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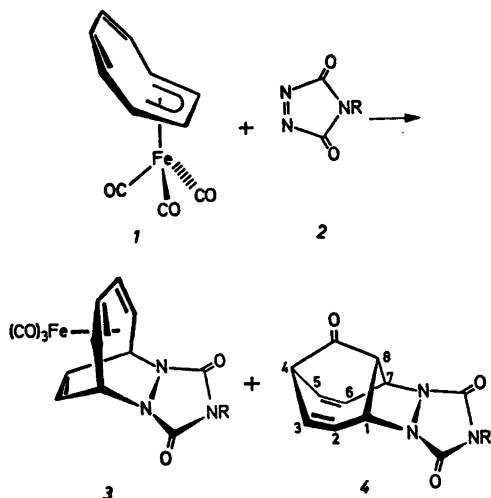
The Formation of Barbaralone Derivatives from the Reaction between Triazolinediones and Cyclooctatetraene-iron Tricarbonyl

HENRIK OLSEN

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Coordination of a polyene to a metal center can lead to drastic modification of its reactivity. Thus cyclooctatetraene (COT) cycloadds to tetracyanoethylene (TCNE) *via* its [4.2.0]-bicyclic valence isomer in classic Diels-Alder fashion,¹ while the iron tricarbonyl complex *1* yields a 1,3-addition product containing an Fe-C σ bond.² The even more powerful dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (*2*, R=Ph, PTAD) is reported to combine with *1* in low yield at 25 °C to give the 1,4-adduct *3*.³ Apart from the Fe(CO)₃ moiety the reaction appears to be completely analogous to that between PTAD and COT under ambient conditions.⁴ We have reinvestigated the transformation with both MTAD and PTAD (*2*, R=CH₃, Ph) and have found that the barbaral-

one derivative *4* is formed along with complex *3*. The result implies carbonyl insertion into an intermediate 1,3-addition product.

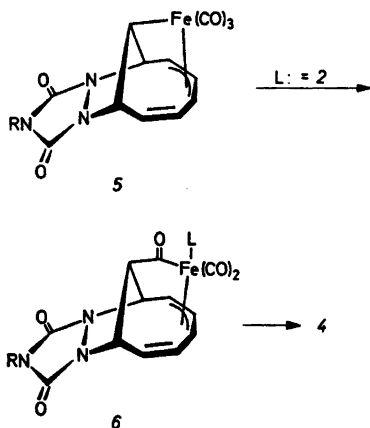


Mixing of equimolar quantities of MTAD and *1* (in CH₂Cl₂, 25 °C, 30 min) followed by chromatography (silica gel, ethyl acetate) leads to the isolation of three compounds. Besides unreacted *1* (22 %) and *3* (R=CH₃, 34 %, m.p. 185 °C, dec.) the barbaralone derivative *4* was obtained (R=CH₃, 16 %, m.p. 214–215 °C). The latter gave a satisfactory elemental analysis and molecular weight (MS). The presence of the keto group was substantiated by derivatization (2,4-DNP) and IR (CHCl₃): 1750 (m), 1772 (s) and 1714 (s) cm⁻¹ (C=O and N-CO-N). ¹H NMR spectrometry (90 MHz, CDCl₃) established the symmetry and structure of *4* by revealing six signals readily analyzable by spin decoupling. The absorption at lowest field is an AB quartet showing additional fine structure [δ 6.41 (2 H, H-3 and H-5) 5.99 (2 H, H-2 and H-6); $J_{23}=J_{56}=9$ Hz; $J_{12}=J_{67}=4$ Hz; $J_{34}=J_{54}=6.5$ Hz; $J_{31}=J_{47}=1$ Hz]. The bridgehead protons α to nitrogen resonate at δ 5.11 (2 H, H-1 and H-7, dd, $J_{18}=J_{78}=8$ Hz). At high field the remaining absorption consists of two doublets of triplets centered at δ 3.68 (1 H, H-8, $J_{48}=2$ Hz) and 3.39 (1 H, H-4) and a singlet at δ 3.08 (N-CH₃). The broad band decoupled ¹³C NMR spectrum (22.63 MHz, CDCl₃) is in complete agreement with structure *4* exhibiting only eight peaks: δ 201.1, 156.2, 134.5, 126.2, 61.7, 50.9, 45.3 and 25.8.

The corresponding reaction with PTAD yielded *1* (22 %), the previously characterized *3* (R=Ph, 33 %, m.p. 156–157 °C; lit.³ m.p. 155 °C) and the barbaralone system *4* (R=Ph, 14 %, m.p. 225–226 °C). The *N*-phenylbarbaralone was characterized as above, its spectro-

scopic properties being analogous with those of the *N*-methyl derivative.

The formation of tetracycle **4** is strongly suggestive that PTAD and MTAD, similar to TCNE, interact with complex **1** to give a 1,3-addition product **5**. Further transformation may proceed by migration of C-8 to CO (**6**) followed by extrusion of the metal component to give **4**. Other polycyclic σ -bonded iron complexes undergo carbonyl insertion in the presence of suitable ligands (e.g. CO,^{2b,3,5} NO,^{2b,3} Ph₃P⁵)^{*} or under the influence of Ce(IV).^{2c} Since cyclic azo compounds react with iron carbonyls to form complexes in which the azo group behaves as a two electron ligand,⁶ it seems plausible that the N=N bond in triazolinedione **2** can function as a ligand in the present instance. Were this the case, less than one equivalent of **2** should be available for combination with **1**. Accordingly we isolate comparable amounts of barbaralone **4** and unreacted **1**.



The combination of triazolinediones with complex **1** is comparable with the corresponding reaction between TCNE and methoxy-COT iron tricarbonyl, where both a 1,3- and a 1,4-addition product have been reported.^{2c} Based on a series of product structure studies the proposal has been advanced that the reaction pathway involves a common zwitterionic intermediate which closes either at the 3- or the 4-position.² It is noteworthy, however, that there is a parallel between the response of complexed and uncomplexed cyclooctatetraenes to treat-

^{*} Green and Wood³ have depicted products derived from **1** and the dienophiles hexafluoroacetone and 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene as tricyclo[6.2.1.0^{4,7}]undeca-2,9-dienes containing a four-membered ring. The reported structural data are consistent with the barbaralone formulation as well. Indirect support favoring the latter is found in the Ce(IV) oxidation of the TCNE/**1** adduct to a symmetrical triquinacene derivative.^{2a,c}

ment with powerful dienophiles. Whereas neither COT-Fe(CO)₃² nor COT⁴ combine with TCNE to give a 1,4-cycloadduct (i.e., structure **3**), both CH₃O-COT-Fe(CO)₃^{2c} and CH₃O-COT⁷ do so. Likewise MTAD/PTAD add 1,4 to COT-Fe(CO)₃ (**1**), to COT⁴ and to CH₃O-COT.^{8,**} Charge separated intermediates have been presumed in the uncomplexed COT adductions as well,^{4,7,8} but it has now been demonstrated by rate studies in various solvents that the proposition was premature.⁹ Consequently the question as to the nature of the preliminary steps in the formation of adducts derived from cyclopolyolefin-Fe(CO)₃ complexes and dienophiles must be regarded as still open.

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^{**} The reaction between MTAD/PTAD and CH₃O-COT-Fe(CO)₃ has to our knowledge not been reported.