Reactions of *pentahapto*-Cyclohexadienyliron Tricarbonyl Cations with Enamines

Robert E. Ireland* and Garth G. Brown, Jr.[1]

Contribution No. 4607 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

Richard H. Stanford, Jr., and Thomas C. McKenzie[2]

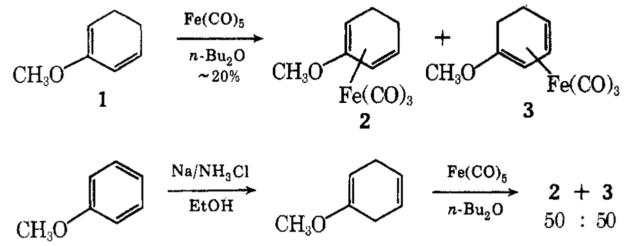
Norman Church Laboratories of Chemical Biology, California Institute of Technology, Pasadena, California 91109

Received May 7, 1973

Complexes of the type $CH_3OC_6H_6Fe(CO)_3{}^+BF_4{}^-$ were reinvestigated. A previously predicted isomer was isolated and identified as **6**. The structure of an isomer of $CH_3OC_6H_5CH_3Fe(CO)_3{}^+BF_4{}^-$ (**8**) was reassigned on the basis of new spectral, chemical, and X-ray evidence. In addition isomers of the salts were shown to react with enamines in ~65% yield.

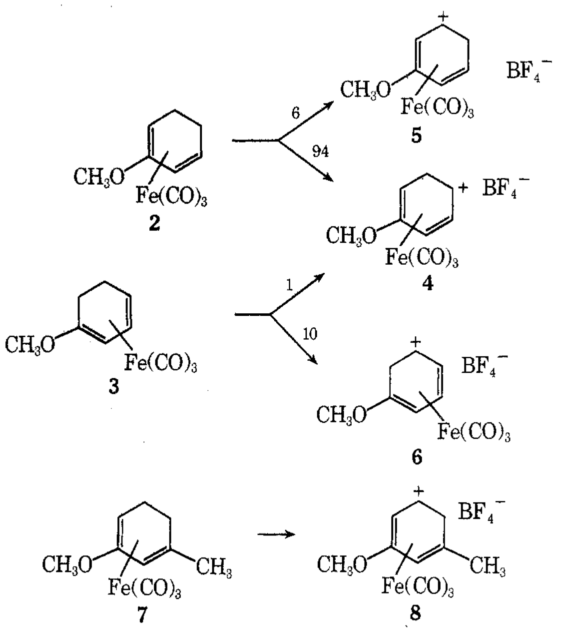
(*pentahapto*-Pentadienyl)(tricarbonyl)iron cations have been studied by a number of investigators.[3-9] The (*pentahapto*-methoxycyclohexadienyl)(tricarbonyl)iron cations have been examined in their reactions with nucleophiles[10] and have been shown to yield substituted anisole compounds on the removal of the iron tricarbonyl group.[3] In addition to extending the scope of the reaction with nucleophiles to enamines, we have oxidatively removed the iron tricarbonyl group with hydrolysis. This seems to be a convenient method of synthesizing cyclohexenones substituted in the 4 position. Such compounds have structural similarities to agents useful in herbicides.[11]

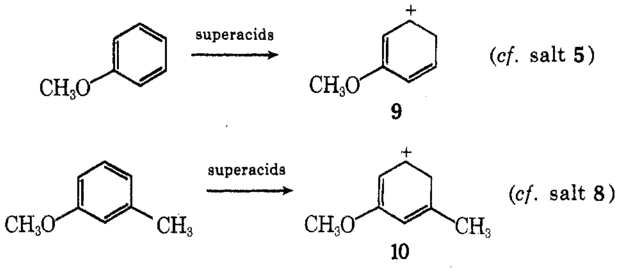
Treatment of 2-methoxycyclohexa-1,3-diene (**1**) with $Fe(CO)_5$ in refluxing di-*n*-butyl ether[5,12] gave a 70:30 mixture of complexes **2** and **3**. Treatment of 1-methoxycyclohexa-1,4-diene with $Fe(CO)_5$ in refluxing di-*n*-butyl ether gave a 50:50 mixture of **2** and **3**. The pure complex **2** and the pure complex **3** each gave a 70:30 mixture of **2** and **3** on heating in refluxing di-*n*-butyl ether. This is despite the report that **2** and **3** do not isomerize upon heating in refluxing benzene or upon irradiation.[3]



Treatment with triphenylmethyl fluoroborate converts complex **2** to a 94:6 mixture of the salts (1,2,3,4,5-*pentahapto*-2-methoxycyclohexadienyl)(tricarbonyl)(iron fluoroborate (**4**) and (1,2,3,4,5-*pentahapto*-3-methoxycyclohexadienyl)(tricarbonyl)iron fluoroborate (**5**). The corresponding reaction of **3** gave a 10:1 mixture of the salts (1,2,3,4,5-*pentahapto*-1-methoxycyclohexadienyl)(tricarbonyl)iron fluoroborate (**6**) and **4**. Treatment of 3-methoxy-1-methylcyclohexa-1,3-dieneiron tricarbonyl (**7**) with triphenylmethyl fluoroborate gave exclusively (1,2,3,4,5-*pentahapto*-3-methoxy-1-methylcyclohexadienyl)(tricarbonyl)iron fluoroborate (**8**).

The directing effect of the methyl group on hydride abstraction from the complex **7** is not clearly understood but may be the result of steric interactions. However, all the abstractions above are likely to be under kinetic control. It is interesting to note that the cations of the salts **4**, **5**, **6**, and **8** can be viewed as protonated anisoles complexed with iron tricarbonyl. The pmr spectra of protonated anisoles have recently appeared.[13] The protonated species presumably form under thermodynamic control and give the predicted products when C-protonation occurs.





The pmr spectra of the salts of **4**, **5**, **6**, **8**, **9**, and **10** are shown in Table I. Salt **4** has been reported previously with its pmr spectrum.[3] Birch and coworkers found that **4** reacts with cyanide, and the product was transformed to

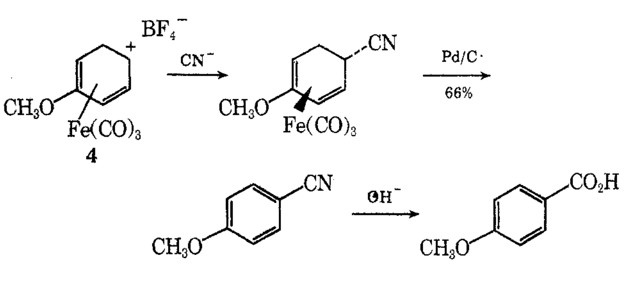
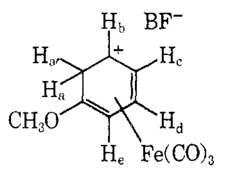
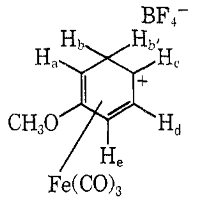
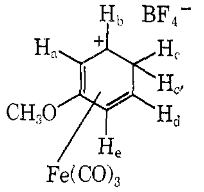
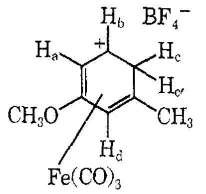
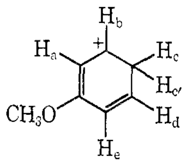
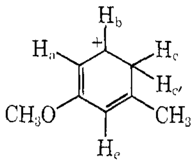
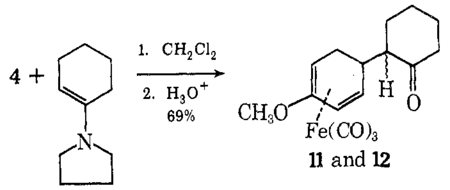


Table I[a]

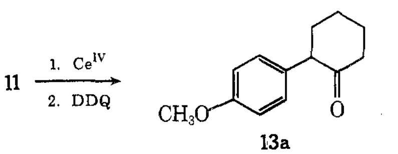
Compd	Structure	H_a	H_b	H_c	R_d	H_e	$H_{x'}$	OCH_3
6 R = H x = a		3.47 (dd) $J = 18$ $J = 6$	4.37 (t) $J = 6$ $J = 6$	6.44 (t) $J = 6$ $J = 6$	7.23 (t) $J = 6$ $J = 6$	4.92 (d) $J = 6$	2.90 (d) $J = 18$	4.05 (s)
4 R = H x = b		4.25 (d) $J = 6$	3.17 (m) $J = 16$ $J = 7$ $J = 6$	4.49 (dd) $J = 7$ $J = 6$	6.23 (t) $J = 6$ $J = 6$	7.34 (d) $J = 6$	2.16 (d) $J = 6$	3.94 (s)
5 R = H x = c		6.46 (d) $J = 7$	4.33 (r) $J = 7$ $J = 7$	3.10 (m) $J = 16$ $J = 7$ $J = 7$	4.33 (d) $J = 7$ $J = 7$	6.46 (d) $J = 7$	2.07 (d) $J = 16$	4.37 (s)
8 R = CH_3 x = c		6.39 (d) $J = 8$	4.10 (dd) $J = 8$ $J = 6$	3.03 (dd) $J = 16$ $J = 6$	1.97 (s)	6.23 (s)	2.28 (d) $J = 16$	4.25 (s)
9 R = H x = c		7.8 (d) $J = 10$	9.0 (d) $J = 10$	4.5 (s)	8.6 (d) $J = 10$	7.5 (d) $J = 10$	4.5 (s)	4.80 (s)
10 R = CH_3 x = c		J.42 (d) $J = 10$	8.5 (d) $J = 10$	4.3 (s)	2.83 (s)	7.50 (s)	4.3 (s)	4.69 es)

[a] The pmr spectra of the iron complexes were taken in CD_3COCD_3. The chemical shifts are given in δ relative to internal TMS. The coupling constants (J) are in hertz. Values for the uncomplexed ions are from ref 13 and were taken in superacids.

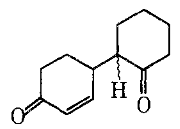
known compounds. We have found that **4** reacts with 1-pyrrolidinocyclohexene to give ketones **11** and **12** after hydrolysis. Pure **11** was converted to the known aromatic compound **13a**.[14] Oxidation of the ketone **12** with Jones reagent or with ferrous perchlorate gave a new compound with a saturated and unsaturated ketone as well as two vinyl hydrogens. The new compound was assigned the diketone structure **13b**.



11 and 12



13a



13b

The C_s symmetry of the cation in the salt **5** was evident in the pmr pattern. This evidence for the structure of the salt **5** was supplemented by the formation of **5** from the diene complex **2** and the absence of the salt **5** in the hydride abstraction products of the diene complex **3**. The structure of the salt **6** is consistent with its formation from the diene complex **3** as is the absence of **6** in the hydride abstraction products of the diene complex **2**. The resonances of the salt **6** at δ 4.37 (proton b) and 6.44 (proton c) were found to be coupled. Resonances at δ 4.92 (proton e) and 7.23 (proton d) were also coupled, justifying the assignments given in Table I.

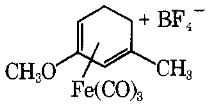
The structure **14** was previously assigned to the salt **8** on the basis of an unreported pmr spectrum.[3] However, our pmr spectrum of **8** is very similar to the spectrum of the salt **5**. Additional new evidence for the identity of the salt **8** was obtained by treating **8** with the pyrrolidine ena-

Table II

Bond Distances and Angles and Their Standard Deviations Involving the Heavier Atoms[a]

Bond	Length, Å	Bond	Angle, deg	Bond	Angle, deg
C(2)–C(1)	1.424 (5)	C(2)–C(1)–C(6)	118.3 (3)	C(2)–C(1)–Fe(23)	67.8 (2)
C(6)–C(1)	1.510 (5)	C(6)–C(1)–C(16)	114.0 (3)	C(6)–C(1)–Fe(23)	109.5 (2)
C(16)–C(1)	1.512 (6)	C(16)–C(1)–Fe(23)	121.0 (2)	C(16)–C(1)–C(2)	118.5 (3)
Fe(23)–C(1)	2.116 (3)				
C(3)–C(2)	1.405 (5)	C(3)–C(2)–C(1)	115.0 (3)	C(3)–C(2)–Fe(23)	70.8 (2)
Fe(23)–C(2)	2.057 (3)	Fe(23)–C(2)–C(1)	72.3 (2)		
C(4)–C(3)	1.421 (4)	C(4)–C(3)–C(2)	115.0 (3)	C(4)–C(3)–O(4)	118.6 (3)
O(14)–C(3)	1.364 (4)	O(14)–C(3)–C(2)	126.3 (3)	O(14)–C(3)–Fe(23)	126.2 (2)
Fe(23)–C(3)	2.074 (3)	Fe(23)–C(3)–C(2)	69.5 (2)	Fe(23)–C(3)–C(4)	71.1 (2)
C(5)–C(4)	1.514 (4)	C(5)–C(4)–C(3)	120.5 (2)	C(5)–C(4)–Fe(23)	110.3 (2)
Fe(23)–C(4)	2.100 (3)	Fe(23)–C(4)–C(3)	69.1 (2)		
C(6)–C(5)	1.540 (5)	C(6)–C(5)–C(4)	108.8 (3)	C(1)–C(6)–C(5)	112.4 (2)
C(7)–C(5)	1.534 (4)	C(7)–C(5)–C(4)	112.9 (2)	C(7)–C(5)–C(6)	112.8 (2)
C(8)–C(7)	1.534 (5)	C(8)–C(7)–C(5)	114.8 (3)	C(8)–C(7)–C(12)	109.8 (3)
C(12)–C(7)	1.519 (5)	C(12)–C(7)–C(5)	113.0 (2)		
C(9)–C(8)	1.524 (5)	C(9)–C(8)–C(7)	111.8 (3)		
C(10)–C(9)	1.511 (6)	C(10)–C(9)–C(8)	110.1 (3)		
C(11)–C(10)	1.519 (6)	C(11)–C(10)–C(9)	111.6 (3)		
C(12)–C(11)	1.500 (6)	C(12)–C(11)–C(10)	113.9 (3)	C(7)–C(12)–C(11)	115.7 (3)
O(13)–C(12)	1.198 (4)	O(13)–C(12)–C(7)	122.4 (3)	O(13)–C(12)–C(11)	121.9 (3)
O(14)–C(15)	1.426 (5)	C(3)–O(14)–C(15)	116.8 (3)		
C(17)–O(18)	1.142 (5)	Fe(23)–C(17)–O(18)	179.3 (3)		
C(17)–Fe(23)	1.788 (4)	C(17)–Fe(23)–C(1)	96.5 (1)	C(17)–Fe(23)–C(2)	93.3 (2)
		C(17)–Fe(23)–C(3)	121.4 (1)	C(17)–Fe(23)–C(4)	161.2 (1)
C(19)–O(20)	1.142 (4)	Fe(23)–C(19)–O(20)	177.3 (3)		
C(19)–Fe(23)	1.774 (3)	C(19)–Fe(23)–C(1)	88.6 (1)	C(19)–Fe(23)–C(2)	128.1 (1)
		C(19)–Fe(23)–C(3)	134.0 (1)	C(19)–Fe(23)–C(4)	97.1 (1)
C(21)–O(22)	1.142 (4)	Fe(23)–C(21)–O(22)	175.9 (3)		
C(21)–Fe(23)	1.780 (3)	C(21)–Fe(23)–C(1)	163.0 (1)	C(21)–Fe(23)–C(2)	126.5 (1)
		C(21)–Fe(23)–C(3)	93.8 (1)	C(21)–Fe(23)–C(4)	89.2 (1)
		C(1)–Fe(23)–C(2)	39.8 (1)	C(1)–Fe(23)–C(3)	69.4 (1)
		C(1)–Fe(23)–C(4)	76.4 (1)	C(2)–Fe(23)–C(3)	39.8 (1)
		C(2)–Fe(23)–C(4)	69.9 (1)	C(3)–Fe(23)–C(4)	39.8 (1)
		C(17)–Fe(23)–C(19)	100.2 (2)	C(17)–Fe(23)–C(21)	94.4 (1)
		C(19)–Fe(23)–C(21)			

[a] The values for the standard deviations in bond lengths have been multiplied by 10^3. The values for the standard deviations in bond angles have been multiplied by 10.



14

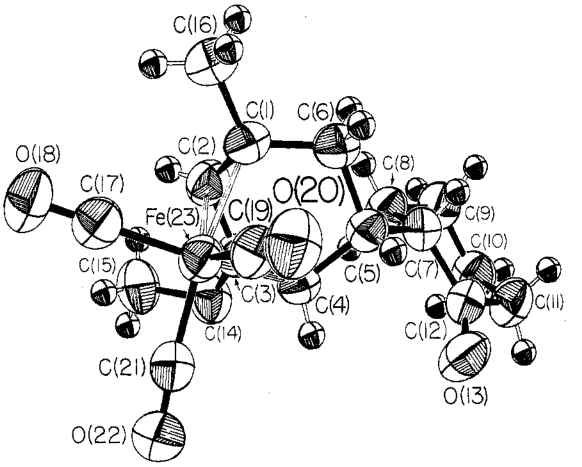


Figure 1. The carbon, iron, and oxygen atoms in the top figure of 3-methoxy-1-methyl-5-(2-oxocyclohexyl)cyclohexadieneiron tricarbonyl are drawn as ellipsoids at 50% thermal probability. The hydrogen atoms are shown as spheres of radius 1 nm.

mine of cyclohexanone. Subsequent hydrolysis of the product gave ketone **15**. Ketone **15** was characterized by single-crystal X-ray structure analysis. The crystal structure was solved by the heavy atom method. Refinement to an *R* factor of 5.7% was obtained by the method of least squares on 1860 nonzero structure factors. The intensity data were collected on a diffractometer (Co Kα radiation).

A view of the ketone **15**, drawn by a Calcomp plotter controlled by an IBM 370/155 computer using the ORTEP program,[15] is shown in Figure 1. The bond distances and angles involving the heavier atoms, along with their respective standard deviations, are listed in Table II. The standard deviations in atomic coordinates (Tables III and IV) correspond to positional uncertainties of approximately 0.004 Å for carbon atoms, 0.003 Å for oxygen atoms, 0.0006 Å for the iron atom, and 0.04 Å for hydrogen atoms. Distances and angles involving hydrogen atoms are listed in Table V.

The cyclohexadiene ring is distorted in the complex. Carbons 1–4 are nearly planar and the methoxy oxygen (O-14) does not deviate much from the best plane through the four carbon atoms. Carbons 5 and 6, the bridging carbon atoms, are bent substantially away from the iron atom, and the methyl group (C-16) is bent toward the metal atom (see Table VI). Also the bond between C-2 and C-3, a formal single bond, is shorter than the formal double bond between C-3 and C-4. This distortion was also found by Churchill and Mason,[16] who studied the structure of octafluorocyclohexa-1,3-dieneiron tricarbonyl, and is discussed at length by them.

Additional reactions of the salts **4** and **8** are shown in Schemes I and II. Of particular interest is the reaction of the salt **4** with the dienamine 3-pyrrolidinocholesta-3,5-diene (**16**). Reagents such as diketone,[17] methyl iodide,[18] *m*-methoxybenzyl bromide,[19] ethyl acrylate,[20] acryloyl chloride,[21] 1,3-dichlorobut-2-ene,[22] methyl vinyl ketone,[23] methyl vinyl sulfone,[23] α,β-unsaturated nitriles,[24] cyano-

Table III
Heavy-Atom Parameters and Their Standard Deviations[a]

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	4125 (4)	6100 (3)	1310 (1)	245 (8)	154 (4)	21 (1)	50 (9)	−39 (3)	2 (2)
C(2)	4030 (5)	7575 (4)	1412 (1)	262 (8)	167 (4)	20 (1)	−44 (10)	−39 (4)	−4 (2)
C(3)	2347 (5)	8263 (3)	1284 (1)	284 (9)	134 (4)	18 (1)	17 (9)	−26 (3)	0 (2)
C(4)	960 (5)	7369 (3)	1094 (1)	234 (8)	136 (4)	18 (1)	51 (9)	−29 (3)	1 (2)
C(5)	1692 (4)	6274 (3)	679 (1)	240 (8)	131 (3)	19 (1)	−10 (9)	−28 (3)	−3 (2)
C(6)	3611 (5)	5583 (4)	802 (1)	288 (9)	150 (4)	20 (1)	55 (10)	−31 (3)	−1 (2)
C(7)	1977 (5)	6869 (3)	123 (1)	277 (8)	136 (4)	16 (1)	2 (8)	−32 (3)	−7 (2)
C(8)	3363 (6)	8158 (4)	24 (1)	289 (10)	174 (4)	21 (1)	−60 (10)	−40 (4)	8 (3)
C(9)	3670 (6)	8637 (4)	−543 (1)	353 (10)	190 (5)	20 (1)	−87 (12)	−21 (4)	13 (3)
C(10)	1676 (6)	9034 (4)	−686 (2)	403 (11)	185 (5)	20 (1)	14 (12)	−34 (4)	14 (3)
C(11)	176 (6)	7831 (5)	−584 (2)	368 (11)	206 (6)	22 (1)	−12 (13)	−68 (4)	9 (3)
C(12)	2 (5)	7184 (4)	−52 (1)	279 (9)	156 (4)	19 (1)	−18 (0)	−43 (3)	−10 (2)
O(13)	−1594 (4)	6889 (3)	208 (1)	269 (7)	266 (5)	25 (1)	−68 (8)	−48 (3)	19 (2)
O(14)	1903 (4)	9661 (2)	1350 (1)	387 (7)	127 (3)	20 (1)	14 (7)	−47 (3)	−4 (2)
C(15)	2810 (7)	10399 (4)	1723 (2)	468 (14)	154 (5)	22 (1)	−54 (12)	−48 (4)	−18 (3)
C(16)	5735 (6)	5245 (5)	1498 (2)	320 (10)	197 (6)	27 (1)	107 (12)	−64 (4)	−2 (3)
C(17)	2455 (5)	6553 (4)	2413 (1)	326 (10)	166 (5)	22 (1)	26 (10)	−48 (4)	−3 (2)
O(18)	3074 (5)	6475 (3)	2792 (1)	517 (10)	272 (5)	22 (1)	109 (11)	−114 (4)	−7 (2)
C(19)	574 (5)	4928 (3)	1782 (1)	306 (9)	151 (4)	17 (1)	3 (10)	−44 (3)	8 (2)
O(20)	74 (4)	3791 (3)	1740 (1)	480 (9)	146 (3)	26 (1)	−68 (8)	−74 (3)	5 (2)
C(21)	−760 (5)	7582 (4)	2126 (1)	297 (9)	159 (4)	17 (1)	1 (10)	−35 (3)	−5 (2)
O(22)	−2238 (4)	8130 (3)	2296 (1)	327 (7)	210 (4)	26 (1)	77 (8)	−32 (3)	−26 (2)
Fe(23)	1456 (1)	6677 (1)	1825 (0)	273 (2)	139 (1)	18 (0)	9 (2)	−40 (1)	1 (0)

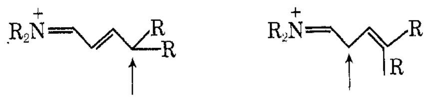
[a] The values have been multiplied by 10^4. The temperature factor is in the form $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table IV
Hydrogen Atom Parameters and Their Standard Deviations[a]

Atom	x	y	z	B
H(24)	475 (4)	802 (3)	158 (1)	46 (7)
H(25)	−22 (4)	780 (3)	107 (1)	38 (6)
H(26)	71 (4)	558 (3)	72 (1)	36 (5)
H(27)	341 (5)	452 (4)	82 (1)	63 (8)
H(28)	478 (4)	584 (3)	54 (1)	46 (6)
H(29)	257 (4)	618 (3)	−10 (1)	42 (6)
H(30)	462 (5)	792 (4)	11 (1)	64 (8)
H(31)	274 (4)	898 (4)	26 (1)	56 (7)
H(32)	430 (6)	780 (4)	−78 (1)	81 (10)
H(33)	469 (6)	939 (4)	−60 (1)	75 (9)
H(34)	191 (5)	934 (4)	−104 (1)	70 (9)
H(35)	121 (6)	985 (4)	−46 (2)	76 (9)
H(36)	70 (5)	716 (4)	−83 (1)	60 (8)
H(37)	−115 (6)	814 (4)	−59 (1)	76 (10)
H(38)	246 (5)	994 (4)	205 (1)	70 (9)
H(39)	217 (6)	1134 (5)	177 (2)	91 (11)
H(40)	422 (6)	1044 (4)	159 (1)	76 (10)
H(41)	596 (5)	561 (4)	182 (1)	71 (9)
H(42)	530 (5)	429 (4)	155 (1)	57 (8)
H(43)	688 (6)	519 (5)	122 (2)	84 (10)

[a] The values for the coordinates have been multiplied by 10^3. The values for the isotropic temperature factors have beed multiplied by 10.

gen chloride,[25] and diethyl azodicarboxylate[26] attack the β carbon of the dienamine.[27] This is a result of attack at the position of greatest electron density. However, the product from attack at the δ carbon gives the more stable product after nucleophilic attack. The relationship between the stability of a cation and its selectivity in reaction has long been appreciated.[27-29] In particular, electrophilic reagents which stabilize positive charge especially well tend to give terminal substitution at the δ carbon with dienamines.[27] Examples include the Vilsmeier reagent $HC(Cl){=}NMe_2^+$,[30] protons,[31] 1,2-diphenyl-3-dicyanomethylenecyclopropene,[32] and benzyl sulfonyl chloride.[26]



δ attack β attack

Since the salt 4 is stable to recrystallization from hot water[3] and is stable in air for several weeks, its chemistry would be expected to display a similar selectivity with the latter reagents. The salt 4 attacked the β carbon atom of isobutyraldehyde enamine, unlike alkyl halides that usually attack the nitrogen of β-disubstituted enamines that are derived from aldehydes.[33]

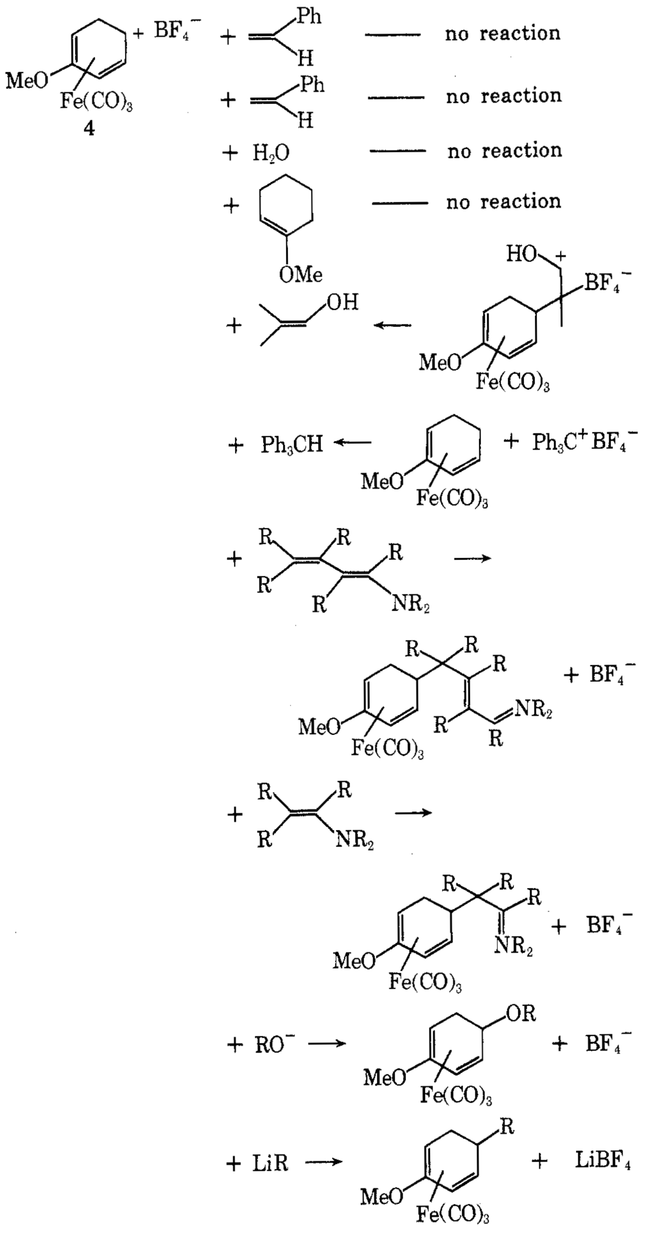
Experimental Section[34]

Preparation of 2-Methoxycyclohexa-1,3-dieneiron Tricarbonyl (2) and 1-Methoxycyclohexa-1,3-dieneiron Tricarbonyl (3).[35] To 146 g (6.35 g-atoms) of sodium in 2 l. of ammonia was added 130 g (1.30 mol) of anisole with 100 ml of ether. The addition required 40 min. The mixture was stirred for an additional 30 min before 600 ml (10.3 mol) of ethanol was added. After the reaction mixture turned colorless, the ammonia was boiled off; then 500 ml of ether was added. The organic layer was separated, washed with 3 × 100 ml of water, and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, leaving 69.3 g of colorless oil: pmr spectrum (CCl_4) δ 3.75 (s, rel intensity 4, methoxy group in anisole), 3.51 (s, rel intensity 15, methoxy group in 1-methylcyclohexa-1,4-diene), 3.43 (s, rel intensity 4, methoxy group in 1-methoxycyclohexene).

To 15.6 g of the colorless oil was added 250 ml of di-*n*-butyl ether and 25 g (128 mmol) of iron pentacarbonyl. The reaction mixture was stirred under argon in an oil bath at 135–145° for 55 hr. The reaction mixture was filtered through Celite. Solvent was removed at vacuum pump pressure. The remaining 14.6 g of crude product contained about a 50:50 mixture of **2** and **3**. Chromatography on 500 g of silica gel with petroleum ether gave a first major yellow band containing 7.2 g (10% yield, two steps) of **2**: pmr spectrum ($CHCl_3$) δ 5.06 (dd, $J = 6, 2$ Hz, 1 H, C_3 H), 3.56 (s, 3 H, methoxy), 3.43 (q, $J = 2$ Hz, 1 H, C_1 H), 2.75 (dd, $J = 6, 3$ Hz, C_4 CH), 2.5–0.8 (m, 4 H); ^{13}C nmr spectrum ($CDCl_3$) δ 201.0 (carbonyl on iron), 133.2 (C_2), 64.4 (C_3), 52.4 (methoxy), 51.3 (C_1), 48.4 (C_4), 23.7, 22.6 (C_5 and C_6); ir spectrum ($CHCl_3$) 3005, 2935, 2925, 2900, 2875 (CH stretch), 2045 (vs, symmetrical carbonyl stretch on iron ligands), 1975 (vs, asymmetrical carbonyl stretch on iron ligands), 1480 cm^{-1} (alkene ligand).

The second major yellow band was eluted with ether–petroleum ether and gave 6.3 g (9% yield) of **3**: pmr spectrum ($CDCL_3$) δ 5.33 (dd, $J = 5, 2$ Hz, 1 H, C_2 H), 5.05 (dd, $J = 7, 5$ Hz, 1 H, C_3 H), 3.47 (s, 3 H, methoxy), 2.98 (m, 1 H, C_4 H), 2.5–0.8 (m, 4 H); ^{13}C nmr spectrum ($CDCl_3$) δ 201.7 (carbonyl on iron), 134.0 (C_1), 74.5 (C_2), 73.6 (C_3), 55.3 (methoxy), 53.5 (C_4), 24.0, 22.3 (C_5 and

Scheme I
Reactivity of (1,2,3,4,5-*pentahapto*-2-Methoxycyclohexadienyl)(tricarbonyl)iron Fluoroborate

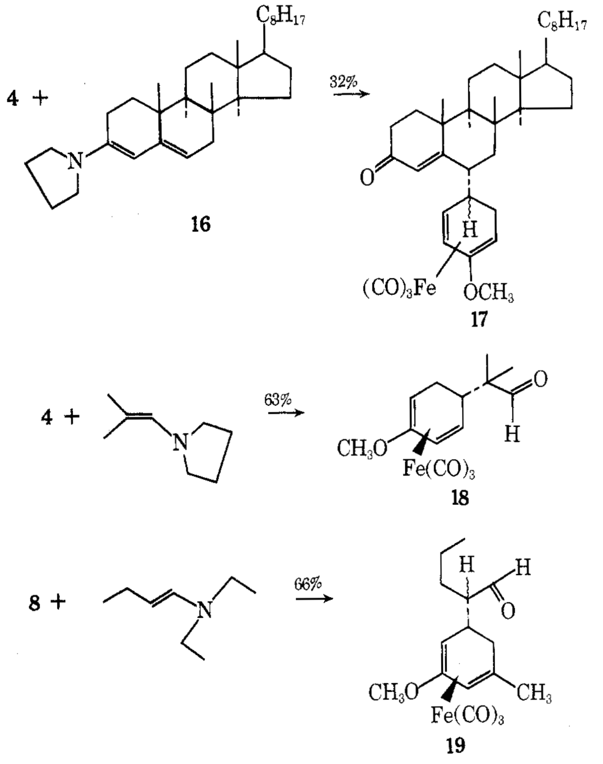


C$_6$); ir spectrum (CHCl$_3$) 3015, 2965, 2940, 2905, 2865 (CH stretch), 2030 (vs, symmetrical carbonyl stretch on iron ligands), 1960 (vs, asymmetrical carbonyl stretch on iron ligands), 1475 cm^{-1} (s, alkene ligands).

Preparation of (1,2,3,4,5-*pentahapto*-2-Methoxycyclohexadienyl)(tricarbonyl)iron Fluoroborate[36,37] **(4) and (1,2,3,4,5-*pentahapto*-3-Methoxycyclohexadienyl)(tricarbonyl)iron Fluoroborate (5).** To a warm solution of 3.22 g (12.4 mmol) of triphenylcarbinol in 32 ml of acetic anhydride was added 1.9 ml (10.4 mmol) of 48-50% aqueous fluoroboric acid under argon. After the solution had stood for 15 min, a 3.11-g (12.4 mmol) portion of 2 was added. The reaction mixture was stirred for 40 min. As 92 ml of ether was added, a precipitate formed. The precipitate was collected and washed with 10 ml of ether. On drying 3.72 g (89% yield) of 4 was obtained: nmr spectrum, see Table I; ir spectrum (mineral oil) 2100, 2055, 2045 (vs, carbonyl stretching), 1515, 1495 (alkene stretching), 1095, 1050, 1025 cm^{-1} (s, fluoroborate).

An additional 100 ml of ether was added to the mother liquor and wash solution. A second precipitate formed. Filtration gave 0.26 g (6% yield) of a yellow powder after washing with 10 ml of ether and drying. The pmr spectrum showed 5 with about 5% of 4 as a contaminant. Purer material was obtained by dissolving the solid in acetone and precipitating the yellow powder with petroleum ether: pmr spectrum, see Table I; ir spectrum (mineral oil) 2100, 2060, 2040 (vs, carbonyl stretching), 1540 (alkene stretching), 1100, 1055, 1045 cm^{-1} (fluoroborate). *Anal.* Calcd for $C_{10}H_9BF_4FeO_4$: C, 35.77; H, 2.70. Found: C, 35.82; H, 2.46.

Scheme II
Hydrolysis Products after Treating 8 and 4 with the Enamines Drawn



Preparation of (1,2,3,4,5-*pentahapto*-1-Methoxycyclohexadienyl)(tricarbonyl)iron Fluoroborate (6).[37] To a warm solution of 1.6 g (6.2 mmol) of triphenylcarbinol in 17 ml of acetic acid was added 0.95 ml (5.2 mmol) of 48-50% aqueous fluoroboric acid under argon. The mixture was stirred with cooling for 15 min. Next 1.55 g (6.2 mmol) of 3 was added with 2 ml of acetic anhydride. After stirring for 30 min under argon, the reaction was quenched with 30 ml of ether. The solid that formed was filtered and washed with 10 ml of ether. On drying the precipitate amounted to 0.647 g. The pmr spectrum showed about 10% impurity of 4. The filtrate and wash solution were treated with a second 30-ml portion of ether and after washing with 10 ml of ether gave 0.296 g of yellow solid with an pmr spectrum identical with that of the first precipitate. The combined solid was dissolved in acetone and precipitated with petroleum ether. The resulting material was redissolved and precipitated twice more. After drying, the resulting residue was a yellow powder: pmr spectrum, see Table I; ir spectrum (mineral oil) 2105, 2030 (vs, carbonyl stretching), 1539 (alkene stretching), 1095, 1050, 1035 cm^{-1} (s, fluoroborate). *Anal.* Calcd for $C_{10}H_9BF_4FeO_4$: C, 35.77; H, 2.70. Found: C, 35.63; H, 2.61.

Preparation of 2-Methoxy-5-(2-oxocyclohexyl)cyclohexa-1,3-dieneiron Tricarbonyl (11, 12). To a solution of 3.35 g (10 mmol) of 4 in 50 ml of dichloromethane was added 1.51 g (10 mmol) of 1-pyrrolidinocyclohexene. The mixture was stirred under argon for 17 hr; then 600 mg of sodium acetate, 10 ml of acetic acid, and 10 ml of water were added. The resulting mixture was stirred and refluxed for 3 hr under an argon atmosphere. The organic layer was separated, washed with 4 × 25 ml of water, and dried over anhydrous MgSO$_4$. Removal of solvent at reduced pressure left 3.46 g of yellow solid. The solid was chromatographed on 400 g of silica gel. Dichloromethane was used to elute 2.40 g (69% yield) of crude product. The crude material was recrystallized from petroleum ether, giving 596 mg of crystals of **11**, mp 97-102°, and 668 mg of less soluble crystals of **12**, mp 108-114°.

The crude 11 was recrystallized twice more from petroleum ether to give yellow crystals: mp 102-103°; pmr spectrum (CDCl$_3$) δ 5.13 (dd, J = 7, 2 Hz, 1 H, C$_3$ H), 3.47 (s, 3 H, methoxy), 3.34 (m, 1 H, C$_1$ H), 2.74 (dd, J = 6, 3 Hz, 1 H, C$_4$ H), 2.5-0.8 (m, 12 H); ^{13}C nmr spectrum (CDCl$_3$) δ 211.8 (carbonyl on iron), 66.7 (C$_3$), 58.7 (C$_{1'}$), 55.3 (C$_4$), 53.1 (methoxy carbon), 51.3 (C$_1$), 42.4

Table V
Bond Distances and Angles and Their Standard Deviations Involving the Hydrogen Atoms[a]

Bond	Length, Å	Bond	Angle, deg	Bond	Angle, deg
H(24)–C(2)	0.82 (3)	H(24)–C(2)–C(1)	126 (2)	H(24)–C(2)–C(3)	118 (2)
		H(24)–C(2)–Fe(23)	118 (2)		
H(25)–C(4)	0.91 (3)	H(25)–C(4)–C(3)	114 (2)	H(25)–C(4)–C(5)	115 (2)
		H(25)–C(4)–Fe(23)	120 (1)		
H(26)–C(5)	0.93 (2)	H(26)–C(5)–C(4)	106 (2)	H(26)–C(5)–C(6)	107 (2)
		H(26)–C(5)–C(7)	109 (2)		
H(27)–C(6)	1.02 (4)	H(27)–C(6)–C(1)	110 (2)	H(27)–C(6)–C(5)	109 (2)
		H(27)–C(6)–H(28)	111 (2)		
H(28)–C(6)	0.98 (3)	H(28)–C(6)–C(1)	105 (2)	H(28)–C(6)–C(5)	111 (2)
H(29)–C(7)	0.91 (3)	H(20)–C(7)–C(5)	107 (2)	H(29)–C(7)–C(8)	106 (2)
		H(29)–C(7)–C(12)	105 (2)		
H(30)–C(8)	0.94 (4)	H(30)–C(8)–C(7)	109 (2)	H(30)–C(8)–C(9)	109 (2)
		H(30)–C(8)–H(31)	108 (3)		
H(31)–C(8)	1.04 (3)	H(31)–C(8)–C(7)	109 (2)	H(31)–C(8)–C(9)	109 (2)
H(32)–C(9)	1.05 (4)	H(32)–C(9)–C(8)	108 (2)	H(32)–C(9)–C(10)	110 (2)
		H(32)–C(9)–H(33)	105 (3)		
H(33)–C(9)	0.98 (4)	H(33)–C(9)–C(8)	110 (2)	H(33)–C(9)–C(10)	114 (2)
H(34)–C(10)	0.95 (4)	H(34)–C(10)–C(9)	108 (2)	H(34)–C(10)–C(11)	113 (2)
		H(34)–C(10)–H(35)	109 (3)		
H(35)–C(10)	0.99 (4)	H(35)–C(10)–C(9)	104 (2)	H(35)–C(10)–C(11)	111 (2)
H(36)–C(11)	0.93 (3)	H(36)–C(11)–C(10)	104 (2)	H(36)–C(11)–C(12)	108 (2)
		H(36)–C(11)–H(37)	116 (3)		
H(37)–C(11)	0.95 (4)	H(37)–C(11)–C(10)	111 (2)	H(37)–C(11)–C(12)	104 (2)
H(38)–C(15)	0.95 (4)	H(38)–C(15)–O(14)	109 (2)	H(38)–C(15)–H(39)	106 (3)
H(39)–C(15)	0.98 (5)	H(39)–C(15)–O(14)	107 (3)	H(39)–C(15)–H(40)	113 (3)
H(40)–C(15)	0.95 (4)	H(40)–C(15)–O(14)	108 (2)	H(40)–C(15)–H(38)	114 (3)
H(41)–C(16)	0.95 (4)	H(41)–C(16)–C(1)	110 (2)	H(41)–C(16)–H(42)	109 (3)
H(42)–C(16)	0.95 (3)	H(42)–C(16)–C(1)	109 (2)	H(42)–C(16)–H(43)	104 (3)
H(43)–C(16)	0.97 (4)	H(43)–C(16)–C(1)	108 (3)	H(43)–C(16)–H(41)	117 (3)

[a] The values for the standard deviations in bond lengths have been multiplied by 10^2.

Table VI
Least-Squares Plane of the Diene Carbon Atoms and Atomic Deviations from the Plane[a]

Atom	Deviation, Å	Atom	Deviation, Å
C(1)	−0.006	C(5)	−0.907
C(2)	0.012	C(6)	−0.946
C(3)	−0.012	O(14)	0.012
C(4)	0.006	C(16)	0.196

[a] Coefficients are direction cosines relative to the crystallographic axis. Plane through atoms C(1), C(2), C(3), and C(4): $-0.3239x - 0.1653y + 0.8563z = 1.068$.

($C_{3'}$), 36.5 (C_5), 32.3 ($C_{6'}$), 31.6 ($C_{4'}$), 28.3 ($C_{5'}$), 25.1 (C_6); ir spectrum ($CHCl_3$) 3030, 3020, 2940, 2865 (CH stretch), 2045 (vs, symmetrical carbonyl stretch of iron ligands), 1965 (vs, asymmetrical carbonyl stretch of iron ligands), 1705 (s, carbonyl of cyclohexanoyl), 1485 cm^{-1} (s, alkene ligand). *Anal.* Calcd for $C_{16}H_{18}FeO_5$: C, 55.51; H, 5.24. Found: C, 55.55; H, 5.46.

The crude 12 was recrystallized twice more from petroleum ether to give crystals: mp 113–114°; pmr spectrum ($CDCl_3$) δ 5.12 (dd, J = 7, 2 Hz, 1 H, C_3 H), 3.47 (s, 3 H, methoxy), 3.28 (m, 1 H, C_1 H), 2.55 (dd, J = 7, 2 Hz, 1 H, C_4 H), 2.4–0.8 (m, 12 H); ^{13}C nmr spectrum ($CDCl_3$) δ 212.2 (carbonyls on iron), 211.2 (cyclohexanoyl carbonyl), 139.7 (C_2), 67.4 (C_3), 57.6 ($C_{1'}$), 54.3 C_4), 52.9 (methoxy), 51.3 (C_1), 42.1 ($C_{3'}$), 37.1 (C_5), 30.6 ($C_{6'}$), 28.7 ($C_{4'}$), 27.8 ($C_{5'}$), 24.3 (C_6); ir spectrum ($CHCl_3$) 3005, 2940, 2865, 2830 (CH stretch), 2040 (vs, symmetrical carbonyl strength of iron ligands), 1960 (vs, asymmetrical carbonyl stretch or iron ligands), 1705 (s, carbonyl of cyclohexanoyl), 1485 cm^{-1} (s, alkene ligands). *Anal.* Calcd for $C_{16}H_{18}FeO_5$: C, 55.51; H, 5.24. Found: C, 55.30; H, 5.09.

Preparation of 5-(1,1-Dimethyl-2-oxoethyl)-2-methoxycyclohexa-1,3-dieneiron Tricarbonyl (18). To a mixture of 336 mg (1.0 mmol) of 4 and 5 ml of CH_2Cl_2 was added 125 mg (1.0 mmol) of 2,2-dimethyl-1-pyrrolidinoethene. The mixture was stirred under argon for 19 hr. A solution of 300 mg of sodium acetate, 6 ml of acetic acid, and 6 ml of water was added to the reaction mixture and stirring was continued for 3 hr. Then the organic layer was separated, washed with 5 × 5 ml of saturated sodium bicarbonate, washed with 2 × 5 ml of water, and dried over anhydrous $MgSO_4$. Removal of the solvent at vacuum pump pressure left 266 mg of a yellow oil.

Bulb-to-bulb distillation of the oil (95°, 0.05 mm) gave 203 mg (63° yield) of 18: pmr spectrum ($CDCl_3$) δ 9.59 (s, 1 H, aldehyde proton), 5.28 (dd, J = 6, 2 Hz, 1 H, C_3 H), 3.76 (s, 3 H, methoxy), 3.44 (m, 1 H, C_1 H), 3.0–0.8 (m, 4 H), 1.12 (s, 3 H, methyl), 1.08 (s, 3 H, methyl); ir spectrum ($CHCl_3$) 3010, 2965, 2940, 2875 (CH stretch), 2760 (CH aldehyde stretch), 2045 (vs, symmetrical carbonyl stretch of iron ligands), 1965 (vs, asymmetrical carbonyl stretch of iron ligands), 1725 (s, aldehyde carbonyl), 1490 cm^{-1} (s, alkene ligand). *Anal.* Calcd for $C_{14}H_{16}FeO_5$: C, 52.52; H, 5.04. Found: C, 52.58; H, 5.03.

Preparation of 6α-(4-Methoxycyclohexa-2,4-dieneiron Tricarbonyl)cholest-4-en-3-one (17). To 1.46 g (4.35 mmol) of 4 with 50 ml of CH_2Cl_2 was added 1.9 g (4.35 mmol) of 3-pyrrolidinocholesta-3,5-diene.[38] The mixture was stirred under an argon atmosphere for 31 hr. A solution of 1 g of sodium acetate, 20 ml of water, and 20 ml of acetic acid was added to the reaction mixture and stirring was continued for 14 hr. The organic layer was separated, washed with 4 × 25 ml of saturated sodium bicarbonate, washed with 25 ml of water, and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, leaving 2.62 g of brown foam, mp 90–93°. A 1.22-g portion of the form was chromatographed on 15 g of silica gel. A solution of 25% ethyl acetate–hexane was used to elute a yellow oil that gave 846 mg of brown foam at vacuum pressure. The foam was then chromatographed on 115 g silica gel H (10–40) in a column 2.54 cm in diameter. A solution of 25% ethyl acetate-hexane was pumped through the column to elute the sample. After an initial 150 ml of solvent was collected from the high-pressure column at the rate of 1.5 ml/min, the fractions were collected every 4 min. Fractions 29–55 contained 431 mg (32% yield) of chromatographically homogeneous foam.

The chromatographed foam was recrystallized from 12 ml of methanol to give 181 mg of white, fibrous solid, mp 167–169°. Repeated recrystallization from methanol gave a white, fibrous solid: mp 172–173°; pmr spectrum ($CDCl_3$) δ 5.63 (s, 1 H, $C_{4'}$ vinyl hydrogen), 5.12 (dd, J = 7, 2 Hz, 1 H, $C_{3'}$ H), 3.63 (s, 3 H, methoxy), 3.26 (m, 1 H, $C_{5'}$ H), 2.80 (m, 1 H, $C_{2'}$ H), 2.5–0.8 (m, 33 H), 1.08 (s, 3 H, methyl), 0.9 (s, 3 H, methyl); ir spectrum ($CHCl_3$) 3010, 2950, 2890, 2870 (CH stretch), 2045 (vs, symmetrical carbonyl stretch of iron ligands), 1965 (vs, asymmetrical carbonyl stretch of iron ligands), 1660 (s, enone carbonyl), 1605 (alkene), 1490 cm^{-1} (s, alkene ligands); uv spectrum λ_{max} (MeOH) 225 nm (ϵ 20,000). *Anal.* Calcd for $C_{37}H_{52}FeO_5$: C, 70.24; H, 8.29. Found: C, 70.48; H, 8.53.

Preparation of 3-Methoxy-1-methylcyclohexa-1,3-dieneiron Tricarbonyl (7), 1-Methoxy-5-methylcyclohexa-1,3-dieneiron Tricarbonyl, and 1-Methoxy-3-methylcyclohexa-1,3-dieneiron Tricarbonyl.[34] To a solution of 21 g (0.875 g-atom) of sodium in 500 ml of ammonia was added 20 g (164 mmol) of 3-methylanisole and 250 ml of ether. The addition was complete in 50 min. The reaction mixture was stirred for 30 min and then 75 ml (1.28 mol) of ethanol was added over a 20-min period. The ammonia was boiled off. After 200 ml of water and 200 ml of ether were added, the organic layer was separated, washed with 4 × 50 ml of water, and dried over anhydrous $MgSO_4$. Removal of solvent at reduced pressure left 16.6 g (82% yield) of 1-methoxy-5-methylcyclohexa-1,4-diene. Distillation gave 12.9 g of a colorless oil: bp 75–77° (aspirator pressure); pmr spectrum (CCl_4) δ 5.35 (m, 1 H, C_4 H), 4.52 (m, 1 H, C_2 H), 3.42 (s, 3 H, methoxy), 2.58 (m, 4 H, C_3 H and C_6 H), 1.68 (s, 3 H, methyl).

To 6.0 g (48.3 mmol) of 1-methoxy-5-methylcyclohexa-1,4-diene in 120 ml of di-*n*-butyl ether was added 26 g (133 mmol) of iron pentacarbonyl. The reaction mixture was stirred and refluxed under argon in a oil bath at 135–145°. The reaction was followed by examining aliquots by ir. The reaction was stopped after 45 hr at reflux when absorption at 1670 and 1710 cm^{-1} had diminished. The reaction mixture was filtered through Celite, which was washed with ether until the wash solution was colorless. The solvents were removed at reduced pressure. After treatment at vacuum-pump pressure, a crude yield of 9.33 g of oil was collected. A 9.05-g portion of oil was loaded onto 500 g of silica gel and eluted with petroleum ether. The petroleum ether was collected in 500-ml fractions. Fractions 5 and 6 consisted of yellow material, 280 mg, of unknown structure. The next three fractions contained a trace of green material, possibly $Fe_3(CO)_{12}$.[39] Fractions 10–18 contained 2.65 g (21% yield) of **7**: pmr spectrum ($CDCl_3$) δ 5.02 (d, J = 2 Hz, 1 H, C_2 H), 3.56 (s, 3 H, methoxy), 3.33 (m, 1 H, C_4 H), 2.0–0.8 (m, 4 H, C_5 H and C_6 H), 1.61 (s, 3 H, methyl); ir spectrum ($CHCl_3$) 3010, 2960, 2940, 2920, 2880, 2860, 2840 (CH stretch), 2035 (vs, symmetrical carbonyl stretch of iron ligands), 1490 cm^{-1} (s, alkene ligand). On elution of the column with ether–petroleum ether, 4.56 g of a mixture of 1-methoxy-5-methylcyclohexa-1,3-dieneiron tricarbonyl and 1-methoxy-3-methylcyclohexa-1,3-dieneiron tricarbonyl was collected.

Preparation of (1,2,3,4,5-*pentahapto*-3-Methoxy-1-methylcyclohexadienyl)(tricarbonyl)iron Fluoroborate (8).[37] To a warm solution of 520 mg (2 mmol) of triphenylcarbinol in 5.2 ml of acetic anhydride was added 0.325 ml (1.7 mmol) of 48–50% aqueous fluoroboric acid under argon atmosphere. The mixture was stirred for 30 min, and then 528 mg (2 mmol) of **7** was added. The reaction mixture was stirred for 1 hr in an ice bath and then quenched with 10 ml of ether. The precipitate was filtered and washed with 2 × 10 ml of ether. Further precipitate which formed in the combined mother liquor and wash solution was collected and added to the original precipitate. Drying the combined precipitates at vacuum pump pressure left 561 mg (80% yield) of yellow powder: pmr spectrum, see Table I; ir spectrum (mineral oil) 2090, 2045, 1975 (vs, carbonyl stretch on iron ligands), 1555 (alkene ligands), 1100, 1060, 1040 cm^{-1} (s, fluoroborate). *Anal.* Calcd for $C_{11}H_{11}BF_4FeO_4$: C, 37.76; H, 3.17 Fe, 15.96. Found: C, 37.87; H, 3.29; Fe, 15,80.

Preparation of 5-(1-Ethyl-2-oxoethyl)-3-methoxy-1-methylcyclohexa-1,3-dieneiron Tricarbonyl (19). To 1.50 g (4.29 mmol) of **8** and 75 ml of CH_2Cl_2 was added 550 mg (4.86 mmol) of 1-(*N*,*N*-diethylamino)-1-butene. The mixture was stirred under argon for 14 hr. The solvent was removed from the reaction mixture at reduced pressure, and then the gummy residue was shaken with 50 ml of ether and 20 ml of water. The ether layer, the water layer, and the remaining gum were separated. The gum was extracted with an additional 50 ml of ether. The combined ether layers were dried over anhydrous $MgSO_4$. A residue remained after the solvent was removed at reduced pressure.

The residue was chromatographed on 20 g of silica gel. Elution of the second band with petroleum ether gave 937 mg (66% yield) of yellow oil. A portion of the oily product was distilled bulb to bulb (95%, 0.05 mm) to give a purer product: nmr spectrum ($CDCl_3$) δ 9.63 (t, J = 2 Hz, 1 H, aldehyde hydrogen), 5.12 (s, 1 H, C_2 H), 3.62 (s, 3 H, methoxy), 3.24 (m, 1 H, C_4 H), 3.0–0.8 (m, 9 H), 1.57 (3 H, methyl); ir spectrum ($CHCl_3$) 3020, 2970, 2940 (CH stretch), 2725 (w, aldehyde CH stretch), 2040 (vs, symmetrical carbonyl stretch on iron ligands), 1960 (vs, asymmetrical carbonyl stretch on iron ligands), 1720 (aldehyde carbonyl), 1490 cm^{-1} (alkene ligands). *Anal.* Calcd for $C_{15}H_{18}FeO_5$: C, 53.91; H, 5.42; Fe, 16.71. Found: C, 54.03; H, 5.41; Fe, 16.63.

Preparation of 3-Methoxy-1-methyl-5-(2-oxocyclohexyl)cyclohexa-1,3-dieneiron Tricarbonyl (15). To 30 ml of CH_2Cl_2 were added 750 mg (.0 mmol) of 1-pyrrolidinocyclohexene and 200 mg (0.573 mmol) of **11**. The reaction mixture was stirred under argon for 20 hr. A solution of 250 mg of sodium acetate, 5 ml of water, and 5 ml of acetic acid was added to the reaction mixture and stirring was continued for 1.5 hr. The organic layer was separated, washed with 2 × 15 ml of water, and dried over anhydrous $MgSO_4$. Removal of the solvents at vacuum-pump pressure left 194 mg of dark oil.

The crude product dissolved in methanol. The methanol solution was filtered and evaporated at reduced pressure to give 139 mg of oily solid (67% yield). A portion of the product was recrystallized twice from methanol to give yellow crystals: mp 142–143°; pmr spectrum ($CDCl_3$) δ 5.12 (d, J = 2 Hz, 1 H, C_2 H), 3.60 (s, 3 H, methoxy), 3.26 (m, 1 H, C_4 H), 3.0–0.8 (m, 12 H), 1.53 (s, 3 H, methyl); ir spectrum ($CHCl_3$) 2945, 2870, 2865 (CH stretch), 2040 (vs, symmetrical carbonyl stretch on iron ligands), 1960 (vs, asymmetrical carbonyl stretch on iron ligands), 1705 (cyclohexanoyl carbonyl), 1490 cm^{-1} (s, alkene ligands). *Anal.* Calcd for $C_{17}H_{20}FeO_5$: C, 56.68; H, 5.60; Fe, 15.50. Found: C, 56.77; H, 5.56; Fe, 15.41.

Collection of the X-Ray Data for Compound 15. Crystals in the form of yellow prisms were obtained from petroleum ether. All the data were obtained from one crystal with dimensions of 0.6 × 0.3 × 0.2 mm. Unit cell parameters were determined from least-squares refinement of the 2θ angles of 27 reflections measured on a General Electric diffractometer. The resulting values were a = 6.769 ± 0.001 Å, b = 9.487 ± 0.002 Å, c = 26.054 ± 0.003 Å, β = 100.57 ± 0.02°. The absence of $0k0$ reflections for k odd and $h0l$ reflections for l odd indicated that the space group was $P2_1/c$. The crystal density, measured by the flotation method, was found to be 1.43 ± 0.02 g cm^{-3}. The calculated density is 1.45 g cm^{-3} for four molecules of molecular weight 360.20 per unit cell.

Intensity data were collected by the θ–2θ scan method on a Datex-automated General Electric diffractometer using iron-filtered Co Kα radiation (λ 1.79021 Å). Reflections were collected to a maximum value of 2θ = 135° with a scan rate of 2°/min. Background counts were taken for 30 sec at the beginning and the end of each scan. The reflections whose peak counting rate exceeded 20,000 counts/sec were remeasured with a lower beam intensity to minimize counting losses. Three reflections, monitored at regular intervals during the data collection, showed no significant variation in intensity.

The intensities of 1875 reflections were measured. The intensities of 15 of these reflections were observed to be less than one standard deviation above background and were assigned a value of zero with zero weight throughout the refinement process. The data were corrected for Lorentz-polarization effects but not for absorption (μ 23 cm^{-1}). The data were placed on an approximately absolute scale by Wilson's method.[40] A Howells', Phillips', and Rogers' plot[41] confirmed that the crystal was centrosymmetric.

Solution and Refinement of the Structure of 15. The phases of the 211 reflections with an E value greater than 1.60 were assigned by Long's program,[42] which uses a reiterative application of Sayre's[43] equation. Long's procedure yielded 16 possible phase assignment combinations for the 211 chosen reflections. Of these 16 combinations, two clearly had much higher consistency indices and of these the more consistent had also converged more quickly.

The reflections whose phases had been determined as described above were used to calculate an E map. The iron atom was easily located in this map. The alternate calculation of structure factors and electron-density maps quickly led to the complete elucidation of the structure.

All calculations were carried out on the IBM 370/155 computer with subprograms operating under the CRYM system.[44] The atomic scattering factors for carbon, oxygen, and iron were taken from "International Tables for X-Ray Crystallography."[45] The atomic scattering factor for hydrogen is that given by Stewart, Davidson, and Simpson.[46] The least-squares routine minimizes the quantity $\Sigma w(F_o^2 - F_c^2)^2$. The weights, w, used throughout the refinement of the structure, were set equal to $1/\sigma^2(F_o^2)$ which were derived from counting statistics. The variance of the intensity was calculated by the formula

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (\mathrm{d}S)^2$$

where S is the total counts collected during the scan, B_1 and B_2 are the numbers of counts collected for each background, α is the scan time to total background time ratio, and d is an empirical constant of 0.02.

Least-squares refinement of the coordinates of the 23 heavier atoms reduced the R index to 0.173. The nonmethyl group hydrogens were introduced at their expected positions. After two cycles of least-squares refinement of the heavier atoms including isotropic temperature factors followed by two additional cycles of refinement with anisotropic temperature factors, a difference Fourier synthesis revealed the positions of the six hydrogens on the two methyl groups. The coordinates of all atoms were placed in one matrix. The temperature factors, including isotropic temperature factors for the hydrogen atoms, and the scale factor were contained in a second matrix, and the refinement was continued. The R index $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0.073 and the weighted R, $\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4$, to 0.040. The "goodness-of-fit" $[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, where m is the number of observations and s is the number of parameters refined, was 7.0

This rather large value for the "goodness-of-fit" and the unreasonableness of some of the refined temperature factors led us to reexamine the data. The most evident error was the fact that the crystal was larger in one dimension than the diameter of the X-ray beam. The crystal was mounted on the diffractometer with its long needle axis coincident with the ϕ axis. Under these conditions it can be easily shown that the volume of the crystal bathed by the X-ray beam is proportional to sec θ and to sin χ. The intensity data were, therefore, all multiplied by $(1 + \tan^2\theta \sin^2\chi)^{-1/2}$; additional least-squares refinement was performed with this corrected data. In the final stages of refinement, a secondary extinction factor[47] was included and the anomalous dispersion contribution was included in the atomic scattering factor for iron. The final value obtained for the secondary extinction factor, g, was $20.1 \pm 0.5 \times 10^{-6}$. The final R index was 0.057, the weighted R was 0.019, and the "goodness-of-fit" was 5.1.

The observed and calculated structure factors $|F_o|$ and F_c are listed in Table VII.[48] The coordinates and anisotropic temperature factors of the heavier atoms and their standard deviations are given in Table III. The positional parameters and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table IV. During the final cycle of refinement, the average parameter shift was less than one-tenth of its standard deviation, and no parameter shifted more than one-quarter of its standard deviation.

Oxidation of 12 to 2-(*p*-Anisyl)cyclohexanone (13a). To a mixture of 190 mg (0.55 mmol) of **12** and 5 ml of methanol was added 1.0 g (1.83 mmol) of ceric ammonium nitrate in 10 ml of methanol. The addition was completed in 5 min. The reaction mixture was stirred for an additional 10 min before 0.125 g (0.55 mmol) of dichlorodicyanoquinone (DDQ) in 20 ml of ether was added over a 5-min period. The reaction mixture was stirred for 1-hr. Then 10 ml of water and 20 ml of ether were added. The ether layer was separated. The aqueous layer was extracted with 3 × 20 ml of ether, and the combined ether layers were washed with 10 ml of brine and dried over anhydrous $MgSO_4$. Removal of the ether at reduced pressure left 198 mg of crude product. After the solid was washed with 1 ml of warm benzene and 6 ml of warm chloroform, the product was eluted on a silica gel plate (EM reagents silica gel F-254, 20 × 200 cm) with ether. The band of higher R_f contained 47 mg (42% yield) of **13a**, mp 69–78°. Four recrystallizations from petroleum ether gave white crystals of **13a**, mp 88–89° (lit.[12] mp 89–89.2°). The 2,4-dinitrophenylhydrazone was prepared[49] and had mp 143–144° (lit.[12] mp 144–145°).

The band of lower R_f contained 32 mg of what was presumably an isomer or a mixture of isomers of 4-(2-oxocyclohexyl)cyclohex-2-en-1-one: ir spectrum ($CHCl_3$) 2940, 2865 (CH stretch), 1710 (unconjugated carbonyl), 1675 (conjugated carbonyl), 1450 cm^{-1} (alkene); pmr spectrum ($CDCl_3$) δ 6.82 (m, J = 10 Hz, 1 H, alkene β to carbonyl), 5.99 (dd, J = 10, 2 Hz, 1 H, alkene α to carbonyl), 3.3–0.8 (m, 14 H).

Conversion of 11 to 4-(2-Oxocyclohexyl)cyclohex-2-en-1-one (13b). To 180 mg (0.52 mmol) of **11** in 5 ml of acetone was added 0.59 ml of Jones reagent (approximately 8 N in chromic acid or about 0.47 mmol of CrO_3). Bubbles evolved from the mixture until the last few drops of oxidant were added. The organic layer was partitioned between ether and saturated aqueous $NaHCO_3$. The ether solution was dried over anhydrous $MgSO_4$. Removal of ether at reduced pressure left 69 mg (69% yield) of a yellow oil which solidified, mp 74–79°. Three recrystallizations from petroleum ether gave crystals of **13b**: mp 85–86°; ir spectrum ($CHCl_3$) 2940, 2865 (CH stretch), 1710 (unconjugated carbonyl), 1675 (conjugated carbonyl), 1450 cm^{-1} (alkene); pmr spectrum ($CDCl_3$) δ 6.83 (m, J = 10 Hz, 1 H, vinyl hydrogen β to carbonyl), 5.99 (dd, J = 10, 2 Hz, 1 H, vinyl hydrogen α to carbonyl), 3.10 (m), 2.8–0.8 (m); uv spectrum λ_{max} (MeOH) 226 nm (ϵ 1.01×10^4). *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.03; H, 8.56.

Acid-Catalyzed Cleavage of 5-(1,1-Dimethyl-2-oxoethyl)-2-methoxycyclohexa-1,3-dieneiron Tricarbonyl. To 160 mg (0.5 mmol) of 5-(1,1-dimethyl-2-oxoethyl)-2-methoxycyclohexa-1,3-dieneiron tricarbonyl in 1.5 ml of acetic anhydride was added 0.08 ml (0.45 mmol) of 48–50% aqueous fluoroboric acid. The mixture turned orange and was stirred under argon for 30 min. Then 5 ml of ether was added. The precipitate was collected and dried at vacuum-pump pressure. The residue contained 103 mg (62% yield) of (1,2,3,4,5-*pentahapto*-2-methoxycyclohexadienyl)(tricarbonyl)iron fluoroborate (**4**).

Rate of Hydride Abstraction from 2-Methoxycyclohexa-1,3-dieneiron Tricarbonyl. To 3.22 g (12.4 mmol) of triphenylcarbinol in a 200-ml flask was added 32 ml of acetic anhydride. The solid was dissolved by heating the mixture on a steam bath. Then 1.9 ml (10.4 mmol) of 48–50% aqueous fluoroboric acid was added. The mixture was stirred and cooled under an argon atmosphere for 15 min. Then 3.11 g (12.4 mmol) of 2-methoxycyclohexa-1,3-dieneiron tricarbonyl was added.

The first 5-ml aliquot was taken 5 min after the addition of reagents was complete. The aliquots were treated with 25 ml of ether. The precipitate formed was collected, washed with 5 ml of ether, and dried at vacuum-pump pressure for each aliquot.

Successive aliquots were taken 10, 20, 30, 40, 60, and 90 min after all reagents had been mixed. The 5-ml aliquoots contained 424, 411, 430, 425, 418, 432, and 448 mg. The last aliquot taken was a 6.8-ml sample at 120 min and contained 549 mg. The total yield of salts was 3.54 g (86%). The pmr spectra of the 5-min aliquot, the 40-min aliquot, and the 120-min aliquot were identical. The spectra showed that the aliquots contained about 90% (1,2,3,4,5-*pentahapto*-2-methoxycyclohexadienyl)(tricarbonyl)iron fluoroborate (**4**) and about 10% of (1,2,3,4,5-*pentahapto*-3-methoxycyclohexadienyl)(tricarbonyl)iron fluoroborate.

Acknowledgments. The authors thank Professor Morton E. Munk for suggesting the use of enamines. Mr. James G. Nourse is also thanked for obtaining the ^{13}C nmr data.

Registry No. 2, 12318-19-3; **3,** 12318-18-2; **4,** 12307-15-2; **5,** 42531-68-0; **6,** 42531-69-1; **7,** 12318-45-5; **8,** 42531-71-5; **9,** 42540-81-8; **10,** 42540-82-9; **11,** 42531-72-6; **13a,** 37087-68-6; **13b,** 42540-84-1; **15,** 42531-73-7; **17,** 42531-74-8; **18,** 42531-75-9; **19,** 42531-76-0; triphenylcarbinol, 76-84-6; 1-pyrrolidinocyclohexene, 1125-99-1; 2,2-dimethyl-1-pyrrolidinoethene, 2403-57-8; 3-pyrrolidinocholesta-3,5-diene, 2309-31-1; 3-methylanisole, 100-84-5; 1-methoxy-5-methylcyclohexa-1,4-diene, 13697-84-2; 1-(*N,N*-diethylamino)-1-butene, 15430-99-6; DDQ, 84-58-2.

Supplementary Material Available. Table VII, listing the observed and calculated structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche, referring to code number JOC-74-51.

References and Notes

(1) Eastman Kodak Summer Fellow, 1971, and Trainee of the National Institutes of Health.

(2) Postdoctoral Fellow of the National Institutes of Health.

(3) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).

(4) E. W. Abel and F. G. A. Stone, *Quart. Rev., Chem. Soc.*, **24**, 498 (1970), and references cited therein.

(5) A. J. Birch and M. A. Haas, *J. Chem. Soc. C*, 2465 (1971).

(6) M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc. A*, 240 (1967).

(7) J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3959 (1963).

(8) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. 1, Elsevier, New York, N. Y., 1966, and references cited therein.

(9) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen and Co. Ltd., London, 1968, and references cited therein.

(10) L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 1602 (1971).

(11) The compound 2-(3-oxocyclohexyl)-2-cyclohexen-1-one synergistically increases the herbicidal effects of 2,4,5-T and atrazine: H. A. Kaufman and R. P. Napier, German Offen. 2,016,666 (1970); *Chem. Abstr.*, **74**, 30977 (1971) ; N. J. Leonard and W. J. Musliner, *J. Org. Chem.*, **31**, 639 (1966).

(12) M. Cais and N. Maoz, *J. Organometal. Chem.*, **5**, 370 (1966); P. L. Pauson, "Organometallic Chemistry," Edward Arnold Ltd., London, 1967, p 120.

(13) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 353 (1973).
(14) W. E. Bachmann, G. I. Fujimoto, and L. B. Wick, *J. Amer. Chem. Soc.*, **72**, 1995 (1950).
(15) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(16) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **301**, 433 (1967).
(17) B. B. Millward, *J. Chem. Soc.*, 26 (1960).
(18) G. Stork and G. Birnbaum, *Tetrahedron Lett.*, 313 (1961).
(19) U. K. Pandit, K. de Jonge, K. Erhart, and H. O. Huisman, *Tetrahedron Lett.*, 1207 (1969).
(20) A. A. Brizzolara, Ph.D. Thesis, Columbia University, 1960.
(21) H. F. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 2320 (1968).
(22) L. Velluz, G. Nominé, R. Bucourt, A. Pierdet, and P. Dufay, *Tetrahedron Lett.*, 127 (1961).
(23) D. Bertin and J. Perronnet, *Bull. Soc. Chim. Fr.*, 1442 (1968).
(24) H. Nozaki, T. Yamaguti, S. Ueda, and K. Kondo, *Tetrahedron*, **24**, 1445 (1968).
(25) M. E. Kuehne and J. A. Nelson, *J. Org. Chem.*, **35**, 161 (1970).
(26) M. E. Kuehne and G. DiVincenzo, *J. Org. Chem.*, **37**, 1023 (1972).
(27) M. J. M. Pollmann, H. R. Reus, U. K. Pandit, and H. O. Huisman, *Recl. Trav. Chim. Pays-Bas.*, **89**, 929 (1970).
(28) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, **88**, 2594 (1966).
(29) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Amer. Chem. Soc.*, **75**, 136 (1953).
(30) R. Sciaky, U. Pallini, and A. Consonni, *Gazz. Chim. Ital.*, **96**, 1284 (1966).
(31) J. L. Johnson, M. E. Herr, J. C. Babcock, A. E. Fonken, J. E. Stafford, and F. W. Heyl, *J. Amer. Chem. Soc.*, **78**, 430 (1956).
(32) J. Ciabattoni and E. C. Nathan, *J. Amer. Chem. Soc.*, **89**, 3081 (1967).
(33) A. G. Cook, "Enamines," Marcel Dekker, New York, N. Y., 1969, p 119.
(34) All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (ir) were taken on a Perkin-Elmer infrared spectrometer, Model 237B, and ultraviolet spectra (uv) were taken on a Cary recording spectrometer, Model 11M. Proton magnetic resonance (pmr) spectra were taken on a Varian Associates Model T-60. Carbon magnetic resonance (^{13}C nmr) spectra were taken on a Varian Associates Model DFS-60. The spectra were noise decoupled. During decoupling the field of the DFS-60 was locked to internal $CDCl_3$. Preparative thin layer chromatography (ptlc) was performed on 20 × 20 cm plates coated with a 2-mm layer of silica gel F 254 (EM Reagents). Dichloromethane was distilled from P_2O_5, and di-*n*-butyl ether was distilled at reduced pressure from lithium aluminum hydride. Petroleum ether refers to that hydrocarbon fraction boiling in the range 30–60° that is supplied by J. T. Baker Co., Phillipsburg, N. J., and labeled "analyzed reagent." Microanalyses for compounds **8**, **19**, and **15** were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Microanalyses for compounds **18**, **11**, **12**, **5**, **13b**, **6**, and **17** were performed by Chemalytics, Inc., Tempe, Ariz.
(35) These compounds were prepared using methods based on procedures found in ref 3 and 12.
(36) This compound was reported in ref 3. It was prepared by essentially the same method.
(37) The preparation of triphenylmethyl fluoroborate was accomplished using a procedure patterned after the one reported by H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
(38) Prepared by the procedure of F. W. Heyl and M. E. Herr, *J. Amer. Chem. Soc.*, **75**, 1918 (1953).
(39) R. Pettit and J. Henery, *Org. Syn.*, **50**, 21 (1970).
(40) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).
(41) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).
(42) R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.
(43) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).
(44) D. J. Duchamp, Program and Abstracts, ACA Meeting, Bozeman, Mont., 1964, Paper B-14, p 29.
(45) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.
(46) R. F. Steward, E. R. Davidson, and W. R. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(47) A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).
(48) See paragraph at end of paper regarding supplementary material.
(49) The derivative was prepared by the procedure of L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 330.

Reaction Intermediates in the Alkylation of Pyridine with *tert*-Butyllithium[1]

Robert F. Francis,* William Davis, and J. T. Wisener

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

Received July 2, 1973

The complex 1,3-dilithio-2,6-di-*tert*-butyl-1,2,3,6-tetrahydropyridine (2) is formed from pyridine and excess *tert*-butyllithium and decomposes on heating to 2,6-di-*tert*-butylpyridine (5). Complex 2 has been isolated as the protonated analog 2,6-di-*tert*-butyl-1,2,3,6-tetrahydropyridine (**10**), which can be catalytically dehydrogenated to **5**. The precursor of 2-*tert*-butylpyridine (3), 1-lithio-2-*tert*-butyl-1,2-dihydropyridine (1), was isolated from a reaction of pyridine with *tert*-butyllithium at −70°. Treatment of **1** with methanol gives a mixture containing 2-*tert*-butyl-1,2-dihydropyridine (6) and 2-*tert*-butyl-2,5-dihydropyridine (7). When heated, dihydropyridines 6 and 7 form 2-*tert*-butylpyridine (3) and 2-*tert*-butyl-1,2,5,6-tetrahydropyridine (8). Pyridine and excess *tert*-butyllithium above room temperature also give 2,4,6-tri-*tert*-butylpyridine (9) which is formed only by alkylation of **5**.

The reactions of pyridine with organolithium compounds have provided a variety of products resulting from monoalkylation or arylation of pyridine α to nitrogen.[2] We recently reported[3] isolation of 4-alkyl- and 2,4- and 2,6-dialkylpyridines in addition to the expected 2-alkylpyridine from reactions in which an excess of the appropriate alkyllithium compound was used. This investigation led to the direct synthesis in good yield of a variety of 2,6-dialkylpyridines.[3] The reaction of pyridine with excess *tert*-butyllithium is significant because it gives 2,4,6-tri-*tert*-butylpyridine (9)[3,4] in addition to other products. However, trialkylated products were not observed in reactions of pyridine with other alkyllithium compounds.

Intermediates which are precursors to dialkyl- and trialkylpyridines have not been reported previously. However, the recent conclusive evidence[5] for the existence of intermediate σ complexes in monoalkylation and arylation of pyridine with organolithium compounds suggested that isolation and characterization of similar complexes leading directly to *tert*-butylpyridines 5 and 9 might also be possible.

Two reaction schemes were considered as the most likely pathways to 2,6-di-*tert*-butylpyridine (5). Direct alkylation of intermediate 1 and alkylation of 2-*tert*-butylpyridine (3) formed by decomposition of 1 could give intermediates 2 and 4, respectively. These intermediates could form dialkylpyridine 5 by loss of lithium hydride. Formation of 5 by decomposition of intermediate 1 followed by a second alkylation step corresponds to the previously utilized[2d] two-step synthesis of 2,6-dialkylpyridines. Intermediate 2 could result from direct alkylation of 1, a reaction not unlike the known[6] addition of *tert*-butyllithium to 1,3-butadiene, or from alkylation of the isomeric 5-lithio-2-*tert*-butyl-2,5-dihydropyridine.