Tetrahedron Letters No.46, pp. 4521-4524, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE CHEMISTRY OF SMALL RING COMPOUNDS IX (1).

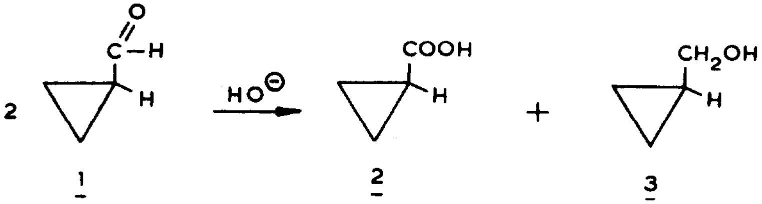
THE BASE CATALYSED REACTIONS OF CYCLOPROPANECARBALDEHYDE AND CYCLOBUTANECARBALDEHYDE*.

F.P.B. van der Maeden, H. Steinberg and Th.J. de Boer
Laboratory for Organic Chemistry,
University of Amsterdam, Nieuwe Achtergracht 129,
Amsterdam, The Netherlands.

(Received in UK 15 July 1967)

Because of the different s-character of the C-H bond of the cyclopropane ring ($sp^{2.28}$) and of the cyclobutane ring (sp^3) (2), it was of interest to investigate whether cyclopropanecarbaldehyde 1 and cyclobutanecarbaldehyde 4 undergo the aldol and/or Cannizzaro reaction.

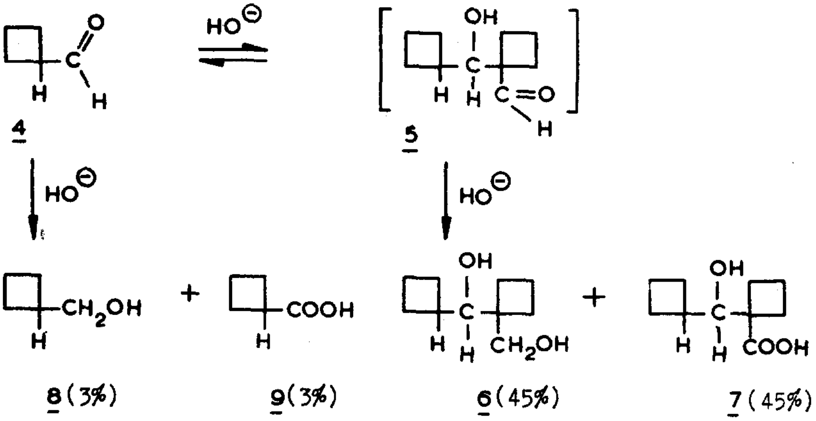
Reaction of cyclopropanecarbaldehyde 1 with an excess of sodium hydroxide for 17 hours at 80°C leads exclusively to an equimolar amount of cyclopropanecarboxylic acid 2 and cyclopropylmethanol 3. On the other hand cyclobutane-



---

[*] Part of the forthcoming thesis of F.P.B. van der Maeden.

carbaldehyde 4 gives under similar conditions after 42 hours cyclobutylmethanol 8, cyclobutanecarboxylic acid 9, cyclobutyl-[1-(1-hydroxymethyl)cyclobutyl]-methanol 6 and 1-(cyclobutylhydroxymethyl)cyclobutanecarboxylic acid 7.



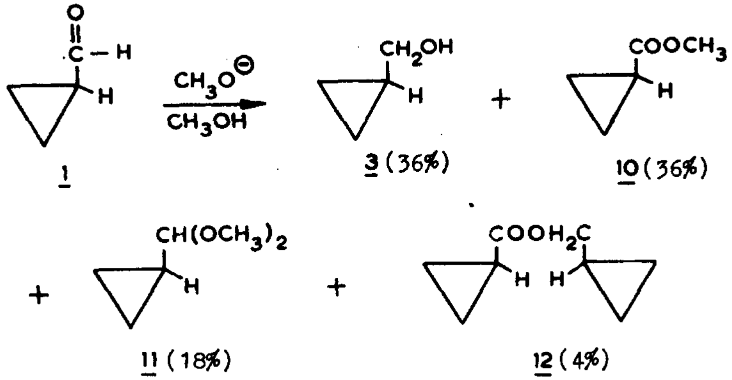
In the older work of Perkin and Coleman (3) it was suggested that only the products 8 and 9 are formed. The products 6 and 7 can arise by a Cannizzaro reaction between two molecules of 5 or by a crossed Cannizzaro reaction with 4, which yields also 8 and 9.

We were unable to isolate the primarily formed aldol 5 from the remaining few percents of unidentified reaction products.

The infrared spectrum of 6 (liq. film) shows the strong associated OH-band between 3600 - 3100 cm^{-1} and CH methylene bands in the 2900 cm^{-1} region. The NMR spectrum ($CDCl_3$) displays a singlet at $\delta = 4.1$ (OH, variable with concentration), a singlet at $\delta = 3.75$ ($-OCH_2$), a doublet centred at $\delta = 3.6$ (>CHO-) and broad absorption bands between $\delta = 1.2 - 2.9$ (cyclobutyl protons).

The infrared spectrum of 7 (KBr) has the characteristic OH, CH and C=O absorption bands. The NMR spectrum of 7 ($(CD_3)_2CO$) shows a broad band at $\delta = 7.1$ (COOH), a doublet centred at $\delta = 3.8$ (>CHO-) and a broad signal between $\delta = 1.4 - 2.8$ (cyclobutyl protons).

At 80°C, the sodium methoxide catalysed reaction of cyclopropanecarbaldehyde 1 in methanol yielded after 96 hours a mixture of cyclopropylmethanol 3, methylcyclopropanecarboxylate 10, cyclopropanecarbaldehyde dimethylacetal 11 in a ratio 2:2:1 approximately and a minor amount of cyclopropylmethyl cyclopropanecarboxylate 12 presumably arising by transesterification between 3 and 10.



The infrared spectrum of 12 (CCl_4) reveals strong bands at 1720 cm^{-1} (C=O), 1170 and 1200 cm^{-1} (C-O). The NMR spectrum (CCl_4) shows a doublet centred at $\delta = 3.9$ (OCH_2) and a broad signal between $\delta = 0.1 - 0.9$ (cyclopropyl protons) with peak areas in the ratio 1:5.

The formation of the dimethylacetal 11 is more difficult to explain. There is no doubt as to its structure because the infrared spectrum of 11 (CCl_4) displays maxima at 3100 and 3000 cm^{-1} (cyclopropyl CH) and at 2820 cm^{-1} (OCH) whereas OH and C=O absorptions are absent. The NMR spectrum of 11 (CCl_4) shows a doublet centred at $\delta = 4.1$ ($\mathrm{H{-}C}\begin{matrix}\scriptstyle O- \\ \scriptstyle O-\end{matrix}$), a singlet at $\delta = 3.3$ (OCH_3) and broad multiplet between $\delta = 0.2 - 1.3$ (cyclopropyl protons) with peak areas in the ratio 1:6:5. Analysis calc. for $C_6H_{12}O_2$:C 62.04; H 10.41; O 27.55. Found C 61.9; H 10.4; O 27.5. A "normal" synthesis of 11 was achieved through reaction of cyclopropanecarbaldehyde with a small amount of hydrogen chloride in methanol for two hours at 80°C. Yield 65% calc. on recovered aldehyde. Two byproducts were formed which were identified as 1,1,4-trimethoxybutane (5%) and 4-chloro-1,1-dimethoxybutane (25%) by elemental analysis, infrared and NMR spectral data.

The mechanism of acetal formation -an exceptional process in alkaline medium- is under investigation.

REFERENCES

1. Preceeding papers: Part VI. S.E. Schaafsma, H. Steinberg and Th.J. de Boer, Rec. Trav. Chim., 86, 651 (1967); Part VII. J. Bus, H. Steinberg and Th.J. de Boer, Tetrahedron Letters, 18, 1979 (1966); Part VIII. W.Th. van Wijnen, H. Steinberg and Th.J. de Boer, Tetrahedron in press.
2. D.J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York-London, 1965, p. 48.
3. H.G. Coleman and W.H. Perkin, J. Chem. Soc., 51, 238 (1887).