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Stereoselection in CO Trapping by the 1-Methyl-3-chlorocyclopentyl Cation. Absence of Chlorine Coordination in a γ-Chloroacyl Cation

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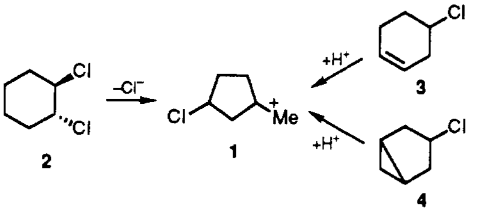
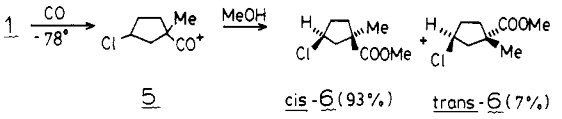
Reaction of the 3-chloro-1-methylcyclopentyl cation with CO at −78 °C gives the two stereoisomers of (3-chloro-1-methylcyclopentyl)carbonyl cation (**5**) in a 93:7 ratio, as established by GLC analysis of the methyl esters formed upon methanol quenching of the acyl cation. The two methyl esters (**6**) were interconverted to a 52:48 ratio by lithium chloride in dimethylformamide. A high-resolution NMR study with homonuclear spin decoupling, heteronuclear C/H chemical shift correlation, and lanthanide shift reagent experiments indicated that the ester predominating in the original mixture had the chlorine cis to the carbomethoxy group. The possibility that the stereoselection is determined by the internal chlorine coordination in the acyl cation, already felt at the transition state of the carbonylation reaction, was tested by examining the ^{13}C NMR spectrum of the 4-chlorobutyryl cation. No indication for the formation of an acyl alkyl chloronium ion was found. Other explanations considered include the interference by an axial hydrogen with the trans attack in the conformation of the five-membered ring favored at low temperature.

One of us has reported preliminary work on the formation of 3-chloro-1-methylcyclopentyl cation (**1**) by the low-temperature ionization of *trans*-1,2-dichlorocyclohexane (**2**) in super acid.[2] Cation **1** was subsequently obtained from 4-chlorocyclohexene (**3**)[3] and also from 3-chlorobicyclo[3.1.0]hexane (**4**).[4] For **3** and **4** protonation of the double bond and protonolysis of the three-membered ring were faster than ionization of chloride.[3]



Upon being warmed above −50 °C, **1** eliminated hydrogen chloride and yielded the 1-methylcyclopentenyl cation. The protium NMR spectrum of **1** was discussed.[2,3]

Reaction of **1** with carbon monoxide at low temperature[2] gave the (3-chloro-1-methylcyclopentyl)carbonyl cation (**5**); upon quenching with methanol the acyl cation **5** afforded the methyl ester of 3-chloro-1-methylcyclopentanecarboxylic acid (**6**) as a 93:7 mixture of stereoisomers. We report here a study of the carbonylation reaction and the determination of the stereochemistry of ester products, and we also give the experimental details of the preparation of **1**. Furthermore, we discuss the possibility of formation of a bicyclic acylchloronium ion by intramolecular coordination of chlorine by the positive CO group in the cis isomer of **5**. In order to look for this type of interaction, a simple model, the 4-chlorobutyryl cation was prepared. The NMR spectra of this model ion were investigated and are discussed below.



$$cis\text{-}\mathbf{6} \xrightleftharpoons{\text{LiCl, 90 °C}} trans\text{-}\mathbf{6}$$

Results and Discussion

Carbonylation of **1** was conducted by reaction with 1.5–3.5 MPa of carbon monoxide at dry ice temperature for 1.5–3 h. To avoid elimination of HCl the solution of **1** was first cooled to −95 °C and then poured into the pressure vessel cooled in liquid nitrogen. The vessel was sealed and pressurized with CO at the same temperature, buried in dry ice, and stirred for the indicated length of time. This procedure made it difficult to measure the progress of carbonylation by following the pressure drop, since CO absorption occurred at the same time with the warming of the solution and gas inside the pressure vessel.

An attempt to conduct ionization and carbonylation in one step by bubbling CO at atmospheric pressure through the acid during the addition of precursor **2** did not give the desired **5**. Carbonylation at −65 to −70 °C appeared to give somewhat lower stereoselectivity, but the results were not reliable, since the purity of the product was low.

The instability of ion **1** prevented any attempt at quantitative transfer of the solution to the carbonylation vessel, therefore recovery was mediocre. An experiment in which cation **1** was prepared directly in the pressure vessel, then 1.5 MPa of CO was introduced, could not be worked out satisfactorily (see the Experimental Section). Variable amounts of solid material (very little in the most successful runs) were formed upon methanol quenching, but pentane extraction led to **6** with less than 10% impurities (GLC). The key to obtaining a pure carbonylation product was avoidance of HCl elimination between ionization and CO trapping. The ester product was purified by column chromatography on silica gel. Since the isomers were partially separated (2–4% ether in pentane as eluent), the major isomer, eluting last, was obtained pure and was used for the NMR measurements. As indicated below, this was established to be the cis isomer.

Treatment of the original ester with LiCl in dimethylformamide at 90 °C led to a mixture containing about equal amounts of the two isomers. By column chromatography, a fraction enriched to about 65% in the originally minor isomer (trans), suitable for obtaining the NMR spectra of the latter, was obtained.

The NMR spectra were obtained for the pure cis isomer and for the mixture, as described in the experimental part. The carbon chemical shifts and lanthanide-induced shifts, the protium chemical shifts and coupling constants are given in Table I. Only a few coupling constants could be determined for the trans isomer investigated in the 65:35

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(1) (a) Clarkson University. (b) Postdoctoral research associate. (c) Exxon Research and Engineering Co.

(2) Fărcaşiu, D. *J. Chem. Soc., Chem. Commun.* **1977**, 394.

(3) Fărcaşiu, D. *J. Am. Chem. Soc.* **1978**, *100*, 1015.

(4) Rees, J. C.; Whittaker, D. *J. Chem. Soc., Chem. Commun.* **1978**, 1096.

0022-3263/89/1954-4582$01.50/0

Table I. Carbon-13 and Protium NMR Spectra of *cis*- and *trans*-6[a]

	carbon atom							
	C-1	C-2	C-3	C-4	C-5	CH_3	OCH_3	C(=O)O
cis-**6**	48.24	47.92	59.35	36.57	35.38	26.18	52.09	177.81
LIS[b]	−0.50	−0.32	−0.21	−0.19	−0.38	−0.43	−0.46	−0.64
trans-**6**[b]	48.74	48.07	59.93	37.01	36.36	26.21	52.09	(178)
LIS[b]	−0.68	−0.47	−0.26	−0.24	−0.44	−0.49	−0.58	*c*

	H[d]								
	OMe	CMe	2c	2t	3	4c	4t	5c	5t
cis-**6**	3.660	1.248	2.512	2.041	4.343	1.962	2.198	2.454	1.536
J,[e] Hz			14.7 (2t) 5.4 (3)	6.4 (3)	5.0 (4c) 5.8 (4t)	7.8 (5c) 14.7 (4t)	7.8 (5c) 6.8 (5t)	13.7 (5t)	5.8 (4c)
trans-**6**[b]	3.646	1.397	2.757	1.800	4.399	2.15–2.2	1.95–2.0	2.15–2.2	1.85
J,[b,e], Hz			6.9 (3)	14.7 (2c)	5.4 (2t)				

[a] Chemical shifts, ppm, from internal TMS. [b] Determined in the mixture of *cis*- and *trans*-**6** (35:65). [c] Shifted to 177.24. [d] Hydrogen at the given carbon atom number, on the same side (c) or on the opposite side (t) to the carbomethoxy group. [e] Coupling with the hydrogen atom indicated.

mixture of stereoisomers, and some of the protium chemical shifts indicated for it in Table I have lower accuracy than the other values. Nevertheless, the spectra were quite satisfactory for assigning unambiguously the stereochemistry of *cis*- and *trans*-**6**.

Stereochemistry Assignment. There are several arguments for the assignment of cis geometry to the major carbonylation product:

1. In the protium NMR spectrum (Table I), the angular methyl group resonates at higher field for the cis isomer (δ 1.248) than for the trans isomer (δ 1.397); conversely, the methoxy group fo the cis isomer (δ 3.660) resonates at lower field than the same group of the trans isomer (δ 3.646). In each case, the hydrogens closer to chlorine are more deshielded. A similar pattern was reported for *cis*- and *trans*-1,5,5-trimethyl-3-hydroxycyclopentanecarboxylic acids.[5] For comparison, the unsubstituted ester, methyl 1-methylcyclopentanecarboxylate has the signals of the corresponding protons at 1.24 and 3.65, respectively.

2. The protium at C-5 on the same side with the methyl group in *cis*-**6** resonates at δ 1.536. The corresponding atom in *trans*-**6** resonates at δ ca. 1.8, because it is cis to chlorine. There is no protium resonance at higher field than 1.8 ppm for *trans*-**6**.

3. Of the geminal pairs at C-2 and C-5 in *cis*-**6**, the hydrogens on the same side with the methyl group should resonate at higher field. Upon addition of the shift reagent $Yb(TFC)_3$, the signals for these hydrogens (and for their counterpart at C-4) should move upfield less than the hydrogens cis to the carbomethoxy group in each pair. The experimental findings (Figure 1 in the supplementary material) match these predictions.

4. The signal of the CHCl group is at slightly higher field for the cis isomer than for the trans isomer. As a more important feature, the lanthanide-induced shift (LIS) is larger for the downfield peak, which overtakes the upfield peak (Figure 2, supplementary material).

5. The ^{13}C NMR signals of both isomers are easily assigned, as chemical shifts match the values calculated based on additivity of substituent effects.[2,6] Only the absorptions for the C-4/C-5 pair, which are very close, could not be assigned in this way, but a decision is possible based on LIS (Table I). It is seen that LIS values are higher for the trans isomer, which is expected, because steric interference from chlorine should result in a weaker complex with the Yb reagent for the cis isomer.

6. The chromatographic behavior of the two isomers is as expected, because the cis isomer, which has a higher dipolemoment, elutes slower on column chromatography on silica gel and on GLC on a polar column. The isomers were only incompletely separated on a non-polar GLC column.

Possible Origin of the Stereoselection in the Carbonylation of 1. The observed selectivity should be kinetically controlled because the carbonylation time was too short to allow isomer equilibration (*cis*-**5** $\rightleftarrows$ *trans*-**5**) by decarbonylation–recarbonylation. Thus, extrapolation to −75 °C of rates of decarbonylation of the pivaloyl cation to *tert*-butyl cation[7] gives a half-life of 10.5 h. Decarbonylation of **5** to the carbocation **1** destabilized by the electronegative chlorine substituent[8] should be even slower. The CO attack is, therefore, faster on the nominally more crowded side of the ring to give the large *cis*-**5**/*trans*-**5** ratio in the product. We have considered three possible explanations for this observation:

(a) The cis isomer is stabilized by coordination of the chlorine substituent in an α-oxochloronium ion (**7**). Such a structure was proposed, albeit without experimental proof, for the monocation derived from succinyl difluoride in SbF_5.[9] Part of this stabilization could be felt already at the transition state of carbonylation, thus making *cis*-**5** the kinetically controlled product.

(b) Ion **1** is tightly paired in solution with the complex anion, which is situated trans to the electronegative chlorine substituent, and prevents the attack by CO from that direction.

(c) In the partially rigid ion **1**, the chlorine substituent occupies a (pseudo)equatorial position (**8**). The trans attack is then made unfavorable by a 1,3-diaxial interaction between the incoming nucleophile and the hydrogen atom at C-3. Molecular mechanics[10] calculations on the model structure, 1,3-dimethylcyclopentyl cation, indicate a

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(5) Faigle, J. W.; Müller, H.; von Philipsborn, W.; Karrer, P. *Helv. Chim. Acta* **1964**, *81*, 741.

(6) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

(7) Hogeveen, H.; Baardman, F.; Roobek, C. F. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 227.

(8) Cation **1** is not expected to be stabilized as a bicyclic chloronium ion, since four-membered chloronium ions are not formed even in less strained systems: Olah, G. A.; Mo, Y. K.; Brinich, J. *J. Am. Chem. Soc.* **1972**, *94*, 1164. See, however: Exner, J. H.; Kershner, L. D.; Evans, T. E. *J. Chem. Soc., Chem. Commun.* **1973**, 361. McManus, S. P.; Smith, M. R.; Smith, M. B.; Worley, S. D. *Tetrahedron Lett.* **1983**, *24*, 557.

(9) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1966**, *88*, 3313.

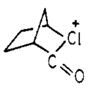
(10) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) For other examples of force field calculations on carbocations see: Fărcaşiu, D.; Jähme, J.; Rüchardt, C. *J. Am. Chem. Soc.* **1985**, *107*, 5717; Fărcaşiu, D. *J. Org. Chem.* **1981**, *46*, 223; Fărcaşiu, D. *Ibid.* **1978**, *43*, 3878 and references therein. (c) The force field for carbocations employed in the ref 10a and 10b was introduced in the computer program BIGSTRAIN3: Nachbar, R. L.; Mislow, K. *QCPE*, **1986**, 514.

Table II. NMR Spectra of Acid Chlorides and Acyl Cations

			^{13}C chemical shifts[b]				^1H chemical shifts[b,c]		
formula	solvent[a]	*T*, °C	C-1	C-2	C-3	C-4	C-2	C-3	C-4
9	$CDCl_3$	37	173.0	44.0	27.7	42.9	3.17 (6.5)	2.17 (6.5)	3.64 (6.5)
10	4:1 FSO_3H-SbF_5	0	152.8	18.7	26.6	42.9	4.61 (5.5)	3.21 (5.5)	4.34 (5.5)[e]
		−60[d]	152.8	18.7	26.5	43.2			
12	$CDCl_3$	0	173.7	48.9	18.7	13.0	2.91 (7.0)	1.76 (7.0)	0.99 (7.0)
13	4:1 FSO_3H-SbF_5	0	152.3	20.4	18.0	12.2	4.44 (7.0)	2.64 (7.0)	1.72 (7.0)[f]

[a] Solute in $CDCl_3$, 10% (v:v); in acid, 0.7 M. [b] Ppm from internal TMS ($CDCl_3$ samples) and external (coaxial) TMS (acid samples). [c] Coupling constants (hertz) given in parentheses. [d] SO_2FCl (0.25 vol.) was added. [e] The values in 1:1 FSO_3H-SbF_5 are 4.77, 3.42, and 4.55, respectively. [f] Literature values: 4.45, 2.75, and 1.60 ppm, respectively (Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1977**, *89*, 3591.

slightly lower steric energy (1 kcal/mol) for the structure with an equatorial 3-substituent.



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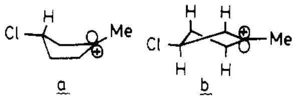

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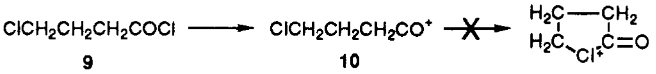
The first hypothesis was tested by a study of the ionization of 4-chlorobutyryl chloride (**9**) in 4:1 FSO_3H-SbF_5. Chlorine coordination by the acyl group of 4-chlorobutyryl cation (**10**) should be more favorable than for **5**, because the resulting ion (**11**) is much less strained than **7**.

Based on the published reports on tetramethylenechloronium ion[11] and on the complex of fluoroacetyl fluoride with antimony pentafluoride,[12] it could be predicted that in the acylalkylchloronium ion **11** the carbon-13 NMR signals of both C-1 and C-4 would be shifted downfield from the position of the corresponding signals in **9** by about 20 ppm. The actual spectrum shows C-1 *upfield* by about 20 ppm, and C-4 unchanged from **9**, corresponding exactly to the spectral changes observed upon ionization of the parent butyryl chloride (**12**) to the butyryl cation (**13**).[13] Thus, the ^{13}C NMR data show conclusively that no significant amount of **11** exists in equilibrium with **10**, both at 0 °C and at −60 °C.[14] The measured chemical shifts are shown in Table II.



9 **10** **11**

$$\underset{\mathbf{12}}{CH_3CH_2CH_2COCl} \rightarrow \underset{\mathbf{13}}{CH_3CH_2CH_2CO^+}$$

The protium NMR spectrum of **10** showed no unusual features, except that in the stronger acid 1:1 FSO_3H-SbF_5 a slight downfield shift of the signals was observed (Table II, footnote *e*), suggesting some complexation $F_5Sb \leftarrow Cl(CH_2)_3CO^+$; the changes are too small, however, to allow for any definite conclusion.[15] In any event, ionization of **9** indicates that chlorine coordination in *cis*-**5** plays no role in the reaction of **1** with CO.

Hypotheses b and c are more difficult to ascertain. Structures **8** should have no hindrance to ion pairing on either side, but an electrostatic interaction between chlorine and the positive charge[8,16] stronger than 1 kcal/mol could bring the chlorine atom in an axial position, thus hindering ion pairing in cis. The published IR and Raman spectra of the 2-methyl-2-propyl cation were consistent with ion pairing in concentrated solution.[17] However, when chemical evidence for ion pairing of carbocations in super acids was specifically sought, this was not found.[18]

For the conformational argument c, one observes that the carbocationic center in **8** is perfectly staggered, and the chlorine-bearing atom (C-3) of the envelope form **8a** is out of the C-5–C-1–C-2 plane. The pseudoaxial hydrogen at C-3 impedes the access of CO. This steric hindrance would be capable of raising the activation energy by 1 kcal/mol[19] (93:7 selectivity) at −78 °C.

The twist conformation of the ring seems less attractive as the ground for an explanation of the observed selectivity, because there are axial hydrogens on either side of the ring. Nonetheless, from an elegant NMR study of partially deuterated 1-(*p*-fluorophenyl)cyclopentyl cations Forsyth and Botkin found that the cyclopentyl cation assumes a twist conformation,[20] as shown in formula **8b**.

The molecular mechanics calculations mentioned above indicate that the twist cyclopentyl cation is somewhat flattened. Dihedral angles involving C–H bonds at adjacent carbons are close to 30° and 90° (C-2–C-3), or 45° and 75° (C-3–C-4), rather than 60° and 60°. The larger chlorine substituent at C-3 could move toward a better staggered arrangement, tilting the axial hydrogens at C-3 and C-5 inward and the axial hydrogens at C-2 and C-4 outward. Such a distortion of the ring might make the side cis to the chlorine atom the more available one for CO attack.

Experimental Section

General. *trans*-1,2-Dichlorocyclohexane and 4:1 FSO_3H-SbF_5 were used as purchased. Freon-11 (trichlorofluoromethane) and dimethylformamide (DMF) were dried on 3A molecular sieves. Sulfuryl chloride fluoride, purchased in ampuls, was transferred on the vacuum line to a Fisher-Porter tube and was stored—as was the acid—under nitrogen, in a dry box. Carbon monoxide (99.5%) was used as purchased. GLC analyses were conducted on a 3 m × 3 mm o.d. column, with 10% Carbowax 20M (polyethyleneglycol) on 60–80 Gaschrom Q, at 125 °C.

NMR Analyses. NMR spectra were obtained on a varian XL-300 spectrometer (300 MHz for ^1H, 75.43 MHz for ^{13}C) and on a JEOL GX-400 spectrometer (400 MHz for ^1H). The DEPT pulse technique was used to distinguish the ^{13}C resonances according to the number of directly bonded hydrogens, and thus it secured the assignments made based on additivity (see text).

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(11) Henrichs, P. M.; Peterson, P. E. *J. Org. Chem.* **1976**, *41*, 362; *J. Am. Chem. Soc.* **1973**, *95*, 7449.

(12) Olah, G. A.; Germain, A.; Lin, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 5481 give δ CO 159.7 in FCH_2COF, and 180.7 in $FCH_2COF \rightarrow SbF_5$.

(13) For ^{13}C NMR spectra of other acyl cations, see: Olah, G. A.; Spear, R. J.; Denis, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 5855.

(14) The equilibrium between cyclic chloronium ions and ω-chloroalkyl cations is appreciably temperature-dependent; see ref 11.

(15) Upon longer standing in either acid, cation **10** eliminates HCl and forms the (*E*)-2-butenoyl (*trans*-crotonyl) cation. That reaction and its complex dependence upon the acidity of the medium will be reported separately: Fărcaşiu, D.; Miller, G., paper in preparation.

(16) This explanation was suggested by a reviewer of the manuscript.

(17) Olah, G. A.; DeMember, J. R.; Commeyras, A.; Bribes, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 459.

(18) Olah, G. A.; Bollinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587.

(19) 1 cal = 4.184 J.

(20) Forsyth, D. A.; Botkin, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4296.

2D COSY experiments, homonuclear spin decoupling ($^1H-^1H$, at 400 MHz), and LIS experiments were conducted in the standard manner.

Preparation of 6. The acid (7 mL) was mixed with 4 mL of SO_2FCl,[21] in a 25-mL round-bottomed flask with a Teflon-coated stirring bar, and then 2 mL of Freon-11 was added as a top layer over the acid solution, and the flask was stoppered and taken out of the dry box. A special dropping funnel was made from a 1.5-cm i.d. glass tube with screw cap and a side arm with stopcock near the top, by connecting to the bottom a 3-cm-long rod with a capillary bore, pointed at the end. A cut up polypropylene bottle was made into a dry ice cooling mantle for the body of the capillary funnel. The latter was attached to the upper end of the straight arm of a distillation adapter. The other arm was fitted to a nitrogen inlet and a nitrogen outlet connected to an oil bubbler. The nitrogen flow was started, and then the reaction flask was attached to the lower end of the adapter and cooled with a toluene liquid nitrogen slush (−95 °C). Vigorous magnetic stirring was maintained throughout the reaction. The capillary funnel was cooled with dry ice placed in the mantle, and a solution of 0.97 g of *trans*-1,2-dichlorocyclohexane in 4 mL of Freon-11, was placed into the funnel, which was then capped. The drops falling from the funnel were very small, and dropping stopped soon, because of the depression created in the funnel. A pipet rubber bulb was fitted on to the side arm (the stopcock was open) and squeezed gently whenever the dropping ceased. The addition was completed in 25–30 min. The cooling bath was allowed to warm to −70 °C and was kept at that temperature for 5 min. The color of the solution changed from orange to brown. The temperature was brought back to −95 °C, and the content of the flask (including the stirring bar) was poured into a 40-mL Hastelloy-C pressure vessel (from Parr, Inc.) lined with Teflon, and precooled in liquid nitrogen. The vessel was sealed, pressurized with CO at 1.5–4.0 MPa, and buried in dry ice in a dish at the top of a magnetic stirring motor. Soon afterwards the movement of the stirring bar inside the pressure vessel was heard, indicating that the content had thawed. As discussed in the text above, measuring accurately the pressure drop was not possible, but CO absorption was definitely complete in less than half an hour. Upon opening the pressure vessel, a light-colored liquid and some solid was found. The suspension was poured into a beaker containing methanol (50 mL) and pentane (10 mL) cooled at −100 °C and vigorously stirred. Water (50 mL) and more pentane (15 mL) were added, the organic layer was isolated, and the acid layer was extracted four times with pentane. The combined organic solution was washed with Na_2CO_3 solution until basic (4 times), with water (4 times), dried on Na_2SO_4, and the solvent was evaporated to give a yellow oil, containing (GLC) 6.9% *trans*-**6**, 88.1% *cis*-**6**, and a combined 5% of minor impurities, beside traces of solvent.

To avoid losses from the transfer of the solution of **1** from the reaction flask to the autoclave, the preparation of **1** directly in the autoclave was also attempted. It was not possible, however, to protect the solution from moisture or (when working inside the drybox) from aerosols of the solvent from the cooling bath. Trying to distill the substrate into the assembled pressure vessel containing the other reagents led to extensive condensation in the inlet line and a very poor yield. We concluded that a specially designed top for the pressure vessel would be necessary to conduct the ionization and carbonylation as a one-pot operation.

The crude ester was purified by chromatography on 40 g of silica gel (Woelm, 0.2–0.5 mm), with pentane, then 98:2, and then 96:4 pentane–ether as eluent. After a mixture of stereoisomers (0.43 g) was eluted, 0.18 g of pure *cis*-**6** was collected.

Epimerization of 6. The chloro ester (0.43 g, ca. 90% cis, 10% trans) was dissolved in 1.6 mL of DMF saturated with LiCl (dried in the oven at 125 °C overnight) and 0.65 mL of DMF in an 8 mm o.d. NMR tube and heated at 90 °C until the *cis*-**6**/*trans*-**6** ratio remained constant (3.5 h). The solution was diluted with water, extracted three times with pentane, the pentane extract was washed three times with water and dried (Na_2SO_4), and the solvent was evaporated. Recovery of ester (52:48 cis/trans by GLC) was nearly quantitative. Chromatography on silica gel (35 g) as above gave in the first fractions 207 mg of a 35:65 mixture of *cis*- and *trans*-**6**.

Acknowledgment. Extensive discussions of the NMR spectra with Tonis Pehk are gratefully acknowledged.

Supplementary Material Available: Copies of NMR spectra showing the effect of the shift reagent on the spectra of *cis*-**6** and of the 65:35 mixture of *trans*- and *cis*-**6** (2 pages). Ordering information is given on any current masthead page.

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[21] Alternatively, liquid SO_2 was used as solvent. It was added to the two-layer mixture of acid and Freon-11 in the reaction flask by distillation on a vaccum line, as described previously: Fărcaşiu, D.; Fisk, S. L.; Melchior, M. T.; Rose, K. D. *J. Org. Chem.* **1982**, *47*, 453.