Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 421 recording spectrometer in Nujol mulls, the NMR spectra were recorded on a Varian A-60D spectrometer, and the mass spectra were determined on an Atlas CH-4 spectrometer.

α-Chloro-o-tolyl Methyl Sulfoxide (3). *m*-Chloroperoxybenzoic acid (85% pure, 40.1 g; 0.186 mol) in chloroform (400 mL) was added dropwise over a 0.5-h period to a stirred solution of **2**[3] (32 g; 0.186 mol) in chloroform (180 mL) maintained at −20 to −10 °C. Stirring was continued for 1.5 h at −20 to −10 °C and the reaction mixture was allowed to stand at 4 °C for 16 h. The precipitate was removed by filtration and the filtrate was extracted with saturated sodium hydrogen carbonate solution containing sodium sulfite (3 × 200 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was recrystallized from hexane to afford 18.96 g (54%) of **3**: mp 65–7 °C; IR 665, 690, 745, 780 (aromatic CH/other), 965, 1020, 1060 (S=O), 1645, and 1670 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.83 (s, 3 H, $SOCH_3$), 4.73 (d of d, 2 H, J = 11 Hz, CH_2Cl), 7.30–7.77 (m, 3 H, aromatic), 7.95–8.17 (m, 1 H, aromatic); mass spectrum *m/e* 188 and 190 (M^+). Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.77; Cl, 18.83; S, 16.98. Found: C, 51.05; H, 4.88; Cl, 18.88; S, 17.08.

1-Methyl-1*H*,3*H*-1,2-benzisothiazole 1-Oxide (4) and Its Hydrochloride (5). A mixture of **3** (7.52 g; 0.041 mol), concentrated sulfuric acid (25 mL), and chloroform (170 mL) was heated to 45 °C and sodium azide (13.9 g; 0.212 mol) was added portionwise over a 2-h period with stirring. The mixture was stirred at 45 °C for an additional 16 h and cooled. The precipitate (I) was removed by filtration, dissolved in water (800 mL), and made basic (pH 12) with 6 N sodium hydroxide. The basic solution was stirred at ambient temperature for 0.5 h and extracted with dichloromethane (3 × 500 mL). The combined extracts were dried (Na_2SO_4) and the solvent was removed in vacuo and the residue was recrystallized from ether to afford 4.44 g (65%) of **4**: mp 81–4 °C; IR 790, 785, 765, 760, 750 (ortho CH), 1255, 1225, 1215, 1185, 1170, 1080, 975, 965, 865 (N=S=O/CH), 1595, 1580 (C=C), 3080, 3060 cm^{-1} (=CH); NMR ($CDCl_3$) δ 3.37 (s, 3 H, CH_3), 4.76 (d of d, 2 H, J = 17 Hz, CH_2), 7.30–8.00 (m, 4 H, aromatic); mass spectrum *m/e* 166 and 167 ($M^+ - 1$) and (M^+). Anal. Calcd for C_8H_9NOS: C, 57.48; H, 5.39; N, 8.38; S, 19.16. Found: C, 57.55; H, 5.70; N, 8.44; S, 18.82.

Compound **4** (3.95 g; 0.0235 mol) was dissolved in ether and treated with ethereal hydrogen chloride. The precipitate was recrystallized from ethanol–ether to afford 4.08 g (85%) of **5**: mp 138–141 °C dec; IR 760 (ortho CH), 990, 1050, 1250 (N=S=O), 1580, 1600 cm^{-1} (C=C); NMR (Me_2SO-d_6) δ 4.32 (s, 3 H, CH_3), 4.95 (s, 2 H, CH_2), 7.76–8.17 (m, 3 H, aromatic), 8.38–8.63 (m, 1 H, aromatic); mass spectrum *m/e* 166 and 167 ($M^+ - 1$) and (M^+) for free base; high resolution mass spectrum *m/e* 167.0409, Calcd for C_8H_9NOS *m/e* 167.0405. Anal. Calcd for $C_8H_{10}ClNOS$: C, 47.17; H, 4.91; Cl, 17.44; N, 6.88; S, 15.72. Found: C, 47.13; H, 5.20; Cl, 17.59; N, 7.04; S, 15.86.

Thermolysis of 5. Compound **5** (1 g; 4.9 mmol) was heated at 155 °C for a period of 20 min to afford 0.62 g (94%) of 1,2-benzisothiazole (**6**). The analytical sample was recrystallized from pentane to afford colorless crystals: mp 34.5–35.5 °C (lit.[9] mp 37 °C); NMR ($CDCl_3$) δ 7.27–7.72 (m, 2 H), 7.87–8.23 (m, 2 H), 8.94 (s, 1 H); mass spectrum *m/e* 135 (M^+);[10] high resolution mass spectrum *m/e* 135.0136, Calcd for C_7H_5NS *m/e* 135.0143. Anal. Calcd for C_7H_5NS: C, 62.22; H, 3.70; N, 10.37; S, 23.70. Found: C, 62.09; H, 3.78; N, 10.52; S, 23.33.

Compound **5** was heated at ca. 150 °C and the gaseous material was analyzed by IR. The IR spectrum consisted of absorptions characteristic of methyl chloride; however, technical difficulties precluded the positive identification of water. Water was identified as a product when **5** was heated at 150 °C in a small flask equipped with a condenser. The liquid which collected in the condenser was identified as water by NMR (neat).

Kinetic Study for Conversion of 5 and 5a to 6. Compounds **5** (1.30 g; 6.40 mmol) and the corresponding hydrobromide (**5a**) (1.59 g; 6.40 mmol) were separately dissolved in Me_2SO (28 mL) and heated at 110 ± 3 °C. At timed intervals aliquots (2.00 mL) were removed and added to water (10 mL) and extracted with dichloromethane (2 × 5 mL). The combined extracts were washed with water (15 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the residues were dissolved in acetone (0.25 mL). GC analyses of 2.0-μL aliquots were performed on a Hewlett Packard Model 5700A gas chromatograph with a Supelco 3 ft 3% OV-225 on 80/100 Supelcoport column. The instrument was previously calibrated with known amounts of 1,2-benzisothiazole. Least-squares analyses of the data showed that **5a** decomposed ca. 4 times more rapidly than did **5**.

Acknowledgment. We are grateful to the Physical and Analytical Department of The Upjohn Company for determining the elemental analyses, infrared spectra, and mass spectra.

Registry No.—**1**, 33384-77-9; **2**, 26190-68-1; **3**, 65442-16-2; **4**, 65442-17-3; **5**, 65442-18-4; **5a**, 65442-19-5; **6**, 272-16-2; I, 65442-21-9.

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Base-Catalyzed Cis–Trans Isomerization of Bis(4-benzylideneaminocyclohexyl)methane

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Exhaustive hydrogenation of bis(4-aminophenyl)methane (**1**) to bis(4-aminocyclohexyl)methane (**2**) in the presence of noble metal catalysts under mild conditions produces predominately the kinetically favored cis,cis isomer **2a.**[1] This is in contrast to the hydrogenation run using cobalt or nickel (or its compounds) as catalyst at high temperature (above 200 °C) and high pressures (above 130 atm) of hydrogen which yields an amine mixture containing larger amounts of the thermodynamically favored cis,trans and trans,trans isomers **2b** and **2c,** respectively.[2,3]

Since an isomer mixture enriched in *trans,trans*-**2c** is a major component of several novel polyamide fibers, attempts have been made to convert cis,cis- and cis,trans-rich isomer mixtures into **2c.** Most processes involve heating of cis-rich products with metal (predominately from group 8) catalysts in the presence of hydrogen but the degree of isomerization to **2c** seldom exceeds 50%.[4] Consequently, hydrogenating **1** in the presence of ruthenium catalysts at high temperature and pressure leads directly to trans-rich mixtures of **2.**[5] In addition, several patented processes deal with the separation of the trans,trans isomer from crude hydrogenation mixtures.[6]

We have found a method to isomerize the bis(benzaldimines) **3a** and **3b** of **2a** and **2b** into *trans,trans*-**3c** on treatment with base under very mild conditions. Deprotonation on C-4 and C-4′ of the cyclohexane rings adjacent to the CN double bonds (giving **4a**) will lead to a partial charge distribution over the C–N–C unit with formation of an isomeric azaallylic carbanion **5** and eventually will result in an enrichment of the thermodynamically favored trans,trans-imine **3c** via **4b.**[7] (See Scheme II.)

Thus greater than 90% yield of **3c** is realized on stirring a suspension of **3a** in 1,2-dimethoxyethane (DME) in the presence of 20 wt % of potassium *tert*-butoxide at room temperature for 60–70 h. No significant amounts of by-products

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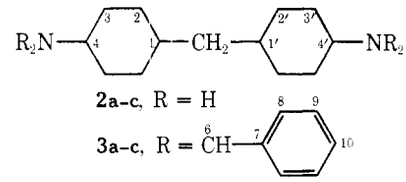
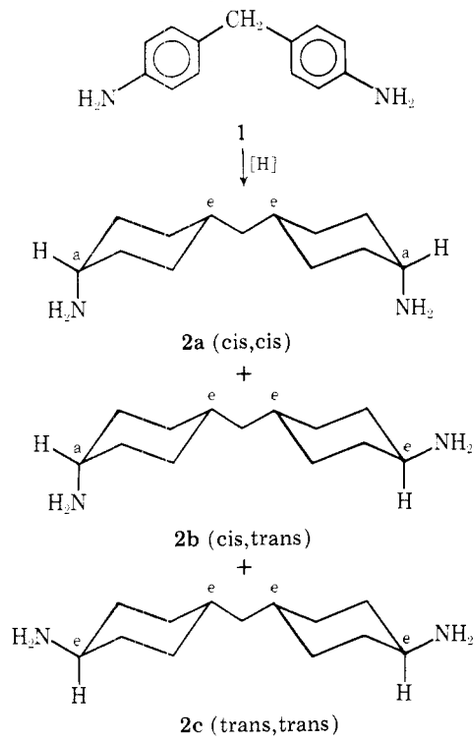
Table I. ^{13}C Chemical Shifts of 2 and 3 (ppm from Me_4Si)[a]



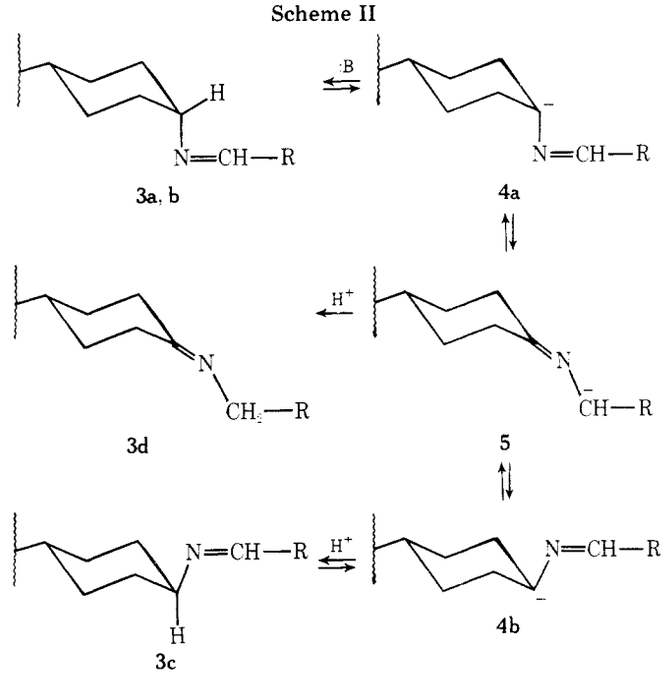
Compd	Registry no.	Cl(Cl′)	C2(C2′) or C3(C3′)	C3(C3′) or C2(C2′)	C4(C4′)	C5	C6(C6′)	C7(C7′)	C8 or C9	C9 or C8	C10
2a	6693-31-8	47.7	32.6	27.9	32.5	40.0					
2b	6693-30-7	50.8 (47.6)	32.3	36.6 (27.8)	33.9	42.2					
2c	6693-29-4	50.8	32.4	36.7	33.9	44.5					
3a	63418-35-9	67.4	31.7	28.5	32.5	39.7	158.0	137.0	128.5	128.1	130.2
3b	63492-46-6	67.4 (70.4)	31.8 (34.3)	32.0 (28.5)	32.4 (34.1)	42.4	158.1 (158.6)	137.0 (136.8)	128.5	128.1	130.2
3c	63492-47-7	70.4	34.2	32.0	33.9	45.0	158.7	136.8	128.5	128.1	130.3

[a] The resonance assignments were made on the basis of the absolute intensities of the resonances, off-resonance coupling experiments, and the chemical shifts of **2** and **3**.

Scheme I



Scheme II



are formed and **3c** can be isolated on diluting the reaction mixture with water. Isomerization conducted with 20 wt % of potassium hydroxide and 2–5 wt % of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) or 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Kryptofix 222) give virtually the same results. In addition we found that the solvent/substrate ratio influences the degree of isomerization: High concentrations of imine tended to give more than 90% yield of **3c** while lower concentrations left some **3a** and **3b** unchanged. Precipitation of **3c** during the reaction seems to push the equilibrium toward the right. Too small amounts of solvent, however, resulted in insufficient mixing of the reagents and hence incomplete isomerization. Many other attempts to conduct the isomerization of cis-rich mixtures of **3** with other bases or base/phase transfer agent combinations ($NaOCH_3$, $NaOC_2H_5$, NaH, $KOCH_3$, KOC_2H_5, LiOH, or KOH/*N,N,N′,N′*-tetramethylethylenediamine or benzyltrimethylammonium hydroxide) or with Schiff bases derived from **2** and carbonyl compounds other than benzaldehyde (salicylaldehyde, *p*-nitrobenzaldehyde, pyridine-2-aldehyde, acetone, isatin) gave less favorable results.

The possibility of forming bis(4-iminocyclohexane)methane derivatives of type **3d** via the anion **5** during base treatment is remote: Isomerization studies on ketimines derived from cyclohexanones and benzylamine in the presence of base showed the almost exclusive formation of mixtures of the isomeric benzylidene cyclohexylamines.[8]

Liberation of the *trans,trans*-**2c** from **3c** is accomplished best by treatment with dilute hydrochloric acid at 50–60 °C; the by-product benzaldehyde can also be recovered quantitatively. Another method of enriching *trans,trans*-**2c** involving no hydrolytic process is based on the ability of imines to add amines to its CN double bond giving aminals in a reversible equilibrium. Dissolving *trans,trans*-**3c** and an isomer mixture of **2** high in cis contents (Σcis:Σtrans ≃ 72:28; sample obtained from low temperature–low pressure hydrogenation of **1** with Ru catalyst) in an inert solvent leads to an exchange

between **2** and **3** via aminals as shown below in eq 1. After standing for about 24 h at room temperature, the trans isomer content of **2** increased to ~65%. Separation of the resulting **2** and **3** was not attempted but should be possible by distillation or fractional crystallization. Repeated equilibration with trans-enriched samples of **2** and **3c** would even further increase the trans content of **2**.

$$R'NH_2 + R''N{=}CHR''' \rightleftarrows \begin{matrix} R'NH \\ \diagdown \\ \quad CHR''' \\ \diagup \\ R''NH \end{matrix} \rightleftarrows R''NH_2 + R'N{=}CHR''' \quad (1)$$

R' = cis-R; R'' = trans-R; R''' = C_6H_5

The isomer distribution in all samples of amine **2** and imine **3** can be measured from the ^{13}C-NMR spectra of the samples. Use of ^{13}C rather than H NMR for the analysis is desirable as shift reagents are needed to separate coincident peaks in the proton spectra of the isomer mixtures.[9] Table I lists the ^{13}C chemical shifts of the compounds studied. The chemical shifts of several carbon positions, especially C-5, differ sufficiently to determine the isomer distribution by integration of peak areas.

Experimental Section[10]

Starting Materials. The required isomeric bis(4-benzylideneaminocyclohexyl)methanes **3a, 3b,** and **3c** were prepared by heating benzene (or toluene) solutions of the corresponding amine **2a, 2b,** or **2c** with 2 mol of benzaldehyde. The reaction flask is connected to a water separator and heating is continued until water separation is completed. Evaporation of solvent yields the imines in colorless crystals. Samples are recrystalized for analysis from chloroform–methanol (**3a** and **3c**) or methanol–water (**3b**); ^{13}C-NMR data are listed in Table I. **3a:** mp 132–133 °C; colorless plates; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.69; H, 9.02; N, 7.07. **3b:** mp 98–99 °C; colorless crystals; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.94; H, 8.83; N, 71.4. **3c:** mp 153–154 °C; colorless needles; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 84.00; H, 8.71; N, 7.19.

Cis–Trans Isomerization of 3a to 3c. (a) With Potassium *tert*-Butoxide. A 3.0-g sample of **3a** is suspended in 6 mL of 1,2-dimethoxyethene (DME). After adding 0.6 g of potassium *tert*-butoxide the mixture is stirred for 64 h under a blanket of nitrogen at room temperature, after which the thick suspension is diluted with water (ca. 40–50 mL). Colorless or nearly colorless crystals are left undissolved which are filtered off and after being washed with water are dried at 70 °C; yield 3.0 g, ^{13}C-NMR analysis gives an overall cis–trans ratio of 7:93. Stirring of the crude product with methanol and filtration leaves essentially pure **3c.**

(b) With Potassium Hydroxide–18-Crown-6. A mixture of 5.0 g of isomeric imines **3** with a cis–trans ratio of 72:28, 1.0 g of powdered potassium hydroxide, and 0.2 g of 18-crown-6 is suspended in 10 mL of DME and stirred for 95 h at room temperature in a nitrogen atmosphere. The resulting suspension is diluted with 50–60 mL of water, filtered, and dried at 70 °C, 5.0-g yield. ^{13}C NMR shows the crude material to contain more than 95% trans imine. Similar experiments with about 2–4 wt % Kryptofix 222 instead of 18-crown-6 give comparable results.

Hydrolysis of 3c. A solution of 10.0 g of **3c** in 100 mL of 2 N hydrochloric acid is kept at 50 °C for ca. 60 min. Hydrolysis is indicated by separation of droplets of benzaldehyde. The resulting mixture is extracted with methylene chloride (4 × 10 mL) after cooling. Drying the extracts with sodium sulfate and evaporation of solvent lead to quantitative recovery of benzaldehyde.

On adjusting the pH of the aqueous phase to 9–10 by adding 30% sodium hydroxide solution the *trans,trans*-amine **2c** is separated in fine droplets, which crystalize on scratching. Extraction with methylene chloride (4 × 10 mL) gives 5.5 g (quantitative) of crude **2c** after evaporation of solvent, mp (hexane) 63 °C (Lit.[11] 64–64.4 °C), identical in IR comparison with authentic **2c.**

Equilibration between 3c and an Isomer Mixture of 2. A mixture of isomers of **2** (1.05 g, 0.005 mol), having an overall cis–trans ratio of 71:29, is dissolved in 6 mL of methylene chloride together with 1.93 g (0.005 mol) of **3c.** ^{13}C-NMR analysis of the mixture after 24 h reveals a change of the cis–trans ratio of the amine **2** to 33:66 and of the imine **3** to 35:65.

Registry No.—**1,** 101-77-9; benzaldehyde, 100-52-7.

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Intramolecular Aldol Condensation of 2,2'-Dimethylbenzil

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During the base-catalyzed condensation of 2,2'-dimethylbenzil (**1**) with 1,3-diphenyl-2-propanone to prepare the reddish-black 2,5-diphenyl-3,4-bis(*o*-tolyl)cyclopentadienone,[1] a crystalline, colorless side product (**2**) was isolated in 9% yield, mp 155–157 °C. Ultimate analysis agreed with the formula $C_{16}H_{14}O_2$, identical with that of the starting material, 2,2'-dimethylbenzil. **2** was insoluble in aqueous alkali. Treatment of **2** with alkali in alcohol restored a yellow color. The infrared spectrum showed the following peaks: 3400 (s, tertiary OH), 1700 cm^{-1} (s, C=O), 1602 (m, Ar), 1210 (s, C—O, C=O), 1055 (s, CO), 960 (w, Ar), and 745, 730, and 715 cm^{-1} (ortho-disubstituted Ar). The 300-MHz NMR spectrum ($CDCl_3$) revealed peaks at δ 2.348 (3 H, s, $ArCH_3$), 2.86 (1 H, s, OH), 3.58 (2 H, s, $ArCH_2$), 7.16 (1 H, m, tolyl H_3), 7.24 (2 H,

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