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THE SYNTHESIS OF TWO DIHYDROPENTALENYL DERIVATIVES[1]

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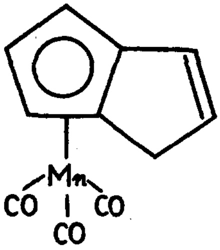
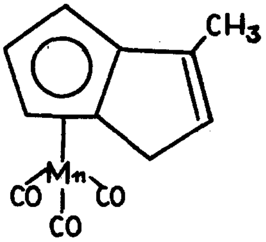
Recently[3] we reported the preparation of several new derivatives of cyclopentadienylmanganese tricarbonyl, to serve as model compounds towards an eventual synthesis of a potential pentalene system. The basic idea of this approach was that metal complexing the double bonds of one ring might stabilise the system sufficiently to enable one to proceed with the introduction of the double bonds (or potential double bonds) in the second cyclopentadiene ring of pentalene. In the present note we wish to report the synthesis of two dihydropentalenyl derivatives I and II



I



II

Reduction of ketone III[3] with aluminum isopropoxide yielded 60% of the alcohol IV, m.p. 90-91° (Found: C, 54.12; H, 4.70; Mn, 19.27. $C_{13}H_{13}MnO_4$ requires: C, 54.18; H, 4.55; O, 19.02%).

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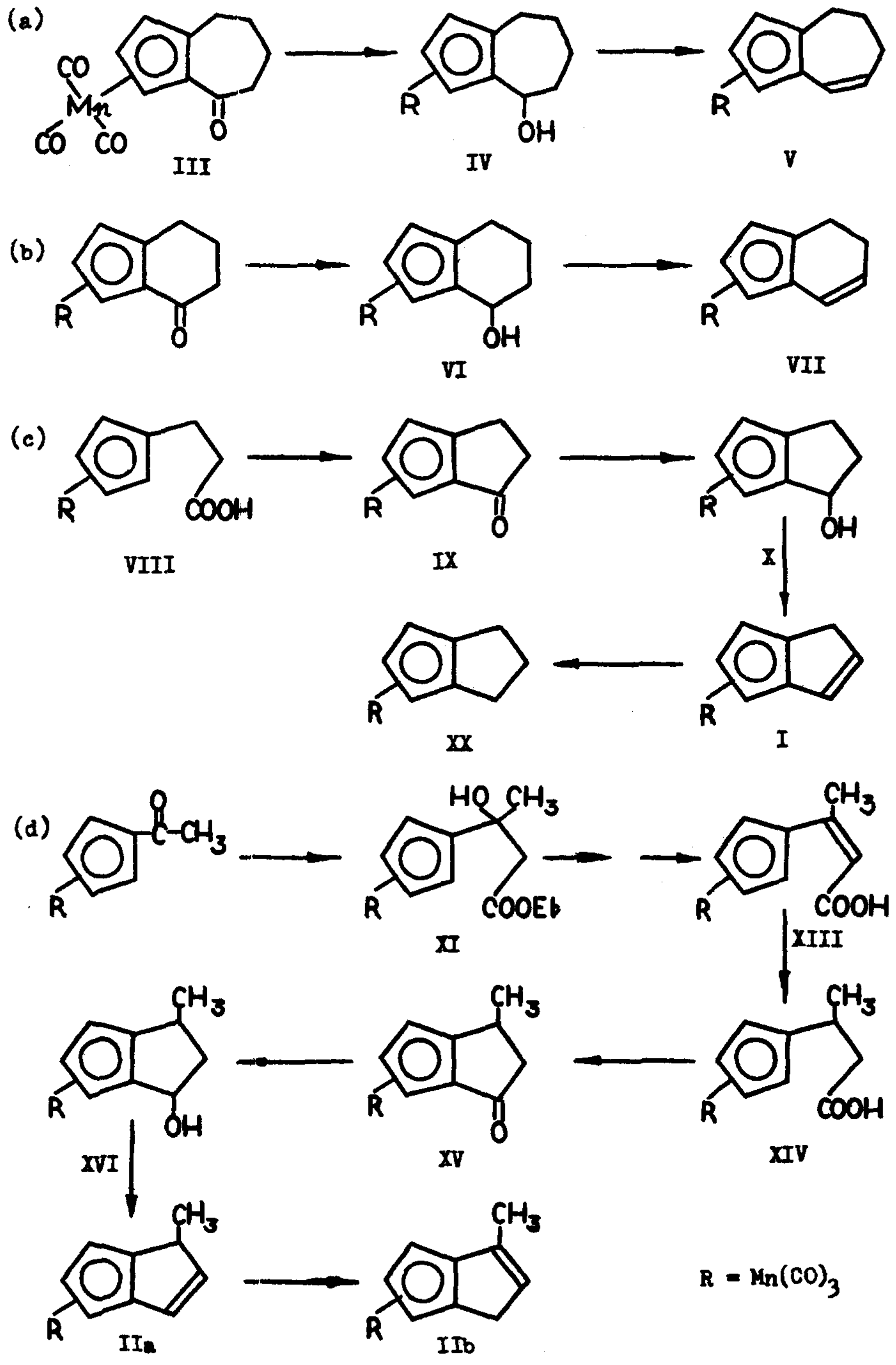
[1] Presented in part at the meeting of Israel Chemical Society, Jerusalem, April 19-20, 1960.

[2] To whom inquiries should be addressed.

[3] M. Cais and A. Modiano, *Chem. and Ind.* 202 (1960).


(a)
CO
Mn
CO
CO
III
R
OH
IV
V
(b)
R
O
VI
VII
(c)
COOH
VIII
IX
X
I
XX
(d)
CH$_3$
HO
COOEt
XI
COOH
XIII
XIV
XV
XVI
IIa
IIb
R = Mn(CO)$_3$

Dehydration of IV yielded 98% of the tetrahydroazulenylmanganese tricarbonyl derivative V, b.p. 90°/0.03 mm. (Found: C, 57.41; H, 4.30; Mn, 20.26. $C_{13}H_{11}MnO_3$ requires: C, 57.79; H, 4.10; Mn, 20.34%). (No OH absorption bands in infrared spectrum). By the same reaction sequence we obtained in 90% yield (after dehydration) the dihydroindenylmanganese tricarbonyl compound VII, b.p. 78-80°/0.05 mm. (Found: Mn, 21.49. $C_{12}H_9MnO_3$ requires: Mn, 21.45%).

The experience gained with the model compounds enabled us to proceed with reaction sequence (c). Cyalisation of the propionic acid derivative VIII[3] produced the ketone IX in 60% yield, m.p. 102-104° (Found: C, 51.30; H, 2.61; Mn, 20.99. $C_{11}H_7MnO_4$ requires: C, 51.19; H, 2.73; Mn, 21.29%). Reduction to the alcohol and dehydration produced in 95% yield (calculated on dehydration reaction) dihydropentalenylmanganese tricarbonyl I, b.p. 74-76°/0.05 mm. (Found: C, 54.71; H, 2.78; Mn, 22.52. $C_{11}H_7MnO_3$ requires[6]: C, 54.57; H, 2.92; Mn, 22.69%). The infrared spectrum[4] of I was similar but not identical with that of the compound from the reaction of acetylene with manganese carbonyl and to which the authors have recently[5] ascribed structure I[6]. In the catalytic hydrogenation of I (PtO_2 catalyst) one mole of hydrogen was absorbed and the infrared spectrum[4] of the reduced compound was identical with that of the compound reported[5] during the preparation of this manuscript and to which the same structure XX was ascribed.

Reaction scheme (d) shows the route for the synthesis of the methyl dihydropentalenyl derivative II. The Reformatzky reaction on (acetylcyclopentadienyl)manganese tricarbonyl[7] yielded 98% (crude) of

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[4] We wish to thank Dr. W.B. Ligett, Director, Chemical Research, Ethyl Corporation, Detroit, Mich., for kindly sending us copies of the infrared spectra of the acetylene-manganese carbonyl derivatives[5].

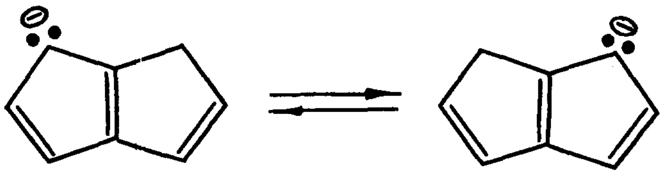
[5] T.H. Coffield, K.G. Ihrman and W. Burns, J. Am. Chem. Soc. 82, 1251 (1960).

[6] The calculated analysis for $C_{11}H_7MnO_3$ as given by above authors[5] appears to be in error.

[7] J. Kozikowski, R.E. Maginn and M. Sizen-Klove, J. Am. Chem. Soc. 81, 2995 (1959).

the β-hydroxy ester XI, m.p. 42.5-43.5°. (Found: C, 50.23; H, 4.59; Mn, 16.59. $C_{14}H_{15}MnO_6$ requires: C, 50.31; H, 4.52; Mn, 16.44%). Dehydration of XI afforded in nearly quantitative yield the corresponding α-β-unsaturated ester XII, m.p. 73.5-74.5° (Found: C, 53.45; H, 3.97; Mn, 17.19. $C_{14}H_{13}MnO_5$ requires: C, 53.18; H, 4.14; Mn, 17.38%). Hydrolysis of XII yielded 66% of the α-β-unsaturated acid XIII, m.p. 171-172.5° (Found: C, 50.19; H, 3.22; Mn, 19.13. $C_{12}H_9MnO_5$ requires: C, 50.02; H, 3.15; Mn, 19.07%). Hydrogenation of XIII (Raney Nickel catalyst) yielded 92% of the butyric acid derivative, XIV, m.p. 105-107° (Found: C, 49.51; H, 3.66; Mn, 18.84. $C_{12}H_{11}MnO_5$ requires: C, 49.67; H, 3.82; Mn, 18.93%). Cyclization to the ketone XV proceeded in 93% yield, b.p. 104°/0.02 mm. (Found: C, 52.84; H, 3.38; Mn, 20.09. $C_{12}H_9MnO_4$ requires: C, 52.96; H, 3.33; Mn, 20.19%). The aluminium isopropoxide reduction to the alcohol XVI proceeded in 98% yield (crude), b.p. 108°/0.04 mm. (Found: C, 52.77; H, 4.10; Mn, 19.99. $C_{12}H_{11}MnO_4$ requires: C, 52.57; H, 4.05; Mn, 20.04%). Dehydration of XVI gave a high yield (98%) of the methyl dihydropentalenyl derivative II, b.p. 98°/0.1 mm. (Found: C, 56.38; H, 3.65; Mn, 21.05. $C_{12}H_9MnO_3$ requires: C, 56.27; H, 3.54; Mn, 21.45%). It is likely that the olefinic double bond in IIa migrates to the position of highest substitution, IIb and we are currently investigating this possibility.

It is interesting to speculate on the possible contributions of the resonating forms of XIXa and XIXb, with eight Π electrons available, to the electronic structure of compounds I and II.



XIXa XIXb

Investigations are in progress for finding methods to transform the organometallic pentalenyl derivatives I and II into the metal-free hydrocarbons.

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