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FORMATION OF A PYRROLE BY CARBENE - CARBENE REARRANGEMENT

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A pyrrole is formed through a carbene-carbene rearrangement, as shown by specific ^{12}C *labelling experiments.*

Reactions of methyllithium with gem-dibromocyclopropane derivatives having an olefinic π-bond adjacent to the ring give rise to cyclopentadienes, most probably through a carbene-carbene rearrangement.[1,2,3] So far the rearrangement has only been described for C-C π-bonds. We want to report the formation of 1-t-butyl-3-methylpyrrole (1) from the reaction of the imine 2 and methyllithium, suggesting that the rearrangement will take place with other π-bonds as well.

The imine 2 was prepared in 68% yield from 2,2-dibromo-1-methylcyclopropanecarbaldehyde (3)[4] and t-butylamine.

2: b.p. 56-58 °C (0.015 mm); IR (film) 1670 cm^{-1}; ^{1}HNMR (CCl_4) δ 1.18 (9H, s, $C(CH_3)_3$) 1.55 (3H, s, CH_3) 1.88 (2H, dd, CH_2) 7.37 (1H, s, -CH=N-); ^{13}CNMR (CCl_4) δ 20.14 (CH_3) 29.37, 31.97 ($C(CH_3)_3$) 32.42 (CH_2) 34.10 (CBr_2), 57.11 (-C-) 156.46 (-CH=N-).

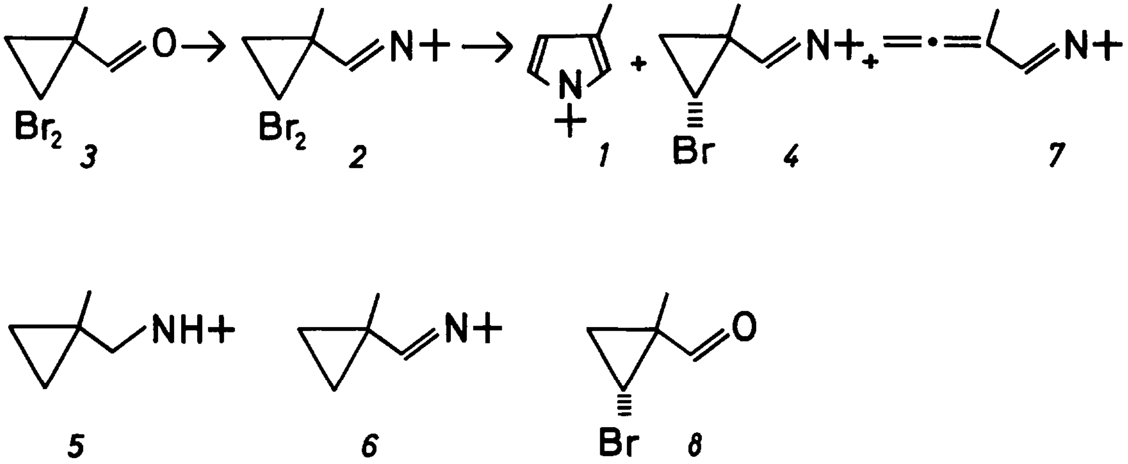
Reaction of 2 at room temperature with methyllithium for 16 hrs. gave a mixture of products. Extensive decomposition took place on attempted separation, but the spectral data indicated that the main components were the pyrrole 1 and the monobromides 4. Reduction of the crude reaction mixture with $Na/NH_3(\ell)/MeOH$ gave 1-methyl-N-t-butylcyclopropanemethanamine (5, 25%) while the pyrrole 1 (67%) remained unaffected. (Scheme 1) Two minor components (8%) were also present but were not isolated. For comparison the amine 5 was also prepared by a similar reduction of the dibromocyclopropane derivative 2.

Pure samples of 1 and 5 were obtained by preparative GC.

1: IR (film) 3140, 3090, 1560, 1580, 750 cm^{-1}; ^{1}HNMR (CCl_4) δ 1.43 (9H, s, $C(CH_3)_3$) 2.00 (3H, s, CH_3) 5.70 (1H, t, = CH-) 6.37 (1H, br. s, = CH-N) 6.50 (1H, t, = CHN); ^{13}CNMR (CCl_4) δ 12.02 (CH_3) 30.67, 53.41 ($C(CH_3)_3$) 108.96 (=CH-) 114.87 (=C-) 116.50 (= CH-N) 117.47 (=CH-N). m/e 137 (M), 122, 81, 57, 53, 41.

5: IR (film) 3080, 1230 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 0.27 (4H, br. s) 1.05 (9H, s) 1.10 (3H, s) 2.35 (2H, s); ^{13}CNMR ($CDCl_3$) δ 12.19 (cycloprop. CH_2) 15.85 (cycloprop. C) 21.83 (CH_3) 28.63, 51.11 ($C(CH_3)_3$) 51.55 (CH_2); m/e 126 (M-15), 57.

Using less reducing agent and shorter reaction time the imine 6 was obtained: ^{1}HNMR (CCl_4) δ 0.62 (4H, br.d, cycloprop. CH_2) 1.07 (9H, s, $C(CH_3)_3$) 1.18 (3H, s, CH_3) 6.88 (1H, s, -CH=N-).

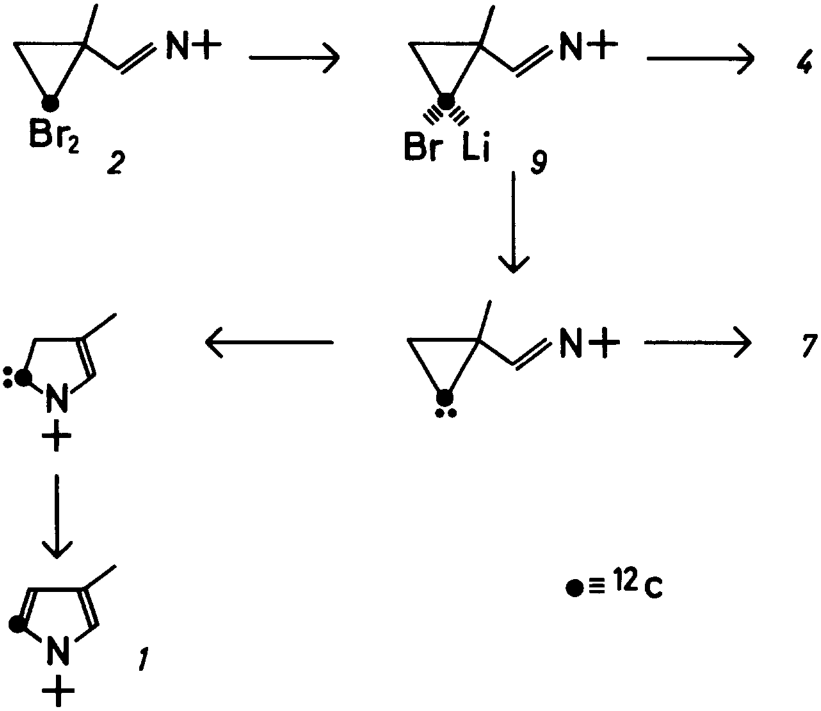


Scheme 1

When the reaction was carried out at -78 °C much less of the pyrrole was formed, the monobromide being the main product; trace amounts of the allene 7 was probably also present as indicated by weak IR absorption at 1970 cm^{-1}. Additional evidence for the monobromides were obtained by treating the reaction mixture with 2,4-DNP reagent; the mixture of hydrazones exhibited a ^{1}HNMR spectrum practically identical to that recorded from the mixture of 2,4-DNP derivatives obtained from the isomeric aldehydes 8.

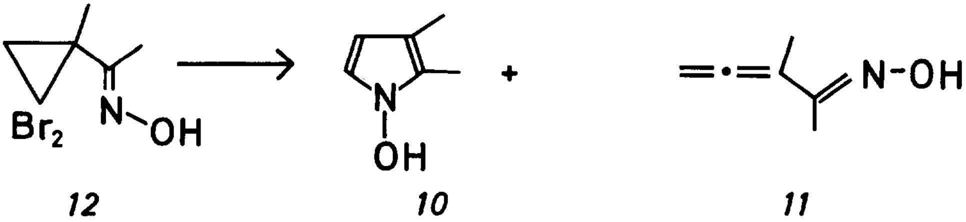
The reaction paths illustrated in Scheme 2 accomodate the results and the carbene-carbene rearrangement is analogous to that proposed for the similar reaction of alkenyl-substituted dibromocyclopropanes.[2,5] Evidence for the scheme was provided by reacting specifically ^{12}C-labelled imine, obtained from labelled aldehyde 3. The latter was prepared from isoprene, $^{12}CHBr_3$ and KOH under phase transfer conditions, followed by oxidation of the addition product with ruthenium tetroxide.

The absence of resonances at δ 34.24 and 116.50 in the ^{13}CNMR spectra of the imine 2 and the pyrrole 1, respectively, proves the positions of labelling as marked in the scheme. The intermediate organolithium derivative 9, the precursor of the monobromides 4, is probably stabilized by the neighbouring nitrogen and temperatures considerably above -78 °C are required for elimination of lithium bromide to occur at a reasonable rate.



Scheme 2

In a recent paper, Santelli reports[6] the formation of the hydroxypyrrole 10 and the allene 11 from treatment of 12 with methyllithium (Scheme 3). It is proposed that the pyrrole derives from the allene, but the present work suggests that the formation of 10 is another example of the carbene rearrangement depicted in scheme 2.



Scheme 3

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