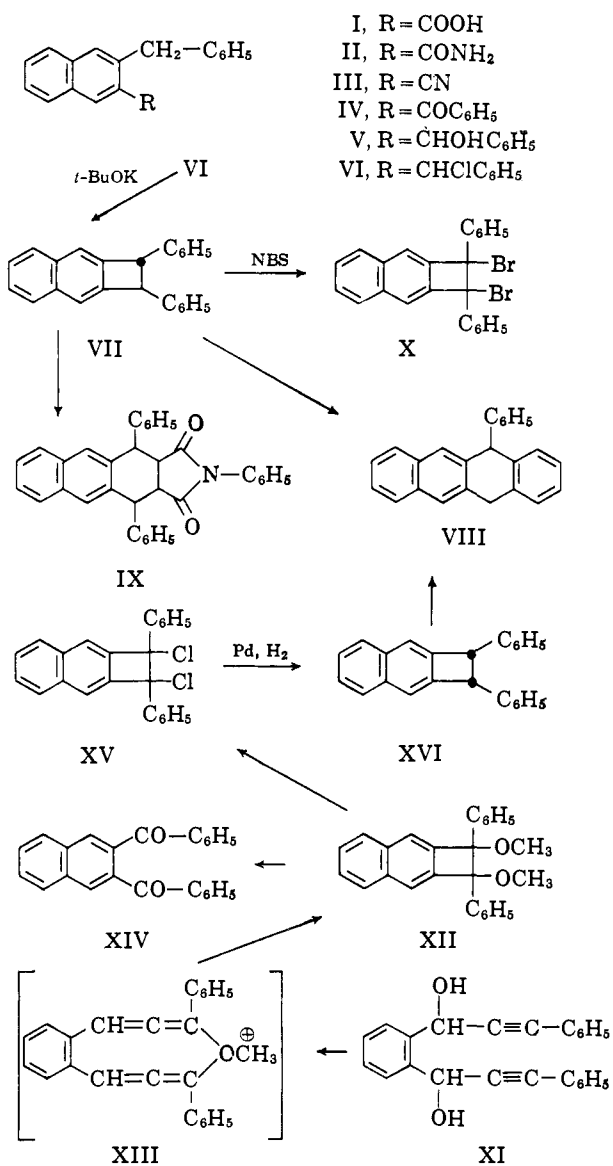


bromination of VII with *N*-bromosuccinimide in carbon tetrachloride proceeds smoothly in the presence of benzoyl peroxide to give, in 89% yield, 1,2-dibromo-1,2-diphenylnaphtho[*b*]cyclobutene (X), m.p. 180–183° dec.⁶

The second entry into the 1,2-diphenylnaphtho[*b*]cyclobutene system employs a novel two-step route from a simple benzene derivative. Thus, *o*-phthalaldehyde reacts with phenylethylnmagnesium bromide to give, in 66% yield, the bispropargylic alcohol XI, m.p. 109–110°. Reaction of diol XI with warm dry methanolic hydrogen chloride affords, in 35–40% yield, 1,2-dimethoxy-1,2-diphenylnaphtho[*b*]cyclobutene (XII)⁶ as colorless crystals, m.p. 150–151° dec.; a diallenic compound such as XIII is assumed to be an intermediate in this cyclization.⁷ The presence of a naphthalene nucleus in XII is indicated not only by the similarity of its ultraviolet spectrum (λ_{\max} 230, 272, 283, 293, 307, 320 m μ) to that of naphtho[*b*]cyclobutene⁸ but also by its slow reaction with bromine in carbon tetrachloride to give (65% yield) 2,3-dibenzoylnaphthalene (XIV), identical with authentic material.¹



(6) The stereochemistry of this compound is as yet undetermined.

(7) Several instances have been recorded of the intermolecular dimerization of acetylenic alcohols to unsaturated cyclobutanes, presumably via allenic intermediates: (a) T. Nagase, *Bull. Chem. Soc. Japan*, **34**, 139 (1961); (b) P. D. Landor and S. R. Landor, *Proc. Chem. Soc.*, 77 (1962).

(8) M. P. Cava and R. L. Shirley, *J. Am. Chem. Soc.*, **82**, 654 (1960).

Reaction of ether XII with acetyl chloride at room temperature affords, in 66% yield, 1,2-dichloro-1,2-diphenylnaphtho[*b*]cyclobutene (XV),⁶ m.p. 149–150° dec. Catalytic reduction of dichloride XV in the presence of palladium-charcoal and triethylamine gives, in 95% yield, *cis*-1,2-diphenylnaphtho[*b*]cyclobutene (XVI), m.p. 141–141.5°. When a solution of XVI in dimethylformamide is refluxed, the compound rearranges (90% yield) to the identical hydrocarbon VIII, formed by thermolysis of the *trans* isomer VII.

As with the corresponding *cis* and *trans* isomers of 1,2-diphenylbenzocyclobutene,⁹ the stereochemistry of XVI and VII may be assigned on the basis of the positions of their benzylic protons in the n.m.r. Thus, the benzylic protons of the *trans* isomer VII are more shielded (4.67 δ) than those of the *cis* isomer XVI (5.34 δ).

The conversion of dihalides XV and X into a stable naphthocyclobutadiene is described in the following communication.

Acknowledgment.—We are grateful to the National Science Foundation for a grant in support of this work. We also express thanks to Mr. R. H. Schlessinger for determining the n.m.r. spectra of compounds in this series.

(9) L. A. Carpino, *ibid.*, **84**, 2196 (1962).

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RECEIVED OCTOBER 21, 1963

A Stable Naphtho Derivative of Cyclobutadiene

Sir:

No example has yet been recorded of a compound containing a cyclobutadiene nucleus which is neither stabilized as a transition metal complex nor fused on both sides, as in biphenylene, to aromatic rings. Attempts to stabilize cyclobutadiene by substituting phenyl groups for all four of its hydrogens,¹ or by fusing one side only of the four-membered ring to a benzene² or a naphthalene³ nucleus, have not led to the formation of isolable monomeric hydrocarbons. We now report the synthesis of 1,2-diphenylnaphtho[*b*]cyclobutadiene (I), a stable crystalline analog of the transient molecule benzocyclobutadiene.

The reaction of 1,2-dichloro-1,2-diphenylnaphtho[*b*]cyclobutene (II)⁴ with zinc dust in boiling benzene for 3 min., followed by chromatography on alumina, affords in 60% yield, bright red needles of 1,2-diphenylnaphtho[*b*]cyclobutadiene (I), m.p. 137–138°; $\lambda_{\max}^{\text{EtOH}}$ 209 m μ (log ϵ 4.71), 257 (4.68), 289 (4.85), 300 (4.87), 436 (3.71), 455 (3.71). The 2,4,7-trinitrofluorenone complex I forms black needles, m.p. 182–183°. Hydrocarbon I is obtained also, in 49% yield, by zinc debromination of 1,2-dibromo-1,2-diphenylnaphtho[*b*]cyclobutene (III).⁴ In the presence of palladium-charcoal catalyst a solution of I in benzene-ethanol is reduced rapidly at room temperature to *cis*-1,2-diphenylnaphtho[*b*]cyclobutene (IV)⁴ in 95% yield. Further confirmation of the structure of I results from its behavior on oxidation with potassium permanganate in acetone, which affords 2,3-dibenzoylnaphthalene (V) in 80% yield; an authentic sample of diketone V (m.p. 143–145°) was synthesized for comparison purposes in 87% yield by the pyridine-chromic oxide oxidation of the previously described lactol VI.⁵

(1) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

(2) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957).

(3) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Ann.*, **653**, 79 (1962).

(4) M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Am. Chem. Soc.*, **85**, 4031 (1963).

(5) M. P. Cava and J. P. Van Meter, *ibid.*, **84**, 2008 (1962).

