1,1-Dimethylcyclopropane from Pyrolysis of Neopentyl Chloride

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THE suggestion that 1,1-dimethylcyclopropane may be formed as an intermediate in the pyrolysis of neopentyl chloride has been made separately by Maccoll and Swinbourne[1] and by Anderson and Benson.[2] The absence of this compound from the C_5H_{10} products of neopentyl chloride pyrolysis at 444° as observed by Maccoll and Swinbourne[1,3] was attributed to rapid isomerization under the reaction conditions, as these products were observed always to consist of a mixture of methylbutenes in equilibrium proportions. These studies were carried out using Pyrex vessels "seasoned" with the pyrolysis products of allyl bromide.

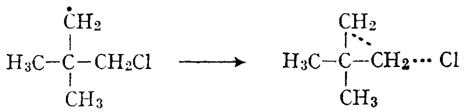
In view of the known catalytic activity of hydrogen bromide,[4] the pyrolysis of neopentyl chloride was re-examined by us with vessels from which brominated hydrocarbons had been carefully excluded. In these vessels, which had been seasoned with the decomposition products of 3-chloro-2-methylpropene, the rate of pyrolysis of neopentyl chloride at 444° ($10^5k_1 = 3{\cdot}2$ sec.$^{-1}$) was slightly lower than that reported by Maccoll and Swinbourne ($10^5k_1 = 3{\cdot}7$ sec.$^{-1}$) but the C_5H_{10} products included 1,1-dimethylcyclopropane as well as the three isomeric methylbutenes in non-equilibrium proportions. These products accounted for 50—55% of the neopentyl chloride decomposition, the remaining products being similar to those reported by Maccoll and Swinbourne. (Analysis was by gas chromatography.)

The composition of the C_5H_{10} products altered during the course of the reaction. In the early stages (<5% decomposition) it was 43% 1,1-dimethylcyclopropane (DMC), 36% 2-methylbut-1-ene (2MB1), 20% 2-methylbut-2-ene (2MB2), 1% 3-methylbut-1-ene (3MB1). Towards the later stages, the relative amount of DMC diminished considerably and the composition of the C_5H_{10} products approached that of an equilibrium mixture (30% 2MB1, 66% 2MB2, 4% 3MB1). Separate studies on DMC and the methylbutenes showed that, although hydrogen chloride catalyzed isomerizations among these compounds, little isomerization had occurred prior to 5% decomposition of neopentyl chloride at 444°. The isomerization of DMC in the presence of hydrogen chloride was expressible as the sum of an uncatalyzed reaction producing mainly 3MB1 and 2MB2, and a catalyzed reaction producing mainly 2MB1. Thus,

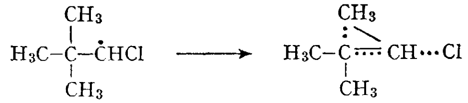
$$-\mathrm{d}[\mathrm{DMC}]/\mathrm{d}t = k_{\mathrm{uncat.}}[\mathrm{DMC}] + k_{\mathrm{cat.}}[\mathrm{DMC}][\mathrm{HCl.}]$$

At 444°, $10^5k_{\mathrm{uncat.}} = 9{\cdot}4$ sec.$^{-1}$, $10^{-2}k_{\mathrm{cat.}} = 1{\cdot}2$ mole^{-1} ml. sec.$^{-1}$. The products and the rate of the uncatalysed reaction were in good agreement with the findings of Flowers and Frey.[5]

The rates of formation of DMC, 2MB2, and 3MB1 in the early stages of neopentyl chloride decomposition at 444° were increased by the addition of hydrogen chloride and decreased by the addition of isobutene or propene, however the initial rate of formation of 2MB1 was little affected by these additions, or by a seven-fold increase in the surface–volume ratio of the reaction vessel. The effect of propene addition upon the rate of DMC formation was particularly marked: when added in an equimolar proportion, it dropped the rate by 80%. This behaviour is consistent with the production of 2MB1 from neopentyl chloride by a unimolecular process (mechanism suggested by Maccoll and Swinbourne[1,3]) and of DMC and 2MB2 *via* a free-radical process (mechanism suggested by Anderson and Benson[2]). The 3MB1 is probably not formed directly from neopentyl chloride, but comes from DMC isomerization. Radical (I) could form DMC by ring-closure associated with the ejection of a chlorine atom. Radical (II) could form 2MB2 by 1,2-migration of a methyl group associated with ejection of a chlorine atom; radical rearrangements of similar types have been reviewed by Fish.[6] It is unlikely that the decomposition of neopentyl chloride involves a t-pentyl type intermediate: pyrolysis of t-pentyl chloride at 444° produced hydrogen chloride and 2MB1 (43%) plus 2MB2 (57%) with no detectable amount of DMC.



(I)



(II)

The presence of traces (~ 10^{-2} mm.) of hydrogen bromide was sufficient to double the rate of formation of C_5H_{10} products from neopentyl chloride at

444°. Decomposition was significantly faster for runs in a vessel after it had been in contact with hydrogen bromide, and isomerizations among the C_5H_{10} products were also more rapid. Other workers[7] have noted the activity of reaction vessel coatings produced from allyl bromide, particularly with respect to their ability to promote isomerization of olefins. The results of the present study suggest that the presence of traces of hydrogen bromide in such coatings may be an important factor contributing to their activity.

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[1] A. Maccoll and E. S. Swinbourne, *J. Chem. Soc.*, 1964, 149.

[2] K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, 1963, **39**, 1673.

[3] A. Maccoll and E. S. Swinbourne, *Proc. Chem. Soc.*, 1960, 409.

[4] V. R. Stimson and E. J. Watson, *J. Chem. Soc.*, 1961, 1392. R. A. Ross and V. R. Stimson, *J. Chem. Soc.*, 1962, 1602; A. Macoll and R. A. Ross, *J. Amer. Chem. Soc.*, 1965, **87**, 4997.

[5] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1959, 3953.

[6] A. Fish, *Quart. Rev.*, 1964, **18**, 248.

[7] A. Macoll and R. H. Stone, *J. Chem. Soc.*, 1961, 2756; K. A. Holbrook, *Proc. Chem. Soc.*, 1964, 41; K. A. Holbrook and J. J. Rooney, *J. Chem. Soc.*, 1965, 247; M. R. Bridge and J. L. Holmes, *J. Chem. Soc.* (*B*), 1966, 713.