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BENZOCYCLOBUTENE VIA CATALYTIC DEHYDROGENATION[1]

James M. Garrett
Stephen F. Austin State College, Nacogdoches, Texas 75961
G. J. Fonken
University of Texas, Austin, Texas 78712

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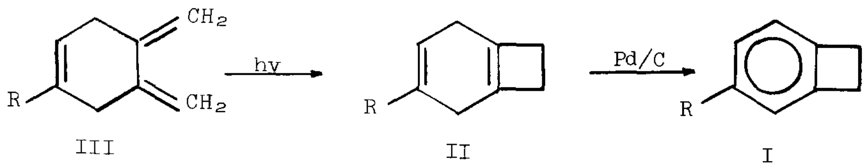
The synthesis of benzocyclobutene was first reported in 1956 by Cava and Napier[2]. Since the initial report, Cava[3] *et al.* and other workers have introduced a variety of synthetic pathways which have led to the aromatic bicyclic hydrocarbon on its derivatives. Other than a recent report[4] of an improvement of the original Cava scheme, these other synthetic routes can be broken down into two main types:

1. intramolecular thermal[5] and photochemical[6] condensations and
2. reactions utilizing proposed benzyne intermediates[7].

With only one exception[8], all previous syntheses involved having substituents on a benzene nucleus which through specific reactions were capable of closure to the required four membered ring.

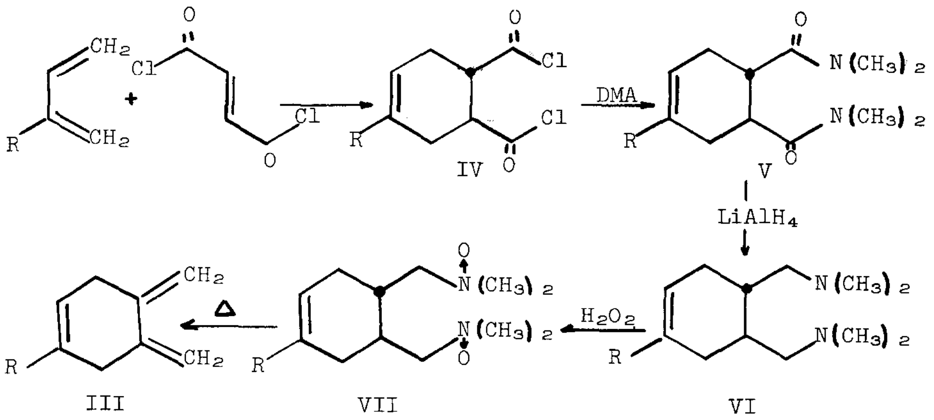
We wish to report the first successful[9] preparation of benzocyclobutene [Ia] and its 3-methyl derivative [Ib] by a dehydrogenation scheme in which aromatic character has been introduced into a compound containing the pre-existing σ structure of the desired product.

The compounds bicyclo [4.2.0] octa-1(6),3-diene [IIa] and 3-methylbicyclo [4.2.0] octa-1(6),3-diene [IIb] were chosen as precursors since they contained the desired fused ring systems and were readily accessible from the photolysis[10] of 4,5-dimethylenecyclohexene [IIIa] and 1-methyl-4,5-dimethylenecyclohexene [IIIb] respectively.



a: R=H
b: R=CH_3

Precursors to the triene [III] were prepared by an Alder[11] type scheme in which an appropriate diene [1,3-butadiene or isoprene] was added to fumaryl chloride. The resulting acid chloride [IV] was converted to the diamide [V] using dimethylamine and subsequently reduced to the amine [VI] using an ethereal lithium aluminum hydride solution. The amine [60% yield through three steps] was oxidized to an amine oxide [VII] which upon pyrolysis gave a Cope type elimination and the desired triene [III].



a: R=H
b: R=CH_3

The triene [III] which had been characterized earlier[12], was dissolved [6.0 g.; 0.057 mole in 400 ml. of solvent] in anhydrous ether and placed in a quartz flask equipped with water condenser and a nitrogen inlet tube. The contents were irradiated[a] for a period of 42 hours[b] at which time the cyclic diene [II] was obtained in 60% yield along with polymeric material. An intimate mixture of II and 5% palladium on charcoal which was heated to 100°C. under nitrogen atmosphere for 6-7 hours gave a mixture of products, the major one [52-72% yield] being I. I was isolated from the mixture using gas-liquid chromatography[c]. The infrared and ultraviolet absorption spectra of benzocyclobutene obtained in this manner were identical to those published earlier by Cava[13]. The 3-methylbenzocyclobutene had an nmr spectrum similar to benzocyclobutene. Sharp singlets were observed in the benzylic region at τ6.91(4H) and 7.72(3H); two broad signals were obtained downfield in the aromatic region at τ 3.75(2H) and 3.25(1H). Both benzocyclobutene and its derivative were further characterized and compared to authentic samples prepared by another synthesis route[14].

Investigations of similar systems should lead to a variety of benzocyclobutene derivatives. Additional work in this area of photochemical and dehydrogenation reactions is currently in progress and will be reported at a later date.

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[a] A water cooled General Electric AH-6 high intensity mercury vapor lamp was used as an external source of ultraviolet light.

[b] Irradiation time varied with the age of the lamp used.

[c] A 3/8 in. by 10 ft. column packed with 15% carbowax 20 M on chromosorb W-terephthalic acid was used for preparative purposes.

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