Reduction by Dissolving Metals. Part XVI.[1] Reactions of Some Aromatic Amines with Metal–Ammonia Solutions

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The reduction in liquid ammonia, preferably by lithium and t-pentyl alcohol, of some *NN*-dimethylanilines and some *N*-arylmorpholines has been examined. The products normally isolated are conjugated cyclohexadienamines, except in the case of *ortho*-substituted amines, from which stable unconjugated cyclohexadienamines can be obtained. In some other cases, with sufficient care, unconjugated dienamines can be isolated, but they undergo ready thermal conjugation at temperatures above *ca.* 30°. The morpholine derivatives are easier to handle and more stable than the *NN*-dimethylamino-derivatives. The conjugated and unconjugated dienamines have characteristic u.v., i.r., and n.m.r. spectra.

In Part III [2] the reductions of some *NN*-dimethylaniline derivatives with sodium and ethanol in ammonia were briefly discussed. Owing to their rather unstable nature, the products were not examined directly, but were hydrolysed to ketones with acid. The resulting ketones were qualitatively identical with those obtained by similar treatment of the corresponding methoxybenzenes, so it was inferred that the orientations of hydrogen addition to the rings were the same in both series. A quantitative difference from the behaviour of the methoxybenzenes was the frequent formation of a higher proportion of (undesirable) cyclohexanone compared with cyclohexenone,[3] thus indicating the formation of a larger proportion of tetrahydro-derivative under these reduction conditions.

Stork [4] and Millward [5] isolated the reduction products from *NN*-dimethylaniline and *NN*-dimethyl-*p*-toluidine and showed that they contained a large proportion of 2,3- rather than the 2,5-dihydro-derivatives analogous to those obtained by similar reductions of anisole and *p*-methylanisole. This was a surprising result, since such conjugated dienes are usually more readily reducible than the aromatic precursors, and their formation as kinetically controlled intermediates would have been expected to lead to tetrahydro-derivatives as the isolable products. Although 2,5-dihydroanisoles can be converted fairly readily by strong bases into the 2,3-dihydroanisoles, appropriate basic conditions are not encountered during the amine reductions. We have accordingly re-examined the process to find out whether the initial products are the expected unconjugated dienamines, and whether these are then converted with unexpected ease into the conjugated dienamines.

The best experimental conditions to obtain the dihydro-derivative, not normally contaminated with more than 5% of tetrahydro-derivative except in the cases noted later, involved the use of lithium and t-butyl or t-pentyl alcohol.[6] The use of ethanol gave a considerably higher proportion of further-reduced product. The reason for this is not clear, although Smith [7] showed in the case of anisoles that the more highly acidic the proton source the higher the proportion of further-reduced products which could be attributed to reduction of an intermediate conjugated diene. Methanol had a particularly marked effect. This was attributed to less specific protonation of intermediate anions, yielding higher proportions of the conjugated isomer as a kinetically controlled intermediate. Stork,[4] using the Wilds–Nelson [8] technique (ethanol) with *NN*-dimethylaniline, also obtained a high proportion of tetrahydro-derivative.

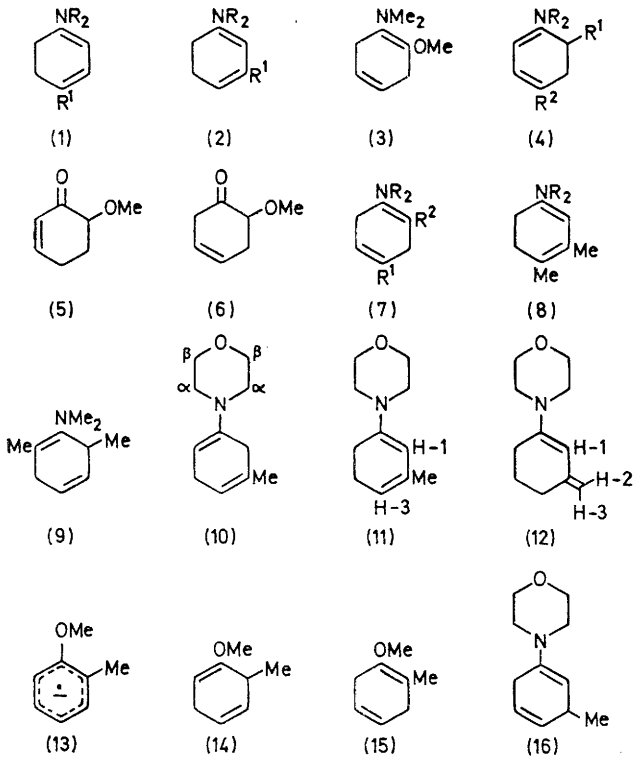
Initially, *NN*-dimethylaniline derivatives were employed, but these were later replaced by substituted *N*-phenylmorpholines since the products from these compounds were found to be more stable and more readily handled. They were easily made in high yield by treating aromatic primary amines with 2,2′-dichlorodiethyl ether, by a technique superior to that described.[9]

The u.v. and i.r. spectra of the products, discussed later, enable ready differentiation between the conjugated and unconjugated isomers. Individual assignments were confirmed by n.m.r. spectroscopy, and the products were also examined by g.l.c.

NN-Dimethylaniline was found to yield the conjugated dienamine (1; R^1 = H, R = Me), even after cold extraction of the reduction mixture with light petroleum. The assignment of structure rests on the u.v., i.r., ^{1}H n.m.r., and mass spectra. Hydrolysis with acid gave mainly cyclohex-2-enone, containing only a little cyclohexanone. In other reductions, in ethanol instead of t-butyl alcohol, a higher proportion (*ca.* 40%) of tetrahydro-derivative (*NN*-dimethylaminocyclohexene) resulted (*m/e* 125) and was quantitatively estimated from the resonances at δ 2·56 (s, 6H, NMe_2), 1·5—2·0 (m, 8H), and 4·52 (t, *J* 3·5 Hz, 1H, $CH_2{\cdot}C\overset{\cdot}{H}{:}C{\cdot}NMe_2$) p.p.m., identical with those of an authentic specimen, and by hydrolysis to cyclohexanone.

NN-Dimethyl-*p*- and *m*-anisidines gave compounds (1; R^1 = OMe, R = Me) and (2; R^1 = OMe, R = Me),

[1] Part XV, A. J. Birch and G. Subba Rao, *Austral. J. Chem.*, 1970, **23**, 1641.
[2] A. J. Birch, *J. Chem. Soc.*, 1946, 593.
[3] A. J. Birch, unpublished work.
[4] G. Stork and D. N. White, *J. Amer. Chem. Soc.*, 1956, **78**, 4604.
[5] B. B. Millward, *J. Chem. Soc.*, 1960, 26.
[6] A. J. Birch, *J. Chem. Soc.*, 1944, 430; E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, 1968, **90**, 5618.
[7] M. Smith, Ph.D. Thesis, University of Manchester, 1961.
[8] A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360.
[9] J. G. Erickson and J. S. Keps, *J. Amer. Chem. Soc.*, 1954, **76**, 3589.



respectively, in high yield. Acid hydrolysis, gave, respectively, cyclohexane-1,4-dione and cyclohexane-1,3-dione. *NN*-Dimethyl-*o*-anisidine, however, gave the unconjugated diene (3), accompanied by small proportions of a tetrahydro-amine, *NN*-dimethylaniline, and 2,5-dihydroanisole. The diene (3) was identified by its u.v., i.r., n.m.r., and mass spectra (Table 1; experimental section). Distillation, injection into a g.l.c. apparatus, or treatment with potassium t-butoxide in dimethyl sulphoxide readily converted it into the conjugated isomer (4; $R^1 = OMe$, $R^2 = H$, $R = Me$), the structure of which is supported by its u.v., i.r., n.m.r., and mass spectra. Mild acid hydrolysis gave 6-methoxycyclohex-2-en-1-one (5), which was stable to further treatment with acid, unlike the isomeric ketone (6), which readily gave a mixture of phenol and anisole on heating with aqueous acid.[10] The ketone (6) cannot therefore be an intermediate, and hydrolysis is almost certainly initiated by protonation at the 4-position, not the 2-position. The mild hydrolysis of other alkyl conjugated dienamines gave unconjugated ketone in those examples with a 4-substituent only; possibly this directs protonation to the 2-position. The general picture resembles that presented by Rogers[11] for the acid hydrolysis of 1-methoxycyclohexa-1,3-dienes.

NN-Dimethyl-*p*-toluidine gave the conjugated dienamine (1; $R = Me$, $R^1 = Me$), hydrolysed by acid to 4-methylcyclohex-3-enone. *NN*-Dimethyl-*o*-toluidine, like the *o*-anisidine, gave an unconjugated dienamine (7; $R^1 = H$, $R = R^2 = Me$), converted by oxalic acid into 2-methylcyclohex-5-en-1-one. The unconjugated dienamine on distillation, or on treatment with potassium t-butoxide in dimethyl sulphoxide, produced the conjugated dienamine by a pivoting of the double bond around the carbon carrying the nitrogen atom, as in other cases.

NN-Dimethyl-*m*-toluidine gave a product (isolated) containing two dienamines (88%) and a monoenamine (12%). The dienamines have structures analogous to those of the corresponding morpholine derivatives discussed later.

TABLE 1

^{1}H N.m.r. data for dimethylaminocyclohexadienes

	NMe_2	CH_2 [b]	H-1 [c]	H-2 [c]	H-3 [c]	Others
(1; $R^1 = H$, $R = Me$)	2·70(s)	2·28br(s)	4·75 (d, *J* 6 Hz)	5·97 (d, *J* 6 Hz)	5·28(m)	
(1; $R^1 = R = Me$)	2·65(s)	2·24(m)	4·68 (d, *J* 6 Hz)	5·63 (d, *J* 6 Hz)		=C·CH_3, 1·75(s)
(1; $R^1 = OMe$, $R = Me$)	2·62(s)	2·37(s)	4·64 (d, *J* 6 Hz)	4·96 (d, *J* 6 Hz)		O·CH_3, 3·56(s)
(2; $R^1 = R = Me$)	2·68(s)	2·25(m)	4·57(s)	4·95(m)		=C·CH_3, 1·72(s)
(2; $R^1 = OMe$, $R = Me$)	2·73(s)	2·26(m)	4·24(m)	4·64(m)		O·CH_3, 3·55(s)
(3)	2·56(s)	2·84(m)	5·65br(s)	5·65br(s)		O·CH_3, 3·60(s)
(7; $R^1 = H$, $R = R^2 = Me$)	2·38(s)	2·64(m)	5·59br(s)	5·59br(s)		=C·CH_3, 1·69(s)
(4; $R = R^1 = Me$, $R^2 = H$)	2·72(s)	2·42(m)	4·60 (d, *J* 10 Hz)	5·85(m)	5·07(m)	CH·CH_3, 1·00(d)
(4; $R^1 = OMe$, $R^2 = H$, $R = Me$	2·77(s)	2·90br(s)	4·95 (d, *J* 6 Hz)	6·07(m)	5·33(m)	O·CH_3, 3·32(s) C*H*·O·CH_3, 3·98(t)
(8; $R = Me$)	2·62(s)	2·18(m)	4·58(s)			=C·CH_3, 1·70(s)
(9)	2·56(s)	2·33(s)	5·60br(s)	5·60br(s)		CH·CH_3, 1·0(d) =C·CH_3, 1·74(s)

[a] α- and β-Methylene protons as shown in (10). [b] Protons in the ring. [c] H-1 represents the vinylic hydrogen in $R_2NC{:}CH{\cdot}$; H-2 and H-3 are the vinylic protons next to H-1 in clockwise order.

The 3,4- and the 2,6-dimethyl derivatives gave products which were now to be expected: in the former case the conjugated dienamine (8) and in the latter case

[10] A. J. Birch, *J. Chem. Soc.*, 1947, 102.
[11] N. A. J. Rogers and A. Sattar, *Tetrahedron Letters*, 1964, 1311.

the unconjugated isomer (9), which is unique so far in the series because it could be distilled without causing conjugation.

The corresponding *N*-arylmorpholines gave similar results. The behaviour of *N*-(*m*-tolyl)morpholine was particularly interesting, since the unconjugated isomer (10) was sufficiently stable to be isolated and characterised. The action of heat on compound (10) caused its conversion into a mixture of two other isomeric dienes, (11) and (12). The diene (10) had $\nu_{max.}$ 1698 and 1650 cm.$^{-1}$; heating caused the development of u.v. absorption, initially at 287 nm, changing to 277 nm., and shifted the i.r. bands to 1650 and 1585 cm.$^{-1}$, with subsequent development of bands at 1620 and 1579 cm.$^{-1}$, indicating conjugation first to an endocyclic diene and then conversion into the exocyclic diene. The analogue of (11) having OMe instead of NR_2 has bands at 1660 and 1610 cm.$^{-1}$, and that of (12) has bands at 1640 and 1620 cm.$^{-1}$,[12] showing the expected direction of shifts. Analysis by g.l.c. showed the presence of two compounds (46 and 34%), which are (11) and (12) respectively if the quantitative interpretation of the n.m.r. spectrum of the mixture is correctly attributed as follows: (11) δ 2·90 (m, 4H, morpholine), 3·72 (m, 4H, morpholine), 2·16br (s, 4H, $2CH_2$); 4·77 (s, 1H, H-1), 5·07 (m, 1H, H-3), and 1·73 (s, Me); (12) δ 2·90 (m, 4H, morpholine), 3·72 (m, 4H, morpholine), 2·2 (m, 4H, $2CH_2$), 5·30 (s, 1H, H-1), and 4·50 (d, 2H, $=CH_2$) p.p.m. These assignments agree with the conclusions of Hickmott [13] for the morpholine dienamines of isophorone. Acid hydrolysis of the mixture gave 3-methylcyclohex-2-enone only, and ozonolysis gave a notable proportion of formaldehyde.

N-(2,4-Dimethylphenyl)morpholine gave exclusively the unconjugated diene, which could be converted by distillation into the conjugated isomer, and *N*-(3,4-dimethylphenyl)morpholine gave two products, separated by g.l.c., one of which proved to be the tetrahydro-derivative in rather high proportion (22%); the other was the expected conjugated dienamine.

N-(*p*-Methoxyphenyl)morpholine also gave initially an unconjugated diene (7; $R^2 = H$, $R^1 = OMe$, $R_2 = [CH_2{\cdot}CH_2]_2O$), which was crystalline, but which was immediately converted into the oily conjugated isomer (1; $R^1 = OMe$, $R_2 = [CH_2{\cdot}CH_2]_2O$) on heating or attempted recrystallisation.

The further reduction of the conjugated dienamines was found to occur readily, as expected, the products being the tetrahydro-compounds, *i.e.* monoenamines, produced without the hydrogenolysis which accompanies reduction in the analogous methoxy-series.[1] The detailed results will be discussed in a later paper.

TABLE 2

^{1}H N.m.r. data for *N*-(cyclohexadienyl)morpholines

$R_2 = {\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}$	α-CH_2 [a]	β-CH_2 [a]	CH_2 [b]	H-1 [c]	H-2 [c]	H-3 [c]	Others
(1; $R^1 = Me$)	2·84(m)	3·72(m)	2·20(m)	4·86 (d, *J* 6 Hz)	5·61 (d, *J* 6 Hz)		=C·CH_3, 1·75(s)
(7; $R^1 = H$, $R^2 = Me$)	2·68(m)	3·72(m)	2·68(m)	5·67br(s)	5·67br(s)		=C·CH_3, 1·73(s)
(4; $R^1 = Me$, $R^2 = H$)	2·92(m)	3·72(m)	2·0—2·7(m)	4·83 (q, *J* 6 Hz)	5·89 (q, *J* 3 Hz)	5·27(m)	CH·CH_3, 1·01(d)
(11)	2·90(m)	3·72(m)	2·16br(s)	4·77(s)	5·07		=C·CH_3, 1·73(s)
(12)	2·90(m)	3·72(m)	2·2(m)	5·30(s)	4·50 (d, *J* 7 Hz)	4·50 (d, *J* 7 Hz)	
(8)	2·87(m)	3·74(m)	2·19(m)	4·78(s)			=C·CH_3, 1·70(s)
(7; $R^1 = R^2 = Me$)	2·64(m)	3·72(m)	2·64(m)	5·41br(s)			=C·CH_3, 1·66(s) =C·CH_3, 1·73(s)
(4; $R^1 = R^2 = Me$)	2·82(m)	3·66(m)	2·2—2·60(m)	4·83 (d, *J* 6 Hz)	5·69(m)		=C·CH_3, 1·75(s) CH·CH_3, 1·0(d)
(1; $R^1 = OMe$)	2·56(m)	3·54(m)	2·0—2·4(m)	4·56(t)	4·90(s)		O·CH_3, 3·55(s)
(1; $R^1 = OMe$	2·80(m)	3·72(m)	2·30(s)	4·90(s)	4·90(s)		O·CH_3, 3·60(s)

Footnotes as in Table 1

The conclusions are that the initial reduction products must in all cases be the unconjugated dienes, with a similar orientation of hydrogen-addition to the methoxy-series, but that the products undergo conjugation with extraordinary ease, often during work-up and almost invariably on distillation. A difference is observed with the *ortho*-methyl series, compared with the methoxy-compounds, since only the 3,6-dihydro-isomer (7; $R^1 = H$, $R^2 = Me$, and R = Me or $R_2 = [CH_2{\cdot}CH_2]_2O$) is detectable, whereas in the case of the methoxy-analogues a considerable proportion of the 2,5-dihydro-derivative (14) is present as well as (15).[14] This result must be related to selectivity in the addition of the first proton to the initial radical-anion (13). It is still not clear, despite much discussion,[15] whether this is directed as we previously suggested [16] by the charge distribution, and if so whether it would be expected to occur *ortho* or

[12] A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 1961, 5376.
[13] N. F. Firrell and P. W. Hickmott, *J. Chem. Soc.* (*B*), 1969, 293.
[14] A. J. Birch and M. Smith, unpublished work.
[15] A. J. Birch and D. Nasipuri, *Tetrahedron*, 1959, **6**, 148; A. P. Krapcho and A. A. Bothner-by, *J. Amer. Chem. Soc.*, 1959, **81**, 3658; J. K. Brown, D. R. Burnham, and N. A. J. Rogers, *Tetrahedron Letters*, 1966, 2621; H. E. Zimmermann, *Tetrahedron*, 1961, **16**, 169.
[16] A. J. Birch, *Trans. Faraday Soc.*, 1947, 246.

meta to OMe or NR_2. Part of the argument favouring *meta*-addition was in fact the production of both (14) and (15). It seems possible however that initial addition may occur at *ortho* and *meta* positions at similar rates, and that small differences in the effects of groups may shift predominant attack from one to the other position. The formation of compound (7) is clearly best explained by attack *ortho* to NR_2. In that case however the formation of compound (10) from the *meta*-derivative as the sole product is not readily explicable, since some of the alternative product of *ortho*-attack (16) could well have been expected. The question seems unlikely to be settled until an experimental method can be devised to decide which of the two hydrogens is added first.

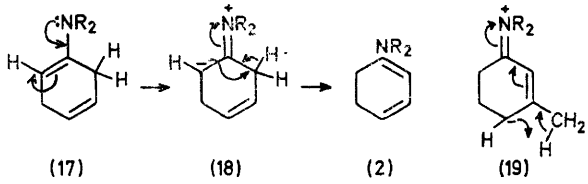
Spectra.—(i) *U.v.* The presence of NMe_2 at the 1-position of the cyclohexa-1,3-diene clearly results in extension of conjugation with absorption at *ca.* $\lambda_{max.}$ 302 nm. (*cf. ca.* 275 nm. for the corresponding hydrocarbon). The morpholine derivatives absorb at about 294 nm. The 1,4-dienes have no selective absorption above 220 nm.

(ii) *I.r.* The unconjugated dienes have two bands, one at *ca.* 1690, the other at *ca.* 1650 $cm.^{-1}$, and the conjugated dienes absorb at about 1650 and 1580 $cm.^{-1}$; the exocyclic transoid dienes such as (12) show bands at 1620 and 1580 $cm.^{-1}$.

(iii) *N.m.r.* The ^1H n.m.r. spectra of the unconjugated and conjugated dienamines were useful in indicating structures. The high-field proton resonance at δ 4·70 p.p.m. is assigned [17] to the vinylic $R_2NC{=}CH$; the assignment is confirmed by its absence in the spectra of the 2-substituted compounds. Tables 1 and 2 show that the olefinic protons of the unconjugated dihydro-*o*-tolymorpholine appear as a broad singlet at δ 5·67, while in the spectrum of the conjugated isomer three resonances appear, at δ 4·83, 5·27, and 5·89 p.p.m. The upfield shift can be attributed to further delocalisation of the *p*-electrons of the nitrogen atom in interaction with the extended π-system; similar effects are observed in the corresponding methoxycyclohexadienes. A discussion of the spectra of similar systems has appeared.[13]

Conjugation of Cyclohexa-1,4-dienes.—1-Methoxycyclohexa-1,4-dienes are equilibrated with the 1,3-dienes (75—80%) by means of very strong bases such as potassamide in ammonia [18] or potassium t-butoxide in dimethyl sulphoxide.[19] The intermediate in the equilibrium is the anion produced by loss of a proton from the methylene group in the 6-position, and weak external bases such as amines have no effect because of the very low acidity of the group. The methoxycyclohexa-1,4-dienes have a high degree of thermal stability except in the presence of dienophiles, which apparently act as electron-acceptors in charge-transfer complexes.[20] The astonishing ease of the thermal conjugations in the present series is unlikely to be explicable by external base catalysis, and acid catalysis, known to equilibrate enamines rapidly, is ruled out by the method of work-up, which is alkaline throughout.

A possible mechanism involves the effect of the nitrogen as an internal base, *e.g.* structure (17) polarised to (18) with subsequent proton transfer to the more stable (2). The thermodynamic stability of the conjugated isomer is attested by the fact that, in contrast to results in the methoxy-series, no unconjugated isomer remains. Further equilibration to the transoid dienes in the case of the 3-methyl series may proceed by proton migration in the polarised form (19).



(17) (18) (2) (19)

The reduction process described leads readily to both dienamines and enamines, and further reactions of these products will be described (see ref. 21).

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer; u.v. spectra were examined for solutions in ethanol with a Unicam SP 800 instrument. ^1H n.m.r. spectra were recorded with a Varian HA 100 spectrometer for solutions in deuteriochloroform, with tetramethylsilane as internal standard. Mass spectra were examined with an A.E.I. MS902 instrument. In cases of doubt n.m.r. assignments were checked by double resonance experiments.

Analytical g.l.c. was performed with a Varian Aerograph 202-1C instrument [stainless steel columns (6 ft. × 0·25 in.); carrier gas helium; stationary phase SE30 (3%) on 100—120 mesh Aeropack-30]. Unless otherwise mentioned, all retention times (R_t) reported were measured with reference to an internal standard. 2-Methoxynaphthalene (R_t 13·2 min.) and 4-methoxybiphenyl (R_t 8·8 min.) were used for dimethylamino- and morpholino-cyclohexadienes respectively. Preparative g.l.c. was carried out with the same instrument [SE30 column (20%)]. The percentages recorded represent the relative concentrations determined by cutting and weighing the curves, and were supported by quantitative examination of ^1H n.m.r. spectra.

Liquid ammonia was distilled from sodium directly into the reaction vessel.

Preparation of Aromatic Amines.—Some of these were purchased; the *NN*-dimethylanilines which had to be made were obtained by treatment of the aniline (1 mol.) with trimethyl phosphate (1 mol.) at reflux for 3·5 hr.; the amine was worked up as usual and distilled (yield *ca.* 60%). In the case of the morpholine derivatives, the aniline (1 mol.) and bis-(2-chloroethyl) ether (1 mol.) with anhydrous potassium carbonate (2 mol.) were refluxed for 24 hr., and after the usual work-up the product was dis-

[17] W. D. Gurowitz and M. A. Joseph, *Tetrahedron Letters*, 1965, 4433.
[18] A. J. Birch, *J. Chem. Soc.*, 1947, 1642.
[19] A. Schriesheim, J. E. Hoffman, and C. A. Rowe, *J. Amer. Chem. Soc.*, 1961, **83**, 3731.
[20] A. J. Birch and P. L. Macdonald, unpublished work.
[21] A. J. Birch, E. G. Hutchinson, and G. Subba Rao, *Chem. Comm.*, 1970, 657.

tilled. This method is superior to those previously reported. Compounds prepared were: 1-(*p*-tolyl)morpholine, b.p. 91°/0·4 mm., m.p. 51°, $\lambda_{max.}$ 248 and 289 nm. (ε 12,000 and 1385), $\nu_{max.}$ 1611 and 1576 cm.$^{-1}$ (Found: C, 74·2; H, 8·7; N, 7·8. Calc. for $C_{11}H_{15}NO$: C, 74·5; H, 8·5; N, 7·9%); 1-(*m*-tolyl)morpholine, m.p. 37°, $\lambda_{max.}$ 250 and 287 nm. (ε 10,540 and 1520), $\nu_{max.}$ 1600 and 1581 cm.$^{-1}$ (Found: C, 74·7; H, 8·5; N, 8·0. Calc. for $C_{11}H_{15}NO$: C, 74·5; H, 8·5; N, 7·9%); 1-(*o*-tolyl)morpholine, b.p. 77°/0·4 mm., $\lambda_{max.}$ 242 and 275 nm. (ε 6300 and 1220), $\nu_{max.}$ 1600 cm.$^{-1}$ (Found: C, 74·6; H, 8·6; N, 7·9. Calc. for $C_{11}H_{15}NO$: C, 74·5; H, 8·5; N, 7·9%); 1-(2,4-*xylyl*)*morpholine*, b.p. 87°/0·4 mm., $\lambda_{max.}$ 242 and 281 nm. (ε 7570 and 1240), $\nu_{max.}$ 1605 and 1593 cm.$^{-1}$ (Found: C, 75·5; H, 9·0; N, 7·3. $C_{12}H_{17}NO$ requires C, 75·4; H, 9·0; N, 7·3%); 1-(3,4-*xylyl*)*morpholine*, b.p. 100°/0·1 mm., m.p. 29°, $\lambda_{max.}$ 247 and 289 nm. (ε 11,400 and 1530), $\nu_{max.}$ 1614 and 1573 cm.$^{-1}$, δ 2·15 (s, 3H, Me) 2·20 (s, 3H, Me), 3·01 (m, 4H), 3·76 (m, 4H), 6·62 (m, 2H), and 6·96 (d, *J* 8 Hz, 1H) p.p.m. (Found: C, 75·0; H, 9·2; N, 7·7. $C_{12}H_{17}NO$ requires C, 75·3; H, 9·0; N, 7·3%).

General Procedure for Reductions. To a stirred solution of the amine (1 mol., *ca.* 10 g.) in tetrahydrofuran (1 vol., *ca.* 80 ml.) and ammonia (5 vol., *ca.* 400 ml.) containing the alcohol (preferably t-butyl or t-pentyl alcohol) (1 vol., *ca.* 80 ml.) was added the metal (preferably lithium) (5 atomic proportions) during 20 min. After a further 1 hr. ethanol was added to discharge the blue colour, followed by light petroleum (b.p. 30—40°) and water. The organic layer was rapidly separated, washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The product was examined directly or distilled, as appropriate. The enamines were hydrolysed by dissolution in cold N-hydrochloric acid, and the ketonic products were usually examined as their 2,4-dinitrophenylhydrazones. These were separated when necessary by preparative t.l.c.

1-*Dimethylaminocyclohexa*-1,3-*diene*.—Reduction of *NN*-dimethylaniline gave the 1-dimethylaminocyclohexa-1,3-diene (R_t 2·05 min.; 87%), containing a small proportion of 1-dimethylaminocyclohexene (13%). The former had b.p. 31—33°/0·7 mm., $\lambda_{max.}$ 302 nm. (ε 7300), $\nu_{max.}$ 1676, 1645, and 1574 cm.$^{-1}$, *m/e* 123. Hydrolysis gave cyclohex-2-enone; 2,4-dinitrophenylhydrazone, m.p. 164—165°.

4-*Dimethylamino*-1-*methoxycyclohexa*-1,3-*diene*.—Reduction of the aromatic precursor gave 1-*methoxy*-4-*dimethylaminocyclohexa*-1,3-*diene* (R_t 5·65 min.), b.p. 97—99°/12 mm., $\lambda_{max.}$ 297 nm. (ε 5800), $\nu_{max.}$ 1650 and 1602 cm.$^{-1}$, *m/e* 153 (Found: C, 70·2; H, 9·6; N, 9·0. $C_9H_{15}NO$ requires C, 70·5; H, 9·9; N, 9·2%). Hydrolysis with acid gave cyclohexane-1,4-dione, m.p. 77—78°; bis-2,4-dinitrophenylhydrazone, m.p. 238—239°.

1-*Dimethylamino*-3-*methoxycyclohexa*-1,3-*diene*. This *diene* (R_t 6·10 min.), b.p. 108—109°/11 mm., (92% yield) had $\lambda_{max.}$ 285 nm. (ε 12,200), $\nu_{max.}$ 1691, 1644, and 1595 cm.$^{-1}$, *m/e* 153·1153 ($C_9H_{15}NO$ requires *M*, 153·1154).

1-*Dimethylamino*-2-*methoxycyclohexa*-1,4-*diene*.—Reduction of the aromatic precursor gave the *diene* (62%), R_t 10·8 min., a tetrahydro-amine (21%), R_t 7 min., *NN*-dimethylaniline (5%), R_t 6·2 min., and 1-methoxycyclohexa-1,4-diene (11%), R_t 2·8 min., the last two being identified by g.l.c., mass spectral, and n.m.r. comparison with authentic materials. The g.l.c. data were obtained on a Ucon 550X column at 170° in this case. The diene had $\nu_{max.}$ 1692 and 1632 cm.$^{-1}$, *m/e* 153. On distillation (b.p. 69—73°/1·5 mm.), the conjugated isomer 1-dimethylamino-6-methoxycyclohexa-1,3-diene was obtained, $\lambda_{max.}$ 306 nm. (ε 10,000), $\nu_{max.}$ 1648 and 1575 cm.$^{-1}$, *m/e* 153. Acid hydrolysis gave 6-methoxycyclohex-2-enone, b.p. 84—88°/11 mm., $\lambda_{max.}$ 224 nm. (ε 9400), $\nu_{max.}$ 1690 and 1620 cm.$^{-1}$, *m/e* 126. The 2,4-*dinitrophenylhydrazone* had m.p. 200—201°, $\lambda_{max.}$ 385 nm. (ε 27,700), $\nu_{max.}$ 1614, 1590, and 1573 cm.$^{-1}$ (Found: C, 51·0; H, 4·7; N, 18·2. $C_{13}H_{14}N_4O_5$ requires C, 51·0; H, 4·6; N, 18·3%). The cyclohexene derivative was characterised by its molecular ion, *m/e* 155.

1-*Dimethylamino*-4-*methylcyclohexa*-1,3-*diene*.—Reduction of *NN*-dimethyl-4-methylaniline gave the diene (92%) (R_t 2·85 min.), apparently identical with Millward's product.[5] It had b.p. 70—72°/6·5 mm., $\lambda_{max.}$ 300 nm. (ε 7500), $\nu_{max.}$ 1651 and 1593 cm.$^{-1}$, *m/e* 137. Hydrolysis gave 4-methylcyclohex-3-enone; 2,4-dinitrophenylhydrazone, m.p. 128—129°, $\lambda_{max.}$ 367 nm. (ε 22,700). The reduction product contained *ca.* 8% of 1-dimethylamino-4-methylcyclohexene, δ 2·54 (s, 6H) 4·43 (m, 1H), and 0·95 (d, *J* 6 Hz, 3H, CH*Me*) p.p.m.; acid hydrolysis gave 4-methylcyclohexanone; 2,4-dinitrophenylhydrazone, m.p. 132—133°, separated by preparative t.l.c. The quantitative analysis was based on quantitative estimation of this derivative and examination of the n.m.r. spectrum and g.l.c. curves.

Reduction of NN,3-*Trimethylaniline*. This gave a mixture of three products, as shown by g.l.c., b.p. 64—66°/2·5 mm. One major peak on g.l.c. (88%) was due to a mixture of isomeric dienes which could not be separated; *m/e* 137, $\lambda_{max.}$ 269 nm. (ε 8300), $\nu_{max.}$ 1667, 1650, 1613, and 1581 cm.$^{-1}$. The n.m.r. spectrum of the mixture, in agreement with the results of Hickmott,[13] indicated the presence of dimethylamino-3-methylcyclohexa-1,3-diene, δ 1·72 (s, 3H, =CMe), 2·25 (m, 4H, $CH_2{\cdot}CH_2$), 2·68 (s, 6H, NMe_2), 4·57 (s, 1H), and 4·95 (m, 1H) p.p.m.; and dimethylamino-3-methylenecyclohex-1-ene, δ 2·70 (s, 6H, NMe_2), 2·25 (m, 6H, $CH_2{\cdot}CH_2$), 4·37 (d, *J* 7 Hz, 2H, $C{=}CH_2$), and 5·12 (s, 1H) p.p.m., in the ratio 5 : 3. The mixture on acid hydrolysis gave 3-methylcyclohex-2-enone, identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 171—173°.

The other reduction product, of lower R_t value was the dimethylamino-3-methylcyclohexene (12%), which was separated by preparative g.l.c. It had *m/e* 139 and on hydrolysis gave 3-methylcyclohexanone; 2,4-dinitrophenylhydrazone, m.p. 156—157°, $\lambda_{max.}$ 367 nm. (ε 24,500).

1-*Dimethylamino*-2-*methylcyclohexa*-1,4-*diene*.—Reduction of *NN*,2-trimethylaniline gave the unconjugated diene, $\nu_{max.}$ 1692 and 1630 cm.$^{-1}$. Hydrolysis with aqueous oxalic acid gave 2-methylcyclohex-4-enone; 2,4-dinitrophenylhydrazone, m.p. 139—140° (lit.,[22] m.p. 139°) $\lambda_{max.}$ 365 nm. (ε 23,300). This diene on treatment with potassium t-butoxide in dimethyl sulphoxide under nitrogen gave 1-dimethylamino-6-methylcyclohexa-1,3-diene, b.p. 57—58°/2·5 mm., $\lambda_{max.}$ 305 nm. (ε 6000), $\nu_{max.}$ 1657 and 1570 cm.$^{-1}$, *m/e* 137.

1-*Dimethylamino*-3,4-*dimethylcyclohexa*-1,3-*diene*.—The aromatic precursor gave the *diene*, b.p. 54—56°/0·3 mm., $\lambda_{max.}$ 290 nm. (ε 9600), $\nu_{max.}$ 1666 and 1593 cm.$^{-1}$, *m/e* 151 (Found: C, 79·6; H, 11·2; N, 9·3. $C_{10}H_{17}N$ requires C, 79·4; H, 11·3; N, 9·3%). Hydrolysis with acid gave 3,4-dimethylcyclohex-3-enone; 2,4-dinitrophenylhydrazone, m.p. 142—143° (lit.,[12] 143°), $\lambda_{max.}$ 368 nm. (ε 23,000) [lit.,[12] 366 nm. (ε 24,000)].

[22] E. A. Braude, A. A. Webb, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 1958, 3328.

1-*Dimethylamino*-2,6-*dimethylcyclohexa*-1,4-*diene*.—Reduction of *NN*,2,6-tetramethylaniline gave the unconjugated *dienamine* (98%), R_t 2·0 min., b.p. 68—69°/12 mm., $\nu_{max.}$ 1685 and 1655 cm.$^{-1}$ (Found: C, 79·9; H, 11·7. $C_{10}H_{17}N$ requires C, 79·4; H, 11·4%). Mild acid hydrolysis gave 2,6-dimethylcyclohex-3-enone, $\nu_{max.}$ 1711 and 1612 cm.$^{-1}$, which on treatment with Brady's reagent gave a mixture of 2,4-dinitrophenylhydrazones, separated by preparative t.l.c. and identified as the derivative of the unconjugated ketone, m.p. 161—162°, $\lambda_{max.}$ ($CHCl_3$) 367 nm. (ε 20,600), and that of the conjugated ketone, m.p. 156—157°, $\lambda_{max.}$ ($CHCl_3$) 381 nm. (ε 25,700).

1-(4-*Methylcyclohexa*-1,3-*dienyl*)*morpholine*.—Reduction of the aromatic precursor gave the *diene* (R_t 5·4 min.), b.p. 88°/0·65 mm., $\lambda_{max.}$ 294 nm. (ε 7800), $\nu_{max.}$ 1650 and 1591 cm.$^{-1}$ (Found: C, 73·3; H, 9·4; N, 8·0. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·6; N, 7·8%). Hydrolysis gave the known 4-methylcyclohex-3-enone; 2,4-dinitrophenylhydrazone, m.p. 129°. A small proportion of the monoene was isolated by preparative g.l.c. and gave rise with acid to 4-methylcyclohexanone; 2,4-dinitrophenylhydrazone, m.p. 134°.

1-(5-*Methylcyclohexa*-1,4-*dienyl*)*morpholine*.—Reduction of 1-(*m*-tolyl)morpholine gave the unconjugated *dienamine*, with no initial u.v. absorption. This diene equilibrated rapidly on warming to 50° under nitrogen to a mixture of the endocyclic (46%) and exocyclic (34%) dienamines (R_t 3·40 and 4·80 min.). The mixture had b.p. 104—105°/2·2 mm., $\lambda_{max.}$ 277 nm. (ε 8670), $\nu_{max.}$ 1650, 1620, 1585, and 1579 cm.$^{-1}$, *m/e* 179 (Found: C, 73·7; H, 9·1; N, 7·7. Calc. for $C_{11}H_{17}NO$: C, 73·7; H, 9·5; N, 7·8%). Hydrolysis with dilute acid gave the known 3-methylcyclohex-2-enone; 2,4-dinitrophenylhydrazone, m.p. 173°.

The diene mixture (3·5 g.) in ethyl acetate (50 ml.) was ozonised at −80° for 3 hr. The product was directly hydrogenated over Adams catalyst; the uptake of hydrogen was 2 atoms per mole of the exocyclic dienamine. The mixture was filtered and steam distilled into a solution of dimedone (2·0 g.) in ethanol (25 ml.) and water (3 ml.), giving formaldehyde dimedone adduct (0·80 g.), which was purified by preparative t.l.c. and had m.p. and mixed m.p. 189°.

1-(2-*Methylcyclohexa*-1,3-*dienyl*)*morpholine*.—Reduction of 1-(*o*-tolyl)morpholine gave mainly the unconjugated 1-(2-methylcyclohex-1,4-dienyl)morpholine (95%), $\nu_{max.}$ 1692 and 1658 cm.$^{-1}$, *m/e* 179. On distillation, this was converted into the 1,3-*diene* (80%), R_t 3·70 min., b.p. 83°/0·8 mm., $\lambda_{max.}$ 297 nm. (ε 6400), $\nu_{max.}$ 1634 and 1573 cm.$^{-1}$, *m/e* 179 (Found: C, 73·6; H, 9·8; N, 7·6. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·6; N, 7·8%).

1-(4-*Methoxycyclohexa*-1,3-*dienyl*)*morpholine*.—Reduction of the aromatic precursor gave 1-(4-*methoxycyclohexa*-1,4-*dienyl*)*morpholine* (75%), m.p. 73—74°, $\nu_{max.}$ 1694 and 1651 cm.$^{-1}$ (Found: C, 67·4; H, 8·8; N, 7·2. $C_{11}H_{17}NO_2$ requires C, 67·6; H, 8·7; N, 7·3%). On distillation, this gave the conjugated *dienamine* (R_t 3·0 min.), b.p. 98°/0·2 mm., 292 nm. (ε 8000), $\nu_{max.}$ 1646 and 1605 cm.$^{-1}$ (Found: C, 67·7; H, 8·8; N, 7·2. $C_{11}H_{17}NO_2$ requires C, 67·6; H, 8·7; N, 7·3%).

1-(2,4-*Dimethylcyclohexa*-1,3-*dienyl*)*morpholine*.—Reduction of 1-(2,4-xylyl)morpholine gave the unconjugated dienamine (95%), $\nu_{max.}$ 1675 and 1650 cm.$^{-1}$. During distillation, this was converted into the conjugated *dienamine* (R_t 4·75 min.), b.p. 62°/0·04 mm., $\lambda_{max.}$ 295 nm. (ε 8900), $\nu_{max.}$ 1650 and 1589 cm.$^{-1}$ (Found: C, 74·8; H, 9·9; N, 7·0. $C_{12}H_{19}NO$ requires C, 74·6; H, 9·9; N, 7·3%). Hydrolysis gave 2,4-dimethylcyclohex-4-enone; 2,4-*dinitrophenylhydrazone* m.p. 167—168°, $\lambda_{max.}$ 365 nm. (ε 24,800) (Found: C, 54·9; H, 5·4. $C_{14}H_{16}N_4O_4$ requires, C, 55·2; H, 5·3%).

1-(3,4-*Dimethylcyclohexa*-1,3-*dienyl*)*morpholine*.—Reduction of 1-(3,4-xylyl)morpholine gave the conjugated *diene* (78%), R_t 4·90 min., b.p. 96—98°/0·5 mm., $\lambda_{max.}$ 286·5 nm. (ε 9420), $\nu_{max.}$ 1660 and 1598 cm.$^{-1}$, *m/e* 193 (Found: C, 74·5; H, 10·0; N, 7·2. $C_{12}H_{19}NO$ requires C, 74·6; H, 9·9; N, 7·3%). Hydrolysis with dilute acid gave the known 3,4-dimethylcyclohexa-3-en-1-one, $\nu_{max.}$ 1710 cm.$^{-1}$; 2,4-dinitrophenylhydrazone, m.p. 142—143° (lit.,[12] 143°).

The monoenamine (22%), R_t 3·6 min., also obtained in the reduction was separated by g.l.c. and had δ 1·02 (d, *J* 7 Hz, 3H, CH·CH_3), 1·15 (d, *J* 7 Hz, 3H, CH·CH_3), 1·5—1·8 (m, 6H), 2·80 (m, 4H), 3·75 (m, 4H), and 4·8 (d, 1H) p.p.m., *m/e* 195.

[0/1159 *Received, July 8th,* 1970.]