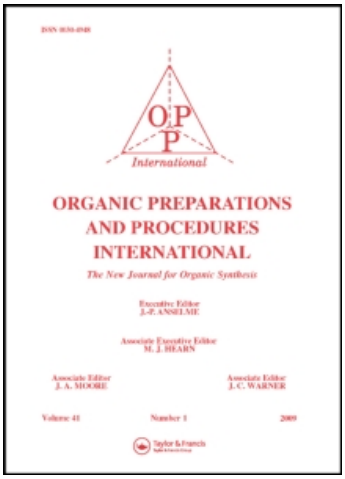

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SELECTIVE PREPARATION. 41. CONVERSION OF 2,2'-DIHYDROXY-3,3'-DI-*t*-BUTYL-5,5'-DIMETHYLBIPHENYL TO SOME NOVEL DIBENZOFURAN

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SELECTIVE PREPARATION. 41.

CONVERSION OF 2,2'-DIHYDROXY-3,3'-DI-t-BUTYL-5,5'-DIMETHYLBIPHENYL TO SOME NOVEL DIBENZOFURAN+

Submitted by Masashi Tashiro* and Haruo Yoshiya++
(10/03/83)

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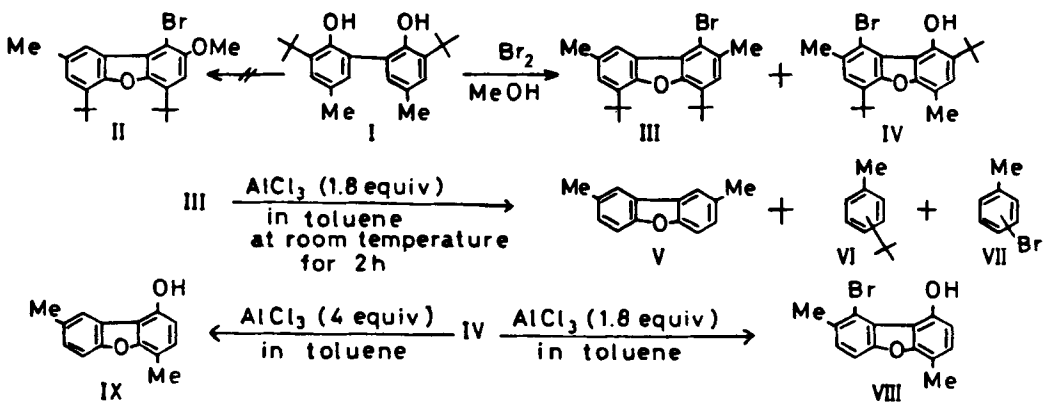
A recent paper described the bromination of 2,2'-dihydroxy-3,3',5,5'-tetra-t-butyl-biphenyl with bromine in methanol to afford 1-bromo-2-methoxy-4,6,8-tri-t-butyldibenzofuran which was converted to 2-hydroxy-dibenzofuran by treatment with $AlCl_3$ in toluene.[1] We now report the preparation of some novel dibenzofurans starting from 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethylbiphenyl (I).

Scheme 1



The bromination of I did not give the product (II) expected from the result described in the previous report[1] but afforded the dibenzofuran derivativees III and IV in 28% and 13% yields, respectively. Treatment of III with 1.8 equivalents of $AlCl_3$ in toluene afforded the anticipated 2,7-dimethyldibenzofuran (V) together with t-butyltoluenes (VI) and bromotoluenes (VII) in 47% yield. However, similar treatment of IV gave only the product VIII and not he expected IX. IX was obtained from IV only when $AlCl_3$ was used in large excess.

The bromination of both 2,2'-dihydroxy-3,3'-dimethyl-5,5'-di-t-butyl- (X) and 2,2'-dihydroxy-3,3'-dibromo-5,5'-di-t-butylbiphenyl (XI) with bromine in methanol did not afford any product giving only tarry materials in the former case and failing to occur in the latter.

EXPERIMENTAL SECTION

All melting points are uncorrected. ^{1}H-NMR spectra were determined at 100 MHz with a Nippon Denshi, JEOL FT-100 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured in KBr pellets with a Nippon Bunko IRA-102 spectrophotometer. Mass spectra were obtained with a Nippon Denshi, JMS-01SA-2 spectrometer at 75 eV, using a direct-inlet system.

Preparation of 2,2'-Dihydroxy-3,3'-dibromo-5,5'-di-t-butylbiphenyl (XI).- To a solution of 2,2'-dihydroxy-5,5'-di-t-butylbiphenyl[2] (800 mg, 2.7 mmol) in 50 ml of methanol was added a solution of bromine (660 mg, 4.1 mmol) in 5 ml of methanol at room temperature. After the reaction mixture was stirred for 30 min, it was poured into a large amount of water and extracted with benzene. The benzene extracts were washed successively with water, aqueous $Na_2S_2O_3$ solution and water, dried over Na_2SO_4 and evaporated in vacuo to leave a residue which was recrystallized from hexane to give 960 mg (78%) of XI as colorless prisms, mp. 175-176°; IR (KBr): 3480 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.30 (s, 18H), 5.76 (s, 2H), 7.17 (d, J = 2.5 Hz, 2H),

7.49 (d, J = 2.5 Hz, 2H); Mass:m/e 454, 456, 458 (M^+).

Anal. Calcd. for $C_{20}H_{24}Br_2O_2$: C, 52.65; H, 5.30

Found: C, 52.43; H, 5.23

Bromination of 2,2'-Dihydroxy-3,3'-di-t-butyl-5,5'-dimethylbiphenyl (I).- To a solution of 1.63 g (5 mmol) of I[3] in 20 ml of methanol was added slowly a solution of 2.8 g of bromine in 3 ml of methanol at room temperature. After the reaction mixture was stirred for 1 hr, it was evaporated in vacuo to leave a residue which was column chromatographed on silica gel using a mixture of hexane and benzene (1:1) to give 540 mg (28%) of III and 260 mg (13%) of IV. Compound III: colorless prisms (methanol), mp. 193-194°; ^{1}H-NMR ($CDCl_3$): δ 1.55 (s, 18H), 2.50 (s, 6H), 7.08 (d, J = 2 Hz, 1H), 7.10 (s, 1H), 8.18 (d, J = 2 Hz, 1H), Mass: m/e 386, 388 (M^+).

Anal. Calcd. for $C_{22}H_{27}BrO$: C, 68.21; H, 7.03

Found: C, 68.51; H, 7.10

Compound IV: colorless prisms (methanol), mp. 247.5-248.5°; IR (KBr): 3460 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$): δ 1.51 and 1.55 (each s, 9H), 2.27 (s, 3H), 7.05 (s, 1H), 7.12 (s, 1H), 7.90 (s, 1H); Mass: m/e 402, 404 (M^+).

Anal. Calcd. for $C_{22}H_{27}Br_2O_2$: C, 65.51; H, 6.75

Found: C, 65.55; H, 6.77

Similar bromination of X[3] and XI was carried out under the conditions described above. However, the former case afforded only tarry materials and the latter compound was quantitatively recovered.

Preparation of 2,7-Dimethyldibenzofuran (V).- To a solution of 450 mg (1.2 mmol) of III in 20 ml of toluene was added 230 mg (1.7 mmol) of $AlCl_3$ at room temperature. After the reaction mixture was stirred for 2 hrs, it was poured into a large amount of ice-water and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave a residue which was column chromatographed on silica gel

using a mixture of hexane and benzene (1:1) as an eluent to give 105 mg (47%) of V as colorless plates (methanol), mp. 62-63°, lit.[4] 64°. IR (KBr): 1480, 1455, 1210, 1185, 810, 795 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 2.48 (s, 6H), 7.19 (dd, J = 8 and 2 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.62-7.69 (m, 2H); Mass: m/e 196 (M^+).

Anal. Calcd. for $C_{14}H_{12}O$: C, 86.68; H, 6.16

Found: C, 85.44; H, 6.04

Treatment of IV with $AlCl_3$ in Toluene.- To a solution of IV (200 mg, 0.5 mmol) in 15 ml of toluene was added finely powdered $AlCl_3$ (110 mg, 0.8 mmol) at room temperature. After the reaction mixture was stirred for 1 hr, it was worked up and treated as described above to give 110 mg (64%) of VIII as colorless needles (methanol), mp. 157-158°; IR (KBr): 3450 cm^{-1}; (OH); ^1H-NMR ($CDCl_3$): δ 1.46 (s, 9H), 2.35 (s, 3H), 2.54 (s, 3H), 3.87 (broad s, 1H, disappeared with D_2O), 7.01 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 8.23 (s, 1H); Mass: m/e 346, 348 (M^+).

Anal. Calcd. for $C_{18}H_{19}BrO_2$: C, 62.25; H, 5.52

Found: C, 62.30; H, 5.55

Treatment of IV with 4 equiv $AlCl_3$ in toluene for 4 hrs was carried out and the reaction mixture was worked up and treated as described above to give 11% yield of IX as colorless prisms (hexane), mp. 110-111.5°; IR (KBr): 3520 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 2.36 (s, 3H), 2.50 (s, 3H), 5.13 (s, 1H, disappeared with D_2O), 6.99 (d, J = 8 Hz), 7.80-7.88 (m, 1H), Mass: m/e Calcd. for $C_{14}H_{12}O_2$ 212.0837 (M^+), Found: 212.0819 (M^+).

Formation of VI and VII was detected by GC analysis.

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SYNTHESIS OF N-ARYL ENAMINOSULFONES AND IMPROVED PREPARATION OF N-SUBSTITUTED ENAMINONITRILES

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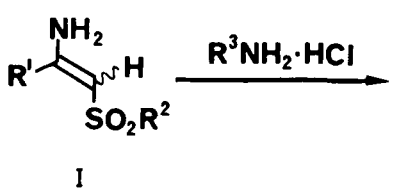
Previously, we have reported a general synthesis of β-iminosulfones or tautomeric enaminosulfones, by the reaction of sulfonyl carbanions with nitriles.[1] It was not possible, however, to extend this method to the



I II

	R^1	R^2	R^3
a)	Ph	Me	Ph
b)	Ph	Me	*p*-tolyl
c)	Ph	Ph	Ph
d)	*m*-tolyl	Ph	Ph
e)	*m*-tolyl	Ph	*p*-tolyl
f)	*p*-tolyl	NMe_2	Ph
g)	*p*-tolyl	NMe_2	*p*-tolyl

synthesis of N-substituted enaminosulfones. There has been no general synthetic method of N-substituted type enaminosulfones so far reported except for the one example by Knorr et al.[2] who prepared 2-anilinopropenyl