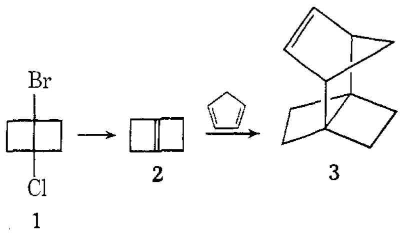
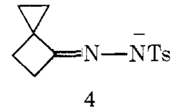
Communications

Electroorganic Chemistry. IV.[1] $\Delta^{1,4}$-Bicyclo[2.2.0]hexene

Summary: Controlled current electroreduction of 1-bromo-4-chlorobicyclo[2.2.0]hexane (**1**) in dimethylformamide at −20° on a mercury cathode gave $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**2**) as the only organic product, identified as the Diels–Alder adduct (**3**) with cyclopentadiene.

Sir: The theoretically interesting $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**2**) represents one of the most highly strained olefins conceivable. Examination of its physical and chemical properties would constitute a valuable contribution to a study of the bonding properties of strained molecules. Convincing evidence has been presented[2] for the presence of **2** during the thermolysis of tosylhydrazone salt **4**. The Diels–Alder adduct (**3**) of olefin **2** was isolated and characterized by Wiberg and coworkers, who also reported the low temperature ^{1}H nmr spectrum of the olefin itself. Subsequently the same research group has reported[3] that **2** can be isolated as the bis(triphenylphosphine)ethylene)platinum π complex (**5**) from which it could be freed by treatment with carbon disulfide.

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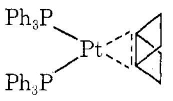
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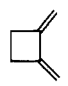
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We wish to report that, when bromochloride **1**[4] [$E_{1/2}$ −2.50 V *vs.* saturated calomel electrode in dimethylformamide (DMF)] was electroreduced at −20° in a compartmented cell similar to one described elsewhere[1,5] and the reaction product treated with excess cyclopentadiene, the only volatile organic product (excepting dicyclopentadiene) was adduct **3**. The yield was nearly quantitative, and the crude reaction mixture was free from the Diels–Alder adduct of 1,2-dimethylenecyclobutane (**6**) and olefin **2**, an adduct reported to be formed during the thermolysis of **4**.[2] That the primary product of the reaction was olefin **2** could be demonstrated in two ways. Controlled current electroreduction was conducted at a stirred mercury cathode at 200 mA and −20° using DMF as solvent and tetraethylammonium fluoborate[6] as supporting electrolyte. Following the passage of 2.0 F, excess cyclopentadiene was added to the cold catholyte. The catholyte was worked up in the usual way[1] after it has stood overnight at room temperature. Compound **3** was separated from dicyclopentadiene by preparative glpc. Alternatively, if the reduction was carried out at −20° under 0.6-Torr pressure in a very gentle stream of dry nitrogen and the volatiles were collected directly on the vacuum line in a trap at −200° which contained excess cyclopentadiene, the same result was obtained after the trap was allowed to warm to room temperature as had been obtained by adding cyclopentadiene directly to the cold reaction mixture. The continuous removal of **2** as it was formed prevented its subsequent thermal decomposition. Such a technique was employed previously by us.[7]

Compound **3** showed ^{1}H nmr signals at τ 3.82 (s, 2 H), 7.46 (s, 2 H), and 7.55–8.75 (m, 10 H), in excellent agreement with the values reported previously.[2] The mass spectrum (rel intensity) *m/e* 146 (M^+, 10%), 131 ($C_{10}H_{11}^+$, 22%), 117 ($C_9H_9^+$, 26%), 91 ($C_7H_7^+$, 100%), 90 ($C_7H_6^+$, 42%), 77 ($C_6H_5^+$, 32%), 66 ($C_5H_6^+$, 35%), 61 ($C_5H_5^+$, 23%), supports earlier structural assignment. With a direct convenient synthesis of this unusual olefin now available, work is in progress directed toward the isolation and study of the physical properties of the pure olefin.

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References and Notes

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A Convenient Synthesis of $\Delta^{1,4}$-Bicyclo[2.2.0]hexene[1]

Summary: The electrochemical dehalogenation of 1-chloro-4-bromobicyclo[2.2.0]hexane gives an almost quantitative yield of $\Delta^{1,4}$-bicyclo[2.2.0]hexene.

Sir: The synthetically and theoretically interesting hydrocarbon, $\Delta^{1,4}$-bicyclo[2.2.0]hexene (I), has been prepared by the thermolysis of the anion derived from spiro[2.3]hexanone-4 tosylhydrazone.[2] 1,2-Dimethylenecyclobutane (II) was formed in similar amount, and, because of the rapid