$J$ = 7.5, 13.5, 1 H), 2.41 (dd, $J$ = 13.0 Hz, 1 H), 2.99 (dd, $J$ = 5.0, 8.0 Hz, 1 H), 3.12 (quintet, $J$ = 8.0 Hz, 1 H), 3.44 (ddd, $J$ = 5.5, 7.5, 13.0 Hz, 1 H), 4.08–4.31 (m, 4 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 14.00, 14.08, 23.44, 23.90, 24.15, 25.54, 25.93, 31.89, 33.19, 33.59, 33.71, 34.16, 34.67, 36.84, 38.43, 43.25, 45.22, 45.96, 46.01, 48.11, 48.36, 48.60, 55.44, 55.79, 57.33, 59.69, 59.73, 60.64, 61.53, 61.63, 61.73, 61.94, 63.26, 63.77, 169.44, 170.42, 170.83, 172.07; exact mass calcd for $C_{21}H_{34}O_6S$ 414.2076, found 414.2122. Anal. Calcd for $C_{21}H_{34}O_6S$: C, 60.84; H, 8.27; S, 7.73. Found: C, 60.90; H, 8.23; S, 7.58.

**Diethyl 4-Methyl-3-(phenylsulfonyl)-1,1-cyclopentanedicarboxylate (5h) and Diethyl 2-(2-Propen-1-yl)-2-[2-(phenylsulfonyl)ethyl]propane-1,3-dioate (5h′).** The general procedure for radical cyclization was followed with use of bromides **3h** (331 mg, 0.740 mmol) in benzene (60 mL), triphenyltin hydride (410 mg, 1.17 mmol) in benzene (10 mL), and AIBN (10.0 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica (2 × 15 cm) using 25% ethyl acetate–hexane gave two fractions. The thick syrupy material of lower $R_f$ was a mixture of **5h** (83 mg,[30] 30% yield; 35% based on conversion) together with **5h′** (51 mg,[30] 19% yield; 21% based on conversion). The fraction of higher $R_f$ (44.9 mg, 13%) was unreacted starting material. The mixture of products **5h** and **5h′** had the following characteristics: FT-IR ($CCl_4$ cast) 1730, 1440, 1305, 1253, 1181, 1149, 1080 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ (signals assigned to reduction product **5h′**) 1.21 (t, $J$ = 7.5 Hz, 6 H), 2.20 (two superimposed dd, $J$ = 4.0, 13.0 Hz and $J$ = 8.0, 9.0 Hz, 2 H), 2.58 (d, $J$ = 7.5 Hz, 2 H), 3.14 (two superimposed dd, $J$ = 4.0, 13.0 Hz, and $J$ = 8.0, 9.0 Hz, 2 H), 4.14 (q, $J$ = 7.5 Hz) and 4.15 (q, $J$ = 7.5 Hz) [both signals together correspond to 4 H], 5.05 (m, 2 H), 5.51 (m, 1 H), 7.54–7.72 (m, 3 H), 7.70 (m, 2 H); (signals assigned to cyclization product **5h**) 0.98–1.49 (m, 9 H), 1.80 (m, 0.30 H), 2.38 (m, 2.3 H), 2.62–2.80 (m, 2.4 H), 3.25 (m, 0.4 H), 3.53 (m, 0.6 H), 4.05–4.32 (m, 4 H), 7.41–8.02 (m, 5 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.5, 15.3, 19.2, 25.4, 34.0, 34.6, 35.2, 35.9, 37.3, 41.0, 41.7, 51.3, 55.4, 57.9, 58.0, 61.2, 61.4, 65.2, 69.0, 119.4, 127.7, 128.1, 128.4, 128.7, 128.8, 130.8, 133.1, 133.3, 135.7, 139.5, 169.5, 170.2, 171.4; exact mass, $m/z$ [$(M - SO_2C_6H_5)^+$] calcd for $C_{12}H_{19}O_4$ 227.1283, found 227.1283.

An authentic sample of **5h′** was prepared by the procedure employed for **3a** with diethyl 2-(2-propen-1-yl)propane-1,3-dioate[29] (248 mg, 1.24 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (66.4 mg, 50% dispersion in oil, 1.38 mmol) in THF (15 mL), and phenyl vinyl sulfone[24] (176 mg, 1.05 mmol) in THF (3 mL + 1-mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **5h′** (172 mg, 44%) as a colorless oil: $^1$H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, $J$ = 7.5 Hz, 6 H), 2.20 (two superimposed dd, $J$ = 4.0, 13.0 Hz and $J$ = 8.0, 9.0 Hz, 2 H), 2.58 (d, $J$ = 7.5 Hz, 2 H), 3.14 (two superimposed dd, $J$ = 4.0, 13.0 Hz, and $J$ = 8.0, 9.0 Hz, 2 H), 4.14 (q, $J$ = 7.5 Hz), and 4.15 (q, $J$ = 7.5 Hz) [both signals together correspond to 4 H], 5.05 (m, 2 H), 5.51 (m, 1 H), 7.54–7.72 (m, 3 H), 7.70 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 14.01, 25.91, 37.80, 51.85, 55.96, 61.72, 119.88, 128.12, 129.32, 131.30, 133.80, 138.70, 169.97; exact mass, $m/z$ calcd for $C_{18}H_{24}O_6S$ 368.1294, found 368.1290.

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**Registry No.** **1a**, 53608-93-8; **1d**, 6305-63-1; **1e**, 118893-25-7; **1f**, 60415-75-0; **1g**, 118920-25-5; **1h**, 2049-80-1; **2a**, 17101-78-9; **2b**, 118893-26-8; **2c**, 75804-36-3; **2d**, 4519-46-4; **3a** (isomer 1), 118893-27-9; **3a** (isomer 2), 118893-46-2; **3b** (isomer 1), 118893-28-0; **3b** (isomer 2), 118893-47-3; **3c** (isomer 1), 118893-29-1; **3c** (isomer 2), 118893-48-4; **3d** (isomer 1), 118893-30-4; **3d** (isomer 2), 118893-49-5; **3e** (isomer 1), 118893-31-5; **3e** (isomer 2), 118893-50-8; **3f**, 118893-32-6; **3g** (isomer 1), 118893-33-7; **3g** (isomer 2), 118893-51-9; **3h**, 118893-34-8; **5a** (isomer 1), 118893-35-9; **5a** (isomer 2), 118893-52-0; **5a′**, 118893-36-0; **5b** (isomer 1), 118893-37-1; **5b** (isomer 2), 118893-53-1; **5c** (isomer 1), 118893-38-2; **5c** (isomer 2), 118893-54-2; **5d** (isomer 1), 118893-39-3; **5d** (isomer 2), 118893-55-3; **5e** (isomer 1), 118893-40-6; **5e** (isomer 2), 118893-56-4; **5f** (isomer 1), 118893-41-7; **5f** (isomer 2), 119007-00-0; **5f** (isomer 3), 119007-01-1; **5f** (isomer 4), 119007-02-2; **5g** (isomer 1), 118893-42-8; **5g** (isomer 2), 119007-03-3; **5h**, 118893-43-9; **5h′**, 118893-44-0; 2-[(1,1-dimethylethyl)thio]ethanol, 5396-50-9; 2-methyl-2-propanethiol, 75-66-1; 2-chloroethanol, 107-07-3; [(1,1-dimethylethyl)thio]ethene, 14094-13-4; [(1,1-dimethylethyl)-sulfonyl]ethene, 18288-23-8; 1,2-dibromoethyl 1,1-dimethylethyl sulfone, 118893-45-1; methyl acrylate, 96-33-3; phenylselenenyl chloride, 5707-04-0; phenyl vinyl sulfone, 5535-48-8.

(30) This weight is calculated from the weight of the mixture and from its composition as determined by $^1$H NMR spectroscopy.

## Reactions of Norbornyl Aldehydes with Diiron Nonacarbonyl: A Stereoselective Pathway to "Geminal-Faced" Esters and Alcohols

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Metal complexes are useful reagents for the synthesis of many organic compounds. The stereoselectivity that often accompanies these reactions[1-3] is of paramount interest, and a focus of this report is on the stereocontrol mediated by iron carbonyl in its reactions with norbornyl aldehydes.

The reported reactions of aldehydes with iron carbonyl reagents have been limited to α,β-unsaturated systems in which stable π-complexes are formed. For example, acrolein coordinates with diiron nonacarbonyl to provide (acrolein)iron tetracarbonyl[4] and cinnamaldehyde gives rise to a heterodieneiron tricarbonyl in which the iron fragment is coordinated to the C=C—C=O linkage.[5] The norbornyl aldehydes chosen for this study were not expected to form stable complexes. Therefore, it was hoped that their carbonyl functions would become reactive sites in the presence of diiron nonacarbonyl, and these expectations were indeed realized.

In the presence of diiron nonacarbonyl in refluxing hexane or tetrahydrofuran (THF), norbornane-2-carboxaldehyde (**1**) was converted to the endo,endo congener (90% isomeric purity) of norbornan-2-ylmethyl norbornane-2-carboxylate (**2**) in 54% and 71% yields, respectively, after 48 h (Scheme I). In addition, a minor amount (4–6%) of the reduction product, *endo*-2-(hydroxymethyl)norbornane (**3**), was generated as well, which possessed an isomeric purity of 85% (Table I).

Under the same reaction conditions, in hexane or THF, 3-methylnorbornane-2-carboxaldehyde (**4**) was converted to (3-methylnorbornan-2-yl)methyl 3-methylnorbornane-2-carboxylate (**5**) in 51% and 77% yields, respectively, after 48 h. The synthesis of **5** occurred without the stereoselectivity associated with **2**, but this lack of stereocontrol possibly resulted from the variation displayed by the 3-methyl functions of the "geminal-faced" ester. An alcohol was not isolated from this reaction, but its presence was suggested by TLC.

Although yield enrichments were observed for esters **2** and **5** with a change of solvent, alcohol formation remained approximately the same. Nevertheless, these results emphasized the importance of solvent characteristics as a parameter for ester synthesis. Indeed, it is well known[6,7] that THF stabilizes iron carbonyl through complexation,

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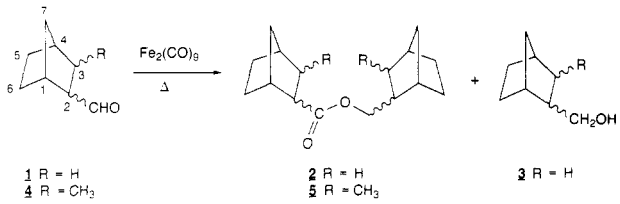
**Scheme I. Reactions of Norbornyl Aldehydes with Diiron Nonacarbonyl**




1 R = H
4 R = $CH_3$

2 R = H
5 R = $CH_3$

3 R = H

**Table I. Product Distribution from the Reaction of Norbornane-2-carboxaldehyde with Diiron Nonacarbonyl[a]**

| solvent | reactn time, h | % ester | % alcohol |
|---|---|---|---|
| hexane | 48 | 54 | 6 |
| THF | 48 | 71 | 4 |
| butyl ether | 24 | – | 48 |
| | 48 | – | 68 |

[a] Each reaction was conducted under a nitrogen atmosphere at the reflux temperature of the solvent. Isomeric purity of ester **2** was ~90% endo,endo; isomeric purity of alcohol **3** was ~85% endo.

and this evidently contributed to the higher ester yields in that medium. Alcohol formation must have been perpetrated by an iron carbonyl hydride, probably dihydroiron tetracarbonyl,[8] which was generated in situ. However, the concentration of such a hydride was apparently small in both hexane and THF based upon the minor yields of alcohol in those solvents. In refluxing *n*-butyl ether, the reaction of **1** with diiron nonacarbonyl gave only a reduction product. This reduction provided **3** in 48% and 68% yields after 24 and 48 h, respectively. The higher reaction temperature achieved with *n*-butyl ether must have been responsible for the sole production of 2-(hydroxymethyl)norbornane (**3**) in that solvent; THF and hexane possess similar boiling points, but their reaction temperatures are dramatically lower. It thus seemed reasonable to assume that the rate of aldehyde reduction is directly proportional to solvent temperature, while lower temperatures—and perhaps more polar solvents, especially those with chelating qualities—enhance ester synthesis.

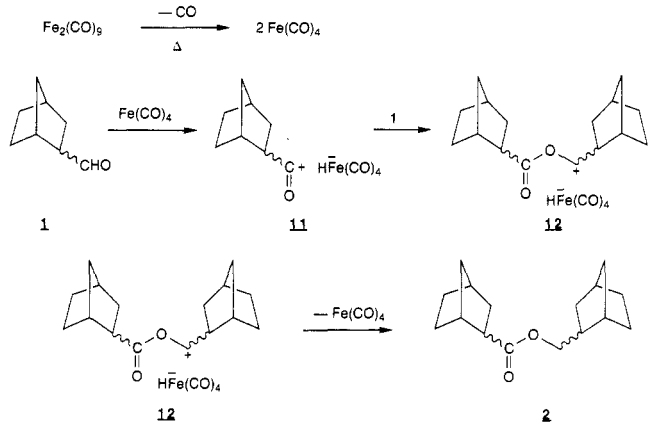
The proton NMR spectrum of ester **2** contained a resonance assigned to the $CH_2O$ fragment ($\delta$ 3.69–4.15), which clearly favors an endo,endo isomer. The sharp doublet at $\delta$ 3.69–3.77 represented about 90% of that isomer, and the remaining absorptions ($\delta$ 3.85–4.15) belonged to the other three possible conformations. Further support for the endo,endo assignment of the major isomer of **2** came from the NMR spectrum of its unsaturated analogue, 5-norbornen-2-ylmethyl 5-norbornene-2-carboxylate (**7**). This ester possessed a major olefinic resonance ($\delta$ 6.10–6.30) that must belong to an endo,endo isomer based upon the olefinic region of 5-norbornene-2-carboxaldehyde (**6**). In addition, subsequent hydrogenation of **7** gave **2** in about the same isomeric purity. The synthesis of **2** by a direct route (acid-catalyzed esterification) provided an ester that did not favor any particular isomer, and this illustrated the lack of stereocontrol offered by that process.

**Table II. Product Distribution from the Reaction of 5-Norbornene-2-carboxaldehyde with Diiron Nonacarbonyl[a]**

| solvent | reactn time, h | % ester | % alcohol | % dimer[b] | % binuclear complex[c] |
|---|---|---|---|---|---|
| hexane | 48 | 19 | 4 | 9 | 13 |
| THF | 48 | 45 | 4 | 3 | 3 |

[a] Each reaction was conducted under a nitrogen atmosphere at the reflux temperature of the solvent. Isomeric purity of ester **7** was ~90% endo,endo; isomeric purity of alcohol **8** was ~75% endo. [b] Dimer represents dicyclopentadiene. [c] Binuclear complex represents [bis($\eta^5$-cyclopentadienyl)di-$\mu$-carbonyl]diiron dicarbonyl.

**Scheme II. Proposed Mechanism for Ester Synthesis from the Reaction of Norbornyl Aldehydes with Diiron Nonacarbonyl**




NMR analysis of alcohol **3** revealed a sharp doublet at $\delta$ 3.21–3.28 (endo $CH_2O$), which represented 85% of the endo:exo mixture. The minor doublet at $\delta$ 3.50–3.57 represented *exo*-2-(hydroxymethyl)norbornane.

The unsaturated analogue of **1**, 5-norbornene-2-carboxaldehyde (**6**), also reacted in the presence of diiron nonacarbonyl to give the expected "geminal-faced" ester **7** as well as the reduction product, 2-(hydroxymethyl)-5-norbornene (**8**). In addition, reverse Diels–Alder products were formed, too. In refluxing hexane, for instance, **7** and **8** were isolated in 19% and 4% yields, respectively, while thermal decomposition of the aldehyde substrate became the major event of this reaction (Table II). This reverse Diels–Alder process seemed to occur via a metal-assisted decomposition of **6**, since pyrolytic rupture of its bonds was not significant in refluxing hexane when diiron nonacarbonyl was absent. The yields of dicyclopentadiene (**9**) and [bis($\eta^5$-cyclopentadienyl)di-$\mu$-carbonyl]diiron dicarbonyl (**10**) were rather small, but most of the cyclopentadiene generated from the reverse Diels–Alder process of **6** evidently escaped the reaction vessel before it could dimerize[9–11] or coordinate with iron carbonyl.[12,13] In THF the yield of ester **7** increased to 45% while reduction remained almost constant. Again, the impact of solvent characteristics was demonstrated. The yields of **7** and **8** were modest, but product formation was stereoselective. Each synthesis favored an endo,endo congener (~90% isomeric purity), and the isolated alcohol was generated

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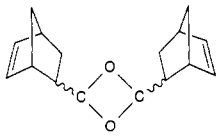

**Figure 1.** Dioxetane (13) generated from the Diels–Alder reaction between acrolein and cyclopentadiene in the presence of $CCl_4$.

in 75% stereochemical yield favoring *endo*-2-(hydroxymethyl)-5-norbornene (8).

A plausible mechanism that supports ester synthesis begins with hydride abstraction from the norbornyl substrate, 1, by iron tetracarbonyl[12,13] to generate an ion pair (11)[14,15] (Scheme II). Hydride abstraction is supported by the gradual disappearance of the endo, followed by the exo, aldehyde resonance when the reaction is followed by $^1H$ NMR spectroscopy, and the accelerated rate of ester formation in THF, as opposed to hexane, indicates the intermediacy of a stable carbocation. Nucleophilic attack on 11 by free norbornyl aldehyde provides a cationic ester, 12, the precursor of ester 2, which is acquired after the hydride ion is returned from the counter anion, hydrotetracarbonylferrate. It is possible that hydrotetracarbonylferrate is converted to dihydroiron tetracarbonyl[8] in the presence of a proton source, perhaps the aldehyde, and such a species would certainly reduce the norbornyl substrate.

The high stereoselectivity observed in these metal-mediated reactions, as compared to preparation by other methods, is not unusual, and many other examples are reported in the literature.[1-3] The preferred synthesis of an endo,endo ester from these manipulations may be related to the fact that endo aldehyde reacted faster than its exo congener. In addition, most of the exo aldehyde must have been isomerized to its endo form prior to its conversion to an ester, since the starting aldehydes are composed of about 40% exo isomer, while the stereochemical yield of endo ester was at least 90%.

An interesting result was observed during the attempted preparation of one of the starting materials, 5-norbornene-2-carboxaldehyde (6). The cycloaddition reaction between acrolein and cyclopentadiene normally proceeds to form 6,[16] but when this reaction was conducted in carbon tetrachloride the aldehyde was dimerized to a dioxetane, 13 (Figure 1). Besides the strong ether absorption at 1100 $cm^{-1}$ in the IR spectrum, structure determination of 13 was based upon the results obtained from $^1H$ NMR, mass spectral, and elemental analysis data.

With respect to the norbornyl fragments, three isomeric structures for 13 are possible: endo,endo; endo,exo; and exo,exo. The NMR spectrum supports the generation of two isomers, tentatively assigned as the endo,endo (major) and endo,exo (minor) congeners.[17] Further investigation may provide additional evidence to substantiate this proposed stereochemistry.

## Experimental Section

**General Procedures.** All solvents were dried over activated 3-Å molecular sieves or distilled over sodium benzophenone ketyl. Catalytic hydrogenation[18] of 3-methyl-5-norbornene-2-carboxaldehyde and 5-norbornene-2-carboxaldehyde (Aldrich Chemicals) provided the starting materials, norbornane-2-carboxaldehyde and 3-methylnorbornane-2-carboxaldehyde. Model esters, for comparison with those generated by iron carbonyl, were prepared by acid-catalyzed esterification using the appropriate alcohols and carboxylic acids. All starting materials were characterized by NMR, IR, and elemental analyses. Diiron nonacarbonyl[19] was prepared by a literature method. $^1H$ NMR spectra were recorded on Varian EM-360 and Varian EM-390 spectrometers, operating at 60 and 90 MHz, respectively. IR data was obtained from a Perkin-Elmer 1320 or a Shimadzu 460 grating spectrometer using NaCl plates or matching KCl cells. GC information was obtained from a Varian Aerograph 1400 or a Hewlett-Packard 5890A gas chromatograph equipped with SP-4270 integrators; samples were injected onto a 6-ft column of 3% SE-30 on Chromosorb WHP 180/100, a 6-ft column of 10% Carbowax 20 M on Varaport-30 100/120, or on a 15M DB-WAX capillary column. Mass spectra were recorded on an AEI MS-902 high-resolution direct-probe instrument. Elemental analyses were performed by Atlantic Microlab, Inc. TLC analyses were conducted on Merck silica gel 60 $F_{254}$ analytical plates.

**Reactions of Norbornyl Aldehydes with Diiron Nonacarbonyl.** Norbornane-2-carboxaldehyde (1, 1.0 g, 8.05 mmol), 3-methylnorbornane-2-carboxaldehyde (4, 1.0 g, 7.24 mmol), and 5-norbornene-2-carboxaldehyde (6, 1.0 g, 8.18 mmol) were each heated to reflux in tetrahydrofuran or hexane in the presence of diiron nonacarbonyl (6.0 g, 16.48 mmol) for 48 h under nitrogen. Each reaction mixture was subsequently filtered over Celite, and the filtrates were concentrated. Chromatography (silica gel 60/$CH_2Cl_2$ eluant) provided the product distributions in pure form. The reaction of 1 in THF provided 710 mg (2.86 mmol, 71%) of norbornan-2-ylmethyl norbornane-2-carboxylate (2), which slowly crystallized to a glass (mp 95–97 °C), and 36 mg (0.29 mmol, 4%) of 2-(hydroxymethyl)norbornane (3). **Ester 2**: $^1H$ NMR (90 MHz, $CDCl_3$) δ 0.55–0.82, 1.10–2.00 (m, 16 H), 2.00–2.37 (m, 4 H), 2.37–2.85 (m, 2 H), 3.69–4.15 [2 H (3.69–3.77, d, *endo*-$CH_2O$, $J$ = 2.4 Hz), 3.85–4.15, m, remaining isomers]; IR ($CH_2Cl_2$) 2950 (s), 1730 (s), 1449 (m), 1213 (m), 1179 (s), 1063 (m), 1034 (sh) $cm^{-1}$; mass spectrum, calcd mass for $C_{16}H_{24}O_2$ 248.1776, found 248.1781. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.23; H, 9.77. **Alcohol 3**: $^1H$ NMR (90 MHz, $CDCl_3$) δ 0.50–0.74, 0.80–1.85 (m, 8 H), 1.97–2.34 (m, 3 H), 2.93 (br s, 1 H), 3.21–3.57 [2 H (3.21–3.28, d, *endo*-$CH_2O$, $J$ = 2.1 Hz), 3.50–3.57, d, *exo*-$CH_2O$, $J$ = 2.1 Hz]; IR (neat) 3345 (s), 2950 (s), 2865 (s), 1042 (s), 1028 (sh), 1002 (m), 735 (s) $cm^{-1}$. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.02; H, 11.09. The reaction of 4 in THF provided 770 mg (2.79 mmol, 77%) of (3-methylnorbornan-2-yl)methyl 3-methylnorbornane-2-carboxylate (5) as an oil: $^1H$ NMR (90 MHz, $CDCl_3$) δ 0.72–2.57 (m, 26 H), 3.72–4.09 (m, 2 H); IR (neat) 2955 (s), 2870 (m), 1730 (s), 1451 (m), 1388 (sh), 1291 (m), 1180 (s), 1153 (m), 1123 (m) $cm^{-1}$; mass spectrum, calcd mass for $C_{18}H_{28}O_2$ 276.2089, found 276.2092. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.18; H, 10.23. The reaction of 6 in THF provided 450 mg (1.84 mmol, 45%) of 5-norbornen-2-ylmethyl 5-norbornene-2-carboxylate (7) as an oil, 37 mg (0.30 mmol, 4%) of 2-(hydroxymethyl)-5-norbornene (8) as an oil, 42 mg (0.12 mmol, 3%) of [bis($\eta^5$-cyclopentadienyl)di-$\mu$-carbonyl]diiron dicarbonyl (9),[12,13] and 18 mg (0.14 mmol, 3%) of dicyclopentadiene (10).[9-11] **Ester 7**: $^1H$ NMR (90 MHz, $CDCl_3$) δ 0.41–0.70, 1.10–2.59 (m, 8 H), 2.60–2.98 (m, 4 H), 2.98–3.20 (m, 2 H), 3.68–4.25 (m, 2 H), 5.76–6.30 [4 H (5.76–6.10, m, isomeric mixture), 6.10–6.30, m, endo,endo isomer]; IR (neat 3140 (w), 3062 (m), 2975 (s), 2875 (m), 1730 (s), 1335 (s), 1272 (m), 1234 (m), 1175 (s), 1110 (m), 1030 (m) $cm^{-1}$. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.57; H, 8.28. **Alcohol 8**: $^1H$ NMR (90 MHz, $CDCl_3$): δ 0.38–0.62, 1.08–2.07 (m, 5 H), 2.07–2.48 (m, 1 H), 2.60–2.99 (m, 2 H), 2.99–3.80 (m, 2 H), 5.85–6.18 [2 H (5.85–6.01, m, exo isomer), 6.01–6.18, m, endo isomer]; IR (neat) 3335 (s), 2960 (s), 2865 (s), 1331 (m), 1056 (m), 1030 (s), 1010 (sh) $cm^{-1}$. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.27; H, 9.79.

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(15) An alternate mechanism, as suggested by a reviewer, involves addition of $Fe(CO)_4$ to the C–H bond of the aldehyde to first give an acyliron tetracarbonyl hydride, which then reacts with free aldehyde to provide intermediate 12. Acylmetal carbonyls are accepted intermediates during the hydroformylation of alkenes (ref 21 and 22).

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**Reaction of 1 with Diiron Nonacarbonyl in Butyl Ether.** A solution of 1 (1.0 g, 8.05 mmol) in 50 mL of *n*-butyl ether was heated to reflux in the presence of 6.0 g (16.48 mmol) of diiron nonacarbonyl for 48 h under nitrogen. The workup, as previously described, gave 691 mg (5.48 mmol, 68%) of 2-(hydroxymethyl)norbornane (**3**) possessing an endo isomeric purity of 85%.

**Reaction of Cyclopentadiene and Acrolein in the Presence of Carbon Tetrachloride.** A solution of freshly prepared[20] cyclopentadiene (26 g, 394 mmol) in 50 mL of $CCl_4$ was added dropwise to a stirred solution of acrolein (22 g, 393 mmol) in 50 mL of $CCl_4$ at 0 °C under a nitrogen atmosphere. The contents were stirred overnight, the solvent was removed at reduced pressure, and the residue was distilled (42–43 °C/7 mmHg), giving 37 g (152 mmol, 77%) of an oil that quickly solidified upon cooling. Recrystallization from acetone gave 32 g of pure product (mp 168–171 °C), identified as a dioxetane, **13**: $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 0.62–1.52 (m, 6 H), 1.55–2.05 (m, 2 H), 2.15–2.58 (m, 2 H), 2.67–3.11 (m, 4 H), 3.88–3.99 (2 H [two isomeric doublets: 3.88–3.97, $J$ = 2.7 Hz, minor isomer; 3.90–3.99, $J$ = 2.7 Hz, major isomer]), 5.69–6.18 (m, 4 H); IR ($CH_2Cl_2$) 3060 (w), 2965 (m), 2890 (m), 1360 (m), 1339 (m), 1207 (m), 1100 (s), 1058 (m) cm$^{-1}$; mass spectrum, calcd mass for $C_{16}H_{20}O_2$ 244.1463, found 244.1460; other fragments at $m/e$ 151, 122, and 93. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65, H, 8.25. Found: C, 78.76; H, 8.29.

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**Registry No.** *endo*-**1**, 3574-54-7; *exo*-**1**, 3574-55-8; **2**, 119337-06-3; *endo*-**3**, 13137-31-0; *exo*-**3**, 13118-79-1; **4**, 19923-87-6; **5**, 119337-07-4; *endo*-**6**, 19926-90-0; *exo*-**6**, 19926-88-6; **7**, 1218-65-1; *endo*-**8**, 15507-06-9; *exo*-**8**, 13360-81-1; **9**, 12154-95-9; **10**, 77-73-6; **13**, 119337-08-5; diiron nonacarbonyl, 15321-51-4; cyclopentadiene, 542-92-7; acrolein, 107-02-8.

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## Facile Stereospecific Synthesis of Deoxyfucosyl Disaccharide Units of Anthracyclines

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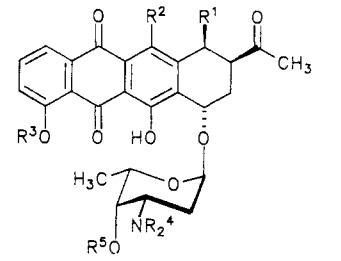
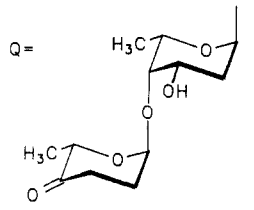
One of the main problems in the clinical application of anthracyclines like, e.g., daunorubicin (**1**) is associated with the considerable cytotoxicity which does affect neoplastic tissue but also causes severe side effects in membranes and the myocardium.[1] An enhanced therapeutic index may be achieved by the use of anthracyclines with oligosaccharide side chains, e.g., aclacinomycin A (**2**).[2] In a number of cases this led to decreased $IC_{50}$ values for the general cytotoxicity. Furthermore, compounds of this type showed an enhanced differentiation inducing activity[3] which can be correlated with a shift of the biological effect from DNA to RNA synthesis inhibition.

**Scheme I**



| # | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|
| 1 | H | OH | $CH_3$ | H | H |
| 2 | $COOCH_3$ | H | H | $CH_3$ | Q |



A survey of the data presently available supports the assumption that typical saccharide structures are required for the construction of such oligosaccharide side chains. This relates to monosaccharide configuration and substitution pattern, as well as their arrangement, and their interglycosidic linkages. Recently, some approaches to trisaccharide syntheses of anthracycline side chains have been described,[4-6] the primary drawback of which was the glycosylation step of the most unreactive axially configurated 4-hydroxy group in either of the deoxyfucose units; e.g., the Koenigs–Knorr glycosylation could be accomplished in only 40% yield.[4,5] The previously introduced *N*-iodosuccinimide glycosylation technique[7] was applied as an alternative approach. Although this procedure was successful in a variety of cases in which $\alpha$-linkages have been required,[8,9] it failed in this particular case for reasons not fully understood at present. Thus, a deviation was recommended via the D-configurated precursor with an equatorial hydroxy group.[6,8,9]

The electrophilicites of both the oxocarbenium ion and the iodonium ion, the former being the intermediate in the Koenigs–Knorr or a similar type glycosylation, the latter being the one in the *N*-iodosuccinimide-mediated glycosylation, respectively, are only slightly influenced by configuration and substitution pattern. Furthermore, the reactivity in the former case may be somewhat dependent on the anomeric leaving group, a feature that does not apply to the *N*-iodosuccinimide glycosylation. Thus, an enhancement of the nucleophilicity of the donor is required for further approaches. There are reports that give evidence for increased nucleophilicites of organotin substituted oxygen derivatives,[10] and experiments along similar lines were successful in classical glycosylations.[11]

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