Tetrahedron Letters No. 3, pp 271 - 274, 1978. Pergamon Press. Printed in Great Britain.

A NOVEL 1,3-DIENE- TO σ,π-ALLYLIRON TRICARBONYL DYOTROPIC REARRANGEMENT. CYCLOADDITION REACTIONS OF CYCLOHEPTATRIENEIRON TRICARBONYL AND DIPHENYLKETENE.

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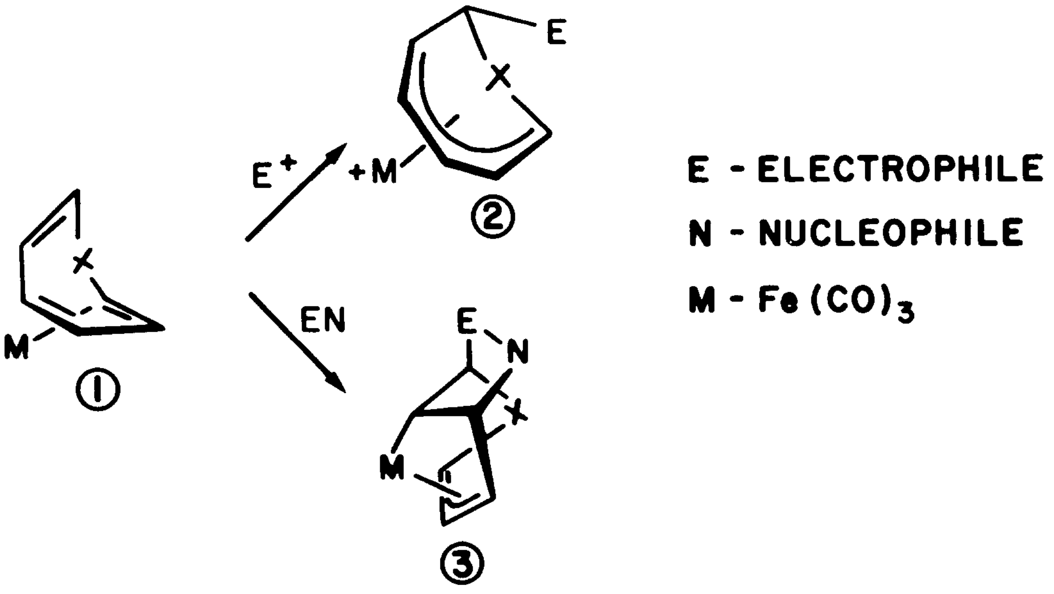
(Received in UK 9 November 1977; accepted for publication 24 November 1977)

The reactivity of cyclic trieneiron tricarbonyl complexes 1 has become a subject of paramount interest.[1] The donor character of the complexed butadiene moiety[2] attached to the free double bond, together with the apparent stability of the cyclic pentadienyliron tricarbonyl cation 2 [3] makes this system extremely useful in reactions with electrophiles.[1]

Uniparticulate electrophiles (EN), e.g., tetracyanoethylene (TCNE), N-phenyl-triazolinedione (NPTD) and hexafluoroacetone (HFA) efficiently enter cycloaddition reactions with 1, to give mainly the exo-1,3-σ,π-allyliron tricarbonyl adducts 3, by either a stepwise[4,5,6] or a concerted[7] mechanism.



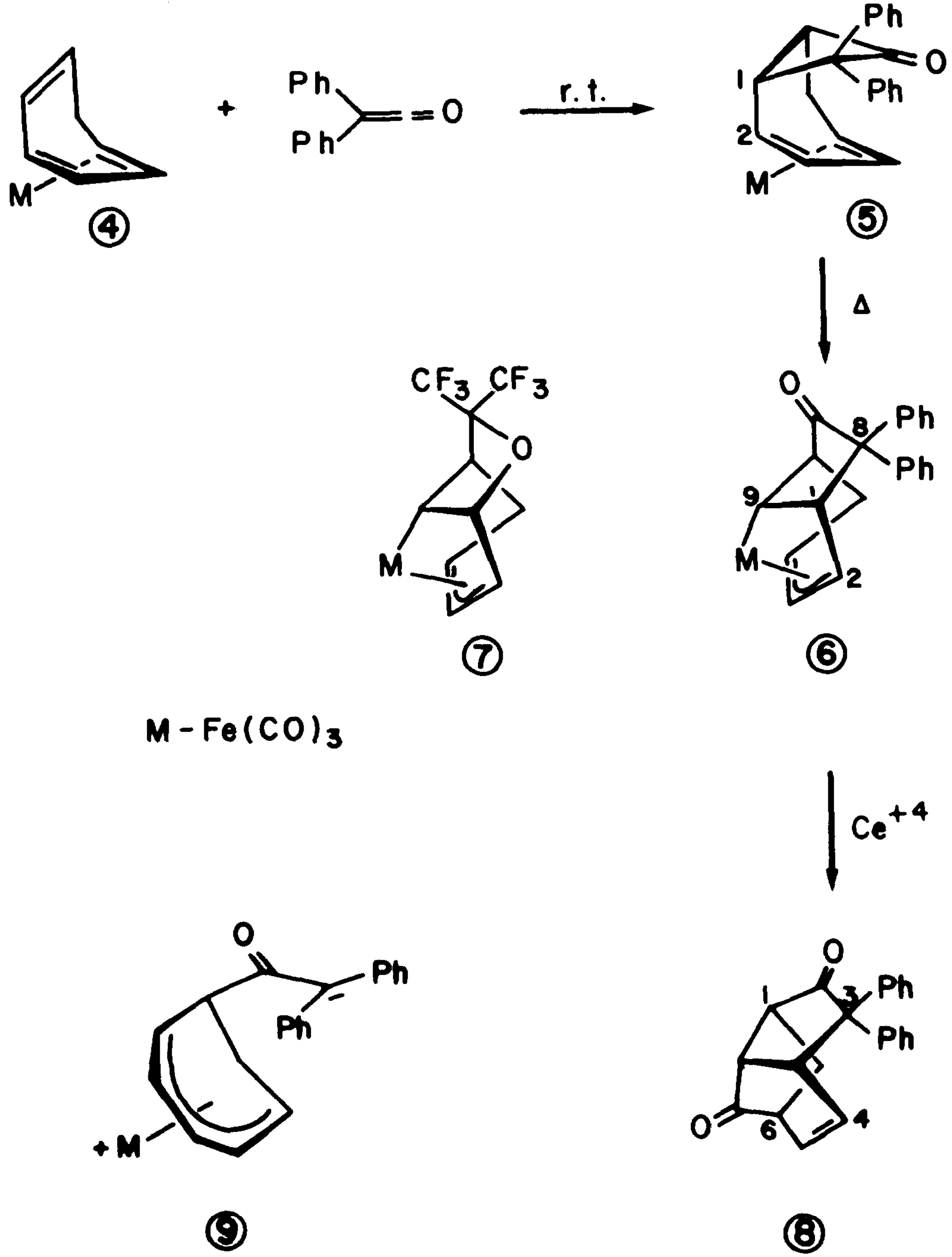
In order further to explore the scope and mechanism of these cycloadditions, we turned to a study of the reaction between triene complexes and ketenes. This communication reports our detailed study of the reaction between cycloheptatrieneiron tricarbonyl (4) and diphenylketene (DPK) which has led to the discovery of a new dyotropic rearrangement[8] and has opened a convenient route to the synthesis of a novel system.

When a benzene solution of complex 4 and DPK was stirred at room temperature under nitrogen, a single crystalline 1:1 adduct could be isolated by column chromatography (mp. 136-8°, from CH_2Cl_2-hexane, 25% yield). The ir spectrum showed in addition to the typical carbonyl ligand absorptions at 2060 and 1980 cm^{-1} a strong signal at 1775 cm^{-1}, clearly indicating the presence of a cyclobutanone ring, consistent with structure 5. This structure was further established by the 100 MHz pmr spectrum ($CDCl_3$), which displayed signals at δ 1.99 (H_6,ddd,2.5,9,18); 2.48 (H_6',dd,5.5,18); 2.72 (H_2,dd,4.5,8); 2.99 (H_5,m); 3.35 (H_7,dd,9,10); 3.83 (H_1,dd,4.5,10); 4.70 (H_3,dd,5,8); 5.10 (H_4,dd,5,8); 7.3 (10H,m, aromatic). These assignments were verified by decoupling experiments.[9]

Upon heating in refluxing benzene dienone complex 5 undergoes a clean thermal rearrangement to an isomeric compound, identified as the σ,π-allyliron tricarbonyl complex 6 (mp. 155-6°, from hexane).[9,10] The pmr spectrum (benzene-d_6) exhibited signals at δ 1.66 (H_9,dd,8,9); 2.02 (H_6,bt,9,10); 2.39 (H_5,ddd,16,10,3.5); 2.69 (H_5',bd,16); 3.35 (H_2,H_3,m); 3.71 (H_1,H_4,m); 7.3 (10H,m,aromatic). This structural assignment was further secured by proton decoupled cmr spectrum which exhibits resonances at δ 22.11 (C_9), 40.49 (C_5), 49.56 (C_6), 55.63 (C_1), 66.41, 72.27 (C_2,C_4), 69.03 (C_8), 98.89 (C_3), 126.4, 127.3, 127.9, 129.9, 139.0, 139.6 (aromatic), 214.1, 212.8, 203.1 (ligand carbonyls), 218.3 (ring carbonyl). This spectrum parallels that of the previously prepared HFA-adduct 7,[4] except for a distinct downfield shift of C_1 in 7 to 82.7 ppm.

These experimental results clearly show that unlike other uniparticulate electrophiles, ketenes prefer to react with cycloheptatrieneiron tricarbonyl through the free double bond in a typical 2+2 concerted cycloaddition. The adjacent diene-$Fe(CO)_3$ moiety, acting as a donor function, facilitates the reaction and determines the observed regiospecificity.[11] More interestingly however, is the subsequent thermal rearrangement of 5 to 6 which is to the best of our knowledge without precedent. Formally, it represents a unique [2,2]-dyotropic rearrangement[8] in which the iron which is attached to C_2 of 5 migrates to the neighbouring carbon, forming the Fe-C_9 σ-bond (in 6), while the diphenylcarbinyl carbon migrates from C_1 to C_2 (in 5) to form the C_1-C_8 σ-bond of 6. Unless we assume an inversion on iron, this rearrangement seems to involve a symmetry forbidden (2_a+2_a) thermal reaction and thus may alternatively involve the intermediacy of a polar zwitterion 9. Finally, we note that while formation of cycloadduct 5 is kinetically controlled, the σ,π-allyl isomer 6 is obtained by a thermodynamically controlled process.

Ceric ion oxidation of complex 6 afforded mainly a single iron free compound which was isolated by preparative tlc (20% yield, mp. 166-167°, cyclohexane). The elemental analysis and the mass spectrum indicated that a carbonyl insertion took place during oxidation. The ir spectrum showed a broad band at 1735 cm^{-1} (cyclopentanone). This data together with the pmr spectrum (benzene-d_6) which displayed signals at δ 1.68 (1H methylene,ddd,5.5,11,13); 1.99 (1H methylene,bd,13); 2.0-2.4 (H_1,H_6,m); 2.78 (H_{7a},dd,5.5,7.5); 3.87 (H_{3a},dd,4,5.5); 4.86 (H_4,dd,4,9); 5.47 (H_5,dd,7.5,9); 7.3 (10H aromatic,m), supported the structural assignment 8.


④
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Thus, in contrast to the behavior of complexed cycloheptatriene-TCNE adducts which undergo an oxidative rearrangement with cerium reagent,[6] complex 6 suffers an unrearranged oxidative collapse accompanied by carbonyl insertion leading to the novel 1,6-methanoindene system 8.[12,13] This convenient synthetic route to the highly condensed tricyclic diketone again reveals the power of transition metal complexes as organic synthons.

References and Footnotes

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9) Satisfactory elemental analysis and appropriate spectroscopic data.

10) Alternatively, 6 could be directly obtained by reacting CHT-Fe(CO)$_3$ and DPK at the temperature of refluxing benzene.

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13) 3,3-Diphenyl-2,3,3a,6,7,7a-hexahydro-1,6-methano-1H-indene-2,7-dione.