Organocobalt Complexes. Part VIII.[1] Specificity of the Cyclopentenone Synthesis from Acetylenehexacarbonyldicobalt Complexes and Norbornene Derivatives

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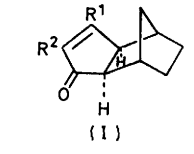
Numerous new examples of the annelation reactions leading to cyclopentenone derivatives are reported. They provide evidence of steric control resulting in preferred substitutions at positions 2 and 5 and placement of the larger substituent at position 2 if the acetylenic precursor is disubstituted. A pathway accounting for such preference is suggested and the bulky trimethylsilyl group is utilized as a removable direction-determining group to allow synthesis of the 3- instead of 2-substituted cyclopentenones. More remote substituents in the norbornene are shown to exert a significant but no longer decisive effect, so that mixtures of isomers result. A ^{1}H n.m.r. study has shown that the ferrocenyl substituent in 7a-ferrocenyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (IX) cannot rotate about the bond joining it to position 7a.

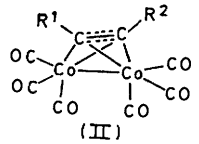
CYCLOPENTENONES having the 4,7-methanohexahydroindenone skeleton (I) have been shown [2] to be the principal organic products from reaction of norbornene with acetylenehexacarbonyldicobalt derivatives (II). The reaction involves annelation of the strained alkene and the acetylenic components with incorporation of a carbonyl group. It was demonstrated that the reaction is stereospecific, furnishing only the ketones with *exo*-configuration (with respect to the new ring junction). Specificity was also noted in the direction of addition of the acetylene component, the two monosubstituted acetylene complexes used [those of propyne (II; R^1 = H, R^2 = Me) and phenylacetylene (II; R^1 = H; R^2 = Ph)] giving exclusively the ketones substituted on C-2 (Ib and c). We have now employed complexes of the unsymmetrically disubstituted acetylenes (Id and e): these as well as (Ig and h) [3] give results which support the deduction that this specificity is sterically determined, the bulkier group becoming the substituent (R^2) at C-2. The trimethylsilyl group was cleaved from the ketone (Ie) by acidic hydrolysis to yield the ketone (If), isomeric with that [(Ib)] derived directly from methylacetylene. Thus either the 2- or the 3-substituted ketones become available from terminal acetylenes by use of a trialkylsilyl group as a masking group if the latter ketones are required.

The only unsymmetrical norbornene components employed in our earlier work [2] were the *exo*-forms of the ketones (IIIk), themselves derived from the condensation of the cobalt complexes (II) with norbornadienes. These reacted further to yield mixtures of the *exo,exo*-analogues of the diketones (IV) and (V) in which the former predominated. Thus even relatively remote substituents markedly influence the direction of reaction.



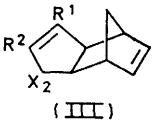
(I)

a; R^1 = R^2 = H
c; R^1 = H, R^2 = Ph
e; R^1 = Me, R^2 = $SiMe_3$
g; R^1 = Me, R^2 = $CH_2{\cdot}C{:}CMe$
i; R^1 = R^2 = Et



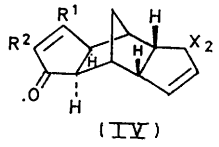
(II)

b; R^1 = H, R^2 = Me
d; R^1 = Me, R^2 = Ph
f; R^1 = Me, R^2 = H
h; R^1 = Me, R^2 = $CH_2{\cdot}CH{:}CHMe$
j; R^1 = R^2 = Ph

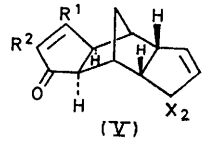


(III)

k; X_2 = O
l; X = H



(IV)



(V)

Less influence might be expected in the case of the corresponding hydrocarbon (IIIal) (cyclopentadiene

[1] Part VII, D. J. S. Guthrie, I. U. Khand, G. R. Knox, J. Kollmeier, P. L. Pauson, and W. E. Watts, *J. Organometallic Chem.*, 1975, **90**, 93.

[2] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, and M. I. Foreman, *J.C.S. Perkin I*, 1973, 977.

[3] F. M. Chaudhari, I. U. Khand, and P. L. Pauson, unpublished observations.

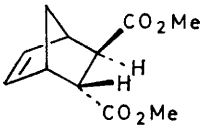
TABLE 1

Preparation of ketones [a]

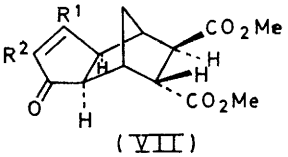
Ketone	Alkene (mmol)	Yield [mg (%)]	B.p. or m.p. (°C) [b]	Found (%) C	Found (%) H	Required (%) C	Required (%) H	Formula
(Id)	7	800 (65)	70—71 (MeOH)	85.9	7.0	85.7	7.6	$C_{17}H_{18}O$
(Ie)	7	430 (38)	100—110 (0.5 Torr)	71.5	9.1	71.7	9.5	$C_{14}H_{22}OSi$ [c]
(If)			90—100 (0.5 Torr)	81.4	8.55	81.45	8.7	$C_{11}H_{14}O$ [c]
(IIIek)	7	480 (42)	140—150 (0.5 Torr)					$C_{14}H_{20}OSi$ [c,d]
(IV/Val) [e]	2.1	200 (74 [f])	57—58	83.8	7.4	83.8	7.6	$C_{13}H_{14}O$ [c]
(IV/Vbl) [e]	2.1	220 (51 [f])	60—62 (C_5H_{12})	83.8	7.7	84.0	8.05	$C_{14}H_{16}O$ [c]
(IV/Vcl) [e]	5	780 (57)	128—130	87.2	7.2	87.1	6.9	$C_{19}H_{18}O$ [c]
(IV/Vdl) [e]	5	450 (32)	135—136	86.9	7.35	87.0	7.3	$C_{20}H_{20}O$ [c]
(IV/Vil) [e]	3.4	150 (18 [f])	155—160 (0.1 Torr)					$C_{17}H_{22}O$ [c]
(IV/Vjl) [e]	6.6	330 (23)		88.4	6.5	88.7	6.6	$C_{25}H_{22}O$ [c]
(IVak)	2	130 (33 [f])	129—130	78.1	6.25	78.0	6.0	$C_{13}H_{12}O_2$ [c]
(Vak)		70 (18 [f])	118—120	78.2	6.1			
(IVbk)	2	100 (24 [f])	171—172	78.4	6.8	78.5	6.6	$C_{14}H_{14}O_2$
(Vbk)		40 (10 [f])	137—139	78.2	6.7			
(IVck)	3.3	300 (32 [f])	212—214	82.1	6.1	82.5	5.8	$C_{19}H_{16}O_2$
(Vck)		80 (9 [f])	180—182	82.2	5.9			
(VII/VIIIal) [g]	1.4	90 (25 [f])	138—139	63.5	6.1	63.7	6.1	$C_{14}H_{16}O_5$ [c]
		43 (8 [f])	102—103	63.8	6.4			
(VII/VIIIbl) [g]	1.4	200 (53 [f])	129—130	64.6	6.5	64.7	6.5	$C_{15}H_{18}O_5$ [c]
		35 (9 [f])	102—103	64.7	6.6			
(VII/VIIIcl) [g]	2.4	375 (44 [f])	153—154	70.3	6.0	70.6	5.9	$C_{20}H_{20}O_5$ [c]
		115 (14 [f])	142—144	70.5	5.9			
(VII/VIIIdl) [g]	2.9	285 (28 [f])	141—142	71.1	6.0	71.2	6.2	$C_{21}H_{22}O_5$ [c]
		135 (14 [f])	149—150	70.9	6.3			
(IX)	1.5	85 (18 [f])	143—144	72.15	5.8	72.3	6.0	$C_{20}H_{20}FeO$
(Xa)	0.34	95 (65 [f])	191—192	74.3	6.7	74.2	6.5	$C_{23}H_{24}FeO$ [c]
(Xb)	0.5	75 (60 [f])	130—131	86.5	7.7	86.3	7.6	$C_{19}H_{20}O$ [c]

[a] The method followed is that described as ' method 1 ' in Part I;[5] benzene was used as solvent (at 60—70 °C) for the ketone (Id), toluene at 60—70 °C for the ketones (VII/VIII), and toluene at 70—80 °C in all other cases; see experimental section for the preparation of the ketone (If). [b] Bath temps. are given for b.p.s followed by the pressure; all other figures are m.p.s of solids recrystallised from benzene–pentane unless another solvent is specified. [c] Confirmed by accurate mass measurement of both the parent (M^+) and $(M + 1)^+$ ions in the mass spectrum. [d] Not obtained pure; the mass spectrum showed a $C_{14}H_{20}O_2Si$ impurity, possibly the 5,6-epoxide. [e] See text; the n.m.r. spectrum of the unsubstituted compound suggests that it is a single compound. The major component of the product may have been purified by crystallisation, but most of these ketones are believed to contain both isomers (IV) and (V). [f] Based on weight of alkene, which is limiting in these cases; in all other cases yields are based on the quantity of complex (II) used. [g] It is not known which isomer is which.

dimer), and although this yielded the crystalline products included in Table 1, these are possibly mixtures of



(VI)



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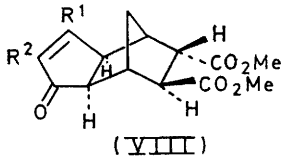

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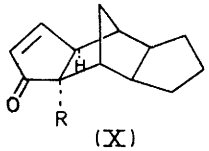
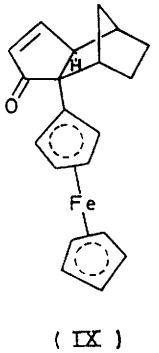


(X)

a; R = ferrocenyl
b; R = Ph



(IX)

the isomers (IVl) and (Vl). The *endo*-isomer of the ketone (IIIak) is also shown to give both types of product (IV) and (V) with only a slight preference for the former. We have also examined the reactions of dimethyl norborn-5-ene-*trans*-2,3-dicarboxylate (VI) with four of the acetylene complexes (II) and in each case separated the isomeric products (VII) and (VIII), but have not determined which is which.

Substitution on the reacting double bond of norbornene was tested by using three derivatives. In each case the cyclopentenone produced [(IX), (Xa), and (Xb)] had the carbonyl group adjacent to the substituent. Although we have no direct evidence concerning the steps involved, all the results can be consistently interpreted on the assumption that the acetylenic and olefinic components are joined at the less hindered position of each, and the carbonyl group is added in a subsequent step. The reaction of alkenes bearing electron-withdrawing groups with the acetylene complexes (II) which we have reported briefly [4] then differs from the reaction of other alkenes in the intervention of a hydrogen transfer in place of the carbonylation step.

The n.m.r. spectrum of ketone (IX) showed four

[4] I. U. Khand and P. L. Pauson, *J.C.S. Chem. Comm.*, 1974, 379.

broad singlets corresponding to the protons (2′, 3′, 4′, and 5′) of the substituted cyclopentadienyl ring. Although these protons are intrinsically different from each other, the clear differentiation of H-2′ from H-5′ and especially of H-3′ from H-4′ would not be expected unless there is severe restriction of rotation about the bond (1′,7a) linking the ferrocenyl group to the methanoindene. Heating did not appear to remove this restriction: the spectrum showed no appreciable change up to at least 100 °C, and at 140 °C there was general deterioration, apparently due to slow decomposition rather than greater rotational freedom. However successive additions of the europium shift reagent $Eu(fod)_3$ resulted in changes (Table 2) which clearly support a rigid structure. The signal due to one of the cyclopentadienyl protons, which we assume to be H-2′ suffers by far the greatest downfield shift, exceeding even that of H-7, and the others (H-3′, -4′, and -5′) shift no more than the unsubstituted cyclopentadienyl ring protons. This is clearly compatible only with a rigid structure in which H-2′ is much closer to the oxygen and hence also to the europium atom. The assignments of the remaining protons follow readily from those in related compounds studied previously.[2] Thus, for example, a very broad two-proton singlet initially at τ 7.82 rapidly separates on addition of the europium compound into a broad singlet which suffers the extensive shift expected for H-7 and a broad singlet shifting very slowly and assignable to H-4. For each of the signals there is a nearly linear correlation of position with amount of added europium compound.

TABLE 2

Effect of $Eu(fod)_3$ on ^1H n.m.r. spectrum of the ketone (IX)

Position of H	2	3	3a	4	7	2′	C_5H_5
Normal ^1H resonance (τ) [a]	3.60	2.48	7.30	7.81	7.82	5.55	6.03
Eu-shifted resonance (τ) [b]	2.14	1.81	6.15	7.33	5.85	2.80	5.45
Difference ($\Delta\tau$)	1.46	0.67	1.15	0.48	1.97	2.75	0.60

[a] Data relate to a solution of the ketone (77 mg) in $CDCl_3$. The protons at C-3′, -4′, and -5′ gave broad singlets at τ 5.85, 5 95, and 6.15; those at C-5, -6, and -8 gave multiplets centred at 8.35 (1H) and 8.8 (5H). [b] Successive portions of the reagent [Eu-($Me_3C{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}C_3F_7)_3$] were added; the first addition (6.5 mg) caused slightly greater shifts but thereafter peak positions varied linearly with weight of reagent. The values quoted are those obtained after addition of *ca.* 45 mg, the maximum quantity which still gave a well resolved spectrum.

EXPERIMENTAL

The reactions were carried out as described [5] in Part I, with the results listed in Table 1. Cyclopentadiene dimer (IIIal) employed for the preparation of the ketones (IV/V) was the crystalline *endo*-isomer filtered from commercial material. The *endo*-ketone (IIIak) was prepared from this by oxidation with chromic acid of the corresponding alcohol.[6] Samples of 2-ferrocenylbicyclo[2.2.1]hept-2-ene,[7] and of the 5-ferrocenyl- and 3a,4,7,7a-tetrahydro-5-phenyl-4,7-methanoindanes were kindly donated by Dr. W. E. Watts.

Hexacarbonyl-μ-(1-trimethylsilylpropyne)dicobalt (IIe) was obtained by the standard method and was independently reported during the course of our work.[8] The other complexes (II) were known compounds.[9]

Desilylation of the Ketone (Ie).—A solution of the ketone (*ca.* 500 mg) in concentrated sulphuric acid (*ca.* 1 ml) was kept at room temperature for 3 days, then heated to 70—80 °C for 30 min. It was then added to water (100 ml); the mixture was extracted with ether and the dried extract evaporated. The residue was chromatographed on neutral alumina, and 3a,4,5,6,7,7a-*hexahydro*-3-*methyl*-4,7-*methanoinden*-1-*one* (If) (*ca.* 145 mg, 42%) was eluted with benzene–chloroform (1 : 1).

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[8] R. S. Dickson and H. P. Kirsch, *Austral. J. Chem.*, 1972, **25**, 1815.

[9] R. S. Dickson and P. J. Fraser, *Adv. Organometallic Chem.*, 1974, **12**, 323.