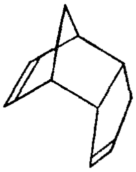
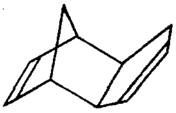
NOTES

exo-Dicyclopentadiene

By Paul D. Bartlett and Irving S. Goldstein

It was discovered by Bruson and Riener[1] that ordinary dicyclopentadiene (I) on addition of hydrogen chloride and other reagents is converted by rearrangement into a set of products (III) later shown[2] to be derived from the *exo*-isomer of dicyclopentadiene (II). The presence of this isomer in heated dicyclopentadiene was established by Alder and Stein,[3] who characterized it by means of its phenyl azide derivative and established its configuration by relating it to the well-studied isomers of the addition product of maleic anhydride to cyclopentadiene.


I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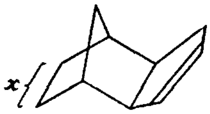

III

The isolation of *exo*-dicyclopentadiene, however, was not successfully accomplished. It was of interest to us to isolate this missing member of the series, in view of the great availability of its isomer and of the many hundreds of its derivatives made available by the method of Bruson and Riener.

exo-Dicyclopentadiene (II) was obtained in 57% yield by the reaction of alcoholic potassium hydroxide with the product of addition of hydrogen iodide to *endo*-dicyclopentadiene. The product boils at 170–172° at 763 mm. and at 51–53° under 12 mm. pressure. It has d_{20} 0.977 and $n^{25}\text{D}$ 1.5070. It does not solidify at 0°. It adds hydrogen chloride and (in the presence of sulfuric acid) water, less cleanly than the *endo*-isomer, yielding the same product as the *endo*-isomer in each case. It reacts with phenyl azide, apparently more vigorously than the *endo*-isomer, to yield a derivative melting at 123–124°.

Experimental

Iodo-dihydro-*exo*-dicyclopentadiene[1] was obtained in a yield of 97 g. (44%) from six hours of stirring on the steam-bath of 110 g. of ordinary (*endo*) dicyclopentadiene with 227 g. of 47% hydriodic acid. The product was distilled at 8–9 mm. and the fraction boiling from 120–130° was taken.

***exo*-Dicyclopentadiene.**—To 97 g. of iodo-dihydro-*exo*-dicyclopentadiene was added a solution of 50 g. of potassium hydroxide in 200 cc. of 95% ethyl alcohol. The mixture was heated under reflux on a steam-bath for twenty-four hours, then diluted with water and extracted with ether. The ether extract was dried with calcium chloride and distilled, yielding a fraction of 28.5 g. (57% yield) boiling at 43–46° under 6–7 mm. pressure. On redistillation the fraction boiling at 51–53° at 12 mm. was retained. This boiled under atmospheric pressure (763 mm.) at 170–172° and did not solidify at 0°. It decolorized bromine water and permanganate solution. It had $n^{25}\text{D}$ 1.5070 and d_{20} 0.977. The original distillation, continued at 5 mm., yielded 16.5 g. of a light yellow oil boiling from 95 to 101° and having an odor like that of hydroxydihydro-*exo*-dicyclopentadiene.

Reaction of *exo*-Dicyclopentadiene with Sulfuric Acid.—Five grams of *exo*-dicyclopentadiene and 15 g. of 25% sulfuric acid were heated on the steam-bath with stirring for five hours. After dilution, extraction with ether, washing with alkali, drying, and distillation there was recovered about 2 g. of starting material and 2 cc. of a colorless viscous oil with a very sweet odor. This product yielded a phenylurethan which, after recrystallization from alcohol, melted at 163–165° alone and at 162–165° when mixed with the phenylurethan of authentic hydroxydihydro-*exo*-dicyclopentadiene.

Reaction with Hydrochloric Acid.—Five grams of the *exo*-dicyclopentadiene and 10 cc. of 37% hydrochloric acid were stirred for five hours on the steam-bath. The mixture turned black. The ether extract was washed with alkali, dried, and distilled, yielding almost 5 cc. of a colorless oil boiling under 10 mm. pressure at 96–98° and having $n^{25}\text{D}$ 1.5206. Chlorodihydro-*exo*-dicyclopentadiene[1] boils under 12 mm. pressure at 100–102°, with $n^{25}\text{D}$ 1.5208. The compound gave slight precipitation of potassium chloride after a day on the steam-bath with alcoholic potassium hydroxide.

Reactions of *exo*- and *endo*-Dicyclopentadienes with Phenyl Azide.—To a 3-g. sample of *exo*-dicyclopentadiene and a similar sample of the *endo* isomer, 2 cc. of phenyl azide was added. After a few minutes the solutions grew warm, the warming being more marked with the *exo* than with the *endo* form. The reaction was moderated by surrounding with water. After standing overnight the flasks both contained crystal cakes. After three recrystallizations from ethanol, in which the *exo* derivative was the more soluble of the two, and decolorization with charcoal, the phenyl azide derivative of the *endo* isomer was obtained as white needles melting at 128–129° and that of the *exo* isomer as white prisms melting at 123–124°. The mixture of the two melted at 95–105°. Alder and Stein[3] report the melting points of both the *endo* and *exo* derivatives as 127–128°.

In a second preparation of the *exo* derivative it was obtained in a yield of 80.6% from *exo*-dicyclopentadiene.

Anal. Calcd. for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82. Found: C, 76.15; H, 6.48.

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[1] Bruson and Riener, This Journal, **67**, 723, 1178 (1945).

[2] Bartlett and Schneider, *ibid.*, **68**, 6 (1946); Bruson and Riener, *ibid.*, **68**, 8 (1946).

[3] Alder and Stein, *Ann.*, **594**, 219 (1933).

The Synthesis of Some New Pteridines

By Gertrude B. Elion and George H. Hitchings

The condensation of 4,5-diaminopyrimidines with di-carbonyl reagents, such as diketones,[1] dicarboxylic acids[2] and α-keto-esters[3] are known

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[1] Kuhn and Cook, *Ber.*, **70**, 761 (1937).

[2] Purrmann, *Ann.*, **544**, 182 (1940).

[3] Purrmann, *ibid.*, **548**, 284 (1941).