The dinickel tetrathiolene-like complex **2** (Figure 1) possesses crystallographic C_{2h}–$2/m$ symmetry; the central $NiS_2C_2S_2Ni$ fragment conforms within experimental error to a planar D_{2h} geometry, which is analogous to that of the organic pentalene dianion. Prime evidence that the π system of the bimetallic-coordinated tetrathiooxalate ligand in **2** is highly delocalized (unlike that of the bimetallic-coordinated dithiooxalato ligand[20]) not only is in accordance with its redox behavior[16] but also is consistent with the Ni–S, S–C, and C–C bond lengths of 2.122 (1), 1.718 (3), and 1.360 (11) Å, respectively, being similar to those found[21] in the neutral nickel bis(1,2-dithiolene) complexes. The selective, facile, *head-to-head*, quantitative dimerization of CS_2 in **2** may be attributed to each Ni(I) in the coreactant $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ functioning as a one-electron reductant as well as a chelating sulfur acceptor. The only previously reported example of a *head-to-head* C–C coupling of another cumulene (or heteroallene) is the reduction of *p*-tolylcarbodiimide by the d^2 Ti(II) $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ to the presumed d^1 Ti(III) tetra-*p*-tolyloxalylamidine complex $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2(NR)_4)$,[2b] whose planar $Ti(RN)_2C_2(NR)_2Ti$ fragment is strikingly similar to the $NiS_2C_2S_2Ni$ fragment in **2**.

The hexanickel molecule **1** (Figure 2) of crystallographic C_s–m site symmetry closely conforms to a centrosymmetric C_{2h} geometry with the pseudo-2-fold axis directed along the C–C′ bond. Direct evidence for the breakdown of the dithiolene-like electron delocalization due to this formal adduct formation of **1** from **2** is given by the similar values of the six independent Ni–S bond lengths of range 2.160 (6)–2.184 (7) Å and mean 2.173 Å being significantly longer than those in **2**. Formal valence electron considerations suggest that this molecule can likewise be viewed as containing a tetrathiooxalato dianion together with six d^8 Ni(II), six $C_5H_5^-$ ligands, and two S^{2-} ligands.[22–24]

Current studies are underway to determine whether **2** may serve as a convenient chemical precursor to other interesting organic species (e.g., tetrathiofulvalene complexes via reactions with acetylenes). So that the reactivity of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ with other cumulenes can be explored, reactions with phenyl isocyanate, diphenylcarbodiimide, various isothiocyanates, COS, and CO_2 are also being carried out.

Acknowledgment. This research was supported by the National Science Foundation. Thanks are due to Mark H. Englert and Mark A. Murphy for their assistance in parts of the experimental work.

Registry No. 1, 82281-75-2; **2**, 82281-72-9; $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2$, 12170-92-2; $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$, 69239-93-6; CS_2, 75-15-0.

Supplementary Material Available: Listings of atomic parameters for both $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}S)]_2(C_2S_4)\cdot C_6H_6$ (Table I) and $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (Table II) (4 pages). Ordering information is given on any current masthead page.

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(19) $[Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (fw 540.16): parallelepiped-shaped crystals acquired from slow evaporation of a benzene solution; the crystal data conform to tetragonal D_{4h} Laue symmetry with $a = b = 12.924$ (6) Å, $c = 14.342$ (5) Å, $V = 2395$ (2) Å^3, $\rho_c = 1.50$ g/cm^3 for $Z = 4$. An incoherent twinning model involving an individual orthorhombic single-crystal component of symmetry *Pbam* was used to solve the crystal structure. The procedures for solving and refining such crystal data which suffer from diffraction enhancement and twinning are given elsewhere.[1a] Least-squares refinement of the twinned structure with RAELS[18] gave $R_1(F) = 4.9\%$ and $R_2(F^2) = 13.8\%$ for 919 independent diffractometry collected reflections with $I > 2.5\sigma(I)$.

(20) Hollander, F. J.; Leitheiser, M.; Coucouvanis, D. *Inorg. Chem.* **1977**, *16*, 1615–1619. Leitheiser, M.; Coucouvanis, D. *Ibid.* **1977**, *16*, 1611–1614 and references cited therein. Coucouvanis, D., In "Transition Metal Chemistry: Current Problems of General, Biological and Catalytic Relevance", Müller, A., Diemann, E.; Eds.; Verlag Chemie GmbH, Weinheim, 1981, pp 59–89.

(21) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295–369.

(22) Alternatively, the bridging C_2S_4 ligand in **1** may be regarded as a tetraanion of ethylenetetrathiol[10,23] coordinated to two electron-coupled d^7 Ni(III) and four d^8 Ni(II). Lappert and co-workers[23,24] have shown that related electron-rich poly(organosulfur) olefins have afforded an extensive metal coordination chemistry via reactions with a variety of transition-metal substrates.

(23) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1975**, 683–684.

(24) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. *J. Chem. Soc., Dalton Trans.* **1979**, 434–440 and references therein.

Studies of Exciplexes in Mixed Crystals. Activation Energy for a Solid-State Photoaddition Reaction Proceeding via an Exciplex

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Exciplex intermediacy has been postulated for many photoaddition reactions, although the number of such reactions where this species has actually been observed is much smaller.[1] Only in recent years has exciplex intermediacy been demonstrated for certain photoadditions;[2] in most cases this was achieved by showing[2a–f] that certain additives quenched exciplex fluorescence and photoaddition in solution to the same extent without quenching the initial monomer excited state.

In this communication we suggest an alternative approach for studying certain exciplex-forming systems and/or heterophotoaddition reactions, which is based on the use of solid solutions.[3] In this approach the system is studied in a mixed crystal of the interacting species.[4a] The main advantages of the present approach over solution studies are (a) the ground-state geometries of the interacting molecules are fixed and can be determined by various techniques,[5] (b) measurements may usually be performed over a wide temperature range (up to the crystal melting point), which enables determination of activation energies, and (c) energy transfer in crystals is frequently very efficient and so exciplex fluorescence may be observed exclusively, enabling determination of exciplex fluorescence quantum yields and, as shown here, evaluation of the role of an exciplex in a photoaddition reaction.

The above approach is demonstrated by studying the solid-state heterophotodimerization between 9-cyanoanthracene (9-CNA) and 9-methoxyanthracene (9-MeOA) in 9-CNA host crystals doped with 9-MeOA. It has been shown[4a,b] that this system also exhibits exciplex emission. At room temperature a 9-MeOA (guest) concentration of 4% causes quenching of about 95% of the host excited states by exciplex formation;[4a] the major channel of energy transfer through the crystal is the 9-CNA excimer level.[4b,c] At low temperatues (<100 K) when excimer-level transfer is inhibited, the exciplex may nevertheless be populated by direct excitation at tail absorption (450 nm) since the absorption of a mixed crystal containing heteropairs is slightly red-shifted with respect to that of the pure host.[4a]

In the present work it is proven (without the need to introduce supplementary quenchers) that the above-mentioned photodimerization proceeds via the exciplex. Arrhenius-type analysis of exciplex fluorescence parameters yields the activation energy for photodimerization as well as a calculated quantum yield of photodimerization in good agreement with experiment.

Exciplex intermediacy in the photodimerization may be proven or eliminated by simultaneously monitoring the exciplex fluorescence quantum yield (ϕ_F) and decay time (τ) as functions of temperature. It has been observed[4a] that the yield of photoproduct, which is measurable at room temperature, is zero at 77

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(1) For recent reviews see: Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45–50. Lewis, F. D. *Ibid.* **1979**, *12*, 152–158.

(2) (a) Caldwell, R. A.; Smith, L. *J. Am. Chem. Soc.* **1974**, *96*, 2994–2996. (b) Creed, D.; Caldwell, R. A. *Ibid.* **1974**, *96*, 7369–7371. (c) Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *Ibid.* **1975**, *97*, 3697–3702. (d) Lewis, F. D.; Hoyle, C. E. *Ibid.* **1977**, *99*, 3779–3786. (e) Pac, C.; Sakurai, H. *Chem. Lett.* **1976**, 1067–1072. (f) Libman, J.; Ludmer, Z.; Lourie, B.; Yakhot, V. *J. Chem. Res., Synop.* **1978**, 472–473. (g) Ferguson, J.; Mau, A. W.-H. *Mol. Phys.* **1974**, *27*, 377–387.

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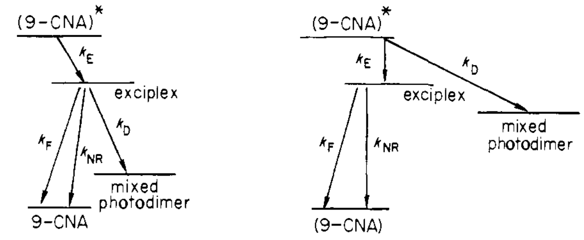
(5) The host crystal structure can be accurately determined by X-ray crystallography; the position and conformation of a low concentration of a guest species may be estimated by molecular force-field calculations; see ref 3, pp 115–121. Craig, D. P.; Markey, B. R.; Griewank, A. O. *Chem. Phys. Lett.* **1979**, *62*, 223–229.

0002-7863/82/1504-4280$01.25/0

Scheme I[a]



(a) photodimerization proceeds via the exciplex

$$\tau^{-1} = k_F + k_{NR} + k_D$$
$$\phi_F = k_F(k_F + k_{NR} + k_D)^{-1} = k_F\tau$$

(b) photodimerization does not proceed via the exciplex

$$\tau^{-1} = k_F + k_{NR}$$
$$\phi_F = k_E(k_E + k_D)^{-1}k_F(k_F + k_{NR})^{-1} = k_E(k_E + k_D)^{-1}k_F\tau$$

k_F = rate of exciplex fluorescence
k_D = rate of photodimerization
k_{NR} = sum of rates of other exciplex relaxation processes
k_E = rate of exciplex formation
τ = exciplex fluorescence decay time
ϕ_F = exciplex fluorescence quantum yield

[a] Direct relaxation of (9-CNA)* to its ground state is not included since at the guest concentration employed (4%) exciplex formation quenches about 95% of (9-CNA)*.

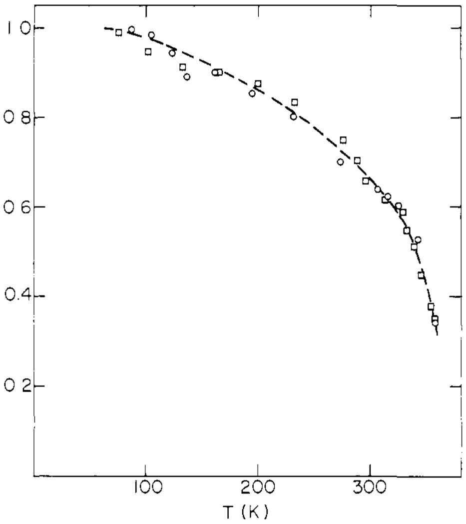


Figure 1. Relative exciplex fluorescence quantum yield, $\phi_F/\phi_F{}^\circ$ (○), and relative exciplex decay time, τ/τ° (□), are plotted as a function of temperature. Both sets of data may be fitted within experimental error (±3%) to a single curve.

K; thus the rate of photodimerization (k_D) increases with temperature. In Scheme Ia it is shown that if the exciplex is an intermediate in the photodimerization, then

$$\phi_F = k_F\tau \tag{1}$$

i.e., ϕ_F and τ, which decrease with increasing temperature as the yield of photoproduct increases, should remain proportional to one another for constant k_F (rate of exciplex fluorescence). If, however, dimerization and exciplex formation occur by independent paths, it is predicted (Scheme Ib) that

$$\phi_F = k_E(k_E + k_D)^{-1}k_F\tau \tag{2}$$

i.e., ϕ_F will decrease more rapidly on heating than does τ.

The measurement[6] of ϕ_F and τ has been extended to the range 5–360 K. These parameters, normalized with respect to their limiting low-temperature values[7a] ($\phi_F{}^\circ$, τ°), show identical behavior on variation of temperature (see Figure 1). However, this is insufficient to validate Scheme Ia; it remains to be shown that a significant portion of the quenching of ϕ_F and τ is due to photodimerization.

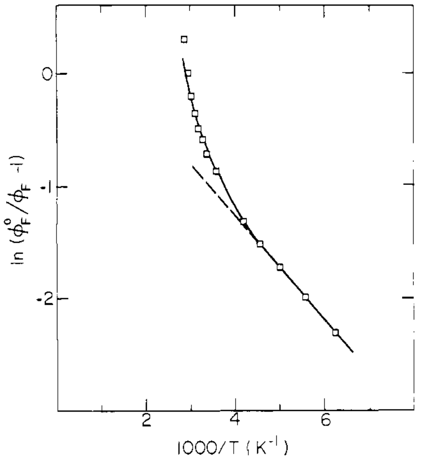


Figure 2. Plot of $\ln(\phi_F{}^\circ/\phi_F - 1)$ against $1/T$ is linear at low T (broken line). The entire data may be satisfactorily fitted by using two exponents (full curve—see text).

At 293 K $\phi_F/\phi_F{}^\circ = \tau/\tau^\circ = 0.68$ and so it is deduced that the sum of the quantum yields of the thermally activated relaxation processes, which are ineffective at low temperatures, is 0.32. By direct measurement we have determined[8] at 293 K that the quantum yield of photodimerization $\phi_D = 0.12 \pm 0.05$. Direct determination of ϕ_D at higher temperatures was not attempted due to the rapid thermal decomposition of the photoproduct formed.[4a,9] However, since photodimerization accounts for about a third of the thermally activated quenching at 293 K and a much greater proportion at higher temperatures (see below) it is concluded that the data of Figure 1 do indeed prove that Scheme Ia is correct and the exciplex is an intermediate in the photodimerization.

The various exciplex relaxation rates of Scheme Ia may be divided[10] into temperature-independent (k_F, $k_{NR}{}^\circ$) and thermally activated (k_D, $k_{NR}{}'$) processes, where $k_{NR} = k_{NR}{}^\circ + k_{NR}{}'$. We may formally write[10]

$$k_D = \alpha e^{-A/RT} \tag{3}$$

and

$$k_{NR}{}' = \sum_i \beta_i e^{-B_i/RT} \tag{4}$$

It is easily shown[10] that

$$\ln(\phi_F{}^\circ/\phi_F - 1) = \ln\left(\alpha e^{-A/RT} + \sum_i \beta_i e^{-B_i/RT}\right) - \ln(k_F + k_{NR}{}^\circ) \tag{5}$$

The left-hand side of eq 5 is plotted against $1/T$ in Figure 2.[7b] The plot is linear below 220 K, indicating that only one thermally activated quenching process is dominant in this region. However, at higher temperatures the curve deviates markedly, indicating that another mechanism is becoming significant. The entire data in Figure 2 can, however, be satisfactorily fitted[11] by using only

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[6] Determination of these quantities at room temperature and 77 K and experimental details are found in ref 4.

[7] (a) From ref 4b, τ° = 78 ns and $\phi_F{}^\circ$ = 0.3. (b) We thus derive $k_F = 3.8 \times 10^6$ s^{-1} and $k_{NR}{}^\circ = 8.9 \times 10^6$ s^{-1}.

[8] After irradiation the sample (approximately 5 mg) was dissolved in toluene (to about 10^{-4} M). A portion of the solution was warmed (50 °C, 15 min) in order to thermally monomerize any heterophotodimer present (ref 9); the remainder was kept at 0 °C. The absolute and difference absorbances were measured in the region 360–420 nm (Carey 118 spectrophotometer, 1-cm cells; typical values of the absorbances were 1.0 and 0.005, respectively) in order to determine the number of molecules that underwent photodimerization. The number of irradiation photons was determined by actinometry; see: Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.

[9] Castellan, A.; Lapouyade, R.; Bouas-Laurent, H.; Lallemand, J. Y. *Tetrahedron Lett.* **1975**, 2467–2470.

[10] See, for example: Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; pp 111, 146. Sakurovs, R.; Ghiggino, K. P. *Aust. J. Chem.* **1981**, *34*, 1367–1372.

two quenching mechanisms (i.e., only one term in the summation for k_{NR}') where

$$\alpha = 1.4 \times 10^{10}\ \mathrm{s}^{-1} \qquad A = 5.4\ \mathrm{kcal/mol}$$

$$\beta = 2.3 \times 10^{7}\ \mathrm{s}^{-1} \qquad B = 0.95\ \mathrm{kcal/mol}$$

The mechanism, which starts to influence the quenching only above 220 K, is assigned to photodimerization. The value obtained for the activation energy of photodimerization (A = 5.4 kcal/mol) is similar to those reported for other photocycloadditions shown to proceed via an exciplex.[2g,12] Using the rate parameters determined here,[7b] we calculate that at 293 K $\phi_D = 0.08 \pm 0.02$, which is compatible with the independent value found by direct measurement.

Registry No. 9-CNA, 1210-12-4; 9-MeOA, 2395-96-2.

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(11) The experimental uncertainty is estimated to be 5% for activation energies and 20% for the preexponential factors.

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New Synthetic Route to (1*R*)-*trans*-Chrysanthemic Ester and to the (1*R*)-*cis*-*gem*-Dibromovinyl Analogue from a Common Intermediate

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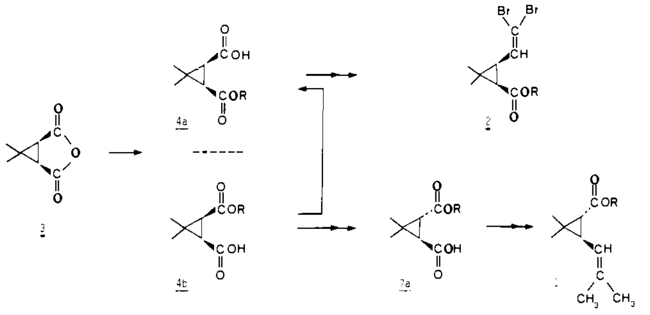
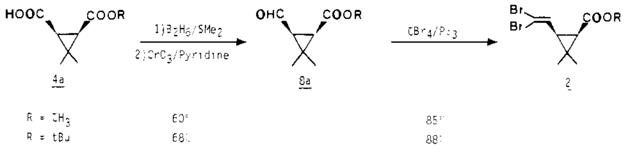
Suitable esters of the (1*R*)-*trans*-chrysanthemic acid (**1**) and its dihalogeno (1*R*)-cis analogue **2** are potent insecticides,[1] safe to mammals,[1] and biodegradable.[1] The higher photostability of **2** (half-life 10 days instead of 5 h for **1**) has opened an important market in agriculture for pest control, especially in fruits, vegetables, and cotton crops, the natural derivative **1** being mainly used for its knock-down effect.[1] A total of 3000 tons of **1** and **2** was manufactured in 1979 and increased production (up to 10000 tons/year) is expected in the near future.[2] We report here on a new synthetic approach[3] that allows the preparation of the most active[1] optical isomers **1** and **2** from the chiral cis monoester of caronic acid **4** (R = CH_3), which is derived from the prochiral caronic anhydride **3** by methanolysis (1 equiv) of CH_3ONa/CH_3OH, 0 °C, 0.1 h, then 10% aqueous HCl)[4] and resolution with optically active α-methylbenzylamine.[5] The proposed methodology not only allows the completely stereoselective interconversion of the two cis-intermediates **4a** and **4b** but also provides simple and stereoselective access to each enantiomer of the trans-series **7a** and **7b**. It completely utilizes the racemate **4**, which can be transformed as desired to one and only one of the four isomers **4a**, **4b**, **7a**, and **7b** and thus to the desired chrysanthemic esters **1** or **2** (Scheme I).

Typically the (1*R*,3*S*)-enantiomer **4a** (R = CH_3) was isolated in pure form as its ammonium salt (mp 143 °C, orthorhombic crystals) in 25% yield (not optimized) after reaction of the racemate **4** (R = CH_3) with (+)-α-methylbenzylamine in acetone and selective precipitation from the same solvent (0.23 M solution, 20 °C, 24 h).

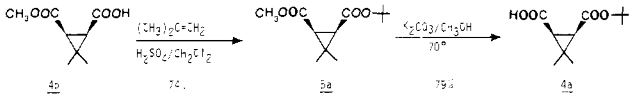
Scheme I



Scheme II



Scheme III



The enantiomer **4b** (R = CH_3) was also isolated as its ammonium salt (mp 139 °C, monoclinic) in pure form in 25% yield (not optimized) on reaction of the material left in the filtrate (after destruction of the remaining ammonium salt) with (−)-α-methylbenzylamine,[5] applying a workup identical with the one used for **4a** (R = CH_3).

The recovery of **4a** and **4b** from their respective ammonium salt was best achieved by treatment with an aqueous potassium carbonate solution (0.5 M, 2 equiv, 20 °C, 0.1 h) followed by careful acidification [HCl, 10%, 1.01 equiv (titration)] and rapid extraction from the acidic medium, which was found to rapidly racemize the product. Under these conditions **4a** and **4b** were each quantitatively isolated in 98% enantiomeric excess.[6a]

The **4a** isomer was directly transformed (Scheme II) to the exceedingly active insecticide **2** by using a set of reactions that we already described on the racemate[4,7] and that proved to be completely stereoselective on the pure enantiomer (Scheme II, R = CH_3).

The "wrong" enantiomer **4b** (R = CH_3) has also been utilized to produce stereoselectively, as desired, **4a** (R = *t*-Bu) or the trans isomer **7a** (R = *t*-Bu), respectively, precursors of **2** (Scheme II) or of the natural chrysanthemic acid.[1,4]

The stereoselective isomerization of the hemicaronic ester **4b** to **4a** (Scheme I), which formally requires a double inversion at the C_1 and C_3 carbons of the cyclopropane ring, was in fact achieved by using the rather simple observation that interconversion of the ester and acid groups on the cyclopropyl ring will give the same result.

This was effectively achieved as follows (Scheme III): the monomethyl ester **4b** (R = CH_3) was readily transformed to the optically active mixed (1*R*,3*S*)-*tert*-butyl methyl diester **5a** (isobutene, trace of H_2SO_4 in CH_2Cl_2, 20 °C) isolated in 74% yield (enantiomeric excess 99.6%),[4b] which contains two ester groups different in both nature (for optical reasons) and reactivity. We took advantage of these differences to achieve the selective hydrolysis[8] of the methyl ester [K_2CO_3 (5 equiv), $MeOH/H_2O$

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(1) M. Elliott and N. F. Janes, *Chem. Soc. Rev.*, **7**, 473 (1978).

(2) We thank Dr. Punja, ICI (PPD) Jealott's Hills Research Station, for valuable discussions, during the sabbatical leave of A.K.

(3) D. Arlt, M. Jautelat, and R. Lantzsch, *Angew. Chem., Int. Ed. Engl.* **20**, 703 (1981).

(4) M. J. Devos, J. N. Denis, and A. Krief, *Tetrahedron Lett.*, 1847 (1978).

(5) (+)-α-Methylbenzylamine, $\alpha^{20}{}_D$ +39° (neat) (Aldrich); (−)-α-methylbenzylamine, $\alpha^{20}{}_D$ −39° (neat) Aldrich).

(6) Comparison has been made with authentic samples prepared from pure (1*R*,3*S*) chrysanthemic acid, kindly provided by Roussel Uclaf Co. (Romainville, France). A full account of this work will appear in the full paper. (a) **4a** (R = CH_3), $\alpha^{20}{}_D$ +29.95° (wet ethanol); (b) **5a** (R = *t*-Bu), $\alpha^{20}{}_D$ −32.91 (acetone); (c) **4a** (R = *t*-Bu), $\alpha^{20}{}_D$ +1.78 (wet ethanol).

(7) F. Ramirez and N. McKelvie, *J. Am. Chem. Soc.*, **84**, 174 (1962).

(8) The use of KOH instead of K_2CO_3 (1 equiv KOH, MeOH, reflux) completely epemerizes the product.

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