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STEREOSPECIFIC SYNTHESIS OF DIENONE IRON TRICARBONYL COMPLEXES BY FRIEDEL—CRAFTS ACYLATION

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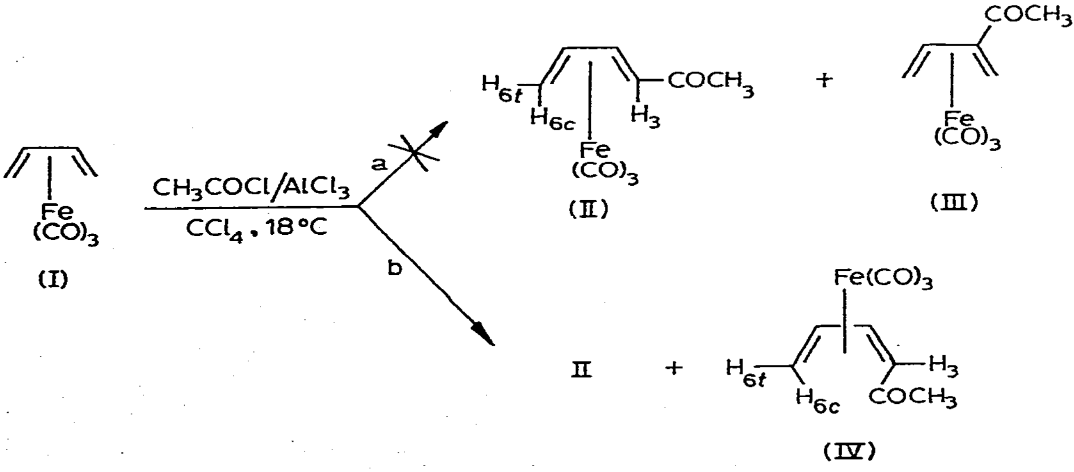
Summary

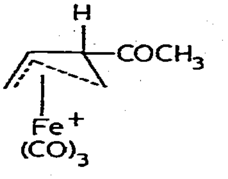
Acylation of diene $Fe(CO)_3$ complexes using the Perrier complexes $RCOCl/AlCl_3$ in methylene chloride at 0°C gives dienone complexes in high yield. Substitution occurs only at unsubstituted terminal carbons of the diene unit. Quenching the reaction mixtures in cold aqueous ammonia gives *cis* dienone complexes only. *Trans* dienone complexes are prepared by subsequent isomerization in methanolic sodium methoxide. Formylation of diene $Fe(CO)_3$ complexes proceeds in modest yield using dichloromethylmethylether/$AlCl_3$ in methylene chloride to give *trans*-dienal complexes. Reduction of the dienone and dienal complexes as well as those of dienols and dienoic esters with 4 : 1 $AlCl_3/LiAlH_4$ results in complete removal of the oxygen function to give *trans*-diene complexes in good yield.

Electrophilic substitution of diene $Fe(CO)_3$ complexes was first described by Ecke who reported the acylation of butadiene $Fe(CO)_3$ to give 1- and 2-acetyl derivatives (eqn. 1a) [1]. Subsequent work suggested that the second product



(1)

was not III but IV [2,3]. The homoallyl $Fe(CO)_3$ cation V is expected to be considerably less stable than a conjugated derivative (e.g. VI). Thus, electrophilic attack at the internal carbon would not be expected to compete with attack at the terminal carbon. Consistent with this expectation, electrophilic H—D exchange in acyclic diene $Fe(CO)_3$ complexes occurs exclusively at the terminal carbons [4]. During the course of our work, Knox et al. published data



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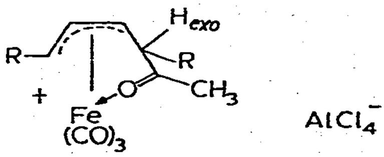


(VI)

which showed that the products were II and IV (eqn. 1b) and that intermediate (VI, R = H) could be isolated prior to quenching. We report here a study of the synthetic utility of this reaction and some useful transformations of the resulting dienones.

Results

Optimum acylation yields were obtained using methylene chloride which gave homogeneous reaction mixtures. Acylations were carried out at 0°C for ca. 20 min

TABLE 1

EFFECT OF QUENCH CONDITIONS ON THE PERCENTAGE OF *trans* KETONE IN ACETYLATION OF BUTADIENE $Fe(CO)_3$ [a]

Quench conditions	% *trans* Ketone
A. Weak bases	
Diisopropylethyl amine	1
Diethyl amine	3
30% aqueous ammonia	1
Dry sodium bicarbonate	5
5% aqueous potassium carbonate	8
B. Strong acids or bases, heterogeneous quench	
Water [b]	22
10% aqueous H_2SO_4	23
20% aqueous HCl	25
20% aqueous NaOH	20
Solid NaOH	22
Solid sodium methoxide	18
C. Strong acids or bases, homogeneous quench	
10% methanolic H_2SO_4	38
Methanolic sodium methoxide	30
Potassium t-butoxide in t-butanol	91

[a] Quenches were run for 3 min at 0°C. The reaction mixture was then partitioned between water and methylene chloride and analyzed immediately by liquid chromatography. [b] Hydrolysis of $AlCl_3$ produces an aqueous HCl solution.

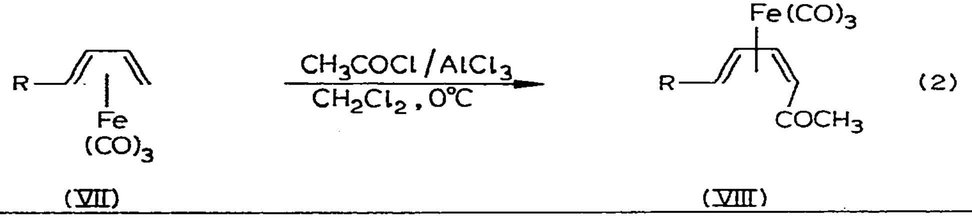
followed by quenching. As shown in Table 1, the *cis/trans* (i.e., *anti/syn*) ratio is highly dependent on the method of quenching. Quenching with cold 28% aqueous ammonia gives high yields of *cis*-dienone complexes. Liquid chromatographic analysis [6] of the crude products revealed 1%or less of the *trans* isomers.

Dienone $Fe(CO)_3$ complexes have been thoroughly characterized in previous work [5,7]. The structures of the acylation products were assigned on the basis of IR, NMR, and mass spectral data, elemental analysis, and chromatographic behavior. The *trans* isomer of each *cis—trans* pair exhibited the following distinguishing characteristics: (1) higher NMR chemical shifts for H_3 and H_{6t} (see II); (2) a higher ketone carbonyl stretching frequency by 5—15 cm^{-1}; (3) a 10—20% higher TLC R_f value (silica gel/methylene chloride); and (4) a longer liquid chromatography retention time. ^1H NMR spectroscopy can be used to identify one isomer in the absence of the other.

Acetylation results using the ammonia quench are given in Table 2 (eqns. 2 and 3). Substitution occurred only at unsubstituted terminal carbons. The behavior of VIId was unusual in that quenching with aqueous potassium carbonate gave only *trans*-dienone (XXV, $R_1 = R_2 = H$, $R_3 = p\text{-}CH_3COC_6H_4$—). This compound was also prepared by acetylation of *trans,trans*-6-phenyl-3,5-hexadien-2-one $Fe(CO)_3$ complex (XXV, $R_1 = R_2 = H$, $R_3 = C_6H_5$) and by acetyla-

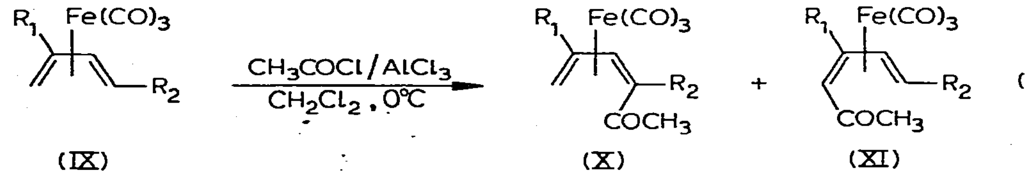
TABLE 2

ACETYLATION OF DIENE $Fe(CO)_3$ COMPOUNDS [a]



(2)

	R	Yield (%) [b]
a	H	86
b	CH_3	84
c	$p\text{-}BrC_6H_4$	97
d	$p\text{-}CH_3COC_6H_4$	90 [c]

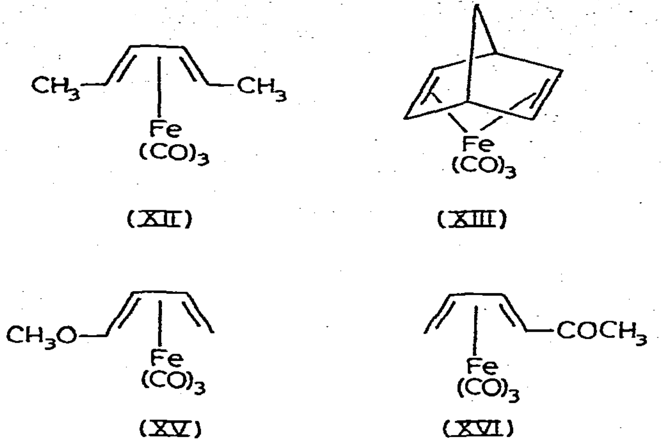


(3)

	R_1	R_2	Total yield (%)	Isomers
a	CH_3	H	90	65% 10a, 35% 11a
b	CH_3O	H	38	10b only [d]
c	CH_3	CH_3	91 [e]	11c only [e]

[a] Quenched with 28% aqueous ammonia with exception of VIIId. [b] Isolated yield. [c] *trans,trans*-Dienone complex, XXV ($R_1 = R_2 = H$, $R_3 = p\text{-}CH_3COC_6H_4$) only isolated after quenching with 5% aqueous potassium carbonate. [d] 5—10% of the *trans* isomer Xb was present after ammonia quench. [e] Unpublished work of D.G. Gresham.

SCHEME 1

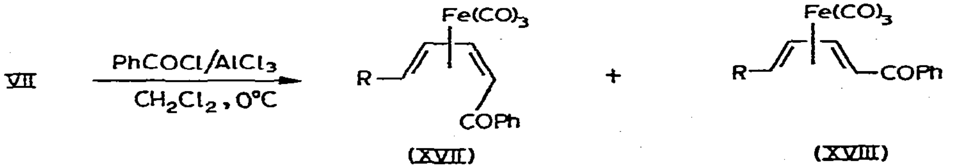


XII—XV: Reaction occurred but no product could be isolated.
XVI : No reaction, starting material recovered

tion of 1-phenylbutadiene $Fe(CO)_3$ complex (VII, R = C_6H_5) with excess acetyl chloride/aluminum chloride.

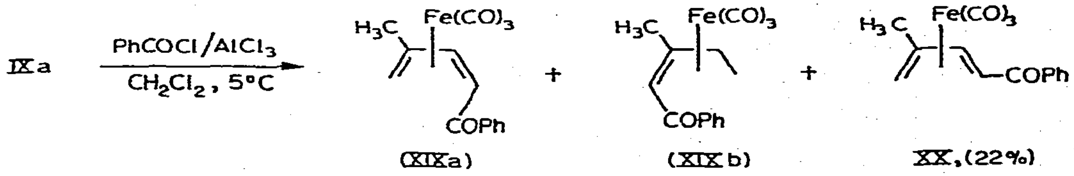
Scheme 1 contains compounds which could not be successfully acylated under our conditions. The dienone complex XVI is totally unreactive and the 2,4-hexadiene complex XII even after 24 h gave only decomposition products and a little starting material. Compounds XIII and XIV appeared to react more readily. Ketone carbonyl IR absorption was detected in the crude reaction mixtures, but no pure products could be isolated. Compound XV was destroyed under acylation conditions.

Benzoylation results are depicted in eqns. 4 and 5. These reactions were quenched with 5% aqueous potassium carbonate. Both *cis* and *trans* dienone products were observed.



(4)

VII a, R = H, yield 12% XVII, 10% XVIII
VII b, R = CH_3, yield 30% XVII, 9% XVIII

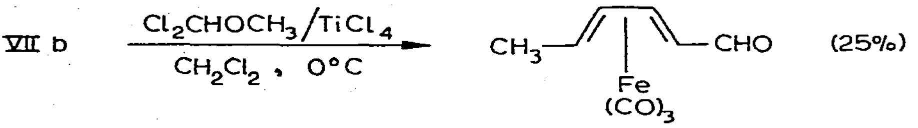


(5)

The yields are those isolated after separation of products by preparative TLC. Reaction 5 gave *cis* isomers XIXa and b as the major initial products along with

XX. However after standing 3 days the crude product was mostly XX. The pattern of substitution is identical to that observed for acetylation.

Electrophilic formylation proceeded in modest yield when diene $Fe(CO)_3$ complexes were treated with dichloromethylether/titanium tetrachloride in methylene chloride at 0° C as shown in eqns. 6 and 7 [8].



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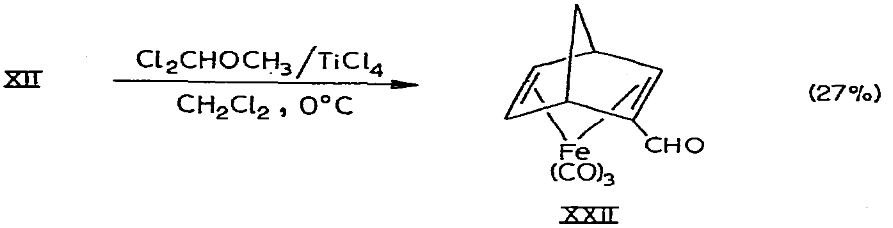
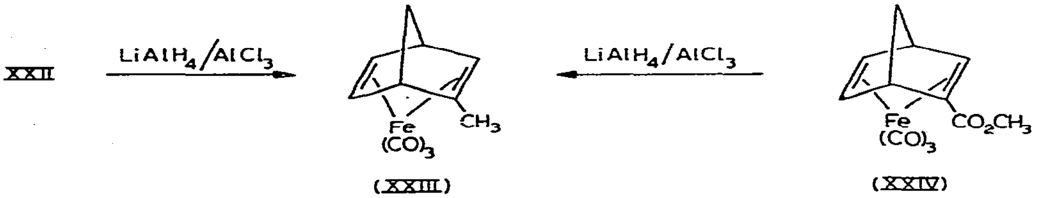


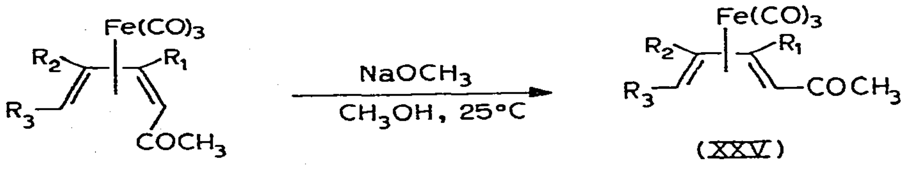
(7)

Quenching in ice water gave exclusively *trans*-aldehyde XXI, identical to authentic material prepared by complexation of *trans,trans*-2,4-hexadienal [9]. Structure XXII was in agreement with all spectral data for this compound. Further proof of structure was accomplished by reduction with 1 : 4 $LiAlH_4/AlCl_3$ (see below) to give XXIII which was identical to a sample of XXIII produced by a similar reduction of the known compound XXIV (eqn. 8) [8].



(8)

Knox et al. have reported that *cis* dienone $Fe(CO)_3$ complexes are converted to their *trans* isomers by aqueous alkali or acid at room temperature [5]. We have found that these isomerizations proceed smoothly in methanolic sodium methoxide or methanolic sulfuric acid. Table 3 shows results of preparative isomerizations, eqn. 9 *. Analogous isomerizations of all other *cis* dienone $Fe(CO)_3$ complexes reported here were run on a small scale and followed by liquid chromatography [6].



(9)

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* Bottled sodium methoxide was a poor catalyst. Solutions were always prepared by dissolving sodium in dry methanol.

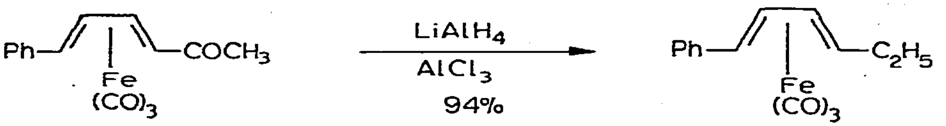
TABLE 3

cis TO *trans* ISOMERIZATION OF DIENONE $Fe(CO)_3$ COMPLEXES IN METHANOLIC SODIUM METHOXIDE [a]

Starting *cis* dienone	Yield of *trans* dienone (%)
VIIIa	69
VIIIb	71
VIIIc	79 [b]
Xb	60
XIc	75 [c]
Xa & XIa [d]	67 [d]

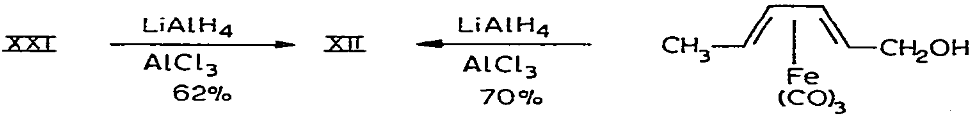
[a] 1.0 *M* sodium methoxide in methanol under nitrogen for 3 h. [b] Crude yield. [c] D.G. Gresham, unpublished data. [d] Run as a mixture, the yield is reported for a mixture of XXV ($R_1 = CH_3$, $R_2 = R_3 = H$) and XXV ($R_1 = R_3 = H$, $R_2 = CH_3$).

Another general reaction of dienone $Fe(CO)_3$ complexes is their reduction by excess 1 : 4 $LiAlH_4/AlCl_3$ which causes complete removal of the oxygen function (eqns. 8, 10, 11). The reaction can also be extended to esters (eqn. 8) and alcohols (eqn. 11).



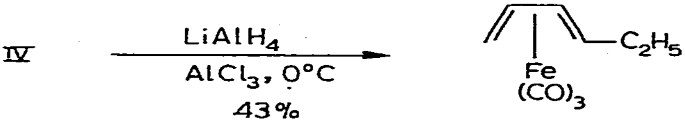
(XXVI)

(10)



(11)

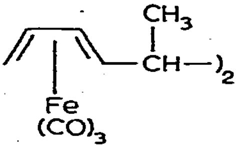
An attempt to prepare a *cis*-diene $Fe(CO)_3$ complex failed. Reduction of the *cis* dienone complex IV produced only the known [10] *trans*-1,3-hexadiene $Fe(CO)_3$ (XXVII) (eqn. 12).



(XXVII)

(12)

Aluminum chloride alone in methylene chloride causes only a slow conversion of IV to its *trans* isomer II. When reaction 12 was run using only a stoichiometric



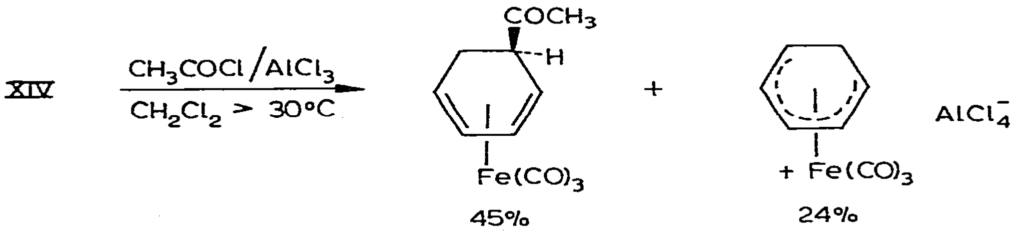
(XXVIII)

amount of $AlHCl_2$ [4,11], liquid chromatographic analysis of remaining dienone after 1 min and after 2 h gave *cis/trans* ratios of 9 : 1 and 1 : 5, respectively. TLC analysis showed 5 components in the crude reaction mixture after quenching. Compounds II, IV, XXVII and XXVIII [12] were identified. A minor component could not be separated from XXVII.

Discussion

Electrophilic substitution of transition metal complexed dienes and polyenes now qualifies as a familiar reaction [13]. Tricarbonyliron complexes of cycloheptatriene [14], cyclooctatetraene [15], cyclobutadiene [16], azepine [17], allene [18] and trimethylenemethane [19] have been acylated and or formylated. Acylation of tricarbonyliron complexes of butadiene [1,5,20], 2,3-dimethylbutadiene [21] and pentadiene [20c] have been described, and we have reported partial rate factors for acetylation at individual carbons in complexes I, VIIb, VIIc, and IXa [22]. 2-Acetoxybutadiene $Fe(CO)_3$, like our 2-methoxybutadiene $Fe(CO)_3$ (IXb), is reported to acylate at the 4 position [23]. Selective acetylation of 1-phenylbutadiene $Fe(CO)_3$ in the *para* position of the phenyl ring has been demonstrated [24].

Under our mild conditions substitution occurs only at unsubstituted terminal carbons. No diacylation occurs. Other reports conform to this pattern, and attempts to acylate the terminally substituted complexes XII and XIV (Scheme 1) failed. Acylations of VIIa—c and competition experiments [25] make it clear that substitution lowers the reactivity of a terminal carbon toward electrophiles. Steric hindrance to attack by the bulky solvated acylium ion electrophile [26] is probably responsible. However, failure of compounds XII—XV (Scheme 1) to give acyl derivatives is not caused by lack of attack by the electrophile. These complexes consume acylating agent and cannot be recovered from acylation reaction mixtures in good yield. 1-Acetoxybutadiene $Fe(CO)_3$ is reported to be unstable under acylating conditions [23], in accord with our observations with the 1-methoxy derivative XV. Tricarbonyl(anisole) chromium undergoes ether cleavage faster than acetylation under conditions similar to ours [27]. More conclusive is the report of Gubin et al. that XIV can be acylated when more vigorous conditions are employed (eqn. 13) [28,29].



(13)

Finally, Knox et al. have confirmed that XII is attacked by isolation and characterization which includes a crystal structure, of intermediate VI, R = CH_3 [30]. The acylations in Scheme 1 fail because the intermediate cations do not decompose to give acyl derivatives under our quenching conditions.

Quenching of butadiene $Fe(CO)_3$ acetylation mixture with water has been reported to give 80% *cis* and 20% *trans* dienone while dicyclohexylamine quenching gave only *cis* dienone [5]. The explanation suggested was that the bulky base removes H_{exo} from the intermediate VI, R = H stereospecifically to give *cis* dienone only. Our more complete data (Table 1), while entirely consistent with the above observations, suggest a different interpretation. It is clear that any weak base, even one as small as ammonia, produces *cis* dienone almost exclusively. Significant amounts of *trans* dienones are produced only when strong acids or bases are used in the quench. More *trans* dienone is produced by homogeneous quenching than by heterogeneous quenching; and in the presence of strong acids and bases, the percentage of *trans* dienone increased as the quench time was increased. All of these observations are in accord with the proposal that the initial quench always produces *cis* dienone with very high stereoselectivity, and that any substantial amounts of *trans* dienones are simply the product of acid or base catalyzed isomerization. Failure to observe *cis* formylation products (eqn. 6) may be attributed to the fact that the carbonyl group, which holds the acetylation intermediates (VI) in a cisoid geometry by coordination to iron [5,30], is generated only during quenching in formylation.

Mixed lithium aluminum hydride/aluminum chloride reductions of acids, esters, ketones and aldehydes with complete removal of the oxygen function is well documented [13,31]. Despite the fact that reduction of dienone complex II with $LiAlH_4$ alone results in decomposition with formation of 2-hexanol [20], mixed hydride reductions of the norbornadiene aldehyde XXII and ester XXIV proceeded smoothly (eqn. 8) [8]. The reaction was easily extended to complexes of conjugated dienes (eqns. 10—12). In the case that a diene precursor is expensive or difficult to prepare, mixed hydride reduction may be the method of choice for preparation of its tricarbonyliron complex (e.g. XII). Synthesis of XII by mixed hydride reduction of ethyl *trans*-sorbate and *trans*-muconic acid tricarbonyliron derivatives has been reported [30] and Gubin et al. have reported reduction of an acylated diene $Fe(CO)_3$ complex under similar conditions [28].

In summary, Friedel—Crafts acylation of diene $Fe(CO)_3$ complexes and subsequent quenching with aqueous ammonia leads with high stereoselectivity to dienone $Fe(CO)_3$ complexes with *cis* geometry about the α,β-double bond Substitution occurs only at unsubstituted terminal carbons of the diene ligand. The corresponding *trans* dienone $Fe(CO)_3$ complexes can be prepared by acid or base catalyzed isomerization of the *cis* dienone complexes in methanol. Reduction of the dienone complexes with 4 : 1 lithium aluminum hydride/aluminum chloride produces the corresponding complexed hydrocarbon with *trans* geometry about the original α,β-double bond. Efficient removal of the $Fe(CO)_3$ moiety from these complexes is possible [9,32]. Thus these acylations provide stereospecific routes to α,β-*cis*- and α,β-*trans*-dienones and their transformation products.

Experimental section

General

IR spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated with the 1601 cm^{-1} polystyrene band. NMR spectra were recorded

TABLE 4

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	b.p. (°C/ Torr)	M.p. (°C)	Found (calc.) (%)		
			C	H	Fe
XV	106—108/15		42.85	3.57	24.9
			(42.80)	(3.57)	(24.9)
IXb	110/15		42.81	3.53	24.6
			(42.80)	(3.57)	(24.9)
VIIIc [a]		110.5—111.5	46.45	3.10	14.2
			(46.08)	(2.84)	(14.3)
XXV		118 —118.5	57.63	3.82	15.75
			(57.66)	(3.99)	(15.77)
XVII (R = H)		87.5— 88.5	56.17	3.20	18.60
		[lit. [5] 86—88]	(56.41)	(3.38)	(18.74)
XVIII (R = H)		82.5— 83.0	56.65	3.38	18.70
		[lit. [5] 82—83]	(56.41)	(3.38)	(18.74)
XVII (R = CH_3)		87 — 88	57.94	3.97	17.9
			(57.73)	(3.88)	(17.9)
XVIII (R = CH_3)		91.5— 92.0	58.00	4.15	18.0
			(57.73)	(3.88)	(17.9)
XX		99.5—100	57.90	3.82	17.6
			(57.73)	(3.88)	(17.9)
XV (R_1 = R_2 = H [b], R_3 = p-BrC_6H_4)		162 —162.5	46.30	2.86	13.97
			(46.08)	(2.84)	(14.28)
XXII [c]			45.80	3.92	17.69
			(45.46)	(3.50)	(17.61)
XXIV		46.5— 47	49.55	3.33	19.20
			(49.69)	(3.48)	(19.25)
XXVI		52 — 53	60.42	4.90	18.7
			(60.43)	(4.73)	(18.7)
XXIII			53.55	3.93	22.53
			(53.70)	(4.10)	(22.70)

[a] Analysis for bromine, calcd. 20.44%, found 20.38%. [b] Analysis for bromine, calcd. 20.44%, found 20.38%. [c] Analysis performed on semicarbazone derivative, m.p. 204°C dec., % N calcd. 13.25, found 13.00.

on Varian Associates A-60 or a Perkin—Elmer R-12 spectrometer, and chemical shifts are referred to internal tetramethylsilane. IUPAC numbering is used to report NMR data (see II and IV for *cis* and *trans* designations). Mass spectra were recorded on a Hitachi RMU-6L spectrometer. Melting points are uncorrected. Elemental analyses were performed by the University of Massachusetts Research Services Microanalytical Laboratory under the direction of Mr. Charles Meade. Thin layer chromatography was performed using Camag silica gel. Preparative plates were coated to a thickness of 1 mm and were activated at 100°C for 8 h prior to use. Tricarbonyl(butadiene)iron was prepared in 44% yield (based on iron pentacarbonyl) using a method similar to that reported by Koerner von Gustorf et al. [33]. Analytical and spectral data are collected in Tables 4—6.

Tricarbonyl(1-methoxy-1,3-butadiene)iron (XV) and tricarbonyl(2-methoxy-1,3-butadiene)iron (IXb)

To a 16.9 g (46.6 mmol) diiron enneacarbonyl in 100 ml of Skellysolve F was added 3.58 g (42.7 mmol) 1-methoxy-1,3-butadiene [34] in 100 ml of

TABLE 5

IR AND MASS SPECTRA

Compound	IR		Mass spectrum, m/e (rel. intensity) [b]
	Solvent	ν (cm^{-1}) [a]	
XV	film	2040, 1950—1980	224(6), 196(18), 168(16), 140(31), 110(42), 84(100)
IXb	film	2050, 1965	224(24), 196(88), 168(87), 140(85), 84(100)
IV	CCl_4	2055, 1990, 1672	
VIIIc	CCl_4	2055, 1989, 1672	392(2), 390(2), 364(5), 362(5), 336(24), 334(24), 308(88), 306(88), 252(14), 171(32), 128(100)
Xa & XIa [c]	CCl_4	2052, 1981, 1669	
Xb	CCl_4	2059, 1982, 1668	
XXV, $R_1 = R_2 = H$; $R_3 = p\text{-}CH_3\text{-}COC_6H_4$	CCl_4	2060, 1922, 1687	354(1), 326(2), 298(19), 270(57) 214(30), 171(15), 128(22)
XVII, R = H	CCl_4	2055, 1987, 1648	
XVIII, R = H	CCl_4	2055, 1990, 1653	
XVII, R = CH_3	CCl_4	2045, 1970, 1645	
XVIII, R = CH_3	CCl_4	2050, 1985, 1652	
XX	CCl_4	2050, 1990, 1650	
XXV, $R_1 = R_2 = H$; $R_3 = p\text{-}BrC_6H_4$	CCl_4	2060, 1990, 1686	392(2), 390(2), 364(6), 362(6), 336(27), 334(27), 308(93), 306(93), 265(23), 263(23), 252(18), 250(18), 171(47), 128(100)
XXV, $R_1 = R_2 = H$; $R_3 = OCH_3$	CCl_4	2060, 1982, 1678	
XXV, $R_1 = R_2 = H$; $R_3 = CH_3$	CCl_4	2060, 1982, 1681	250(5), 222(8), 194(49), 166(97), 110(100), 95(98)
XXV, $R_1 = CH_3$; $R_2 = R_3 = H$	CCl_4	2055, 1981, 1680	250(3), 222(6), 194(24), 166(50), 110(98), 95(100)
XXII	film	2040, 1960—1980, 1658	260(6), 232(11), 204(33), 176(38), 148(50), 122(80) [d]
XXIV	CCl_4	2039, 1950—1990, 1700	290(5), 262(13), 234(60), 206(98), 150(37), 148(100), 122(78)
XXVI	CCl_4	2045, 1960—1985, 1600, 1380	298(6), 207(26), 242(48), 214(100), 158(41)
XXIII	film	2025, 1945, 1380	246(1), 218(8), 190(11), 162(18), 106(96), 91(100), 80(76), 66(96)

[a] Calibrated using the 1601 cm^{-1} polystyrene band, wavelengths accurate to ±3 cm^{-1}. [b] Ionizing voltage 80 eV. [c] Recorded as a mixture. [d] $C_6H_5Fe^+$ from loss of HC≡CCHO via retro Diels Alder.

Skellysolve F. The mixture was stirred under nitrogen at 30° C for 24 h. A small amount of brown sediment was removed by filtration. The solvent and unreacted starting materials were removed by distillation up to 50° C (15 mmHg). Continued vacuum distillation gave 3.58 g of XV (40% yield) as a yellow oil. Compound IXb was prepared in an identical fashion and isolated as a yellow oil in 26% yield.

General procedure for acylation of diene complexes: tricarbonyl-(cis-3,5-hexadien-2-one)iron (IV)

To 60 ml of dry dichloromethane cooled to 0° C was added 2.5 ml (35 mmol) of acetyl chloride and 3.2 g (24 mmol) of anhydrous aluminum chloride. The

TABLE 6. ^1H NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Spectrum [a], τ (multiplicity [b], relative intensity, assignment)
XV [c]	4.5—5.1 (m, 2, H_2, H_3), 6.52 (s, 3, —OCH_3), 6.89 (d, 1, $J_{12} = 6$ Hz, H_1), 8.43 (m, 1, H_{4t}), 10.12 (1, q, $J_{34c} = 8$ Hz, $J_{4c4t} = 2.5$ Hz, H_{4c})
IXb	4.86 (t of d, 1, $J_{34t} = 6$ Hz, $J_{34c} = 7$ Hz, $J_{1t3} = 1$ Hz, H_3), 6.34 (s, 3, —OCH_3), 7.85 (q, 1, $J_{1c1t} = 4$ Hz, $J_{1t3} = 1$ Hz, H_{1t}), 8.83 (d of d, 1, $J_{34t} = 6$ Hz, $J_{4c4t} = 1$ Hz, H_{4t}), 9.77 (d, 1, $J_{1t1c} = 4$ Hz, H_{1c}), 10.28 (d of d, 1, $J_{34c} = 7$ Hz, $J_{4c4t} = 1$ Hz, H_{4c})
IV	4.25—4.8 (m, 2, H_4, H_5), 6.84 (d, 1, $J_{34} = 6$ Hz, H_3), 7.75 (q, 1, $J_{56t} = 6$ Hz, $J_{6c6t} = 3$ Hz, H_{6t}), 7.91 (s, 3, —$COCH_3$), 8.62 (q, 1, $J_{6c6t} = 3$ Hz, $J_{56c} = 9$ Hz, H_{6c})
VIIIc	2.75 ($AA'BB'$ multiplet, 4, —C_6H_4Br), 4.0 (q, 1, $J_{45} = 5$ Hz, $J_{56} = 7$ Hz, H_5), 4.62 (t, 1, $J_{34} = 6$ Hz, $J_{45} = 5$ Hz, H_4), 6.87 (d, 2, $J_{34} = 6$ Hz, $J_{56} = 7$ Hz, H_3, H_6), 7.82 (s, 3, —$COCH_3$)
Xa [d]	4.82 (d, 1, $J_{34} = 6$ Hz, H_4), 7.02 (d, 1, $J_{34} = 6$ Hz, H_3), 7.83 (s, 3, —$COCH_3$), 7.95 (obscured, 1, H_{6t}), 7.97 (s, 3, 5-CH_3), 8.67 (d, 1, $J_{6c6t} = 3$ Hz, H_{6c})
XIa [d]	4.52 (t, 1, $J_{56c} = 9$ Hz, $J_{56t} = 8$ Hz, H_5), 6.83 (s, 1, H_3), 7.83 (s, 3, —$COCH_3$), 7.95 (obscured, 1, H_{6t}), 7.97 (s, 3, 4-CH_3), 8.80 (q, 1, $J_{56c} = 8$ Hz, $J_{6c6t} = 2$ Hz, H_{6c})
Xb [e]	5.1 (d, broad, 1, $J_{34} = 6$ Hz, H_4), 6.37 (s, 3, —OCH_3), 7.08 (d, 1, $J_{34} = 6$ Hz, H_3), 7.58 (q, 1, $J_{46t} = 2$ Hz, $J_{6c6t} = 5$ Hz, H_{6t}), 8.77 (d, 1, $J_{6c6t} = 5$ Hz, H_{6c})
XXV $R_1 = R_2 = H$; $R_3 = p$-CH_3CO-C_6H_4	2.70 ($AA'BB'$ multiplet, 4, —C_6H_4—), 4.25 (d, 2, $J_{34} = 7$ Hz, $J_{56} = 7$ Hz, H_4, H_5), 7.65 (s, 3, —C_6H_4CO—CH_3), 7.7 (d, 1, $J_{56} = 7$ Hz, H_6), 7.88 (s, 3, 1-CH_3), 8.40 (d, 1, $J_{34} = 7$ Hz, H_3)
XVII, R = H	2.2 and 2.5 (m, 5, —C_6H_5), 4.42 (m, 2, H_3, H_4), 6.20 (d, 1, $J_{23} = 6$ Hz, H_2), 7.7 (m, 1, H_{5t}), 8.55 (m, 1, H_{5c})
XVIII, R = H	2.1 and 2.5 (m, 5, —C_6H_5), 3.75 (q, 1, $J_{23} = 8$ Hz, $J_{34} = 5$ Hz, H_3), 4.42 (m, 1, H_4), 7.75—8.10 m, 2, analyzed as 7.8 (d with additional coupling, $J_{45t} = 7$ Hz, H_{5t}), 8.08 (d, 1, $J_{23} = 8$ Hz, H_2), 9.12 (q, 1, $J_{45c} = 10$ Hz, $J_{5c5t} = 2.5$ Hz, H_{5c})
XVII, R = CH_3	2.10 and 2.50 (m, 5, —C_6H_5), 4.58 (q, 2, $J_{23} = J_{45} = 6$ Hz, $J_{24} = 2$ Hz, H_3, H_4), 6.30 (d, 1, $J_{23} = 6$ Hz, H_2), 7.74 (m, 1, H_5), 8.47 (d, 3, $J_{56} = 5$ Hz, —CH_3)
XVIII, R = CH_3	2.10 and 2.50 (m, 5, —C_6H_5), 3.95 (t, 1, $J_{23} = J_{34} = 8$ Hz, H_3), 4.67 (t, 1, $J_{34} = J_{45} = 8$ Hz, H_4), 8.08 (d, ca. 1, $J_{23} = 8$ Hz, H_2) 8.3—8.8 [m, ca. 4, analysed as 8.45 (d, —CH_3) and ca. 8.5 (m, H_5)]
XX	2.10 (m, 2, H_{ortho}), 2.48 (m, 3, H_m and H_p), 3.90 (d, 1, $J_{2t3} = 8$ Hz, H_3), 7.72 (s, 3, CH_3), 7.89 (t, 1, $J_{5c5t} = J_{35t} = 2$ Hz, H_{5t}), 8.25 (d, 1, $J_{2c3} = 8$ Hz, H_2), 9.08 (d, 1, $J_{5c5t} = 2$ Hz, H_{5c})
XXV, $R_1 = R_2 = H$; $R_3 = p$-BrC_6H_4	2.75 ($AA'BB'$ multiplet, 4, —C_6H_5Br), 4.10 (d, 2, $J_{34} = 8$ Hz, $J_{56} = 8$ Hz, H_4, H_5), 7.68 (d, 1, $J_{56} = 8$ Hz, H_6), 7.8 (s, 3, —$COCH_3$), 8.48 (d, 1, $J_{34} = 8$ Hz, H_3)
XXV, $R_1 = R_3 = H$; $R_2 = OCH_3$	4.48 (d, 1, $J_{34} = 7$ Hz, H_4), 6.32 (s, 3, —OCH_3), 7.71 (d, 1, $J_{6c6t} = 4$ Hz, H_{6t}), 7.91 (s, 3, —$COCH_3$), 9.18 (d, 1, $J_{34} = 7$ Hz, H_3), 9.33 (d, 1, $J_{6c6t} = 4$ Hz, H_{6c})
XXV, $R_1 = R_3 = H$; $R_2 = CH_3$	4.22 (d, 1, $J_{34} = 7.5$ Hz, H_4), 7.83 (s, 3, —$COCH_3$), 7.92 (s, 3, 5-CH_3), 7.95 (d, 1, $J_{6c6t} = 2.5$ Hz, H_{6t}), 8.93 (d, 1, $J_{34} = 7.5$ Hz, H_3), 9.29 (d, 1, $J_{6c6t} = 2.5$ Hz, H_{6c})
XXV, $R_1 = CH_3$ $R_2 = R_3 = H$	4.80 (t, 1, $J_{56t} = 8$ Hz, $J_{56t} = 7$ Hz, H_5), 7.46 (s, 3, 4-CH_3), 7.88 (s, 3, —$COCH_3$), 8.16 (q, 1, $J_{56t} = 7.0$ Hz, $J_{6c6t} = 2.5$ Hz, H_{6t}), 9.12 (s, 1, H_3), 9.42 (q, 1, $J_{56c} = 8$ Hz, $J_{6c6t} = 2.5$ Hz, H_{6c})
XXII	1.3 (s, 1, —CHO), 4.0—4.8 (m, 5, H_1, H_{3-6}), 8.4—8.8 (m, 2.2 analyzed as ca. 8.6 (d, 1, $J_{7a7b} = 10$ Hz, H_{7a}), 8.65 (d, 1, $J_{7a7b} = 10$ Hz, H_{7b}), 8.75 (m, 0.2, impurity)]
XXIV	6.3—6.6 [m, 8, analyzed as 6.32 (s, 3, —OCH_3), 6.3—6.6 (m, 5, H_1, H_{3-6})], 8.7 (s, 2, H_{7a}, H_{7b})
XXVI	2.85 (s, 5, —C_6H_5), 4.38 (q, 1, $J_{12} = 9$ Hz, $J_{23} = 5$ Hz, H_2), 4.91 (q, 1, $J_{23} = 5$ Hz, $J_{34} = 8$ Hz, H_3), 8.05 (d, 1, $J_{12} = 9$ Hz, H_1), 8.2—9.2 [m, 6, analyzed as 8.45 (m, —CH_2—), 8.93 (t, $J_{56} = 7$ Hz, —CH_3), H_4 obscured]
XXIII	6.8 (m, 4, H_1 or H_3, H_{4-6}), 7.13 (d, 1, $J = 3$ Hz, H_1 or H_3); 8.28 (s, 3, —CH_3), 8.73 (s, broad, 2, H_{7a}, H_{7b})

[a] Solvent is deuteriochloroform unless otherwise indicated. [b] d = doublet, t = triplet, q = quartet, m = multiplet. [c] In carbon tetrachloride solvent. [d] Xa and XIa were examined as a mixture. [e] Assignments confirmed by double resonance experiments.

mixture was stirred under nitrogen for 20 min at 0°C. Then 4.1 g (21 mmol) of tricarbonyl-(1,3-butadiene)iron (I) dissolved in 25 ml of dichloromethane was added dropwise over a 5 min period. The reaction mixture was stirred for an additional 15 min at 0°C and then was poured rapidly into a stirring mixture of 75 ml of 28% aqueous ammonia and 50 g of ice. The color of the resulting mixture was deep red. After the mixture was stirred for 5 min, the layers were separated. The aqueous layer was diluted with 75 ml of water and was extracted with four 25-ml portions of dichloromethane. The combined organic extracts were washed with four 50-ml portions of water and were dried (Na_2SO_4). The solvent was removed under reduced pressure on a rotary evaporator, leaving 4.3 g (86%) of a red oil which was shown by TLC to consist of two components. LC showed that the crude material had a *cis/trans* isomer ratio of 98.5 : 1.5 and only traces of other impurities. The small amounts of impurities could be removed by column chromatography on alumina or silica gel with dichloromethane as the eluant, but a small amount of *cis* to *trans* isomerization of the product was always observed during this procedure. Pure *cis* product was obtained by preparative thin layer chromatography using dichloromethane as the developing solvent. The easily resolved lower band (R_f 0.35) was scraped from the plates and extracted with dichloromethane. Filtration and removal of the solvent under reduced pressure left IV as a deep orange oil.

Tricarbonyl(2-methoxy-1,3-butadiene)iron was an exception in that considerable decomposition took place during its acylation. A compound which exhibited IR bands at 2100 and 2020 cm^{-1}, characteristic of hydrogen chloride adducts of diene complexes [35], was isolated in addition to the product dienone (Xb).

General procedure for cis to trans isomerization of acylated diene complexes: tricarbonyl(trans-3,5-hexadien-2-one)iron (II)

To 25 ml of 1.0 *M* sodium methoxide in dry methanol (sodium metal was added to dry methanol) was added 2.0 g (8.4 mmol) of tricarbonyl(*cis*-3,5-hexadien-2-one)iron (IV). The solution was stirred at 25°C under nitrogen for 3 h and then was poured into 50 ml of dichloromethane. Water (150 ml) was then added, and the layers were separated. The aqueous layer was extracted three more times with dichloromethane and then discarded. The combined organic extracts were washed with four 50-ml portions of water and then dried over sodium sulfate. The solvent was removed under reduced pressure, leaving a red-brown oil which contained none of the *cis* starting material according to LC. The product was purified by column chromatography on alumina. A greenish yellow forerun was eluted with 5% dichloromethane in Skellysolve B. A single yellow band was then eluted with 120 ml of 50% dichloromethane in Skellysolve B. A small amount of black residue remained at the top of the column. Removal of the solvent under reduced pressure left 1.38 g (69% yield) of an orange oil: IR (5% in CCl_4) 2052, 1985 ($C\equiv O$), and 1681 cm^{-1} ($C=O$); NMR ($CDCl_3$) τ 4.04 (m, 1, tentatively H_4) 5.55 (m, 1, tentatively H_5), 7.86 (s, 3, $-COCH_3$), 8.75 (d, 1, $J_{34} = 7$ Hz, H_3), 9.18 (q, 1, $J_{6c6t} = 2$ Hz, $J_{56t} = 8$ Hz, H_{6t}), 9.26 (q, 1, $J_{6c6t} = 2$ Hz, $J_{56c} = 12$ Hz, H_{6c}). These data are in accord with previously reported but less complete data [2,5].

A 2,4-dinitrophenylhydrazone derivative was prepared which sintered at

194°C, [lit. [1] m.p. 194°C d].

The preparative scale base-catalyzed isomerizations were run with 1 *M* base for speed and convenience. A much better overall recovery was possible by running the reaction with 0.1 *M* base. The time necessary to obtain 99% conversion in this case was at least 24 h; the recovery was about 85%. A sampling of the 0.1 *M* reaction at three half-lives showed that about 94% of the original complexed dienone could be accounted for between the two isomers.

Tricarbonyl(*trans*-5-methyl-3,5-hexadien-2-one)iron (XXV, $R_1 = R_3 = H$, $R_2 = CH_3$) and tricarbonyl(*trans*-4-methyl-3,5-hexadienone)iron (XXV, $R_1 = CH_3$, $R_2 = R_3 = H$) were prepared by isomerization of a mixture of the corresponding *cis* dienone complexes (Xa and XIa) and subsequent separation by preparative TLC (silica gel/dichloromethane).

General formylation procedure: tricarbonyl(2-formylbicyclo-[2.2.1]-hepta-2,5-diene)iron (XXII)

To 25 ml of dichloromethane was added 1.5 ml (13 mmol) of titanium tetrachloride and 1.08 g (10 mmol) of dichloromethyl methyl ether [36]. The solution was stirred at 0°C for 10 min under nitrogen. Then 2.3 g (10 mmol) of tricarbonyl(bicyclo[2.2.1]hepta-2,5-diene)iron [8] (XIII) dissolved in 10 ml of dichloromethane was added dropwise with stirring. The solution immediately became dark brown. The mixture was stirred at 0°C for 30 min and then allowed to warm to room temperature; it was then poured over ice. The layers were separated and the aqueous layer was extracted with one 25-ml portion of dichloromethane. The combined organic layers were washed with six 30-ml portions of water. After drying (Na_2SO_4), the solvent was removed on a rotary evaporator under reduced pressure leaving a viscous brown oil. Analytical TLC showed a major spot at R_f 0.25. The oil was chromatographed on alumina (activity II, 40 g). Elution with 10% dichloromethane in Skellysolve B gave a green fraction of decomposed material along with a small amount of unreacted diene. Continued elution with 1 : 1 dichloromethane in Skellysolve B gave a yellow fraction in 150 ml of solvent. The solvent was removed on a rotary evaporator under reduced pressure yielding 0.175 g (27%) of an orange oil which was shown to be homogeneous by TLC.

Tricarbonyl(2-carbomethoxybicyclo[2.2.1]hepta-2,5-diene)iron [37] (XXIV)

To 39.0 g (0.26 mol) of the corresponding uncomplexed ester [38] was added 87.0 g (0.45 mol) of iron pentacarbonyl. The mixture was stirred and heated at reflux under nitrogen for 20 h. A black sediment was removed by suction filtration, and the unreacted starting materials were removed by distillation up to 100°C (12 mmHg). The residue (52.0 g) was cooled and then was dissolved in 200 ml of benzene. Fitlration of this solution through 40 g of alumina (activity II) removed most of the decomposition products. The resulting red-brown, viscous oil was then dissolved in boiling Skellysolve F and crystallized at —78°C yielding 21 g (27% yield) of yellow powder. An analytical sample was prepared by recrystallization from pentane at —78°C.

General procedure for lithium aluminum hydride/aluminum chloride reductions: tricarbonyl(trans,trans-1-phenyl-1,3-hexadiene)iron (XXVI)

To 100 ml of anhydrous diethyl ether cooled to 0°C in a 250-ml flask equipped with a condenser, mechanical stirrer, and addition funnel was added 14.30 g (107 mmol) of anhydrous aluminum chloride. The slurry was stirred for 10 min, then a slurry of 0.98 g (25.8 mmol) of lithium aluminum hydride in 75 ml of anhydrous ether was added slowly. The resulting mixture was stirred for 30 min at 0° C. Tricarbonyl(*trans,trans*-6-phenyl-3,5-hexadien-2-one)iron (2.44 g, 7.73 mmol) in 35 ml of anhydrous ether was added over a period of 5 min, and the mixture was stirred at 0° C for an additional 15 min. Analytical TLC showed that no starting material remained by this time. Excess hydride was destroyed by the addition of 5 ml of ethyl formate. Dropwise addition of 35 ml of water completed the quenching of the reaction, after which the mixture was stirred for 20 min. The ether layer was separated, was washed with four 100-ml portions of water, dried (Na_2SO_4), and was evaporated on a rotary evaporator under reduced pressure leaving a brown oil.

The product was purified by column chromatography (35 g alumina-activity II, Skellysolve B). The yellow product eluted as the first and only fraction (200 ml). Removal of the solvent under reduced pressure left an orange-red oil which solidified on standing to yield 2.19 g (94%) of a yellow powder.

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