Published on 01 January 1968. Downloaded by University of California - Santa Cruz on 30/10/2014 08:24:48.

Hydrogenolysis of Cyclopropane Derivatives. Application to the Synthesis of an Axial t-Butylcyclohexane, 2-t-Butyladamantane

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THE hydrogenolysis of substituted cyclopropane rings is a reaction whose ease, specificity, and considerable synthetic utility for the preparation of compounds containing quaternary carbon atoms (gem-dialkyl, t-butyl and other t-alkyl groups, and angular methyl substituents) is not adequately appreciated.¹⁻⁴ The drastic conditions sometimes recommended² are not generally needed;^{3,4} the hydrogenolyses reported here were carried out at 3 atm. pressure in a Parr apparatus at 50° using PtO₂ catalyst and acetic acid solvent.

Catalytic reduction of simple, unconjugated cyclopropane derivatives usually results in the

preferential cleavage of the least-substituted ring bonds,^{2,3}[†] unless isomerization on the catalyst takes place prior to hydrogenation.^{2,3} Such isomerization is avoided with mild conditions, and we have observed apparently complete specificity in the illustrations reported here.

1-t-Butyladamantane (I) has proved unexpectedly difficult to prepare by conventional procedures.⁵ Compound (I), m.p. 112—113°, was obtained in 96% yield by hydrogenolysis of 1-(1-adamantyl)-1-methylcyclopropane (II) which in turn had been prepared by Simmons-Smith cyclopropanation⁶ of 1-isopropenyladamantane (III).⁷

 \dagger Exceptions, of course, are found in very strained substrates, where cleavage of the *most strained* bond often occurs (cf. ref. 3 and 4).

The n.m.r. spectrum confirmed the structure:8 δ 0.8 (9 H, sharp s, t-butyl), 2.0 (3 H, b, bridgeheads), 1.6 (12 H, methylene groups).



By an analogous procedure, 2-methyleneadamantane (IV)⁹ was converted through cyclopropanoadamantane (V), m.p. 113-114°, to 2,2-dimethyladamantane (VI), m.p. 144-145°. The cyclopropane resonances of (V) appeared as a sharp singlet at $\delta 0.2$, two protons, presumably at the adjacent bridgeheads, had δ 0.9 and the other protons δ 1.8. Compound (VI) gave the diffuse n.m.r. spectrum typical of 2-alkyladamantane derivatives,8 but the sharp signal due to the two methyl groups appeared at δ 1.04.[±]



The generality of this method of introducing quaternary carbon atoms was put to a challenging test: the synthesis of 2-t-butyladamantane (VII), a highly strained compound¹⁰ with the t-butyl group axial to a cyclohexane ring. No other unambiguous example of such an axial t-butyl group is known to us.10,11 Methyl 2adamantane carboxylate¹² was treated with excess

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methyl Grignard reagent, and the resulting tertiary alcohol dehydrated. The desired product, 2-isopropenyladamantane (VIII) (b.p. 109-110°/9 mm.) was separated from its by-product, 2-isopropylideneadamantane (b.p. 104-105°/9 mm.), by fractional distillation. The same sequence of reactions as before $[(VIII) \rightarrow (IX) \rightarrow (VII)]$ sufficed to prepare (VII), an oil (b.p. 258°), which was purified by preparative gas chromatography. The n.m.r. spectrum of (VII) showed a sharp t-butyl signal at δ 1.0 and the usual diffuse 2-alkyladamantane absorptions⁸ down to δ 2.2.



In addition to the n.m.r. data reported above, all new compounds gave satisfactory elemental analyses, and mass and i.r. spectra consistent with the assigned structures.

This work was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, and from the National Institutes of Health. C.W.W. was supported by an N.I.H. Predoctoral Fellowship. The mass and n.m.r. spectrometers were purchased by grants from the National Science Foundation and the departmental instrument laboratory was funded in part by N.I.H. Biochemical Sciences Support Grant.

(Received, March 4th, 1968; Com. 270.)

‡ Professor S. Landa has recently informed us of similar preparations of (V) and (VI), (J. Vais, J. Burkhard, and S. Landa, Z. Chem., in the press).

¹ Unpublished examples, pertinent to the present paper, have been reported to us: a t-butyl substituted sesquiterpene derivative (Prof. A. Eschenmoser, see B. Gubler, Thesis, E. T. H. Zurich, 1965) and 7,7-dimethyl-norbornane derivatives (Prof. P. D. Bartlett). During the course of our work, the preparation of 1-methyl-1-alkylcyclohexanes was reported by S. I. Khromov, G. P. Kochnova, O. I. Guseva, and E. S. Balenkova, Neftekhimiya, 1966, 6, 809 (Chem. Abs., 1967, 66, 104733v).

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³ The earlier literature is well summarized in two reviews: M. Yu Lukina, Russ. Chem. Rev., 1962, 31, 419; J. Newham, Chem. Rev., 1963, 63, 123.

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¹⁰ N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, J. Amer. Chem. Soc., 1967, 89, 4345, have estimated a strain energy of 12.32 kcal./mole for (VII).

¹¹ Cf., E. L. Eliel and Sr. M. C. Knoeber, J. Amer. Chem. Soc., 1966, 88, 5347; A. Haaland and L. Schäfer, Acta Chem. Scand., 1967, 21, 2474.

¹² H. Stetter, H. Held, and J. Mayer, Annalen, 1962, 658, 151; the compound was actually prepared by the convenient method of I. Tabushi, J. Hamuro, and R. Oda, private communication.