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Cycloreversion of Quadricyclane to Norbornadiene Catalyzed by Tin (II) Complexes

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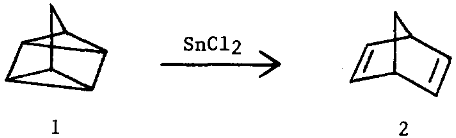
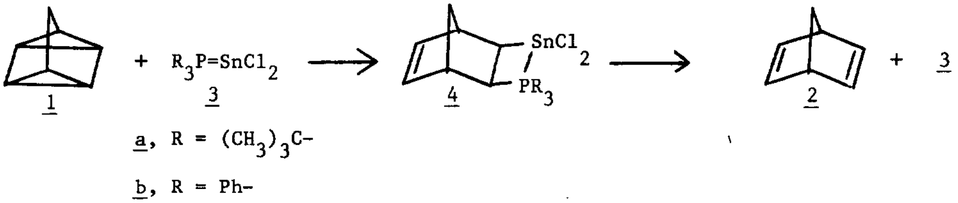
Summary. The conversion of quadricyclane (1) to norbornadiene (2) is catalyzed by stannous chloride and stannous chloride-phosphine complexes. A newly synthesized polymer-bound phosphine-stannous chloride complex also proved effective in the catalytic conversion of 1 to 2.

The unique chemical reactivity of quadricyclane 1 toward $[2\pi + 2\sigma + 2\sigma]$ cycloadditions with olefinic dienophiles[2] indicates significant electronic interaction[3] between the two most strained cyclopropane sigma bonds. Azodicarboxylates[4] and diaroyldiazines[5] also cycloadd to 1 producing four-membered ring hydrazines, 1,2-diazetidines. In attempting to determine the scope of these cycloadditions with regard to the reactivity of 1 toward non-carbon dienophiles, we have discovered an unusual and potentially useful cycloreversion of 1 to nonbornadiene and heat by the action of stannous chloride-derivatives.



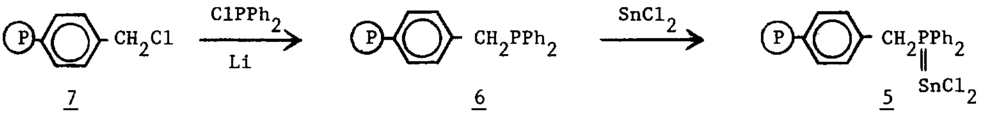
Addition of stannous chloride (10 mol %) to 0.1 M 1 in CD_3OD rapidly converts 1 to 2 ($t_{1/2}$ 1min). Insoluble stannous chloride (slurried in a solution of 1 in benzene-d_6 or $CDCl_3$) is unreactive. A similar reaction occurs when tri-t-butylphosphine or triphenylphosphine-stannous chloride complexes[6] (3, 0.5 mol %) are added to 1.0 M 1 in $CDCl_3$ ($t_{1/2}$~5 sec). Phosphines alone are inert. It is possible that an initial cycloadduct 4, or a



charge-transfer complex preceding its formation[5], rapidly regenerates the tin-complex and norbornadiene. Low temperature ^{1}H NMR spectra of reaction mixtures of 1 and 3 fail to display unique absorbances attributable to 4 (only 1 and 2 observed).

The rapid cycloreversion of 1 and 2 by these tin-derivatives suggests their potential use in the norbornadiene-quadricyclane solar energy storage system.[7,8] Photo-conversion of 2 to 1 by polymer-anchored sensitizers proceeds with high efficiency[7], and conversion of 1 and 2 can be achieved with polymer-based catalysts.[8] We therefore prepared a polymer-supported stannous chloride complex in order to examine its catalytic activity toward 1.

A polymer-bound phosphine-stannous chloride complex 5 was prepared by reaction of stannous chloride with polymer-bound phosphine[9] 6 as shown below.



A solution of 2.39 g of stannous chloride dihydrate (10 mmol) in 50 mL of tetrahydrofuran was added to a stirred slurry of 11.5 g phosphine 6[9] (0.87 mmol phosphine/g), and the mixture was refluxed under nitrogen for 24 h. The polymer was filtered, washed sequentially with 100 mL each of 2:3, 3:1, 9:1 chloroform: methanol, and washed finally with 100 mL of chloroform. After drying *in vacuo*, polymer 5 gave the following analysis: C, 77.61; H, 6.63; P, 2.25; Sn, 6.83; Cl, 3.84 (0.57 mmol Sn/g; 0.72 mmol P/g; 1.08 mmol Cl/g). The data indicate 79% conversion of phosphine groups into tin complexes with little or no loss of chlorine from tin.

Tin-polymer 5 catalyzes the conversion of quadricyclane to norbornadiene. Neither synthetic precursor (6 or 7) is active. Slurries of 0.1 g of 6 (0.057 mmol Sn) in 5.0 mL

$CDCl_3$ with 0.9 g 1 (10 mmol) at 25 ^{o}C, were monitored for conversion to 2 by ^1H NMR spectroscopy. Plots of ln[1] versus time gave straight lines through 50-70% conversion. Deviations from linearity toward slower rate at higher conversion suggests poisoning[8] of the catalyst by norbornadiene. Pseudo first order rate constants for the catalysis are 1-2 x 10^{-5} sec (range of five experiments). Halving the catalyst amount (to 0.05 g 6 per 10 mmol 1) decreases the rate constant to 5-10 x 10^{-6} sec^{-1} (range of five experiments). The catalysis by polymer 5 ($t_{\frac{1}{2}} \sim$ 3-7 x 10^4 sec for 0.57 mol % Sn per 1) is less spectacular than by monomeric complex 3b ($t_{\frac{1}{2}} \sim$ 15 sec for 0.5 mol % Sn per 1), but it nevertheless indicates the utility of a tin-based polymer as a functional catalyst for the quadricyclane-norbornadiene conversion.

Research on regenerating the catalytic activity of polymer-tin complex 5 and on developing more active tin complexes is in progress.

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References and Footnotes

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