However, under appropriate conditions where kinetic control is favored, the hydroxyl group produced by ring opening, which remains covalently bound in close proximity to the phosphoryl function, can act as an intramolecular nucleophile, attacking the phosphorus, blocking the attack of water (which would cause the destruction of cyclic AMP), and causing re-formation of cyclic AMP with the release of free enzyme.[19] Our mechanistic proposal shows how cyclic AMP could regulate the action of many enzymes in a very effective way. We are actively investigating this hypothesis further.

(19) The re-formation of the six-membered cyclic ester, cyclic AMP, could be more favorable from a thermodynamic point of view than the cyclization reaction we have described for the five-membered system I.

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Photochemistry with Circularly Polarized Light. The Synthesis of Optically Active Hexahelicene

Sir:

The use of circularly polarized light in photochemistry has led to three types of asymmetric transformations: asymmetric photodestructions,[1] partial photoresolutions,[2] and asymmetric synthesis.[3,4] The latter until now have been unsuccessful, since the observed optical rotations have usually been very small and were always near the limit of the experimental error.

We now wish to report a synthesis of optically active hexahelicene 8 induced by circularly polarized light.[5] The method chosen for this synthesis is the photocyclization of 1,2-diarylethylenes to dihydrohelicenes. This reaction, if carried out in the presence of oxidants such as I_2 and O_2, has been shown to be an easy access to a series of helicenes.[6,7]

Our preliminary results concern the asymmetric synthesis of hexahelicene, starting from 1-(β-naphthyl)-2-(3-phenanthryl)ethylene (3a), or 1-(2-benzo[c]phenanthryl)-2-phenylethylene (3b),[8] which were prepared (Scheme I) from 1 and 2 by the method described by Siegrist and coworkers.[9] The alkene 3a (162 mg) was

(1) W. Kuhn and E. Knopf, *Z. Phys. Chem. Abt. B*, 7, 292 (1930).

(2) (a) K. L. Stevenson and J. K. Verdieck, *J. Amer. Chem. Soc.*, 90, 2974 (1968); (b) *Mol. Photochem.*, 1, 271 (1969).

(3) T. L. Davis and J. Ackerman, *J. Amer. Chem. Soc.*, 67, 486 (1945).

(4) T. L. Davis and R. Heggie, *ibid.*, 57, 377, 1622 (1935).

(5) The reasons for having chosen helicenes and a discussion concerning the use of circularly polarized light in this type of photochemical synthesis will be given in a forthcoming publication.

(6) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *Tetrahedron Lett.*, 3507 (1968).

(7) R. H. Martin, M. Defay, H. P. Figeys, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke, and J. J. Schurter, *Tetrahedron*, 25, 4985 (1969).

(8) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *ibid.*, 26, 4865 (1970).

(9) A. E. Siegrist, P. Liechti, H. R. Meyer, and K. Weber, *Helv. Chem. Acta*, 52, 2521 (1969).

irradiated[10] for 10 hr in 750 ml of benzene in the presence of 10 mg of iodine to give a maximum yield of 25% hexahelicene 8. On the other hand, irradiation of the alkene 3b (62 mg) for 6 hr under the same conditions

Scheme I
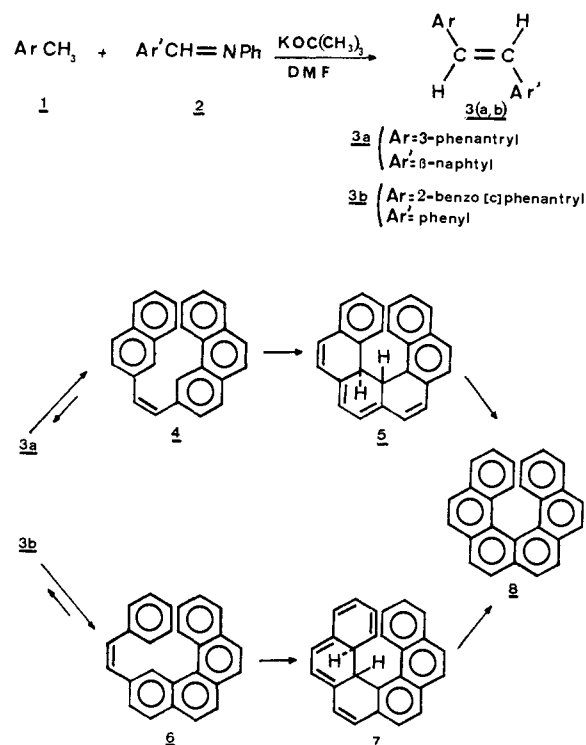
gave a maximum yield of 85% of hexahelicene 8. After purifications by chromatography on alumina using n-hexane as an eluent, the optical rotations of hexahelicene (Table I) were directly measured without recrystallization. The optical yields thus obtained are

Table I. Optical Rotations of Hexahelicene 8 Synthesized by Photocyclization of Alkenes 3a and 3b

Alkene	Irradiations with right circularly polarized light, deg	Irradiations with left circularly polarized light, deg
3a	$[\alpha]^{23}{}_{589} = -7.5 \pm 0.3$ $[\alpha]^{23}{}_{436} = -30.0 \pm 0.3$ (c 2.08, CHCl₃)	$[\alpha]^{23}{}_{589} = +7.9 \pm 0.6$ $[\alpha]^{23}{}_{436} = +30.5 \pm 0.9$ (c 0.77, CHCl₃)
3b	$[\alpha]^{23}{}_{589} = -1.8 \pm 0.4$ $[\alpha]^{23}{}_{436} = -7.6 \pm 0.4$ (c 1.29, CHCl₃)	$[\alpha]^{23}{}_{436} = +1.9 \pm 0.5$ $[\alpha]^{23}{}_{436} = +8.4 \pm 0.5$ (c 0.99, CHCl₃)

(10) A mercury super-high-pressure arc lamp was used. After focalization with a quartz lens, the 290–370-nm band was isolated, using a nickel chloride–cobalt chloride solution (see W. W. Wladimiroff, *Photochem. Photobiol.*, 5, 243 (1966)) as a filter, and then linearly polarized with a PL 40 filter (Polacoat, Inc.). Finally circular polarization was achieved by traversing the light beam through an isotrope silica plate, which was made birefractive by compression. All irradiations were carried out with a circularly polarized light at 313 nm. Therefore the ellipticity of the frontiers of the band are |1,16| for 290 nm and |0,79| for 370 nm. With this system we repeated Kuhn's asymmetric destruction experiment[1] and obtained optical rotations that were comparable to those reported. We are grateful to the "Laboratoire de Spectroscopie Herzienne" at the E.N.S. (Paris) for helpful suggestions that allowed us the realization of this system.

low ($\leq 0.20\%$),[11] but the observed optical rotations were always significant.

To demonstrate that the induced optical activity comes from some form of asymmetric synthesis and not from a partial asymmetric photodestruction of a racemic hexahelicene, the following experiments were carried out: 45 mg of racemic hexahelicene was irradiated under the same experimental conditions as previously employed. A slow photodestruction was observed that transformed after 110 hr photolysis about 25% of the starting material.[12] The remaining hexahelicene appeared to have undergone an asymmetric photodestruction (Table II). Nevertheless, the optical

Table II. Optical Rotations of Hexahelicene **8** after Its Partial Asymmetric Photodestruction

Right circularly polarized light, deg	Left circularly polarized light, deg
$[\alpha]^{23°}{}_{589} = +2.6 \pm 0.3$	$[\alpha]^{23°}{}_{589} = -1.1 \pm 0.2$
$[\alpha]^{23°}{}_{436} = +7.5 \pm 0.3$	$[\alpha]^{23°}{}_{436} = -5.2 \pm 0.2$
(c 1.99, CHCl₃)	(c 2.23, CHCl₃)

activities obtained are opposite to those induced during photocyclizations.

The optical activities obtained by photocyclization of alkenes **3a** and **3b** are *obviously not induced by asymmetric photodestruction* of hexahelicene. The asymmetric destruction of hexahelicene formed by asymmetric synthesis is not large, but exists simultaneously with the latter, thus reducing its optical yield.

From a mechanistic point of view, we cannot exclude at the present time[5] the possibility of rapid racemization equilibriums of enantiomeric *chiral intermediates* (thermal or photochemical), followed by partial photoresolutions or asymmetric photodestructions prior to the formation of hexahelicene **8**. Further work is in progress on the mechanism of this type of photochemical asymmetric synthesis.

(11) M. S. Newman, R. S. Darlak, and L. Tsai, *J. Amer. Chem. Soc.*, **89**, 6191 (1967).
(12) The amounts of photodestruction were calculated using glc with an internal standard, detail of which will be published elsewhere.

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Chiral Bornadiene. Its Synthesis and Characterization

Sir:

Chiral bornadiene-*d* is an essential substrate for an investigation of the stereochemical course of the

bornadiene–trimethyltropilidene rearrangement.[1] We wish to report a stereospecific synthesis, the comprehensive characterization, and pyrolysis of optically active ($-$)-(7R)-8-deuteriobornadiene (**1**).

Camphor-9-*d* (**4**) was prepared from ($+$)-9-bromocamphor (**3**)[2] *via* its ethylene ketal, reduction with sodium in methanol-*d*, and acid hydrolysis.[3] The recovered ($+$)-camphor (**4**) (99% optically pure) contained 0.98 deuterium atom/molecule exclusively at the C-9 position.[4] This 9-deuteriocamphor was converted to ($+$)-9-deuteriobornylene (**5**) (98% optically, isotopically, and stereochemically pure) using Shapiro's tosylhydrazone method.[5] The overall yield of bornylene-*d* from camphor was 35%.
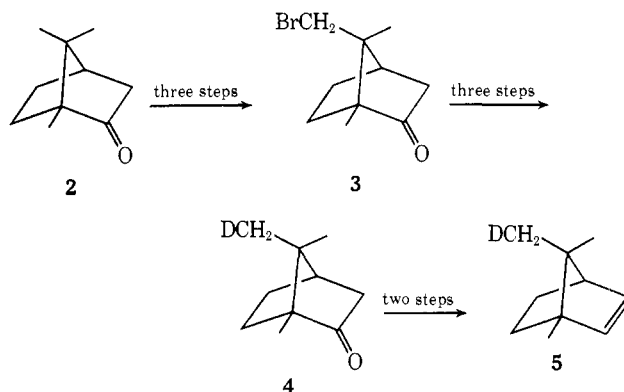
Cautious pyrolysis of the optically pure bornylene-*d* (1 min at 345° in a gas-phase stirred flow reactor) gave 20% conversion to a mixture of 1,5,5-trimethylcyclopentadiene-*d* (**6**) and 1,2,3-trimethylcyclopentadiene.[6] Diels–Alder reaction of gas chromatographically purified **6** with ethyl propiolate afforded a 1:1 mixture of compounds **7** and **8** in 85% yield. The esters were hydrolyzed in 25% KOH and the corresponding acids were decarboxylated with copper chromite in quinoline. The bornadiene thus obtained was identical with an authentic sample except for isotopic composition (98.5% d_1, 1.5% d_0). The positions of the deuterium atom (86% at C-8, 14% at C-10) were evident in the 100-MHz deuterium-decoupled proton nmr spectrum because the C-10 methyl group exhibited resonances at δ 1.20 and 1.18 (CH₃ and CH₂D, respectively) while the C-8 and C-9 resonances appeared at δ 1.02 and 1.00.[7] Integration of this spectral region specified that 86% of the deuterium was in either the C-8 or C-9 position.

(1) M. R. Willcott and C. J. Boriack, *J. Amer. Chem. Soc.*, **90**, 3287 (1968).
(2) E. J. Corey, S. W. Chow, and R. A. Scherrer, *ibid.*, **79**, 5773 (1957).
(3) This route was suggested by the synthesis of ($+$)-(7R)-camphor-9,9,9-d_3: W. L. Meyer, A. P. Lobo, and R. N. McCarty, *J. Org. Chem.*, **32**, 1754 (1967).
(4) Determination of optical, isotopic, and stereochemical purity was accomplished by precision polarimetry, mass spectroscopy, and nmr spectroscopy, respectively. Optical purities are based on the literature values for the unlabeled substances and are not corrected for the (unknown) deuterium isotope effect.
(5) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967).
(6) Determination of these conditions was greatly aided by the kinetic parameters reported by W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33**, 4504 (1968). An indication of the subtlety of the pyrolytic problem can be found by reading the account of W. C. Herndon and J. M. Manion, *Tetrahedron Lett.*, 6327 (1968); cf. also ref 8.
(7) The isotope shift is discussion by H. Batiz-Hernandez and R. A. Bernaheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 63 (1967).