

mated³⁹ from reactivity measurements to have a negligible σ_R value. It is difficult to escape the conclusion, also argued recently by Sheppard,²¹ that the π -inductive effect is, at most, very small. Our present evidence does not allow any general conclusions to be made as to the relative contributions of the other two factors.

The values reported here for alkylbenzenes show a slight increase in disturbance in the series Me < Et < *i*-Pr < *t*-Bu. This order is in contrast to that obtained⁴⁰ for σ_R values, but a larger value of σ^0_R has been

(39) C. F. Wilcox, Jr., and J. S. McIntyre, *J. Org. Chem.*, **30**, 777 (1965).

(40) R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

found²³ for ethylbenzene than methylbenzene by fluorine-19 nmr experiments. We are investigating a series of alkylbenzenes and *p*-nitroalkylbenzenes in both carbon tetrachloride and more polar solvents and defer further discussion on hyperconjugation until we report these results.

Other current investigations include measurements on cycloalkyl- and cycloheteroalkyl-substituted benzenes, on the solvent and temperature dependence of π -electron disturbances in mono- and disubstituted benzenes, and on monosubstituted pyridines. We are also studying the use of the method as a tool to investigate hydrogen bonding and complex formation between aromatic and aliphatic molecules.

The Absolute Configuration of an Axially Dissymmetric Compound. (*S*)-(+)-1-Benzylidene-4-methylcyclohexane¹

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Abstract: (*R*)-(+)-3-Methylcyclohexanone was converted to the (*R*)-(–)-5-benzal derivative and this was reduced by use of aluminum chloride–lithium aluminum hydride to a separable mixture of (*S*)-(+)-1-benzylidene-4-methylcyclohexane and (*R*)-(+)-4-methyl-1-benzylcyclohexane. The benzalketone and the benzylidenecyclohexane show strong negative Cotton effects, indicating that their chromophores are twisted. The relationship of these results to several models of optical activity is discussed, and configurations of several additional cyclohexylidene compounds are predicted.

Dissymmetric spiranes, cycloalkylidene compounds, and allenes² are of interest because some of them cannot show either "atomic"³ or "conformational"³ dissymmetry and so must owe their optical rotatory properties to longer range, or "permolecular,"³ dissymmetry effects. As one step in a program aimed at defining more sharply the concept of "permolecular" dissymmetry,⁴ we have now determined the absolute configurations of a series of 1-benzylidene-4-methylcyclohexanes (III) and measured their optical rotatory dispersion curves (see Figure 1 and Table V).

Our starting material, (+)-3-methylcyclohexanone (I), is available, without need for resolution, by hydrolysis of (+)-pulegone,⁵ the major constituent of oil of pennyroyal.⁶ Its absolute configuration (*R*)⁷ has been

(1) A Useful Model of Optical Activity, part VI; for part V see Hydrogenolyses with Chloroaluminum Hydrides, J. H. Brewster, *Tetrahedron*, **13**, 106 (1961); for part IV see J. H. Brewster, S. F. Osman, H. O. Bayer, and H. B. Hopps, *J. Org. Chem.*, **29**, 121 (1964).

(2) For a review see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 307–317.

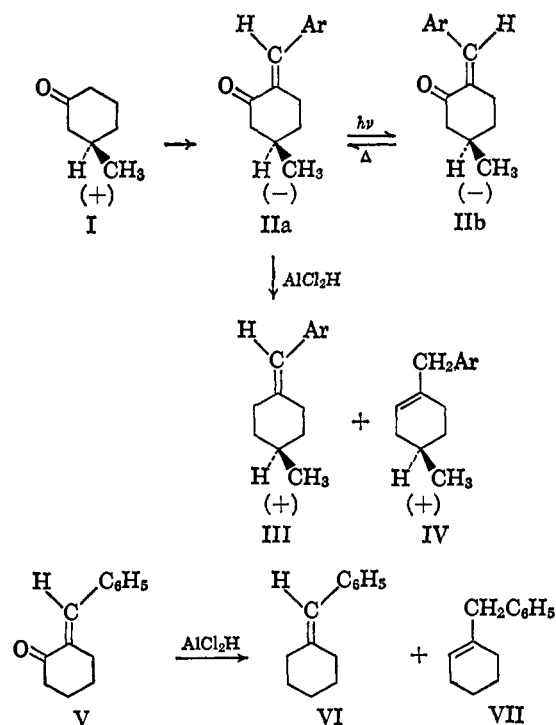
(3) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

(4) For useful criticisms of our failure to develop this aspect of our work in more detail see: (a) W. Kauzmann, F. B. Clough, and I. Tobias, *Tetrahedron*, **13**, 57 (1961); (b) J. A. Berson, J. S. Walla, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961). (c) A paper dealing with this matter at more length is in preparation.

(5) O. Wallach, *Ann.*, **289**, 337 (1895).

(6) E. Guenther, "The Essential Oils," Vol. III, D. van Nostrand Co., Inc., New York, N. Y., 1949, p 575.

(7) Notation of R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).



established in several ways.^{8–10} Condensation with

(8) A. Fredga, *Arkiv Kemi Mineral. Geol.*, **14B**, No. 27 (1941); **15B**, No. 23 (1942); A. Fredga and E. Leskinen, *ibid.*, **19B**, No. 1 (1944).

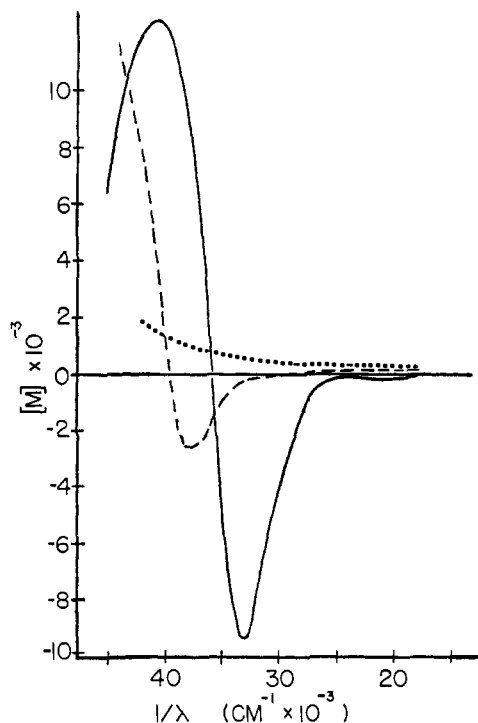


Figure 1. Optical rotatory dispersion of *R*-(-)-2-benzylidene-5-methylcyclohexanone (IIa) in isooctane (—), of *S*-(+)-1-benzylidene-4-methylcyclohexane (III) in isooctane (---), and of *R*-(+)-1-benzyl-4-methylcyclohexene (IV) in cyclohexane (.....). Wave numbers are in kilokaysers and may be converted to millimicrons by division into 10^4 .

benzaldehyde can be controlled to give the mono-benzylidene ketone (IIa).^{11,12} The large ultraviolet extinction coefficient ($\lambda_{\text{max}}^{\text{EtOH}}$ 286 $m\mu$ (ϵ 13,700)) and the nearly equal intensities of its carbonyl and olefinic stretching bands in the infrared (see Table I) indicate¹³ that IIa has the *trans* configuration shown. Photoisomerization¹³ gave an isomer which had $\lambda_{\text{max}}^{\text{EtOH}}$ 276 $m\mu$ (ϵ 8420) and a weak olefinic band in the infrared, indicating¹³ that it was the *cis* isomer IIb. The positions of the vinyl proton peaks in the nmr spectra of IIa (δ 7.28, under the aromatic proton peak) and IIb (δ 6.18) are also consistent with these assignments, reflecting deshielding by the carbonyl group^{13,14} in IIa. So is the fact that IIb was converted to IIa (isolated) on all attempts at gas chromatographic analysis.

Bayer has shown¹⁵ that hydrogenolysis of α,β -unsaturated ketones or the corresponding allylic alcohols with 3:1 aluminum chloride-lithium aluminum hydride¹⁶ ("AlCl₂H") gives the olefins to be expected by reduction of the allylic carbonium ion, with *predominating retention of configuration at the olefinic double bond in transoid systems such as IIa*. Phenyl-sub-

Table I. Spectroscopic Data for Aromatic-Substituted (*R*)-(-)-2-Benzylidene-5-methylcyclohexanones

Substituent	Ultraviolet		Infrared, cm^{-1}		Nmr vinyl H (CCl ₄), δ
	$\lambda_{\text{max}}^{\text{EtOH}}$, $m\mu$	($\epsilon \times 10^{-3}$)	$\nu_{\text{C=O}}^{\text{melt}}$	$\nu_{\text{C=C}}^{\text{melt}}$ (γ^a)	
None ^b	286 (13.7)		1680	1592	7.28 ^k
4'-Methyl ^c	292 (18.8)		1675	1590	7.35
4'-Isopropyl ^d	292 (18.0)		1675	1590	7.36
4'-Chloro ^e	292 (17.9)		1675	1585	7.30 ^k
4'-Methoxy ^e	318 (18.1)		1680	1590	7.38
4'-N,N-Dimethyl-amino ^g	372 254	(13.6) (10.5)	1665	1605	7.43
3',4'-Methylene-dioxy ^f	325 (10.3)		1670	1575	7.28
2',3'-Dimethoxy ^h	288 (15.1)		1675	1590	7.42
2'-Chloro ⁱ	278 (12.4)		1685	1600	7.38
2',3'-C ₆ H ₄ ^j (1'-naphthylidene)	223 300	(49.0) (8.5)	1685	1600	<i>k</i>

^a γ = absorbance of C=C/absorbance of C=O. ^b O. Wallach, *Ber.*, **29**, 1595 (1896). ^c F. Nerdel, B. Gnauck, and G. Kresze, *Ann.*, **580**, 35 (1953). ^d A. Haller, *Compt. Rend.*, **136**, 1225 (1892). ^e F. Nerdel, B. Gnauck, and G. Kresze, *Chem. Ber.*, **88**, 1006 (1955). ^f C. Striegler, *J. Prakt. Chem.*, [2] **86**, 267 (1912). ^g *Anal.* Calcd for C₁₆H₂₁NO: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.06; H, 8.68; N, 5.85; mp 117–118°. ^h *Anal.* Calcd for C₁₈H₂₀O₂: C, 73.82; H, 7.74. Found: C, 73.52; H, 7.54; bp 189–195° (5 mm). ⁱ *Anal.* Calcd for C₁₄H₁₅OCl: C, 71.64; H, 6.44; Cl, 15.11. Found: C, 71.96; H, 6.52; Cl, 15.24; bp 163–167° (7 mm); mp 47–48°; $[\alpha]_D^{25}$ -87.5° (c 1, ethanol). ^j *Anal.* Calcd for C₁₈H₁₅O: C, 86.36; H, 7.25. Found: C, 86.33; H, 7.44; bp 208–210° (5 mm); $[\alpha]_D^{25}$ -120° (c 1, ethanol). ^k Under signal for aromatic protons.

stituted allylic alcohols were found¹⁵ to give large amounts of the more highly conjugated product; thus, cinnamyl alcohol gave about 70% of *trans*-1-phenylpropene and 30% of allylbenzene. It was, finally, shown¹⁵ that this reducing system did not produce a significant equilibration of olefins under the conditions ordinarily used. Bayer's results¹⁵ suggested, then, that IIa might be reduced in this way to a mixture rich in III, without loss of either relative or absolute configuration. Preliminary studies showed that reduction of 2-benzylidene-cyclohexanone¹⁷ (V) gave, in 88% yield, a mixture containing 70% of benzylidene-cyclohexane¹⁸ (VI) and 30% 1-benzylcyclohexene²⁰ (VII), both of which products could be isolated *via* gas chromatography. The two products are readily distinguished. The *exo* isomer VI, being conjugated, shows styrenoid absorption ($\lambda_{\text{max}}^{\text{EtOH}}$ 245 $m\mu$ (ϵ 13,500)) and a higher refractive index. The vinyl proton peak of the *exo* isomer VI (δ 6.18) and the vinyl (δ 5.42) and benzyl (δ 3.19) peaks of the *endo* isomer VII were especially important in assigning structure. It is of

(17) W. S. Emerson, G. Birum, and R. L. Longley, Jr., *J. Am. Chem. Soc.*, **75**, 1312 (1953).

(18) C. Prévost, P. Donzelot, and E. Balla, *Compt. Rend.*, **198**, 1041 (1934). A comparison sample was also prepared from α -cyclohexylbenzyl alcohol¹⁹ by pyrolysis of its acetate.

(19) A. Sabatier and H. Mailhe, *ibid.*, **139**, 345 (1904).

(20) D. N. Kursanov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **62**, 1691 (1930); *Chem. Abstr.*, **25**, 2698 (1931). A comparison sample, prepared from α -cyclohexylbenzyl alcohol¹⁹ by acidic dehydration, was purified by gas chromatography.

(9) D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **76**, 768 (1954); D. S. Noyce and J. H. Canfield, *ibid.*, **76**, 3630 (1954).

(10) K. Freudenberg and J. Geiger, *Ann.*, **575**, 145 (1952); K. Freudenberg and W. Hohmann, *ibid.*, **584**, 54 (1953).

(11) O. Wallach, *Ber.*, **29**, 1595 (1896).

(12) L. Tétray, *Bull. Soc. Chim. France*, [3] **27**, 302 (1902).

(13) A. Hassner and T. C. Mead, *Tetrahedron*, **20**, 2201 (1964), and references cited therein.

(14) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 28, 66.

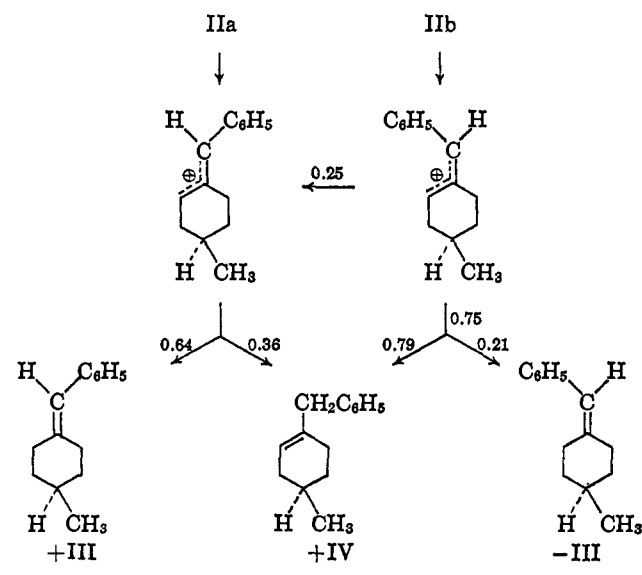
(15) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105, 116 (1964).

(16) See E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961), for a review of other applications of this reagent.

incidental interest that either acid- or base-catalyzed isomerization gave a mixture containing about 80% of the *endo* (unconjugated) isomer VII, pointing up the useful fact¹⁵ that the product of a "mixed hydride" reduction may be relatively rich in thermodynamically less stable isomers. The position of this equilibrium is not unexpected²¹ and presumably reflects internal crowding and entropy effects²² and also (see below) steric interference with full coplanarity of the conjugated system.²³

Mixed hydride reduction of IIa gave, routinely, about 80% of a mixture of two olefins, separable by gas chromatography. The principal constituent (64%) had n_D 1.5512, styrenoid absorption ($\lambda_{\max}^{\text{EtOH}}$ 246 $m\mu$ (ϵ 12,000)), and a vinyl proton peak at δ 6.17 (see Table III) and is therefore assigned the structure and absolute configuration III (*S*);⁷ it had $[\alpha]_D +60^\circ$ (ethanol) and showed what is probably the first extremum of a negative Cotton effect at 263 $m\mu$ (see Table V and Figure 1). The lesser constituent (36%) had n_D 1.5257, no strong absorption above 220 $m\mu$, a vinyl proton peak at δ 5.37, and benzylic proton peaks at δ 3.18 (see Table III) and is therefore assigned the structure and absolute configuration IV (*R*);⁷ it had $[\alpha]_D +68^\circ$ ²⁴ (ethanol) but showed only a plain positive dispersion curve (Table IV, Figure 1). Equilibration of the initial olefin mixture with potassium *t*-butoxide in dimethyl sulfoxide gave a mixture containing 85% of the *endo* and 15% of the *exo* isomer, completing the analogy with the model system (V–VII).

Bayer¹⁵ had found that while transoid systems (such as IIa) tended to preserve their geometric configuration, cisoid systems (such as IIb) often gave significant amounts of transoid product, larger amounts of the less conjugated isomer also being formed. Consistent with this, the *cis*-benzylidene ketone (IIb) gave a mixture containing 68% of the dextrorotatory *endo* olefin (IV) and only 32% of the *exo* olefin, which was almost wholly racemic. These results can be interpreted, in



(21) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954); H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

(22) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.*, **82**, 1750 (1960).

(23) R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

(24) Consistent with the Mills rule: J. A. Mills, *J. Chem. Soc.*, 4976 (1952); see also, J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).

the same fashion as Bayer's,¹⁵ by use of the hypothesis that the *cis* (from IIb) carbonium ion is less stable than the *trans* (from IIa) and is partially converted to it during the reduction.

Experimental Section^{25,26}

2-Benzylidenecyclohexanone was prepared from benzaldehyde and cyclohexanone in dilute aqueous sodium hydroxide.¹⁷ It had bp 185–200° (20 mm), mp 53–54° (lit¹⁷ bp 165–171° (9 mm), mp 51–53°), $\lambda_{\max}^{\text{EtOH}}$ 292 $m\mu$ (ϵ 17,200) (lit²⁷ $\lambda_{\max}^{\text{EtOH}}$ 290 $m\mu$ (ϵ 16,800)), $\nu_{\text{C=O}}^{\text{meit}}$ 1682 cm^{-1} (s), $\nu_{\text{C=C}}^{\text{meit}}$ 1605 cm^{-1} (s), vinyl proton under aromatic protons at δ 7.26, 2,4-dinitrophenylhydrazone mp 186° (lit²⁷ mp 184°).

Aromatic-substituted 2-benzylidene-5-methylcyclohexanones (as IIa) were prepared by condensation of (+)-3-methylcyclohexanone²⁸ with aromatic aldehydes in dilute alkali.¹⁷ Four of the products were new (see Table I, footnotes *g*–*j*, for properties and analyses); the properties of the others were in adequate agreement with those reported in the literature. The characterizing spectroscopic properties are shown in Table I; they are comparable to those of 2-benzylidenecyclohexanone. All of these compounds showed negative Cotton effects; multiple Cotton compounds were shown by the *p*-dimethylaminobenzylidene—and the 1-naphthylidene—derivatives. The significant ORD values are shown in Table II.

(–)-2-Isobenzylidene-5-methylcyclohexanone (IIb). A solution of 2.0 g of (–)-2-benzylidene-5-methylcyclohexanone in 40 ml of absolute ethanol in a Pyrex flask was irradiated with a 500-w mercury lamp for 55 hr. Most of the ethanol was distilled; the residue was crystallized by cooling and collected by suction filtration. It had mp 23°, $[\alpha]_D^{27} -72^\circ$ (*c* 1.89, ethanol), $\lambda_{\max}^{\text{EtOH}}$ 276 $m\mu$ (ϵ 8420), $\nu_{\text{C=O}}^{\text{alt}}$ 1690 cm^{-1} (s), $\nu_{\text{C=C}}^{\text{alt}}$ 1620 cm^{-1} (w), vinyl proton at δ 6.18.

ORD in isoctane: (*c* 0.0515) $[M]_{588} -101^\circ$; (*c* 0.00343) $[M]_{513} -1832^\circ$ (trough), $[M]_{286} +7638^\circ$ (peak), $[M]_{227} -8972^\circ$.

Mixed hydride reagent (3:1) was prepared essentially as described by Bayer.^{15,29} Solutions of 82 g of aluminum chloride and of 8.3 g of lithium aluminum hydride, each in 400 ml of anhydrous ether, were cooled to -10° . The solutions were carefully mixed and allowed to stand for 6 hr at 0° ; the mixture was filtered through glass wool and stored at -10° . The solutions were standardized by collection of hydrogen over water and found to be 0.75–1.0 *M* in hydride. They maintained this activity for 1 month when stored in the cold.

Mixed hydride reductions were carried out by dropwise addition of a solution of the unsaturated ketone (0.01 mole) in ether to a solution containing the equivalent of 0.05 mole of dichloroaluminum hydride in ether (0.75–1.0 *M*) with stirring and keeping the temperature below 35° . The reaction mixture was allowed to stand for 4 hr. Water was added, to destroy excess hydride, until all of the solids had dissolved. The ether layer was separated, washed several times with water, concentrated, and distilled under vacuum.

Reduction of 2-benzylidenecyclohexanone as described above gave 88% of hydrocarbon, bp 138–142° (15 mm). Vapor phase chromatography (vpc) on Craig polysuccinate at 133°, with helium at 36 cc/min, gave two peaks with retention times of 16.5 and 20.0 min. The component giving the first peak (30% of the mixture) was collected and found to be 1-benzylcyclohexene, $n_D^{26} 1.5396$ (lit²⁰ $n_D^{26} 1.5400$); its infrared and nuclear magnetic resonance spectra were identical with those of a sample prepared *via* dehydration of α -cyclohexylbenzyl alcohol with sulfuric acid (below).

(25) All melting points are uncorrected. Microanalyses were performed by Dr. C. S. Yeh and Mrs. M. Hudgens. Infrared and ultraviolet spectra were determined by Miss S. Hall and Mrs. D. Aguilar. Nuclear magnetic resonance spectra were determined by Mr. W. Baitinger and Mrs. D. Aguilar, using a Varian A60 instrument operating at 60 Mc/sec; the data are reported in δ units.

(26) Specific rotations were determined on absolute ethanol solutions (unless otherwise specified) on a Zeiss polarimeter. Optical rotatory dispersion data were recorded on an automatic recording Bendix spectropolarimeter with a 250-w xenon arc-light source. The sensitivity ranged from 0.0002° at 546 $m\mu$ to 0.0019° at 200 $m\mu$ and the slit width remained at 1 mm throughout the scan. A standard 1-cm three-piece cell with silica end plates was used.

(27) B. Eistert, W. Reiss, and H. Wirtzler, *Ann.*, **650**, 133 (1961).

(28) From (+)-pulegone by the method of Wallach;⁵ distilled at 169–174°; $[\alpha]_D^{26} +12.9^\circ$ (*c* 1, ethanol).

(29) H. O. Bayer, Ph.D. Thesis, Purdue University, 1961.

Table II. Optical Rotatory Dispersion Data for Aromatic-Substituted (*R*)-(-)-2-Benzylidene-5-methylcyclohexanones

Substituent	Initial (588 m μ)	[M] $\times 10^{-2}$ (λ , m μ) [c, isoctane]		
		Extrema		Final
		Trough	Peak	
None	-1.70 [0.0365]	-188.6 (303)	+246.3 (244)	+126.9 (222)
		[0.00243]		
4'-Methyl	-2.63 [0.0630]	-158.5 (303)	+218.3 (244)	+204.7 (238)
		[0.00252]		
4'-Isopropyl	-2.06 [0.0451]	-181.6 (313)	+297.6 (263)	+194.4 (238)
		[0.00226]		
4'-Chloro	-3.26 [0.0695]	-237.9 (303)	+290.8 (244)	+198.4 (227)
4'-Methoxy	-4.95 [0.0400]	-187.5 (323)	+238.2 (263)	+134.6 (233)
		[0.0010]		
4'-N,N-Dimethyl- amino	-6.49 [0.00106]	-92.1 (370)	+104.7 (313)	+50.8 (233)
		+70.2 (278)	+88.8 (250)	+50.8 (233)
		[0.00106]		
3',4'-Methylene- dioxy	-3.03 [0.0400]	-93.7 (333)	+111.3 (270)	+61.8 (232)
		[0.00383]		
2',3'-Dimethoxy	-2.25 [0.0555]	-118.4 (313)	+467.4 (244)	+426.8 (238)
		[0.00152]		
2'-Chloro	-0.91 [0.0476]	-190.9 (294)	+320.0 (244)	+270.6 (233)
		[0.00238]		
2',3'-C ₆ H ₄ (1'- naphthylidene)	-3.13 [0.0520]	-100.6 (333)	+74.3 (278)	+107.3 (250)
		+25.9 (263)		+107.3 (250)

The component giving the second peak (70% of the mixture) was collected and identified as benzylidenecyclohexane, n_D^{20} 1.5586 (lit¹⁸ n_D^{20} 1.5567), by comparison of its ultraviolet, infrared, and nuclear magnetic resonance spectra with those of a sample prepared by pyrolysis of the acetate of α -cyclohexylbenzyl alcohol (below). Quantitative ultraviolet spectroscopy indicated that the hydrocarbon mixture first obtained contained 67% of the *exo* (conjugated) isomer.

Benzylidenecyclohexane. α -Cyclohexylbenzyl alcohol¹⁸ (bp 156–160° (12 mm), mp 44–45°; lit¹⁹ mp 41°) (9.5 g) was heated with acetic anhydride (15.3 g) and pyridine (1.3 ml) on a steam bath for 20 hr. The mixture was treated with sodium bicarbonate to destroy excess anhydride and acid and then extracted with two 500-ml portions of ether. There was obtained by distillation 11.1 g (96%) of acetate, bp 166–168° (15 mm). Nine grams of the acetate was introduced slowly into the top of a 2-ft column loosely packed with small glass helices and maintained at a temperature of 500–512°. The products of pyrolysis were collected in a Dry Ice trap connected to the bottom of the column. On distillation the pyrolyzate gave 5.8 g (98%) of benzylidenecyclohexane, bp 136–140° (15 mm), n_D^{20} 1.5576 (lit¹⁸ n_D^{20} 1.5567), $\lambda_{\text{max}}^{\text{EtOH}}$ 245 m μ (ϵ 13,500), $\nu_{\text{C}=\text{C}}^{\text{alm}}$ 1645 cm⁻¹ (w); vinyl proton at δ 6.18, aromatic protons at 7.14, and methylene protons at 1.62 and 2.31. Vpc on Craig polysuccinate gave only one peak.

Anal. Calcd for C₁₂H₁₆: C, 90.64; H, 9.36. Found: C, 90.88; H, 8.99.

Benzylcyclohexene. A mixture of 5.0 g of α -cyclohexylbenzyl alcohol¹⁸ and 0.3 ml of concentrated sulfuric acid was heated at 100° for 1 hr. The reaction mixture was washed with water and with sodium carbonate solution, dried, and distilled to give 2.1 g of hydrocarbon, bp 130–140° (12 mm). The mixture was separated into its two main components by vpc over Craig polysuccinate. The component giving the first peak (75% of the mixture) showed only aromatic absorption above 220 m μ , one vinyl proton at δ 5.42, five aromatic protons at 7.12, and two benzylic protons at 3.19.

The component giving the second peak (25%) had infrared and nmr spectra identical with those of benzylidenecyclohexane (above).

Reduction of (*R*)-(-)-2-benzylidene-5-methylcyclohexanones with mixed hydride as described above gave yields of distilled hydrocarbons of the order of 80%. Clean separations of the two olefins by vpc could not be achieved with the products derived from the 2'-chlorobenzylidene, 2',3'-dimethoxybenzylidene, 1-naphthylidene, or 4'-N,N-dimethylaminobenzylidene ketones. The properties of the olefins which could be separated by vpc are summarized in Tables III–V.

In several cases a third component could be separated by vpc; this may be a diene formed by dehydration of the allylic alcohol intermediate.

Reduction of (*R*)-(-)-2-isobenzylidene-5-methylcyclohexanone by the method described above gave 91% of a hydrocarbon mixture. Vpc showed the presence of 68% of the *endo* olefin and 32% of the *exo*, reversing the ratios obtained with the other geometric isomer. The isolated 1-benzyl-4-methylcyclohexene had $[\alpha]_D^{27}$ +74° (c 1, ethanol), n_D^{27} 1.5240; the infrared and nmr spectra were identical with those obtained above. The isolated 1-benzylidene-4-methylcyclohexane had n_D^{27} 1.5420 and spectra identical with those obtained above. It was essentially completely optically inactive down to 240 m μ .

Equilibration Studies. A mixture containing 66% of (+)-1-benzylidene-4-methylcyclohexane and 34% of (+)-1-benzyl-4-methylcyclohexene (100 mg) was added to 100 mg of potassium *t*-butoxide in 2 ml of dimethyl sulfoxide and the mixture was let stand at room temperature in a sealed tube for 16 hr. Water (5 ml) was added and the mixture was extracted with ligroin. The washed ligroin solution was distilled to give a mixture of the two olefins containing (by vpc analysis) 85% of 1-benzyl-4-methylcyclohexene and 15% of 1-benzylidene-4-methylcyclohexane.

When either 1-benzylcyclohexene or benzylidenecyclohexane was allowed to stand for 2 weeks with a small amount of concentrated sulfuric acid there was formed a mixture containing, by vpc analysis, 80% of 1-benzylcyclohexene and 20% of benzylidenecyclohexane.

Discussion of Results

The rotatory dispersion curves of the substituted benzylidene ketones (IIa) are all similar to that of the parent compound, shown in Figure 1 (see Table II for numerical values). This shows a strong negative Cotton effect curve superimposed on a positive background, the Cotton effect curve being dominant in the visible as well as in the near-ultraviolet. The positions of the extrema (303, 244 m μ) indicate that the Cotton effect is attributable to the conjugated system³⁰ (λ_{max} 286 m μ), while the large amplitude (43,000) suggests that the chromophore is twisted and, thus, inherently dissymmetric.³¹ The sign of the Cotton effect shows that the chromophore is twisted in the sense of VIII,^{31,32} whence it follows that the preferred conformation of the ring is "twist like" (IXa) rather than "chair like" (IXb). An inspection of models reveals that one of the *ortho* aromatic hydrogen atoms will be sterically crowded by an equatorial hydrogen atom in IXb if the *styrene* chromophore is coplanar, but will not be crowded in this way in IXa.

The substituted 1-benzylidene-4-methylcyclohexanes (III, Table V) all show what is probably the first extremum of a negative Cotton effect at about 270 m μ . In the case of the 3',4'-methyleneedioxy derivative the second extremum was also observed, at 244 m μ . This Cotton effect appears to be associated with

(30) See P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism," Holden-Day, Inc., San Francisco, Calif., 1965, pp 191–224, for a recent review of Cotton effects in α,β -unsaturated ketones.

(31) See ref 30, pp 180–190.

(32) This levorotatory conformational unit, regarded solely as a collection of *bonds*, has the geometry of a fragment of a left-handed helix. In our empirical analysis,³ a preoccupation with the polarizabilities of *atoms* led us to describe the saturated and singly unsaturated analogs of VIII (which are also levorotatory) as "right-handed screw patterns of *atoms*." It is theoretically preferable to describe all of these levorotatory units of structure as "left-handed screw patterns of *bonds*" and we shall do so henceforth.

Table III. Mixed Hydride Hydrogenolyses of Aromatic-Substituted (*R*)-(-)-2-Benzylidene-5-methylcyclohexanones

Substituent Formula	Double bond	% in product	Anal, %				<i>n</i> _D	$\lambda_{\max}^{\text{EtOH}}$, $m\mu$ ($\epsilon \times 10^{-3}$)	Nmr, δ	
			C		H				Vinyl H	Benzyl H
None	<i>endo</i>	36	90.31	90.66	9.69	9.90	1.5257	...	5.37	3.18
(C ₁₄ H ₁₈)	<i>exo</i>	64	...	90.24	...	9.97	1.5512	246 (12.0)	6.17	...
4'-Methyl	<i>endo</i>	44	89.94	90.25	10.06	9.95	1.5265	235 (2.8)	5.34	3.13
(C ₁₅ H ₂₀)	<i>exo</i>	56	...	90.26	...	10.04	1.5422	248 (14.6)	6.16	...
4'-Isopropyl	<i>endo</i>	33	89.47	89.28	10.76	10.25	1.5245	270 (2.4)	5.40	3.16
(C ₁₇ H ₂₄)	<i>exo</i>	67	...	89.41	...	10.59	1.5320	249 (14.6)	6.15	...
4'-Chloro	<i>endo</i>	36	76.15	76.17	7.75	7.77	1.5346	280 (2.8)	5.37	3.16
(C ₁₄ H ₁₇ Cl) ^a	<i>exo</i>	64	...	76.39	...	7.52	1.5490	252 (17.2)	6.08	...
4'-Methoxy	<i>endo</i>	36	83.29	83.17	9.30	9.19	1.5283	227 (10.2), 277 (2.1), 285 (1.9)	5.40	3.14
(C ₁₅ H ₂₀ O)	<i>exo</i>	64	...	83.15	...	9.18	1.5479	252 (15.8)	6.14	...
3',4'-Methylene-dioxy	<i>endo</i>	33	78.23	77.95	7.88	7.90	1.5400	236 (5.3), 288 (5.7)	5.32	3.08
(C ₁₅ H ₁₈ O ₂)	<i>exo</i>	67	...	78.18	...	8.04	1.5580	258 (11.4), 295 (5.9)	6.04	...

^a Anal. Calcd for C₁₄H₁₇Cl: Cl, 16.09. Found (*endo*): Cl, 16.02. Found (*exo*): Cl, 15.99.

Table IV. Optical Rotatory Dispersion Data for Aromatic-Substituted (*R*)-(+)-1-Benzyl-4-methylcyclohexenes (*endo*-Olefins) in Cyclohexane

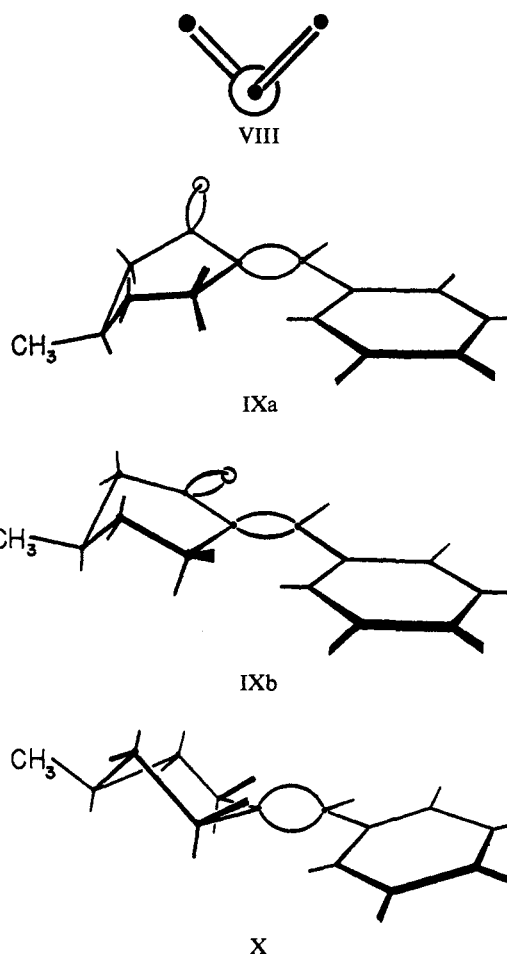
Substituent	<i>c</i>	[M] ^o × 10 ⁻²		
		588 $m\mu$	303 $m\mu$	238 $m\mu$
None	0.0470	0.74	5.13	18.4
4'-Methyl	0.0368	0.40	3.44	10.6
4'-Isopropyl	0.0434	0.65	4.01	12.2
4'-Chloro	0.0480	1.95	12.8	49.0
4'-Methoxy	0.0178	1.35	7.62	24.3
3',4'-Methylene-dioxy	0.0575	1.52	12.0	41.3
	0.00383			

Table V. Optical Rotatory Dispersion Data for Aromatic-Substituted (*S*)-(+)-1-Benzylidene-4-methylcyclohexanes (*exo*-Olefins) in Cyclohexane

Substituent	[M] ^o × 10 ⁻²		
	Initial (588 $m\mu$) [<i>c</i>]	Extrema (λ , $m\mu$) [<i>c</i>]	Final (λ , $m\mu$) [<i>c</i>]
None	+0.42 [0.0720]	-26 (263) [0.0024]	+114.8 (227) [0.0024]
4'-Methyl	+0.15 [0.0620]	-37 (267) [0.0062]	+98 (227) [0.0021]
4'-Isopropyl	+0.42 [0.0330]	-41.7 (263) [0.0022]	+99.9 (233) [0.0022]
4'-Chloro	+0.21 [0.1335]	-38.7 (278) [0.0134]	+111.6 (244) [0.0020]
4'-Methoxy	+0.27 [0.0725]	-69.3 (270) [0.0018]	+85.8 (233) [0.0018]
3',4'-Methylene-dioxy	+0.74 [0.0764]	-281 (+957) (278) (244) [0.00306]	+356 (277) [0.00306]

the styrene absorption band (245–260 $m\mu$) and its intensity suggests that the chromophore is inherently dissymmetric³¹ too. This is consistent with the suggestions (above), following Turner and Garner,²³ that steric hindrance to coplanarity of the conjugated system is a factor influencing the position of the *exo-endo* equilibrium of III and IV. The direction of twist about the styrene single bond can be predicted by assuming that the cyclohexane ring of III is largely in that chair conformation in which the methyl group is equatorial (X) and that this conformation resembles cyclohexanone geometrically.³³ If so, then the equa-

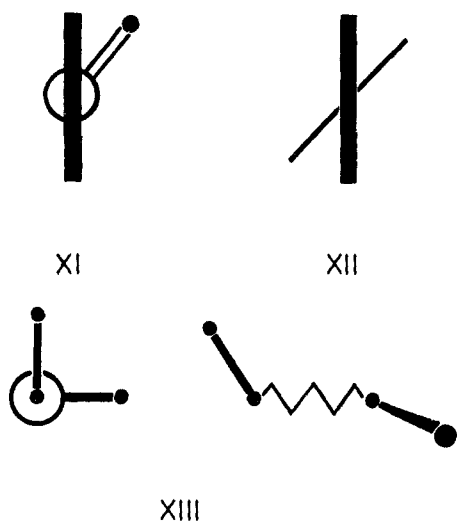
(33) W. Moffitt, R. B. Woodward, A. Moscovitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).



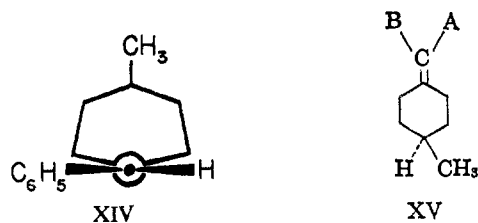
torial hydrogen atoms adjacent to the exocyclic double bond are slightly above it and a downward tilting of the crowded *ortho* hydrogen provides the most efficient relief of strain. It appears, on this basis, that the styrene chromophore will give a negative Cotton effect near 250 $m\mu$ when it has the absolute conformation XI. This is consonant with the finding that biphenyl gives a negative Cotton effect at the conjugation band (245 $m\mu$) when in the absolute conformation XII.³⁴

(34) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962); 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).

The dextrorotation of the benzylidenecyclohexanes (III, Table V) and the general appearance of their dispersion curves (Figure 1, Table V) suggest that the negative Cotton effect curve is superimposed on a strong positive background. A strong positive background curve is, indeed, to be expected from the Kirkwood polarizability theory,³⁵ which indicates that the system XIII will, in general, be dextrorotatory with respect to contributions from electric dipole moment allowed transitions.³⁶ In the present case, the skew pattern XIII is observed when



one looks along the length of the olefinic double bond (XIV). We may, then, predict on this basis that the

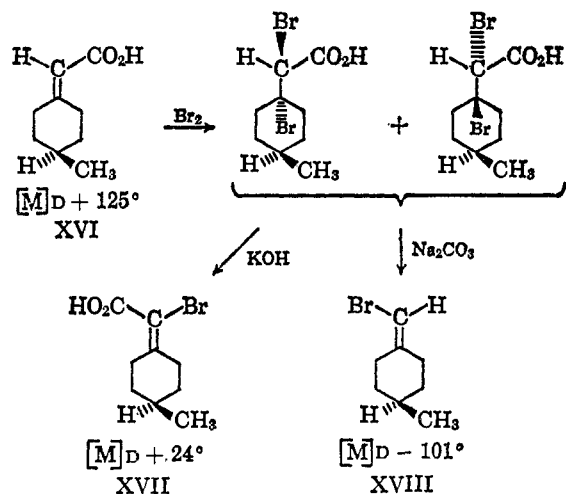


cycloalkylidene XV will be dextrorotatory when A is more polarizable than B, provided only that some near-ultraviolet Cotton effect does not control rotation in the visible³⁶ (as, for example, in IIa). This allows a tentative assignment of absolute configuration to three other

(35) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, **20**, 561 (1952); W. Heller and D. D. Fitts, "Physical Methods of Organic Chemistry," Vol. I, part III, A. Weissberger, Ed., 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1960, pp 2165-2180; see also, W. Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957, pp 616-635, 703-723.

(36) While this manuscript was being written, G. Lowe, *Chem. Commun.* (London), 411 (1964), suggested a rule for relating the sign of rotation and absolute configuration of allenes. This rule can be obtained from the Kirkwood model, via XIII, and the same kind of arithmetical operations used in predicting the sign of rotation of a full dissymmetric conformation.³ Lowe's suggestion that such a rule should also apply to the cycloalkylidenes is not without hazard (see text).

members of this series (XVI--XVIII);³⁷ these compounds would not be expected to show Cotton effects of the sort shown by III except at considerably lower wavelengths. Indeed, Perkin and Pope³⁷ suggested that the acid (XVI) and the bromo compound (XVIII) had the (relative) configurational relationship shown on the grounds that their rotations were opposite in sign. Such an assignment is consistent with the view that the addition of bromine gives the *trans* products shown,³⁸ either of which by *trans* elimination of the elements of carbon dioxide and hydrogen bromide³⁹ would give XVIII; *trans* elimination of the elements of hydrogen bromide, from either dibromo acid, would give XVII. The absolute configuration shown is consistent with dextrorotation, if bromine is considered to be more highly polarizable than the carboxy carbon.³ Perkin and Pope³⁷ assigned the opposite relative configuration, essentially on the ground that the sum of the molecular rotations of XVI and XVIII is +24°. Since, however, the decarboxylation reaction leading to XVIII might give partial racemization,³⁹ it is by no means clear that the molecular rotation of optically pure XVIII should, in fact, be numerically smaller than that of XVI.



Acknowledgments. We wish to thank the Petroleum Research Fund for a grant in support of this work and also the National Science Foundation for Grant GP1688 for purchase of the spectropolarimeter.

(37) W. H. Perkin and W. J. Pope, *J. Chem. Soc.*, **99**, 1510 (1911).

(38) See J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 214-223.

(39) E. Grovenstein, Jr., and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2645 (1953). This reaction appears to be highly stereospecific when it involves a concerted fragmentation. When it is initiated by ionization of the β -bromine atom (as with cinnamic acid dibromide in polar solvents), the more stable olefin is produced. In the present case such a stepwise mechanism would be expected to lead to racemization, but not to predominant formation of the enantiomer of XVIII.