

Organocobalt Complexes. Part II.¹ Reaction of Acetylenehexacarbonyldicobalt Complexes, $(R^1C_2R^2)Co_2(CO)_6$, with Norbornene and its Derivatives

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Tetra- and hexa-hydro-4,7-methanoinden-1-ones and the analogous indacenediones (VIII)—(X) are formed stoichiometrically by the title reaction or catalytically from acetylenes, norbornene derivatives, and carbon monoxide in the presence of octacarbonyldicobalt. The process leads stereoselectively to ketones of the *exo*-series and methyl or phenyl groups derived from the appropriate monosubstituted acetylenes are always found adjacent to the carbonyl group. The ¹H n.m.r. spectra of the products are discussed and the use of an europium shift reagent together with spin decoupling is shown to allow clear distinction of the isomeric methanoindacenediones (VIII) and (IX).

NORBORNENE and similarly reactive alkenes behave not unlike alkynes in some of their reactions with metal carbonyls,² and since alkynes are known to react further with their hexacarbonyldicobalt complexes (I), we

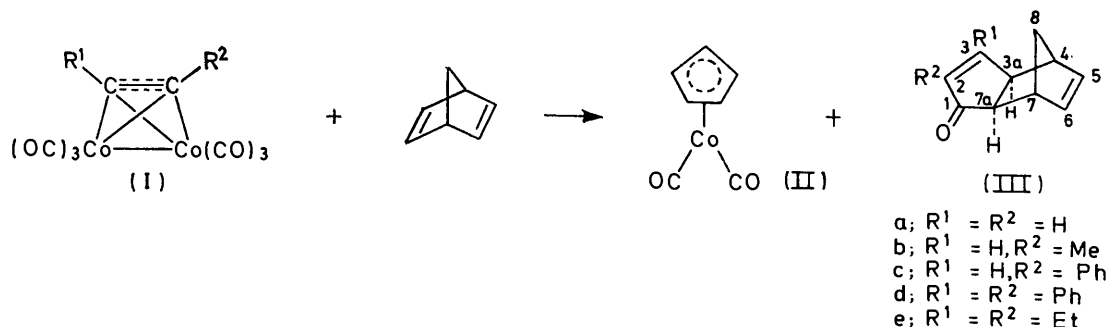
undertook a study of the behaviour of norbornadiene with the latter. When the reactions were conducted in aromatic solvents, a new class of arenecobalt complexes was formed.¹ But in dimethoxyethane as solvent, most

¹ Part I, I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, preceding paper.

² See *e.g.* C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 1963, 410.

of the cobalt was found as dicarbonylcyclopentadienylcobalt (II) as already reported.³ The cyclopentadienyl group in this product (II) must arise from reverse Diels-Alder type cleavage of the norbornadiene. Since simple thermal cleavage does not occur under the mild conditions of these reactions, it must either be strongly

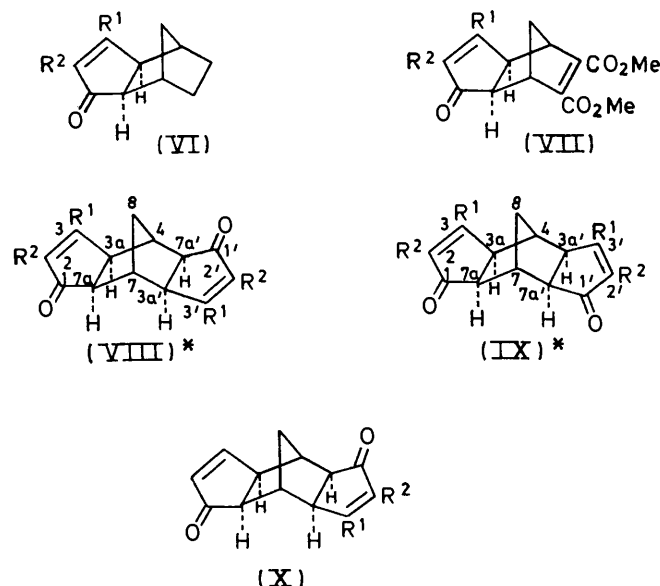
respectively. 2,3-Bismethoxycarbonylbicyclo[2.2.1]-hept-2-ene does not react. In each case one stereoisomer is formed exclusively, or at least predominantly (see later), and when the products are derived from unsymmetrical acetylenes (MeC≡CH or PhC≡CH) only a single position isomer is isolated. Since the hydrogen



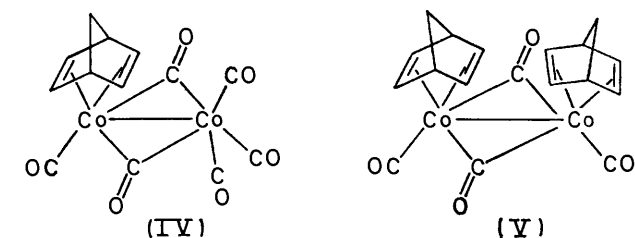
catalysed by one of the cobalt complexes or occur *via* an intermediate norbornadienecobalt complex. We have encountered the same cobalt-assisted cleavage in the reaction⁴ of norbornadiene with benzyldynonacarbonyltricobalt, PhCCo₃(CO)₉. The nature of this cleavage is being studied in more detail and will be discussed later.

In the reactions with acetylenehexacarbonyldicobalt complexes only part of the norbornadiene suffers this cleavage and, whether in arene or other solvents, a major portion of the diene is found in the form of ketonic products. This paper is chiefly concerned with the preparation and characterisation of these ketonic products, which are shown by analysis to contain the acetylene and one carbonyl group from the initial complex (I) as well as the diene. In some of the reactions the norbornadiene cobalt complexes (IV) and (V) are

atoms R¹ and R² in complex (IIIa) give the widely different proton resonance signals characteristic of αβ-unsaturated ketones, it is readily shown that the single substituent always occurs on the carbon atom adjacent to the carbonyl group.



* Numbered for easy comparison of n.m.r. spectra with those of monoketones.



formed as by-products by simple displacement of the acetylenic ligand (and CO). Authentic samples⁵ of these do not give significant yields of the ketones (III) when treated with acetylenes and they can therefore be discounted as likely intermediates.

The principal ketonic products are readily shown by their spectra to have the structure (III), and norbornene and 2,3-bismethoxycarbonylbicyclo[2.2.1]hepta-2,5-diene afford the analogous ketones (VI) and (VII),

The unsubstituted ketones (IIIa) and (VIa) from norbornadiene and norbornene were readily hydrogenated to the same saturated ketone and spectral correlations strongly support the deduction that all the ketones belong to the same stereochemical series. Both *endo*- and *exo*-forms of (IIIa) and (VIa) are known, and although the published properties⁶ of the *exo*-forms do

³ I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, *Chem. Comm.*, 1971, 36.

⁴ I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, unpublished results.

⁵ G. Winkhaus and G. Wilkinson, *J. Chem. Soc.*, 1961, 602.

⁶ P. D. Bartlett and A. Schneider, *J. Amer. Chem. Soc.*, 1946, **68**, 6; *cf.* R. R. Sauers and A. Shurpik, *J. Org. Chem.*, 1967, **32**, 3120.

not permit ready comparison, our predominant product (IIIa) was identical with a sample supplied by Professor R. C. Cookson and Dr. J. Hudec⁷ and clearly different from an authentic sample⁸ of the readily available *endo*-isomer. However the latter isomer was present in the sample and n.m.r. spectra of the ketones from different runs revealed wide variations in the proportions. While this may have been partly due to fortuitous separation (the *exo*-ketone is slightly less strongly adsorbed on alumina), further experiments showed that it is largely the result of isomerisation. When a sample of the ketone mixture was heated with octacarbonyldicobalt the proportion of *endo*-isomer increased markedly. Moreover when the samples of the mixture from the condensation reaction were withdrawn at intervals and examined by g.l.c. it was found that the *endo*-isomer was barely detectable after 1 h but increased steadily with increasing reaction time. Thus

corresponds with the behaviour of norbornadiene in related condensation reactions.⁷ Both the stereochemistry of the product and the ability of norbornene to undergo the reaction suggest that a single double bond of the alkene or diene becomes co-ordinated to cobalt during the condensation.

The ketones (III) or (VI) can be produced by this route from the acetylene, norbornadiene or norbornene, and carbon monoxide, in an inert hydrocarbon solvent with only a catalytic amount of carbonylcobalt. In addition to the monoketone, substantial amounts of the corresponding diketones (VIIIa) and (VIIIc) were formed under these conditions. The isomeric diketones (IX) were formed in small yield. In the 'stoichiometric' reactions the diketones (VIII) and (IX) have also been isolated, especially by use of more vigorous reaction conditions. As the ketones (III) retain a norbornene system, their further reaction with complex

TABLE 1
N.m.r. spectra of ketones (τ values; CDCl₃ solutions)

Compound	3-H	8-H	R ²	5- and 6-H	3a-, 4-, 7-, and 7a-H
(IIIa)	2.56 (dd)	8.78 (m)	3.88	3.88 (m)	7.22 (2H, m), 7.40br (s), 7.88 (d)
(IIIb)	2.81br (s)	8.74 (q)	8.24 (t)	3.78 (m)	7.13br (s), 7.35br (2H, s), 7.75br (d)
(IIIc)	ca. 2.25 (? ^a)	8.62 (m)	2.25, 2.55 (m),	3.66 (m)	6.98br (s), 7.21 (2H, m), 7.53 (d)
(IIId)		8.53 (s)	2.64 (m)	3.62br (s)	6.64 (d), 6.85br (s), 7.36 (2H, m)
(VIa)	2.48 (dd)	9.00 (m)	3.74 (dd)	8.28—8.77 (m)	7.31 (m), 7.62br (s), 7.84 (2H, m)
(VIb)	2.89br (s)	9.05 (s)	8.24 (t)	8.23—8.80 (m)	7.47br (s), 7.63br (s), 7.87br (2H, d)
(VIc)	2.42 (d) ^b	8.98 (m)	2.33, 2.67 (m)	8.28—8.78 (m)	7.37 (m), 7.53br (s), 7.68 (d), 7.77br (s)
(VIId)		8.90 (q)	2.74 (m)	8.28—8.70 (m)	6.82 (d), 7.46 (2H, m), 7.90br (s)
(VIIa)	2.38 (dd)	8.44	3.79 (m)	(6.22) ^e	6.30 (m), 6.75 (2H, m), 7.32 (m)
(VIIb)	2.79	8.35 (dm), 8.69 (m)	8.21 (t)	(6.21) ^e	6.71br (s), 6.95 (m), 7.43br (d), 7.8 (m)
(VIIc)	ca. 2.33 (? ^a)	8.40 (m)	2.33, 2.66 (m)	(6.20) ^e	6.58br (s), 6.82 (2H, m), 7.23br (d)
(VIIId)		8.35 (m)	2.69 (m)	(6.18) ^e	6.33 (d, <i>J</i> 6 Hz), 6.47br (s), 6.91br (s), 7.10br (d)
(VIIIa) ^d	2.48 (dd)	9.08 (s)	3.72 (dd)		7.12 (2H, m, H-3a,3a'), 7.65 (4H, m)
(VIIIc) ^d	ca. 2.31 (? ^a)	9.02br (s)	2.31, 2.65br		7.0—7.5br (m)
<i>endo</i> -(IIIa)	2.62 (dd)	8.33 (q)	4.23 (dd)	4.06br (d)	6.60 (m), 6.81br (s), 7.05 (m), 7.23 (t)

^a Under Ph signal. ^b Identified by separation from the phenyl-protons using the Eu(fod)₃ shift reagent which shifts the τ 2.33 multiplet (2H) of the phenyl group more, but the τ 2.67 (m) (3H) less than this doublet. ^c CO₂Me at C-5 and C-6. ^d Numbered as for equivalent monoketones (VI); for (VIIIb) and (IXb) see Table 2.

the *endo*-isomer apparently arises by catalysed isomerisation of the *exo*-isomer formed in the initial reaction. This isomerisation is irreversible: a sample of pure *endo*-ketone heated in the presence of octacarbonyl dicobalt for 18 h showed no trace of *exo*-isomer on g.l.c. examination. It is also highly solvent-dependent: condensations carried out in toluene and dimethoxyethane gave a much greater proportion of *endo*-isomer in the latter case.

The isomerisation, unlike the condensation reaction, must require the second double bond since no *endo*-isomer of ketone (VIa) was found. Moreover it is strongly hindered by substitution: we did not detect peaks attributable to *endo*-isomers in the ketones from substituted acetylenes; moreover the methyl derivative (IIIb) gave a single peak on g.l.c. even after a sample had been heated with octacarbonyldicobalt in refluxing dimethoxyethane, and apparently isomerised very slowly, if at all, under these conditions. The almost exclusive formation of *exo*-ketones in the present system

(I) is to be expected. This stepwise formation of the diketones has been verified by showing that the monoketone (IIIa) reacts with the substituted acetylene complexes (Ib and c) to give chiefly the diketones (Xb and c).

The 'catalytic' version of the reaction is the best route available for the preparation of such tricyclic ketones. The literature methods involve several steps and are less flexible.

Proton Resonance Spectra.—The ¹H n.m.r. spectra were invaluable in assigning structures to the ketones and are summarised in Table 1. Several features deserve comment. Particularly detailed study was necessary to distinguish with certainty between the isomeric diketone series (VIII) and (IX) and this was undertaken for the methyl compounds (VIIIb) and (IXb). Although compounds (IX) have a mirror-plane of symmetry whereas compounds (VIII) only possess a twofold axis, the latter are 'more symmetrical' in an n.m.r. sense, as the two bridgehead protons (H-4 and H-7) are equivalent; in (IX) they are different. All other protons occur in equivalent pairs. Although a corresponding difference in the complexity of the spectra was readily apparent,

⁷ R. C. Cookson, J. Henstock, and J. Hudec, *J. Amer. Chem. Soc.*, 1966, **88**, 1059.

⁸ M. Rosenblum, *J. Amer. Chem. Soc.*, 1957, **79**, 3179.

TABLE 2
Assignment of chemical shift parameters

Position of H	Compound (VIII)			Compound (IX)		
	τ (CDCl ₃)	Shifted τ value ^a	Δ ^b	τ (CS ₂) ^c	Shifted τ value ^a	Δ ^b
3, 3'	2.88 ^d	1.86	1.02	2.99	1.72	1.27
3a, 3a'	7.27 ^e	5.42	1.85	7.25	5.66	1.59
7a, 7a'	7.64	4.05br(d)	3.59	7.83	4.64	3.19
7	7.64	4.67br(s)	2.97	7.54	3.69	3.85
4				7.92	6.54	1.38
(CH ₃)	8.22(t)	6.25	1.97	8.28(t)	6.35	1.93
8	9.19br(s)	6.54	2.65	9.25br(s)	7.04	2.21

^a On addition of an arbitrary quantity of Eu(fod)₃. Intermediate spectra with smaller quantities of this reagent were taken to follow the gradual peak movement; spectra run at 60 MHz. ^b Difference between previous columns, *i.e.* the largest observed shift. ^c Spectra were also run in CDCl₃ at 100 MHz; peak positions are almost identical. ^d Four lines collapsing to two on irradiation at the frequency of the methyl resonance. ^e Broad and very complex multiplet; better resolved on irradiation at the frequency of the methyl resonance.

possible accidental coincidences made a firm assignment appear risky without further study. However, use of a lanthanide shift reagent [tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium(III)]⁹ [Eu(fod)₃] not only removed such coincidences, but made

auxiliary tool and was found to be readily applicable to the europium-shifted as well as the original spectra. The shift parameters observed and the assignments based on these are given in Table 2.

Although the hydrogen atom at C-7a is α to a carbonyl group, it is rigidly held at a large angle to that group, which has a comparable effect on the β -proton at C-7. In all the methyl-substituted compounds the methyl signal is finely split into a 'triplet.' Decoupling has confirmed that in addition to the expected allylic splitting by the proton at C-3, there is homoallylic splitting of comparable magnitude by that at C-3a, an effect previously noted in a methylcyclopentenone system.¹⁰

EXPERIMENTAL

Preparation of Ketones.—The reaction procedure was that described in Part I¹ (Method 1). The use of arene solvents gave the best yields although iso-octane could be substituted with little change; in this case most of the metal was recovered as dodecacarbonyltetracobalt. All the cobalt compounds were less strongly adsorbed on neutral alumina than the ketones and could be removed by elution with

TABLE 3
Properties of products

Ketone	Yield in g ^a (%)	B.p. or m.p. (with recryst. solvent)	ν_{CO} /cm ⁻¹	Found (%)		Required (%)		Formula
				C	H	C	H	
(IIIa)	(T) 0.45 (43)	100—101° at 15 mmHg	1700 (f)	82.0	7.1	82.25	6.85	C ₁₆ H ₁₆ O
(IIIb)	(T) 0.34 (33)	80—85° at 0.5 mmHg ^c	1700 (f)	82.7	7.4	82.5	7.5	C ₁₁ H ₁₂ O
(IIIc)	(B) 0.50 (45)	70—71° (C ₅ H ₁₂)	1688 (n)	86.6	6.6	86.5	6.3	C ₁₆ H ₁₄ O ^d
(IIId)	(B) 0.38 (28)	117—118° (C ₅ H ₁₂)	1690 (k)	88.55	6.1	88.5	6.05	C ₂₂ H ₁₈ O ^d
	(T at 100°) 0.315							
(IIIe)	(T) 0.25 (23)	100—105° at 0.1 mmHg ^c	1695 (f)	82.9	8.7	83.1	8.9	C ₁₄ H ₁₈ O
(VIa)	(T) 0.5 (52)	101—102° at 15 mm	1695 (f)	81.0	8.3	81.1	8.1	C ₁₆ H ₁₄ O
	(B) (55)	32° (C ₅ H ₁₂)						
(VIb)	(T) 0.38 (33)	110—115° at 0.5 mmHg ^c	1700 (f)	81.4	8.4	81.55	8.7	C ₁₁ H ₁₄ O ^d
(VIc)	(M) 0.64 (59)	93—95° (C ₅ H ₁₂)	1695 (n)	85.5	7.2	85.6	7.1	C ₁₆ H ₁₆ O
(VIId)	(T) 0.47 (35)	130—131° (C ₅ H ₁₂)	1695 (n)	87.8	6.7	87.9	6.7	C ₂₂ H ₂₀ O ^d
(VIe)	(T) 0.25 (23)	110—115° at 0.1 mmHg ^c	1690 (f)	82.0	9.6	82.3	9.8	C ₁₄ H ₂₀ O ^d
(VIIa)	(T) 0.39 (23)	145—150° at 0.5 mmHg ^c	1715br (f)	63.8	5.3	64.0	5.35	C ₁₄ H ₁₄ O ₅
(VIIb)	(T) 0.33 (38)	175—180° at 0.1 mmHg ^c	1695 1700 (f) 1730	64.9 6.0 6.0		65.2	5.8	C ₁₅ H ₁₆ O ₅
(VIIc)	(T) 0.62 (31)	113—114° (CHCl ₃ -C ₅ H ₁₂)	1695 1720 (n) 1735	70.8 5.6		70.8	5.6	C ₂₀ H ₁₈ O ₅
(VIId)	(T) 0.52 (28)	188—189° (C ₅ H ₈ -C ₅ H ₁₂)	1690 1715 (n) 1735	75.75 5.4		75.4	5.3	C ₂₆ H ₂₂ O ₅
(VIIIa)	(T) 0.175 ^e (29)	138—139° (C ₅ H ₁₂)	1690 (n)	77.9	6.1	78.0	6.0	C ₁₃ H ₁₂ O ₂ ^d
(IXa)	(T) 0.025 (4)	185—188° (decomp.) (C ₅ H ₈ -C ₅ H ₁₂)	77.75	6.15		78.0	6.0	C ₁₃ H ₁₂ O ₂ ^d
(VIIIb)	(T) 0.135 (17)	171—172° (C ₅ H ₁₂ -C ₅ H ₈)	1690 (n)	79.0	7.2	78.9	7.1	C ₁₅ H ₁₆ O ₂ ^d
(IXb)	(T) 0.035 (4.4)	218—220° (C ₅ H ₈ -C ₅ H ₁₂)	1693 (n)	79.1	7.1	78.9	7.1	C ₁₆ H ₁₆ O ₂ ^d
(VIIIc)	(T) 0.172 (13) ^f	250—251° (CHCl ₃ -C ₅ H ₈)	1690 (n)	84.9	5.6	85.3	5.7	C ₂₅ H ₂₀ O ₂ ^d
(Xb)	(T) 0.30 (21) ^g	145—147° (C ₅ H ₈ -C ₅ H ₁₂)	1690 (n)	78.1	6.3	78.5	6.5	C ₁₄ H ₁₄ O ₂ ^d
(Xc)	(T) 0.43 (23) ^g	202—203° (C ₅ H ₈ -C ₅ H ₁₂)	1690 (n)	82.1	6.1	82.5	5.8	C ₁₉ H ₁₆ O ₂ ^d

^a By Method 1 (Part I¹) from 2 g of complex (I) with benzene (B), toluene (T), or mesitylene (M). ^b (f) = film; (n) = Nujol; (k) = KCl. ^c Bath temp. ^d Confirmed by accurate mass measurements of both the parent (*M*⁺) and *M*⁺ + 1 ions in the mass spectrum. ^e Reaction time 10 h. ^f Reaction for 7—8 h at 80—90°. ^g Ketone (IIIa) (1.0 g) treated with excess of complex (I) (3 g) in toluene at *ca.* 90° for *ca.* 8 h; yields are based on the ketone.

a rigorous assignment possible by observation of the variation in downfield shift experienced by protons according to their distances from the polar carbonyl function. Decoupling of selected peaks was used as an

benzene. The ketones were then eluted with benzene-chloroform or pure chloroform and the diketones (VIII) and (IX) [or (X)] followed the monoketones in that order. They were further purified by recrystallisation or distillation as

⁹ R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

¹⁰ P. Bladon, S. McVey, and P. L. Pauson, *J. Chem. Soc. (C)*, 1966, 306.

appropriate. Details are given in Table 3, which also lists the physical properties and analytical data.

Ketone (VIa) gradually dimerises at room temperature in liquid form or dissolved in inert solvents. The *dimer*, m.p. 51° (from light petroleum), was characterised by its mass spectrum (Found: M , 296·1785. $C_{20}H_{24}O_2$ requires M , 296·1776), which showed ready breakdown back to $C_{10}H_{12}O$, the base peak (Found: m/e 148·0891. Calculated: 148·0888).

A sample of ketone (IIIb) which had been stored in air had been apparently largely epoxidised when its mass spectrum was obtained (Found: m/e 176·0830. Calc. for $C_{11}H_{12}O_2$: 176·0837).

Reaction of Complex (Ia) with Norbornadiene in Dimethoxyethane.—The complex (2 g, 6 mmol) and norbornadiene (0·8 g, 8 mmol) in 1,2-dimethoxyethane (100 ml) were heated at 60–70° for 4 h under nitrogen. The solvent was removed under reduced pressure and the residue chromatographed on neutral alumina. Light petroleum (b.p. 40–60°) eluted a viscous oily hydrocarbon (45 mg), presumably a dimer or dimers of norbornadiene (a similar sample from reaction in iso-octane was identified as $C_{14}H_{16}$ by mass spectrometry). Light petroleum–benzene then eluted dicarbonylcyclopentadienylcobalt (0·355 g), identified by its i.r. spectrum and showing only the expected single peak (τ 5·0) in its n.m.r. spectrum. Chloroform then eluted the ketone (IIIa) (75 mg), identical with the sample described in Table 3.

Formation of endo-3a,4,7,7a-Tetrahydro-4,7-methanoinden-1-one (IIIa).—The presence of this isomer was first noted from the n.m.r. spectrum, where the peaks of the 4-H and 8-H of the *endo*-isomer are clearly separated from those of the *exo*-ketone. These peaks were particularly large in spectra of samples from the catalytic reactions (see later), when slow gas absorption necessitated a long reaction time. Preparations from complex (Ia) (2 g) and norbornadiene (0·6 g) were therefore repeated and the reaction monitored by withdrawing samples at intervals for g.l.c. examination. This was carried out on a Perkin-Elmer F11 instrument with a 2 m glass column packed with phenyl methyl silicone (2·5%) on Chromosorb G, on which the *exo*- and *endo*-isomers had retention times of *ca.* 28 and *ca.* 33 min, respectively, at 80°. A reaction in toluene (100 ml) gave *exo*-ketone, accompanied after 1 h by a barely detectable quantity of *endo*-isomer the ratio of which had increased after 8 h reaction time to 1 : 6. In dimethoxyethane as solvent the ratio was already *ca.* 1 : 3 after 1 h and reached *ca.* 1 : 1 after 8 h. That gradual isomerisation occurs in the presence of carbonylcobalt derivatives was confirmed when a sample (0·5 g) initially containing *ca.* 4 : 1 *exo* : *endo* was heated with octacarbonyldicobalt (0·3 g) in mesitylene (15 ml) at 65–70°. After 8 h the ratio had changed to 5 : 2. Similar heating of pure *endo*-ketone for 18 h produced no detectable quantity of *exo*-isomer.

The 4 : 1 mixture was also used to show that separation is possible by column chromatography, with 2% chloroform–benzene as eluant.

Catalytic Preparations of the Ketones.—(a) *exo*-3a,4,5,6,7,7a-Hexahydro-4,7-methanoinden-1-one (VIa) A solution of octacarbonyldicobalt (1 g, 3 mmol) and norbornene (3 g, 32 mmol) in iso-octane (100 ml) was stirred first under acetylene, and then under 1 : 1 acetylene–carbon monoxide at 60–70° until gas absorption ceased (total *ca.* 1550 ml). The mixture was then concentrated and the residue chromatographed on neutral alumina. Light

petroleum (b.p. 40–60°)–benzene (1 : 1) eluted acetylene-hexacarbonyldicobalt (*ca.* 70 mg). Benzene–chloroform (1 : 1) then eluted a yellow oil which was distilled at 101–102° and 15 mmHg to give the ketone (VIa) (3·54 g, 74%), identical with the sample described in Table 3. It solidified on prolonged storage in a refrigerator.

A run with a lower proportion of catalyst [0·52 g $Co_2(CO)_8$ for 6·05 g C_7H_{10}] gave a lower yield (5·8 g, 61·5%).

(b) 3a,4,7,7a-Tetrahydro-4,7-methanoinden-1-one (IIIa). Acetylene and carbon monoxide were simultaneously passed for 7–8 h through a mixture of octacarbonyldicobalt (*ca.* 1 g, 3 mmol) and norbornadiene (12 g) in iso-octane (150 ml), maintained at 60–70°. Work-up as in (a) yielded acetylenehexacarbonyldicobalt (25 mg) and the ketone (IIIa) (2·65 g, 14%), identical with the product described in Table 3. Further elution of the chromatogram with chloroform–benzene (2 : 1) yielded impure solid products which were not fully investigated, and finally chloroform eluted the diketone (VIIIa) (15 mg).

An experiment carried out by the procedure in (a) showed that much longer reaction time is required for complete gas absorption but gave [from 0·96 g $Co_2(CO)_8$ and 7 g C_7H_{10}] a much better yield of ketone (IIIa) (4·33 g, 47%), b.p. 100–101° at 15 mmHg.

(c) 2-Phenyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (IIIc). A mixture of octacarbonyldicobalt (0·8 g, 2·3 mmol), phenylacetylene (5 g, 50 mmol), norbornadiene (3 g, 32·5 mmol), and iso-octane (15 ml) was heated in an autoclave under 50 atm of carbon monoxide for 5 h at 70°. Chromatography of the product yielded successively the ketone (IIIc) (1·9 g, 8·6 mmol) and the diketones (VIIIc) (1·2 g, 3·4 mmol) and (IXc) (70 mg). The first two products were identical with the samples described in Table 3; the last has not been fully purified or characterised.

Hydrogenation and Characterisation of the Ketones (IIIa) and (VIa).—Both these ketones were reduced in ethanol over 10% palladium–charcoal. The products were oils having identical i.r. [ν_{CO} (film) 1730 cm^{-1}] and n.m.r. spectra, and both samples were converted into the 2,4-dinitrophenylhydrazone of 4,7-methanoperhydroinden-1-one, orange crystals, m.p. 234–236° (from ethanol) (Found: C, 58·25, 58·3; H, 5·4, 5·4; N, 16·7, 17·0. $C_{16}H_{18}N_4O_4$ requires C, 58·2; H, 5·4; N, 17·0%). The two samples of this derivative had identical i.r. spectra and identical m.p. (separately or mixed). The hydrogenation of the ketone (IIIa) proceeded without obvious interruption corresponding to the formation of the presumed intermediate (VIa). These two ketones were further characterised by formation of the 2,4-dinitrophenylhydrazone of ketone (IIIa), deep orange crystals, m.p. 228–230° (from benzene–ethanol) (Found: C, 58·95; H, 4·5; N, 16·9. $C_{16}H_{14}N_4O_4$ requires C, 58·9; H, 4·3; N, 17·2%); and the 2,4-dinitrophenylhydrazone of ketone (VIa), deep orange crystals, m.p. 239–241° (from benzene–ethanol) (Found: C, 58·6; H, 5·3; N, 16·9. $C_{16}H_{16}N_4O_4$ requires C, 58·5; H, 4·9; N, 17·1%).

The 2,4-dinitrophenylhydrazone prepared from a sample of the ketone (IIIa) supplied by Professor R. C. Cookson and Dr. J. Hudec was identical (m.p., mixed m.p., and i.r. spectrum) with the aforementioned sample.

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