

Simple, Stereospecific Syntheses of Some Insect Pheromones using the $-\text{Fe}(\text{CO})_3$ Protecting Group

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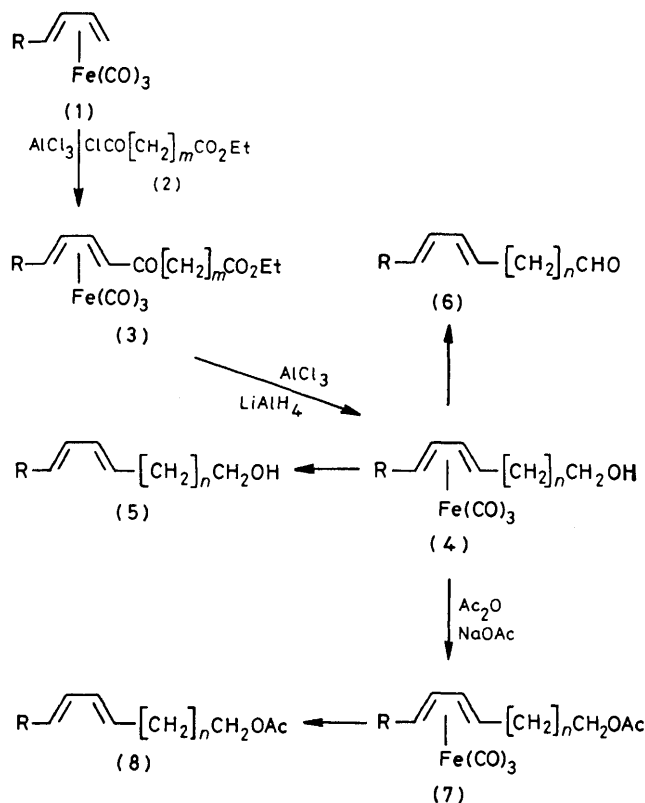
Summary (Diene) $\text{Fe}(\text{CO})_3$ complexes have been used for totally stereospecific syntheses of insect pheromones having (*E*)- and (*E,E*)-1,3-diene skeletons.

AN increasingly large number of insect pheromones are being shown to possess a 1,3-diene skeleton, usually incorporated into a C_{12} , C_{14} , or C_{16} alcohol, acetate, or aldehyde and having variously (*E*)-, (*Z*)-, (*E,E*)-, (*E,Z*)-, or (*Z,Z*)- configurations.¹ Several alternative procedures for the synthesis of these compounds have been developed but the reaction for introducing the 1,3-diene unit has often been stereochemically unsatisfactory, although some authors^{2a} have used ingenious procedures for subsequent isomer separation. *E.g.* three different Wittig-type syntheses² of (*E*)-9,11-dodecadienyl acetate (**8a**), the pheromone of the red bollworm moth (*Diparopsis castanea* Hmps), have given products having 80–96% stereochemical purity; a synthesis³ based upon Grignard coupling gave a product which contained 85% of (*E*)-isomer. This communication describes a general, totally stereospecific procedure for preparing several pheromones using a pre-

formed, simple 1,3-diene, locked into an (*E*)-configuration by an $-\text{Fe}(\text{CO})_3$ protecting group.

We have shown previously that tricarbonyl(butadiene)iron^{4a} and derivatives undergo electrophilic addition under Friedel–Crafts conditions and that stereochemically pure (dienone) $\text{Fe}(\text{CO})_3$ complexes may be obtained;⁵ oxidative cleavage of the $-\text{Fe}(\text{CO})_3$ group yields the dienone.⁶ This general procedure has been applied to the synthesis of the pheromones (**8a**), (**8c**), (**8d**), (**5d**), and (**6f**). The synthesis of (*E*)-9,11-dodecadienyl acetate (**8a**) illustrates a typical sequence. Acylation of tricarbonyl(butadiene)iron (**1a**) with the acid chloride $\text{ClCO}[\text{CH}_2]_6\text{CO}_2\text{Et}$ (**2a**) and AlCl_3 gave the *syn*-keto-ester (**3a**) [(*E*)-isomer], together with the *anti*-isomer [(*Z*)-isomer] which was thermally isomerised to (**3a**) without previous isolation; the overall yield was *ca.* 70%. Mixed hydride reduction [$\text{LiAlH}_4(1) : \text{AlCl}_3(4)$] converted (**3a**) into (**4a**) (*ca.* 60% yield) which was acetylated ($\text{Ac}_2\text{O}-\text{NaOAc}$) to give (**7a**) and cleaved (*ca.* 80%) with trimethylamine *N*-oxide† in benzene⁷ to give (*E*)-(**8a**), shown to possess > 99% stereochemical purity by g.c. analysis on 4-(*p*-methoxycinnamyl)-4'-methoxyazoben-

† Although other reagents [*e.g.* Ce^{IV} , MnO_2 , BaMnO_4 , $(\text{C}_5\text{H}_5\text{N}^+\text{H})(\text{CrO}_3\text{Cl}^-)$] were examined we found that Me_3NO was the most satisfactory reagent for effecting this cleavage; the published conditions (ref. 7) are ideal for small scale reactions under aprotic conditions since the byproducts are gaseous (Me_3N , CO , CO_2) or easily removed by filtration.



	R	m	n	Moth species
a;	H	6	7	red bollworm moth
b;	MeCO	—	7	—
c;	Et	—	7	light-brown apple moth
d;	Me	5	6	pea moth; pitch pine tip moth; codling moth
e;	EtCO	—	—	—
f;	Pr ⁿ	7	8	spiny bollworm moth

zene, a nematic liquid crystal stationary phase.⁸ Intermediate (7a) was also utilised as a precursor for the synthesis of (8c), one of the pheromones of the light-brown apple moth (*Epiphyas postvittana*)⁹. Friedel-Crafts acetylation of (7a) gave, after thermal isomerisation, (7b) which was reduced to (4c), reacylated to (7c), and cleaved to give > 96.4% stereochemically pure (*E,E*)-9,11-tetradecadienyl acetate^{2c} (8c). A similar sequence of reactions starting with tricarbonyl(1,3-pentadiene)iron^{4b} (1d) allowed a high yield, stereospecific [$> 97\%$ (*E,E*)] synthesis *via* (3d), (4d), and (7d) of (*E,E*)-8,10-dodecadienyl acetate (8d),[†] the principal pheromone of both the pea moth (*Cydia nigricana*)¹⁰ and the pitch pine tip moth (*Rhyacionia rigidana*).¹¹

Trimethylamine *N*-oxide is not a specific reagent for the cleavage of $-\text{Fe}(\text{CO})_3$ groups but will also oxidise primary alcohols. Thus, cleavage of complex (4d) yielded not only (*E,E*)-8,10-dodecadienol (5d), the pheromone of the codling moth [*Laspeyresia (Carpocapsa) pomonella*],¹² but after prolonged reactions (> 1 h) increasing amounts of aldehyde (6d) and corresponding carboxylic acid. This observation was utilised in a synthesis of the aldehyde (6f), the pheromone of the spiny bollworm (*Earias insulana*).¹³ Complexed alcohol (4f) was obtained from (1a) *via* (1e), (1f), and (3f). Concomitant cleavage of the $\text{Fe}(\text{CO})_3$ and oxidation of (4f) was achieved with pyridinium chlorochromate but (6f) was contaminated with other ketonic material. This is in contrast with the clean oxidation¹³ of uncomplexed (5f) and suggests that the $\text{Fe}(\text{CO})_3$ protecting group may also influence chemistry at sites remote from those of co-ordination.

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[†] Before oxidative cleavage compounds (4d), (4f), (7a), (7c), (7d), and (7f) were shown (chromatography, ¹H n.m.r. spectroscopy) to be totally free of contamination by *anti*-isomers. The small amounts of (*Z*)-dienes present in cleaved ligands [(8c) and (8d)] are assumed to have arisen by isomerisation *after* cleavage; significant isomerisation is revealed by g.l.c. analysis of acetate (8f) [$> 87\%$ (*E,E*)].

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