

DICHLOROMETHYLDIAMANTANES, HOMODIAMANTANONES, AND HOMODIAMANTANE

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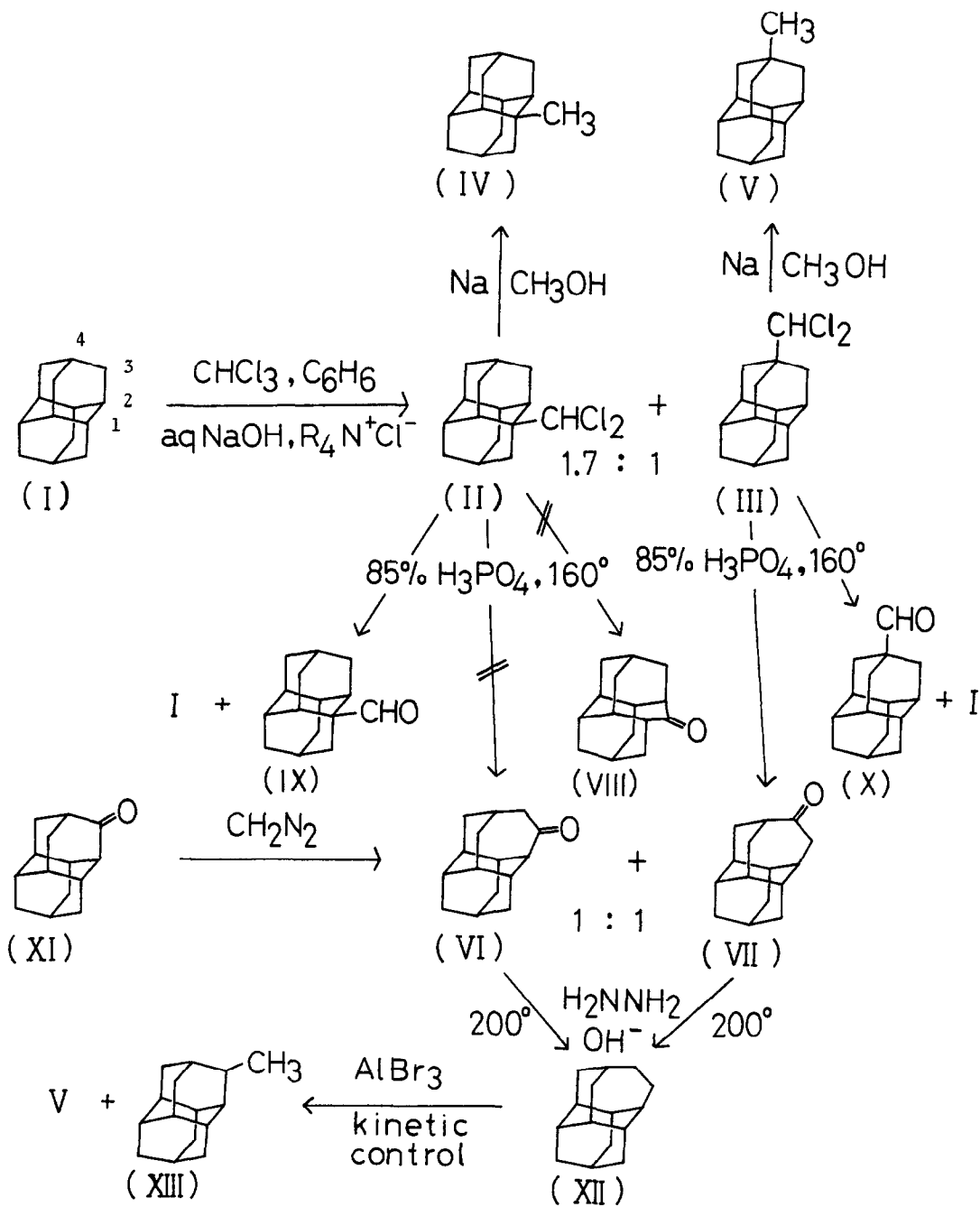
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(Received in Japan 27 November 1972; received in UK for publication 8 December 1972)

The selective functionalization of the two different kinds of bridgehead positions in diamantane (I)¹ is a synthetic challenge. Ionic reagents attack the 1-position of I preferentially under conditions of kinetic control.^{2,3} Equilibration appears to be the best published route to 4-derivatives,²⁻⁴ but entropy factors tend to counterbalance enthalpy, and mixtures are obtained.⁵ Dichlorocarbene insertion, already applied to adamantane,⁶ appeared to offer another approach. We hoped that the conditions of micelle encapsulation⁶ would favor attack at the less hindered 4-bridgehead.

These expectations were realized, but only in part. Reactions of diamantane with dichlorocarbene generated in an alkaline medium containing detergent⁶ gives practically quantitative yield of a mixture of 1- and 4-dichloromethyl diamantanes (II) and (III) in a 1.7:1 ratio. Isomer II, m.p. 110.5-112°, was isolated by recrystallization from pentane, while III, m.p. 70° was difficult to prepare pure and was obtained by preparative g.l.c. separation. The structures of II and III were proved by conversion to the corresponding 1- and 4-methyldiamantanes (IV^{5,7} and V^{2,5}) by reduction with sodium in methanol. The statistically corrected ratio of 1- to 4-dichloromethyl isomer indicates that the 4-position is more reactive by a factor of 1.8. As with adamantane,⁶ no significant attack at non-bridgehead positions was observed.

Interestingly, treatment of dichloromethyl diamantanes II and III under conditions where dichloromethyladamantane forms homoadamantanone⁶ did not give rise either to homodiamantanones VI and VII or to isohomodiamantanone (VIII); both II and III were unreactive. Under more vigorous conditions (160°, 20 hr., 85% phosphoric acid, sealed tube) II gave only diamantane and a small amount of 1-diamantane carboxaldehyde (IX) in 65% combined yield,⁸ but a 1:1 mixture of



II and III gave homodiamantanone VII (mass spect. P^+ at m/e 216, ir ν C=O 1698 cm^{-1} ; nmr (CCl_4) δ ca. 2.64 (1H, broad s) 2.58 (2H, d, $J=4$ Hz), 1.6-2.1 (broad); m.p. 168°, after recrystallization from hexane-methanol in 20% yield, together with diamantane (30-40% yield),⁸ the diamantane carboxaldehydes IX and X (10-20%),⁸ and a small amount of acidic material.

Diazomethane ring homologation of diamantanone (XI)² affords a convenient alternative method of entry into the homodiamantanone system, a 1:1 mixture of the two homodiamantanone isomers VI and VII being obtained in 96% yield.^{9,10} The isomer of lower retention time (carbowax) was identical to VII, obtained unambiguously by rearrangement of III. The other homodiamantanone was assigned structure VI.

The Mixture of homodiamantanones VI and VII was reduced¹¹ to homodiamantane (XII), m.p. 136.2-137.4°, in 88% yield. The 60 MHz nmr spectrum consists of a single peak at δ 1.78 with broadening at the base. The 220 MHz nmr spectrum [CDCl_3 : δ 2.37 (broad d, $J=12.5$ Hz-half AB), 2.29 (broad s), 2.16 (broad d, $J=12.5$ Hz-half AB), 2.04 (d, $J=5$ Hz), 1.91 (broad s), 1.86 (d, $J=1.8$ Hz), 1.76 (s), 1.62 (m), 1.56 (broad s), 1.22 (broad d, $J=12$ Hz)] was similar to that of homoadamantane¹² but with more complex splitting over a broader range.

Treatment of homodiamantane with aluminum bromide leads to the formation of methyl diamantanes. Interestingly, the least stable 3-methyl isomer (XIII)^{2,5,13} predominates at short reaction times (0° and 25°); 4-methyl diamantane (V) is also produced, but none of the 1-isomer. At higher temperatures and longer reaction times, the equilibrium^{2,5,13} composition containing more than 95% V is achieved. Homoadamantane and homoadamantene behave similarly in giving predominantly the less stable 2-methyl adamantane under conditions of kinetic control.¹⁴

The micelle dichlorocarbene insertion reaction shows only a modest selectivity for the less hindered 4-position of diamantane. The insertion product mixture (II and III) affords a specific route to homodiamantanone VII, but the diazomethane ring homologation is synthetically better suited for the preparation of homodiamantane (XII) itself.

Acknowledgements — This work was supported at Princeton University by grants from the National Institute of Health, the National Science Foundation, and Hoffmann-LaRoche, Nutley, New Jersey. Japanese authors are grateful to Prof. Yoshida for his helpful discussions.

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