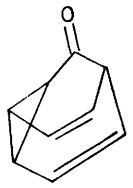
Synthesis of Barbaralone from $C_8H_8Fe(CO)_3$

By VAL HEIL, BRIAN F. G. JOHNSON, JACK LEWIS,* and DAVID J. THOMPSON
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

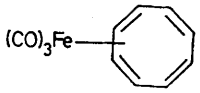
Summary A synthesis of barbaralone from $C_8H_8Fe(CO)_3$ is described.

CURRENTLY available synthetic routes to barbaralone (**1**) are inefficient giving low yields from a multistage synthesis.[1] We now report a two-stage synthesis from the readily available (cyclo-octatetraene)tricarbonyliron (**2**).

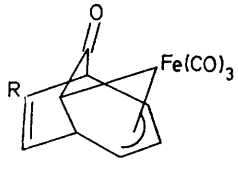
The reaction of (**2**) and anhydrous aluminium trichloride in benzene at 10°C gave a yellow complex (*ca.* 40%). This product was purified by chromatography and recrystallization from hexane and identified as (**3**; R = H), previously obtained[2] from the reaction between barbaralone and di-ironnonacarbonyl, on the basis of its analytical and spectroscopic properties [m.p. 133°C $\nu_{M\text{-}CO}$ (hexane) 2058, 2000, 1922 cm^{-1}, ν_{CO} (ketone), 1670 cm^{-1}, *m/e* 272 (M^+), 244 ($M - CO^+$), 216 ($M - 2CO^+$), 188 ($M - 3CO)^+$, 160 ($M - 4CO^+$), 134 ($160-C_2H_2^+$)]. The structure proposed for this complex is largely based on its ^1H n.m.r. spectrum



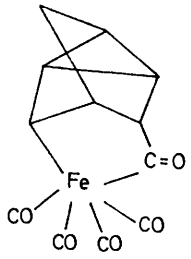
(1)



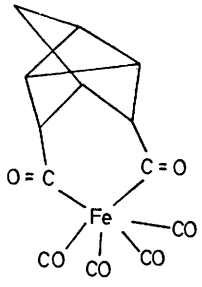
(2)



(3)



(4)



(5)

which is in complete agreement with that reported previously.[2] Reaction of (**3**; R = H) with carbon monoxide under moderate temperature (120°C) and pressure (100 ats.) liberates barbaralone, C_9H_8O (**1**) (90%) and thus provides a convenient preparative route of this ketone from the readily available complex (**2**). The analytical and spectroscopic properties of ketone (**1**) were as described elsewhere.[1]

The use of substituted cyclo-octatetraene derivatives has been briefly explored; good yields of complex (**3**; R = Me) may be obtained from methylcyclo-octatetraene, whilst the phenylcyclo-octatetraene yields a variety of products which are under current investigation.

Alternative Lewis acids have also been employed but the above reaction appears to occur only in the presence of aluminium trichloride. This reaction does, however, appear to occur with systems other than cyclo-octatetraenetricarbonyliron. Thus we have established that cyclo-octatrienetricarbonyliron also undergoes CO insertion on reaction with $AlCl_3$ to yield a ketone complex, $C_9H_{10}OFe(CO)_3$ and norbornadienetricarbonyliron react to yield products of probable structures (**4**) and (**5**). Compound (**4**) can also be synthesised by reaction of quadricyclane with $Fe_2(CO)_9$. Cycloheptatrienetricarbonyliron does not undergo CO insertion under these conditions. We are currently investigating the mechanism and generality of these reactions.

We thank M. H. Mitchell for experimental assistance and one of us (D.J.T.) thanks the Royal Commissioners for the Exhibition of 1851 Fellowships for an award.

(*Received, 24th January* 1974; *Com.* 095.)

[1] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 197, **23**, 3943.
[2] A. Eisenstadt, *Tetrahedron Letters*, 1972, 2005.