New Synthesis of Diphenylmethane Derivatives

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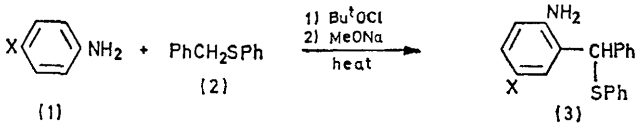
Summary A new, general synthesis of *o*-benzylanilines (2-aminodiphenylmethanes) from anilines has been developed, which involves the sequential reaction of an aniline with (i) t-butyl hypochlorite, (ii) phenyl benzyl sulphide, and (iii) sodium methoxide, followed by desulphurization with lithium aluminium hydride or Raney-nickel.

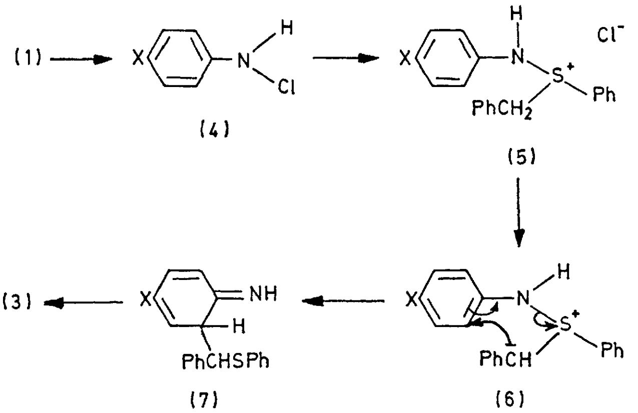
Although *o*-benzylanilines are useful synthetic intermediates (*e.g.*, in the synthesis of fluorenes[1]), the available methods[2] of preparation of *o*-benzylanilines have limitations. We have developed a new method for the *o*-alkylation of aromatic amines,[3] and report here a modification of this



	X	yield(%)
a;	Me	73
b;	H	72
c;	Cl	76
d;	CO_2Me	61
e;	NO_2	65

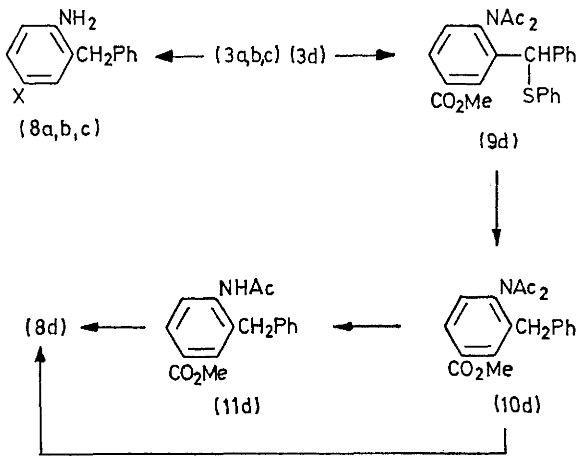
procedure which provides a general, high yield synthesis of *o*-benzylanilines.

In a general procedure, the aniline (**1**) (1 equiv.) and phenyl benzyl sulphide (**2**) (2 equiv.) were dissolved in a 3:1 mixture of MeCN–CH_2Cl_2 and the solution cooled to −40°. A solution of 1·3 equiv. of Bu^tOCl in CH_2Cl_2 at −78° was added dropwise and the reaction mixture was stirred for *ca.* 4 h at −40° and then allowed to warm to −20° over 3 h. A methanolic solution of sodium methoxide was then added and the reaction mixture was heated. Work-up and purification gave (**3**).†



Mechanistically, the reaction involves initial chlorination of (**1**) to give (**4**) followed by reaction of (**4**) with (**2**) to give the azasulphonium salt (**5**). Treatment with base yields the ylide (**6**) which on heating undergoes a Sommelet–Hauser type rearrangement[4] to give the dienone imine (**7**). Hydrogen shift and accompanying re-aromatization gave (**3**).

Desulphurization of (**3**) was readily accomplished *via* reduction with lithium aluminium hydride. When (**3a**), (**3b**), or (**3c**) was stirred with an equimolar amount of lithium aluminium hydride at 25° for 12 h, we obtained (**8a**) (89%), (**8b**) (95%), and (**8c**) (83%), respectively. Since lithium aluminium hydride desulphurization of (**3d**) could not be accomplished without reduction of the methoxycarbonyl group, an alternative desulphurization process was developed. Direct Raney-nickel reduction of (**3d**) was complicated by extensive reduction of the activated aromatic ring. In order to avoid this difficulty (**3d**) was converted into (**9d**) according to the method of Brown.[5] Reduction of (**9d**) with W-2 Raney-nickel in ethanolic tetrahydrofuran gave (**10d**) (93%). Treatment of (**10d**) with BF_3–MeOH in methanol removed the acetyl protecting groups to give (**8d**) in 79% overall yield from (**3d**). The selective removal of one acetyl group could be accomplished by treating (**10d**) with sodium methoxide in methanol under reflux for 12 h, which gave 91% of (**11d**).



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† All new compounds had satisfactory elemental analyses and spectra.

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