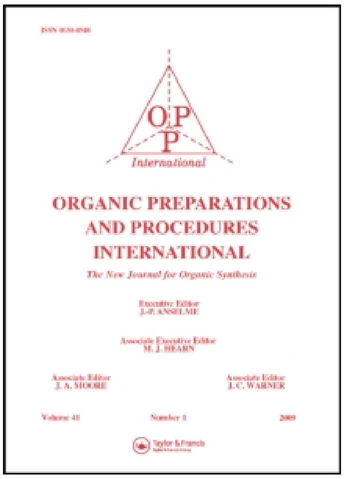


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

POLYETHERS. 2. PREPARATION OF ω,ω'-DISUBSTITUTED POLYARYLETHERS

Masashi Tashiro[a]; Haruo Yoshiya[a]; Gouki Fukata[a]
[a] Research Institute of Industrial Science, Kyushu University, Fukuoka, JAPAN

To cite this Article Tashiro, Masashi , Yoshiya, Haruo and Fukata, Gouki(1981) 'POLYETHERS. 2. PREPARATION OF ω,ω'-DISUBSTITUTED POLYARYLETHERS', Organic Preparations and Procedures International, 13: 2, 87 — 92

To link to this Article: DOI: 10.1080/00304948109356100

URL: http://dx.doi.org/10.1080/00304948109356100

ORGANIC PREPARATIONS AND PROCEDURES INT. 13(2), 87-92 (1981)

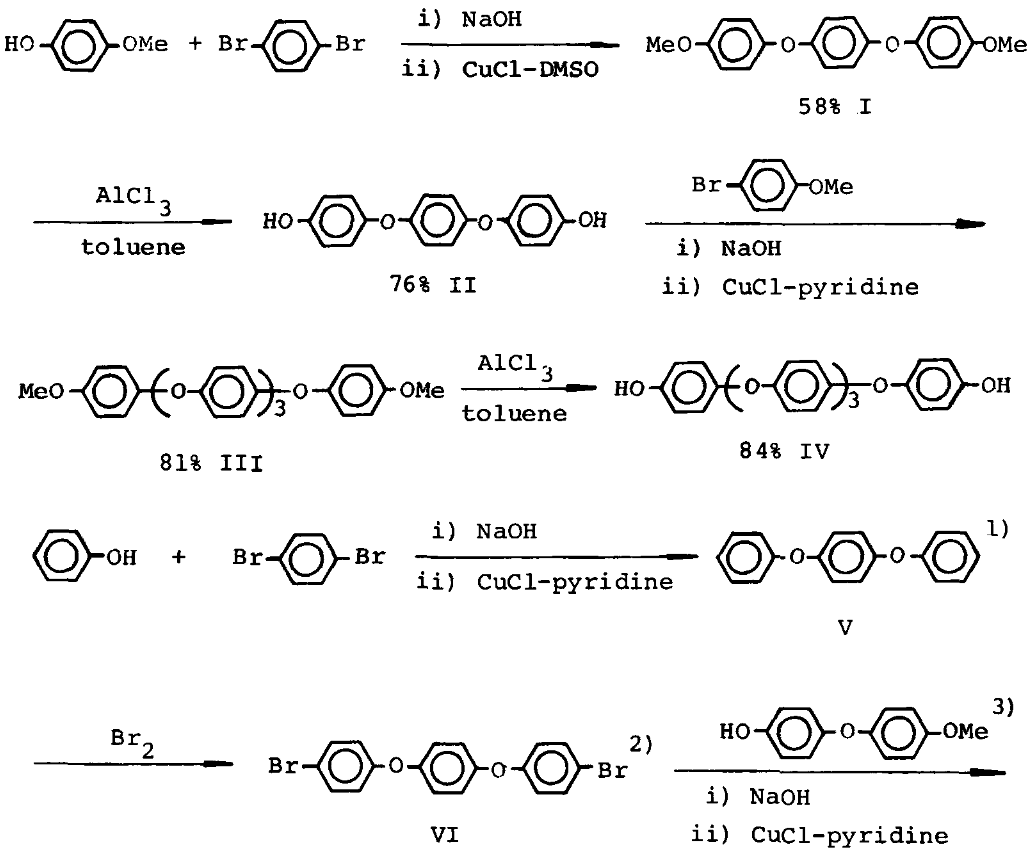
POLYETHERS. 2.

PREPARATION OF ω,ω'-DISUBSTITUTED POLYARYLETHERS†

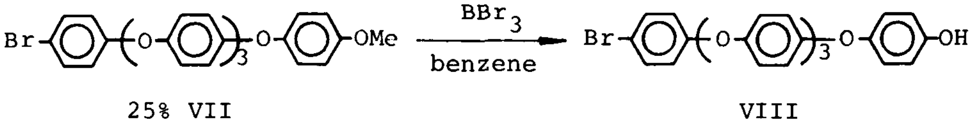
Masashi Tashiro*, Haruo Yoshiya and Gouki Fukata

Research Institute of Industrial Science, Kyushu University 86,
Hakozaki, Higashi-ku, Fukuoka 812, JAPAN

We report the syntheses of ω,ω'-disubstituted polyarylethers which seem to be good starting compounds for the preparations of macrocyclic and acyclic polyarylethers.

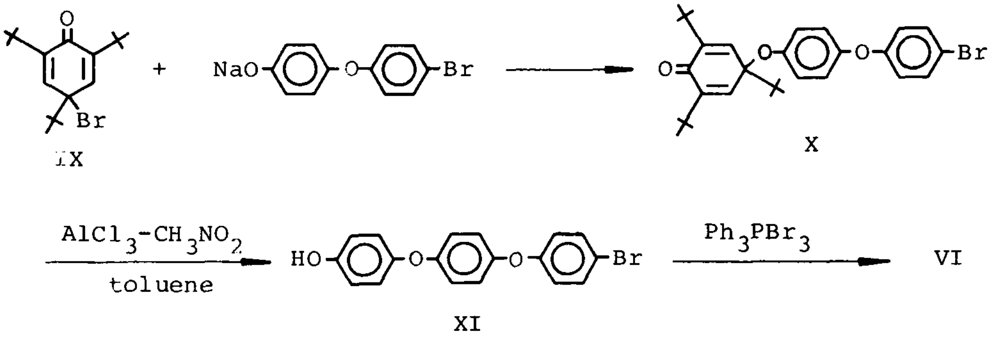


[continued]



Scheme 1

Compound I was prepared by Ullmann reaction of 4-methoxyphenol with 1,4-dibromobenzene in the presence of CuCl in DMSO. Its demethylation with $AlCl_3$ in toluene afforded the corresponding dihydroxy compound II in 76% yield. Compounds III and IV were obtained via a similar route (as depicted in Scheme 1) in 81 and 84% yields, respectively. The asymmetric polyarylethers such as VII and VIII were prepared by reactions that are also shown in Scheme 1. Compounds V and VI were prepared according to reported methods,[1,2] but the positions of the two bromo groups of VI are not described in the literature.[2] Therefore, the positions of these groups were confirmed by comparison of our sample of VI with a sample of authentic compound which was prepared by the reactions shown in Scheme 2.



Scheme 2

EXPERIMENTAL

All melting points are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrometer and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal reference.

Preparation of I.- A mixture of 74.3 g (1.86 mole) of NaOH and 236.8 g (1.9 mole) of 4-methoxyphenol in 300 ml of DMSO was heated at 80°C until a clear solution was obtained. 1,4-Dibromobenzene (75 g, 0.3 mole) and 49 g (0.49 mole) of CuCl were then added to this solution. After the mixture was heated at 130° for 36 hrs with stirring, it was poured into a large amount of water. The precipitate was filtered, washed with 10% HCl, 10% NaOH solution, water and benzene and extracted with THF. The THF extract solution was dried over Na_2SO_4 and evaporated *in vacuo* to give 59.4 g (58%) of I as colorless plates (from benzene), mp. 142-143°, IR: ν_{C-O-C} 1230 cm^{-1}, NMR ($CDCl_3$): δ 3.78 (6H, s, $OC\underline{H}_3$), 6.90 (12H, s, aromatic protons).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63.
Found: C, 74.36; H, 5.47.

Demethylation of I.- After a mixture of 3.0 g (9.3 mmol) of I and 3.72 g (27.9 mmol) of $AlCl_3$ in 50 ml of toluene was heated at refluxing temperature for 3 hrs, it was poured into a large amount of ice-water. The colorless precipitate formed was collected and washed with water to give 2.08 g (76%) of II as colorless plates (from benzene), mp. 193-194°, IR: ν_{OH} 3080-3460 cm^{-1}, NMR (CD_3COCD_3): δ 6.82-6.87 (12H, m, aromatic protons), 8.12 (2H, s, $O\underline{H}$).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.40; H, 4.30.
Found: C, 73.31; H, 4.79.

Preparation of III.- After a mixture of 14.3 g (76.4 mmol) of 4-bromoanisole, 3.1 g (9.1 mmol) of the sodium salt of II (prepared from I and NaOH), and 1.89 g (19.1 mmol) of CuCl in 30 ml of pyridine was refluxed for 24 hrs under a stream of N_2 gas, the pyridine was distilled under reduced pressure. The residue was poured into 100 ml of 2N HCl solution. The precipitate that formed was collected and washed with water and acetone to give 3.76 g (81%) of III as colorless plates (from benzene), mp. 197-198°; IR: ν_{C-O-C} 1220 cm^{-1}; NMR ($CDCl_3$): δ 3.78 (6H, s, O$\underline{CH}_3$), 6.88-6.92 (20H, m, aromatic protons).

Anal. Calcd for $C_{32}H_{26}O_6$: C, 75.87; H, 5.17.
found: C, 75.59; H, 5.12.

Demethylation of III.- Compound III was treated and worked up as was compound I to afford IV in 84% yield as colorless plates (from benzene), mp. 211-212°, IR: ν_{OH} 3080-3680 cm^{-1}, NMR (CD_3COCD_3): δ 2.87 (2H, s, OH), 6.80-6.96 (20H, m, aromatic protons).

Anal. Calcd for $C_{30}H_{22}O_6$: C, 75.30; H, 4.63.
found: C, 75.16; H, 4.58.

Preparation of VII.- To a mixture of 6 g (14 mmol) of VI, 4.2 g (42 mmol) of CuCl and 500 ml of pyridine was added a solution of 9.8 g (41 mmol) of the sodium salt of 4-(4-methoxyphenoxy)-phenol[3] and 17.5 g (41 mmol) of VI in 75 ml of pyridine at refluxing temperature over a period of 1.5 hr. After the mixture was refluxed for an additional 35 hrs, the pyridine was distilled under reduced pressure, and the residue was poured into a large amount of water. The resulting precipitate was collected and washed with 10% HCl solution, Claisen alkali[4] and water and extracted with THF. The THF solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue which was chromatographied on silica gel (Wako, C-300) using benzene as eluent to give 6.0 g (26.5%) of VII as colorless plates (from benzene), mp. 191-192°, IR: ν_{C-O-C} 1220 cm^{-1}, NMR (DMSO-d_6): δ 3.72 (3H, s, OCH_3), 6.88-7.55 (20H, m, aromatic protons).

Anal. Calcd for $C_{31}H_{23}O_5Br$: C, 67.04; H, 4.44.
Found: C, 67.22; H, 4.17.

Demethylation of VII.- After 0.98 g (1.76 mmol) of VII was dissolved in 350 ml of hot benzene, it was cooled to room temperature. To the solution was added a solution of 2.5 g (9 mmol) of BBr_3 in 5 ml of benzene at room temperature. After the solution was stirred for 5 hrs, it was poured into a large amount of water. The resulting precipitate was collected to give 0.67 g (71%) of VIII as colorless prisms (from benzene), mp. 179.5-180.5°, IR: ν_{OH} 3100-3700 cm^{-1}. NMR (DMSO-d_6): δ 6.70-7.55 (20H, m, aromatic protons), 9.25 (1H, s, OH).

Anal. Calcd for $C_{30}H_{21}O_5Br$: C, 66.56; H, 3.91.
Found: C, 66.76; H, 4.13.

Preparation of X.- After a mixture of 1.29 g (3.8 mmol) of IX and 1.09 g (3.8 mmol) of the sodium salt of 4-(4-bromophenoxy)-phenol[3] in 30 ml of THF was refluxed for 15 min, it was poured into a large amount of water. The organic layer was extracted with benzene. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo at room temperature to afford 0.57 g (30%) of X as a pale yellow crystalline powder (mp. 88-92°) which is so unstable that its purification could not be carried out by recrystallization and chromatography, IR: $\nu_{C=O}$ 1645, 1670 cm^{-1}.

The trans-tert-butylation of X.- To a solution of 0.567 g (1.43 mmol) of X in 40 ml of toluene was added a solution of 0.6 g (4.5 mmol) of $AlCl_3$ in 10 ml of nitromethane at -15°. After the reaction mixture was stirred for 30 min, it was poured into a large amount of water. The organic layer was extracted with ether. THe ether solution was extracted with 10% NaOH solution. The alkaline extract was acidified with 10% HCl solution and then extracted with ether. The ether solution was dried over Na_2SO_4 and evaporated *in vacuo* to give 10.6 mg (3%) of XI as colorless plates (hexane), mp. 132-135°, IR: ν_{OH} 3080-3460 cm^{-1}.

Treatment of XI with dibromotriphenylphosphine.- When compound XI was treated with dibromotriphenylphosphine according to the method of Schaefer and Higgins,[5] VI was obtained in 2% yield.

REFERENCES

†. Part 1. M. Tashiro, T. Sumida and G. Fukata, J. Org. Chem., 45, 1156 (1980).

1. F. Ullmann and S. Spanagel, Ber., 38, 2212 (1905).
2. H. Staudinger and F. Stalger, Ann., 517, 67 (1935).
3. M. Tashiro, H. Yoshiya and T. Yamato, Synthesis, 1978, 399.
4. L. Claisen, Ann., 418, 89 (1919).
5. J. P. Schaefer and J. Higgins, J. Org. Chem., 32, 1607 (1967).

(Received April 22, 1980; in revised form June 23, 1980)