10c: mp 61.5 °C (from petroleum ether); NMR see Table IV; IR (KBr pellet) 1690, 1670, 1440, 840, 780, 760, 680 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.02; H, 8.05; N, 9.32.

Oxidation of 5, 10, and 11 with Nitric Acid. Oxidation was carried out by heating **5**, **10**, or **11** together with excess 30–60% nitric acid in a sealed unit such as the glass tube or the autoclave at 115–145 °C for several hours. The sealed unit was cooled to room temperature and opened, and then the reaction mixture was freed from nitric acid by distillation under reduced pressure to give **12** or dihydrate of **9** as residue.

Preparation of 9 from 5b. 5b (0.5 g, 2.31 mmol) was sealed in a glass tube together with 30% nitric acid (10 mL), and the tube was heated at 115 °C for 20 h. The reaction mixture was concentrated under reduced pressure to give the dihydrate of **9** (0.55 g, 1.88 mmol, 81%) as white crystals; mp >250 °C (lit.[13] mp 273 °C). The IR spectrum was identical with that of an authentic sample. Anal. Calcd for $C_{10}H_{10}O_{10}$: C, 41.39; H, 3.47. Found: C, 41.39; H, 3.48.

Preparation of 9 from 5d. 5d (0.5 g, 1.7 mmol) was treated with 30% nitric acid (10 mL) at 130 °C for 4 h to give the dihydrate of **9** (0.481 g, 1.7 mmol, 99%).

Preparation of 12 from 10b. 10b (0.75 g, 3.1 mmol) was sealed in a glass tube together with 30% nitric acid (10 mL) and heated at 140 °C for 4 h. **12** (0.72 g, 2.8 mmol, 92%) was obtained as white crystals; mp 236–237 °C (lit.[14] mp 236 °C). The IR spectrum was identical with that of an authentic sample. Anal. Calcd. for $C_{10}H_6O_8$: C, 47.26; H, 2.38. Found: C, 47.08; H, 2.57.

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Preparation of 9 from 11b. 11b (0.5 g, 2.0 mmol) was oxidized with nitric acid to give dihydrate of **9** (0.54 g, 1.86 mmol, 92%).

Oxidation of 5b to 8b by $Na_2Cr_2O_7$ and Acid and Alkaline Hydrolysis of 8b to 9. A mixture of **5b** (2.0 g, 2.31 mmol) and glacial acetic acid (30 mL) was heated at 90 °C, and $Na_2Cr_2O_7$ (5.0 g) was added in a small portion with stirring in 1 h. Heating at 90 °C was continued for 14 h, and then the mixture was cooled to room temperature to precipitate white needles (1.72 g) of **8b**. Concentration of the filtrate and dilution with water gave 0.3 g of **8b**. Total amount of **8b** was 2.02 g (8.85 mmol, 95.7%); mp >250 °C. The IR spectrum was identical with that of an authentic sample. Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 58.83; H, 3.41; N, 11.46.

A mixture of **8b** (0.7 g, 3.07 mmol) and 36% hydrochloric acid (10 mL) was heated in a sealed glass tube at 160 °C for 10 h to give 0.7 g (2.41 mmol, 78.5%) of the dihydrate of **9** by concentration of the reaction solution. The IR spectrum was identical with that of an authentic sample.

A mixture of **8b** (2.0 g, 8.76 mmol) and 30% KOH solution (30 mL) was heated under reflux and then neutralized with concentrated hydrochloric acid. The solution was concentrated, and the residue was extracted twice with hot EtOH, which was further concentrated to give the dihydrate of **9** (1.5 g, 5.17 mmol, 59%).

Registry No. **1**, 623-27-8; **2**, 626-19-7; **3a**, 14326-69-3; **3b**, 41464-83-9; **3c**, 72891-08-8; **3d**, 30862-11-4; **4a**, 85067-98-7; **4b**, 85067-99-8; **4c**, 85068-02-6; **5a**, 19048-38-5; **5b**, 85067-95-4; **5c**, 85067-97-6; **5d**, 85067-96-5; **6a**, 85067-94-3; **8b**, 26011-79-0; **9**, 89-05-4; **10a**, 23966-19-0; **10b**, 85068-01-5; **10c**, 85068-04-8; **11a**, 23966-18-9; **11b**, 85068-00-4; **11c**, 85068-03-7; **12**, 476-73-3; $Co_2(CO)_8$, 10210-68-1; aniline, 62-53-3; methylamine, 74-89-5; ethylamine, 75-04-7; butylamine, 109-73-9.

A Novel Reaction Type Promoted by Aqueous Titanium Trichloride. Synthesis of Allylic Pinacols

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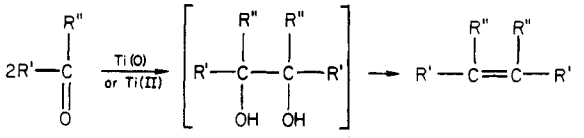
Electron-withdrawing substituted carbonyl compounds which are allowed to react with 2 equiv of aqueous titanium trichloride selectively add to the carbonyl carbon atom of α,β-unsaturated aldehydes. Highly functionalized allylic pinacols are obtained in good yields under very simple experimental conditions. The fundamental role played by the titanium(III) ion is discussed.

Low-valent titanium species such as Ti(0) or Ti(II), prepared by reduction of anhydrous titanium trichloride with either lithium aluminum hydride[1] or reactive metals,[2-4] efficiently induce reductive coupling of carbonyl compounds to olefins, diols being the reaction intermediates (Scheme I).

For some time, now, we have been carrying out investigations regarding the reducing properties of titanium trichloride in aqueous acidic[5,6] or basic[7] solution. The Ti(III) species, certainly a milder reducing agent, has no effect in aqueous acidic medium ($E^\circ = -0.1$ V) on aliphatic and aromatic ketones and aldehydes but easily[5,6] couples

Scheme I



carbonyl compounds **1**, activated toward reduction by an electron-withdrawing group, to the corresponding symmetrical diols **3** (Scheme II, eq 1).

Next[8] we have observed that an interesting mixed pinacol reaction takes place between **1** and simple aldehydes (Scheme II, eq 2) or ketones (Scheme II, eq 3), affording the mixed diols **4** and **5** in very good yields.

All the reactions in eq 1–3 can be schematically shown to involve a common radical intermediate, **2**. Radicals of this type[9] enjoy a particular stabilization, being simulta-

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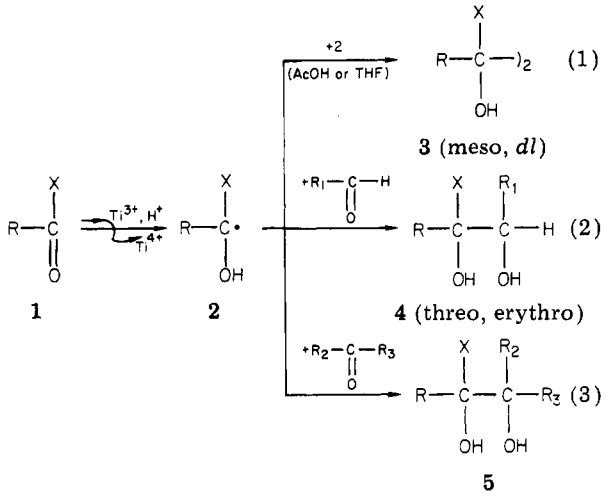
Table I. Yields of Isolated Products

run	substrate RC(O)X (1)	R_4 of aldehyde $R_4CH=CHCHO$	product isolated yield,[a] % 6	7	3	overall yield,[a] %	reaction time, h
a	PhC(O)CN	H	27		10	37[b]	1.30
b	PhC(O)CN	CH_3	53	12	traces	65[c]	1.30
c	PhC(O)$COOCH_3$	H	61		15	76	2
d	PhC(O)$COOCH_3$	CH_3	78	10	traces	88	2
e	PhC(O)COOH	H	71		*d*		1
f	PhC(O)COOH	CH_3	87		*d*		1
g	PhC(O)COOH	Ph	67		*d*		1
h	CH_3C(O)(2-Py)	H	56		27	83	2
i	CH_3C(O)(2-Py)	CH_3	52		27	79	2
j	CH_3C(O)(2-Py)	Ph	40		46	86	2.30
k	CH_3C(O)(4-Py)	H	72		20	92	2
l	CH_3C(O)(4-Py)	CH_3	70		22	92	2
m	CH_3C(O)(4-Py)	Ph	46		44	90	2.30

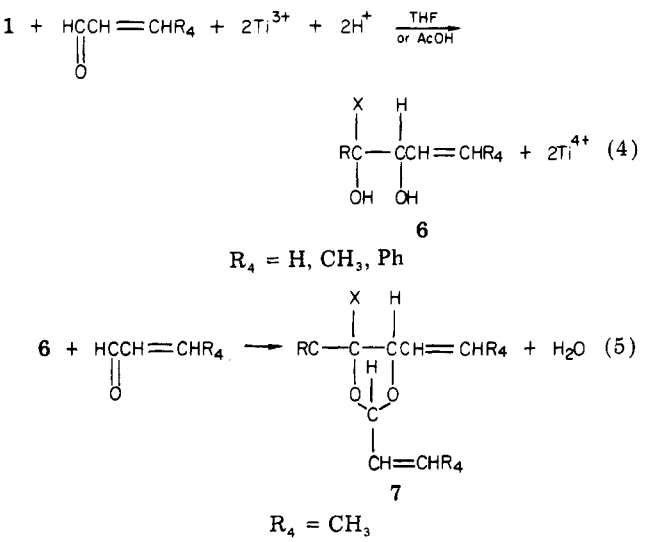
[a] Products isolated and overall yields are based on the starting substrate 1. [b] 45% of the substrate is recovered as benzoic acid. [c] 32% of the substrate is recovered as benzoic acid. [d] Not determined.[10]

Scheme II[a]



[a] X = CN, COOH, $COOCH_3$, 2- and 4-Py;[8] R = H, CH_3, Ph; R_1 = CH_3, Ph; R_2 = R_3 = CH_3; R_2, R_3[8] = $(CH_2)_4$, $(CH_2)_5$.

Scheme III



neously substituted by a donor (OH) and an acceptor (X) group. Additional stabilization comes from the presence of an aromatic ring (R = Ph) directly bonded to the radical center.

Capto-dative substitution seems to favor mainly the dimerization process[9] (Scheme II, eq 1); the fact that dimerization is almost suppressed in the presence of an excess of simple ketones or aldehydes (acetone, acetaldehyde, etc.) in favor of the addition of **2** to the carbonyl carbon atom is to be ascribable to the preeminent role played by the Ti(III) ion in determining the fate of these reactions.

We now report on the extension of the reaction to α,β-unsaturated aldehydes: addition is always at the carbonyl carbon atom, and the reaction provides an exceptionally simple synthesis of highly functionalized allylic pinacols.

Results

An aqueous acidic 15% solution of titanium trichloride promotes the addition of benzoyl cyanide, benzoylformic acid, methyl benzoylformate, 2- and 4-acetylpyridine either to acrolein, crotonaldehyde, or cinnamaldehyde with complete selectivity of attack according to Scheme III.

Allylic pinacols **6** are in some cases accompanied by 1,3-dioxolanes **7**, which result from subsequent condensation of **6** with the starting aldehydes (Scheme III, eq 5). Symmetrical diols **3** are always obtained as byproducts in variable amounts. Isolated yields of **6**, **7**, and **3**, based on the starting substrate **1**, are summarized in Table I. The structural assignments for the products obtained are completely consistent with the spectral and analytical data reported in the Experimental Section.

The ^1H NMR spectra of the crude allylic pinacols **6** suggest that these compounds are formed as a mixture of threo and erythro isomers. Column chromatography, followed by preparative thin-layer chromatography, allowed the separation of the two isomeric forms of **6d,f,l**; any attempt to separate the other isomeric mixtures or analyze their stereochemistry by spectroscopic methods were unsuccessful. ^1H NMR spectra of the crude dioxolanes **7** revealed that two out of four (*dl* pairs) possible stereoisomers were obtained in higher yield.

The overall stoichiometry for the reaction in eq 4 (Scheme III) is 2:1 with respect to the Ti(III)/**1** ratio (determined by back-titration of Ti(III) excess). We have observed[11] that the relative amounts of diol **5** (R_2 = R_3 = CH_3, X = CN, R = Ph) and dimer **3** depend on the amount of ketone used, so in order to minimize the formation of **3** in favor of **6**, all the reactions have been carried out by using an excess of α,β-unsaturated aldehydes. Optimum

(10) Compound **3e** (diphenyltartaric acid) was obtained as a Ti complex. Its mass spectrum shows *m/e* 398, corresponding to M + 2Ti. Any attempt to crystallize the dusty product, in order to determine its structure, was unsuccessful.

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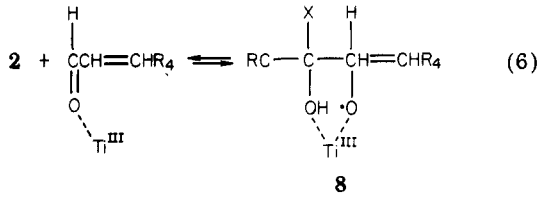
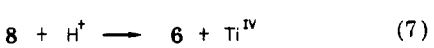
Scheme IV



(6)



(7)

reaction conditions involve rapid addition of the reducing solution; dropwise addition increases the yields of symmetrical diols **3**. The lower yields obtained with cinnamaldehyde are in accord with its low solubility in the reaction medium.

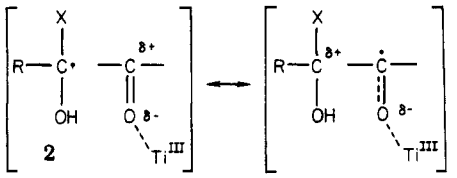
Discussion

Addition of the substrate **1** to acrolein, crotonaldehyde, and cinnamaldehyde is always at the carbon atom of the carbonyl group. No products of addition to the double bond were ever detected. Beyond the synthetic potential, the reaction is of interest in relation to the operating mechanism: a mixed radical coupling is to be discarded because only a lower titanium species (Ti(II) from $TiCl_4/Mg$) is able[12] to reduce the carbonyl group of α,β-enones to the corresponding pinacols; a nucleophilic addition to the carbonyl carbon is quite improbable either because radical **2**, owing to its capto-dative nature,[9,13] is not prone to be reduced by a very mild reducing agent such as Ti(III) ion ($E^\circ = -0.1$ V in acidic medium) or because the presence of an anion would lead, under our reaction conditions (pH ≤ 1), to the corresponding carbinol instead of the addition product **6**. The most likely sequence of reactions to rationalize the formation of **6** is presented in Scheme IV. It involves the addition of the intermediate radical **2** to the carbonyl carbon atom of the α,β-unsaturated aldehyde (eq 6) followed by rapid reduction of the strong electrophilic alkoxyl radical **8** by the Ti(III) ion (eq 7).

Addition of alkyl radicals to the carbonyl carbon has been previously proposed,[14-16] but alkyl radical additions to enones, if they ever proceed, give 1,4-type products. The abnormality observed in the present reaction is ascribable to the fundamental role played by the Ti(III) ion both in determining the direction of addition (Ti(III) coordination with the carbonyl group) and in minimizing the reversibility of the reaction in eq 6 (easy reduction of **8** by Ti(III) ion).

(a) That strong carbonyl oxygen–Ti(III) ion coordination could take place in aqueous acidic solution also is demonstrated by the quantitative recovery of a 1:2 complex[17] between titanium trichloride and acetylacetone. β-Diketone complexes of titanium are well-known,[18] but rigorously anhydrous conditions were always employed in their preparation. The capability[12,19] of Ti(III) ion to strongly coordinate with the carbonyl oxygen of enones rather than the π system (as for low-valent forms of Cr, Fe, and Zn) would enhance the electrophilicity of the carbonyl group by increasing the positive carbon charge and lowering the energy level of the LUMO[20] (lowest unoccupied molecular orbital, π^* (C=O)), thus favoring the 1,2-addition of **2**.

Scheme V



(b) On the supposition that a stabilized radical such as **2** may add to the double bond and compete with the carbonyl carbon addition, this process should be reversible as well. The direction of attack will have to do with the ease with which the radicals formed by the carbonyl and double bond addition are subsequently reduced by the Ti(III) ion. The alkoxyl radical **8**, owing to its strong electrophilic nature, will be reduced in an especially rapid process, thus minimizing the reversibility of the reaction in eq 6. A preexistent Ti(III) ion–carbonyl oxygen coordination further on contributes to the easy reduction of **8**.

(c) Polyfunctional radicals like **2** (e.g., CH_3–Ċ(OH)–COOH, CH_3–Ċ(OH)–COOR, H–Ċ(OH)–COOH) have been shown[13,21] to transfer an electron to a whole range of acceptor molecules instead of dimerize. A strong interaction[22] between the LUMO of the aldehydic carbonyl group and the SOMO (singly occupied molecular orbital) of the alkyl radical **2** favors some degree of charge transfer in the transition state (Scheme V), thus lowering the activation energy of the reaction in eq 7.

Experimental Section

General Data. The physical data were obtained as follows: melting points in a Koffler apparatus (uncorrected); IR spectra on a Perkin-Elmer E 177; mass spectra on a Hitachi Perkin-Elmer RMU 6D at 70 eV; ^1H NMR spectra on a Varian A-90 and HA-100 with Me_4Si as an internal standard. All new compounds gave satisfactory elementary (C, H, N) analyses. Column and preparative chromatography were carried out by using Merck silica gel 60 (0.06–0.34 mm) and Merck Kieselgel G F-254 (2 mm) plates, respectively. All chemicals employed were reagent grade. The $TiCl_3$ solution (15% v/v in acidic water) was standardized against a 0.1 N Ce(IV) solution. Organic extracts were washed with distilled water, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residual oils were treated as indicated in each run.

General Procedures. All reactions took place at room temperature by rapid addition, under N_2, of an aqueous acidic 15% $TiCl_3$ solution (30 mmol, ca. 30 mL) to a well-stirred solution of **1** (15 mmol) and α,β-unsaturated aldehyde (100 mmol) in THF (10 mL). With cinnamaldehyde (runs **g**, **j**, and **m**) glacial CH_3-COOH (20 mL) was used in order to have, as much as possible, a homogeneous mixture. The reaction times are reported in Table I. Because of the different acidic, neutral, or basic properties of the reaction products, the respective procedures for their isolation are given.

Runs a–d. After evaporation of the excess of acrolein or crotonaldehyde at room temperature in vacuo, the mixture was

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(17) By X-ray diffraction analysis the complex was found to be μ-oxo-bis[chlorobis(2,4-pentanedionato)titanium(IV)]: $[TiCl(C_5H_7O_2)_2]_2O$; yellow crystals; mp 242–245 °C (from chloroform/ethylether). Bruckner, S.; Clerici, A.; Malpezzi, L.; Porta, O., unpublished results.
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extracted with ethyl acetate (3 × 100 mL). The chromatography of the crude oil on a silica gel column by using the gradient elution method (hexane/ethyl acetate from 9:1 to 1:1) afforded the following fractions: run **a**, dimer **3a** (benzyldicyanohydrin), benzoic acid, **6a**; run **b**, **7b**, **3a**, benzoic acid, **6b**; run **c**, **6c**, dimer **3c** (methyldiphenyltartarate); run **d**, **7d**, **6d**, **3c**. Complete separation of the two isomers of **6d** was achieved by subsequent preparative chromatography (eluant hexane/ethyl acetate, 7:3).

Runs e–g. Runs e and f. The crude reaction mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer, reduced to a small volume, was made alkaline with a 10% sodium hydroxide solution. The resulting aqueous solution, extracted with ethyl ether (3 × 50 mL) to remove the unreacted aldehyde, was acidified with a 10% hydrochloric acid solution and extracted with ethyl acetate (3 × 100 mL). The concentrated organic extracts afforded almost pure products **6e** and **6f**.

Run g. The crude reaction mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer, reduced to small volume, was made alkaline with a 30% sodium hydroxide solution. Extraction with ethyl ether (3 × 100 mL) of the resulting aqueous solution afforded the unreacted cinnamaldehyde along with the sodium salt of **6g**. This was recovered as white powder by allowing the ethereal extracts to stand overnight. Upon filtration, the precipitate was dissolved in boiling distilled water, and the solution was acidified with 20% hydrochloric acid solution. The free acid **6g**, precipitated in quantitative yield from the aqueous solution, was recrystallized from chloroform/hexane.

Runs h–m. The crude reaction mixture was extracted with ethyl ether (3 × 100 mL) to remove the excess of unreacted α,β-unsaturated aldehyde. The residual aqueous solution, with the addition of 20 mL of a 30% dibasic ammonium citrate solution to prevent hydrolytic precipitation of titanium dioxide and foaming, was made alkaline with a 10% sodium hydroxide solution and extracted with ethyl acetate (3 × 100 mL). The residual oil consisted of products **6h–m** slightly contaminated with dimer **3h** [2,3-bis(2-pyridyl)-2,3-butanediol] or **3k** [2,3-bis(4-pyridyl)-2,3-butanediol]. Subsequent purification of the crude oil by column chromatography (eluant ethyl ether) afforded the following fractions: run **h**, **3h**, **6h**; run **i**, **3h**, **6i**; run **j**, **3h**, **6j**: run **k**, **6k**, **3k**; run **l**, **6l**, **3k** (complete separation of the two isomers of **6l** was achieved only by subsequent preparative chromatography); run **m**, **6m**, **3k**. Owing to the limited solubility of **3h** and **3k** in the most common organic solvents, their quantitative recovery was obtained by continuous extraction of the alkaline aqueous solution with ethyl acetate. The isolated yields of pure products **6**, **7**, and **3** are reported in Table I.

Spectroscopic Data. For the spectroscopic assignments of **3a** see ref 11, for those of **3c** see ref 6, and for those of **3h** and **3k** see ref 5. The structures of the products **6** and **7** were deduced from the following data.

1-Phenyl-1-cyano-1,2-dihydroxy-3-butene (6a): threo and erythro mixture; NMR ($CDCl_3$) δ 4.25 (1 H, CH, d), 4.5–5.0 (2 H, 2 OH, br, D_2O exch), 5.2 (2 H, CH_2=C, m), 5.5–5.9 (1 H, C=CH, m), 7.5 (5 H, Ph H, m); IR[23] (film) ν_{max} 3400 (OH), 960 cm^{-1}; MS,[24] *m/e* 162 (M – HCN), 133, 105, 77, 57, 27 (HCN, base peak).

1-Phenyl-1-cyano-1,2-dihydroxy-3-pentene (6b): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.42–1.72 (3 H, CH_3, 2 d), 4.15–4.32 (1 H, CH, 2 d), 3.75–5.0 (2 H, 2 OH, br, D_2O exch), 5.2–6.0 (2 H, CH=CH, m), 7.25–7.70 (5 H, Ph H, m); IR[23] (film) ν_{max} 3400 (OH), 960 cm^{-1} (CH=CH out of the plane); MS,[24] *m/e* 176 (M – HCN), 107, 105 (base peak), 79, 77, 27 (HCN).

2,4-Dipropenyl-5-phenyl-5-cyano-1,3-dioxolane (7b): mixture of two stereoisomers; oil; NMR ($CDCl_3$) δ 1.5–1.8 (6 H, 2 CH_3, 4 d), 4.2 (1 H, CH, 2 d), 5.6–6.2 (5 H, 2 CH=CH and CH, m), 7.3–7.7 (5 H, Ph H, m); IR (film) ν_{max} 2210 (CN), 1250–1000 (5 characteristic bands of dioxolane ring[25]), 960 cm^{-1}.

Methyl 2-phenyl-2,3-dihydroxy-4-pentenoate (6c): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 3.7 and 3.8 (3 H, CH_3O, 2 s), 4.1 (1 H, CH, d), 4.3–4.9 (2 H, 2 OH, br, D_2O exch), 5.2 (2 H, CH_2=C, m), 5.8 (1 H, C=CH, m), 7.35 (3 H, Ph H, m), 7.7 (2 H, Ph H, m); IR (film) ν_{max} 3500 (OH), 2550 (intramolecular H bond with C=O), 1730 (CO), 1250, 930 cm^{-1}; MS, *m/e* 222 (M), 205 (M – OH), 166 (base peak), 163 (M – $COOCH_3$), 105, 77, 57.

Methyl 2-Phenyl-2,3-dihydroxy-4-hexenoate (6d). The threo and erythro isomers were separated by preparative chromatography (eluant hexane/ethyl acetate, 7/3). One isomer: NMR ($CDCl_3$) δ 1.46 (3 H, CH_3, d), 3.78 (3 H, CH_3O, s), 3.5 and 4.4 (2 H, 2 OH, br, D_2O exch), 4.9 (1 H, CH, d), 5.4–5.8 (2 H, CH=CH, m), 7.3 (3 H, Ph H, m), 7.7 (2 H, Ph H, m). The other isomer: NMR ($CDCl_3$) δ 1.68 (3 H, CH_3, d), 3.68 (3 H, CH_3O, s), 3.3–4.3 (2 H, 2 OH, br, D_2O exch), 4.7 (1 H, CH, d), 5.6–6.0 (2 H, CH=CH, m); IR (film) ν_{max} 3500 (OH), 1730 (CO), 960 cm^{-1}; MS, *m/e* 236 (M), 166, 117 (M – $COOCH_3$), 107, 105 (base peak), 79, 77, 71, 59.

2,4-Dipropenyl-5-phenyl-5-(methoxycarbonyl)-1,3-dioxolane (7d): stereoisomeric mixture; oil; NMR ($CDCl_3$) δ 1.52 and 1.80 (3 H, CH_3, 2 d), 3.68–3.72 (3 H, CH_3O, 4 s), 4.65 (1 H, CH, m), 5.35–6.10 (5 H, 2 CH=CH and CH, m), 7.35 (3 H, Ph H, m), 7.62 (2 H, Ph H, m); IR (film) ν_{max} 1730 (CO), 1250–1000 (5 characteristic bands of dioxolane ring[25]), 960 cm^{-1}; MS, *m/e* 288 (M), 287, 229 (M – $COOCH_3$), 218, 202, 159, 131, 105, 85 (base peak), 77.

2-Phenyl-2,3-dihydroxy-4-pentenoic acid (6e): threo and erythro mixture; mp 150–157 °C (from hexane/chloroform, 7/3); NMR (CD_3OD) δ 3.7 (3 H, 3 OH, s, D_2O exch), 4.8 (1 H, CH, d), 5.2–5.6 (2 H, CH_2=C, m), 5.8–6.2 (1 H, C=CH, m), 7.4 (3 H, Ph H, m), 7.7 (2 H, Ph H, m); IR (Nujol) ν_{max} 3300 (OH), 2580 (intramolecular H bond with C=O), 1690 (CO), 1240, 940 cm^{-1}; MS, *m/e* 208 (M), 191 (M – OH), 163 (M – COOH), 152 (base peak), 105, 77, 57.

2-Phenyl-2,3-dihydroxy-4-hexenoic Acid (6f). The threo and erythro isomers were separated by preparative chromatography. One isomer: mp 135–136 °C (from petroleum ether/chloroform, 9/1); NMR ($CDCl_3$) δ 1.74 (3 H, CH_3, d), 4.75 (1 H, CH, d), 4.0–6.0 (3 H, 3 OH, br, D_2O exch), 5.8 (2 H, CH=CH, m), 7.3 (3 H, Ph H, m), 7.75 (2 H, Ph H, m); IR (Nujol) ν_{max} 3300 (OH), 1690 (CO), 970 cm^{-1}. The other isomer: vitreous substance; NMR ($CDCl_3$) δ 1.5 (3 H, CH_3, d), 4.92 (1 H, CH, d), 5.3–5.8 (2 H, CH=CH, m), 6.6 (3 H, 3 OH, s, D_2O exch), 7.3 (3 H, Ph H, m), 7.65 (2 H, Ph H, m); IR (film) ν_{max} 3350 (OH), 1680 (CO), 960 cm^{-1}; MS, *m/e* 222 (M), 204 (M – H_2O), 160, 159, 105 (base peak), 77, 71.

2,5-Diphenyl-2,3-dihydroxy-4-pentenoic acid (6g): mp 165–168 °C (from hexane/chloroform, 7/3); NMR (CD_3OD) δ 3.1 (3 H, 3 OH, s, D_2O exch), 4.95 (1 H, CH, d, J = 6 Hz), 6.35 (1 H, CH=C, dd, J = 6, 17 Hz), 6.8 (1 H, C=CH, d, J = 17 Hz), 7.4 (8 H, Ph H, m), 7.8 (2 H, Ph H, m); IR (Nujol) ν_{max} 3300 (OH), 1690 (CO), 960 cm^{-1}; MS, *m/e* 284 (M), 266 (M – H_2O), 239, 222, 151, 133 (base peak), 105, 77.

Sodium salt of 6g: mp 220–225 °C; NMR (CD_3OD) δ 4.75 (2 H, 2 OH, br, D_2O exch), 4.85 (1 H, CH, d, J = 6 Hz), 6.2 (1 H, CH=C, dd, J = 6, 17 Hz), 6.55 (1 H, C=CH, d, J = 17 Hz), 7.25 (8 H, Ph H, m), 7.8 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500–3200 (OH), 1600 (COO^- asymmetric stretching, strong), 1390 cm^{-1} (COO^- symmetric stretching, strong); MS, *m/e* 238 (M – COOH), 132, 131 (base peak), 105, 77.

2-(2-Pyridyl)-2,3-dihydroxy-4-pentene (6h): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.5 and 1.6 (3 H, CH_3, 2 s), 4.25 (1 H, CH, d), 4.5 (2 H, 2 OH, s, D_2O exch), 5.2 (2 H, CH_2=C, m), 5.8 (1 H, C=CH, m), 7.2 (1 H, Py β-H, m), 7.6 (2 H, Py H, m), 8.5 (1 H, Py α-H, d); IR (film) ν_{max} 3400 (OH), 1590, 990, 920; MS, *m/e* 180 (M + 1),[26] 179, 162, 160, 122 (base peak), 104, 80, 79, 78, 59.

2-(2-Pyridyl)-2,3-dihydroxy-4-hexene (6i): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.45 and 1.52 (3 H, CH_3, 2 s), 1.53–1.65 (3 H, CH_3, 2 d), 4.2 (1 H, CH, d), 4.5–4.7 (2 H, 2 OH,

(23) The apparent absence of the CN group absorption may be explained with its triple bond character which can be greatly modified by interaction with neighboring hydroxyl groups: Raaen, V. R. *J. Org. Chem.* **1966**, *31*, 3310, footnote 9.

(24) The mass spectra of **6a** and **6b** do not show the molecular ion because of the complete loss of HCN due to its thermal decomposition. The presence of the CN group is confirmed by the very intense *m/e* 27 ion corresponding to HCN loss.

(25) Barker, S. A.; Bowrne, E. J.; Pinkard, R. M.; Whiffen, D. H. *J. Am. Chem. Soc.* **1959**, *81*, 807.

(26) This compound shows a very abundant M + H parent ion due to intramolecular reactions occurring at low pressure in the mass spectrometer.

br, D_2O exch), 5.3–5.8 (2 H, CH=CH, m), 7.1–7.8 (3 H, Py H, m), 8.5 (1 H, Py α-H, d); IR (film) ν_{max} 3400 (OH), 1590, 960 cm^{-1}; MS, *m/e* 193 (M), 178, 177, 176, 160, 144, 123, 122 (base peak), 80, 79, 70.

2-(2-Pyridyl)-2,3-dihydroxy-5-phenyl-4-pentene (6j): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.5 and 1.6 (3 H, CH_3, 2 s), 4.45 (1 H, CH, d, *J* = 6 Hz), 4.8 (2 H, 2 OH, br, D_2O exch), 6.25 (1 H, CH=C, 55, *J* = 6, 15 Hz), 6.6 (1 H, C=CH, d, *J* = 15 Hz), 7.2 (5 H, Ph H, m), 7.6 (3 H, Py H, m), 8.5 (1 H, Py α-H, m); IR (film) ν_{max} 3400 (OH), 1590, 690 cm^{-1}; MS,[27] *m/e* 255 (M), 237 (M – H_2O), 220, 208, 194, 132, 131, 122 (base peak), 104, 103, 80, 79, 78, 77.

2-(4-Pyridyl)-2,3-dihydroxy-4-pentene (6k): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.42 and 1.55 (3 H, CH_3, 2 s), 4.2 (1 H, CH, d), 5.0–5.3 (2 H, CH_2=C, m), 5.2 (2 H, 2 OH, s, D_2O exch), 5.5–5.8 (1 H, C=CH, m), 7.4 (2 H, Py β-H, m), 8.5 (2 H, Py α-H, d); IR (film) ν_{max} 3500–3100 (OH, br), 1600, 1410, 1000, 920 cm^{-1}; MS, *m/e* 180 (M + 1),[28] 179, 164, 162, 146, 122 (base peak), 78, 77, 55.

2-(4-Pyridyl)-2,3-dihydroxy-4-hexene (6l). The threo and erythro isomers were separated by preparative chromatography (eluant hexane/ethyl acetate, 9/1). One isomer: oil; NMR ($CDCl_3$) δ 1.58 (3 H, CH_3, s), 1.60 (3 H, CH_3, d), 4.12 (1 H, CH, d), 4.4 (2 H, 2 OH, s, D_2O exch), 5.1–5.8 (2 H, CH=CH, m), 7.4 (2 H, Py β-H, m), 8.5 (2 H, Py α-H, d); IR (film) ν_{max} 3400–3100 (OH, br), 1600, 960 cm^{-1}; MS, *m/e* 193 (M), 178, 149, 123, 122 (base peak), 106, 80, 79, 78, 71. The other isomer: oil; NMR ($CDCl_3$) δ 1.44 (3 H, CH_3, s), 1.72 (3 H, CH_3, d), 3.45 (2 H, 2 OH, s, D_2O exch), 4.16 (1 H, CH, d), 5.5–5.7 (2 H, CH=CH, m), 7.4 (2 H, Py β-H, m), 8.5 (2 H, Py α-H, d).

2-(4-Pyridyl)-2,3-dihydroxy-5-phenyl-4-pentene (6m): threo and erythro mixture; oil; NMR ($CDCl_3$) δ 1.46 and 1.6 (3 H, CH_3, 2 s), 4.35 (1 H, CH, d), 5.15 (2 H, 2 OH, s, D_2O exch), 6.0–6.7 (2 H, CH=CH, m), 7.32 (7 H, 5 Ph H and 2 Py β-H, m), 8.43 (2 H, Py α-H, d); IR (film) ν_{max} 3400–3000 (OH, br), 1600, 960, 750 cm^{-1}; MS,[27] *m/e* 255 (M), 237 (M – H_2O), 220, 209, 208, 194, 132, 131, 122 (base peak), 104, 103, 80, 79, 78, 77.

(27) Primary loss of water (M – H_2O) leads to unusual formation of an epoxide structure. Clerici, A.; Traldi, P. *Org. Mass Spectrom.* **1983**, *18*, 114.

Registry No. 1 (R = Ph; X = CN), 613-90-1; 1 (R = Ph; X = $COOCH_3$), 15206-55-0; 1 (R = Ph; X = COOH), 611-73-4; 1 (R = CH_3; X = 2-Py), 1122-62-9; 1 (R = CH_3; X = 4-Py), 1122-54-9; **6a** (isomer 1), 85097-67-2; **6a** (isomer 2), 85097-68-3; **6b** (isomer 1), 85097-69-4; **6b** (isomer 2), 85097-70-7; **6c** (isomer 1), 85097-71-8; **6c** (isomer 2), 85097-72-9; **6d** (isomer 1), 85097-73-0; **6d** (isomer 2), 85097-74-1; **6e** (isomer 1), 85097-75-2; **6e** (isomer 2), 85097-76-3; **6f** (isomer 1), 85097-77-4; **6f** (isomer 2), 85097-78-5; **6g**, 85097-79-6; **6g**·Na, 85097-80-9; **6h** (isomer 1), 85115-78-2; **6h** (isomer 2), 85097-81-0; **6i** (isomer 1), 85097-82-1; **6i** (isomer 2), 85097-83-2; **6j** (isomer 1), 85097-84-3; **6j** (isomer 2), 85097-85-4; **6k** (isomer 1), 85097-86-5; **6k** (isomer 2), 85097-87-6; **6l** (isomer 1), 85097-88-7; **6l** (isomer 2), 85097-89-8; **6m** (isomer 1), 85097-90-1; **6m** (isomer 2), 85097-91-2; **7b**, 85097-92-3; **7d**, 85097-93-4; acrolein, 107-02-8; crotonaldehyde, 4170-30-3; cinnamaldehyde, 104-55-2; titanium trichloride, 7705-07-9.

Synthesis and Reactions of Cyclic Carbodiimides

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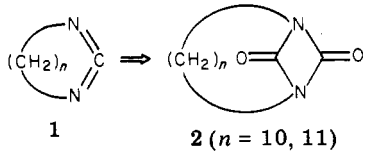
Modified Tiemann rearrangement on cyclic amidoxime *O*-methanesulfonates **4** has been used to synthesize cycloalkylene carbodiimides **1** and 4,5,6,7-tetrahydrobenzo-1,3-diazonine (**1g**). 1,3-Diazacycloocta-1,2-diene (**1b**, *n* = 5) was also prepared by dehydrosulfuration of pentamethylenethiourea. [2 + 2] cycloadducts of the type **20** and **21** are readily formed from **1** as well as **1g** with aryl isocyanates and *N,N'*-diphenylcarbodiimide. Hexafluoroacetone and **1d** (*n* = 7) give a dioxazane, **24b** (*n* = 7), while **1c** (*n* = 6) produces inseparable mixtures of **24a** (*n* = 6) and oxazetidine **23**. 1,3-Diazacyclohepta-1,2-diene (**1a**, *n* = 4) oligomerizes on preparation from tetramethylenethiourea, giving predominantly cyclodimer **7** and trimer **8** (not isolated); it can also be trapped with *N,N'*-diphenylcarbodiimide to give **20a** (*n* = 4, X = NC_6H_5).

We have recently reported about the synthesis of two novel intramolecular alkylene diisocyanate dimers with structure **2**, both of which were prepared from the corresponding cycloalkylene carbodimides in a three-step synthesis.[1]



1 **2** (*n* = 10, 11) (1)

Knowledge about compounds of type **1**, which contain the carbodiimide moiety as part of a ring system, was limited at the time we started our investigation,[2] although several recent publications are testimony to renewed interest in this area.[3-5] Especially lacking was an efficient synthetic method which would allow the preparation of larger quantities of cycloaliphatic carbodiimides for further studies. This need has consequently led us to (a) attempt to find an improved route to **1** and (b) study the chemistry of these carbodiimides as well as some of their precursors.

Synthesis of Cycloaliphatic Carbodiimides

The only method available for the preparation of alkylenecarbodiimides **1** with *n* ≥ 5 until 1979 consisted of dehydrosulfuration of the corresponding thioureas.[2] Cy-

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(2) Behringer, H.; Meier, H. *Justus Liebigs Ann. Chem.* **1957**, *607*, 67.
(3) Hiatt, R. R.; Shaio, M. J.; George, F. *J. Org. Chem.* **1979**, *44*, 3265.
(4) Recently, several very labile seven-membered-ring carbodiimides were prepared and spectroscopically identified by flash vacuum pyrolysis of heteroaromatic azides (which are generated from tetrazolopyridines or pyrimidines and other benzo-annealated systems) at elevated temperatures: Wentrup, C.; Winter, H. W.; *J. Am. Chem. Soc.* **1980**, *102*, 6159. Wentrup, C.; Thetaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitschke, B.; Winter, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566.
(5) Damrauer, R.; Soucy, D.; Winkler, P.; Eby, S. *J. Org. Chem.* **1980**, *45*, 1315.

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