

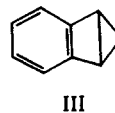
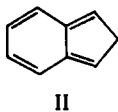
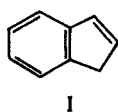
THE REACTION OF BENZOCYCLOBUTADIENE WITH THE SIMMONS-SMITH REAGENT.
PSEUDOINDENE AS A POSSIBLE INTERMEDIATE

Hiroshi Tanida and Shuji Teratake

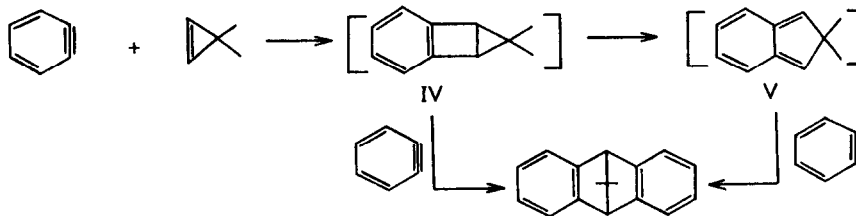
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan

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There have been proposed for indene (I) two valency tautomers, isoindene (II) and pseudoindene (III).



As a reactive intermediate, II was originally suggested by Alder* (1) in the reaction of maleic anhydride with indene, leading to benzonorbornene derivatives. The possibility that a III derivative may be capable of existence was studied in the reaction of α -benzenediazonium carboxylate with 3,3-dimethylcyclopropene (3). The formation of 7,7-dimethyldibenzonorbornadiene (in only 5% yield) was explained as a cycloaddition of benzyne to 3,3-dimethylcyclopropene to give 2,2-dimethylpseudoindene (IV), followed

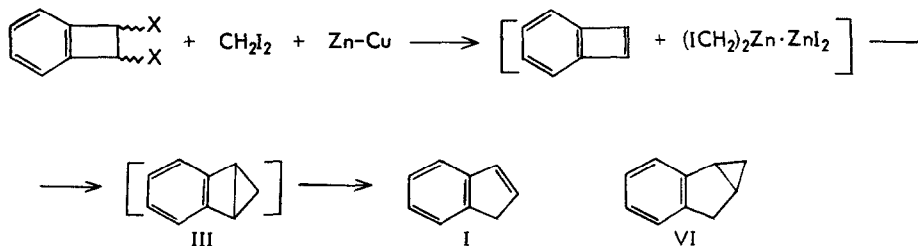


by the reaction with a second mole of benzyne, either directly on IV or after its preliminary isomerization to 2,2-dimethylisoindene (V). If this explanation is correct, it follows that benzyne (or a related transient species) of only a fleeting existence has trapped one or both of the valency tautomers. Therefore, at least one tautomer (more probably V) should exist in the reaction mixture with a considerable life time. Because of the presence of two mobile hydrogens at C₂ instead of the methyl group, the unsubstituted III might

* Also, in the zinc debromination of 1,3-dibromoindane in the presence of maleic anhydride (2).

behave differently. In this connection and also, in order to gain further insight into the nature of this unknown ring system, we were interested in a reaction, even in which III is only a transient intermediate.

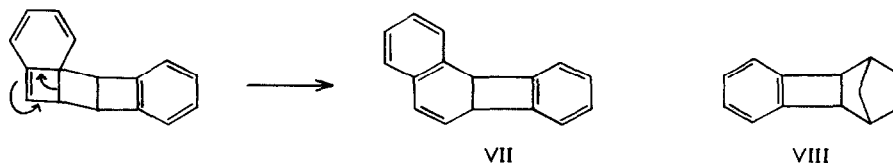
Pseudoindene (III) is a formal addition product of transient benzocyclobutadiene and carbene. To the



Simmons-Smith reagent, prepared from ~20 mmoles each of methylene diiodide and zinc-copper couple in anhydrous ether under nitrogen (4), were alternatively added an ether solution of ~20 mmoles of a mixture composed of 1,2-dibromo and 1,2-diiodobenzocyclobutene in a ratio of 1 to 1 (prepared by Cava's procedure (5)) and 12 g of zinc dust, and the mixture was refluxed for 2 hr. From the products mixture of considerable complexity, indene (~8%) and benzobicyclo[3.1.0]hex-2-ene (VI, ~3%) (6) were isolated by distillation under a reduced pressure, followed by preparative gas chromatography. The compound VI was identified by comparison to an authentic material synthesized by the method of Goodman and Eastman (6).

The formation of indene is most simply rationalized as formation and capture of benzocyclobutadiene** by a rather stable carbene source (4) to give III, followed by isomerization into I. The isolation of VI

** The reaction with 1,2-dibromo or 1,2-diiodobenzocyclobutene alone has been reported to produce 6a,10a-dihydrobenzo[a]biphenylene (VII) (5). This result has been interpreted as involving a Diels-Alder



condensation between two molecules of generated, rabil benzocyclobutadiene followed by a simple electron shift to transform to an aromatic system. In the presence of such an active dienophile as cyclopentadiene or furane, the reaction leads to an adduct having such a structure as the hydrocarbon (VIII) (7). This means trapping of the benzocyclobutadiene intermediate. Accordingly, the generation of benzocyclobutadiene under these conditions has been reasonably assumed.

indicates the attack of excess $(\text{ICH}_2)_2\text{Zn}\cdot\text{ZnI}_2$ for indene already existing in the reaction mixture (at the boiling point of ether). It is not clear whether the indene came totally from the reaction mixture or partially due to the work-up procedure. In either case, however, the present results evidence a very facility of the hypothetical isomerization, pseudoindene \rightarrow indene. It is in sharp contrast to the very slow ring cleavage of ordinary benzocyclobutene derivatives.***

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*** For example, refluxing benzocyclobutene for 1 hr under nitrogen at 150° produced no change in its boiling point or infrared spectrum (8). When benzocyclobutene was heated for 5 days at 200°, 1,2:5,6-dibenzocyclooctadiene was obtained in 24% yield, supposedly via o-xylylene, along with other higher molecular weight products (9).