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1,2-DIMAGNESIUM DERIVATIVES OF CYCLOPROPANE

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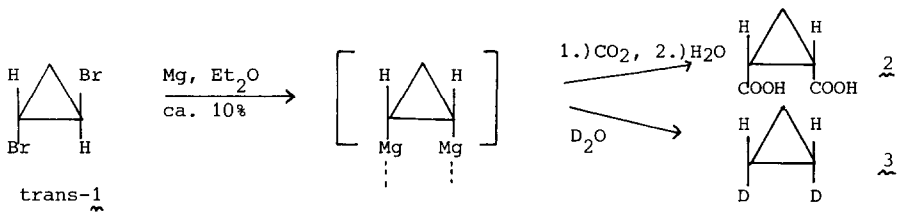
Abstract: cis-1,2-Dibromomagnesiocyclopropane (cis-4) was isolated from the reaction of both trans- and cis-1,2-dibromocyclopropane (1) with magnesium. The corresponding dialkylmagnesium species (7), an oligomer of 2-magnesabicyclobutane, was obtained from cis-4 by precipitation in THF; it forms a soluble complex 8 with $MgBr_2$.

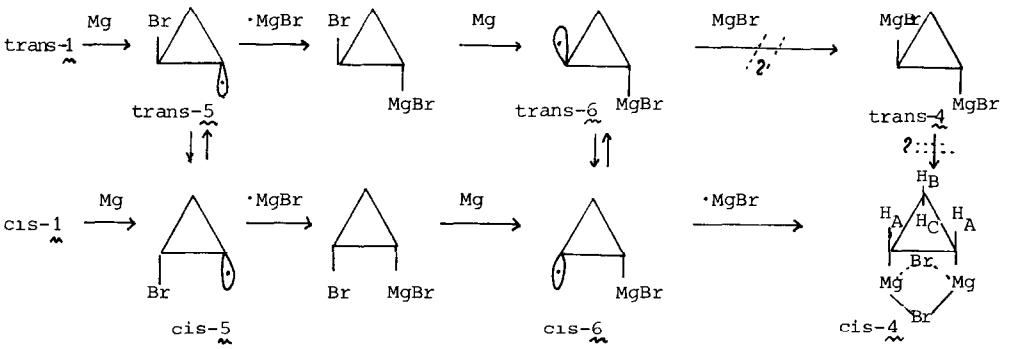
In 1960, Wiberg and Bartley[1] reacted trans-1,2-dibromocyclopropane (trans-1) with magnesium and observed, on treatment of the reaction mixture with CO_2 or D_2O, the formation of 2 and 3, respectively. As the latter reactions are known to occur with retention of configuration, they postulated the intermediacy of a cis-dimagnesiumorganic species.



trans-1

However, vicinal dimetalorganic compounds have been reported to react abnormally in some cases[2]. For this reason, and because of the intrinsic interest of simple compounds of this type, we decided to investigate the organomagnesium compound involved directly.

Both trans-1 and cis-1[3] were treated with magnesium in Et_2O in a fully sealed and evacuated glass apparatus[4]. According to the product analysis after carboxylation or deuterolysis, 15-17% cis-1,2-dibromomagnesiocyclopropane (cis-4) were formed; no indications for the presence of trans-4 were obtained. The solubility of cis-4 in pure Et_2O is low; it precipitates from the reaction mixture and can thus be obtained in pure form, analyzing correctly by acid and complexon titration. Addition of $MgBr_2$ increases the solubility; the best NMR spectra were obtained in liquid $MgBr_2/Et_2O$-d_{10} "underlayer". The ^1H NMR spectrum (250 MHz; broad lines without fine structure: δ = 1.53 ppm (2H, H_A), 0.58 ppm (1H, H_C), 1.26 ppm (1H, H_B) was assigned by comparison with the spectrum of cyclopropylmagnesium bromide[5]; it proves the cis-configuration, as in trans-4 H_B and H_C are equivalent.



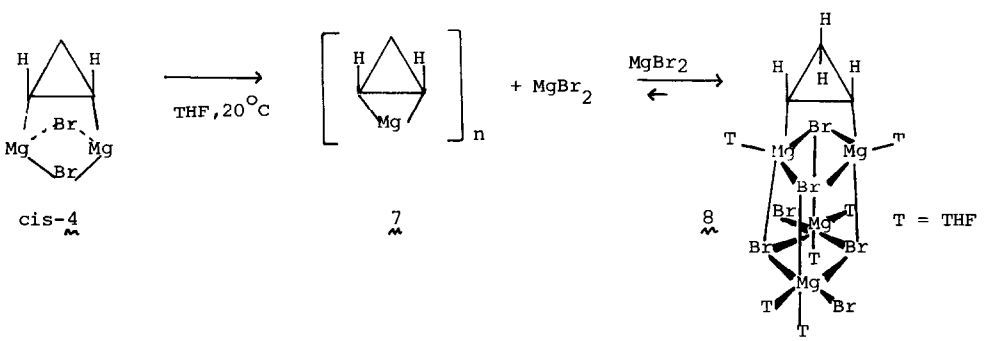
It is not clear which factors are responsible for the exclusive formation of the cis-isomer. Two alternatives may be considered:

1) The stereochemistry is determined <u>during</u> the formation reaction itself, which may be expected to occur via more or less free radicals[6], such as 5 and 6. In view of the conversion of trans-1 to cis-4, it would appear that the radicals are "free" and not partly surface-bound as in the formation of monovalent cyclopropylmagnesium bromides[6b,c]. As the configurational stability of 5 in the Hunsdiecker reaction is low[3], it must be postulated that the stereochemistry is largely determined in the last steps: it may be envisaged
   a.) that cis-6 is favoured in the cis-trans equilibrium (e.g. because of favourable interactions between the unpaired electron and the positively charged magnesium), or
   b.) that ·MgBr reacts faster with cis-6 (because in the transition state the greater thermodynamic stability of cis-4 (see below) is felt), while cis-6 is rapidly supplemented by the equilibrium with trans-6.
2) The stereochemistry is determined thermodynamically <u>after</u> the formation by interconversion of the probably less stable trans-4 to cis-4. While steric factors and dipolar interactions may be expected to favour trans-4, cis-4 may derive its greater stability to double bromine bridging (chelate effect; simple bromine bridging has already been considered by Wiberg and Bartley[1]), and to the entropic advantage of less ether fixation in cis-4 (1 Et_2O/Mg) compared to trans-4 (2 Et_2O/Mg). Although Walborsky and Aronoff have shown that monovalent cyclopropylmagnesium bromides are configurationally stable[6b], the vicinal divalent 4 may have a novel pathway available for interconversion[7]. As long as trans-4 has not been obtained independently, this possibility cannot be excluded.

At present, we consider 1a.) as the most probable possibility.

The proposed double bromine bridged structure of cis-4 is analogous to those observed in dimeric Grignard reagents[8]. It may also in part explain the observed down field shift of the signals in the ^1H and ^{13}C NMR spectra (62.89 MHz: δ = -5.5 ppm, d, $^1J_{CH}$ = 120 Hz, C_α; 14.3 ppm, t, $^1J_{CH}$ = 164 Hz, C_β) relative to those of cyclopropylmagnesium bromide[5]. A priori, one would have expected a high field shift due to the accumulation of negative charge in the ring. In comparison to ether oxygen, bromine is a relatively weak Lewis base and will increase the positive charge on magnesium, thereby decreasing the negative charge on carbon and other atoms at the ring. However, anisotropy may also be quite important.

Unexpectedly, cis-4 furnished the corresponding dialkylorganomagnesium derivative in the following way. Pure, solid cis-4 rapidly dissolved in THF to give a clear solution, but within a few minutes a white precipitate was formed. This precipitate was very sparingly soluble in ethers but soluble in HMPT; however, the HMPT solution decomposed ($T_{\frac{1}{2}}$ ca. 16 days). The precipitate in THF showed the composition of 7 by acid and complexon titration, and on deuterolysis produced pure 3. The ^1H NMR spectrum of 7 (90 MHz, HMPT-d_{18}) showed a broad (ca. 1 ppm) signal centered at δ = -2 ppm; on standing for several days, this signal sharpened somewhat and partially revealed a multiplet structure. We attribute this to the simultaneous presence of several oligomers of 7, some of which are favoured in an equilibrium which is gradually established. The rest of the ^1H NMR signals could not be assigned because of the aforementioned instability of 7.



cis-4 7 8

Of interest is the behaviour of 7 towards $MgBr_2$. While 7 is slightly soluble in pure THF (c_f = 0.6 mmol/l), again $MgBr_2$ increases the solubility. Thus, the solution obtained after addition of THF to cis-4 retains 1/3 of the "basic" magnesium (titration), the rest precipitating as pure 7; this solution contains formally 1 mol of cis-4 and 2 moles of $MgBr_2$. This might indicate the formation of the soluble complex 8, the structural features of which have precedent[9] in organomagnesium chemistry.

References and Notes.

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5. Cyclopropylmagnesium bromide (THF-d_8: ^{1}H NMR spectrum (250 MHz): δ = -2.0 ppm (t of t, J = 11 and 8.5 Hz, 1H, CHMgBr), -0.1 ppm (d of d, J = 8.5 and 1.8 Hz, 2H cis to MgBr), 0.3 ppm (d of d, J = 11 and 1.8 Hz, 2H trans to MgBr); ^{13}C NMR spectrum (62.89 MHz): δ = -10.8 ppm (d, $^1J_{CH}$ = 118.2 Hz, C_α), 2.1 ppm (t of d of t, $^1J_{CH}$ = 155 Hz, $^2J_{CH}$ = 4.2 (H gem. to MgBr), $^2J_{CH}$ = 2.6 Hz, C_β).

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