Nickel-catalysed Stereospecific Cyclocarbonylation of Cyclopentadiene Dimer. Crystal and Molecular Structure of 2-(Tetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-9-en-4-yl)propionic Acid

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The reaction of *endo*-cyclopentadiene dimer with but-2-enyl chloride, carbon monoxide, and tetracarbonylnickel in acetone–water at room temperature gives a tetracyclic acid and co-oligomers. *X*-ray structural determination of the acid shows a selective *cis-exo* attack at the strained double bond. Some aspects of the mechanism are discussed.

It has been recently reported that cycloalkanone structures can be easily synthesised by insertion and carbonylation of strained double bonds or of 1,5-double bonds into allylnickel bonds.[1,2]

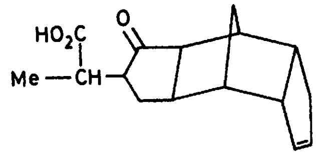
We deemed it useful to test the behaviour of *endo*-cyclopentadiene dimer, which has two potential chelating double bonds, one of which is a strained double bond. The latter has long been known to undergo attack by acids leading to a Wagner–Meerwein rearrangement and eventually to derivatives of the *exo*-form of cyclopentadiene dimer.[3] In the present case formation of a cycloalkanone ring should not imply rearrangement if the attacking allyl group has nucleophilic character. The reaction was also expected to be stereoselective.[1,2] Norbornene has been previously reported to undergo a *cis,exo*-attack by allyl group and carbon monoxide on a nickel complex to give an allylnorbornanylcarboxylic acid.[4] In the present case, however, the influence of another double bond on the direction of attack could not be predicted.

RESULTS AND DISCUSSION

Under our standard conditions[1,2] (acetone–water solution containing KPF_6, room temperature, atmospheric pressure) *endo*-cyclopentadiene dimer reacted with but-2-enyl chloride, carbon monoxide, and tetracarbonylnickel to give a white solid (I) in 10% yield. Only minor amounts of probable isomers could be detected by g.l.c. The bulk of the product was crystalline and melted between 140 and 143 °C. ^{1}H N.m.r. spectroscopy of the methyl ester revealed absorptions due to the protons of the cyclopentene double bond in the region τ 4.1—4.6. ^{13}C N.m.r. spectroscopy revealed three signals due to the double bond carbons (131.0, 131.7, and 132.0 p.p.m. from tetramethylsilane), and two signals due to the carbonyl carbon (224.4 and 223.7 p.p.m.), suggesting the presence of the positional isomer of (I) with the double bond on the adjacent carbon atom.

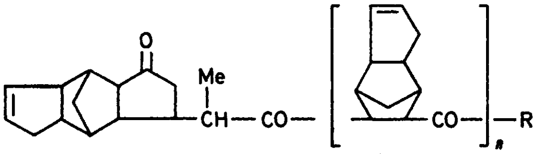
Crystals (m.p. 142—143 °C) suitable for *X*-ray analysis were obtained by dissolving the solid in light petroleum and cooling.

The remaining product was a neutral polymeric material, probably derived from attack of another



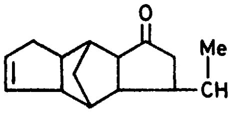
(I)

cyclopentadiene dimer molecule at the acylnickel derivative of (I), followed by alternate co-oligomerisation with carbon monoxide. A tentative formula is (III):



(III)

where R can be:



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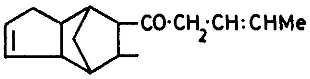

and the cyclopentene double bond can also occupy the adjacent position.

A fraction was obtained, m.p. not <340 °C, whose average molecular weight determined by osmometry was 935. Elemental analysis is roughly in accord with structure (III) for $n = 4$. Mass fragmentation gives the highest peak at m/e 883. If mass of group R is added, M becomes 1 098.

The i.r. spectrum of the solid polymer shows absorptions both at 1 740 and 1 710 cm^{-1}. ^{13}C N.m.r. gives a broad signal of the double-bond carbon atoms (centred at 130.2 p.p.m.) in the same area as the acid absorptions.

Under the same conditions as those for the *endo* isomer, *exo*-cyclopentadiene dimer,[5,6] containing *ca.* 15% of the *endo*-form, mainly gave a polymeric material and a 10% yield of an acid oil, from which a small amount of solid (m.p. 150—155 °C) separated. It had the same mass as

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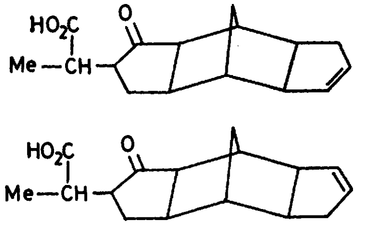
compound (I) but showed depression at the mixed m.p. Its structure could not be determined but analogy with formation of (I) suggests structures (II). G.l.c. of the acid portion gave two poorly resolved peaks of (I) and (II). In addition to the peaks observed for compound (I), ^{13}C n.m.r. spectroscopy revealed two other peaks due to carbonyl carbons at 221.8 and 222.0 p.p.m. and four other peaks due to double-bond carbons at 131.5, 131.9, 132.5, and 133.0 p.p.m.



(II)

The solid polymeric material showed many poorly resolved absorptions due to double-bond carbons in the same area as those for the acid absorptions (128.4—133.6 p.p.m.). When compared with the spectrum of the polymer obtained from *endo*-cyclopentadiene dimer, this region, as well as the entire spectrum (whose frequencies are difficult to attribute), appears to be quite different, thus showing that distinct polymers arise from *endo*- and *exo*-isomers.

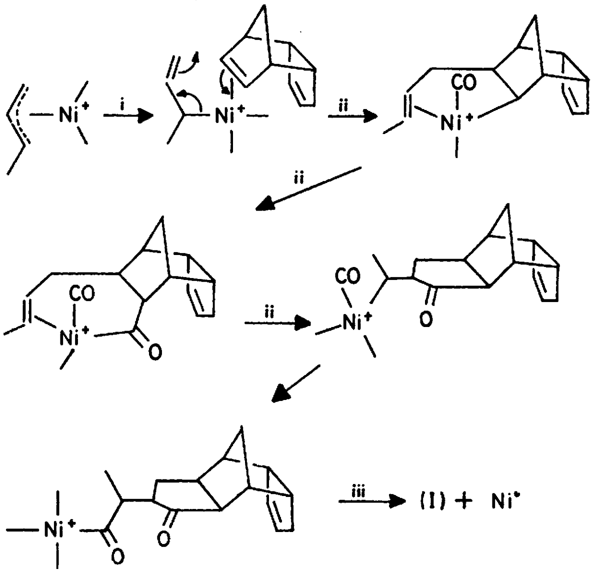
Since most of the acid obtained from *endo*-cyclopentadiene dimer corresponds to structure (I) it can be concluded that the reaction is: (i) selective, only the strained double bond being attacked; (ii) stereoselective, the cyclopentanone ring resulting from a *cis,exo*-attack at the strained double bond; and (iii) stereospecific, the *endo*-configuration giving a product different from the one obtained from the *exo*-configuration. Furthermore, the distances C(10)–C(11) 1.376(9) and C(11)–C(12) 1.439(8) Å indicate preferential localisation of the double bond at the C(10)–C(11) position. A final difference–Fourier map showed no particular features in the region near these atoms and the peaks considered as being due to the hydrogen atoms H(10)—(13) were rather smeared, certainly more so than those corresponding to other hydrogen atom positions. Moreover the thermal parameters of C(10)—(12) are significantly higher than those of the nearest atoms. All these facts seem to be in agreement with a disordered crystal structure with a double bond at C(10)–C(11) in a majority and at C(11)–C(12) in a minority of the molecules, suggesting a partial regioselective attack of the but-2-enyl group and carbon monoxide at the strained double bond.

We suggest that the formation of compound (I) takes place by *exo*-attack at the strained double bond by the vinylic end of the co-ordinated but-2-enyl group in its σ-form (a cationic nickel complex is assumed). In order to form a *cis,exo*-adduct, co-ordination of the sole strained double-bond is required. The observed regiospecificity, however, should be ascribed to a preferred orientation of dicyclopentadiene within the complex. After insertion of carbon monoxide, cyclisation and further carbonylation follow, according to previously described patterns.[7] The Scheme shows a simplified version of the reaction (ligands not reacting with the substrate are omitted).*

Molecular Geometry.—Bond distances and angles are reported in Table 1 and the arbitrary numbering scheme, used in the crystal analysis is shown in the Figure.

Bond lengths in the tetracyclic system are as expected from the hybridisation of the atoms involved, while bond angles suggest that the molecule is somewhat strained, particularly in the norbornane portion. These distortions are similar to those observed in the related compounds of ref. 8.

The folding of the *endo*-cyclopentene ring A with respect to the norbornane part (C) is significantly different from that of the *exo*-cyclopentanone ring E (angles between A–C 123.2, B–E 115.5°), as expected considering the repulsion of the bridgehead C(13) atom. Also the dihedral angles (C–B 113.6, C–D 121.4, and D–B 124.9) are certainly influenced by the *endo*- and *exo*-positions of the fused five-membered rings, so that D–B is larger than D–C. Ring A is planar, while severe distorsions from planarity are observed in ring E.



SCHEME Reagents: i, cyclopentadiene dimer; ii, CO; iii, H$_2$O

The orientation of the 1-carboxyethyl group with respect to ring E is such that the plane C(14), C(15), C(16) is almost parallel (165.5°) and the carboxy-group practically perpendicular (87.0°) to the ring.

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* *Note added in proof:* An insertion reaction of cyclopentadiene dimer and of carbon monoxide into an acylmanganese bond has been described recently (B. B. Booth, M. Gardner, and R. N. Haszeldine, *J.C.S. Dalton*, 1975, 1856, 1863).

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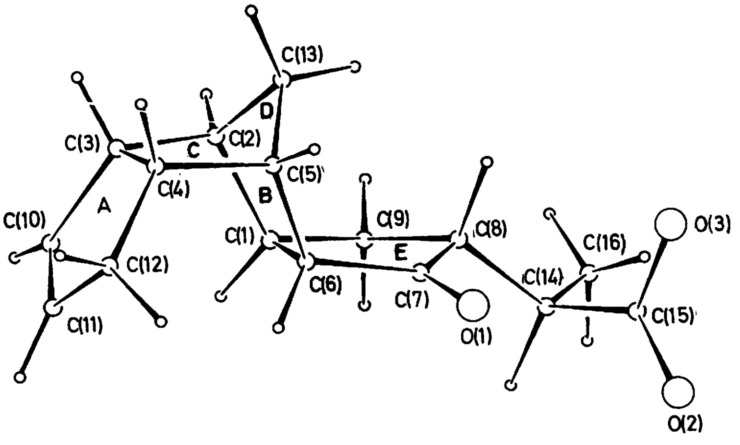
The molecules are joined in centrosymmetric dimers by hydrogen bonds O(2) · · · O(3^I) 2.67 Å (I is at 1 − x, 2 − y, 1 − z). All contacts are in agreement with values for van der Waals radii.

TABLE 1

(*a*) Intramolecular distances (Å)			
O(1)–C(7)	1.206(5)	C(4)–C(12)	1.536(6)
O(2)–C(15)	1.243(4)	C(5)–C(6)	1.554(4)
O(3)–C(15)	1.295(4)	C(5)–C(13)	1.532(6)
C(1)–C(2)	1.543(5)	C(6)–C(7)	1.508(5)
C(1)–C(6)	1.556(6)	C(7)–C(8)	1.525(6)
C(1)–C(9)	1.549(4)	C(8)–C(9)	1.536(6)
C(2)–C(3)	1.557(5)	C(8)–C(14)	1.535(4)
C(2)–C(13)	1.548(6)	C(10)–C(11)	1.376(9)
C(3)–C(4)	1.569(8)	C(11)–C(12)	1.439(8)
C(3)–C(10)	1.528(7)	C(14)–C(15)	1.525(6)
C(4)–C(5)	1.545(5)	C(14)–C(16)	1.538(6)
(*b*) Bond angles (°)			
C(2)–C(1)–C(6)	102.7(5)	O(1)–C(7)–C(6)	124.9(8)
C(2)–C(1)–C(9)	115.3(5)	O(1)–C(7)–C(8)	124.5(10)
C(6)–C(1)–C(9)	106.8(6)	C(6)–C(7)–C(8)	110.7(6)
C(1)–C(2)–C(3)	109.4(5)	C(7)–C(8)–C(9)	105.0(6)
C(1)–C(2)–C(13)	102.0(5)	C(7)–C(8)–C(14)	112.2(5)
C(3)–C(2)–C(13)	99.9(6)	C(9)–C(8)–C(14)	114.8(6)
C(2)–C(3)–C(4)	103.6(7)	C(1)–C(9)–C(8)	108.2(6)
C(2)–C(3)–C(10)	118.1(8)	C(3)–C(10)–C(11)	110.4(8)
C(4)–C(3)–C(10)	103.4(7)	C(10)–C(11)–C(12)	113.3(10)
C(3)–C(4)–C(5)	102.4(6)	C(4)–C(12)–C(11)	106.5(7)
C(3)–C(4)–C(12)	106.2(7)	C(2)–C(13)–C(5)	94.8(6)
C(5)–C(4)–C(12)	117.7(7)	C(8)–C(14)–C(15)	113.0(6)
C(4)–C(5)–C(6)	109.0(5)	C(8)–C(14)–C(16)	112.1(6)
C(4)–C(5)–C(13)	100.6(5)	C(15)–C(14)–C(16)	107.8(7)
C(6)–C(5)–C(13)	102.1(5)	O(2)–C(15)–O(3)	122.6(6)
C(1)–C(6)–C(5)	103.9(6)	O(2)–C(15)–C(14)	119.7(7)
C(1)–C(6)–C(7)	106.3(6)	O(3)–C(15)–C(14)	117.5(7)
C(5)–C(6)–C(7)	112.5(5)		
(*c*) Carbon–hydrogen bonds (Å)			
C(1)–H(1)	1.03(4)	C(11)–H(11)	1.02(4)
C(2)–H(2)	1.04(4)	C(12)–H(12)	1.05(3)
C(3)–H(3)	1.06(5)	C(12)–H(13)	1.05(5)
C(4)–H(4)	1.06(4)	C(13)–H(14)	1.02(4)
C(5)–H(5)	1.02(5)	C(13)–H(15)	1.05(4)
C(6)–H(6)	1.04(4)	C(14)–H(16)	1.15(4)
C(8)–H(7)	1.07(4)	C(16)–H(17)	0.96(4)
C(9)–H(8)	1.00(4)	C(16)–H(18)	0.95(5)
C(9)–H(9)	1.02(4)	C(16)–H(19)	0.90(4)
C(10)–H(10)	0.99(5)		



Projection of the structure on (010)

EXPERIMENTAL

I.r. spectra were measured on a Perkin-Elmer 21, ^1H n.m.r. spectra on a Jeol C60NL spectrometer, and ^{13}C n.m.r. spectra on a Bruker 2262, 90 MHz instrument. G.l.c. analysis of the methyl esters was achieved with a Varian Aerograph 700 on a Carbowax 20 M column (polyethylene glycol succinate on sylanised Chromosorb terminated with terephthalic acid).

Reactions of endo- *and* exo-*Cyclopentadiene Dimer with But-2-enyl Chloride and Tetracarbonylnickel.*—Two solutions, containing but-2-enyl chloride (5.9 g, 0.065 mol) in acetone (10 ml), and tetracarbonylnickel (6 ml) in acetone (10 ml) were dropped at the same time into a stirred solution, kept at 45 °C under carbon monoxide and containing *endo*-cyclopentadiene dimer (9 g, 0.07 mol) and KPF_6 (12 g) in acetone (80 ml) and water (20 ml). After 5 h, a white neutral solid (2.5 g) which had separated was filtered off. Volatile compounds, consisting of but-2-enyl chloride (0.017 g), but-2-enyl dimers (0.22 g) (determined by g.l.c.), acetone, and tetracarbonylnickel were distilled off in a dry carbon dioxide trap. Extraction with diethyl ether gave 1.76 g of an acid and 12.5 g of a neutral solid portion.

The acid portion consisted essentially of compound (I) (10%); M^+ 274, m/e 242 (M^+ −32, MeOH), 214 (M^+ −60, HCO_2Me), 208 (M^+ −66, cyclopentadiene), 188 (M^+ −86, $CH_2{:}CH{\cdot}CO_2Me$), 187 (M^+ −87, $MeCH{\cdot}CO_2Me$), 186 (M^+ −88, $Et{\cdot}CO_2Me$), 120 (M^+ −66−88). ^1H N.m.r. ($CDCl_3$) after esterification with diazomethane showed absorptions in the region τ 4.1—4.6, corresponding to two of the original four protons of cyclopentadiene dimer (cyclopentene protons).

The neutral part had a polymeric nature. Mass fragmentation revealed fragment m/e 215 and several peaks differing by 160, probably the repeating unit of a cyclopentadiene dimer–carbon monoxide copolymer. A fraction obtained by precipitation with methanol from a xylene solution of the polymer had elemental analysis C, 80.8; H, 8.05; O, 11.0; structure (III) (n = 4) requires C, 81.7; H, 7.8; O, 10.2%. Osmometric molecular weight 935.

An analogous reaction was carried out under the same conditions on *exo*-cyclopentadiene dimer,[5] containing 15% of the *endo*-isomer. An acid oil (1.8 g) was obtained, together with a neutral solid polymer (12.5 g). A white solid slowly crystallised from the acid oil, and after recrystallisation from methanol–water melted at 150—155 °C. Mixed m.p. with the solid derived from the *endo*-isomer was depressed. ^1H N.m.r. spectroscopy of the methyl ester revealed a broader area of absorption (τ 4.0—4.68) of the double-bond protons than that observed for the product derived from the *endo*-isomer

Crystal Structure of 2-(*Tetracyclo*[5.5.1.$0^{2,6}$.$0^{8,12}$]*tridec*-9-*en*-4-*yl*)*propionic Acid* (I).—Crystals were colourless tabular prisms, elongated on [001]. Preliminary cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were refined by least-squares by use of $13(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{16}H_{20}O_3$, $M = 260.3$. Triclinic, $a = 14.81(1)$, $b = 6.63(1)$, $c = 7.54(1)$ Å, $\alpha = 107.5(2)$, $\beta = 81.5(2)$, $\gamma = 104.7(2)°$, $Z = 2$, $D_m = 1.27$ g cm^{-3}, $U = 681.5$ Å^3. Cu-K_α radiation, $\lambda = 1.541\ 8$ Å, μ (Cu-K_α) = 7.03 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensity data were collected up to θ 70° by use of the ω—2θ scan method and the five-point technique,[9] with nickel-filtered Cu-K_α radiation on the same single-crystal diffractometer. Throughout data collection a standard reflection checked every twenty measurements indicated practically no decomposition of the specimen. 2 558 Independent reflections were measured of which 159 were not used in the crystal analysis having intensities $<2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal roughly in the x,y,z directions were 0.15, 0.32, 0.41 mm. Absorption was ignored.

Structure Analysis and Refinement.—Data were put on absolute scale by Wilson plot,[10] and normalized structure-factor magnitudes $|E_{hkl}|$ derived. The structure was solved by use of 400 reflections with $|E| \geqslant 1.43$ by the multisolution and phase permutation technique, the reflections in the base set being chosen by use of the programme Multan.[11] An E map computed by use of the most consistent set of signs obtained clearly revealed the position of all atoms in the molecule except hydrogen. A structure-factor calculation carried out at this stage gave R 0.29. The structure was refined by block-diagonal least-squares cycles, first with isotropic and then with anisotropic thermal parameters, reducing R to 0.081. A difference-Fourier synthesis was then computed and revealed significant residual peaks near the positions where hydrogen atoms were expected to occur, except for that attached to the carboxylic group. A few further least-squares cycles were then computed, hydrogen atoms being included with isotropic thermal parameters, a final R value of 0.074 being obtained. Positional parameters together with their standard deviations are given in Table 2. Atom scattering factors were taken from ref. 12 for non-hydrogen atoms and from ref. 13 for hydrogen. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21875 (14 pp, 1 microfiche).*

TABLE 2

(*a*) Fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses, for non-hydrogen atoms

	x	y	z
O(1)	6 483(2)	2 610(4)	−887(4)
O(2)	4 635(1)	−616(4)	−2 963(3)
O(3)	5 992(2)	−860(4)	−4 639(3)
C(1)	7 577(2)	112(5)	1 602(4)
C(2)	8 645(2)	303(6)	1 313(5)
C(3)	9 130(2)	2 214(6)	2 891(5)
C(4)	9 037(3)	4 280(6)	2 391(5)
C(5)	8 485(2)	3 292(6)	631(5)
C(6)	7 469(2)	2 199(5)	1 194(4)
C(7)	6 843(2)	1 451(5)	−392(4)
C(8)	6 700(2)	−992(5)	−1 248(4)
C(9)	6 993(2)	−1 836(5)	215(4)
C(10)	8 672(3)	2 501(8)	4 878(6)
C(11)	8 348(4)	4 383(9)	5 472(6)
C(12)	8 568(3)	5 633(7)	4 139(6)
C(13)	8 916(2)	1 330(6)	−337(5)
C(14)	5 701(2)	−2 041(5)	−1 836(4)
C(15)	5 419(2)	−1 054(5)	−3 196(4)
C(16)	5 565(3)	−4 496(5)	−2 741(4)

(*b*) Fractional co-ordinates ($\times 10^3$) for hydrogen atoms

	x	y	z
H(1)	732(3)	6(6)	294(5)
H(2)	886(3)	−113(6)	108(5)
H(3)	985(3)	217(6)	273(5)
H(4)	969(3)	516(6)	195(5)
H(5)	854(3)	431(6)	−18(5)
H(6)	715(3)	318(6)	232(5)
H(7)	717(3)	−127(6)	−248(5)
H(8)	737(3)	−295(6)	−42(5)
H(9)	641(3)	−253(6)	91(5)
H(10)	860(3)	144(6)	560(5)
H(11)	796(3)	485(6)	670(5)
H(12)	902(3)	713(6)	468(5)
H(13)	796(3)	600(6)	389(5)
H(14)	863(3)	37(6)	−155(5)
H(15)	964(3)	178(6)	−62(5)
H(16)	523(3)	−187(6)	−47(5)
H(17)	613(3)	−495(6)	−278(5)
H(18)	537(3)	−492(6)	−398(5)
H(19)	503(3)	−442(6)	−201(5)

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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