

residual "infinity" rotations were obtained by heating to constant rotation and did not exceed 1-2% of the original values, or about 0.05°. Excellent straight-line relationships resulted from each

set of readings. The values of k obtained from the slopes of the curves are listed in Table XIII, along with other information pertaining to the rate measurements.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, NEW YORK 53, N. Y.]

Conformational Kinetic Isotope Effects in the Racemization of 9,10-Dihydro-4,5-dimethylphenanthrene^{1,2}

BY KURT MISLOW, ROLF GRAEVE, ARNOLD J. GORDON, AND GEORGE H. WAHL, JR.

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The synthesis of specifically deuterated, optically active derivatives of 9,10-dihydro-4,5-dimethylphenanthrene (II-*d*₄, II-*d*₆, and II-*d*₁₀) is described. It has been demonstrated that small inverse isotope effects accompany the rates of racemization of these hydrocarbons. Since the racemizations are purely conformational changes, and since replacement of protium by deuterium atoms in the 4,5-methyl positions has an accelerating effect, it has therefore been unambiguously demonstrated that in severely overcrowded transition states the deuterium atom has a smaller steric requirement than the protium atom.

Although secondary kinetic isotope effects resulting from the substitution of protium by deuterium have been extensively studied,³ one outstanding ambiguity has persisted in the interpretation of some of the observed effects.

It is generally accepted that isotope effects arise to a major extent from differences in zero point energy between the isotopic bonds.⁴ Since the vibrational level of the heavier isotope is always below that of the lighter one and since ΔE_0 decreases as the bond is stretched and weakened, it follows that $\Delta E_{\text{act}}^{\text{H}} < \Delta E_{\text{act}}^{\text{D}}$ and that $k_{\text{H}}/k_{\text{D}}$ is greater than unity. This description means in effect that the C-H bond is loosened more easily than the C-D bond, even if the site of isotopic substitution is not directly involved in the reaction. In carbonium ion reactions such effects have been discussed in terms of hyperconjugative interactions.⁵ Alternatively, however, the lower zero point energy of deuterium also signifies a smaller amplitude of vibration and, effectively, a smaller van der Waals radius than that of protium.⁶ Accordingly, it might be supposed that reactions which involve an increase in bond angles and/or a decrease in coordination number at the reaction center should also exhibit secondary deuterium isotope effects with $k_{\text{H}}/k_{\text{D}}$ greater than unity since relief of nonbonded interactions should be more pronounced in the more congested molecule, *i.e.*, the one containing protium in place of deuterium. Conversely, a decrease in bond angles and/or an increase in the coordination number would imply a $k_{\text{H}}/k_{\text{D}}$ of less than unity. It has been argued⁷ that steric acceleration or deceleration accounts for the major portion of many effects which have been discussed heretofore from the point of view of hyperconjugation.⁵ However, the relative merit of the two alternative and rival hypotheses has thus far remained undecided.

(1) This work was supported in part by a grant from the Alfred P. Sloan Foundation.

(2) Portions of this work have been reported in preliminary form in *J. Am. Chem. Soc.*, **85**, 1199 (1963), and at the 18th National Organic Symposium, Columbus, Ohio, June 19, 1963.

(3) For recent reviews, *cf.* A. Streitwieser, Jr., *Ann. N. Y. Acad. Sci.*, **84**, 576 (1960), and R. E. Weston, Jr., *Ann. Rev. Nuclear Sci.*, **11**, 439 (1961).

(4) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(5) V. Shiner, *Tetrahedron*, **5**, 243 (1959), and references cited therein.

(6) A. R. Ubbelohde, *Trans. Faraday Soc.*, **32**, 525 (1936).

(7) L. S. Bartell: (a) *Tetrahedron Letters*, No. 6, 13 (1960); *J. Am. Chem. Soc.*, **83**, 3567 (1961); (b) *Iowa State J. Sci.*, **36**, 137 (1961). For related discussions, *cf.*, *e.g.*, M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, pp. 141-143.

We have been interested for some time in the possibility of isolating the steric factor and assessing its importance in secondary kinetic isotope effects. The first crucial experiment in this direction⁸ involved the partial asymmetric Meerwein-Ponndorf-Verley reduction of ketone I with (+)-(*S*)-2-propanol-*d*₃. No evidence for the operation of an isotope effect was detected, and it was concluded⁸ that methyl and trideuteriomethyl groups appear to have the same size in this particular reaction. It was recognized, however, that more highly crowded transition states might be required for the exhibition of the steric isotope effect.⁸ The present paper describes the first unambiguous demonstration of this elusive effect.

9,10-Dihydro-4,5-dimethylphenanthrene (II-*d*₀) racemizes in benzene with an activation energy of 23.1 kcal./mole.⁹ Since the corresponding barrier in 9,10-dihydrophenanthrene is estimated¹⁰ at *ca.* 4 kcal./mole, the replacement of the hydrogens in the 4,5-positions by methyl groups introduces a 19 kcal./mole increase in activation energy. N.m.r. spectroscopic evidence indicates¹⁰ that the 4,5-methyl groups in II-*d*₀ are deflected out of the planes of the attached benzene rings, no doubt as a consequence of strain in the ground state. Since the ground-state energy of II-*d*₀ is therefore raised above that of 9,10-dihydrophenanthrene, it follows that the difference in transition-state energies of the comparison substances must be even greater than 19 kcal./mole. This very large energy increment is unquestionably the result of severe molecular deformations which accompany the extreme congestion of the two methyl groups along the reaction coordinate of racemization. The value of the deformation energy is compatible with the measured strain energy (12.6 ± 1.5 kcal./mole) of 4,5-dimethylphenanthrene.^{11a} Since this system has also been obtained in optically active form,^{11b} the energy requirement for the transition state of racemization must be even greater.

Introduction of the methyl groups into the 4,5-positions therefore gives rise to the extreme steric

(8) K. Mislow, R. E. O'Brien, and H. Schaefer, *J. Am. Chem. Soc.*, **82**, 5512 (1960); **84**, 1940 (1962).

(9) K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).

(10) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. W. Wahl, Jr., *ibid.*, **86**, 1710 (1964).

(11) (a) M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *ibid.*, **85**, 2356 (1963); (b) M. S. Newman and A. S. Hussey, *ibid.*, **69**, 3023 (1947).

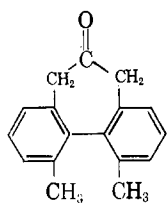
TABLE I
SCHEME FOR THE SYNTHESIS OF OPTICALLY ACTIVE 6,6'-BIS(TRIDEUTERIOMETHYL)-2,2'-DIPHENIC ACID.^a ESTIMATED DEUTERIUM CONTENT BY N.M.R.^b AND COMBUSTION ANALYSIS^c

Type of proton	IV				V-d ₆
Aromatic	2.13 (2.0)	2.06 (2.0)	2.35 (3.0)	2.17 } (6.0)	2.12 } (6.0)
	2.72 (2.0)	2.58 (2.0)		2.69 } (6.0)	2.69 } (6.0)
O-CH ₃	6.15 (3.0)	6.50 (6.0)	...
O-H	...	-2.8 (1.0)	-2.3 (2.0)
C-CH ₃	7.77 (0.14)	7.64 (0.15)	7.57 (0.14)	8.12 (0.31)	8.21 (0.24)
Av. atoms of D in C-CH ₃ by n.m.r.	2.86	2.85	2.86	5.69	5.76
Av. atoms of D per molecule by combustion	2.84	2.87	2.84	5.64	5.71

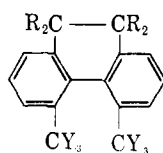
^a Steps: (a) = NaOH; (b) = fum. HNO₃, -15°; (c) = FeSO₄-NH₃, NaNO₂-HCl, CuSO₄-H₂NOH, CH₃OH-H₂SO₄; (d) = NaOH, optical resolution with morphine. ^b Chemical shifts are reported in p.p.m. on the τ -scale, followed by the integrated relative intensity in parentheses. Aromatic absorptions are generally complex and the reported values are estimated centers of the multiplets. ^c Determined by J. Nemeth, Urbana, Ill., by the falling drop method.

compression which is presumably essential for the manifestation of the putative steric isotope effect, and replacement of the -CH₃ groups in II-d₀ by -CD₃ groups should therefore provide the ideal companion substance (II-d₆) for a comparative rate study.

The following section describes the synthesis of optically active II-d₆ and of the closely related compounds II-d₄ and II-d₁₀.



I



II-d₀, R = Y = H
d₆, R = H, Y = D
d₄, R = D, Y = H
d₁₀, R = Y = D

Synthesis.—The synthesis of II-d₆, II-d₄, and II-d₁₀ posed a twofold problem. First, it was necessary to deuterate specifically the desired positions in the molecule and to maximize the deuterium content in those positions. Second, and equally important considering the ultimate goal of the synthesis, it was necessary to obtain II-d₆, II-d₄, and II-d₁₀ in optically active form with high optical purity (in order to maximize the precision of the rate measurements). The second of these two requirements placed a limitation on the synthetic approaches, since it had been shown⁹ that II is optically quite labile, even at room temperature; II-d₀ has an optical half-life of only 108 min. at 28°. As a result, the most reasonable synthetic pathways are those which have as their last step the closure of the six-membered ring from an optically active (and preferably optically pure) precursor under conditions

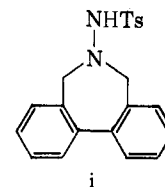
mild enough to prevent extensive racemization.¹² Two such closures had been reported. In one,⁹ optically active 2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl (III) had been ring closed; in the other,¹³ optically active I had been photochemically decarbonylated. In both reactions II-d₀ had been obtained in a state of high optical activity.¹⁴ Because I is prepared from III,¹⁵ the dibromide is the most direct precursor in the synthesis of II, and our efforts were therefore oriented toward a synthesis of suitably deuterated, optically pure III.¹⁶

The reaction scheme is outlined in Tables I-III, which also give n.m.r. and combustion analyses of the intermediates. The starting material (Table I) was methyl 3-(trideuteriomethyl)benzoate (IV), which was prepared in 69% yield from methyl 3-(trichloromethyl)benzoate¹⁷ by reduction¹⁸ with zinc and acetic acid-d. Saponification of IV, followed by (a) nitration in fuming nitric acid¹⁹ at -15°, (b) reduction with ferrous sulfate in aqueous ammonia,²⁰ and (c) diazotization and

(12) The problem of optical lability also renders unattractive alternative approaches such as the LiAlD₄ reduction of 9,10-dihydrophenanthrene-4,5-dicarboxylic acid, even if ether formation (to give the second bridge) could be obviated.

(13) K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3521 (1963).

(14) L. A. Carpino (*Chem. Ind. (London)*, 172 (1957)) has prepared 9,10-dihydrophenanthrene in excellent yield, starting from the tosylhydrazine i. The optically active dimethyl derivative could in principle be used to provide a third route to optically active II-d₀.



i

(15) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

(16) The following two-step synthesis of optically active II-d₁ from I remains as an attractive alternative: exchange¹⁰ of the enolizable hydrogens of I by chromatography on alumina-D₂O, followed by photochemical decarbonylation.¹²

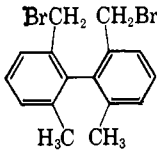
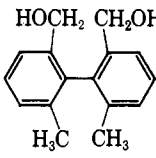
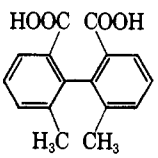
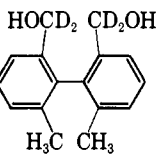
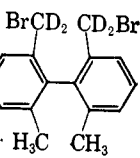
(17) W. Davis and W. H. Perkin, Jr., *J. Chem. Soc.*, 2202 (1922).

(18) This step is based on the procedure of R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956), who reduced α,α,α -trichlorotoluene to toluene- α -d₃ by use of zinc and acetic acid-d.

(19) E. Müller, *Ber.*, **42**, 430 (1909); S. Gabriel and A. Thieme, *ibid.*, **52**, 1079 (1919).

TABLE II


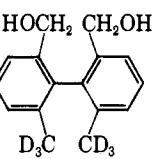
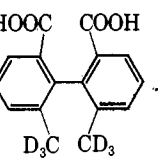
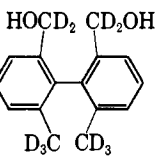

SCHEME FOR THE SYNTHESIS OF BIS(BROMOMETHYL) DERIVATIVES OF 6,6'-DIMETHYL-2,2'-DIPHENIC ACID.^a ESTIMATED DEUTERIUM CONTENT BY N.M.R. ANALYSIS^b

					
Type of proton					
Aromatic	2.64 (6.0)	2.76 (6.0)		2.75 (6.0)	2.64 (6.0)
Hydroxyl	...	6.41 (2.0)		6.48 (2.0)	...
Methylene	5.85 (4.0)	5.85 } (4.0) ^c 6.02		... (≤0.1)	... (≤0.1)
Methyl	8.01 (6.0)	8.16 (6.0)		8.17 (6.0)	8.01 (6.0)
Av. atoms of D in CH ₂	0.0	0.0		≥3.9	≥3.9
Av. atoms of D in CH ₃	0.0	0.0		0.0	0.0

^a Steps: (a) = PBr₃; (b) = LiAlH₄; (c) = LiAlD₄. ^b See footnote b in Table I. Methylene τ -values given for the AB quartet of VI-*d*₀ are calculated centers of gravity. Methylene proton signals of VI- and III-*d*₄ are too weak and diffuse to permit an accurate estimate of τ -values. ^c $J = 11.6$ c./sec.

TABLE III

SCHEME FOR THE SYNTHESIS OF BIS(BROMOMETHYL) DERIVATIVES OF 6,6'-BIS(TRIDEUTERIOMETHYL)-2,2'-DIPHENIC ACID.^a ESTIMATED DEUTERIUM CONTENT BY N.M.R. ANALYSIS^b

					
Type of proton					
Aromatic	2.66 (6.0)	2.76 (6.0)		2.77 (6.0)	2.64 (6.0)
Hydroxyl	...	6.28 (2.0)		6.35 (2.0)	...
Methylene	5.85 (4.0)	5.83 } (4.0) ^c 6.00		... (≤0.1)	... (≤0.1)
Methyl	8.04 (0.35)	8.19 (0.28)		8.21 (0.27)	8.06 (0.27)
Av. atoms of D in CH ₂	0.0	0.0		≥3.9	≥3.9
Av. atoms of D in CH ₃	5.65	5.72		5.73	5.73

^{a,b} See footnotes a and b in Table II. ^c $J = 11.8$ c./sec.

reductive coupling, gave racemic 6,6'-bis(trideuterio-methyl)-2,2'-diphenic acid (V-*d*₆). The crude acid was purified by distillation and recrystallization of the ester,^{21,22} followed by hydrolysis.²² The highly efficient optical resolution with morphine^{22,23} afforded the (+)- and (-)-forms of V-*d*₆. The over-all yield of (+)-V-*d*₆ was 7% based on *m*-(trichloromethyl)-benzoic acid.

The four dibromides (III) were prepared²² in 70–80% over-all yield from the appropriate precursor acids V-*d*₀ or V-*d*₆, by lithium aluminum hydride or deuteride reductions followed by treatment of the diols VI with phosphorus tribromide, as shown in Tables II and III. Finally, the four optically active hydrocarbons (Table IV) were prepared in 90–100% yields by ring closure of the appropriate III with phenyllithium⁹ (*i.e.*, II-*d*₀ from III-*d*₀, II-*d*₄ from III-*d*₄, etc.). This very significant improvement in yield over the previously reported⁹ 30% was achieved by reversing the order of addition previously employed, *i.e.*, by slowly adding solutions of III in ether to ethereal solutions of phenyllithium at 0 to –10°.

A comparison of the deuterated compounds with those of the nondeuterated counterparts revealed no differences in melting point, ultraviolet spectra, or specific rotations.

The n.m.r. analyses, which are supported by the combustion analyses, provide satisfactory evidence for the specific placement of the deuterium atoms in the molecules. The starting ester IV, the derived acid, and 2-nitro-3-methylbenzoic acid (Table I) all have 2.84–2.87 D atoms per molecule by combustion analysis and 2.85–2.86 D atoms per C-methyl group by n.m.r., and it follows that all of the deuterium atoms are on the methyl group. After coupling, the ester and the acid V-*d*₆ have the 5.70 atoms of deuterium per molecule (combustion), specifically located in the methyl groups (n.m.r.), which are calculated on the assumption that the scheme in Table I does not involve any exchange of methyl deuterium atoms. As seen in Tables III and IV, the derivatives of V-*d*₆, *i.e.*, diols VI-, dibromides III-, and hydrocarbons II-*d*₆ and *d*₁₀, also maintain a deuterium content of 5.70 ± 0.05 in the methyl groups.

The chemical shifts of the C-methyl groups show the anticipated¹⁰ variations. The starting material IV and its derivatives prior to the coupling reaction (Table I) have methyl τ -values of 7.6–7.8. After coupling, the unbridged biphenyls have methyl τ -

(20) W. J. Hickinbottom, "Reactions of Organic Compounds," 3rd Ed., Longmans, Green and Co., London, p. 456; W. H. Jacobs and M. Heideberger, *J. Am. Chem. Soc.*, **39**, 1435 (1917).

(21) E. D. Bergmann and Z. Pelchowicz, *ibid.*, **75**, 2663 (1953).

(22) G. Wittig and H. Zimmerman, *Chem. Ber.*, **86**, 629 (1953).

(23) F. Bell, *J. Chem. Soc.*, 835 (1934).

TABLE IV
 9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENES. ESTIMATED DEUTERIUM CONTENT BY N.M.R.^a AND COMBUSTION ANALYSIS^b

Type of proton	II-d ₀	II-d ₄	II-d ₆	II-d ₁₀
Aromatic	2.89 (6.0)	2.90 (6.0)	2.89 (6.0)	2.90 (6.0)
Methylene	7.37 (4.0)	... (≤0.1)	7.37 (4.0)	... (≤0.1)
Methyl	7.75 (6.0)	7.75 (6.0)	7.77 (0.32)	7.70 (0.35)
Av. atoms of D in CH ₂ by n.m.r.	0.0	≥3.9	0.0	≥3.9
Av. atoms of D in CH ₃ by n.m.r.	0.0	0.0	5.68	5.65
Av. atoms of D per molecule by combustion	...	3.90	5.63	9.59

^a See footnote *b* in Table I. Methylene proton signals of II-d₄ and II-d₁₀ are too weak and diffuse to permit an accurate estimate of τ -values. ^b See footnote *c* in Table I.

 TABLE V
 MASS SPECTRAL^a ANALYSIS OF SYNTHETIC PRODUCTS AND PRECURSOR

Compound no.	Isotopic composition		Calcd. atoms of D per molecule	Predicted ^b isotopic composition	
	Component	Abundance, %		Components	Abundance, %
IV	<i>d</i> ₃	85.8	2.574		
	<i>d</i> ₂	13.6	0.272		
	<i>d</i> ₁	0.6	0.006		
	Total		2.852		
II-d ₄	<i>d</i> ₄	92.4	3.696		
	<i>d</i> ₃	7.3	0.219		
	<i>d</i> ₂	0.3	0.006		
	Total		3.921		
II-d ₆	<i>d</i> ₆	73.3	4.398	<i>d</i> ₆ = <i>d</i> ₃ + <i>d</i> ₃	73.6
	<i>d</i> ₅	23.2	1.160	<i>d</i> ₅ = <i>d</i> ₃ + <i>d</i> ₂	23.3
	<i>d</i> ₄	3.3	0.132	<i>d</i> ₄ = (<i>d</i> ₂ + <i>d</i> ₂) + (<i>d</i> ₁ + <i>d</i> ₃)	2.9
	<i>d</i> ₃	0.2	0.006	<i>d</i> ₃ = <i>d</i> ₂ + <i>d</i> ₁	0.1
	Total		5.696		
II-d ₁₀	<i>d</i> ₁₀	69.7	6.970	<i>d</i> ₁₀ = (<i>d</i> ₆ + <i>d</i> ₄) +	67.7
	<i>d</i> ₉	25.0	2.250	<i>d</i> ₉ = (<i>d</i> ₆ + <i>d</i> ₃) + (<i>d</i> ₅ + <i>d</i> ₄)	26.8
	<i>d</i> ₈	3.9	0.312	<i>d</i> ₈ = (<i>d</i> ₆ + <i>d</i> ₂) + (<i>d</i> ₅ + <i>d</i> ₃) + <i>d</i> ₄ + <i>d</i> ₄	5.0
	<i>d</i> ₅₋₇	1.4	0.1-0.07		
	Total		9.60-9.63		

^a Measurements were kindly performed by Mr. E. B. Miller on a CEC Type 21-103C mass spectrometer operated at 7-8 e.v. Under these conditions of operation fragmentation reactions were completely suppressed. ^b Assuming no isotope effect in the coupling reaction of step (c), Table I, the calculated values for II-d₆ are derived from the composition of IV, and the calculated values for II-d₁₀ are combinations derived from the compositions of II-d₄ and of II-d₆.

values of 8.1-8.2 (ester and acid V, Table I; diols VI, Tables II and III) and 8.0-8.1 (dibromides III, Tables II and III). After bridging, hydrocarbons II have methyl τ -values of 7.7-7.8. This change in methyl τ -values reflects the change in shielding of the methyl groups by the π -electrons of the distal benzene ring, and this change in turn is a function of the biphenyl angle of torsion (ϕ).¹⁰ It is noteworthy that the τ -values of the compounds in Table II are uniformly lower, by 0.02-0.05 p.p.m., than those in Table III, showing that the methyl protons in the latter are more shielded than those of the former.

The shielding effect of the distal benzene ring is also seen in the chemical shift of the O-methyl protons of the ester derived from V (Table I), *i.e.*, τ 6.50, as compared to τ 6.15 for the "half-molecule" IV. The upfield shift of 0.35 p.p.m. is comparable to a similar shift of 0.40 p.p.m. which had previously been observed by Meyer in a closely related case.²⁴

(24) Prof. W. L. Meyer, private communication.

Mass spectral analyses gave a further insight into the composition of hydrocarbons II. Analyses of II-d₄, -d₆, and -d₁₀ (Table V) gave a deuterium content of 3.92, 5.70, and 9.6 deuterium atoms per molecule, respectively, which agreed within experimental error with the values found by n.m.r. and combustion (Table IV) analyses. The mass spectral analysis of IV showed 2.85 atoms of deuterium per molecule, in perfect accord with the values determined by n.m.r. and combustion analyses (Table I). The last column in Table V shows the isotopic composition of II-d₆ which was calculated from the composition of IV, and the isotopic composition of II-d₁₀ which was calculated from the compositions of IV and II-d₄. Both calculations were based on the assumption that the coupling step (c) in Table I is a purely statistical process. From the gratifying agreement between calculated and found values for II-d₆ it may be concluded that *no isotope effect accompanies the coupling reaction*. The accord between the abundances found (3.3%) and calculated

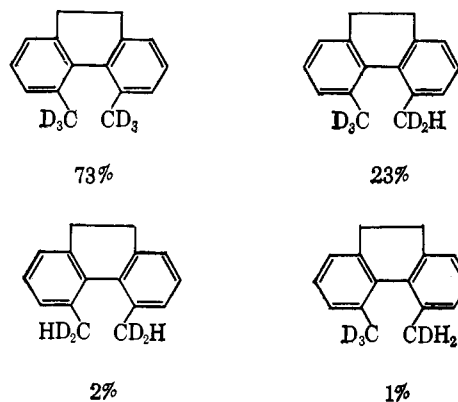
TABLE VI

RATE DATA FOR THE RACEMIZATION OF 9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENES IN BENZENE AT 42.0°

Run no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Concentration, g./100 ml.	1.895	4.82	0.986	3.72	5.10	4.58	3.52	3.22	5.27	4.12	4.42	2.84	2.80
α_{∞} at t_0^a ($l = 2$ dm.)	-20.24°	-24.21°	-10.15°	-35.89°	+45.07°	+25.54°	+33.62°	+17.06°	+55.36°	+43.30°	+40.81°	+30.81°	+26.87°
$t_1 \times 10^4$, sec. ^{-1b}	5.83	5.94	5.87	5.92	6.18	6.24	6.20	6.73	6.73	6.70	7.01	7.01	7.02
$t_{0.5}$, min. ^b	19.82	19.47	19.69	19.5	18.70	18.52	18.60	17.17	17.17	17.21	16.48	16.48	16.45
Span of observations (in units of $t_{0.5}$)	4.27	3.46	1.47	3.09	3.21	3.46	3.58	3.04	3.26	3.17	3.08	3.23	3.02
No. of measurements recorded	31	31	15	34	37	32	43	31	37	32	32	32	31

^a t_0 was taken as the time of the first measurement, usually about 3 min. after the sample had been placed in the jacketed polarimeter tube. ^b Calculated from the slope of the line drawn through the points of the plot of $\log \alpha$ vs. time. The infinity rotation was measured in each case and was indistinguishable (within experimental error) from the instrumental null point.

(2.9%) for the d_4 portion of II- d_6 exposes the detailed composition of that portion, since the calculated figure was arrived at by adding the abundances calculated for the ($d_2 + d_2$) fraction (1.9%) and for the ($d_1 + d_3$) fraction (1.0%). The constituent species of II- d_6 and their abundances are therefore



The agreement between calculated and found values for the isotopic composition of II- d_{10} is less satisfactory; this is in part due to the error introduced in extrapolating mass spectral results obtained for II- d_4 and in part to the fact that II- d_{10} was contaminated by d_{5-7} fractions to the extent of 1.4%.

Rates of Racemization and Isotope Effects.—The rates of racemization were measured in benzene at 42° as described before,⁹ but since it was anticipated that the isotope effects would be small (as indeed they proved to be), special care was taken to achieve a maximum in precision and reproducibility. This was accomplished in several ways (see Table VI). First, thanks to the high initial rotations at the wave length employed (Table VI),²⁵ the measured α_{435} never fell below 2.00° over the span of observations (which varied from 1.47 to 4.27 half-lives); the error in the readings ($\pm 0.01^\circ$) therefore never exceeded and was usually less than 1% of the measured value. Second, in each run with the exception of run 3, 30–40 measurements were taken over the span of observations. Finally each run was repeated at least in triplicate and different samples or different chromatographic cuts were used in most of the triplicate sets. In each case excellent straight-line relationships resulted from the plot of $\log (\alpha_t - \alpha_\infty)$ vs. time. The first-order rate constants computed from the slopes of the plots are recorded in Table VI. First-order rate constants were also computed by a program developed by Lietzke at ORNL²⁶ and are recorded in Table VII.

For each hydrocarbon the rate constants in the separate runs agree with each other regardless of the method of computation, i.e., whether computed graphically (Table VI) or by the methods of linear or nonlinear least squares (Table VII). The small differences between the average rate constants of the four hydrocarbons are therefore significant and the observed inverse isotope effects are real. In summary

(25) The highest rotation observed in the present study was that of a sample of II- d_6 which had $[\alpha]_{25}^{25} = -643^\circ$ (c 2.74) immediately after dissolution in benzene.

(26) M. H. Lietzke, "Oak Ridge National Laboratory Report No. 3259," Oak Ridge, Tenn., March 21, 1962. We are obliged to Drs. C. J. Collins and M. H. Lietzke for bringing this program to our attention and for performing the computations.

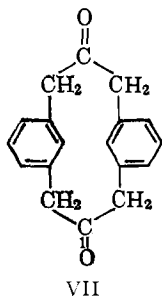
$k_1^{42} \times 10^4 (\text{sec.}^{-1})$	5.92	6.21	6.70	6.99
k_D/k_H		1.05	1.13	1.18

TABLE VII
9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENES. COMPUTED^a RATE CONSTANTS OF RACEMIZATION IN BENZENE AT 42.0° REPORTED AS $k_1 \times 10^4 \text{ SEC.}^{-1}$

Method ^b	Runs 1-4	Runs 5-7	Runs 8-10	Runs 11-13
LLS	5.850 ± 0.01	6.191 ± 0.011	6.667 ± 0.03	7.012 ± 0.002
(1)	5.918 ± .005	6.234 ± .005	6.744 ± .002	6.989 ± .004
	5.891 ± .012	6.214 ± .002	6.734 ± .003	7.003 ± .004
	5.944 ± .002			
LLS	5.852 ± .005	6.199 ± .003	6.700 ± .006	7.011 ± .0006
(α)	5.924 ± .002	6.233 ± .002	6.741 ± .0005	6.993 ± .001
	5.893 ± .005		6.728 ± .001	6.996 ± .001
	5.945 ± .0005			
NLLS	5.880 ± .03	6.234 ± .02	6.690 ± .02	7.000 ± .008
(1)	5.940 ± .01	6.199 ± .006	6.731 ± .006	7.010 ± .01
	5.921 ± .06		6.683 ± .008	6.962 ± .01
	5.937 ± .007			

^a M. H. Lietzke, ORNL Report No. 3259; cf. ref. 26. ^b LLS = linear least squares code; NLLS = nonlinear least square code; (1) = equal weight is assigned to each measurement; (α) = weight assigned to each measurement is proportional to the value of the measurement. Standard errors are listed.

The finding that $k_D \neq k_H$ further exemplifies the operation of *conformational kinetic isotope effects*. Such an effect had first been observed¹⁰ in the case of the doubly bridged diketone VII, but it should be noted that the effects in VII and in II are in opposite directions.



The present study has revealed that substitution of deuterium in either the 9,10-bridge positions (II-*d*₄) or in the 4,5-blocking positions (II-*d*₆) gives rise to a kinetic isotope effect. These isotope effects appear to be additive, since the 18% effect in II-*d*₁₀ is the sum of the 5% effect in II-*d*₄ and the 13% effect in II-*d*₆. Although the detailed source of these effects still remains a subject of speculation, certain conjectures and general conclusions are permissible.

The 5% effect in II-*d*₄ and II-*d*₁₀ is possibly related to a change in the potential barrier to torsion around the 9,10-bond,²⁷ or possibly it may be a nonbonding "steric" isotope effect resulting from isotopic dif-

(27) In a related situation, the potential barrier to internal rotation fluctuates within about 10% of the average barrier height of 3030 cal./mole for variously deuterated ethanes (D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958)).

ferences in interaction between 9,10-hydrogens and the nearest aromatic hydrogens at the 1- and 8-positions.²⁸

The 13% effect in II-*d*₆ and II-*d*₁₀ must be steric in origin, and we believe that *the present observations provide the first unambiguous evidence for the operation of steric kinetic isotope effects*. The fact that this is an inverse isotope effect supports the contention that the *effective* steric requirement of protium is greater than that of deuterium. However, it is not clear whether this effect arises exclusively from isotopic differences in nonbonded repulsions,⁷ and to what extent other factors need also be considered.

The rates of racemization of II-*d*₀ and II-*d*₆ vary only very slightly with solvent (heptane, benzene, ethanol) and the corresponding isotope effect is also essentially independent of solvent (Table VIII). This supports our view that any charge displacements along the reaction coordinate of racemization are negligibly small and that the process studied, *i.e.*, a molecular vibration, is exceptionally free of complicating features.

The rates of racemization of II-*d*₀ and II-*d*₆ were measured in benzene and in heptane at four temperatures (Table VIII). Calculated Arrhenius parameters are listed in Table IX. The temperature dependence of k_{rac} of II-*d*₀ in benzene agrees with that previously reported.⁹ Somewhat unexpectedly, the temperature dependence of the two hydrocarbons is solvent dependent in the sense that E_{act} and A for II-*d*₀ and II-*d*₆ are slightly greater in benzene than in heptane, and

(28) Steric interaction between vicinal hydrogens at the 9,10-positions is probably negligible; cf. E. B. Wilson, Jr., "Advances in Chemical Physics," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1959, p. 367.

that below 39° II-*d*₀ and II-*d*₆ racemize faster in heptane than in benzene whereas above 39° they racemize more slowly. We have no explanation for this observation.

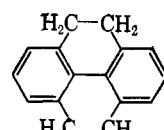
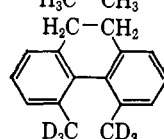
TABLE VIII
KINETIC ISOTOPE EFFECTS IN THE RACEMIZATION OF
9,10-DIHYDRO-4,5-BIS(TRIDEUTERIOMETHYL)PHENANTHRENE
(II-*d*₆): RATES

Solvent	Temp., °C.	$k_t \times 10^4, \text{sec.}^{-1}$		k_D/k_H
		H ^a	D ^b	
Heptane	22.0	0.502	0.584	1.163
Heptane	32.0	1.806	2.075	1.149
Heptane	42.0	5.836	6.629	1.136
Heptane	52.0	17.80	20.04	1.126
Benzene	22.0	0.483	0.564	1.168
Benzene	32.0	1.771	2.041	1.153
Benzene	42.0	5.910	6.720	1.137
Benzene	52.0	18.71	20.99	1.121
Ethanol	42.0	5.76	6.62	1.149

^a Refers to II-*d*₀. ^b Refers to the title compound.

The difference in the enthalpies of activation (in benzene or heptane) of II-*d*₀ and II-*d*₆ is about 0.2 kcal./mole (Table IX), and this factor has the effect of slowing the racemization of II-*d*₀ relative to that of II-*d*₆. However, since the entropy factor (Table IX) has the opposite effect of slowing the racemization of II-*d*₆ relative to that of II-*d*₀, the value of $\Delta G_H^\ddagger - \Delta G_D^\ddagger$ is only about one-third to one-half that of $\Delta H_H^\ddagger - \Delta H_D^\ddagger$ over the temperature range studied, e.g., $\Delta \Delta G^\ddagger$ at 42° is 0.08 kcal./mole.

TABLE IX
KINETIC ISOTOPE EFFECTS IN THE RACEMIZATION OF
9,10-DIHYDRO-4,5-BIS(TRIDEUTERIOMETHYL)PHENANTHRENE
(II-*d*₆): ACTIVATION PARAMETERS^a

	Benzene	Heptane	
	$E_{\text{act.}}, \text{kcal./mole}$	23.1	22.5
	$A \times 10^{-12}, \text{sec.}^{-1}$	6.5	2.5
	$E_{\text{act.}}, \text{kcal./mole}$	23.0	22.4
	$A \times 10^{-12}, \text{sec.}^{-1}$	5.8	2.3
	$\Delta H_H^\ddagger - \Delta H_D^\ddagger, \text{kcal./mole}$	0.24	0.19
	$\Delta S_H^\ddagger - \Delta S_D^\ddagger, \text{e.u.}$	0.53	0.36

^a Calculated from the data in Table VIII. The subscripts H and D refer, respectively, to II-*d*₀ and to the title compound.

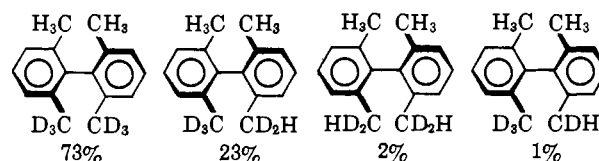
When the magnitude of these values is considered, it must be borne in mind that II-*d*₆ is a mixture of molecules, 73% of which contain two -CD₃ groups, 23% of which contain a -CD₃ and a -CHD₂ group, and 3% of which contain only four deuterium atoms among the six hydrogens in the blocking positions. The complete absence of curvature in the straight line relationship of $\log \alpha$ vs. time for II-*d*₆ and II-*d*₁₀ indicates, however, that the first-order rate constants of the two major components in II-*d*₆ must be virtually identical. The composite rate constants reported for II-*d*₆ in Tables VI-VIII are therefore applicable to "pure" II-*d*₆, though in fact they refer to a mixture having an average of 5.7 deuterium atoms per molecule, i.e., 95% of the full complement of 6.0. An entirely different consideration leads to the same conclusion.

It is reasonable to suppose that only two out of the three hydrogens on each methyl group are capable of being compressed against the opposite methyl group,²⁹ so that one-third of the interactions in the (*d*₃ + *d*₂) fraction of II-*d*₆ are essentially identical with those in the (*d*₃ + *d*₃) fraction. Since the former fraction constitutes 23% and the latter 73% of the mixture, it follows that two deuterium atoms oppose two deuterium atoms in 81% of the interactions, and two deuterium atoms oppose one deuterium plus one hydrogen atom in 15% of the interactions. It seems unlikely that the last named interaction differs greatly from the first, and the isotope effect may therefore be safely referred to 95% of the interactions.

The steric isotope effect (as reflected in the enthalpy of activation term) corresponds to ca. 50 cal./D atom, assuming that only four out of the six hydrogen atoms are effective in nonbonded repulsive interactions. It may not be valid to extrapolate these results to systems and reactions as different from ours as are the solvolyses studied by Shiner⁵; nevertheless, to the extent that a *qualitative* judgment is permissible, it does not seem likely that steric factors are responsible to a major extent for the deuterium isotope effects observed in SN1 reactions. In these reactions the hydrogens are far less compressed (and the differences in nonbonded interactions between ground and transition state conformations appear to be far smaller) than in the systems employed in the present study.

In summary: from the experimental evidence gathered thus far in this and the preceding⁸ investigation, we conclude that steric hydrogen isotope effects are plainly operative only under special conditions of severe overcrowding.³⁰

Absence of Optical Activity in a Dissymmetric Biphenyl.—The availability of dibromide III-*d*₆ suggested the preparation of another compound which might be suitable for gaging the difference in the size of protium and deuterium. Reduction of optically pure (+)-III-*d*₆ with lithium aluminum hydride in tetrahydrofuran gave 2,2'-dimethyl-6,6'-bis(trideuteriomethyl)-biphenyl (VIII) whose isotopic components had the identical abundances as those of II-*d*₆ (Table V and Experimental part). The composition of VIII is therefore



Each of the above components is dissymmetric, and this dissymmetry might give rise to optical activity for two reasons: first, even if the phenyl rings were perpendicular, the methyl or deuteriomethyl groups in each of the four components shown would constitute a dissymmetric assembly and their interaction might give rise to optical activity. Second, even if the above interactions were purely of the nonbonding repulsive type, a dif-

(29) The precise topology of interaction is unknown and the possibility of "ganging" (i.e., a geared motion of the opposing methyl groups) cannot be excluded; cf., e.g., O. Schnepp and D. S. McClure, *J. Chem. Phys.*, **26**, 83 (1957).

(30) See also E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963).

ference in size between $-\text{CH}_3$ and $-\text{CD}_3$ groups should give rise to a slight dissymmetric twist in the biphenyl moiety and hence to optical activity. We have been unable to detect any optical activity over the whole of the instrumentally accessible spectral region, from the visible to below $250\ \mu$. Evidently the average biphenyl angle of torsion (ϕ) still remains essentially 90° . This conclusion is supported by the chemical shift of the methyl protons (τ 8.11) which is indistinguishable from that of the methyl protons in the nondeuterated analog¹⁰ (τ 8.12). Again we have failed to find evidence for a steric isotope effect in a non-overcrowded situation.³¹

The absolute configuration of (+)-III- d_0 is (*S*),³² and since deuterium substitution has had no detectable effect on the rotation of related members in the series $\text{V} \rightarrow \text{VI} \rightarrow \text{III}$, it follows that (+)-III- d_6 also has the (*S*)-configuration. The absolute configuration of derivative VIII is therefore established and the (*S*)-configuration of the major d_6 component is indicated in the drawing, as are the corresponding absolute configurations of the minor components.

There can be no question that the starting material is optically pure, in view of the many interdependent resolutions and correlations in the family of biphenyls of which III is a member.³² Racemization under the mild conditions of the reduction is also inconceivable. We are left with no alternative but to assert that we are dealing with an isotopic mixture of dissymmetric molecules which are enantiomerically homogeneous and whose absolute configuration has been firmly established, yet which, under the conditions of solvents and concentrations used in the present work, manifest no optical activity in spectral regions which are open to scrutiny by existing polarimeters.

Experimental³³

3-(Trideuteriomethyl)benzoic Acid.—A solution of 250 g. of methyl 3-(trichloromethyl)benzoate¹⁷ in 1 l. of absolute ether was added, over a period of 8 hr. and under rigorous exclusion of moisture, to a stirred mixture of dried and degassed zinc dust (300 g.), 2 l. of absolute ether, and 480 g. of acetic acid- d_4 at $0-30^\circ$. After standing overnight, the ether layer was decanted and the residue was extracted with ether. The ether layers were washed with water, saturated sodium bicarbonate solution, and dried. Distillation afforded 104 g. (69%) of methyl 3-(trideuteriomethyl)benzoate (IV), b.p. $104-106^\circ$ (23 mm.), whose n.m.r., combustion, and mass spectral analyses are recorded in Tables I and V. Saponification in 20% sodium hydroxide at 90° gave the acid in 90% yield, m.p. $111.5-112^\circ$ after recrystallization from aqueous methanol and sublimation at 100° (0.1 mm.); n.m.r. and combustion analyses are recorded in Table I.

2-Amino-3-(trideuteriomethyl)benzoic Acid.—Nitration of the deuterated *m*-toluic acid with fuming nitric acid¹⁹ (d^{23} 1.486) at -15 to -20° gave 2-nitro-3-(trideuteriomethyl)benzoic acid in 52% yield, m.p. $221.5-222.5^\circ$ after sublimation at 160° and 0.05 mm.; n.m.r. and combustion analyses are recorded in Table I. A solution of the nitro acid (20 g.) in 225 ml. of 5 *M* aqueous ammonia was added dropwise to a well-stirred, refluxing solution of 220 g. of ferrous sulfate heptahydrate in 550 ml. of water blanketed

(31) L. S. Bartell has suggested^{7b} that "if the *ortho* hydrogens in biphenyls were replaced by deuterium, the rings could approach coplanarity more closely by perhaps 0.5° and increase the extinction coefficient slightly." No experimental evidence bearing on this point has appeared thus far.

(32) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(33) Melting points are corrected; n.m.r. spectra were measured on a Varian A-60 spectrometer, using 8-10% w./v. solutions in deuteriochloroform with tetramethylsilane serving as internal standard; O.R.D. curves were measured on a Rudolph spectropolarimeter Model 260/655, 850/810-614 unless otherwise specified.

(34) Acetic acid-*d* was prepared from heavy water (99.81 mole % D_2O) and acetyl chloride which had been distilled from dimethylaniline. The acid contained 5% of CH_3COOH by n.m.r.

under a nitrogen atmosphere. The reaction mixture was made basic by dropwise addition of 15 *M* aqueous ammonia with vigorous stirring. After 10 min. of refluxing, the hot mixture was filtered through Celite. The filtrate was concentrated to 300 ml., made acid to pH 4 with acetic acid, and cooled in ice. The precipitated amino acid (15 g., m.p. $166-171^\circ$) was recrystallized from aqueous isopropyl alcohol to give 13 g. (78%) of needles, m.p. $173-175.5^\circ$. Unrecrystallized material obtained in other preparations was used in the coupling step described below.

(±)-6,6'-Bis(trideuteriomethyl)-2,2'-diphenic Acid Dimethyl Ester.—A solution of 24.5 g. of sodium nitrite in 100 ml. of water was slowly added to a suspension of 50.0 g. of crude amino acid (preceding section) in 335 ml. of 3 *N* hydrochloric acid. The temperature was kept between 0 and 3° . The reaction mixture was filtered through Celite to give solution A. A solution of 33.0 g. of hydroxylamine hydrochloride in 110 ml. of water was mixed with a solution of 19 g. of sodium hydroxide in 80 ml. of water, and this solution was added in a single portion with vigorous stirring to a cold solution made by mixing 117 g. of copper sulfate pentahydrate in 450 ml. of water and 195 ml. of 15 *M* aqueous ammonia. To the resulting mixture was added solution A, care being taken to maintain the temperature of the reaction mixture below 5° . The mixture was heated to 95° and 200 ml. of 12 *N* hydrochloric acid was added. After standing overnight the precipitated product was collected by filtration and extracted with 100 ml. of hot acetone. The insoluble residue was removed by filtration. After removal of solvent, the acetone-soluble fraction was esterified by refluxing in a mixture of methanol (500 ml.) and concentrated sulfuric acid (35 ml.). The ester, worked up in the usual manner, was purified by Kugelrohr distillation at $130-140^\circ$ (0.3 mm.), followed by recrystallization from ligroin. There was thus obtained 30.5 g. (66%) of product, m.p. $56-57^\circ$; n.m.r. and combustion analyses are recorded in Table I.

(±)-, (+)-, and (-)-6,6'-Bis(trideuteriomethyl)-2,2'-diphenic Acid (V- d_6).—Saponification of the ester in hot 15% aqueous sodium hydroxide gave the desired acid in 97% yield, m.p. $236-237^\circ$. Resolution *via* the morphine salt^{22,23} gave the enantiomeric acids. The (+)-acid had m.p. $212.5-213^\circ$ and $[\alpha]^{25\text{D}} + 22^\circ$ (*c* 1.3, methanol). The (-)-acid had m.p. $209-213^\circ$ and $[\alpha]^{25\text{D}} - 20^\circ$ (*c* 1.2, methanol); n.m.r. and combustion analyses of the (+)-acid are recorded in Table I.

(+)- and (-)-2,2'-bis(hydroxymethyl)- and 2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyls VI- and III- d_4 , - d_6 , and - d_{10} were prepared according to the procedure described for the d_0 analogs²² using appropriate precursors (V- d_0 or V- d_6) and reagents (LiAlH_4 or LiAlD_4) as schematized in Tables II and III. The melting point and specific rotation of the deuterated products were indistinguishable from the corresponding properties of the undeuterated counterparts. A typical preparation of VI- d_6 had m.p. $122-123.5^\circ$, $[\alpha]^{25\text{D}} - 107.5^\circ$ (*c* 1.2, benzene); a typical preparation of III- d_6 had m.p. $51.5-53.5^\circ$, $[\alpha]^{25\text{D}} + 52.6^\circ$ (*c* 1.1, benzene); two typical preparations of III- d_4 had m.p. $53.8-54.2^\circ$, $[\alpha]^{25\text{D}} + 50.8^\circ$ (*c* 1.7, benzene), and m.p. $53-54.5^\circ$, $[\alpha]^{25\text{D}} + 52.0^\circ$ (*c* 1.0, benzene); two typical preparations of VI- d_4 had m.p. $121.0-122.0^\circ$, $[\alpha]^{25\text{D}} - 113^\circ$ (*c* 1.3, benzene), and m.p. $121.8-122.5^\circ$, $[\alpha]^{25\text{D}} - 104^\circ$ (*c* 0.9, benzene); a preparation of VI- d_{10} had m.p. $122-123^\circ$, $[\alpha]^{25\text{D}} - 108.5^\circ$ (*c* 1.2, benzene); a preparation of III- d_{10} had m.p. $52.0-54.5^\circ$, $[\alpha]^{25\text{D}} + 54.2^\circ$ (*c* 1.2, benzene). Nuclear magnetic resonance spectra are recorded in Tables II and III.

9,10-Dihydro-4,5-dimethylphenanthrenes II- d_4 , - d_6 , and - d_{10} were prepared from the appropriate dibromide precursors III according to the procedure described before.⁹ Almost quantitative yields of the hydrocarbons were obtained when the ethereal solutions of III were slowly added to phenyllithium, instead of the reverse order previously employed.⁹

Racemizations were carried out as described before.⁹ The first reading (t_0 , Table VI) was usually made 5 min. after solution of the sample. After each kinetic run the solution was refluxed for 90 min. and the residual rotation (α_∞) was measured at $435\ \mu$. In no case did the value of α_∞ differ by more than $\pm 0.02^\circ$ from the instrumental null point.

2,2'-Dimethyl-6,6'-bis(trideuteriomethyl)biphenyl (VIII).—The title compound was prepared by the reduction of (+)-2,2'-bis(bromomethyl)-6,6'-bis(trideuteriomethyl)biphenyl (III- d_6 , $[\alpha]^{25\text{D}} + 53.5^\circ$ (*c* 1.2, benzene)) with a mixture of lithium aluminum hydride and lithium hydride in tetrahydrofuran as described for the undeuterated counterpart.¹⁰ The compound, m.p. $65-66^\circ$, gave a negative Beilstein test and was homogeneous³⁵ by g.l.c.

(35) In particular, 9,10-dihydro-4,5-bis(trideuteriomethyl)phenanthrene (II- d_6) was shown to be absent.

on a 6-ft. \times 0.25-in. column of 10% Dow 710-on-Chromosorb-P at 200° and 200 cc. He/min. The mass spectrum at 8-10 e.v. showed the composition: 73.3% of d_6 , 23.1% of d_5 , 3.2% of d_4 , and 0.4% of d_3 . The combustion analysis (by the falling drop method) gave 5.65 atoms of deuterium per molecule. The integrated intensity of the methyl p.m.r. signal, 6.36 methyl protons per molecule relative to 6.0 aromatic protons, showed that all of the deuterium atoms were distributed among the methyl groups. The chemical shifts are: aromatic multiplet at τ 2.87, methyl singlet at τ 8.11; optical rotations: α^{25} 0.0 \pm 0.02° (c 5.0, isooctane, l 2) at 589, 435, and 365 $m\mu$; α^{24} 0.0 \pm 0.02° (c 3.1, chloro-

form, l 2) at 589 and 435 $m\mu$; α^{25} 0.00 \pm 0.01° (c 5.0, isooctane, l 0.5) between 350 and 275 $m\mu$; α < 0.0005° (above 230 $m\mu$ (c 0.0176, isooctane, l 0.0108).³⁶

Acknowledgments.—It is a pleasure to acknowledge the many fruitful and stimulating discussions with Dr. Clair J. Collins, Oak Ridge National Laboratory, and Dr. Max Wolfsberg, Brookhaven National Laboratory.

(36) This measurement was kindly performed for us by Dr. J. J. Duffield, Applied Physics Corp., using a Cary Model 60 spectropolarimeter.

[CONTRIBUTION FROM THE COLLEGE OF SCIENCE, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

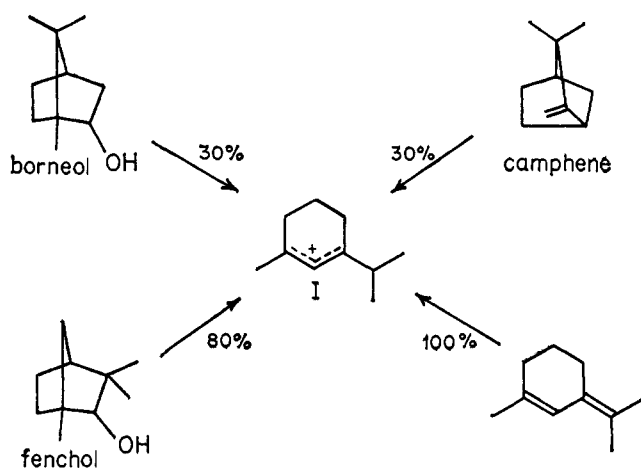
Carbonium Ions. XIV. The Opening of Bicyclic Alcohols to Cyclohexenyl Cations and the Further Conversion to Cyclopentenyl Cations

BY N. C. DENO AND JOHN J. HOUSER

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Fenchol and borneol open to the 1-isopropyl-3-methylcyclohexenyl cation in 96% H_2SO_4 . 2-Methylfenchol and 2-methylborneol open to the 1-isopropyl-3,4-dimethylcyclohexenyl cation, which subsequently rearranges to the 1-isobutyl-2,3-dimethylcyclopentenyl cation. Similar reactions occur with 2,3,3-trimethylborneol, 2-phenylborneol, and 2-phenylfenchol. The yields are generally over 80% and the reactions are of synthetic value.

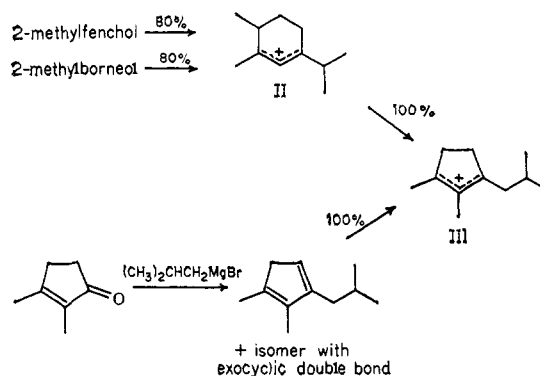
The following conversions are complete within minutes in 96% H_2SO_4 .



The n.m.r. spectrum of I (Table I) is in exact accord both with the areas calculated for structure I and with the characteristic band positions established for cyclohexenyl cations.¹ In 96% H_2SO_4 at 25°, the half-time for conversion of fenchol to I is 4.6 min. in 10^{-5} M solution and 4.0 min. in 10^{-4} M solution. The rates exhibit first-order kinetics over the entire course of the reaction. The half-time for conversion in 82% H_2SO_4 is 5 min.

The following reactions, homologous to the above, introduce as an added feature an interesting collapse of a cyclohexenyl cation to a cyclopentenyl cation. The half-life for the conversion of II to III at 25° is 63 min. in 96% H_2SO_4 and 7 min. in 83% H_2SO_4 . The n.m.r. spectrum of II appears in Table I and that of III is presented in Fig. 1. As pointed out by a referee, methylfenchyl and methylbornyl cations should rapidly interconvert and give the same yield of II and this was found.

(1) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).



The structure of III can be deduced from the n.m.r. spectrum (Fig. 1) alone. However, the assignment was confirmed by an independent synthesis of III, using the more conventional route shown in the above diagram.

A similar collapse of a cyclohexenyl cation to a cyclopentenyl cation probably takes place when 1,2,3,3,7,7-hexamethylbicyclo[2.2.1]heptan-2-ol (IV), trimethylborneol, is added to 96% H_2SO_4 . After 35 days, product VI is present which has only CH_3 at C-2. In the interim, three intermediate cations with only H at C-2 can be recognized by the appearance and disappearance of n.m.r. bands at 7.43, 7.48, and 7.62 p.p.m. At 67 sec. after addition, 7.43 predominates and this must be a cyclohexenyl cation because of its ultraviolet absorption maximum at 320 $m\mu$. At 500 sec., all three are nearly equal. At 7000 sec., 7.62 is strongly dominant. The 7.62 band also dominates at 20 hr. and is provisionally identified as V on the basis of the n.m.r. spectrum (Fig. 2) and the λ_{max} at 296 $m\mu$, typical of highly alkylated cyclopentenyl cations.

The final product VI is a cyclopentenyl cation as shown by λ_{max} at 302 $m\mu$. The n.m.r. spectrum (Fig. 3) is provisionally interpreted as a mixture of the general structure shown in Fig. 3. The two CH_3 groups at C-4 and C-5 are interpreted to be partly on each carbon and partly on a single carbon.