such as α-halo esters (both isomers without loss of optical activity),[7] glycols,[8] epoxides,[9] amino acids,[10] etc. Their importance in natural product synthesis is well documented by their application for the synthesis of several chiral pheromones.[11]

The following experimental procedure is typical. An oven-dried, 50-mL, round-bottom flask equipped with a septum-capped side arm, magnetic stirring bar, and stopcock adaptor was cooled to room temperature in a stream of nitrogen. The flask was charged with 2.5 g of solid 9-BBN (20 mmol), and 3.5 mL (22 mmol) of (+)-α-pinene ($[\alpha]^{25}_D$ +47.3°, 92% ee, distilled from $LiAlH_4$) were added to the flask. The hydroboration was completed by heating the flask to 65 °C for 5 h.[3] The flask was cooled to room temperature and 2.16 g (15 mmol) of *tert*-butyl pyruvate (prepared according to the general procedure[12] from pyruvoyl chloride[13]) was injected into the flask. The reaction was complete in 4-5 h, as indicated by ^1H NMR. Acetaldehyde (0.5 mL) was added to destroy the excess reagent, and the liberated α-pinene was pumped off at 40 °C (0.01 mm). The residue was dissolved in 30 mL of dry ether and cooled to 0 °C, and 1.32 mL (22 mmol) of ethanolamine was added to displace the 9-BBN moiety. The white solid was separated by filtration and washed twice with dry ether. From the combined filtrate, ether was removed by distillation at atmospheric pressure and the product distilled in a Kügelrohr oven at 100 °C (20 mm), yield 2.14 g (98%). GC analysis on both Carbowax 20M and SE-30 columns showed a single peak and traces of ethanol. ^1H NMR ($CDCl_3$) δ 1.37 (d, J = 7 Hz, 3 H), 1.48 (s, 9 H), 2.3 (broad, 1 H, exchanges with D_2O), 4.12 (q, J = 7 Hz, 1 H). The compound was further purified by preparative GC on a Carbowax column at 75 °C, isothermal, and the rotation taken: $[\alpha]^{23}_D$ -8.08° (neat), 85% ee, $[\alpha]^{23}_D$ -4.92° (c 5.02, CCl_4). Repeating the reaction at 0 °C (24 h) gave the distilled product again in 98% yield. The specific rotation in this case was $[\alpha]^{23}_D$ -8.76° (neat), 92.4% ee; $[\alpha]^{23}_D$ -5.36° (c 5.04, CCl_4). Our experimental results are summarized in Table I.

In other cases, no attempt was made to optimize the chemical yields. It is probable that with such efforts comparable yields could be realized.

Acknowledgment. Originally, we were also examining the reduction of acyl cyanides. However, we learned from M. M. Midland that he and his co-workers had also noted the facile reduction of these two groups of compounds, the keto esters and acyl cyanides. To minimize the overlap, we have restricted our study to the keto esters, and he is examining the acyl cyanides. His results will be reported shortly. We thank David N. Whittern for his assistance in obtaining ^{19}F spectra of MTPA esters on the Varian XL-200 Spectrometer (NSF Grant CHE-8004246). The financial support of the National Institutes of Health, GM 10937-20, is gratefully acknowledged.

(7) Lee, J. B.; Downie, I. M. *Tetrahedron* **1967**, *23*, 359.
(8) Prelog, V.; Wilhelm, M.; Bright, D. B. *Helv. Chim. Acta* **1954**, *37*, 221. We have carried out this reduction using $LiBH_4$ according to the procedure by: Brown, H. C.; Narasimham, S. *J. Org. Chem.* **1982**, *47*, 1604.
(9) Mori, K.; Takigawa, T.; Matsuo, T. *Tetrahedron* **1979**, *35*, 933.
(10) Jones, J. H. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 2, pp 819-823.
(11) Mori, K. In "Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley-Interscience: New York, 1981; Vol. 4, pp 1-183.
(12) Raha, C. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, 263.
(13) Ottenheijm, H. C. J.; De Man, J. H. M. *Synthesis* **1975**, 163.
(14) Mislow, K.; O'Brien, R. E.; Schaefer, H. *J. Am. Chem. Soc.* **1962**, *84*, 1940.
(15) Mislow, K.; Bleicher, K. *J. Am. Chem. Soc.* **1954**, *76*, 2825.
(16) Levene, P. A.; Haller, H. L. *J. Biol. Chem.* **1928**, *77*, 555.
(17) Bartlett, P. D.; Kuna, M.; Levene, P. A. *J. Biol. Chem.* **1937**, *118*, 513.
(18) Wood, C. E.; Such, J. E.; Scarf, F. *J. Chem. Soc.* **1926**, 1928.

An Alternate Path to Reductive Elimination for Group 4B Metals: Mechanism of Cyclopropane Formation from Titanacyclobutanes

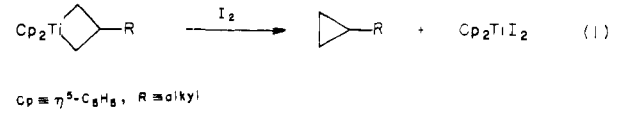
Suzzy C. H. Ho, Daniel A. Straus, and Robert H. Grubbs*

Contribution No. 6919, Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

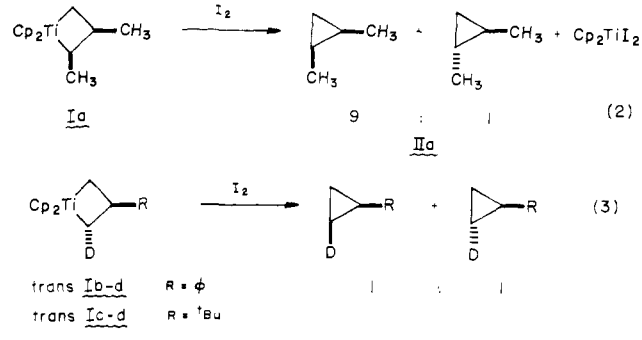
Received October 3, 1983

Reductive elimination of alkanes from dialkylmetal complexes is a key step in numerous catalytic reactions. In many cases, this reaction is accelerated by prior oxidation of the metal complex.[1,2] We now report a clean example of alkane elimination from an early transition-metal dialkyl and describe the stereochemistry of formation and reaction of an observed intermediate.

The readily available titanacyclobutanes[3] provide the complexes required for such a study since treatment of these with iodine produces cyclopropanes cleanly and in good yield (eq 1).[4]



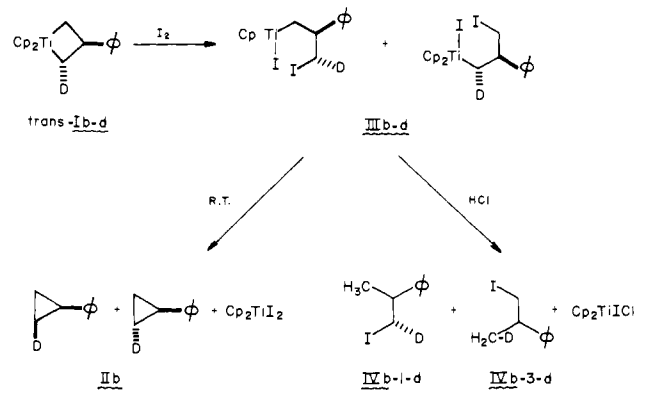
Initial sterochemical studies of these iodinations were puzzling. *cis*-2,3-Dimethyltitanacyclobutane (Ia) gave mostly retention, favoring the less stable dimethylcyclopropane (IIa, 9:1 cis/trans).[5] In contrast, *trans*-2-deuterio-3-phenyltitanacyclobutane (*trans*-Ib-*d*), which was expected to show even greater stereospecificity, gave an essentially nonstereospecific mixture of deuterated phenylcyclopropanes (IIb) under similar conditions (eq 2 and 3).[6]



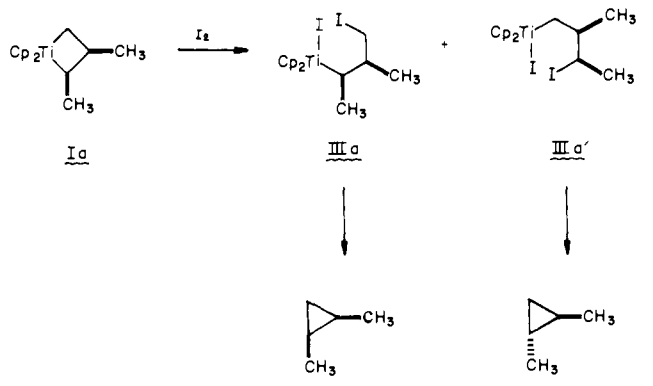
(1) (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. (b) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *Ibid.* **1972**, *94*, 4018. (c) Noyori, R.; Kumagai, Y.; Takaya, K. *Ibid.* **1974**, *96*, 634. (d) Parshall, G. W. *Ibid.* **1974**, *96*, 2360. (e) Morrel, D. E.; Kochi, J. K. *Ibid.* **1975**, *97*, 7262. (f) Miyashita, A.; Grubbs, R. H. *Ibid.* **1978**, *100*, 7416.
(2) (a) Yamamoto, A.; Morifuji, K.; Ikeda, S.; Saito, T.; Uchida, Y.; Misono. A. *Ibid.* **1968**, *90*, 1878. (b) Uchino, M.; Yamamoto, A.; Ikeda, S. *J. Organom. Chem.* **1970**, *24*, C63. (c) Uchino, M.; Asagi, A.; Yamamoto, A.; Ikeda, S. *Ibid.* **1975**, *84*, 93. (d) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1643. (e) Gillie, A.; Stille, J. K. *Ibid.* **1980**, *102*, 4933.
(3) (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6878. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7359.
(4) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733-1744.
(5) (a) Dimethylcyclopropanes and $C_5H_{10}I_2$ were characterized by GC and GC/MS in 32% and 65% yields. Straus, D. A. Ph.D. Thesis, California Institute of Technology, 1983. (b) $\Delta H_c°$ = -804.49 kcal/mol (*trans*-Ib), $\Delta H_c°$ = -805.55 kcal/mol (*cis*-Ib). Good, W. D. *J. Chem. Thermodyn.* **1971**, *3*, 539.
(6) Phenylcyclopropane was isolated in 60% yield. Integration of the 500-MHz ^1H NMR spectrum of phenylcyclopropane-*2-d* in C_6D_6 indicated that the ratio of hydrogens trans to phenyl (0.69 ppm) to hydrogens cis to phenyl (0.52 ppm) was 1.1:1.0. Casey, C. P., Scheck, D. M., Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

0002-7863/84/1506-1533$01.50/0 © 1984 American Chemical Society

Scheme I



Scheme II



To resolve this apparent contradiction, a methylene chloride solution of *trans*-Ib-*d* was treated with 1 equiv of I_2 at −50 °C. An intermediate was observed which upon warming formed a mixture of deuterated phenylcyclopropanes. The thermal instability of the intermediate (IIIb-*d*) precluded its isolation and necessitated spectroscopic and chemical characterizations.[7,8] Treatment of a solution of IIIb-*d* with gaseous HCl at −78 °C produced a 1:1 mixture of IVb-*1*-*d* and IVb-*3*-*d*.[9] By comparison with an authentic sample, IVb-*1*-*d* was shown to be exclusively the threo isomer as shown in Scheme I.[10] These results demonstrate (a) that there is no isotope effect in cleavage of Ib to the diiodide IIIb and (b) that this Ti–C bond cleavage proceeds with retention of sterochemistry.[11]

Formation of a 1:1 mixture of cyclopropane isomers from intermediates III-b-*d* suggests two possible pathways: (a) complete scrambling occurs at both the α- and γ-carbons of III before extrusion of cyclopropane; (b) the reaction of III proceeds with retention of the α-carbon and inversion at the γ-carbon (or vice versa). Scrambling at only one carbon center would give diastereomeric cyclopropanes in a 3:1 ratio, and scrambling of products has been ruled out.[12] To test for racemization at the γ-carbon of III a solution of IIIb-*d* was allowed to react on warming to <50% completion and then quenched with anhydrous HCl. The IVb-*1*-*d* recovered from the reaction was shown by ^2H NMR analysis to have retained the threo stereochemistry.

Since the second Ti–C bond cleavage appears to proceed without prior scrambling of the γ-carbon, b is the most likely mechanism of formation of cyclopropane from IIIb-*d* and IIIc-*d*. Mechanism b is also consistent with our intial observation in the *cis*-2,3-dimethyltitanacyclobutane (Ia) system. Here, it is likely that intermediate IIIa is favored over IIIa′ due to preferential attack of iodine on the less hindered Ti–C bond. Formation of cyclopropane from IIIa by an intramolecular S_N2 process, with retention at α- and inversion at γ-carbons, will yield the observed *cis*-1,2-dimethylcyclopropane (Scheme II). Alternatively, if equal amounts of IIIa and IIIa′ formed, IIIa might react faster due to the ease of nucleophilic displacement at primary halides, and IIIa′ would be preferentially scavenged by iodine to give $C_5H_{10}I_2$ products.[13]

We have shown that the elimination of cyclopropanes from the reaction of titanacyclobutane and iodine occurs with sequential, stereospecific Ti–C bond cleavages.[14] This process provides an alternate path to simple oxidation and reductive elimination, a sequence that should be highly unfavorable in these d^0 metal complexes.

Acknowledgment. We acknowledge the financial support of the National Science Foundation and technical aid by the Southern California High Field NMR Facility supported by the NSF and the helpful discussions of T. R. Howard and K. C. Ott.

(7) Rettig has postulated intermediates in reaction of Cp_2ZrHCl with allylic chlorides to give cyclopropanes. Tam, W.; Rettig, M. F. *J. Organomet. Chem.* **1976**, *108*, C1–C4.

(8) IIIb: ^1H NMR (C_7D_8, 90 MHz, −20 °C) δ6.75–7.10 (5 H, m), 5.91 (5 H, s), 5.70 (5 H, s), 2.65–3.10 (3 H, m), 1.28 (1 H, d of d, J = 10.0, 2.0 Hz), 0.31 (1 H, d of d, J = 10.0, 7.5 Hz). IIIc: ^1H NMR (C_7D_8, 90 MHz, −20 °C) δ 5.96 (5 H, s), 5.89 (5 H, s), 3.01 (1 H, d of d, J = 10, 4 Hz), 2.85 (1 H, d of d, J = 10, 4 Hz), 2.08 (1 H, d, J = 10 Hz), 1.87 (1 H, d, J = 10 Hz), 0.79 (9 H, s), H on the β-carbon was not located. IVb: ^1H NMR (C_6D_6, 90 MHz) δ 6.70–7.10 (5 H, m), 2.53–3.10 (3 H, m), 1.07 (3 H, d, J = 6.3Hz). IVc: ^1H NMR (C_6D_6, 90 MHz) δ 3.24 (1 H, d of d, J = 9.3, 2.0 Hz), 2.47 (1 H, d of d, J = 9.3, 10.7 Hz), 1.36 (1 H, m), 0.91 (3 H, d, J = 6.8 Hz), 0.58 (9 H, s).

(9) IVb-*3*-*d*, IVb-*1*-*d*: ^2H NMR (C_6H_6, 77 MHz) δ 2.82 (1 D), 1.05 (1 D). IVc-*3*-*d*, IVc-*1*-*d*: ^2H NMR (C_6H_6, 77 MHz) δ 3.21 (1 D), 0.87 (1 D).

(10) *erythro*-1-Iodo-2-phenylpropane-*1*-*d* and *threo*-1-iodo-2-phenylpropane-*1*-*d* were prepared by established methods. Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. Van Horn, D. E.; Negishi, E.-I. *Ibid.* **1978**, *100*, 2252. ^2H NMR (C_6H_7, 77 MHz) δ 2.82 (threo isomer) and 2.94 (erythro isomer). IVc-*1*-*d* was assigned as the threo isomer on the basis of proton coupling constants and the deuterium chemical shift. Similar results were obtained for *tert*-butyltitanacyclobutane IV.

(11) Bromination of zirconocene alkyl chlorides, the only other stereochemical study of metal–carbon bond clevage in a d^0 complex, proceeds with retention at the carbon center. Labinger, J. A.; Hart, D. W.; Seibert W. E., III; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

(12) *trans*-(2-Deutero-1-methylcyclopropyl)benzene was not epimerized under reaction conditions ruling out scrambling after the formation of cyclopropane.

(13) Intermediates IIIa could not be observed.

(14) (a) Titanacyclobutanes provide the only existing system to test the stereochemistry of C–C bond formation by Ti–alkyl cleavages. (b) other reactions, including carbonylation, are being investigated. Straus, D. A.; Buchwald, S. L.; Gajda, G. J.; Schaefer, W. P.; Grubbs, R. H., manuscript in preparation.