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A SIMPLE ROUTE FROM DICYCLOPENTADIENE TO TRISHOMOCUBANONE

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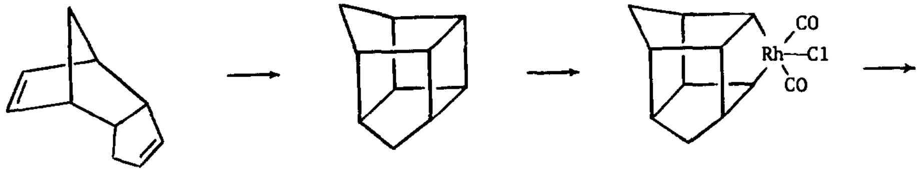
The preparation of trishomocubanone (5) in six steps from cyclopentadiene has recently been reported by Eaton, Hudson and Giordano[1] This intrinsically chiral ketone is a convenient precursor of the parent caged hydrocarbon, D_3-trishomocubane (pentacyclo$[6.3.0.0^{2,6}0^{3,10}0^{5,9}]$-undecane)[1,2]

We wish to report now a most simple synthesis of 5 that is based on photocyclization of dicyclopentadiene (1)[3] and carbonylation of the 1,3-bishomocubane (2), so formed

When a solution of 1 55 g (11 7 mmole) of 2 and 2.28 g (5 85 mmole) $[Rh(CO)_2Cl]_2$ in 40 ml dry benzene was heated under nitrogen at 60° for 24 hr, a pale yellow solid separated Partial evaporation of the solvent and washing the residue with cold benzene afforded complex 4 in quantitative yield (3 80 g) Mp 168-170° (dec)(from heptane). Found C, 44.4, H, 3 7, Cl, 11 2 Calcd for $C_{12}H_{12}ClO_2Rh$ C, 44.1, H, 3.7, Cl, 10.9 IR (KBr) (CO) 1720, 2058 cm^{-1} The molecular weight of the complex could not be established but has been assumed, by analogy with some other acylrhodium compounds[4], to have a Cl-bridged polymeric structure.

Pyrolysis of 4 yields 40-50% trishomocubanone (5). A DMSO or CCl_4 solution of the rhodium complex can simply be injected onto a GLC column packed with 10% OV-101 on Chromosorb W (Injection port 250°, column temp. 140°)

Alternatively 5 can be obtained in 90-95% yield by treatment of a CCl_4 suspension of 4 with a stoichiometric amount (2 moles) of PPh_3 at 60° for 15 min By this method the



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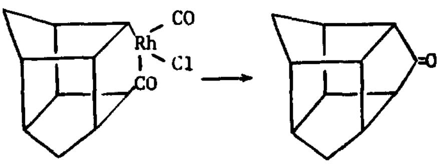

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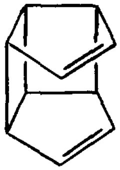

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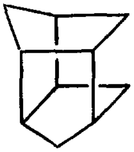

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rhodium is regenerated as chlorocarbonylbis(triphenylphosphine)rhodium, $RhCl(CO)(PPh_3)_2$ The trishomocubanone formed (mp 163-4°) proved to be identical in every respect with an authentic sample kindly provided to us by Professor P.E Eaton[1].

The acylrhodium complexes that have previously been isolated from $[Rh(CO)_2Cl]_2$ and caged hydrocarbons, could be regarded as derivatives of bicyclo[2.2.0]hexane fused with at least one additional cyclobutane ring[5]. In the 1,3-bishomocubane the two adjacent cyclobutanes are surrounded only by cyclopentane structures. By analogy with the cubane system[4a] it could well be predicted that 2 will undergo oxidative addition to dichlorotetracarbonyldirhodium. However, since the 1,3-bishomocubane system has proved able to open up either to hypostrophene (6)[6] or, under reductive conditions, to tetracyclo[5.2.1 $0^{2,6}0^{4,8}$]decane (7)[7,8], the bond to be cleaved in 2 could not be foretold with certainty. The sequence of reactions 2 → 3 → 4 → 5 proves that the insertion occurs exclusively at the central bond of the bicyclo[2 2.0]hexane system

The great stability of 4 has been demonstrated by the recovery of the entire amount of unchanged acylrhodium complex after refluxing its solution in xylene for 24 hr Conversion of 4 into the metal-free ketone takes place only above the mp of the complex. It should be recalled that pyrolysis of the analogous acylrhodium derivatives of bicyclo[2.2 0]hexane[5], *syn*-tricyclo[4.2 $0.0^{2,5}$]octane[9] and cubane[4a] yields cyclohexene, bicyclo[4.2 0]oct-2-ene and *syn*-tricyclo[4.2 0 $0^{2,5}$]octa-3,7-diene, respectively, rather than the corresponding ketones

Further studies on the reaction of transition metal complexes with "isolated" bicyclo[2 2 0]hexane systems in caged compounds are currently at hand.

Acknowledgements. We thank Professor Phillip E Eaton for a sample of trishomocubanone and for informing us of his results prior to publication Thanks are also extended to the Central Fund of the Hebrew University for financial support.

FOOTNOTES AND REFERENCES

1 P.E. Eaton, R.A. Hudson and C Giordano, *J C.S. Chem. Comm.*, in press.

2. G R Underwood and B Ramamoorthy, *Tetrahedron Lett* , 4125 (1970).

3 The photocyclization of dicyclopentadiene to give 2 according to G.U Scheneck and R. Steinmetz, *Chem. Ber* , *96*, 520 (1963), proved to be capricious unless the diene has been freshly purified by chromatography on alumina The best results were obtained when a solution of 1 (17 g) in acetone (250 ml) was photolyzed under nitrogen through quartz with a Hanovia 450 W high pressure mercury lamp No 679A-36

4. Cf., e.g., (a) L Cassar, P E. Eaton and J Halpern, *J. Amer Chem. Soc* , *92*, 3515 (1970), (b) L Cassar and J. Halpern, *J.C S. Chem. Comm.*, 1082 (1970)

5. Recently J. Halpern and M Sohn prepared a rather unstable acylrhodium complex from $[Rh(CO)_2Cl]_2$ and the unsubstituted bicyclo[2 2.0]hexane which proved to react in an unusual manner with triphenylphosphine (Private communication).

6. (a) J.S. McKennis, L. Brener, J.S. Ward and R Pettit, *J. Amer Chem. Soc.*, **93**, 4957 (1971), (b) L.A. Paquette, R.F. Davis and D.R. James, *Tetrahedron Lett.*, 1615 (1974).

7 K.-I. Hirao, T Iwakuma, M. Taniguchi, E. Abe, O Yonemitsu, T. Date and K Kotera, *J.C.S. Chem. Comm.*, 691 (1974).

8. E. Ōsawa, P von R. Schleyer, L W.K. Chang and V.V. Kane, *Tetrahedron Lett.*, 4189 (1974)

9 Pyrolysis of the acylrhodium derivative of *syn*-tricyclo[4 2.0.0^{2,5}]octane at 140° yields 90% bicyclo[4.2.0]oct-2-ene and 10% cycloocta-1,5-diene A full report on the reaction of the tricyclooctane and [Rh(CO)$_2$Cl]$_2$ by J. Halpern and J Blum will be published elsewhere