The 2,3-Homopyrrole Ring System

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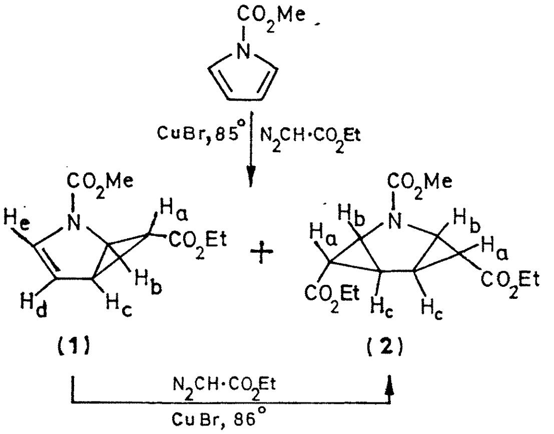
Summary The 2,3-homopyrrole ring system has been prepared by the copper(I) bromide decomposition of ethyl diazoacetate in the presence of *N*-methoxycarbonylpyrrole.

FURAN AND THIOPHEN behave as dienes toward carbenes and carbenoids giving 1,2-addition products, whereas pyrrole and its derivatives have previously yielded only substitution products.[1] We report what we believe to be the first carbene or carbenoid addition to a pyrrole derivative providing the first synthesis of the 2-azabicyclo-[3,1,0]hex-3-ene ring system (2,3-homopyrrole).

When ethyl diazoacetate was decomposed with copper(I) bromide at 85° in the presence of *N*-methoxycarbonylpyrrole (1 equiv.) a complex mixture of products was obtained. T.l.c. of this mixture using silica gel provided a

14% yield of the mono-adduct (**1**) and 5% of the bis-adduct (**2**).† The n.m.r. spectrum (CCl_4) of (**1**) showed τ 3·47 (d, br, 1H, *J* 4·5 Hz., H_e), 4·52—4·70 (m, 1H, H_d), 5·56—6·08 (m, 3H, H_b and OCH_2Me), 6·23 (s, 3H, OCH_3), 7·12—7·40 (m, 1H, H_c), 8·75 (t, 3H, *J* 7·0 Hz., OCH_2CH_3), and 9·08 (t, 1H, *J* 2·0 Hz., H_a). Irradiation of H_a causes the signal due to H_c to collapse into a doublet (*J* 7·0 Hz.) of doublets (*J* 2·5 Hz.). Irradiation of H_c causes the H_d signal to collapse into a doublet (*J* 4·0 Hz.). The i.r. spectrum (neat) showed important absorptions at 3120, 3060 (vinyl and cyclopropyl hydrogens), 1720 (C=O), and 1590(C=C) cm.$^{-1}$ The u.v. spectrum (95%) EtOH) showed λ_{max} 244 (ϵ 195). The mass spectrum showed a molecular ion at *m/e* 211 (12%) and the base peak at *m/e* 138 ($M^+ - CO_2C_2H_5$).



The bis-adduct (**2**) was recrystallized from ether–pentane to give colourless crystals, m.p. 97—98°. The n.m.r. spectrum (CCl_4) showed τ 5·83 (q, 4H, *J* 7·5 Hz., OCH_2Me), 6·28 (s, 3H, OCH_3), 6·60 (d broad, 2H, *J* 7 Hz., H_b), 7·52—7·78 (m, 2H, H_c), 8·17—8·30 (m, 2H, H_a), and 8·72 (t, 6H, *J* 7·5 Hz., $-OCH_2CH_3$). Irradiation of H_a caused the signal due to H_c to collapse into a doublet (*J* 7 Hz.). The i.r. spectrum (KBr) showed important absorptions at 3090, 3063 (cyclopropyl hydrogens) and 1712 cm.$^{-1}$ (C=O).

The ethoxycarbonyl group would be predicted to occupy the *exo*-position since this is the stereochemistry of the main adduct from cyclopentadiene and ethyl diazoacetate.[2] The n.m.r. spectrum of (**1**) also suggests this configuration since the proton α to the ethoxycarbonyl group (H_a) is probably shielded by the double bond and occurs at τ 9·08. This proton (H_a) appears downfield at approximately τ 8·23 in the bis-adduct consistent with the above hypothesis and the carbocyclic analogue.[3]

When ethyl diazoacetate is decomposed with copper(I) bromide at 86° in the presence of (**1**) (1 equiv.) a 10% yield of (**2**) is obtained. This suggests that the ethoxycarbonyl groups are *exo* to the five-membered ring in (**2**). However, the configuration of the cyclopropyl groups with respect to each other cannot be assigned with certainty.

Irradiation of an equimolar mixture of ethyl diazoacetate and *N*-methoxycarbonylpyrrole using a quartz filter and a 500 w Hanovia high-pressure mercury lamp gave no detectable amount of (**1**). Irradiation using a Pyrex filter gave only a trace of (**1**).

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† Satisfactory elemental analyses for (**1**) and (**2**) have been obtained.

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