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Preliminary communication

AN UNUSUAL CYCLOBUTANONE RING CLEAVAGE IN TRICARBONYL-[(η-2,3,4,5)-9,9-DIPHENYLBICYCLO[5.2.0]NONA-2,4-DIEN-8-ONE]IRON

ZEEV GOLDSCHMIDT* and SHLOMO ANTEBI
Department of Chemistry, Bar-Ilan University, Ramat-Gan (Israel)

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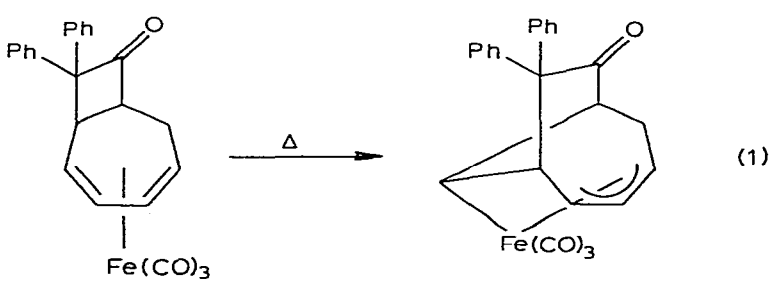
Summary

Isomerization of tricarbonyl[(η-2,3,4,5)-9,9-diphenylbicyclo[5.2.0]nona-2,4-dien-8-one]iron to tricarbonyl [(η-1,2,3,4)-6-(diphenylacetyl)-1,3,5-cycloheptatriene]iron is induced by catalytic amounts of acid or base.

Recently we reported a novel thermal dyotropic rearrangement of the 2+2 adduct of cycloheptatrieneiron tricarbonyl and diphenyl ketene [1,2] (eq. 1). The unusual expansion of the cyclobutanone ring conjugated to a dieneiron tricarbonyl complex led us to study the reactivity of this system toward acid and base.



(1)

(I) (II)

Brookhart has recently shown that the homologous bicyclo[4.2.0]octadienone complex III reacts with base to form the acetic acid derivative V by a mechanism involving a nucleophilic attack at the cyclobutanonecarbonyl group [3] (eq. 2).

We wish to report a different ring opening route of cyclobutanone I in-

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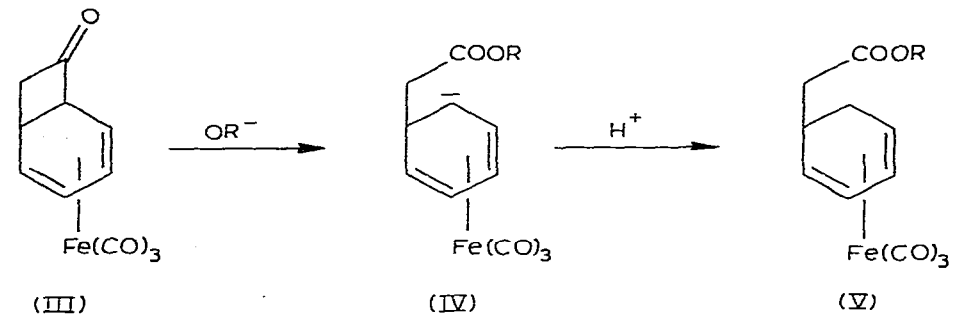


(2)

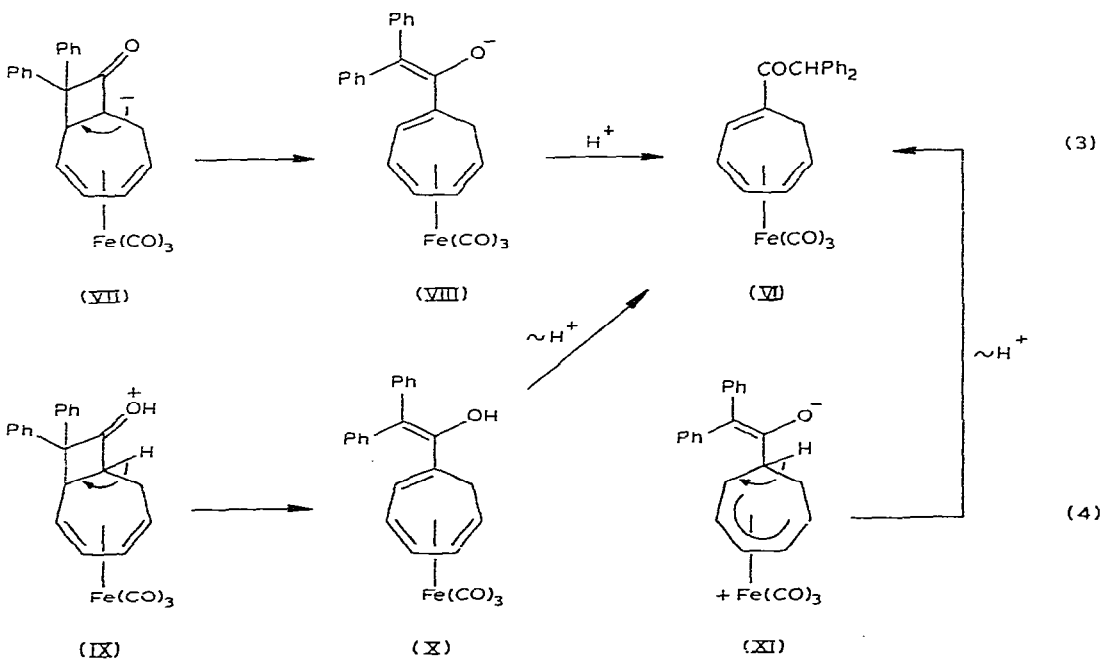
(III) (IV) (V)

(R = H, Me)

duced by either base or acid. Treatment of I with NaOMe in dry MeOH, at room temperature, afforded a single product (by TLC) identified as ketone VI (m.p. 160—161°C, from CH_2Cl_2/hexane): IR (Nujol): 2020, 1975, 1955 (ligand CO), 1640 (ketone CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.60 (2H, ABX, *J* 22, 3 Hz), 2.99 (1H, t, *J* 8 Hz), 3.49 (1H, m), 5.34 (2H, m), 5.61 (1H, s), 6.84—7.52 (11H, m).

The identical ketone VI was also the sole product obtained by treatment of I with a catalytic amount of *p*-TsOH in refluxing benzene. Attempts to chromatograph I over acid washed silica gel likewise resulted in isomerization to VI.

The base induced isomerization may involve a ElcB mechanisms [5] whereby the bridged *endo* proton adjacent to the carbonyl is first abstracted to give carbanion VII, followed by an unusual ring cleavage to give enolate VIII, (eq. 3).



(3)

(4)

(VII) (VIII) (VI)

(IX) (X) (XI)

The alternative acid catalyzed isomerization requires protonation at the ring carbonyl group followed by analogous ring opening to enol X (eq. 4).

The ready abstraction of the *endo* proton in both reactions suggests that the thermal dyotropic rearrangement (eq. 1) follows a concerted pathway [2] since the zwitterion intermediate XI, expected to be formed in a stepwise mechanism, would readily deprotonate leading subsequently to VI. For the same reason it may also be concluded that the cycloaddition of diphenyl ketene to cycloheptatrieneiron tricarbonyl (to form I) is concerted, as previously suggested [1].

Further studies aimed at elaborating the mechanistic aspects of these reactions are currently in progress.

References

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