Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 93, No. 4, May 1984, pp. 625–634.

Mechanism of aromatic lithiation reactions—Importance of steric factors

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Abstract. N,N-Dimethyl-1-naphthylamine and N,N-dimethyl-2-aminobiphenyl do not undergo *ortho*-lithiation although lithiation at a distant, but sterically close, position does occur. The result, although apparently anomalous, can be explained by Roberts-Curtin mechanism, taking into consideration the steric strain present at the transition state corresponding to the proton abstraction process.

Keywords. Aromatic lithiation; Roberts-Curtin mechanism; N,N-dimethyl-1-naphthylamine; N,N-dimethyl-2-aminobiphenyl; Steric factors; Transition state.

Compounds like anisole, N-methylbenzamide, N,N-dimethylbenzylamine etc which carry functional groups bearing heteroatoms with unshared electron pair are readily lithiated, specifically at *ortho* position, on treatment with *n*-BuLi in ether or hexane (Gschwend and Rodriguez 1979). Under these conditions benzene itself is not lithiated to any significant extent†. In recent times these heteroatom-directed atomatic lithiation reactions have been extensively used for the synthesis of several condensed heterocyclic compounds (Narasimhan and Mali 1983).

The intimate mechanism of this important reaction is as yet not fully established. There are indeed difficulties in this regard (Mallan and Bebb 1969). In the first instance, the nature of the lithiating species, RLi, *as present in the reaction medium*, is not known. RLi exists in different polymeric states in different solvents. However, it is very likely that monomeric RLi, although in only small concentration, is also present, in equilibrium with the oligomers, in the reaction medium. Is it the polymeric RLi or the monomeric (presumably more reactive) species which is the lithiating agent? In most of the lithiation reactions, lithium salts (*e.g.* LiBr) are also present in the reaction medium. What is the influence of these on the mechanism of the reaction, particularly on the nature and reactivity of the lithiating species? Finally what is the role of the solvent on the stability of the lithiating species, the transition state and the final organolithium compound formed in the reaction?

Remarkably, however, aromatic lithiation reactions show a large regioselectivity (Gschwend and Rodriguez 1979), as in the exclusive *ortho*-lithiation of anisole, N-methylbenzamide, N,N-dimethylbenzylamine etc.

A widely accepted mechanism, which explains *ortho* lithiation, is due to Roberts and Curtin (1946). This is shown in scheme 1. In this, the first step is the reversible

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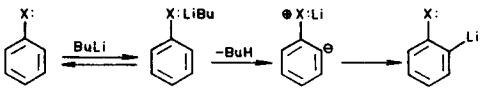
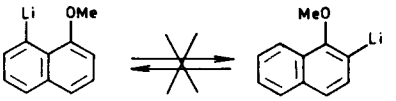
† Benzene can be lithiated when tetramethylethylenediamine (TMEDA) is additionally present (Mallan and Bebb 1969).



Scheme 1



Scheme 2

complexation of the RLi reagent with the electron donor atom present on the substituent in the aromatic ring. In the second step, which is rate determining, the *complexed* RLi abstracts the sterically close *ortho* hydrogen as a proton, presumably by a collinear attack from the back side of the hydrogen in the C–H bond*. This step, in which R is converted to RH, is expected to be irreversible when *n*-BuLi or PhLi is the lithiating agent and hence would be under kinetic control†. The last step is the shift of the lithium atom from oxygen to the *ortho* carbon atom. The organolithium compound would be, presumably, stabilised by internal coordination‡.

Where there is a possibility of the lithiation reaction occurring at more than one position in the aromatic substrate, as in the case of 1,3-dimethoxybenzene *or* 1- and 2-methoxynaphthalenes, it is possible to visualise a scheme in which the different organolithium species formed are under equilibrium control. (Scheme 2)

Equilibration of the aromatic lithium species was indeed suggested for the lithiation of 1-methoxynaphthalene (Barnes and Nehmsmann 1962), where it was stated that the initial product was the 8-lithio compound, which then isomerised to the 2-lithio compound. This experiment has been disputed and it is now well established that the 2-lithio compound is directly formed and not *via* the 8-lithio compound (Graybill and Shirley 1966).

Recently Cram and coworkers (Wilson and Cram 1982) have reported another experiment in which there is an *apparent* isomerisation of 1-lithio-2-methoxynaphthalene. Thus when 1-lithio-2-methoxynaphthalene, generated from 1-bromo-2-methoxynaphthalene by treatment with *n*-BuLi in THF, was reacted with an electrophile, the products formed corresponded to reaction at 1- and also at 3-positions in the naphthalene ring, the latter predominating. Obviously 3-lithio-2-methoxynaphthalene is also formed in this reaction. The formation of 3-lithio-2-methoxynaphthalene, however, is not an isomerisation reaction. It is formed by an alternate mechanism, as shown in scheme 3 (Wilson and Cram 1982), in which, in the first instance, 1-lithio-2-methoxynaphthalene reacts with the solvent to produce 2-methoxynaphthalene and the latter is further lithiated by 1-lithio-2-methoxynaphthalene.

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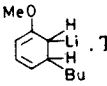
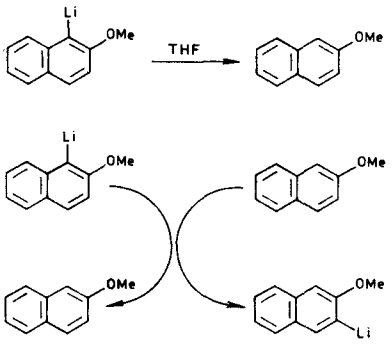
* To the extent collinear approach is not possible, the energy of the proton abstraction process will be larger.

† Indeed, the products BuH and PhH (pK_a 45–50 and 35–37 respectively) cannot be lithiated under the experimental conditions. Substituted benzenes, such as anisole, N-methylbenzamides would have lower pK_a value for the *ortho* hydrogen.

‡ An alternate mechanism was proposed for the lithiation reaction a few years back (Shirley and Hendrix 1968). This involved intermediacy of radical ions and the species 

. This mechanism has since been disproved by us (Narasimhan and Chandrachood 1973) and by the authors themselves (Shirley *et al* 1974) and has since been withdrawn.



Scheme 3

The mechanism is in agreement with the well-known fact that organolithium compounds are less stable in THF and 2-methoxynaphthalene is lithiated predominantly to give the 3-lithio compound.

The above observation, however, is not general. Literature abounds with examples where organolithium compounds, obtained *via* halogen-metal exchange, do not isomerise. Indeed, for this reason, organolithium compounds, obtained this way, have been extensively used in organic synthesis. Specifically now we find that when 1-lithio-2-methoxynaphthalene, obtained from 1-bromo-2-methoxynaphthalene by treatment with *n*-BuLi in *ether solvent*, is treated with dimethylformamide (DMF), no product corresponding to substitution at 3-position is obtained. In this reaction, thus, no 3-lithio compound was formed in the reaction mixture *i.e.* no isomerisation had occurred. Again, when 1-lithio-2-methoxynaphthalene, as obtained above in *ether* solution, was treated with 2-methoxynaphthalene, no 3-lithio compound was obtained (as evidenced by further reaction with DMF). The latter experiment indicated that, *in ether solution* 1-lithio-2-methoxynaphthalene cannot lithiate 2-methoxynaphthalene.

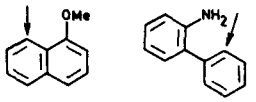
In similar experiments it was found that 4-lithio-1,3-dimethoxybenzene, obtained by treatment of 4-bromo-1,3-dimethoxybenzene with *n*-BuLi *in ether*, did not isomerise to 2-lithio-1,3-dimethoxybenzene, as evidenced by further reaction with benzophenone, although the latter was expected to be thermodynamically the more stable. And also, 4-lithio-1,3-dimethoxybenzene did not lithiate 1,3-dimethoxybenzene.

The above experiments* indicate that organolithium corresponds, once formed, do not undergo any isomerisation *at least in ether solution.* Their formation, then, is under kinetic control.

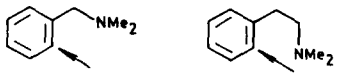
The other observed orientation (Gschwend and Rodriguez 1979) in aromatic lithiation reactions are in accord with the mechanism of lithiation reaction given above. Thus,

(i) lithiation occurs not only at the *ortho* position, but also at other sterically close positions (scheme 4). This is to be expected, for the RLi reagent, complexed to the

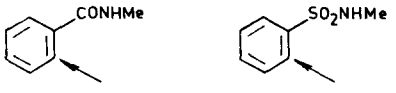
* Several lithiation reactions have been repeated in our laboratory to have uniform experimental conditions so that the conclusions derived are valid. The results are, however, qualitatively similar to what is reported in literature.



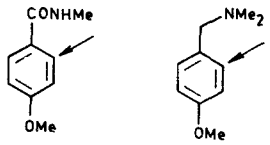
Scheme 4



Scheme 5



Scheme 6



Scheme 7

electron donor atom on the substituent, can abstract hydrogen atoms also from other positions, provided they are sterically accessible to it;

(ii) lithiation occurs even when the heteroatom is not directly attached to be aromatic ring, but is one or two atoms away (scheme 5). The RLi reagent would still complex with the electron donor atom and the transition state corresponding to proton abstraction can be readily formed. However, when the number of intervening atoms is more than two, there will be difficulty in achieving the transition state;

(iii) lithiation occurs at the *ortho* or other sterically close positions even when the lithiation directing group, as a whole, is electron withdrawing, provided it still carries an electron donor atom with which the RLi reagent can complex (scheme 6). Interestingly, such groups, which are meta-orienting in acid catalysed electrophilic substitution reactions, are found to be better *ortho* lithiation-directing. It may be noted that some of these groups, *e.g.* $-CONHCH_3$, would have negative charge on them on treatment with the RLi reagents. Presumably, despite the negative charge, the electron-withdrawing ability of such groups is substantial, which then leads to increased acidity of the *ortho* hydrogen atom*, a condition favourable for the aromatic lithiation reaction;

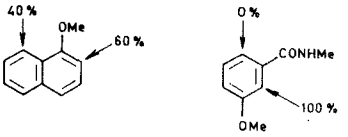
(iv) when more than one lithiation directing group is present, lithiation is directed by that group which complexes better with the RLi reagent (scheme 7);

(v) when more than one position for lithiation is present, lithiation occurs predominantly at that position which carries the more acidic hydrogen atom *from among those which are ortho or sterically close with respect to the better complexing group* (scheme 8).

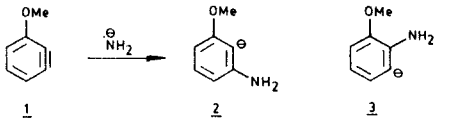
It may be noted here that the acidity to be considered, in these reactions, where *n*-BuLi is the lithiating agent, is the kinetic acidity. This is because, in the rate-determining step, the proton abstraction itself is under kinetic control. Further, in these cases (aromatic lithiations), the acidity of the hydrogen is determined essentially by the inductive effect and not, to any significant extent, by the resonance effect†. The

* It may be noted that dianions are readily formed from CH_3CONHR in contrast to, for example, even monoanions from CH_3OR (House 1972).

† This is presumably because the negative charge on the benzene carbanion is present on the σ-orbital, which is orthogonal to the π-orbital of the aromatic system. Where the π-orbital can assume parallel conformation, as in $PhCH_2^-$, resonance factor will be also important.



Scheme 8



Scheme 9

situation is similar to the formation of similar types of species when substituted benzynes react with strong bases such as NH_2^-. The benzyne 1, for example, reacts with NH_2^- to give 2 rather than 3 (March 1977) (scheme 9). Had the resonance factors been important, the negative charge on the species 2 would have been destabilised by the methoxyl group at the *ortho* position.

In summary it may be stated that complexation and acidity of the hydrogen atom *ortho* or sterically close to the complexing group are the two important factors which govern orientation in aromatic lithiation reactions. Complexation is more important. Thus, *p*-methoxy-N,N-dimethylbenzylamine is lithiated at *ortho* position with respect to the dimethylaminomethyl group despite the fact that the hydrogen atom *ortho* to this group is less acidic than that *ortho* to the methoxyl group (Gschwend and Rodriguez 1979).

Steric factors in aromatic lithiation reactions

Steric factors, evidently, would be also important in lithiation reactions. Steric factors can come into play at three stages: (i) complexation of RLi with the electron-donor group, (ii) attainment of the transition state leading to lithiation and (iii) reaction of the organolithium compound with the electrophilic reagent. The influence of the steric factors on the first and the last stages, however, would be on the rate rather than on the orientation*. The orientation in aromatic lithiation is then essentially governed by the steric factors in the transition state.

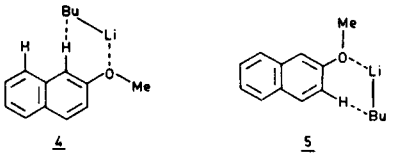
The role of steric factors on orientation in lithiation reactions can be seen in the lithiation of 2-methoxynaphthalene. Here there are two alternate *ortho* positions, 1 and 3, for lithiation. The hydrogen at 1-position would be more acidic since the double bond at the 1(2) position would transmit the inductive effect of the oxygen function better to this than to 3-position. Lithiation is then expected to occur at 1-position. Experimentally, however, lithiation occurs predominantly at 3-position.

The above observation can be rationalised on the basis of the steric strain in the transition states, corresponding to lithiation at 1- and 3-positions. These transition states are shown in scheme 10. In both the transition states a linear approach of the Bu to H–C bond is assumed, since this would be the most favoured pathway for the reaction.

It may be now noted that, of the two transition states 4 and 5, 4 would be more

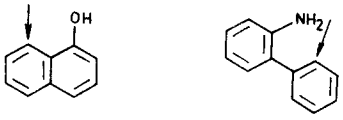
* Complexation can influence orientation in the sense that lithiation will occur *ortho* or sterically close to that group which complexes better with the lithiating agent. This aspect has already been referred to.

It has already been mentioned that formation of the aromatic lithio compounds in ether solution is irreversible. The reaction of the aromatic lithium compounds with electrophiles such as H_2O, CO_2, DMF, PhCOPh are also irreversible and no instance of reversibility has been reported.



4 5

Scheme 10



Scheme 11

strained due to steric repulsion between the hydrogen at 8-position and the butyl group. The lithiation reaction would be then favoured *via* the transition state 5 and would occur predominantly at 3-position.

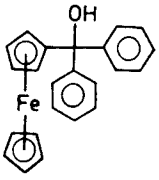
Gilman and Sunthankar (1981) had explained the preferential lithiation of 2-methoxynaphthalene at 3-position invoking resonance factors. According to this, the methoxyl group would increase the electron density (presumably π-electron density) at 1-position, which in turn would decrease the acidity of the hydrogen at that position. The hydrogen at 3-position would be then relatively more acidic, leading to lithiation there. It has already been pointed out that π-electron density is not important for the acidity of the aromatic hydrogen*.

Apparently anomalous lithiation reactions

There are certain lithiation reactions which apparently do not fit in the above scheme of mechanism. Thus 1-naphthol and 2-aminobiphenyl are lithiated exclusively at 8- and 2'-position respectively (scheme 11). In the above, one would have expected lithiation to occur at 2- and 3-positions respectively, since these positions, having an oxygen or nitrogen at the adjacent position, would carry the more acidic hydrogen. A closer examination, however, would indicate that this is not so. The first event that occurs when the above compounds are treated with RLi reagent would be formation of ArO^- and $ArNH^-$ species (or corresponding ion pairs ArOLi, ArNHLi). Aromatic lithiation actually occurs on these species. Now, in these species, the negative charge on the oxygen or nitrogen would indeed decrease the acidity of the hydrogen at the adjacent (*ortho*) position, while those at the distant 8- and 2'-position would be relatively unaffected. The latter would be relatively more acidic and hence lithiation would be more favoured at these positions. The observed orientation in the lithiation of 1-hydroxynaphthalene and 2-aminobiphenyl, thus, is not anomalous but is in agreement with the Roberts–Curtin mechanism.

Lithiation of N,N-dimethyl-1-naphthylamine and N,N-dimethyl-2-aminobiphenyl

On the basis of Roberts–Curtin mechanism, lithiation of N,N-dimethyl-1-naphthylamine and N,N-dimethyl-2-aminobiphenyl was expected to occur more at the *ortho*-

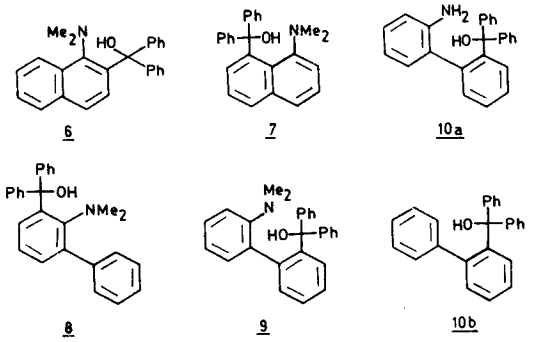
* It may be noted that lithiation of 

occurs on the ferrocene ring, although it has more π-electron density than benzene (Benkeser *et al* 1961).

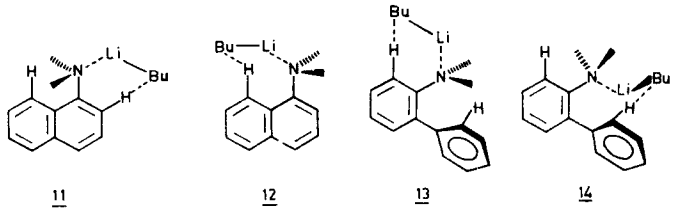
positions (at 2- and 3-positions respectively) which were adjacent to the electronegative nitrogen atom, than at the distant, but sterically close, 8- and 2′-positions respectively. However, actually the lithiation occurred at the distant positions. Thus when N,N-dimethyl-1-naphthylamine was lithiated with *n*-BuLi in ether solution and the metalation mixture treated with benzophenone, the benzhydrol obtained was 7 and not 6. The structure of the compound was established by its NMR spectrum. Here, there was a doublet of doublet (J = 8 and 2 Hz) at 6·92 δ, which was typical for an aromatic proton with an *ortho* and a *meta* proton neighbours, which was possible only for structure 7. The NOE experiments further established that this was not the proton *ortho* to the NMe_2 group but that *ortho* to the benzhydrol group. Thus no intensity enhancement for the signal at 6·92 δ was observed when the signal at 2·2 δ, which corresponded to the $-NMe_2$ group, was irradiated.

Similarly lithiation of N,N-dimethyl-2-aminobiphenyl followed by treatment with benzophenone furnished only the benzhydrol 9 and not 8. In this case, the NMR spectrum was uninformative, but the structure was established by chemical transformation to 10b by first demethylation and then deamination.

Lithiation of N,N-dimethyl-1-naphthylamine and N,N-dimethyl-2-aminobiphenyl at 8- and 2′-positions respectively was surprising. However, it was still consistent with the Roberts–Curtin mechanism and can be explained by taking into account the steric strain present in the transition states corresponding to lithiation at alternate positions. For the lithiation of N,N-dimethyl-1-naphthylamine the transition states, corresponding to lithiation at 2- and 8-positions, are shown in 11 and 12; for the lithiation of N,N-dimethyl-2-aminobiphenyl at 3- and 2-positions they are 13 and 14. It may be seen that in 11, the two methyl groups on the nitrogen atom are very close to the C-8



Scheme 12



Scheme 13

and H-8 atoms of the naphthalene ring (peri positions) and in 13, they are close to phenyl group at 1-position. The transition states 11 and 13 would be relatively more strained than 12 and 14 respectively. Lithiation then occurs according to the latter, at the distant 8- and 2'-positions respectively, despite the greater acidity of the *ortho*-protons at 2- and 3-positions respectively.

In summary it may be stated that Roberts–Curtin mechanism does explain the orientation observed in all lithiation reactions, reported to date.

Experimental

The m.p.'s are uncorrected; the NMR chemical shifts are in δ scale.
n-BuLi in ether was prepared according to Gilman's procedure (Gilman 1954).

Halogen metal exchange reaction of 1-*bromo*-2-*methoxynaphthalene*

(i) *in THF solution*

To a solution of 1-bromo-2-methoxynaphthalene (2·37 g, 0·01 mole) in THF (50 ml) was added *n*-BuLi (0·01 mole) in ether. The metalation mixture was stirred at room temperature for 1 hr and then treated with DMF (0·73 g, 0·01 mole) in ether (10 ml) during 15 min. It was decomposed with water. The ether layer was separated, and the aqueous layer extracted with ether (3 × 25 ml). The combined ether layer was washed with water, dried (Na_2SO_4) and the solvent removed. The residue (1·8 g, 96%) contained only 2-methoxy-1-naphthaldehyde (Narasimhan and Mali 1975) and 2-methoxy-3-naphthaldehyde no other constituents (identified by NMR).

(ii) *in ether solution*

To a stirred solution of 1-bromo-2-methoxynaphthalene (2·37 g, 0·01 mole) in ether (50 ml) was added *n*-BuLi 0·01 mole in ether. The metalation mixture was stirred for 20 hr at room temperature. It was divided into two approximately equal portions.

One portion was treated with DMF (0·365 g, 0·005 mole) in ether during 30 min. Work-up, as usual, gave a residue which on crystallisation from hexane gave 2-methoxy-1-naphthaldehyde (0·992 g, quantitative yield based of 1-bromo-2-methoxynaphthalene used), m.p. 85° (Narasimhan and Mali 1975, m.p. 85°); NMR identical with authentic sample.

The second portion was treated with a solution of 2-methoxynaphthalene (0·799 g, 0·005 mole) in ether. The reaction mixture was stirred for another 20 hr. It was then treated with DMF (0·365 g, 0·005 mole) during 30 min and then decomposed with water. Usual work-up gave a residue, whose NMR indicated it to be a mixture of 2-methoxy-1-naphthaldehyde and 2-methoxynaphthalene. Chromatographic separation of the residue on silica gel using pet ether for elution gave 2-methoxynaphthalene (0·782 g, 99%) in the first fraction and 2-methoxy-1-naphthaldehyde (0·876 g, quantitative yield based on 1-bromo-2-methoxynaphthalene used), m.p. 85°.

Halogen metal exchange of 4-*bromo*-1,3-*dimethoxy benzene in ether solution*

To a stirred solution of 4-bromo-1,3-dimethoxy benzene (2·17 g, 0·01 mole) in ether (50 ml) was added a solution of *n*-BuLi (0·015 mole) in ether (80 ml). The reaction mixture was stirred for 4 hr.

(i) *reaction with benzophenone*

The metalation mixture was treated with a solution of benzophenone (2·73 g, 0·015 mole) in ether (20 ml), stirred for 10 min, and decomposed with water (50 ml). The aqueous layer was extracted with ether (3 × 25 ml). The combined ether layer was washed with water and dried (Na_2SO_4). Removal of solvent furnished residue (4·05 g), which was chromatographed on silica gel (150 g) using pet ether for solution. The first fraction gave benzophenone (0·910 g). Further fractions gave 2,4-dimethoxy-α,α-diphenylbenzyl alcohol (3·03 g, 95%), m.p. 138° (Wittig and Pokels 1939, 137·8–138·6).

(ii) *reaction with* 1,3-*dimethoxy benzene*

The metallation mixture, prepared as above using 4-bromo-1,3-dimethoxy benzene (1·085 g, 0·005 mole), was stirred with the addition of 1,3-dimethoxy benzene (0·690 g, 0·005 mole) for 5 hr at room temperature and then treated with benzophenone (0·910 g, 0·005 mole) in ether during 3 hr. Decomposition with water followed by usual isolation procedure gave a residue which on chromatography over silica gel using pet ether for elution, gave 1,3-dimethoxy benzene (0·675, 98% recovery) in the first fractions and then 2,4-dimethoxy-α,α-diphenylbenzyl alcohol (1·535, 96%), m.p. 138°.

The same result was obtained when the reaction mixture, after addition of 1,3-dimethoxy benzene, was stirred for 24 hr and then treated with benzophenone.

*Lithiation of N,N-dimethyl-*1*-naphthylamine*

To a well stirred solution of N,N-dimethyl-1-naphthylamine (3·0 g, 0·018 mole) in ether (30 ml) was added a solution of *n*-BuLi (0·11 mole) in ether (80 ml). The mixture was stirred for 48 hr at room temperature. Benzophenone (20 g, 0·11 mole) in ether (50 ml) was added and the mixture stirred for 3 hr more, decomposed with water and the ether layer extracted with dil HCl (30 ml). The acid layer was basified with dil NaOH and extracted with ether. Drying (Na_2SO_4) and evaporation of solvent gave residue (4·5 g) which was chromatographed over silica gel (180 g) using benzene for elution. First fractions (500 ml) gave the starting compound (1·5 g, 50%). Next fractions (2000 ml) gave the carbinol 7 (2·8 g, 46%), m.p. 172° (hexane-ethyl acetate); Found: C, 84·72; H, 6·38; N, 3·60; $C_{25}H_{23}NO$ requires C, 84·94; H, 6·50; N, 3·90%; NMR ($CDCl_3$): 2·2 (6H, s, NMe_2), 6·92 (1H, dd, J = 8 and 2 Hz, aromatic H ortho to carbinol), 7·09–7·33 (11H, m, aromatic protons), 7·42 (2H, d, J = 5 Hz, one aromatic proton ortho to NMe_2 and the other para to NMe_2), 7·65–7·86 (2H, m, aromatic protons), 11·28 (1H, s, OH, exchangeable with D_2O).

*Lithiation of N,N-dimethyl-*2*-aminobiphenyl*

Lithiation of N,N-dimethyl-2-aminobiphenyl (2·0 g, 0·01 mole) as above in ether solution, followed by treatment with benzophenone in ether solution gave a basic residue (3·2 g) which was chromatographed on silica gel (100 g) using benzene for elution. First fraction (1000 ml) gave the starting compound (0·44 g, 22%). Further fractions (2000 ml) gave 9 (2·54 g, 70%); m.p. 198° (hexane-ethyl acetate); Found: C, 85·38; H, 6·57; N, 3·43; $C_{27}H_{25}NO$ requires C, 85·45; H, 6·64, N, 3·69%. NMR ($CDCl_3$): 2·55 (6H, s, NMe_2), 6·35–7·7 (18H, m, aromatic protons), 8·49 (1H, s, OH, exchangeable with D_2O).

Demethylation of 9

9 (0·5 g) on heating with HI in sealed tube in N_2 atmosphere at 160°for 36 hr, followed by usual work-up and chromatography on neutral alumina using pet ether for elution gave 10a (0·3 g, 65 %), m.p. 140°; Found: C, 85·35; H, 5·92; N, 3·79; $C_{25}H_{21}NO$ requires C, 85·44; H, 6·02; N, 3·99 %.

Deamination of 10a

10a (0·05 g) was dissolved in ethanol (0·6 ml) and conc. H_2SO_4 (0·13 ml). The solution was cooled to −4° and a solution of $NaNO_2$ (0·1 g) in water (0·5 ml) was added. Copper bronze was added and the mixture refluxed on water bath for 30 min. Ethanol was evaporated and the mixture extracted with ether to furnish 10b (0·03 g), m.p. 232°, identical with synthetic sample (mixed m.p., i.r.).

Synthesis of 10b from methyl biphenyl-2-carboxylate

Reaction of PhMgBr with methyl biphenyl-2-carboxylate gave 10b, m.p. 232° (hexane); Found: C, 89·04, H, 6·22; $C_{25}H_{21}O$ requires C, 89·25; H, 5·99 %.

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