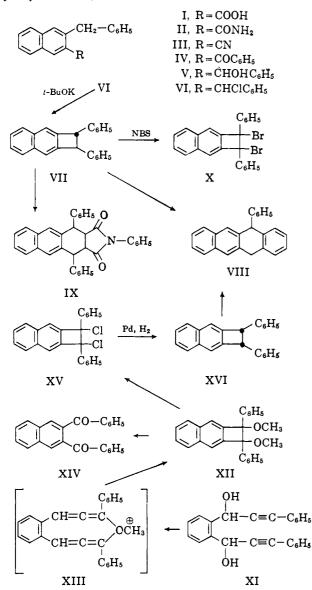
bromination of VII with N-bromosuccinimide in carbon tetrachloride proceeds smoothly in the presence of benzoyl peroxide to give, in 89% yield, 1,2-dibromo-1,2-diphenylnaphtho [b] cyclobutene (X), m.p. 180-183° dec.⁶

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 phenylethynylmagnesium 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 $(\rm XII)^6$ as colorless crystals, m.p. $150-151^\circ$ 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-1,2diphenylnaphtho[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 $(4.67 \ \delta)$ than those of the *cis* isomer XVI $(5.34 \delta).$

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°: λ_{\max}^{EtOH} $209 \text{ m}\mu (\log \epsilon 4.71), 257 (4.68), 289 (4.85), 300 (4.87),$ 436 (3.71), 455 (3.71). The 2,4,7-trinitrofluorenone complex I forms black needles, m.p. $182-183^{\circ}$. 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 palladiumon-charcoal catalyst a solution of I in benzene-ethanol is reduced rapidly at room temperature to cis-1,2diphenylnaphtho [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).

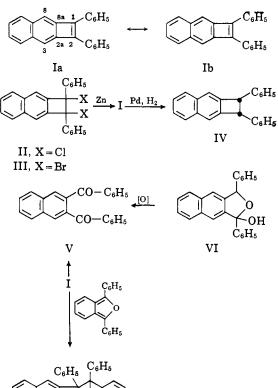
(3) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, Ann., 653, 79 (1962)

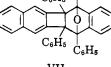
(4) M. P. Cava, B. Hwang, and J. P. Van Meter, J. Am. Chem. Soc., 85, 4031 (1963)

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

Compound I is a reactive dienophile and adds readily to 1,3-diphenylisobenzofuran to give, in 85% yield, a colorless adduct, m.p. $296-297^{\circ}$; the structure VII is assigned tentatively to this adduct. In the crystalline state I has remained unchanged for several weeks at room temperature in the presence of air and ordinary laboratory illumination; molten I retains its blood red color on heating up to about 260° , at which temperature the melt fades to a yellow color.

It is well known that the α,β -bonds of naphthalene have appreciably more double bond character than the β,β -bonds.⁶ This factor might be expected to exert a stabilizing effect on hydrocarbon I, since it should operate to diminish the cyclobutadienoid character of the four-membered ring by increasing the single bond character of the 2a-8a bond. Evidence that bonds 2a-3 and 8-8a in I are fixed to a remarkable degree as in Ia comes from the n.m.r. spectrum of I. In addition to 14 protons in the usual aromatic region, two protons appear as a sharp peak at 6.50 δ ; the position of these protons, undoubtedly those at C-3 and C-8, is very near to that (6.55 δ) of the olefinic protons of *cis*-stilbene.^{7,8}





VII

The correlation of the observed properties of I with molecular orbital calculations for this molecule will be awaited with considerable interest.

A study of the chemistry of I as well as its saturated precursors is continuing. Among the problems under investigation are dimerization and cycloadditions of I, and the possibility of converting I to a stable dianion or dication.⁹

(6) E.g., see L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 880

(7) Spectrum No. 305, Varian Associates N.M.R. Spectra Catalogue. (8) By contrast, in the spectrum of IV, no vinylic protons appear at higher field than the phenyl protons at 6.94δ .

(9) Melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Due to the relative importance of hydrocarbon I, analytical results for this compound are recorded here. Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.41; H, 5.21. Acknowledgment.—We are grateful to the National Science Foundation for a grant in support of this work.

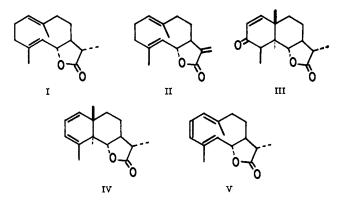
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RECEIVED OCTOBER 21, 1963

Total Synthesis of Dihydrocostunolide

Sir:

The natural sesquiterpenes of the cyclodecane series are noteworthy because of their role as possible biogenetic links between farnesol and the polycarbocyclic sesquiterpenes.¹ In addition, the novel structures of these compounds are interesting to the chemist who seeks to extend synthetic methodology. We describe here a short synthesis of the medium-ring sesquiterpene lactone dihydrocostunolide (I) by a new approach



which also would seem to be applicable to other sesquiterpenoid structures. Dihydrocostunolide was first obtained by catalytic hydrogenation of the related natural product costunolide (II).² However, more recent studies indicate that dihydrocostunolide is also a naturally occurring substance.³

The point of origin for this synthesis was the keto lactone (III), readily available from santonin⁴ by known procedures.⁵ Reduction of III with aluminum isopropoxide in isopropyl alcohol gave the corresponding unsaturated alcohol as a mixture of epimers, oxidation of which (manganese dioxide) regenerated the starting ketone. The mixture of epimeric alcohols was dehydrated by heating with 2.8 parts of neutral alumina (Woelm, activity I), which previously had been treated with 2% of pyridine^{6.7} at 230°, in a slow stream of nitrogen to give the diene IV, m.p. 95–97°, $[\alpha]^{29}$ D +70.5° (chloroform), infrared max. 1785, 1640 cm.⁻¹, ultraviolet max. (methanol) 262 m μ (ϵ 4900). Anal. Found: C, 77.71; H, 8.80.⁸

(1) For recent reviews see F. Šorm, Fort. Chem. org. Naturstoffe, 19, 1 (1961); T. G. Halsall and D. W. Theobald, Quart. Rev. (London), 16, 1 (1962).

(2) A. S. Rao, G. R. Kelkar, and S. C. Bhattacharyya, *Tetrahedron*, 9, 275 (1960), and earlier papers.

(3) A. S. Rao, A. Paul, Sadgopal, and S. C. Bhattacharyya, *ibid.*, **13**, 319 (1961).

(4) Previously made by total synthesis by Y. Abe, T. Harukawa, H Ishikawa, T. Miki, M. Sumi, and T. Toga, *Proc. Japan Acad.*, 28, 425 (1952); 29, 113 (1953); 30, 116, 119 (1954).

(5) See (a) W. Cocker and T. B. H. McMurry, J. Chem. Soc., 4549 (1956),
(b) J. B. Hendrickson and T. L. Bogard, *ibid.*, 1678 (1962); (c) M. Yanagita and A. Tahara, J. Org. Chem., 20, 959 (1955).

(6) E. von Rudloff, Can. J. Chem., 39, 1860 (1961).

(7) L. Beránek, M. Kraus, K. Kochloefl, and V. Bažant, Collection Czech. Chem. Commun., 25, 2513 (1960).

(8) This diene has also been prepared from III by Prof. G. Büchi and Dr. D. W. Hutchinson using different procedures for reduction and elimination (personal communication from Dr. Büchi).