of unlabeled **2**. The quenching factor, 1.3027, was used to normalize the counts of samples of **2** from rearrangement.

Calculations of KIE were made as described earlier.[30]

Irradiation of 4-Methoxyphenyl Acetate (1), 2-Acetyl-4-methoxyphenol (2), and 4-Methoxyphenol for Spectroscopic Measurements. Solutions of these compounds were irradiated in the Rayonet reactor as described above. Samples (3 mL) were withdrawn at timed intervals for recording absorbance at 356 nm. Neither **1** nor 4-methoxyphenol absorb in this region. Data for irradiations of **1** in the absence and presence of propanethiol are given in Figure 1. They show the formation and slow decomposition of **2** in the absence of propanethiol and the formation and stability of **2** in its presence. Data for the prolonged irradiation of **2** alone and in the presence of propanethiol, 2,3-butanedione, and 4-methoxyphenol are given in Figure 2. Included in Figure 2 are data for the irradiation of 4-methoxyphenol alone. This compound was itself decomposed by prolonged irradiation at 300 nm, and the unknown product(s) of decomposition absorbed weakly at 356 nm.

The following absorbance data (λ_{max} [nm], ϵ) are pertinent: **1** (277, 1880; 223, 7030), **2** (356, 3860; 255, 6150; 224, 16,400), 4-methoxyphenol (292, 2990; 225, 5370). Absorbances recorded at 300 nm were as follows: for **1**, 0; for **2**, 500; for 4-methoxyphenol, 2250; for propanethiol, 0; for 2,3-butanedione, 25. Stratenus[18] has reported absorbances for ethanol solutions at particular intervals of wavelength, some of which correspond closely with our data, namely (λ_{max} [nm], ϵ) the following: **1** (275, 1846; 300, 0), **2** (360, 4063; 300, 357), **3** (290, 2880; 300, 2301).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE 8314947) for support of this research.

Registry No. **1**, 1200-06-2; [*o*-^{14}C]-**1**, 108868-06-0; **2**, 705-15-7; [2-^{14}C]azoxybenzene, 104946-11-4; 4-hydroxy[2-^{14}C]azobenzene, 108834-59-9; 4-methoxy[2-^{14}C]azobenzene, 108834-60-2; 4-methoxy[2-^{14}C]phenol, 108834-61-3; ^{18}*O*-4-methoxyphenyl acetate, 108867-96-5; ^{18}*O*-phenol, 108834-62-4; 4-methoxyphenyl [1-^{13}C]-acetate, 92658-26-9; 4-methoxyphenol, 150-76-5; 4-methoxyphenyl [1-^{14}C]acetate, 16282-21-6; [2-^{14}C]azobenzene, 108834-63-5; 4-methoxy[2-^{14}C]aniline, 108834-64-6; [2-^{14}C]aniline, 83548-27-0; 4-methoxybenzenediazonium tetrafluoroborate, 459-64-3; oxygen-18, 14797-71-8; carbon-14, 14762-75-5; carbon-13, 14762-74-4.

Ring–Chain Tautomerism in 1,3-Oxazines

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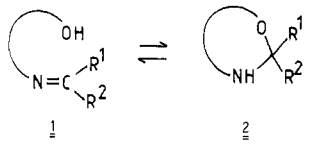
A comparative study on the ring–chain tautomerism of 49 2-(substituted-phenyl) tetrahydro-1,3-oxazines of seven different types, namely, tetrahydro-1,3-oxazines **3**, *r*-8a,*c*-2,*c*-4a- and *r*-8a,*c*-2,*t*-4a-1,3-perhydrobenzoxazines **5** and **7**, *r*-8a,*c*-2,*c*-4- and *r*-8a,*c*-2,*t*-4a-1,3-perhydrobenzoxazines **9** and **11**, 3,4-dihydro-2*H*-1,3-benzoxazines **12**, and 1,2-dihydro-4*H*-3,1-benzoxazines **13**, pointed out that in all cases the equilibria can be described with a simple equation,

$$\log K_X = (0.76 \pm 0.04)\sigma^+ + \log K_{X=H}$$

where K_X = [ring]/[chain] (X ≠ H). A factor *c* illustrating the sum of steric and electronic effects of substituents at C-4, C-5, and C-6 has also been introduced.

Ring–chain tautomerism has been studied extensively.[1b,c] The **1** ⇌ **2** equilibrium (eq 1) represents the ring–chain tautomerism in tetrahydro-1,3-oxazines,[1,2] 1,3-oxazolidines,[1,2] and related systems.[3] In the early reports the



(1)

1 2

tautomeric equilibria were studied with the aid of molecular refraction, IR and UV spectroscopy.[1,2] These methods cannot result in exact tautomer ratios. It has been found that the products from 3-aminopropanol and carbonyl compounds appear in a higher ratio of cyclic vs. chain structures than those from 2-aminoethanol and carbonyl compounds.[4] In both cases the relative amount of the ring form was increased by C-alkylation of the amino alcohols.[4,5] McDonagh and Smith[6] published the first quantitative data for the ring–chain tautomerism of 2-substituted 3,4-dihydro-2*H*-1,3-benzoxazines. Later a clear correlation of log K/K_0 values of 2-aryl-substituted 1,3-oxazolidines to the Hammett σ^+ was found[7] but not to σ values as suggested earlier.[6b]

Since the 1,3-oxazolidine ring formation represents a unfavored 5-endo-trig process according to the Baldwin rules,[9] several investigations of this type of ring–chain

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(7) (a) Paukstelis, J. V.; Hammaker, R. M. *Tetrahedron Lett.* **1968**, 3557. (b) Paukstelis, J. V.; Lambing, L. L. *Tetrahedron Lett.* **1970**, 299.

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Table I. Selected Chemical Shifts and Coupling Constants for Compounds 5d, 7d, 9d, and 11d[18]

compd	chem shifts, ppm				J, Hz		
	H-2	H-4_a	H-4_e	H-8a	4_a,4a	4_e,4a	4_a,4_e
5d							
A	5.18	3.27	2.90	3.97	3.5	1.1	−13.7
B	8.18	3.61	3.92	4.23	5.2	4.1	−12.4
7d							
A	5.22	2.72	3.11	3.40	11.3	4.3	−13.4
B	8.20	3.76	3.55	3.65	10.3	3.9	−12.5
9d							
A	5.16	3.99	3.94	3.22	2.5	ca. 1	−11.3
B	8.24	3.61	3.52	4.05	10.0	4.0	−11.0
11d							
A	5.21	3.51	4.07	2.58	11.0	4.0	−11.0
B	8.32	3.59	3.5	3.12	*a*	*a*	−11.0

[a] Cannot be determined because of the overlapping lines.

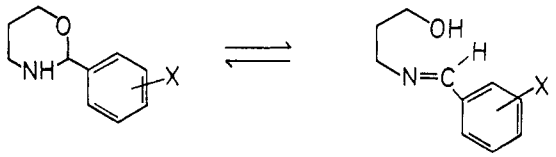
tautomerism have been conducted.[8] It should be noted that the ring–chain tautomeric equilibria depend strongly on solvent[5-7] and temperature[5-7] and that the equilibration occurs very rapidly, within a few seconds. Good linear plots were obtained in different solvents when eq 2 was applied.[8c] The ring–chain tautomerism of 1,3-oxazolidines

$$\log K_X = \rho\sigma^+ + \log K_{X=H} \qquad (2)$$

and 1,3-oxazines has been utilized also to synthesize aldehydes and N-substituted amino alcohols.[10] In hydrolytic decompositions of these ring systems the main routes can be explained by this tautomerism.[11]

In the case of 1,3-oxazines we could, however, find exact data only for 2-aryl-substituted 1,3-benzoxazines.[6b] For monocyclic 2-aryltetrahydro-1,3-oxazines there are only qualitative data for the tautomeric equilibria.[4]

The aim of this work is a quantitative study of the ring–chain tautomerism in 1,3-oxazines **3** and their four possible condensed analogues (**5**, **7**, **9**, and **11**).



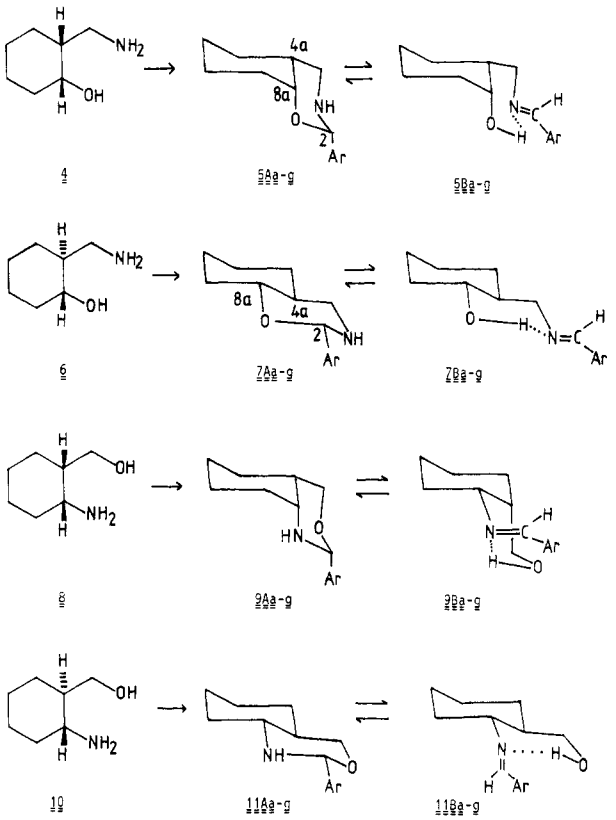
3Aa-g 3Ba-g

X = pNO_2: a, mNO_2: b, pCl: c, H: d, pCH_3: e, $pOCH_3$: f, $pN(CH_3)_2$: g[17]

Results and Discussion

Some 2-aryl-substituted tetrahydro-1,3-oxazines have been prepared earlier and their ring–chain tautomerism studied qualitatively by means of molecular refraction and IR spectroscopy.[4] Several analogous derivatives of perhydrobenzoxazines and their A ring homologues are also known in literature,[12,13] although the ring–chain tautomerism has not been mentioned.

Scheme I



In general, a mixture of an amino alcohol and an oxo compound[13] has been refluxed for a long period of time in different solvents (ethanol, benzene, dioxane, toluene) usually applying some water separation method. Contrary to the above we observed that 3-aminopropanol and amino alcohols **4**, **6**, **8**, and **10**[14] reacted with aromatic aldehydes even at room temperature in ethanolic solution within

(8) (a) Lambert, J. B.; Majchrzak, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3588. (b) Agami, C.; Rizk, T. *Tetrahedron* **1985**, *41*, 537. (c) Alva Astudillo, M. E.; Chokotho, N. C. J.; Jarvis, T. C.; Johnson, C. D.; Lewis, C. C.; McDonnell, P. D. *Tetrahedron* **1985**, *41*, 5919.

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(14) All compounds studied were racemates but in the formulas the C-1 atom of the starting amino alcohol and consequently the C-8a atom of the product has always the *R* configuration.[15]

(15) (a) "IUPAC Nomenclature of Organic Chemistry. Stereochemistry" *Pure Appl. Chem.* **1976**, *45*, 11. (b) Fülöp, F.; Bernáth, G.; Szabó, J. A.; Dombi, G. *J. Chem. Educ.* **1983**, *60*, 95.

Table II. Data for Linear Regression Analysis for Compounds 3, 5, 7, 9, and 11–13

	3	5	7	9	11	12	13
no. of points	7	7	7	7	7	7	7
slope	0.74	0.81	0.73	0.75	0.69	0.82	0.78
intercept	−0.15	0.42	0.50	0.79	1.30	−0.66	1.11
SE of the slope[a]	±0.06	±0.03	±0.04	±0.04	±0.04	±0.04	±0.025
SE of the intercept[a]	±0.05	±0.03	±0.04	±0.03	±0.04	±0.03	±0.02
correlation coefficient	0.984	0.996	0.991	0.993	0.990	0.995	0.997
c (see text)	0	0.57	0.66	0.94_5	1.45	−0.51	1.26_5

[a] SE = standard error.

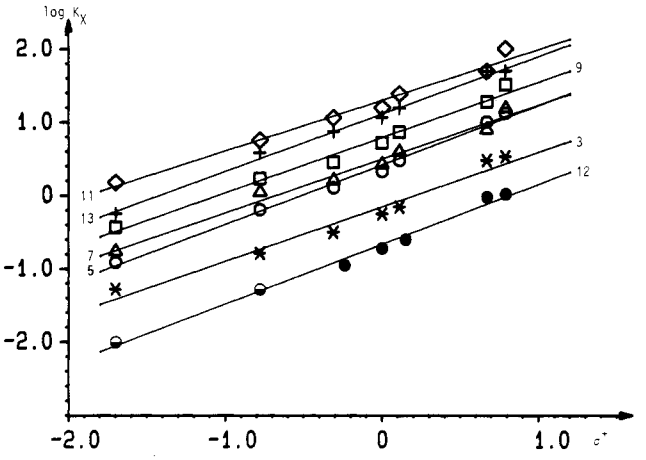


Figure 1. Plots of log K_X against σ^+ values for compounds **3**, **5**, **7**, **9**, and **11–13**.

15–120 min. In accord with earlier findings[12g,16] **4**, **6**, **8**, and **10** resulted in 1,3-oxazines stereospecifically with the following relative configurations: **5**, *r*-8a,*c*-2,*c*-4a; **7**, *r*-8a,*c*-2,*t*-4a; **9**, *r*-8a,*c*-2,*c*-4a; **11**, *r*-8a,*c*-2,*t*-4a.

The tautomer ratios were determined by integrating the signals of suitable, well-separated protons, mainly those of H-2 methine and H-2 methylene protons. In the 400-MHz NMR spectra the signals of the H-2, H-4_a, H-4_e, and H-8a protons were well separated in most cases. The aryl substituent did not cause any significant deviation in chemical shifts and coupling constants. The differences were generally less than 0.1 ppm and 0.2 Hz. Some selected data for 2-phenyl-substituted derivatives are summarized in Table I.

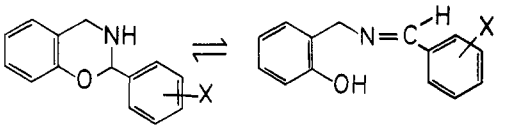
Previously[10b] it has been proven by dynamic NMR measurements that *trans*-2-*p*-nitrophenyl derivatives **7Aa** and **11Aa** attain diequatorial double chair connections and the cis counterparts **5Aa** and **9Aa** are conformationally homogeneous systems with O-in (**5Aa**) and N-in (**9Aa**) conformations. Since the chemical shifts and couplings constants of the other phenyl-substituted derivatives are the same it means that they have similar conformations. The chain forms **5B**, **7B**, **9B**, and **11B** (Table I) are stabilized by strong hydrogen bonds[19,20] and prefer conformations similar to those of the ring forms. It should be noted that **9B** attains the N-outside conformation (Scheme I) like N-substituted 3,1-perhydrobenzoxazines.[12g,21]

Table III. Correlation Parameters for the Linear Regression Analysis of the Rate Data for the N → O Acyl Migration in Compounds 4, 6, 8, and 10 against the c Values for Compounds 5, 7, 9, and 11

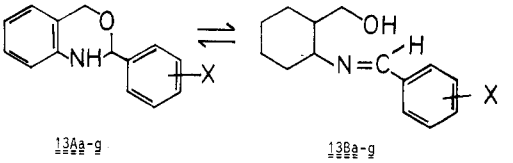
	substituent, X		
	H	NO_2	CH_3
no. of points	4	4	4
slope	0.97	1.12	0.98
intercept	−0.12	−0.49	−0.03
SE of the slope[a]	0.21	0.12	0.09_5
SE of the intercept[a]	0.20	0.11	0.09
correlation coefficient	0.957	0.989	0.991

[a] SE = standard error.

The inspection of the ring–chain tautomeric equilibria (Figure 1) points out that all five series give a good linear fit to eq 2.[22] The plots are practically parallel; therefore, we decided to compare them with the data for benzoxazine series. In case of 1,3-benzoxazines **12** there are some accurate data for ring–chain tautomeric equilibria.[6b] Since no data were available for negative σ^+ values, *p*-methoxy- and *p*-(dimethylamino)phenyl-substituted derivatives **12f** and **12g** were prepared. Although some 3,1-benzoxazine **13** derivatives have been prepared recently by independent authors,[8c,23] only two approximate equilibrium ratios were given (**13Aa/13Ba** = 20:1, **13Af/13Bf** = 4:1).[8c]



12Af,g 12Bf,g



13Aa-g 13Ba-g

Since the ring–chain tautomeric equilibria gave also linear and parallel plots for compounds **12** and **13**, according to eq 2, we conclude that for 1,3-oxazines the σ^+ contributions of the C-2 aromatic substituents are always similar. It means that eq 2 can be modified to eq 3.

$$\log K_X = (0.76 \pm 0.04)\sigma^+ + \log K_{X=H} \quad (3)$$

Because the monocyclic derivatives **3** have no steric and electronic substituent effects, the sum of steric and elec-

(16) (a) Argay, G.; Kálmán, A.; Fülöp, F.; Bernáth, G. *Acta. Chim. Hung.* **1981**, *109*, 39. (b) Pihlaja, K.; Mattinen, J.; Fülöp, F.; Bernáth, G. *Magn. Reson. Chem.* **1986**, *24*, 145.

(17) In compounds **3**, **5**, **7**, **9**, **11**, **12**, and **13** the letters **a–g** have the same meaning.

(18) For easy comparison of the spectroscopic data the same numbering has been used for the ring and chain forms.

(19) (a) Samitov, Yu. Yu.; Zhuk, O. I.; Boiko, I. P.; Unkovskii, B. V.; Malina, Yu. F. *Zh. Org. Khim.* **1974**, *10*, 1283. (b) Danilova, O. I.; Samitov, Yu. Yu.; Boiko, I. P.; Iakusheva, A. D.; Unkovskii, B. V. *Zh. Org. Khim.* **1984**, *20*, 2323.

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(21) (a) Sohár, P.; Gera, L.; Bernáth, G. *Org. Magn. Reson.* **1980**, *14*, 204. (b) Sohár, P.; Fülöp, F.; Bernáth, G. *Org. Magn. Reson.* **1984**, *22*, 527.

(22) Johanson, C. D. *The Hammett Equation*; Cambridge University: Cambridge, 1973; p 33.

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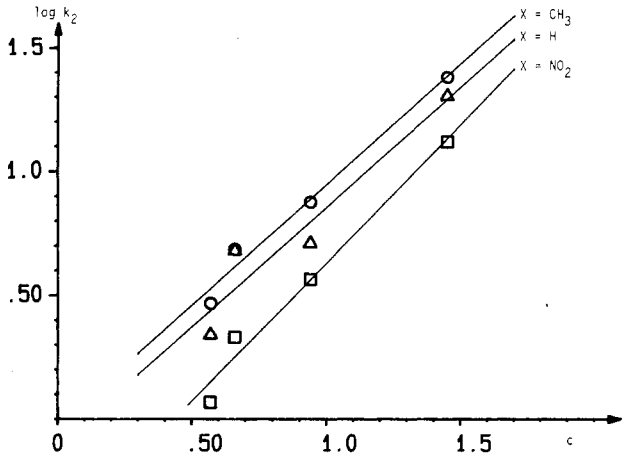


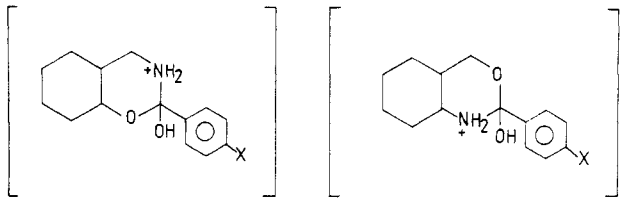
Figure 2. Plots of log k_2 against the c values of compounds **5**, **7**, **9**, and **11** for the acyl migration in compounds **4**, **6**, **8**, and **10**.

tronic effects (c) for substituted derivatives can be obtained from eq 4, where log $K_{X=H}$ = log [ring]/[chain] for phe-

$$\log K_{X=H} - \log K_0 = c \quad (4)$$

nyl-substituted derivatives with substituents on other than phenyl carbons and log K_0 = −0.15, the corresponding c value for **3** (actually the values of the intercepts [$\sigma^+ = 0$] in Table II were used). A positive c value means a stabilization of the ring form, whereas a negative c value indicates destabilization because of the substituents.

In the literature there are thorough kinetic investigations[24] on the N → O acyl migration in benzoyl derivatives of amino alcohols **4**, **6**, **8**, and **10**. Intermediates in this acyl migration are **14**–**17**.[24] When plotting the log of the sec-



ond-order rate constants[24a] (log k_2) of the N → O acyl migration against the c values for compounds **5**, **7**, **9**, and **11** (Figure 2) defined above (Table II), a remarkably good linear correlation was found for the three differently substituted[25] derivatives (Table III). This means that the constant c has a useful physical meaning and at the same time the good linear correlations give an indirect proof that the formation of bicyclic 1,3-oxazine intermediates **14**–**17** can be regarded as the rate-limiting step[26] in the N → O acyl migration process.

Experimental Section

General Methods. Melting points are uncorrected. The ^{1}H NMR spectra were recorded on a JEOL GX 400 FT-NMR spectrometer in $CDCl_3$ (3–5 mg per 2 cm^3), at ambient temperature with Me_4Si as internal standard. The number of scans was 40. If the amount of one of the tautomeric forms was less than 2%, the number of scans was 80. The determination of ring–chain tautomer ratios was generally based on the integrals of methylene and methine protons. If these protons were not well separated, other well-separated signals were used.

Materials. The 3-aminopropanol, *o*-aminobenzyl alcohol, and aromatic aldehydes were commercial products. *o*-Hydroxybenzylamine[27] and the alicyclic 1,3-amino alcohols **4**, **6**, **8**, and **10**[28] were prepared according to literature methods.

General Procedure To React Amino Alcohols with Aromatic Aldehydes. Freshly distilled or crystallized amino alcohol (1 mmol) was dissolved in 10 mL of absolute ethanol, and 1 mmol of freshly distilled or crystallized aldehyde was added. After the mixture was allowed to stand for 2 h, at room temperature, the solvent was evaporated off, and the products were crystallized. If an oily product was formed the evaporation was repeated twice after addition of benzene. All products were dried under vacuum for 24 h. According to their ^{1}H NMR spectra the oily products exhibited more than 97% purity. The yields varied from 85% to 95%. All compounds gave satisfactory microanalyses (C, H, N). Compounds **3**, **5**, **7**, **9**, **11**, and **13** with the exception of **13g** were prepared with this method. Compound **13g** was prepared as reported in the literature[23] by heating fused *o*-aminobenzyl alcohol and *p*-(dimethylamino)benzaldehyde at 150 °C for 5 min (yield, 68%).

Melting points, solvents for recrystallization (H, *n*-hexane; E, ethanol; HA, *n*-hexane/acetone), and the percentage of the ring form (%) are as follows.[17]

3a: 93–94 °C, H, 77% (lit.[4] mp 72–74 °C). **3b**: oil, 75%. **3c**: oil, 41%. **3d**: oil, 36% [lit.[4] bp 146 °C (4 mmHg)]. **3e**: oil, 24%. **3f**: oil, 14% [lit.[4] bp 163–164 °C (4 mmHg)]. **3g**: 96–97 °C, H, 5% (lit.[4] mp 95–95.5 °C).

5a: 101–102 °C, E, 93% (lit.[13a] mp 102.5–103 °C). **5b**: oil, 91%. **5c**: 90–91 °C, H, 75%. **5d**: 68–71 °C, H, 68%. **5e**: 78–70 °C, H, 56%. **5f**: 75–78 °C, H, 39%. **5g**: 96–97 °C, H, 11% (lit.[13b] mp 95–95.5 °C).

7a: 123–124 °C, H, 94% (lit.[13a] mp 123–123.5 °C). **7b**: 86–87 °C, H, 89%. **7c**: 129–131 °C, E, 80%. **7d**: 68–70 °C, H, 73%. **7e**: 70–71 °C, H, 62%. **7f**: 69–71 °C, H, 47%. **7g**: 93–94 °C, H, 15%.

9a: 124–125 °C, H, 97% (lit.[13a] mp 125–125.5 °C). **9b**: 65–66 °C, H, 95%. **9c**: 66–68 °C, H, 88% (lit.[29] mp 62–63 °C). **9d**: oil, 84%. **9e**: oil, 74%. **9f**: oil, 63%. **9g**: 93–95 °C, H, 27%.

11a: 87–88 °C, H, 99% (lit.[13a] mp 88–88.5 °C). **11b**: oil, 98%. **11c**: 115–116 °C, E, 96% (lit.[29] mp 107–108 °C). **11d**: 60–61 °C, H, 94%. **11e**: 85–86 °C, H, 92%. **11f**: oil, 85%. **11g**: 133–135 °C, HA, 60%.

12f: 119–120 °C, H, 5%. **12g**: 149–150 °C, H, 1% (lit.[6b] mp 151–153 °C).

13a: 116–117 °C, E, 98% (lit.[23] mp 114–115 °C, lit.[8c] mp 116–118 °C). **13b**: 93–94 °C, E, 98%. **13c**: 134–135 °C, E, 94% (lit.[23] mp 123–124 °C). **13d**: 119–120 °C, E, 92% (lit.[8c] mp 119–121 °C). **13e**: 125–127 °C, E, 88% (lit.[8c] mp 115–116 °C). **13f**: 147–149 °C, E, 79% (lit.[23] mp 135–136 °C, lit.[8c] mp 147–150 °C). **13g**: 129–132 °C, E, 36% (lit.[23] mp 136–137 °C).

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Registry No. **3Aa**, 109086-73-9; **3Ab**, 109086-74-0; **3Ac**, 109086-75-1; **3Ad**, 17762-72-0; **3Ae**, 109086-76-2; **3Af**, 109086-77-3; **3Ag**, 109086-78-4; (±)-**4**, 109087-13-0; (±)-**4** (*N*-PhC(O)) deriv), 109087-02-7; (±)-**4** (*N*-(*p*-$NO_2C_6H_4C(O)$) deriv), 109087-03-8; (±)-**4** (*N*-(*p*-$MeC_6H_4C(O)$) deriv), 109087-04-9; (±)-**5Aa**, 81969-58-6; (±)-**5Ab**, 109214-78-0; (±)-**5Ac**, 109214-79-1; (±)-**5Ad**, 109214-80-4; (±)-**5Ae**, 109214-81-5; (±)-**5Af**, 109214-82-6; (±)-**5Ag**, 109214-83-7; (±)-**5Bd**, 109087-16-3; (±)-**6**, 109087-14-1; (±)-**6** (*N*-(PhC(O)) deriv), 109087-05-0; (±)-**6** (*N*-(*p*-$NO_2C_6H_4C(O)$) deriv), 109087-06-1; (±)-**6** (*N*-(*p*-$MeC_6H_4C(O)$) deriv), 109087-07-2; (±)-**7Aa**, 109214-66-6; (±)-**7Ab**, 109086-79-5; (±)-**7Ac**, 109086-80-8; (±)-**7Ad**,

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Supplementary Material Available: Analytical and ^1H NMR data for new 1,3-oxazine derivatives **3a–g**, **5a–g**, **7a–g**, **9a–g**, **11a–g**, **12f,g**, and **13a–g** (9 pages). Ordering information is given on any current masthead page.

Dilithiation of α,β-Disubstituted Activated Olefins: α,β-Dilithiocinnamonitrile

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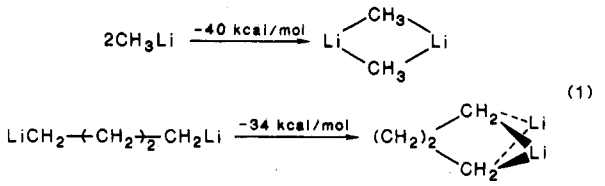
cis- and *trans*-cinnamonitrile were treated with an excess of LDA in an aprotic medium to give a high yield of one preferred isomer of PhC(Li)=C(CN)Li (C.N.-2Li). The chemistry and stereochemistry of its reactions with various electrophiles (MeOD, MeI, IBuI, RCHO, MeSSMe) was studied and discussed. α-Substituted and α,β-disubstituted derivatives of *cis*- and *trans*-cinnamonitrile were obtained. The reaction with MeOD resulted exclusively in a quantitative yield of *trans*-PhCD=CDCN. It is suggested that substitution at C_α takes place first to yield an equilibrium mixture of the corresponding β-lithiated intermediates: *cis*-PhC(Li)=C(E)CN and *trans*-PhC(Li)=C(CN)E. The type and structure of the products obtained in the reaction of this equilibrium mixture with electrophiles depends on factors affecting the nucleophilic reactivity and configurational stability of the C_β–Li bond of each of these two β-lithiated cinnamonitrile derivatives.

Organolithium compounds, usually referred to as "carbanions" because of their chemical behavior, are actually aggregates not only in the solid state but also in solution in coordinating solvents.[1] The tetramerization energy of CH_3Li, for example, is about 125 kcal/mol[2] and even highly coordinating ligands (e.g., TMEDA) are incapable of dissociating this tightly bound cluster. A remarkable number of organic species loosely called "dianions" or "polyanions" are useful synthetic intermediates.[3] The ease of formation of dianions is clearly manifested by the very small ΔpK_a ($pK^2_{CsCHA} - pK^1_{CsCHA}$) values obtained for various carbon acids such as 9,10-dihydroanthracene (pK_a^1 = 30.31, pK_a^2 = 34.1),[4] 2,2′-biindenyl[5] (pK_a^1 = 19.8, pK_a^2 = 20.3), and 9,9′-bifluorenyl (pK_a^1 = 20.5; pK_a^2 = 20.7).[5]

Metallic counterions are intimately involved in stabilizing these polyanionic systems, which might otherwise be unstable because of electrostatic repulsion. Calculations[1,5] and crystallographic studies have clearly shown that double lithium bridging is an extremely common feature of polylithiated compounds. Double lithium bridging might be regarded as the intramolecular equivalent of the dimerization of an organolithium compound. Thus, for example, the cyclization energy for converting extended 1,4-dilithiobutane into the doubly bridged conformation approaches that of the dimerization energy of CH_3Li (eq 1).[6]



(1)

The following are some typical examples of dilithium compounds having a double lithium bridged structure as confirmed by either X-ray crystallography and/or by calculation:

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