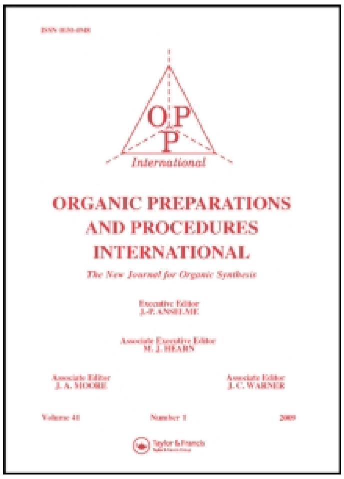

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# PREPARATION OF 4,4'-DI-*t*-BUTYLBIPHENYL DERIVATIVES

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# PREPARATION OF 4,4'-DI-t-BUTYLBIPHENYL DERIVATIVES

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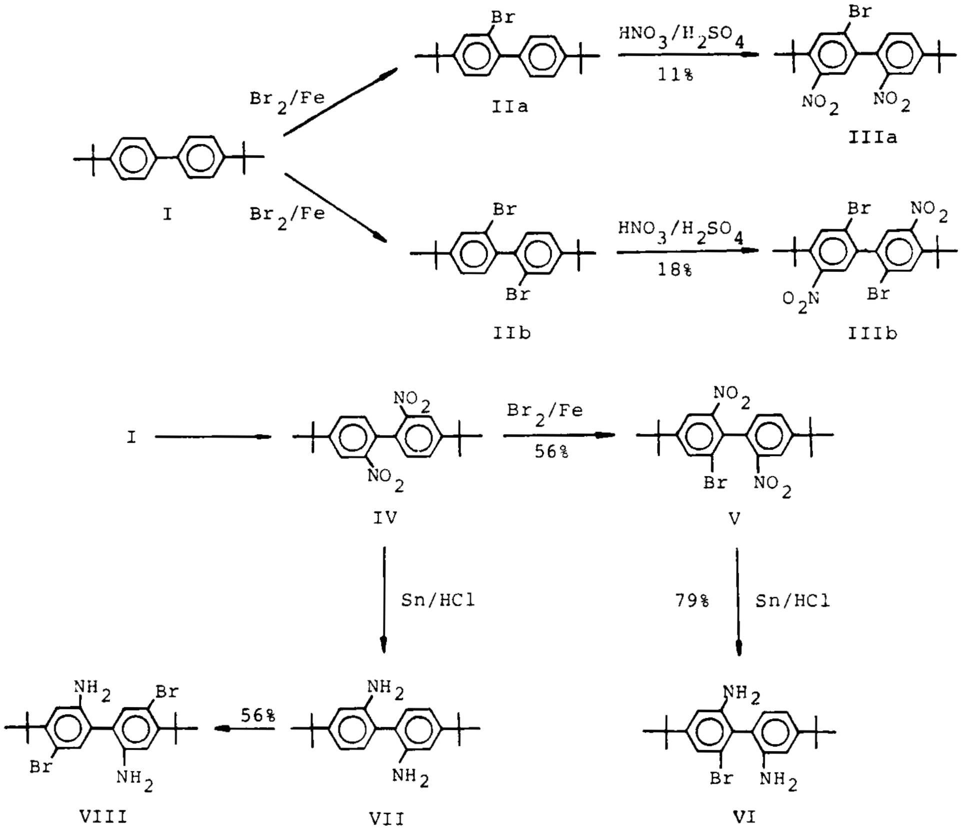
Introduction of functional groups into the positions 2,2' and 6,6' of diphenyl is generally difficult. We have investigated the selective preparation of aromatic compounds using tert-butyl as a positional protective group.[2,3] We now report the nitration of 2-bromo- and 2,2'-dibromo-4,4'-di-t-butylbiphenyl-(IIa and IIb) and bromination of 2,2'-dinitro- and 2,2'-diamino-4,4'-di-t-butylbiphenyl(IV and VII).

Nitration of IIa with a mixed acid of conc. nitric acid and sulfuric acid afforded 2-bromo-5,2'-dinitro-4,4'-di-t-butylbiphenyl (IIIa) in only 11% yield together with an inseparable mixture. Similar reaction of IIb gave 2,2'-dibromo-5,5'-dinitro-4,4'-di-tert-butylbiphenyl (IIIb) in 18% yield with tarry materials. It should be noted that the nitro group attacked position 5 of the ring with the bromo group and position 2' of the other ring in the nitration of IIa and that the two nitro groups attached to the positions 5 and 5' in the case of IIb. However, the bromination of IV resulted in attack at position 2 to give V in 36% yield, which was easily reduced by Sn and HCl to afford VI in good yield. On the other hand, bromination of VII afforded VIII in 49% yield. In this case, the two bromo groups attacked at positions 5 and



Scheme 1

5' rather than positions 2 and 2'. The use of the substituted biphenyls as starting materials for the preparation of carbazoles, dibenzofurans and hydroxybiphenyls with and without prior removal of the t-butyl group is under investigation.

## EXPERIMENTAL SECTION

Nitration of IIa.- To a solution of 300 mg (0.9 mmol) of IIa[4] in 10 ml of $Ac_2O$ was gradually added a mixture of 0.5 ml of fuming $HNO_3$ and 0.1 ml of conc. $H_2SO_4$ at less than 50°C. After the reaction mixture was stirred for 1 hr, it was poured into a large amount of water, stirred overnight and extracted with benzene. The benzene solution was dried and evaporated in vacuo to leave the residue which was chromatographed on silica-gel using benzene as an eluent to afford 40 mg (11%) of IIIa as pale yellow needles (ethanol), mp. 146-147.5°. IR (KBr) 2960, 1530, 1345, 1080, 900 and 885 $cm^{-1}$; $^1H$-NMR ($CDCl_3$) $\delta$ 1.44 (9H, s), 1.46 (1H, s), 7.20 (1H, s), 7.22 (1H, d, J = 8 Hz), 7.69 (1H, dd, J = 8 Hz, J = 2 Hz), 7.76 (1H, s), 8.11 (1H, d). Mass m/e 421 ($M^+-CH_3$).

Anal. Calcd for $C_{20}H_{23}BrN_2O_4$: C, 55.18; H, 5.33; N, 6.44.
Found: C, 55.38; H, 5.38; N, 6.24.

Nitration of IIb.- A solution of 8 g (19 mmol) of IIb[4] in 100 ml of $Ac_2O$ was treated and worked up as described above to give 1.77 g (18%) of IIIb as colorless needles (ethanol); mp. 224-225°. IR (KBr) 2950, 1600, 1520, 1460, 1360, 1345, 890 $cm^{-1}$; $^1H$-NMR ($CDCl_3$) $\delta$ 1.45 (18H, s), 7.22 (2H, s), 7.81 (2H, s); Mass m/e 516 ($M^+$).

Anal. Calcd for $C_{20}H_{22}Br_2N_2O_4$: C, 46.71; H, 4.31; N, 5.44.
Found: C, 46.79; H, 4.35; N, 5.22.

Bromination of IV.- To a mixture of 10 g (28 mmol) of IV[4] and a small amount of Fe powder in 50 ml of $CCl_4$ was added gradually a solution of 3.5 ml of $Br_2$ in 20 ml of $CCl_4$ at room temperature. After the reaction mixture was refluxed for 20 hrs, an additional solution of 3.5 ml of $Br_2$ in 20 ml of $CCl_4$ was added, and then, it was refluxed again for 48 hrs, it was poured into a large amount of water and extracted with $CH_2Cl_2$. The $CH_2Cl_2$ solution was washed with sodium thiosulfate solution and water, dried with $Na_2SO_4$ and evaporated in vacuo to afford 6.83 g (56%) of pure V as yellow prisms (ethanol); mp. 195-198$^o$. IR (KBr) 2950, 1950, 1520, 1340, 1260, 1110, 730 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.42 (18H, s), 7.08 (1H, d, J = 8 Hz), 7.68 (1H, dd, J = 8 Hz, J = 2 Hz), 7.89 (1H, d, J = 2 Hz), 8.03 (1H, d, J = 2Hz), 8.27 (1H, d, J = 2 Hz); Mass: m/e 436 ($M^+$), 434 ($M^+$).

Anal. Calcd for $C_{20}H_{23}BrN_2O_4$: C, 55.18; H, 5.32; N, 6.39.
Found: C, 55.38; H, 5.43; N, 6.39.

Bromination of VII.- To a mixture of 500 mg (17 mmol) of VII[4] and a small amount of Fe powder in 5 ml of $CCl_4$ was added gradually a solution of 0.18 ml of $Br_2$ in 2 ml of $CCl_4$ under ice-cooling. After being stirred for 30 min. at room temperature, the reaction mixture was made alkaline with 10% NaOH and then extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried over $Na_2SO_4$ and evaporated to leave the residue which was recrystallized from hexane to give 30 mg (56%) of VIII as pale brown prisms (hexane); mp. 220-221.5$^o$. IR (KBr) 3450, 3350, 1610, 1375 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.47 (18H, s), 3.63 (4H, s), 6.86 (2H, s), 7.33 (2H, s); Mass m/e 456 ($M^+$), 454 ($M^+$).

Anal. Calcd for $C_{20}H_{26}Br_2N_2$: C, 52.88; H, 5.77; N, 6.17.
Found: C, 52.77; H, 5.83; N, 6.10.

Reduction of V.- To a solution of 5.5 g (13 mmol) of V and 25 ml of conc. HCl in 50 ml of ethanol was gradually added 6 g of Sn powder on water bath (80°). After the reaction mixture was refluxed for 1 hr, it was poured into a large amount of water, made alkaline with 10% NaOH solution and extracted with ether. The ether solution was washed with water, dried over $Na_2SO_4$ and evaporated *in vacuo* to leave the residue which was recrystallized from hexane to give 3.75 g (79%) of VI as colorless needles (hexane); mp. 137.5-140°. IR (KBr) 3450, 3350, 2950, 1610, 1410, 1300, 840 $cm^{-1}$; $^1H$-NMR ($CDCl_3$) $\delta$ 1.31 (9H, s), 1.33 (9H, s), 6.71 (1H, d), 6.78-6.92 (3H, m), 7.07 (2H, d). *Anal*. Calcd for $C_{20}H_{28}BrN_2$: C, 64.00; H, 7.25; N, 7.46.
Found: C, 63.96; H, 7.32; N, 7.36.

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