Preparation of Some Dimethylaminocyclohexa-1,3-dienes and their Reactions with αβ-Unsaturated Ketones

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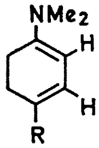
Summary Metal–ammonia reduction of an *NN*-dimethylaniline usually gives the cyclohexadiene of type (**1**). These enamines react with αβ-unsaturated ketones to give initially a 2-substituted cyclohexenone [*e.g.* (**4**)] or a hydronaphthalene ketone [*e.g.* (**3**)].

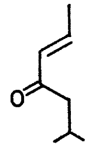
METAL–AMMONIA reduction of a methoxybenzene derivative gives a methoxycyclohexa-1,4-diene, hydrolysable to an unsaturated ketone.[1] Since similar ketones were obtained[2] from *NN*-dimethylanilines, it was assumed that the unstable intermediates were the *NN*-dimethylaminocyclohexa-1,4-dienes. However Millward[3] concluded that the major products of the reduction of *NN*-dimethylaniline and *NN*-dimethyl-*p*-toluidine were the 1,3-dienes (**1**; R = H) and (**1**; R = Me). We have confirmed this, and have shown that many, but not all, products isolated from reactions of substituted dimethylanilines by extraction with light petroleum are the conjugated dienes.

The product of the reduction of *NN*-dimethyl-*p*-toluidine, for example, with lithium and t-pentyl alcohol was the amine[3] (**1**; R = Me): 92%: b.p. 70—72°/6·5 mm, $\lambda_{\max}$ 300 nm (ϵ 7500); $\nu_{\max}$ 1651, 1593 cm.$^{-1}$; n.m.r. δ ($CDCl_3$) 1·75 (s, 3H, $=CCH_3$), 2·65 [s, 6H, $N(CH_3)_2$], 4·68 (d, J = 6 Hz, H-1), 5·63 (d, H-2); *M*, 137. Hydrolysis with dilute acid gave 4-methylcyclohex-3-en-1-one [2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 128—129° $\lambda_{\max}$ 365 nm (ϵ 22,700)].

Reaction of this amine (**1**; R = Me) with but-1-en-3-one in boiling benzene gave the dienone (**3**) in very good yield. The structure of the product rests on spectra: $\lambda_{\max}$ 287 nm, $\nu_{\max}$ 1660 cm^{-1}, δ ($CDCl_3$) 1·1 (d, J 6 Hz, $>CHCH_3$), 1·8—2·8 (m, 9H), 5·75 (s, 1H, $>C=CHC=O$), 5·9 (br d, J = 3 Hz, 1H), *M*, 162; 2,4-dinitrophenylhydrazone, m.p. 182—183°, $\lambda_{\max}$ 397 nm (ϵ 32,200).



(1)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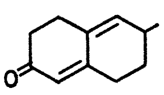
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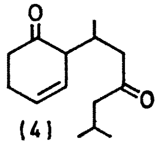
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Reaction of the amine (**1**; R = Me) with 6-methylhept-2-en-3-one (**2**) in refluxing dioxan gave the known[4] diketone (**4**), $\lambda_{\max}$ 225 and 282 nm (ϵ 1200, 212); $\nu_{\max}$ 1710 cm^{-1}; δ ($CDCl_3$) 0·9 (d, J = 6 Hz, 9H, $=CHCH_3$), 1·8 (s, 3H, $>CCH_3$), 2·0—3·0 (m, 11H), 5·4 (s, 1H, *cis*-$CH_3C=CH$), M, 236, identical with an authentic specimen kindly provided by Dr. J. Diekman.

These reactions and one other[3] seem to be the only alkylation of cisoid dienamines recorded, and they occur at the β-, not the δ-position, as observed in a transoid dienamine.[5] The reaction is potentially important because of the ready availability of the compounds, and because the enamine double bond is normally found only in one position because of the specificities of the reduction and migration reactions involved.

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[1] A. J. Birch, *J. Chem. Soc.*, 1944, 430.

[2] A. J. Birch, *J. Chem. Soc.*, 1946, 593.

[3] B. B. Millward, *J. Chem. Soc.*, 1960, 28; see also G. Optz and W. Merz, *Annalen*, 1962, **653**, 139; H. Nozaki, T. Yamaguti, S. Ueda, and K. Kondo, *Tetrahedron*, 1968, **24**, 1445.

[4] A. J. Birch, J. Diekman, and P. L. Macdonald, *Chem. Comm.*, 1970, 52.

[5] G. Stork and G. Birnbaum, *Tetrahedron Letters*, 1961, 313.