

Aromatic Nucleophilic Substitution of $\text{Cr}(\text{CO})_3$ -complexed Halogenoarenes: A New Entry to Dibenzo Crown Ethers

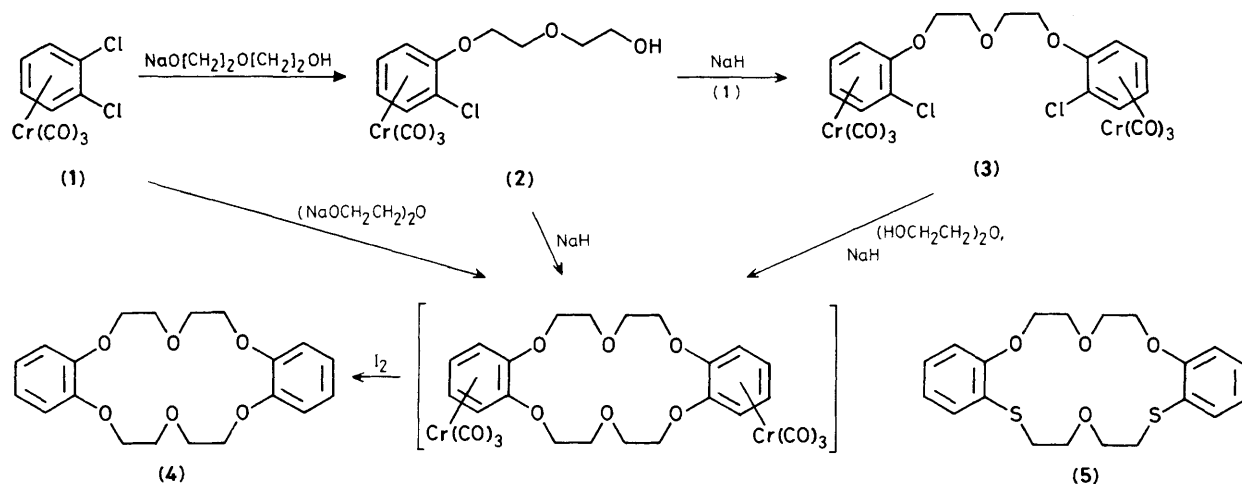
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A new entry to dibenzo crown ethers *via* nucleophilic substitution of $\text{Cr}(\text{CO})_3$ -complexed *o*-dichlorobenzene with the appropriate ethers is reported.

During our work on nucleophilic substitution of the three isomeric dichlorobenzene(tricarbonyl)chromium complexes, we noticed a certain degree of selectivity in the replacement of the two chlorine atoms.^{1,2} Particularly, under phase-transfer conditions (P.T.C.), the substitution of the second chlorine atom with sulphur or oxygen nucleophiles (mainly the latter)

required more severe conditions than for the first substitution, at least for the *ortho*- and *para*-dichloro derivatives. We reasoned that this behaviour could provide a solution to certain synthetic problems; in particular we thought that *o*-dichlorobenzene(tricarbonyl)chromium (**1**) could be treated step-by-step with a variety of bifunctional nucleophilic



Scheme 1

reagents, and we initially focused our attention on the possibility of achieving a new synthesis of dibenzo crown ethers.

We now report that dibenzo-18-crown-6 (DB18C6) (4) was obtained in 27% yield, starting from complex (1) and the sodium salt of diethylene glycol.[†] In a typical experiment, a solution of (1) (3.5 mmol) in 1,2-dimethoxyethane (DME) (30 ml) was added to a slurry of diethylene glycol sodium salt (8 mmol) and tetrabutylammonium bromide (TBAB) (0.3 mmol) as phase-transfer catalyst in DME (10 ml). The mixture was stirred at 50 °C for 8 h, then filtered over Celite. After evaporation, the residue was taken up in CH_2Cl_2 and washed with water. After decomplexation with I_2 the solid residue was thoroughly washed with ether and recrystallized from acetone to give pure (4), identified by comparison with an authentic sample.

Both activation by tricarbonylchromium complexation and the use of phase-transfer conditions were necessary for success in this synthesis. Without phase-transfer catalyst, the reaction was very slow and uncomplexed *o*-dichlorobenzene did not react with the sodium salt of diethylene glycol, either under phase-transfer conditions or on heating in dimethylformamide (DMF) solution at 150 °C for 8 h.

T.l.c. monitoring of the reaction (eluant, Et_2O) showed several products, two of which were clearly intermediates in the formation of DB18C6. Quenching of the reaction with water after 5 h followed by column chromatography (SiO_2 ; eluant, Et_2O) showed, in addition to unchanged (1), two main $\text{Cr}(\text{CO})_3$ complexed products: (2), m.p. 83–84 °C, and (3) (oil).[‡] The $\text{Cr}(\text{CO})_3$ units could be removed by treatment with I_2 . By varying the conditions, either (2) or (3) could be obtained in good yields.

Compound (2) was obtained in 54% yield from (1) (3.53 mmol), NaH (6 mmol), and diethylene glycol (5.3 mmol) in dry tetrahydrofuran (THF) at room temperature for 24 h.

Under the same conditions but with DME as solvent a mixture of (2) and (3) was obtained and (2) was shown to be transformed into (3) by monitoring the reaction by t.l.c. (eluant, Et_2O). Compound (3) was obtained in 84% yield from (1) (3.53 mmol), NaH (7 mmol), and diethylene glycol (2.3 mmol) after 24 h in DME at 50 °C.

Heating of (2) (2 mmol) at 70 °C for 4 h with NaH (3.3 mmol) in DME with TBAB as catalyst gave the expected crown ether (4) in 30% yield after I_2 decomplexation and crystallization from acetone. Reaction of (3) (1.2 mmol) with the sodium salt of diethylene glycol (2.4 mmol) in DME at 70 °C for 5 h with TBAB as catalyst also gave (4), in 33% yield.

We suggest that the reaction takes place by the main paths which are shown in Scheme 1. Complex (2) is the initial product, and could be converted either directly, or *via* (3), into the ether (4).

The possibility of obtaining (3) in good yields is of particular interest in view of its potential for the synthesis of different crown ethers. For example, the dithia compound (5) was prepared by the reaction of (3) (1.3 mmol) with the sodium salt of bis-(2-mercaptoethyl) ether (2.6 mmol) in DME solution (20 ml) at room temperature for 1 h and in the presence of TBAB (0.4 mmol) as catalyst. I_2 decomplexation followed by work-up and crystallization from acetone gave (5) in 15% yield, which is comparable with that obtained by Pedersen⁴ starting from 2-mercapto-phenol.

We thank the Ministero della Pubblica Istruzione for financial support.

Received, 18th March 1985; Com. 362

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[†] This nucleophilic reagent offered also the advantage of disfavoring intramolecular ring closure,³ which would have led to the formation of a highly strained nine-membered ring.

[‡] Microanalytical and spectroscopic data of all new compounds were consistent with the assigned structures.