8-methoxy[2](2,6)-benzoquinono[2]metacyclophane[(5), yellow needles (hexane), mp 208-209°. H^1-nmr ($CDCl_3$); δ 1.35 (9H, s), 2.35-3.14 (8H, m), 3.53 (3H, s), 6.31 (2H, s), 7.01 (2H, s). $\nu_{C=O}$ 1650 cm^{-1}. $\lambda_{max}^{CH_3CN}$ = 257 nm (ε = 18000). Mass spectrum: m/e = 324 (M^+)].



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