Communications to the Editor

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BROMINATION AND OXIDATION OF 5,13-DI-TERT-BUTYL-8,16-DIHYDROXY[2.2]METACYCLOPHANE AFFORDING INTRAMOLECULAR O-C COUPLING PRODUCTS

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Bromination of the title compound **1** with bromine in CCl_4 afforded tetrabromo spiro compound **2** which was also obtained by bromination of spiro compound **4** formed in oxidation of **1** with $K_3Fe(CN)_6$ in benzene.

KEYWORDS ——— 5,13-di-tert-butyl-8,16-dihydroxy[2.2]-metacyclophane; bromination; oxidation; O-C coupling reaction

We previously found that bromination of 5,13-di-tert-butyl-8,16-dialkyl-[2.2]metacyclophanes with bromine afforded novel products, 2,7-di-tert-butyl-4,5,9,10-tetrabromo-10b,10c-dialkyl-10b,10c-dihydropyrenes.[1] We undertook the present work in order to extend the novel reaction mentioned above.

When the titled compound 1[2] was treated with excess bromine in CCl_4 at room temperature for 2 h, a novel product **2** was obtained as colorless prisms in 60% yield and none of the expected dihydropyrene (3) was detected. The structure is deduced from its spectral data[3] and the comparison of its color (λmax: 280 nm) with those of 10b,10c-dihydropyrenes which are deeply colored compounds. Unfortunately the stereochemistry of **2** is still obscure.

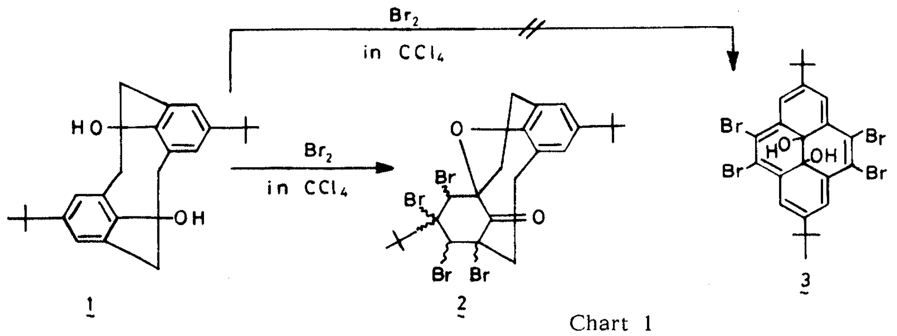
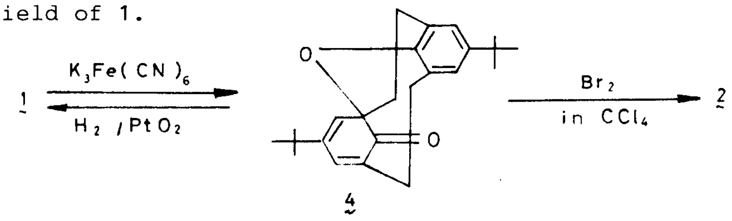


Chart 1

It has been reported that an intramolecular O-C coupling reaction occurs in bromination of 3,3'5,5'-tetra-tert-butyl-2,2'-dihydroxybiphenyl with bromine to give the corresponding hydroxydibenzofuran derivative.[4] This suggests that a similar intramolecular O-C coupling reaction through space in the bromination of **1** might occur to give an intermediate spiro compound **4**, and its bromination might afford the product **2**. To obtain the intermediate **4**, oxidation of **1** with $K_3Fe(CN)_6$, which is well known as an O-C coupling reagent, was carried out according to the reported method.[5]

The expected compound **4** was obtained as pale yellow prisms in 65% yield. Bromination of **4** under the same conditions as described above afforded 2 in 90% yield. It was also found that hydrogenation of **4** in the presence of PtO_2 gave a 74% yield of 1.



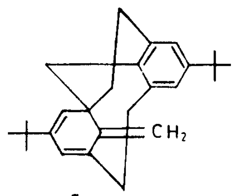


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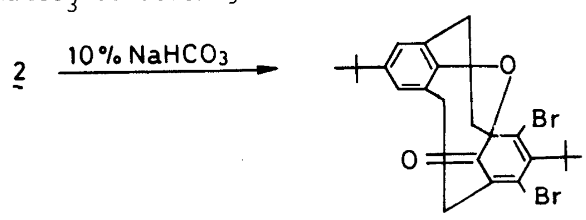
Chart 2

The structure of **4** was deduced from its spectral data[6] and comparison with those of the related compound 5.[7]

REFERENCES

1) M. Tashiro and T. Yamato, J. Am. Chem. Soc., 104, 3701 (1982).
2) M. Tashiro, K. Koya, and T. Yamato, J. Am. Chem. Soc., 104, 3707 (1982).
3) 2; mp 238-240°C (dec.); ^{1}H-NMR ($CDCl_3$) δ: 1.24 (9H, s), 1.33 (9H, s), 2.16-3.60 (6H, m), 4.95 (1H, d, J = 2 Hz), 5.20-5.27 (2H, m), 6.10 (1H, d, J = 2 Hz), 6.99 (1H, d, J = 4 Hz); 7.25 (1H, d, J = 4 Hz); MS m/e: 662, 664, 666, 668, 670 (M^+), IR(KBr): 3040, 2950, 1740, 1480, 1360, 1215, 1190, 1170, 1020, 870, 760 cm^{-1}.
This compound 2 is too labile to purify by recrystallization and column chromatagraphy using silica gel or alunina. However, treatment of 2 with aqueous 10% $NaHCO_3$ solution gave stable comound 2' in good yield.



2'

2': colorless prisms (hexane:benzene), mp 228°C (d), IR (KBr): 3040, 2960, 1740, 1480, 1430, 1360, 1300, 1250, 1220, 1200, 1180, 1030, 990, 940, 870 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.24 (9H, s), 2.0-3.3 (6H, m), 4.83 (1H, d, J = 2 Hz), 6.10 (1H, d, J = 2 Hz), 6.87 (1H, d, J = 2 Hz), 7.0 (1H, d, J = 2 Hz). Anal. Calcd for $C_{24}H_{28}O_2Br_2$: C, 56.71; H, 5.56. Found: C, 56.37; H, 5.86. UV (chloroform) λmax (log ε): 260 nm (4.24), 310 nm (3.72), 358

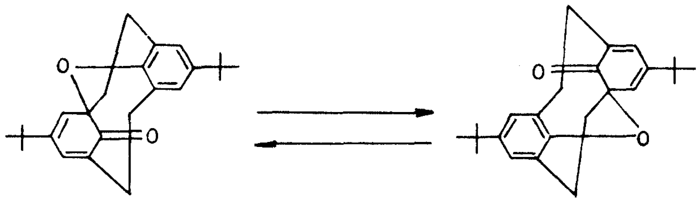
nm (2.64).

4) M. Tashiro, H. Yoshiya and G. Fukata, J. Org. Chem., 47, 4425 (1982).

5) E. Müller and R. Mayer, Ann. Chem., 645, 25 (1961).

6) **4**: mp 280°C (dec.); ^{1}H-NMR ($CDCl_3$) at 25°C, δ: 1.18 (18H, broad s), 2.54 (8H, broad s), 6.42 (4H, broad s); at -50°C, δ: 1.09 (9H, s), 1.24 (9H, s), 1.90-3.20 (8H, m), 5.70 (1H, d, J = 1.5 Hz), 6.23 (1H, d, J = 1.5 Hz), 6.93 (1H, d, J = 2 Hz), 7.03 (1H, d, J = 2Hz); MS m/e: 350 (M^+); IR (KBr): 3020, 2900, 2850, 1718, 1445, 1430, 1190, 1170, 1060, 1445, 1430, 1190, 1170, 1060, 840, 810, 780, 700 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.63; H, 6.01. UV (cyclohexane) λmax (log ε): 380 mm (2.19), 280 nm (3.31), 355 nm (2.39), 370 nm (2.32).

As shown above the protons of **4** were observed as broad signals at room temperature, 25°C, but at -50°C these protons were observed as sharp signals except the bridged methylene protons. These results suggest that there is the following equilibrium at room temperature:



7) M. Tashiro and T. Yamato, Chem. Lett., 1982, 61.

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