Communications to the Editor

Chem. Pharm. Bull.
31(5)1809—1811(1983)

THE MASKING AND ACTIVATING EFFECTS OF TRICARBONYL(TROPONE)IRON IN PERICYCLIC REACTIONS WITH o-QUINODIMETHANE

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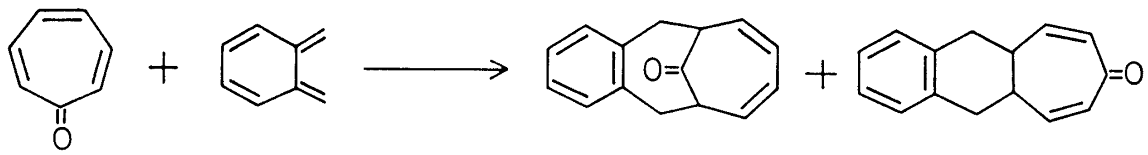
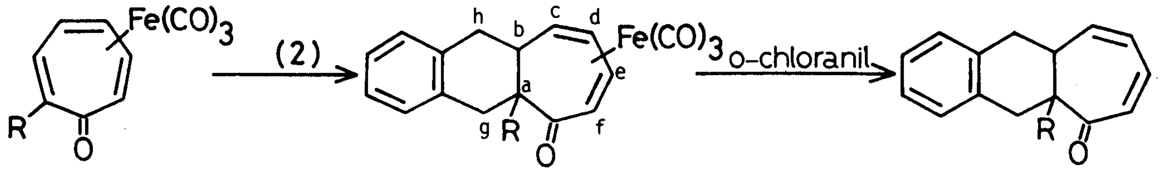
The reaction of tricarbonyl(tropone)iron (5a) and o-quinodimethane (2) followed by decomplexation with o-chloranil gives the previously unobtainable [4+2] adduct (7a) in good yield.

KEYWORDS——pericyclic reaction; masking effect; site-selectivity control; peri-selectivity control; tricarbonyliron complex; tropone; o-quinodimethane; o-chloranil

The new finding of the unique biological activity of 7-hydroxytropolone as a prototype of "antibiotic potentiator" 1) stimulates further studies on highly selective chemical transformations of tropones. Although much effort has been made to establish the control of peri- and site-selectivities in cycloaddition reactions of tropone (1), this cyclic polyene compound variably behaves as the 2π-, 4π-, 6π-, and 8π-cycloaddends, often giving a mixture of products.2)-5) Indeed, Fujise et al.6) reported that (1) underwent non-selective reaction with o-quinodimethane (2), generated by zinc dehalogenation of o-xylene dibromide, to give [6+4]- (3) and [4+2] adduct (4), but no [4+2] adduct reacting at the 2,3-position, *i.e.*, (7), was formed at all. We report now the effective formation of (7a) by using the masking effect of the tricarbonyliron complex.7)

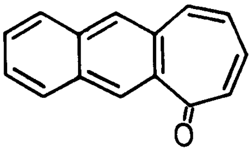

(1) (2) (3) [6+4] (4) [4+2]



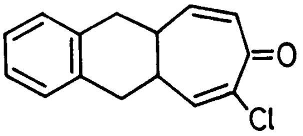
(5)a:R=H
b:R=Cl

(6)a:R=H (92%)
b:R=Cl(55%)

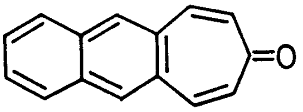
(7)a:R=H (50%)
b:R=Cl(33%)



(8)



(9)



(10)

At first, the reaction of tropone and (2) was reinvestigated using the new generation method of (2) developed by Ito et al.[8)] from [o-(trimethylsilylmethyl)benzyl]trimethylammonium iodide and cesium fluoride, and similar results were obtained [3 (26%) and 4 (24%)] with no formation of (7a). When tricarbonyl(tropone)iron (5a) was similarly treated with (2) at room temperature, a smooth reaction occurred to give exclusively the 1:1 adduct (6a) (92%) as yellow crystals, mp 121-122 °C (n-hexane); ν_{max} 2090, 2000, and 1645 cm^{-1}; m/e 350 (M^+), 322 (M^+-CO), 294 (M^+-2CO), and 266 (M^+-3CO); δ ($CDCl_3$) 2.5-2.9 (m, 6H), 2.96 (d, J = 7.0 Hz, H_f), 3.30 (m, H_a), 5.14 (dd, J = 8.0, 5.5 Hz, H_d), 5.67 (dd, J = 7.0, 5.5 Hz, H_e), and 7.0-7.2 (m, 4H). These assignments were fully confirmed by spin-decoupling experiments. Although removal of the tricarbonyliron moiety from tropone adducts is sometimes troublesome,[7),8)] treatment of (6a) with o-chloranil in refluxing methylene chloride gave previously unobtainable (7a) in 50% yield, mp 52-53 °C (n-hexane); ν_{max} 1665 and 1645 cm^{-1}; m/e 210 (M^+); δ (C_6D_6) 2.4-2.9 (m, 5H), 3.11 (dd, J = 14.0, 9.0 Hz, H_g), 5.3-5.7 (m, 2H), 5.85 (ddd, J = 12.0, 6.0, 2.0 Hz, H_e), 6.07 (br d, J = 12.0 Hz, H_f), and 6.7-7.1 (m, 4H).

When (6a) was treated with trimethylamine oxide, aromatized product (8)[6)] (15%) was formed along with (7a) and its isomers.

The similar reaction of tricarbonyl(2-chlorotropone)iron (5b)[10] and (2) at room temperature afforded a sole product (6b) (55%), mp 129-130 °C (dec.) (n-hexane); ν_{max} 2120, 2020, and 1670 cm^{-1}; m/e 386 (M^++2) and 384 (M^+); δ (C_6D_6) 2.16 (d, J = 16.5 Hz, H_h), 2.24 (d, J = 8.0 Hz, H_c), 2.84 and 3.17 (AB-q, J_{AB}= 19.0 Hz, 2H_g), 2.84 (d, J = 6.5 Hz, H_f), 3.13 (d, J = 6.0 Hz, H_b), 3.37 (dd, J = 16.5, 6.0 Hz, H_h), 4.13 (dd, J = 8.0, 6.0 Hz, H_d), 4.70 (dd, J = 6.5, 6.0 Hz, H_e), and 6.6-7.1 (m, 4H). The spin-decoupling experiments confirmed these assignments, and the appearance of H_b as a doublet was only compatible with the structure (6b). Treatment of (6b) with o-chloranil gave (7b) (33%), mp 97-98 °C (n-hexane); ν_{max} 1665 cm^{-1}; m/e 246 (M^++2) and 244 (M^+); δ ($CDCl_3$) 2.95 (d, J = 11.0 Hz, H_h), 2.99 (d, J = 6.0 Hz, H_b), 3.18 and 3.91 (AB-q, J_{AB} = 16.0 Hz, 2H_g), 3.42 (dd, J = 11.0, 6.0 Hz, H_h), 6.0-6.4 (m, 3H), 6.57 (dd, J = 12.0, 6.5 Hz, H_e), and 6.9-7.2 (m, 4H). In contrast, 2-chlorotropone poorly reacted with (2) to give (10)[6),10)] (13%) as the only isolable product, probably via the hydrogen migration and aromatization of the initially formed [4+2] adduct (9).

In summary, the use of the tricarbonyliron complex provides a promising way of controlling the site- and peri-selectivities of tropone cycloaddition reaction. It should be also noted that the reactivity of tropone toward the electron-rich diene is enhanced by this complexation.

We thank Mr. Hirofumi Samemoto for his technical assistance.

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(Received April 4, 1983)