

CARBONYLATION OF (+)-2-CARENE INDUCED
BY IRON-PENTACARBONYL.

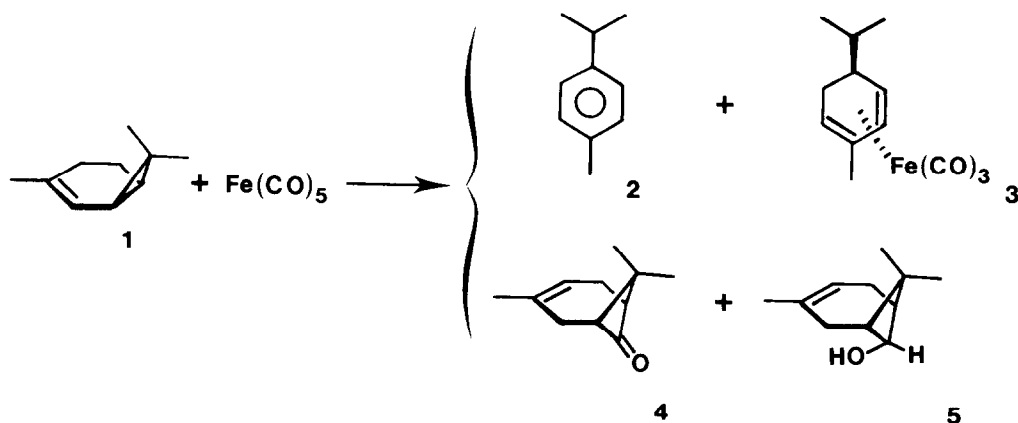
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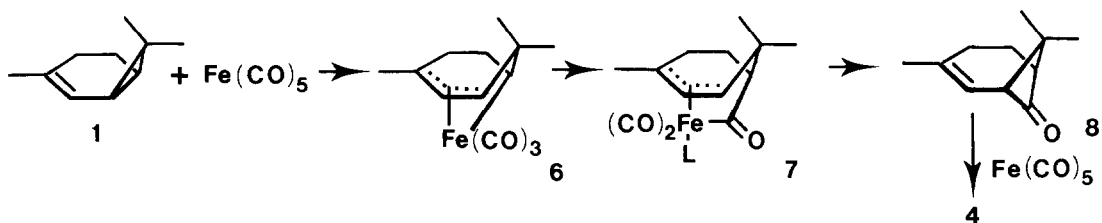
Summary : (+)-2-Carene heated neat with iron pentacarbonyl leads to α -phellandrene-Fe(CO)₃ complex (~15 %), p. cymene (~15 %), (-)-(1S)-3,8,8-trimethylbicyclo (4.1.1.) oct-3-ene-7-one (~50 %) and (+)-(1S,7S)-3,8,8-trimethylbicyclo (4.1.1.) oct-3-ene-7-ol (~20 %).

Expansion of carbon skeletons via introduction of the highly versatile carbonyl function is a major synthetic importance (1). Metal assisted carbonyl insertion reactions are becoming increasingly frequent in particular from iron pentacarbonyl and cyclopropyl compounds : it has been reported that the reaction of some polycyclic olefins containing a cyclopropane group with iron carbonyl compounds gave complexes where the bonding was proposed to involve π -allyl and σ -components to the Fe(CO)₃ unit (2). On the other hand, vinyl cyclopropane treatment produced substituted diene-Fe(CO)₃ complex (2e) (3) (see also (4)).

We now describe the reaction between (+)-2-carene 1 (5) and iron pentacarbonyl (7) : five compounds are isolated : 1 (~50-60 %), p. cymene 2 (~6 %), α -phellandrene-Fe(CO)₃ complex 3 (~6 %) (8), (-)-(1S)-3,8,8-trimethylbicyclo (4.1.1.) oct-3-ene-7-one 4 (~25 %) (10) and (+)-(1S,7S)-3,8,8-trimethylbicyclo (4.1.1.) oct-3-ene-7-ol 5 (~10 %) (12) :

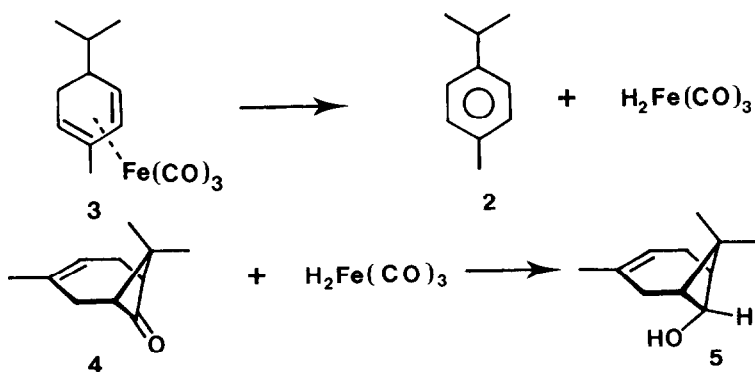


Cleavage of the cyclopropane ring occurs to give a complex involving π and σ bonds to the $\text{Fe}(\text{CO})_3$ unit **6**. Acyl π allyl intermediate **7** is formed by migratory insertion of a carbonyl group (13). The elimination of iron atom leads to ketone **8** :



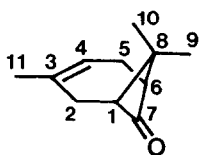
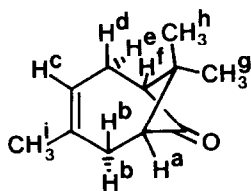
The migration of the double bond of **8** can be catalysed by $\text{Fe}(\text{CO})_5$ (14). Diene- $\text{Fe}(\text{CO})_3$ complex **3** is the product previously obtained from vinyl cyclopropanes and $\text{Fe}(\text{CO})_5$ (2d) (3abc).

Alcohol **5** is a possible result of the reduction of ketone **4** by $\text{H}_2\text{Fe}(\text{CO})_4$ (16). This hydride can be obtained from **3** (17) :



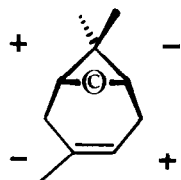
This carbonylation of terpenic hydrocarbons comprises a remarkable advantage for the synthesis of optically strained ketones. We are continuing in our studies of the synthetic potential of this reaction.

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C ¹ : 51.45	C ⁷ : 217.19
C ² : 44.91	C ⁸ : 34.44
C ³ : 142.83	C ⁹ : 32.88
C ⁴ : 117.92	C ¹⁰ : 25.49
C ⁵ : 34.29	C ¹¹ : 22.24
C ⁶ : 54.37	

(α)_D: -32.70°; (α)₅₇₈: -43.7°; (α)₅₄₆: -52.6°; (α)₄₃₆: -134.7°; (α)₃₆₄: -389.3°; (hexane, c=3.6). Circular dichroism showed **4** to have a negative Cotton effect



curve which from the octant rule and analogy with some closely related cyclobutanones (11) implies structure proposed : CD : λ_{max} : 300 nm, $\theta = -9.2 \cdot 10^3$ (hexane).

Ms : 164 (18%), 163 (32%), 149 (32%), 109 (30%), 107 (30%), 93 (50%), 91 (50%), 83 (65%), 55 (50%), 43 (100%), 41 (50%).

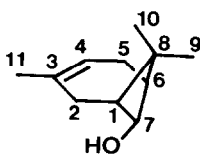
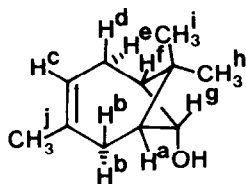
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b J. GORE, C. DJERASSI and J.M. CONIA, *ibid.*, **1967**, 950.

c R.B. BATES, M.J. ONORE, S.K. PAKNIKAR, C. STEELINK and E.P. BLANCHARD, *J. Chem. Soc. Chem. Comm.*, **1967**, 950.

d D. VAN LEUSEN, P.H.F.M. ROUWETTE and A.M. VAN LEUSEN, *J. Org. Chem.*, 1981, **46**, 5159.

12 **5** : m.p. : 74 °C (hexane); IR (CCl₄) : 3500 and 1075 cm⁻¹. RMN ¹H (200 MHz, CDCl₃, δ ppm/TMS) : H^a, H^d, H^f : 2.17 (m.); H^b : 1.60 (part A of AB pattern, ²J = 13.5 Hz, d. J = 6.4 Hz); H^{b'} : 1.44 (part B, ²J = 13.5 Hz); H^c : 5.31 (s. (br.)); H^e : 1.70 (s. (br.)); Hⁱ : 1.02 (s.); H^h : 1.05 (s.); H^j : 1.65 (d. J = 2.4 Hz). RMN ¹³C (50.309 MHz, CDCl₃, δ ppm/TMS) :



C ¹ : 46.42	C ⁷ : 72.85
C ² : 44.76	C ⁸ : 37.27
C ³ : 137.57	C ⁹ : 33.38
C ⁴ : 118.51	C ¹⁰ : 27.79
C ⁵ : 25.26	C ¹¹ : 22.98
C ⁶ : 46.65	

(α)₅₇₈: +61.2°; (α)₅₄₆: +70.8°; (α)₄₃₆: +133.6°; (α)₃₆₄: +233.6° (hexane, c=7.6). HRMS : calcd for C₁₁H₁₈O : 166.13576, found : 166.1367, (11%), 148 (7%), 133 (12%), 92 (100%), 85 (18%), 67 (9%), 41 (13%).

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14 Double bond isomerisations catalyzed by iron (0) are well known (15).

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17 In mass spectra, the loss of H₂ occurs in the case of 1.3-cyclohexadienetricarbonyl iron before all the CO ligands have been removed (9) (18).

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References and Notes :

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- 5 (+)-2-Carene : $(\alpha)_{578}$: +92.5 °; $(\alpha)_{546}$: +107.5 °; $(\alpha)_{436}$: +203 ° (hexane, c=5).
These values as compared to literature values indicate a high optical purity (6).
- 6a W. COCKER, P.V.R. SHANNON and P.A. STANILAND, *J. Chem. Soc.*, 1966, 41.
- b S.P. ACHARYA and H.C. BROWN, *J. Amer. Chem. Soc.*, 1967, 89, 1925.
- 7 (+)-2-Carene and 1.1 equivalent of $\text{Fe}(\text{CO})_5$ are heated neat during 80 hours at 160 °C. After filtration of black slightly pyrophoric iron, crude product is distilled in two fractions : the first (65-75 °C/25 mmHg) contains 1 and 2, the second (80-90 °C/0.2 mmHg) is chromatographed on silica gel (3 is eluted with pentane, 4 with pentane-Et₂O (9/1) and 5 with pentane-Et₂O (1/1).
- 8 3 : This product was identified by comparison with the published ¹H NMR and IR data (9acd). The absolute configuration of 3 is attributed according to the known (R)-(-)- α -phellandrene-Fe(CO)₃ complex (9acd). The enantiomeric excess is low ($(\alpha)_{578}$: +1.5 °; $(\alpha)_{546}$: +1.95 ° (CHCl₃, c=7); $(\alpha)_D$: +11.9 (CHCl₃, c=3) by direct complexation of (R)-(-)- α -phellandrene (9abc). The thermodynamic stability of diene-Fe(CO)₃ complexes, as related to substitution with alkyl groups, is found predominantly in the 2-position of the diene (9d).
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- b A.J. BIRCH, W.D. RAVERTY and G.R. STEPHENSON, *J. Chem. Soc. Chem. Comm.*, 1980, 857.
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- 10 Purification of ketone 4 is very difficult. Pure 4 is obtained by oxidation of the corresponding alcohol 5 (pyridinium-chromate, r.t. 3 h.). IR (CCl₄) : 1755 cm⁻¹ (s.), 1665 cm⁻¹ (w.). RMN ¹H (200 MHz, CDCl₃, δ ppm/TMS) : H^a and H^f: 2.65 (m.); H^b: 1.80 (d. J = 3.8 Hz); H^c: 5.18 (s.(br.)); H^d: 1.92 (t. J = 3.7 Hz, q. J = 2.2 Hz, d. J = 1.6 Hz); H^e: 2.30 (t. J = 3.7 Hz, q. J = 2.2 Hz, d. J = 1.6 Hz); H^g: 1.01 (s.); H^h: 1.20 (s.); Hⁱ: 1.70 (t. J = 2.2 Hz, d. J = 1.6 Hz). RMN ¹³C (50.309 MHz, CDCl₃, δ ppm/TMS) : (assignment confirmed by J modulation, off-resonance and the use of shift reagent (Profod)) :