COMMUNICATIONS

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Synthesis of 6*H*-Dibenzo[*b,f*]oxocin

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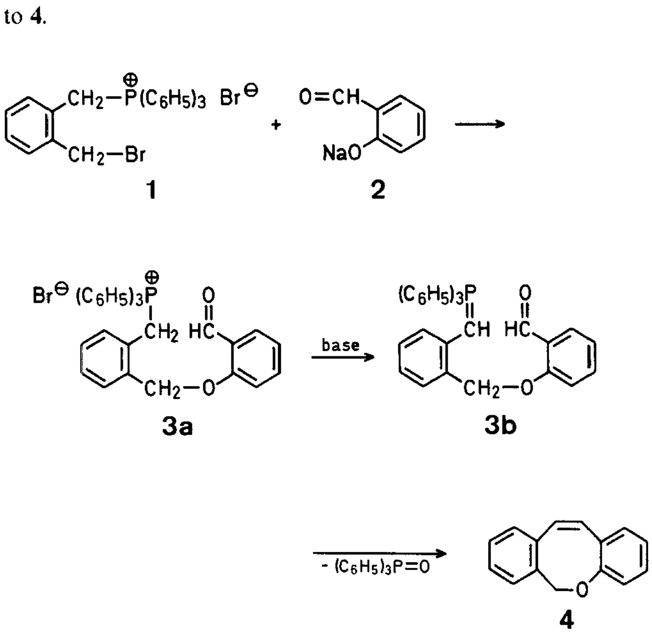
Neutral or charged heterocyclic 10-π-electron systems are the source of considerable interest[1,2,3]. We report here the first synthesis of 6*H*-dibenzo[*b,f*]oxocin (**4**) whose carbanion is potentially aromatic. Previously, 6-oxo-11,12-dihydro-6*H*-dibenzo[*b,f*]oxocin had been reported[4]. The first step of our synthesis involves condensation of the sodium salt of salicylic aldehyde (**2**) with the phosphonium salt **1**[5,6] to give **3a** in 90% yield. The second step involves intramolecular Wittig condensation of **3b** to **4**.



The structure of 6*H*-dibenzo[*b,f*]oxocin (**4**) was confirmed by microanalysis and by I.R., ^{1}H-N.M.R., and ^{13}C-N.M.R. spectral data. The latter spectrum shows signals for fourteen quaternary carbon atoms and one primary carbon atom. The proposed structure for **4** is further supported by the epoxidation of **4** with *m*-chloroperbenzoic acid to give the 11,12-epoxy derivative.

2-(Bromomethyl)-benzyltriphenylphosphonium Bromide (1)[5,6]:
To a stirred solution of 1,2-bis[bromomethyl]benzene (52.8 g, 0.2 mol) in toluene (420 ml) is added a solution of triphenylphosphine (52.4 g, 0.2 mol) in toluene (150 ml). The mixture is heated under reflux for 4 h and the phosphonium salt is collected by filtration; yield: 102 g (98%); m.p. 250 °C; Lit.[5], m.p. 253–256 °C.

2-(2-Formylphenyloxymethyl)-benzyl-triphenylphosphonium Bromide (3a):
To a stirred suspension of the phosphonium salt **1** (31.5 g, 60 mmol) in acetone (250 ml) is added a solution of the sodium salt of salicylic aldehyde (**2**; 10.4 g, 72 mmol) in water (66 ml). After 5 min, the acetone is removed under vacuum and water (120 ml) is added. The mixture is extracted with dichloromethane (200 ml). The organic layer is dried with sodium sulfate and evaporated under normal pressure (azeotropic elimination of water). The residue is triturated with toluene (200 ml) and the toluene is removed by distillation under atmospheric pressure to give the crude salt **3a**; yield: 29.75 g (90%). This dried material is sufficiently pure for the following step, but pure **3a** can be obtained by recrystallisation from acetonitrile; m.p. 226 °C (dec).

$C_{33}H_{28}BrO_2P$	calc.	P 5.46	Br 14.08
(567.5)	found	5.34	13.95

^{1}H-N.M.R. (CDCl$_3$): $\delta=4.93$ (s, 2H); 5.60 (d, 2H, $J_{P-H}=14.5$ Hz); 10.30 ppm (s, 1H).

6*H*-Dibenzo[*b,f*]oxocin (4):
Sodium methoxide in methanol (23 ml of 2.6 normal solution) is added dropwise over a 50 min period to a stirred suspension of phosphonium salt **3a** (34 g, 0.06 mol) in boiling toluene (340 ml). After the addition is complete, the solid product is filtered off. The solvent is evaporated and the residual product is extracted with pentane (3 × 100 ml). The solvent is removed under vacuum giving **4**; a pure sample is obtained by two recrystallisations from ethanol; yield: 7.25 g (62%); m.p. 60–62 °C.

$C_{15}H_{12}O$	calc.	C 86.51	H 5.80	O 7.68
(208.3)	found	86.42	5.65	7.76

^{1}H-N.M.R. (CDCl$_3$): $\delta=5.20$ (s, 2H); 6.55 (s, 2H); 6.8–7.5 ppm (m, 8H).

^{13}C-N.M.R. (CDCl$_3$); $\delta=120.9$; 122.1; 125.7; 127.6; 128.2; 128.6; 128.8; 129.9; 130.0; 131.4; 135.4; 135.5; 138.7; 158.8 ppm (C—O).
I.R. (CCl$_4$): $\nu=1602$ cm^{-1} (C=C).

11,12-Epoxy-11,12-dihydro-6*H*-dibenzo[*b,f*]oxocin:
To a stirred solution of 85% *m*-chloroperbenzoic acid (3.6 g, 0.017 mol) in dichloromethane (50 ml) is added dropwise a solution of 6*H*-dibenzo[*b,f*]oxocin (**4**; 3.38 g, 0.016 mol) in dichloromethane (20 ml). After the addition, the mixture is kept to room temperature for 24 h. The filtered solution is washed with aqueous sodium hydroxide solution (30 ml) and then with water (30 ml). The solvent is evaporated and the residual product recrystallised from methanol; yield: 3.21 g (90%); m.p. 124–125 °C.

$C_{15}H_{12}O_2$	calc.	C 80.34	H 5.39
(224.3)	found	80.02	5.18

^{1}H-N.M.R. (CCl$_4$): $\delta=4.16$ (d, 1H, $^3J_{H-H}=4$ Hz); 4.31 (d, 1H, $J=4$ Hz); 4.98 (d, 1H, $^2J_{H-H}=12$ Hz); 5.61 ppm (d, 1H, $^2J_{H-H}=12$ Hz).

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