Valence Rearrangements of Hetero-systems. A Novel Synthesis of a Dipyrrylmethane

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Summary Rearrangement of a 1,2-dihydropyridazine, generated ***in situ,*** provides a reactive intermediate which is directly converted into a dipyrrylmethane.

IN our study of the general valence rearrangement, (I) → (II), where X and Y are hetero-atoms of higher electronegativity than carbon,[1] we have examined the particular case of a 1,2-dihydropyridazine (III), and have observed an unexpected transformation of such a compound into a dipyrrylmethane. Thus, although Schenk[2] had reported that *trans*-4,5-diacetylcyclohexane reacted with hydrazine to yield a polymer, we found the reaction proceeded cleanly to the pyridazine (IV), [mass spectral *M* 160; ν_{max} (Nujol) 1360, 1400, 1550, 1575, 2900, and 3040 cm.$^{-1}$; λ_{max} (EtOH) 254 nm. (ϵ 2550); n.m.r. (CCl_4) δ 2·42 (s, 6H), 3·08 (d, 4H, *J* 1 Hz), 5·78 (t, 2H, *J* 1 Hz.),] presumably the result of ready oxidation of the intermediate 1,2-dihydropyridazine (III). Avoiding this redox process by use of *sym*-dimethylhydrazine we observed transformation of the same diketone into the di-*N*-methyldipyrrylmethane (V), in 30% yield.†

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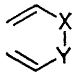
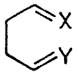
† All new compounds have given satisfactory analytical data.

The structure of (V) is based on its analysis and a comparison of its spectral properties with those of 1,2,3,4,5-pentamethylpyrrole.[3] The mass spectral M is 306 and the n.m.r.



(I)



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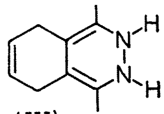

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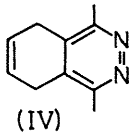
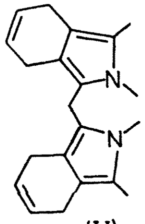
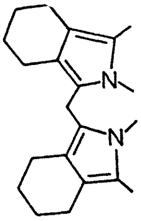


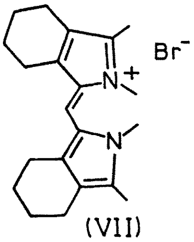
(IV)



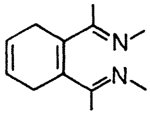
(V)



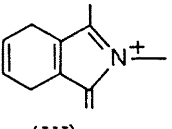
(VI)



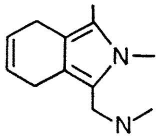
(VII)



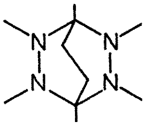
(VIII)



(IX)



(X)



(XI)

spectrum ($CDCl_3$): δ 2·06 (s, 6H), 2·90 (m, 4H), 3·25 (s, 6H), 3·72 (s, 2H), and 5·76 (s, 4H) p.p.m. showed identical chemical shifts for the 1- and 2-methyl substituents as those observed in pentamethylpyrrole. The u.v. spectrum (EtOH), λ_{max} 210 nm. (ϵ 15,000) and the i.r. spectrum (Nujol), ν_{max} 1535 and 1600 cm.$^{-1}$, were also in good agreement with those of pentamethylpyrrole. The dipyrrylmethane (V) was cleanly hydrogenated (PtO_2) to a tetrahydro-derivative (VI) [ν_{max} (CCl_4) 1380, 1440, 2840, 2860, and 2920 cm.$^{-1}$; n.m.r. (CCl_4) δ 1·60 (m, 8H), 1·96 (s, 6H), 2·26 (m, 8H), 3·13 (s, 6H), 3·56 (s, 2H) p.p.m.; mass spectral M 310] by saturation of the cyclohexene-type double bonds. This compound (VI) afforded definitive evidence for a dipyrrylmethane structure since it was readily oxidized by bromine to the deep red dipyrrylmethene salt (VII), λ_{max} 545 nm. (ϵ 21,500), similar to that reported for 1,3,5,1′,3′,5′-hexamethyl-4,4′-bisethoxycarbonyldipyrrylmethene perchlorate.[4] This process was readily reversed by hydrogenation.

The mechanism of formation of (V) is of some interest since it involves the ejection of one carbon atom and concurrent formation and linkage of two pyrrole rings. It seems reasonable to assume a preliminary formation of a 1,2-dihydropyridazine, (III), followed by decomposition as expected[1] by valence rearrangement to a compound (VIII), which can readily rearrange to the species (IX) and (X). Subsequent coupling of (IX) and (X) followed by retro-aldol reaction accounts for structure (V), and in keeping with this suggestion we have demonstrated the presence of formaldehyde by formation of its 2,4-dinitrophenylhydrazone in the reaction mixture. It may be that this process, through its simplicity, could have application in the synthesis of substituted dipyrrylmethenes. In the absence of substituents on the diketone precursor, however, a different path is followed, since when treated with acetonylacetone, dimethylhydrazine gave the bicyclic hydrazine (XI): ν_{max} (CCl_4) 1375, 1450, 2850, 2960, and 3020; n.m.r. (CCl_4) δ 0·98 (s, 6H), 1·86 (bs, 4H), 2·40 (s, 12H) p.p.m.

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[2] G. O. Schenk, *Ber.*, 1944, **77**, 741.

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