

Our data appear in agreement with a recent experimental study on diazomethane.<sup>14</sup>

In conclusion we have shown a new class of dications with the general structure I, methonium ions with a cationic substituent. Their formation both from  $\text{CH}_4^{2+}$  with *n* donors and from hydrogenation of precursor dications is highly exothermic. The experimental verification of I depends on the balance of the heats of reaction vs. the activation energy of fragmentation and isomerization and further on how excess potential energy can be accommodated otherwise. We encourage mass spectroscopists to search for I.

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**Registry No.**  $\text{H}_4\text{C}^+-\text{CO}^+$ , 62655-44-1;  $\text{H}_3\text{C}-\text{C}^+=\text{O}$ , 15762-07-9;  $\text{H}_2\text{C}^+-\text{C}^+=\text{O}$ , 85491-02-7;  $\text{H}_4\text{C}^+-\text{NH}_3^+$ , 91158-04-2;  $\text{H}_2\text{C}^+-\text{N}_2^+$ , 91158-05-3;  $\text{H}_4\text{C}^+-\text{N}_2^+$ , 91158-06-4;  $\text{H}_2\text{C}=\text{N}^+=\text{N}^+\text{H}_2$ , 91158-07-5;  $\text{H}_3\text{C}-\text{N}_2^+$ , 20404-06-2;  $\text{H}_4\text{C}^+-\text{OH}_2^+$ , 91158-08-6.

(13) Niemeyer, H. M. *Helv. Chim. Acta* 1976, 59, 1133. Griengl, H.; Janoschek, R. *Tetrahedron* 1977, 33, 445.

(14) McGarrity, J. F.; Cox, D. P. *J. Am. Chem. Soc.* 1983, 105, 3961.

### Chiral Recognition of the Twisted Cyclohexene Conformation in $\beta$ -Cyclocitral Schiff Bases

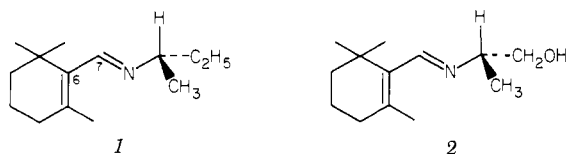
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Steric interactions cause the well-documented<sup>1-4</sup> nonplanarity between the cyclohexene double bond and the polyene chain in retinal-type molecules. We now wish to report what we believe is proof of the twist inherent in the  $\beta$ -ionyl system in solution.

Starting with  $\beta$ -cyclocitral and optically active amines the two chiral Schiff bases **1** and **2**<sup>5</sup> were prepared by standard procedures.<sup>6</sup>



The UV and CD spectra of both compounds show a remarkable solvent and temperature dependence. For **1** the results are collected in Table I. In methanol the extinction of the only prominent absorption band (maximum at 241 nm) is less than 40% the value in isopentane with little change when the temperature is lowered. In isopentane on the other hand the extinction drops significantly between -50 and -100 °C, approaching at even lower temperatures the value found in methanol. A prominent feature of the CD spectrum is a negative band with maximum at 264 nm in methanol (267 nm in isopentane), which, however, develops only at low

(1) Honig, B.; Hudson, B.; Sykes, B. D.; Karplus, M. *Proc. Natl. Acad. Sci., U.S.A.* 1971, 68, 1289. Honig, B.; Warshel, A.; Karplus, M. *Acc. Chem. Res.* 1975, 8, 92.

(2) For a summary of X-ray data, see, e.g.: Noack, K.; Thomson, A. J. *Helv. Chim. Acta* 1979, 62, 1902.

(3) Lienard, B. H. S.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. 2* 1977, 1400.

(4) Christensen, R. L.; Kohler, B. E. *Photochem. Photobiol.* 1973, 18, 293. Paritosh, K. D.; Becker, R. S. *J. Phys. Chem.* 1978, 82, 2081. Honig, B.; Dinur, U.; Birge, R. R.; Ebrey, T. G. *J. Am. Chem. Soc.* 1980, 102, 488. Birge, R. R.; Bocian, D. F.; Hubbard, L. M. *Ibid.* 1982, 104, 1196.

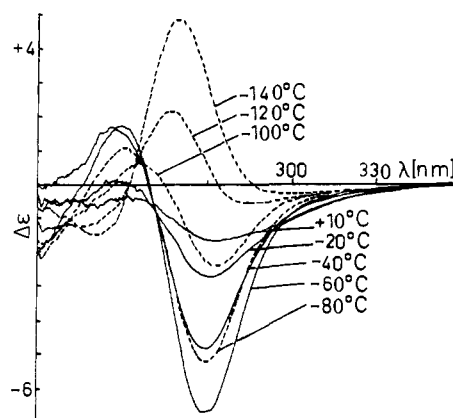
(5) (S)-N-(1-Methylpropyl)- $\beta$ -cyclocitrylideneamine (**1**), (S)-N-(2-hydroxy-1-methyl-ethyl)- $\beta$ -cyclocitrylideneamine (**2**).

(6) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* 1967, 32, 3246.

**Table I.** Solvent and Temperature Dependence of the UV (241 nm) and CD Spectra of **1**

T, °C	$\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup>		10 <sup>40</sup> R, cgs	
	isopentane	methanol	isopentane	methanol
10	13700	5150	-0.58	-3.9
-20	13000	5400	-1.3	-4.6
-40	12300	5200	-1.6	-6.2
-60	11400	5000	-2.0	-7.2
-80	9300	4400	-4.2	-9.0
-100	7100	4300 <sup>a</sup>	-8.2	-10.6 <sup>a</sup>
-120	6600		-12.0	-12.6 <sup>a</sup>
-140	6200		-16.6	-14.6 <sup>a</sup>
-150	5900		-18.5	
-160				-17.0 <sup>a</sup>

<sup>a</sup>Methanol/ethanol (1:4).



**Figure 1.** Temperature-dependent CD spectra of **2** in isopentane.

temperatures and at a different rate in both solvents. The methanol data can be interpreted on the basis of a temperature-dependent equilibrium between two chiral species.<sup>7</sup> In a plot of  $1/(1 + e^{-\Delta G^\circ/(RT)})$  against the observed rotatory strength, excellent linearity (0.998) is obtained for  $\Delta G^\circ = -2.0$  kJ/mol corresponding to rotatory strengths for the two components of  $-2.4$  and  $+4.5 \times 10^{-39}$  cgs, respectively. In isopentane, the same  $\Delta G^\circ$  and rotatory strengths of the same order of magnitude result<sup>8</sup> if only the data below -60 °C are considered.

To interpret these results, we have to consider and evaluate the different conformational equilibria that might play a role in **1**. Hindered rotation around the C-N single bond cannot account for the observed effects since open-chain analogues of **1** which we synthesized do not show them. The *E/Z* equilibrium at the C=N double bond may be ruled out because of the high barrier to inversion or rotation at a doubly bonded nitrogen.<sup>9</sup> We conclude that it is the presence of the ring or, more specifically, the *s-cis/s-trans* equilibrium about the C(6)-C(7) bond that is responsible for the observed changes the *cis* form being favored in methanol and at low temperatures in isopentane.

Twist of this bond makes the chromophore inherently chiral. In addition the asymmetric carbon atom serves as a chiral anchor to distinguish between the twists of opposite chirality, and circular dichroism is observed. Our data indicate, moreover, that it is mainly the *s-cis* form that gives rise to the CD spectra<sup>10</sup> due

(7) Moscowitz, A.; Wellman, K.; Djerassi, C. *J. Am. Chem. Soc.* 1963, 85, 3515.

(8) The calculated rotatory strength of the dominant conformer is -3.6, of the other  $+10.6 \times 10^{-39}$  cgs (linearity 0.998).

(9) A large-scale CI treatment of allylideneimine gives, for the C=N double bond, a barrier to planar inversion of 128 kJ/mol and to rotation of 245 kJ/mol: Bonacic-Koutecky, V.; Persico, M. *J. Am. Chem. Soc.* 1983, 105, 3388.

(10) For the allylideneimine chromophore of **1** twisted by 40° from *s-cis*, we calculate for *p* helicity a rotatory strength of  $+2.2 \times 10^{-39}$  cgs for the  $n\pi^*$  transition and  $1.4 \times 10^{-39}$  cgs for the  $\pi\pi^*$  transition in the CNDO approximation. It is tempting, moreover, to speculate that the different absolute values of rotatory strengths which we obtain by the linearity test correspond to conformations that differ not only in their sense of helicity, but also in the degree of twist.

probably to the smaller deviation from planarity of the *s*-trans form. Thus in methanol we observe the temperature-dependent equilibrium between the chiral *s*-cis forms the calculated value of 2.0 kJ/mol representing the free energy difference between the two conformers involved. In isopentane the *s*-cis portion of **1** becomes dominant at the cost of *s*-trans only at lower temperatures, and only then do we observe the development of the prominent CD band at 267 nm.

The spectra of **2** confirm our hypothesis up to a point. The extinction coefficient in isopentane decreases most rapidly between -30 and -60 °C, reaching the low methanol value already at -70 °C. This behavior is reflected in the temperature-dependent CD spectra (Figure 1). The negative band at 269 nm grows much faster than in **1** resulting in a rotational strength of  $-1.7 \times 10^{-39}$  cgs already at -60 °C. At lower temperatures there appears another band with opposite sign the intensity of which increases at the expense of the negative band. In methanol the CD spectra of **2** exhibit only this band at 259 nm, with the amplitude slowly increasing upon cooling. At -90 °C  $\Delta\epsilon$  is about one-fifth the value in isopentane at -140 °C.

These spectra indicate that in isopentane at temperatures down to -60 °C the same equilibrium between chiral *s*-cis forms is involved as in **1**. Then a second equilibrium begins to establish itself, which completely takes over from about -140 °C on. The nature of the conformers involved is still unknown to us. Since no absorptivity change in the UV spectrum is observed they should be *s*-cis conformers with reserved stabilities of the opposite helicities caused perhaps by hydrogen bonding.

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**Registry No.** **1**, 91112-30-0; **2**, 91112-31-1;  $\beta$ -cyclocitral, 432-25-7; (*S*)-NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>, 513-49-5; (*S*)-NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>OH, 2749-11-3.

**Supplementary Material Available:** Plot of the dependence of UV extinction on temperature and CD spectra of **1** in methanol and isopentane (1 page). Ordering information is given on any current masthead page.

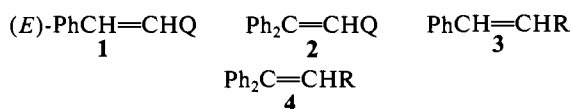
### Alkylation of $\beta$ -Substituted Styrenes by a Free Radical Addition-Elimination Sequence<sup>1</sup>

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We have found that the  $\beta$ -styrenyl or  $\beta,\beta$ -diphenylvinyl derivatives **1** and **2** undergo a free radical chain reaction with al-



a, Q = Bu<sub>3</sub>Sn; b, Q = HgCl; c, Q = HgBr; d, Q = I; e, Q = PhSO<sub>2</sub>; f, Q = PhSO; g, Q = PhS

kylmercury halides (RHgX) to yield alkenes **3** and **4** (Table I).

The reaction involves regioselective addition of R· to **1** or **2** followed by the  $\beta$ -elimination of Q·. The chain reaction continues by virtue of the attack of Q· upon RHgX to regenerate the alkyl

Table I. **1** or **2** + RHgCl → **3** or **4**

sub- strate	R (equiv)	conditions <sup>a</sup>	% <b>3</b> or <b>4</b> (E/Z)
<b>1a</b>	<i>i</i> -Pr (1.2)	PhH, S, 18 h	86 (11.5)
<b>1a</b>	<i>i</i> -Pr (1.2)	PhH, AIBN, 80 °C, 16 h	73 (15)
<b>1a</b>	<i>i</i> -Pr (1.2)	PhH, dark, 50 °C	0
<b>1a</b>	<i>i</i> -Pr (1.2)	PhH, S, DTNO, 16 h	35 (10)
<b>1a</b>	<i>i</i> -PrI (5)	PhH, R, 15 h	18
<b>1b</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 12 h	83
<b>1d</b>	<i>i</i> -Pr (2)	Me <sub>2</sub> SO, R, 14 h	76 (10)
<b>1d</b>	<i>i</i> -Pr (2)	Me <sub>2</sub> SO, Bz <sub>2</sub> O <sub>2</sub> , 100 °C	68 (19)
<b>1d</b>	<i>i</i> -Pr (2)	Me <sub>2</sub> SO, dark, 25 °C	0
<b>1e</b>	<i>i</i> -Pr (2)	Me <sub>2</sub> SO, R, 38 h	68 (6)
<b>1f</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R	20
<b>1g</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 18 h	35 <sup>b</sup> (6.5)
<b>2a</b>	<i>i</i> -Pr (5)	PhH, R, 28 h	73
<b>2c</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 12 h	96
<b>2c</b>	<i>i</i> -PrMgBr (2)	PhH, R	35
<b>2d</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 8 h	89
<b>2e</b>	<i>i</i> -Pr (2)	Me <sub>2</sub> SO, R	62
<b>2e</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R	87
<b>2g</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 96 h	55 <sup>c</sup>
<b>5</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R	55 <sup>d</sup>
<b>6</b>	<i>i</i> -Pr (5)	Me <sub>2</sub> SO, R, 38 h	35 <sup>d</sup>
<b>1a</b>	<i>t</i> -Bu (1.2)	PhH, S, 14 h	83 (49)
<b>1a</b>	<i>t</i> -BuBr (5)	PhH, AIBN, 80 °C	0
<b>1a</b>	<i>t</i> -BuBr (5)	PhH, R	0
<b>1b</b>	<i>t</i> -Bu (5)	Me <sub>2</sub> SO, R, 12 h	40
<b>1e</b>	<i>t</i> -Bu (2)	Me <sub>2</sub> SO, R, 16 h	43 (81)
<b>1f</b>	<i>t</i> -Bu (5)	Me <sub>2</sub> SO, R	32
<b>2a</b>	<i>t</i> -Bu (2)	PhH, 18 h	78
<b>2a</b>	<i>t</i> -BuBr (5)	PhH, R	0
<b>2c</b>	<i>t</i> -Bu (5)	Me <sub>2</sub> SO, R, 12 h	100
<b>2d</b>	<i>t</i> -Bu (5)	Me <sub>2</sub> SO, R, 14 h	86
<b>2e</b>	<i>t</i> -Bu (5)	Me <sub>2</sub> SO, R	88
<b>1a</b>	<i>n</i> -Bu (1.2)	PhH, R, 40 h	46 (6)
<b>1a</b>	<i>n</i> -BuI (2)	PhH, R, 30 h	62 (7)
<b>1d</b>	<i>n</i> -Bu (2)	Me <sub>2</sub> SO, R, 48 h	22
<b>5</b>	<i>n</i> -Bu (5)	Me <sub>2</sub> SO, R, 43 h	38 <sup>d</sup>
<b>1a</b>	$\Delta^3\text{-C}_6\text{H}_{11}$ (1.2)	PhH, 32 h	55 <sup>e</sup> (7)
<b>1a</b>	<i>c</i> -C <sub>5</sub> H <sub>9</sub> CH <sub>2</sub> (1.2)	PhH, R, 48 h	52 <sup>e</sup> (6)
<b>1a</b>	$\Delta^3\text{-C}_4\text{H}_7$ (1.2)	PhH, R, 36 h	45 (7)
<b>1a</b>	Cl <sub>3</sub> CCl	CCl <sub>4</sub> , R, 38 h	62 (19)
<b>1a</b>	MeO <sub>2</sub> CCH <sub>2</sub> Br	PhH, R, 44 h	38 (5)
<b>1b</b>	(EtO) <sub>2</sub> PO (1) <sup>f</sup>	Me <sub>2</sub> SO, R, 8 h	65 (10)
<b>1d</b>	(EtO) <sub>2</sub> PO (1) <sup>f</sup>	Me <sub>2</sub> SO, R, 8 h	85
<b>2a</b>	(EtO) <sub>2</sub> PO (3)	Me <sub>2</sub> SO, R	65
<b>2a</b>	(EtO) <sub>2</sub> PO (1) <sup>g</sup>	Me <sub>2</sub> SO, R	14
<b>2c</b>	(EtO) <sub>2</sub> PO (1) <sup>f</sup>	Me <sub>2</sub> SO, R, 12 h	85
<b>2c</b>	(EtO) <sub>2</sub> PO (3)	Me <sub>2</sub> SO, R, 2 h	59
<b>2c</b>	(EtO) <sub>2</sub> PO (3)	Me <sub>2</sub> SO, R, DTNO, 2h	0
<b>2d</b>	(EtO) <sub>2</sub> PO (3)	Me <sub>2</sub> SO, R, 2h	84
<b>2d</b>	(EtO) <sub>2</sub> PO (1) <sup>g</sup>	Me <sub>2</sub> SO, R	86
<b>2d</b>	(EtO) <sub>2</sub> PO (1) <sup>g</sup>	Me <sub>2</sub> SO, dark	0
<b>2c</b>	<i>c</i> -C <sub>6</sub> H <sub>11</sub> (1) <sup>h</sup>	PhH, S, 18	36
<b>2b</b>	<i>c</i> -C <sub>6</sub> H <sub>11</sub> (5) <sup>h</sup>	PhH, R, 2 h	37
<b>2e</b>	<i>c</i> -C <sub>6</sub> H <sub>11</sub> (5) <sup>h</sup>	PhH, R	23
<b>1f</b>	<i>c</i> -C <sub>6</sub> H <sub>11</sub> (5) <sup>h</sup>	PhH, R	33
<b>1d</b>	PhS (1) <sup>i</sup>	Me <sub>2</sub> SO, R	97
<b>2d</b>	PhS (1) <sup>i</sup>	Me <sub>2</sub> SO, R	100
<b>2c</b>	PhSO <sub>2</sub> (5) <sup>j</sup>	Me <sub>2</sub> SO, R, 12 h	100
<b>2c</b>	PhCOCH <sub>2</sub> (1) <sup>k</sup>	Me <sub>2</sub> SO, R, 13 h	64

<sup>a</sup> Typical conditions involved 1 mmol of substrate in 10 mL of nitrogen-purged solvent at 35-40 °C for 24 h unless otherwise specified: S = radiation by a 275-W sunlamp; R, radiation in a Rayonet reactor at 350 nm; DTNO = 10 mol% di-*tert*-butyl nitroxide; AIBN = azobisisobutyronitrile; Bz<sub>2</sub>O<sub>2</sub> = benzoyl peroxide. <sup>b</sup> A 50% yield of *i*-PrSPh observed. <sup>c</sup> 26% yield of *i*-PrSPh. <sup>d</sup> 2-Alkylbenzothiazole (7). <sup>e</sup> Only cyclopentylcarbinyl product observed. <sup>f</sup> (EtO)<sub>2</sub>POHgCl or ((EtO)<sub>2</sub>PO)<sub>2</sub>Hg. <sup>g</sup> ((EtO)<sub>2</sub>PO)<sub>2</sub>Hg. <sup>h</sup> (*c*-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>B. <sup>i</sup> (PhS)<sub>2</sub>Hg. <sup>j</sup> (PhSO<sub>2</sub>)<sub>2</sub>Hg. <sup>k</sup> (PhCOCH<sub>2</sub>)<sub>2</sub>Hg.

radical by either S<sub>H</sub>2 attack upon Hg for Q· = I, PhS·, PhSO·, PhSO<sub>2</sub>· or electron transfer and/or halogen atom transfer from RHgX to Q· in the case of Bu<sub>3</sub>Sn· or HgCl (Scheme I).<sup>3,4</sup> The

(3) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.

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