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 activities obtained are opposite to those induced during photocyclizations.

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, $CHCl_3$)	(*c* 2.23, $CHCl_3$)

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.

Acknowledgments. We wish to thank Professor R. H. Martin and Dr. W. Renold for fruitful discussions and the Centre National d'Etudes des Télécommunications for financial support to build the photochemical system. One of us (A. M.) thanks the Centre National de la Recherche Scientifique for a fellowship.

(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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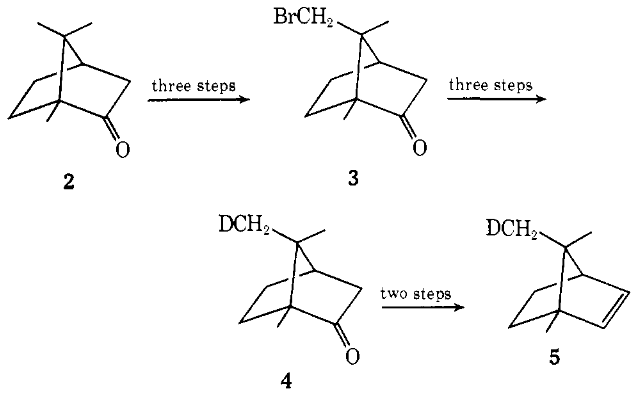
Received February 22, 1971

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 (−)-(7*R*)-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 (CH_3 and CH_2D, 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).

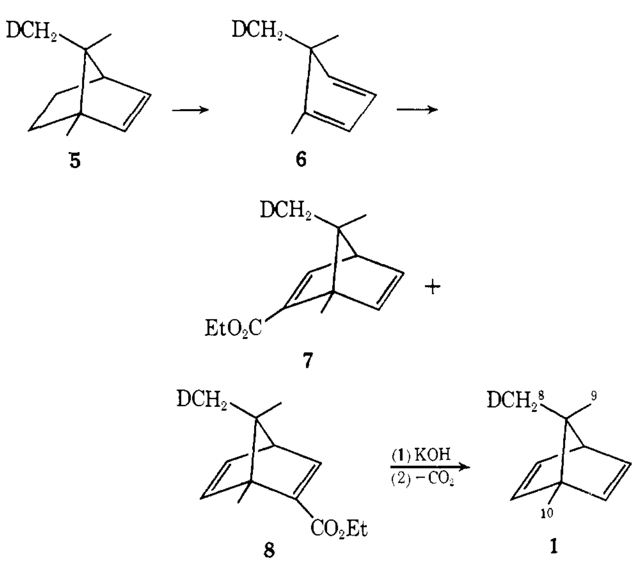
(3) This route was suggested by the synthesis of (+)-(7*R*)-camphor-9,9,9-d_3: W. L. Meyer, A. P. Lobo, and R. N. McCarty, *J. Org. Chem.*, **32**, 1754 (1967).

(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.

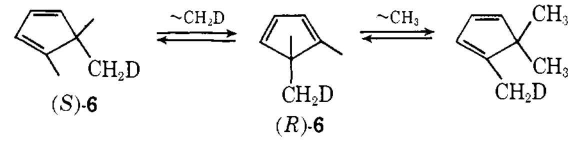
(5) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967).

(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.

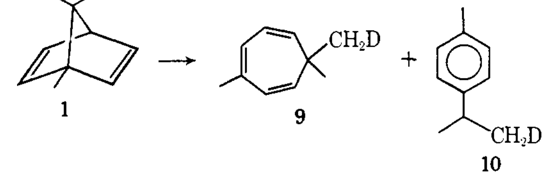
(7) The isotope shift is discussion by H. Batiz-Hernandez and R. A. Bernaheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 63 (1967).



Determination of the optical purity of (−)-(7*R*)-8-deuteriobornadiene (**1**) rests on the reasonable premise that any thermally induced racemization of (5*R*)-1,5-dimethyl-5-(deuteriomethyl)cyclopentadiene will occur *via* a hitherto unobserved 1,5 methyl migration.[8,9] If the isotope effect for the CH$_3$ *vs.* CH$_2$D migration is ignored, then the racemizing event (*i.e.*, (*R*)-**6** $\rightleftarrows$ (*S*)-**6**) is quantitatively measured by the allylic CH$_2$D resonance (*i.e.*, the mole % of the allylic CH$_2$D is equal to the mole % of enantiomeric 1,5,5-trimethylcyclopentadiene-*d* (**6**) in the mixture). Obviously, the bornadiene-*d* derived from this material can be assayed for optical purity by comparing the C-10 resonances with C-8 and 9-C resonances. Experimentally, we find that our bornadiene-*d* contains 72, 14, and 14% of the deuterium at C-8, -9, and -10, respectively. Moreover, since the stereochemistry of interest is at C-8 and C-9, we can conclude that our bornadiene-*d* is $^{72}/_{86}$ or 84% enantiomerically pure.

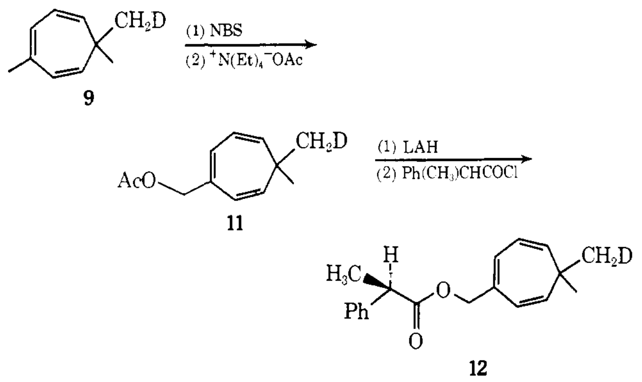


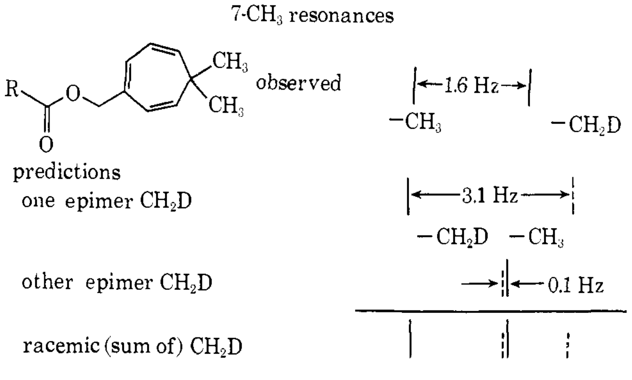
A final demonstration of the stereochemical integrity of the synthesis of bornadiene-*d* was made by observing an $[\alpha]^{25}_{365}$ of −18 ± 1 mdeg. This value corresponds to $[\alpha]^{25}_{365}$ −0.30° (*c* 10, C$_6$H$_{12}$) when account is taken of optical and chemical purity.



Pyrolysis of (−)-8-deuteriobornadiene (80 mg) in an evacuated, carefully cleaned, sealed ampoule for 7 min at 280 ± 5° resulted in an 87% conversion to a 3.5:1 mixture of 3,7,7-trimethyltropilidene-*d* and *p*-cymene-*d* (**10**). That the 30 mg of glc-purified trimethyltropilidene still had the deuterium label in the geminal dimethyl position was obvious from the integrated intensities of the methyl region in the deuterium-decoupled 100-MHz proton nmr spectrum.

In an exploratory operation, unlabeled 3,7,7-trimethyltropilidene was converted to 3-hydroxymethyl-7,7-dimethyltropilidene[10] and esterified with hydratropyl chloride. The diastereotopic 7-methyl groups of the resulting ester **12** exhibited a chemical shift difference of 0.016 ppm (1.6 Hz at 100 MHz) in the nmr spectrum and assured the analysis of the deuteriated material,[11] especially when the deuterium region is decoupled. Thus, treatment of 3,7,7-trimethyltropilidene-*d* successively with *N*-bromosuccinimide, tetraethylammonium acetate, lithium aluminum hydride, and (+)-(*S*)-hydratropyl chloride produced the requisite diastereomeric compounds. By considering both the diastereotopic chemical shift difference and the deuterium isotope effect, by which the CH$_2$D group is shifted upfield 0.015 ppm relative to the corresponding CH$_3$ group, three limiting cases for the outcome of the trimethyltropilidene-*d* stereochemistry can be codified as shown below.





The predicted spectra for the two epimeric arrangements at C-7 would show the two methyl groups separated either by 3.1 Hz (the sum of the diasterotopic differ-

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(8) The formation of nondegenerate products is well authenticated: J. W. DeHaan and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **87**, 289 (1968).

(9) The absolute configurations are all based on that of camphor and are correctly indicated in the structural formulas.

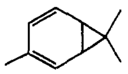
(10) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

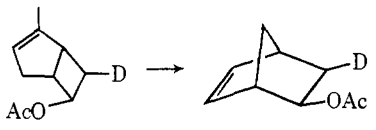
(11) M. Raban and K. Mislow, *Top. Stereochem.*, **2**, 199 (1967).

ence and the isotope effect) or by 0.1 Hz (the difference). The experimentally observed spectrum is the sum of these two spectra, and consists of three lines *ca.* 1.5 Hz apart in the intensity ratio 3:5:2. Trimethyltropilidene is *racemic.*[12]

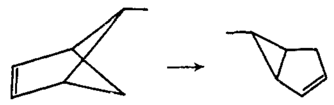
The optical stability of bornadiene-*d* [82.6 mg, $[\alpha]_{365}$ $-0.18°$ (*c* 10, C_6H_{12})] was demonstrated by recovering bornadiene-*d* (32 mg) from partial pyrolysis and observing the same specific rotation. The racemization must occur during the formation of trimethyltropilidene-*d*.

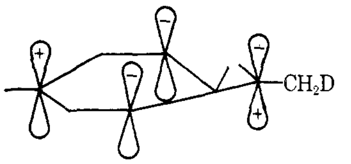
Transformation of bornadiene to 3,7,7-trimethyltropilidene surely proceeds *via* the as-yet-undetected caradiene **13** and is thereby another example of the rather rare 1,3 sigmatropic shifts.[13] Two selected cases, those of Berson[14] (**14** → **15**) and Roth[15] (**16** → **17**), maintain stereochemistry by means of a surprising inversion of configuration at the migrating carbon atom, while a 3-methyl derivative of **14**[16] and the epimer of **16** give products of somewhat randomized stereochemistry. By analogy, reasonable reaction paths for bornadiene consist of stretching the C-1–C-7 bond, then either (a) rotating the geminal dimethyl group about its pivot several times, or (b) rotating the geminal dimethyl group only 90°, and finally forming the C-3–C-7 (or C-5–C-7) bond. The two possible modes a and b can probably be distinguished by determining the optical purity of the *p*-cymene formed in competition with the trimethyltropilidene. Lacking this experiment we can still speculate that the molecular arrangement b obtains.


13



14 **15**


16 **17**



Note well that the six electrons involved form a degenerate MO system and offer no way to control the concerted rearrangement. Bornadiene thermolysis is distinguished from the analogous 1,3 shifts by the presence of six, and not four, electrons. In this way, the occurrence of racemic trimethyltropilidene is completely rationalized.

Acknowledgment. The Varian HA-100 nmr instrument was purchased with a National Science Foundation Institutional Grant (Grant No. GP-3761), and the Perkin-Elmer Model 141 spectropolarimeter was purchased with funds awarded by a University of Houston Faculty Research Support Program Grant in Aid. Support of this work by the National Science Foundation is gratefully acknowledged.

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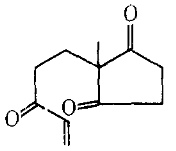
Received November 19, 1970

A Novel Construction of the Steroid Skeleton. The Utility of Di-*tert*-butyl Acetonedicarboxylate

Sir:

The potentialities of the enetrione I as a building block in steroid synthesis were recently suggested.[1]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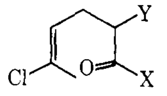
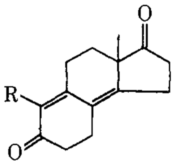
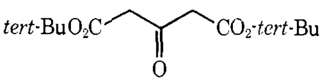


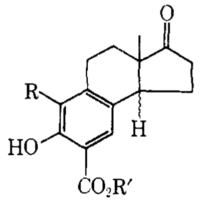
II, $X = Me$; $Y = H$
III, $X = CH_2CO_2Me$; $Y = H$
IV, $X = Me$; $Y = CO_2Me$
IX, $X = OH$; $Y = H$
X, $X = Cl$; $Y = H$
XI, $X = CH(Ac)CO_2$-*tert*-Bu; $Y = H$
XII, $X = CH_2CO_2$-*tert*-Bu; $Y = H$
XIV, $X = CH_2CO_2$-*tert*-Bu; $Y = CO_2$-*tert*-Bu



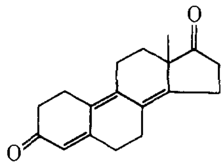
V, $R = CH_2CH{=}C(Cl)Me$
VII, $R = Me$
XV, $R = CH_2CH_2Ac$



XIII



VI, $R = CH_2CH{=}C(Cl)Me$; $R' = Me$
VIII, $R = Me$; $R' = Et$


XVI

In this communication we relate some new results which translate this possibility to practice.

Carbomethoxylation (sodium hydride–dimethyl carbonate–benzene) of compound II gave a 9:1 mixture

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[12] The prediction of the intensities must take into account the isotopic and optical purity of the starting material and of the hydratropic acid. When this is done, the corrected ratio is 3.2:5.0:1.8 for racemic material and 5.1:1.2:2.8 or 1.7:8.0:0.6 for the two products of retained optical activity. Using reasonable error limits, our experimental ratio of 3.4:4.8:1.9 indicates 50 ± 5% of each epimer.

[13] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[14] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967).

[15] W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

[16] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970).

[1] S. Danishefsky and B. H. Migdalof, *J. Amer. Chem. Soc.*, **91**, 2806 (1969).