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A SIMPLE ROUTE FROM CYCLOPENTADIENE TO HYPOSTROPHENE

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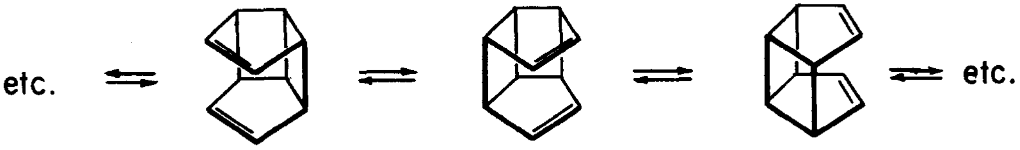
The laterally fused divinyl bicyclo[2.2.0]hexane **1**, assigned the trivial name hypostrophene by Pettit and coworkers,[2] is an exciting newcomer to alicyclic chemistry. As a consequence of its geometry and orbital construct, **1** is capable of sequential degenerate Cope rearrangement at temperatures of 35° and below,[2] and so joins its $(CH)_{10}$ isomer bullvalene as the only known neutral substances which endlessly interchange all of their constituent atoms with regeneration of the starting structure. Additionally, although the two nonconjugated double bonds in **1** bear a close face-to-face relationship, photocyclization to pentaprismane has not been successfully effected. This lack of reactivity has been attributed to the presence of an exceptionally high lying cyclobutane σ level which is ideally oriented for effective through-bond coupling, the consequence of which is to transform the customarily allowed $({}_{\pi}2_s + {}_{\pi}2_s)$ photochemical closure to a symmetry-forbidden process.[3]



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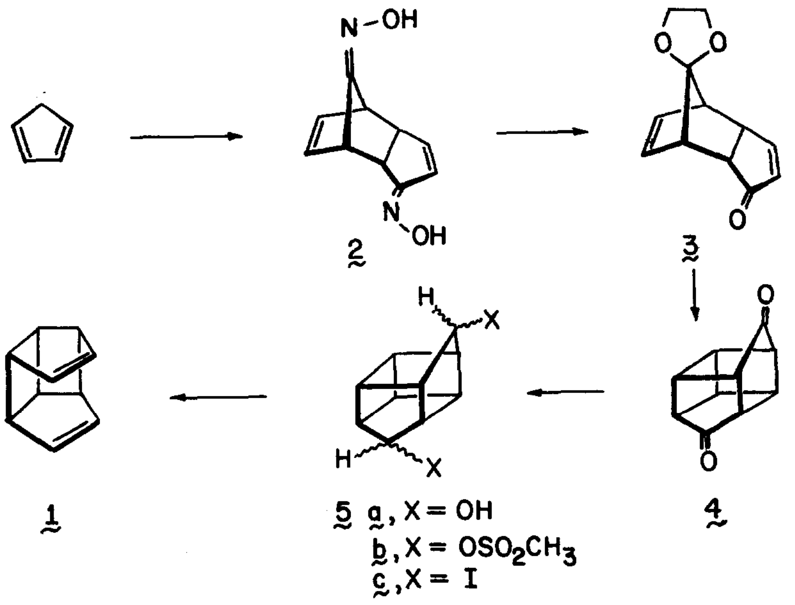
These findings suggest that **1** and closely related molecules hold great promise as possible sources of new theoretical and mechanistic understanding. However, Pettit's original elegant synthetic route to **1** furnishes the hydrocarbon in 3.4% yield from cyclobutadieneiron tricarbonyl,[2] or, more realistically, in 0.7% yield from cyclooctatetraene.[4] As manipulative operations go, this route is costly, tedious, and rather inflexible. In connection with a number of problems now under study in this Laboratory, an efficient and inexpensive route to **1** was required. This note describes a series of interconversions beginning with cyclopentadiene and culminating in the ready production of **1** in 12% overall yield. The new synthetic scheme has proven to be highly satisfactory and convenient for either small or large scale preparations of 1.

The first step, conversion of cyclopentadiene to dicyclopentadienone dioxime (2), was accomplished with ease in 77% yield by nitrosation ($NaOC_2H_5$,C_2H_5ONO) according to the directions of Doering and DePuy.[5] The dioxime was transformed into keto ketal 3 by sequential transoximation with levulinic acid (78%)[6] and selective ketalization with ethylene glycol in benzene containing p-toluenesulfonic acid (81%).[7] Upon irradiation of ether solutions (250 ml) of 3 (5.15 g, 25.2 mmoles) under nitrogen through quartz with a Hanovia 200 W lamp, photoclosure to the structurally related caged keto ketal was realized in 95% yield. Subsequent deketalization of this intermediate proved to be capricious; however, exposure of (typically) 2.39 g (11.7 mmoles) of the keto ketal to a mixture of 10% sulfuric acid (110 ml) and tetrahydrofuran (20 ml) at 80-90° for three hours repeatedly gave rise to the desired ketone 4 in 76% yield. This route to 4 is vastly superior than that involving direct photocyclization of dicyclopentadienone,[8] chiefly as the result of the fact that no competing photochemical side reactions arise upon photoexcitation of 3.

Lithium aluminum hydride reduction of 4 produced in 84% yield the caged diol 5a, whose epimeric composition was revealed clearly by the pmr spectrum (in $CDCl_3$): δ 2.10 (br s, 2, -OH), 2.68 (m, 4), 2.88 (m, 4), and three broadened singlets of differing intensity centered at 3.98, 4.20, and 4.36 (total 2H, $\supset$CHOH). Treatment of 5a with sulfene using the method outlined by Crossland and Servis[9] gave the crystalline dimesylate 5b, mp 151.5-153°,[10] in 85% yield [pmr ($CDCl_3$): δ 2.8 (m,4), 3.02 (s, 6), 3.2 (m, 4), and three broadened singlets of unequal area at 4.74, 4.90, and 5.04 (2, $\supset$CHO-)]. S_N2 displacement of the methanesulfonate groups in 5b (200 mg, 0.6 mmole) by iodide to produce 5c, mp 171-173°,[10] was achieved most conveniently by reaction with dry sodium iodide (1.88 g, 12.5 mmoles) in freshly distilled anhydrous hexamethylphosphoramide (4 ml) at 130-140° for 2 days under a nitrogen atmosphere. Due to the unsolvated nature of the iodide ion in this medium, its effective steric bulk is reduced and its nucleophilicity enhanced such that displacement of the mesylate groups operates at a reasonable rate and without obvious side reactions (90% isolated yield). This nicely crystalline substance, mp 171-173°,[10] again gave spectral evidence of being an epimeric mixture: pmr ($CDCl_3$) δ 2.44-3.60 (br m, 8), 3.76, 3.88, and 4.02 (br s, total 2H, $\supset$CHI).

The dehalogenation procedure preferred by us for the direct conversion of 5c to 1 consists in exposure of the diiodide (106 mg, 0.28 mmol) to sodium-potassium alloy (180 mg, 2:1) in



anhydrous tetrahydrofuran (10 ml) at room temperature. After 75 minutes, filtration and partitioning of the filtrate between water and pentane provides a pentane solution of the desired hydrocarbon which is free of contaminants. Other methods such as those involving sodium naphthalide or sodium-phenanthrene suffer from the problem of ultimate separation of 1 from aromatic byproducts and are accordingly less desirable. Hypostrophene so produced can be isolated by sublimation or preparative gas chromatography in 54% yield as a white solid exhibiting the characteristic pair of pmr singlets (in $CDCl_3$) at δ 3.20 (6H) and 6.12 (4H).[2]

The approach to 1 outlined here can be used to good advantage in extending the chemistry of hypostrophene. Such studies are currently receiving attention.

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FOOTNOTES AND REFERENCES

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(10) Acceptable (±0.3%) combustion analysis data were obtained for all new compounds described herein.