Dehydrooligopeptides. III. Synthesis of (*Z,Z*)- and (*Z,E*)-Geometric Isomers of Dehydrodipeptides and Their Base-catalyzed Transformation to the Hydantoin Derivatives[1)]

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N-Benzyloxycarbonyl (Cbz)-(*Z,E*)-dehydrodipeptides, comprised of both (*Z*)- and (*E*)-α-dehydroamino acid residues, were first synthesized by dehydrochlorination of Cbz-(*Z*)-dehydrodipeptides containing an erythro-3-chloro-2-aminobutanoate moiety. Base-catalyzed transformation of the individual Cbz-(*Z, Z*)- and (*Z, E*)-dehydrodipeptides was carried out to give the corresponding new hydantoin derivatives. The NMR spectroscopic differences between the geometric isomers of both dehydrodipeptides and their hydantoin derivatives were elucidated.

In the previous papers,[1-3)] we reported some useful synthetic methods for the currently interesting dehydropeptides which contain more than one α-dehydroamino acid (DHA) or ΔAA[4)] residue. The syntheses of the dehydrodipeptides (DHP), which consist of a (*Z*)-DHA and an α-amino acid (AA) or two (*Z*)-DHAs, were performed by the coupling of (*Z*)-DHA with AA, by the coupling between two (*Z*)-DHAs, or by the base-catalyzed β-elimination of (*Z*)-DHP including a serine (Ser) or a threonine (Thr) residue.

Although the preparation of (*E*)-geometric DHA has been reported,[5)] dehydropeptide containing (*E*)-DHA residue has not yet been synthesized and few studies on the reactivity of ordinary DHP have been undertaken. Here, we will report on the first synthesis of *N*-benzyloxycarbonyl (Cbz)-(*Z,E*)-DHP, composed of (*Z*)-ΔAA-(*E*)-ΔAA sequence, by dehydrochlorination of erythro-3-chloro-2-aminobutanoate [But(Cl)] moiety in (*Z*)-DHP and base-catalyzed transformations of both (*Z,Z*)- and (*Z,E*)-DHP to the corresponding new (*E*)- and (*Z*)-hydantoin derivatives. After the isomerization of the (*E*)-hydantoin derivative to the (*Z*)-isomer, the NMR spectroscopic differences between the (*E*)- and (*Z*)-isomers of both DHPs and the hydantoin derivatives were unambiguously characterized.

Results and Discussion

(Z,E)-Dehydrodipeptides. According to the method which we previously reported,[3)] Cbz-(*Z*)-ΔAA-(*Z*)-ΔAA-OMe [(*Z,Z*)-**6**: **b**, R=C_2H_5; **c**, R=*n*-C_3H_7; **e**, R=C_6H_5], except for **6a** (R=CH_3) and **6d** (R=*i*-C_3H_7),[1)] was prepared by the triethylamine-catalyzed elimination of Cbz-(*Z*)-ΔAA-Thr(Mes)-OMe, derived by the coupling of Cbz-(*Z*)-ΔAA-OH with Thr-OMe, followed by the mesylation of the dipeptide (**4**) obtained with methanesulfonyl (mesyl) chloride. On the other hand, Cbz-(*Z*)-ΔAA-(*E*)-ΔAA-OMe [(*Z,E*)-**7a**—**e**] was also obtained by the similar base-catalyzed β-elimination of Cbz-(*Z*)-ΔAA-But(Cl)-OMe (**5**) as follows. According to the dicyclohexylcarbodiimide (DCC) method,[1)] the coupling of Cbz-(*Z*)-DHA (**1**) with methyl erythro-3-chloro-2-aminobutanoate (**3**)[6)] as an amine component in CH_2Cl_2 at room temperature for 24 h gave the expected (*Z*)-dehydrodipeptide (**5**) as colorless needles in *ca.* a 64% yield. The subsequent β-elimination of **5** with triethylamine occurred stereoselectively to give the desired (*Z,E*)-isomer of DHP (**7**) in a fairly good yield.

In the IR spectral data of **6** and **7**, the characteristic differences between the (*Z,Z*)- and (*Z,E*)-isomers could not be recognized. In the spectrum of **6**, the absorption bands of NH (3375—3280 cm^{-1}), the ester carbonyl (1734—1718 cm^{-1}), the secondary amide (1700—1670 and 1648—1620 cm^{-1}), and the carbon-carbon double bond (1665—1638 cm^{-1} region) functions all appeared. On the other hand, from comparison with the IR spectrum of **6**, the appearances of a similar pattern of bands due to NH (3300—3250 cm^{-1}), the ester carbonyl (1725—1714 cm^{-1}), the secondary amide (1680—1663 and 1640—1623 cm^{-1}), and the C=C bond (1655—1623 cm^{-1} region) functions indicate clearly the formation of the dehydrodipeptide (**7**) structure.

As mentioned above, although the IR spectra of **6** and **7** are similar, in the NMR spectrum of **7**, the chemical shifts of *C*-terminus alone were found to be considerably different from those of **6**. Therefore, it is supposed that the two compounds **6** and **7** are geometrically isomeric.

From the NMR spectral data, the disappearance of the characteristic methine proton signals coupled as double-doublet in the δ 4.81—4.90 (J=4.0—4.2 and 8.2—8.5 Hz) region in the *C*-terminus of **5** (Table 1) and the appearance of olefinic proton signals in the δ 7.24—7.03 region of **7** (Table 2) indicate unambiguously the formation of a DHA moiety in the *C*-terminus of **7**. In particular, both the olefinic [at δ 6.80—7.24 (q, J=7.5 Hz)] and the methyl protons (at δ 2.04—2.08 region) in the *C*-terminus of **7** resonate at a lower magnetic field than those of **6** [at δ 1.72—1.77 (q, J=7.2 Hz) and 6.77—6.82 regions], whereas the γ-alkyl and β-olefinic protons of *N*-terminus of **6** and **7** resonate at almost the same magnetic fields, in the δ 1.73—2.80 and 6.30—7.24 regions respectively. Hence, it was found that the olefin moiety newly formed in **7** was consistent with an (*E*)-geometric structure.

From the above results, in the NMR spectrum of DHP, the chemical shifts of γ-alkyl and β-olefinic protons of (*Z*)-configurational DHA residue were found

Table 1. Cbz-(*Z*)-⊿AA-But(Cl)-OMe (**5**)

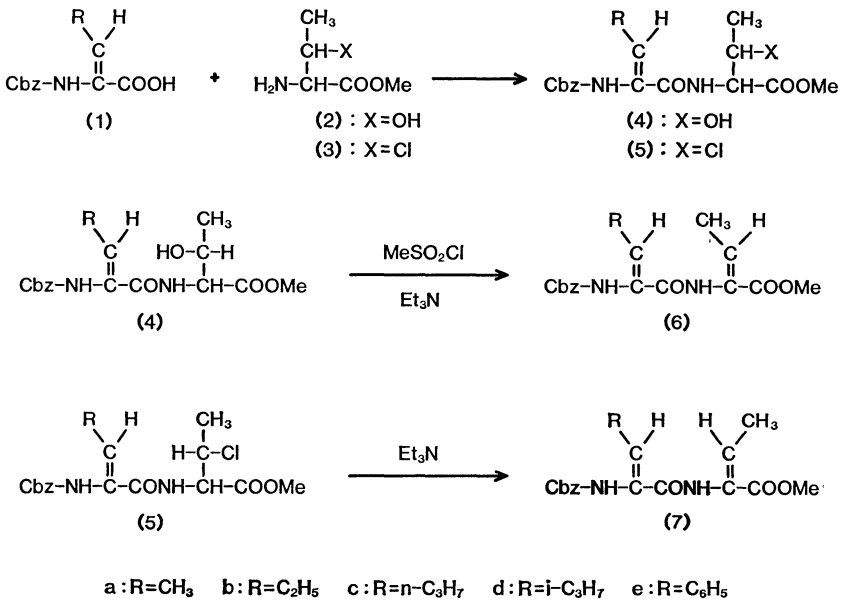
Compd No.	Yield %	Mp θ_m/°C[a]	Formula	Found (Calcd)(%) C	H	N	IR, ν/cm^{-1} in KBr NH	COOMe (C=C)	C=O	NMR, δ in $CDCl_3$ -CH= (J_{Hz})	-N-CH- (J_{Hz})	NH
5a	66	91— 92	$C_{17}H_{21}N_2O_5Cl$	55.30	5.80	7.65	3350	1740	1685	6.55 q	4.87 dd	6.88 bs
				(55.36	5.74	7.60)		(1655)	1686	(7.0)	(8.5, 4.2)	7.14 d
5b	62	87— 88	$C_{18}H_{23}N_2O_5Cl$	56.55	6.11	7.39	3235	1743	1680	6.34 t	4.89 dd	6.47 bs
				(56.47	6.06	7.32)		(1660)	1628	(7.2)	(8.2, 4.0)	6.92 d
5c	67	87— 88	$C_{19}H_{25}N_2O_5Cl$	57.54	6.30	7.10	3325	1745	1687	6.52 t	4.86 dd	6.48 bs
				(57.50	6.35	7.06)	3260	(1643)	1628	(7.5)	(8.5, 4.2)	7.00 d
5d	65	99—100	$C_{19}H_{25}N_2O_5Cl$	57.55	6.31	7.12	3300	1735	1696	6.34 d	4.90 dd	6.44 bs
				(57.50	6.35	7.06)	3200	(1655)	1620	(10.5)	(8.5, 4.2)	7.05 d
5e	70	100—101	$C_{22}H_{23}N_2O_5Cl$	59.98	5.40	6.51	3220	1740	1685	7.10 s	4.88 dd	6.66 bs
				(61.32	5.38	6.50)		(1657)	1625		(8.5, 4.2)	7.20— 7.52[b]

a) Colorless needles from diisopropyl ether. b) Overlapped on phenyl protons.

Table 2. Cbz-(*Z*)-⊿AA-(*Z*) and -(*E*)-⊿But-OMe (**6** and **7**)

Compd No.	Yield %	Mp θ_m/°C[a]	Formula	Found (Calcd)(%) C	H	N	NMR spectrum, δ in $CDCl_3$ R-C<u>H</u>=	R-CH= (J_{Hz})	Me-C<u>H</u>=	Me-CH= (J_{Hz})	-OCONH-	-CONH-
7a	78	syrup	$C_{17}H_{20}N_2O_5$	61.60	6.15	8.40	6.52 q	1.87 d	7.10 q	2.08 d	6.82	8.16
				(61.43	6.07	8.43)		(7.0)		(7.5)		
7b	79	syrup	$C_{18}H_{22}N_2O_5$	62.77	6.95	8.00	6.52 t	2.10 q[b]	7.03 q	2.04 d	7.20	8.30
				(62.41	6.40	8.09)		(7.0)		(7.5)		
6c	69	syrup	$C_{19}H_{24}N_2O_5$	63.38	6.88	7.59	6.52 t	2.11m	6.80 q	1.72 d	6.76	7.73
				(63.32	6.71	7.77)		(7.2)		(7.2)		
7c	81	syrup	$C_{19}H_{24}N_2O_5$	63.48	6.89	7.61	6.52 t	2.80 q	7.04 q	2.04 d	7.24	8.36
				(63.32	6.71	7.77)		(7.0)		(7.5)		
7d	82	syrup	$C_{19}H_{24}N_2O_5$	63.50	6.79	7.62	6.32 d	2.60m	7.10 q	2.10 d	6.82	8.22
				(63.32	6.71	7.77)		(10.0)		(7.5)		
6e	79	112—113	$C_{22}H_{22}N_2O_5$	66.97	5.78	7.23	7.24 s	2.58— 1.73	6.82 q	1.77 d	6.72	7.85
				(66.99	5.62	7.10)				(7.2)		
7e	80	75— 77	$C_{22}H_{22}N_2O_5$	67.05	5.65	7.17	7.20 s	2.80— 1.87	7.24 q	2.07 d	7.20	8.35
				(66.99	5.62	7.10)				(7.5)		

a) Colorless syrup and colorless needles from isopropyl ether. b) Quintet.



Scheme 1.

to resonate at higher magnetic fields than those of the (*E*)-DHA residue, as in the case of the differences between (*Z*)- and (*E*)-DHA derivatives.[7]

The melting points, physical constants, and spectral data of **5**, **6**, and **7** are summarized in Tables 1 and 2.

Hydantoin Derivatives. Recently, Srinivasan *et al.*[8] commented that, in the case of *N,N*-diacyl DHA, *e.g.*, alkyl 2-(phthalimido)crotonate, the protons of alkyl group in the γ-position of (*E*)-isomer shift to a lower magnetic field than that of (*Z*)-isomer, contrary to the *N*-free and *N*-monoacyl DHAs. They claimed that this is a reliable criterion for the confirmation of the geometric structure of DHA.

In order to further explain the differences of the chemical shifts of γ-alkyl protons between the *N*-monoacyl and *N,N*-diacyl DHAs and to study whether we can generalize the above criterion or not, compounds **6** and **7** were converted individually into the corresponding (*E*)- and (*Z*)-2-(hydantoin-3-yl)crotonate derivatives, which were the expected *N,N*-diacyl DHA structures. Instead of triethylamine,[9] sodium methoxide was used for the treatment of **6** to give colorless crystals. These were identified as methyl (*Z*)-2-[(*Z*)-5-alkylidenehydantoin-3-yl]crotonate (**8**) in *ca.* a 90% yield. In addition, instead of sodium methoxide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and potassium *t*-butoxide as a stronger base was also used in this reaction to give **8** in a fairly good yield.

On the other hand, the treatment of **7** with the same base as used above was worked up similarly to give the (*E*)-isomer of **8**, methyl (*E*)-2-[(*Z*)-5-alkylidenehydantoin-3-yl]crotonate (**9**), as a colorless syrup or crystals in *ca.* a 76% yield.

Furthermore, it was found that the direct transformation of **4** and **5** with a strong base such as DBU to the hydantoin derivatives also occurred to give **8** and **9** in high yields respectively, *via* the β-elimination and then cyclization reactions. During the prolonged treatment of **7** with the base, **9** was initially

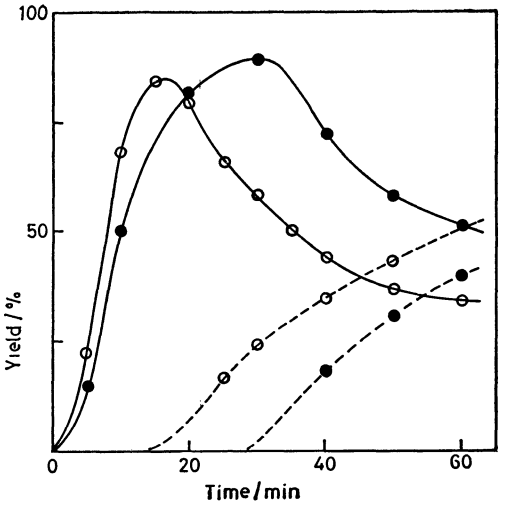


Fig. 1. Yields of **8e** and **9e** *vs.* reaction time and base concentration at room temperature.
8e (——), **9e** (- - -), 0.5 M-DBU (●), 1.0 M-DBU (○).

formed and then isomerization of only the (*E*)-crotonate moiety in **9** gradually occurred to give **8** almost quantitatively. For example, the successive conversion of **7e** to **9e** and **9e** to **8e** for various reaction times and base concentrations were examined in detail. The results are depicted by the curves in Fig. 1. The reaction of **7e** with 0.5 M-DBU (1 M=1 mol dm^{-3}) in $CHCl_3$ at room temperature gave the following results. The formation of **9e** first reached a maximum (*ca.* 90%) yield after 30 min. Then the quantity of **9e** decreased gradually with the isomerization of **9e** to **8e** and the yield of **8e** reached a maximum (*ca.* 80%) after 2 more h. Similarly, when 1.0 M-DBU was employed, the formation of **9e** attained rapidly to the maximum (*ca.* 80%) yield after 15 min; the yield of **8e** thus formed was found to reach its maximum (*ca.* 80%) within 2 h. These results suggested

Table 3. Methyl (*Z*)- and (*E*)-2-[(*Z*)-5-alkylidenehydantoin-3-yl]crotonates (**8** and **9**)

Compd No.	Yield %	Mp θ_m/°C[a]	Formula	Found (Calcd)(%)			NMR spectrum, δ in $CDCl_3$					
				C	H	N	R-C<u>H</u>=	R-CH= (J_{Hz})	Me-C<u>H</u>=	Me-CH= (J_{Hz})	NH[d]	-COOM<u>e</u>
8a	92	121—125	$C_{10}H_{12}N_2O_4$	53.65 (53.57	4.43 4.39	12.61 12.50)	6.05 q	1.88 d (7.8)	7.37 q	1.85 d (7.3)	9.48 s	3.82 s
9a	70	112—115	$C_{10}H_{12}N_2O_4$	53.59 (53.57	4.41 4.39	12.55 12.50)	6.10 q	2.25 d (8.0)	6.52 q	2.24 d (7.0)	9.38 s	3.78 s
8b	91	121—123	$C_{11}H_{14}N_2O_4$	55.49 (55.45	5.99 5.92	11.81 11.76)	6.00 t	2.25m (8.0)	7.40 q	1.86 d (7.0)	9.50 s	3.82 s
9b	73	128—129	$C_{11}H_{14}N_2O_4$	55.47 (55.45	5.97 5.92	11.80 11.76)	5.91 t	2.12m (7.5)	6.44 q	2.26 d (7.6)	9.10 s	3.80 s
8c	93	125—128	$C_{12}H_{16}N_2O_4$	57.18 (57.13	6.47 6.39	11.15 11.11)	6.02 t	2.24 dt (7.3)	7.37 q	1.86 d (7.3)	9.62 s	3.82 s
9c	71	syrup	$C_{12}H_{16}N_2O_4$	57.32 (57.13	6.51 6.39	11.23 11.11)	5.95 t	2.11 q (7.0)	6.48 q	2.23 d (7.7)	9.32 s	3.78 s
8d	90	54— 55	$C_{12}H_{16}N_2O_4$	57.22 (57.13	6.36 6.39	11.18 11.11)	5.82 d	2.64m (10.0)	7.45 q	1.87 d (7.5)	9.50 s	3.84 s
9d	72	syrup	$C_{12}H_{16}N_2O_4$	57.39 (57.13	6.45 6.39	11.34 11.11)	5.78 d	2.23 d (10.0)	6.44 q	2.24 d (7.7)	9.48 s	3.82 s
8e	85	166—167[b]	$C_{15}H_{14}N_2O_4$	63.08 (62.93	5.00 4.93	9.91 9.79)	6.84 s		7.34 q	1.84 d (7.0)	9.70 s	3.79 s
9e	92	212—213[c]	$C_{15}H_{14}N_2O_4$	62.90 (62.93	4.97 4.93	9.72 9.79)	6.74 s		6.50 q	2.28 d (7.5)	9.00 s	3.73 s

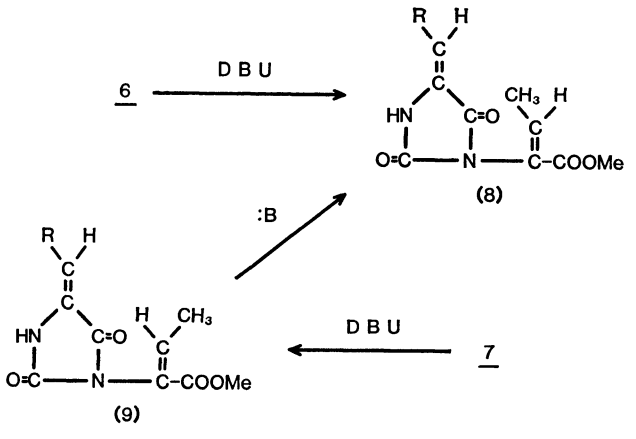
a) Colorless fibers from isopropyl alcohol. b) Colorless needles from CCl_4–isopropyl alcohol. c) Colorless needles from CCl_4–ethanol. d) Broad singlet.

to us that the higher the concentration of DBU or the other similar strong base was, the faster **7** transformed to **8** *via* **9**. In consequence, the expected (*Z*)- and (*E*)-2-(hydantoin-3-yl)crotonate [(*Z*,*Z*)-**8** and (*Z*,*E*)-**9**] were prepared readily as the *N*,*N*-diacyl DHA or enamine in high yields.

In the IR spectrum of **8** and **9**, the appearances of absorption bands of NH (3430—3230 cm^{-1}), ester carbonyl (1736—1715 cm^{-1}), carbon-carbon double bond (1660—1640 cm^{-1}), in particular, the characteristic hydantoin carbonyl bands (1778—1760 and 1720—1673 cm^{-1} regions) at higher wavenumber indicate the formation of the hydantoin ring and the presence of a crotonate moiety. Moreover, from the NMR spectral data of **8** and **9**, the disappearance of NH proton in peptide bonding at δ 6.72—7.20 and that of benzyl protons at about δ 7.20—7.34 (phenyl) and 5.06—5.14 (methylene) in **6** and **7** support the occurrence of a ring closure for hydantoin formation,[9] after the elimination of benzyl alcohol from **6** and **7**. In addition, we have compared the NMR spectrum of **8** with that of **9**. The olefinic proton of the crotonate moiety in (*Z*)-isomer (**8**) resonates at lower magnetic field (at δ 7.34—7.45) than that of (*E*)-isomer (**9**; at δ 6.44—6.52): $\Delta\delta$ *ca.* 0.9. But γ-methyl protons of (*Z*)-isomer shift at higher field (at δ 1.84—1.87) than that of (*E*)-isomer (at δ 2.23—2.28), $\Delta\delta$ *ca.* 0.4, whereas the chemical shifts of β- and γ-protons of the alkylidene group in the hydantoin rings of both **8** and **9** are similar (at δ 5.78—6.84 and δ 1.88—2.64 regions).

These facts are consistent with the Srinivasan comment. Consequently, the criterion became reliable for the confirmational assignment of the geometric structures for *N*-monoacyl and *N*,*N*-diacyl DHAs.

The yields, physical constants, and NMR spectral data of **8** and **9** are summarized in Table 3.



Scheme 2.

Experimental

All the melting points are uncorrected. The IR spectra were recorded with a Hitachi EPI-G3 Spectrometer. The NMR spectra were measured with a JNM-PS-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.), using tetramethylsilane as the internal standard.

Materials. Compounds **3** and **4** were prepared according to the methods reported previously by Kinoshita and Umezawa[6] and by us.[7]

Preparation of **5**. First the hydrochloride of **3** (20 mmol) and triethylamine (20 mmol) in dry CH_2Cl_2 (20 ml) were stirred below 0 °C for 10 min. Into the resulting solution we stirred successively **1** (20 mmol) and DCC (20 mmol), portion by portion; stirring was continued at room temperature for 24 h and the *N*,*N*′-dicyclohexylurea which separated out was filtered off. Into the reaction solution was added CH_2Cl_2 (30 ml); the resulting solution was washed once with successive 1 M HCl, saturated aqueous $NaHCO_3$, and water and then dried over anhydrous Na_2SO_4. Removal of CH_2Cl_2 gave a syrupy residue, which was purified on a silica-gel column using a mixture of benzene and ethyl acetate (4:1 v/v) to give **5** as colorless crystals. See Table 1.

Preparation of **6**. According to the method reported previously,[1,10] compound **4** was subjected to the mesylation, followed by the elimination. Into a solution of **4** (4 mmol) and mesyl chloride (5 mmol) in dry CH_2Cl_2 (20 ml) we stirred triethylamine (12 mmol), drop by drop, at 0—2 °C for 1 h; stirring was continued at room temperature for 12 h. Into the reaction solution was added CH_2Cl_2 (20 ml); the resulting solution was worked up as above. The reaction solution thus obtained was concentrated under reduced pressure to give a crude syrupy substance: this was then purified on a silica-gel column using a mixture of benzene and ethyl acetate (3:1 v/v) as the eluent to give **6** as a colorless syrup or crystals. See Table 2.

Preparation of **7**. Into a solution of **5** (10 mmol) in dry CH_2Cl_2 (15 ml) we stirred triethylamine (30 mmol), drop by drop, under cooling for 2 h; stirring was continued at room temperature for 15 h. Dichloromethane (20 ml) was added to the reaction solution and the resulting solution was washed twice with 1 M HCl, once with saturated aqueous $NaHCO_3$, and three times with water, and finally dried over anhydrous Na_2SO_4. Evaporation of CH_2Cl_2 gave a syrupy residue; this was purified on a silica-gel column using a mixture of benzene and ethyl acetate (4:1 v/v) as the eluent to give **7** as a colorless syrup or crystals. See Table 2.

Preparation of **8**. Into a solution of **6** (10 mmol) in dry $CHCl_3$ (15 ml) we stirred DBU (10 ml) at room temperature for 3 h. To the reaction solution was added $CHCl_3$ (15 ml); this was then washed with 2 M HCl and three times with water and then dried over anhydrous Na_2SO_4. After removal of $CHCl_3$ and the small amount of benzyl alcohol formed as a by-product under reduced pressure, the residual syrup was purified on a silica-gel column using a mixture of benzene and ethyl acetate (4:1 v/v) as the eluent to give **8** as colorless crystals. See Table 3.

Preparation of **9**. Into a solution of **7** (10 mmol) in $CHCl_3$ (15 ml) we stirred some DBU (5 ml) at room temperature for half an hour. The reaction solution was acidified weakly with 1 M HCl. $CHCl_3$ (15 ml) was added and the resulting solution was worked up as the case of **8** mentioned above, to give **9** as a colorless syrup or crystals. See Table 3.

Isomerization of **9** *to* **8**. *From* **9**: A solution of **9** (10 mmol) in $CHCl_3$ (15 ml) in the presence of triethylamine (10 mmol) was stirred at room temperature for 3 d. The reaction solution was washed once with 2 M HCl and three times with water and then dried over anhydrous Na_2SO_4. Removal of $CHCl_3$ gave **8** quantitatively.

A similar isomerization of **9** to **8** was accomplished completely within only 10 h, by using DBU, sodium methoxide,

or potassium *t*-butoxide, instead of triethylamine.

From ***5*** via ***9***: Into a solution of **5** (20 mmol) in methanol (15 ml) we stirred sodium methoxide (12 mmol), drop by drop, below 0 °C; stirring was continued at room temperature for 6 h. After removal of methanol, the residual syrup thus obtained was dissolved in ethyl acetate (40 ml). The resulting solution was washed twice with 1 M HCl and three times with water and finally dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residual substance, which was worked up as the case of **6** to give **8** in *ca.* an 85% yield.

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