Synthesis, characterization and reactions of novel cycloketones \( C_6H_2(CH_2)_4(CO)_2 \) and \( C_6(CH_2)_6(CO)_3 \)

S S Ullah*, F R Alam & M R Haque
Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh

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Reactions of \( \text{AlCl}_3 \) with 2,3,5,6-tetramethylenebicyclo[2.2.0]-hexadienironhexacarbonyl \( 3 \) and 1,2,3,4,5,6-hexamethyleneacyclohexanemonocarbonyltririon \( 5 \) in refluxing THF yield cycloketones \([C_6H_2(CH_2)_{4}(CO)]_4 \) and \([C_6(CH_2)_{6}(CO)]_6 \) respectively. The novel cycloketones 4 and 6 along with 2,4-dinitrophenylhydrazine derivative of the 4 have been characterized by IR, \(^1\)H NMR and mass spectra.

Many organo-iron complexes play an important role in organic synthesis. Some diene \( \text{Fe(CO)}_3 \) complexes can be converted to cyclopentanones by treatment with \( \text{AlCl}_3 \). For example, 2-indanone 2 may be isolated according to the reaction given in Scheme I. Preparation of \( \text{exo-} \) and \( \text{endo-} \)-complexes\(^2 \) of \( \text{R-(-)} \) phellandrene 2 and subsequent ring expansion showed complete retention of chirality as shown in Scheme II. In view these observations, we report herein the results of our investigation on the reaction of \( \text{AlCl}_3 \) with 2,3,5,6-tetramethylenebicyclo[2.2.0]-hexadienironhexacarbonyl \( 3 \) and 1,2,3,4,5,6-hexamethyleneacyclohexanemonocarbonyltririon \( 5 \). The main objective was to achieve the synthesis of some novel cycloketones and their derivatives.

The reaction of \( \text{AlCl}_3 \) with 2,3,5,6-tetramethylenebicyclo[2.2.0]-hexadienironhexacarbonyl \( 3 \) resulted in the isolation of a colourless solid, \([C_6H_2(CH_2)_{4}(CO)]_4 \) \( 4 \) in 43% yield. This compound was characterized by IR, \(^1\)H NMR and mass spectroscopic data. The IR spectrum of \( 4 \) in \( n \)-hexane showed one \( \nu \text{C}=\text{O} \) band at 1725 cm\(^{-1} \). This upward ketonic frequency is characteristic of a cycloketone in which no mesomeric and inductive effects are indicated. Generally, cyclic ketones tend to increase in \( \nu \text{C}=\text{O} \) absorption frequency as the strain of the ring becomes greater\(^3 \). This absorption frequency of \( \nu \text{C}=\text{O} \) gives strong evidence for the product being a cycloketone. The \(^1\)H NMR spectrum of compound \( 4 \) in \( \text{CDCl}_3 \) exhibited signals at \( \delta 0.85 \) (s, 2H) and \( 1.23 \) (s, 8H) with the intensity ratio 1:4 and no absorption in the aromatic region. The high-field singlet at \( 0.85 \) is due to the proton \( \text{H}_8 \), attached to the bridging sp\(^3 \) carbon atoms which is responsible for their high field shift. The singlet at \( \delta 1.23 \) accounts for the presence of methylene protons \( \text{H}_8 \) which are magnetically equivalent. Magnetic anisotropic effect of the C=O group is not particularly significant on the methylene protons. The mass spectrum of \( 4 \) showed the molecular ion peak \( (M^+) \) at \( m/z \) 186, by initial ionization, which favourably fits into the proposed molecular formula \( C_{12}H_{10}O_2 \). Other important peaks appeared at \( m/z \) 172, 158, 130 and 102 indicating successive loss of two \( \text{CH}_2 \) units and two \( \text{CO} \) groups from the molecular ion peak \( M^+ \). The peaks at \( m/z \) 144 and 115 are due to the sequential loss of \( \text{CH}_2 \) and \( \text{C}=(\text{O}+\text{H}) \) from 172. This type of fragmentation pattern is observed in cyclic ketones, for example in 3,3,5-trimethylcyclohexanone\(^4 \). Thus, on the basis of above arguments and spectral evidences the structure of the compound 4 is proposed as shown in Scheme III.

The mechanism of ketone formation\(^5 \) is believed to be the electrophilic attack of an activated carbonyl group of the (diene) \( \text{Fe(CO)}_3 \) moiety of complex 3 as shown in Scheme IV. \( \text{AlCl}_3 \) here acts as strong Lewis acid. The transition intermediate [B], which contains a metal to carbon \( \sigma \)-bond rapidly undergoes cyclization to give the cycloketone 4.

The reaction of \( \text{AlCl}_3 \) with 1,2,3,4,5,6-hexamethyleneacyclohexanemonocarbonyltririon \( 5 \) in 3:1 molar ratio was carried out in distilled THF at reflux temperature for 12 hr. It resulted in the
isolation of a colourless solid compound 

\[ \text{[C}_6\text{H}_2\text{(CH}_2)_6\text{(CO)}_3\text{]}\text{6, which was characterized by IR,} \]

\[ ^1\text{H NMR and mass spectroscopic data. The IR} \]

spectrum of 6 in n-hexane exhibited one \(\nu_{\text{C}=\text{O}}\) band at 1746 \(\text{cm}^{-1}\). This upward stretching frequency is due to the cyclic ketone. The \(^1\text{H NMR of 6 in CDCl}_3\)

exhibited only one singlet at 81.24 (s, 12H) and no peak in aromatic region. This highfield singlet accounted for the presence of methylene protons which are attached to the aromatic ring and are magnetically equivalent.

The mass spectrum of 6 did not exhibit the expected molecular ion peak at m/z 240; instead it showed peaks at m/z 239 arising by rapid loss of one H atom from molecular ion peak (M'). Other important peaks at m/z 225, 211, 197, 169, 141, 113,

99, 85 and 72 are due to the sequential loss of three \(\text{CH}_2\) units, three \(\text{CO}\) units, two \(\text{CH}_2\) units and a \(\text{CH}\) unit from (M' - 1) or peak at m/z 239. Therefore, on the basis of the foregoing discussion and spectroscopic evidences the structure of the complex was proposed as 6 (cf Scheme V). The reaction is believed to have proceeded according to the same scheme as shown for the reaction in Scheme VI.

The reaction of novel cycloketone 4 

\[ \text{[C}_6\text{H}_2\text{(CH}_2)_6\text{(CO)}_3\text{]}\text{4 with 2,4-dinitrophenylhydrazine} \]

in ethanol in 1:1 molar ratio at room temperature, resulted in the isolation of a reddish-yellow crystalline hydrazone 7. The \(^1\text{H NMR spectrum of 7 in CDCl}_3\)

exhibited peaks at 80.86 (s, 2H), 1.24 (s, 8H), 4.59 (s, H) and 7.86 (m, 3H). The high-field singlet at 80.86 is due to the protons attached to the bridging \(sp^3\)

carbon atoms (responsible for high field shift). But, the singlet at 81.24 accounts for the presence of methylene protons which are magnetically equivalent. The peak at 4.59 (s, H) is due to the proton which is attached to nitrogen atom. The multiplet at 7.86 is due three aromatic protons. The absence of a signal due to protons of NH\(_2\) group of hydrazine provides further evidence for the formation of hydrazone derivative.

**Experimental Section**

**General.** All reactions and operations were conducted under dry nitrogen atmosphere. THF was distilled under nitrogen from sodium benzophenone ke-
tly prior to use. Hydrocarbon solvents were dried over sodium wire. AlCl₃ was purchased from Aldrich and was used after sublimation. 2,3,5,6-Tetramethylenecyclo-
1-2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron 5 were prepared according to the methods reported earlier by us. IR spectra were recorded on a Shimadzu 8010 spectrometer, ¹H NMR spectra on a Bruker 250 MHz spectrometer and mass spectra on a high resolution mass spectrometer.

Reaction of AlCl₃ with 2,3,5,6-tetramethylenecyclo-
1-2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron 5. To the freshly sublimed AlCl₃ (0.065g, 0.48 mmole) in dis-
tilled THF (20 mL) was added dropwise a solution of 2,3,5,6-tetramethylenecyclo-
1-2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron 5 (0.1g, 0.24 mmole) in THF (30 mL) from a dropping funnel under nitrogen atmosphere. The re-
ation mass was then refluxed for about 12 hr, and by this time its colour became yellowish-red to colour-
less. The course of reaction was monitored by TLC analysis. After the completion of reaction, the solvent was removed under vacuum and the residue extracted twice with pet.ether (40-60 °C). The pet.ether extract was then filtered on kieselguhr. The filtrate was concen-
trated to dryness to give a colourless mass which was dissolved in minimum volume of diethyl ether and chromatographed over silica gel TLC plates. Elution with pet.ether (40-60 °C) gave
[C₆H₄(CH₂)₄(CO)₂]₄ as colourless solid (0.0195g, 43%). IR (n-hexane): νC=O at 1725 cm⁻¹; ¹H NMR (CDCl₃): 80.85 (s,2H), 1.23 (s,8H); MS : m/z 186 (M⁺), 172[M⁺-CH₃], 158[M⁺-2CH₃], 144 [M⁺-
(CH₂+CO)], 130[M⁺-(2CH₃+CO)], 116[M⁺-(CH₂+2CO)], 115[M⁺-(CH₂⁺ 2CO+H)], 102[M⁺-
(2CH₂+2CO)].

Reaction of AlCl₃ with 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron 5. To the freshly sublimed AlCl₃ (0.0347g, 0.26 mmole) in dis-
tilled THF (20 mL) was added dropwise a solution of 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbo-
ylniiron 5 (0.05g, 0.086 mmole) in THF (20 mL) from a dropping funnel under nitrogen atmosphere. It was then refluxed for about 12 hr, and by this time colour of this mixtures became reddish-yellow to colourless. The course of the reaction was monitored by TLC analysis. The rest of the procedure adopted was the same as described above yielding
[C₆(CH₂)₆(CO)₃]₆ as a colourless solid (0.085g, 40.8%). IR(n-hexane): νC=O at 1746 cm⁻¹; ¹H NMR (CDCl₃): 81.24 (s,12H); MS : m/z 239 (M⁺-H), 225[M⁺-(H+CH₂)], 211[M⁺-(H+2CH₂)], 197[M⁺-
(H+3CH₂)], 169[M⁺-(H+3CH₂+CO)], 141 [M⁺-
(H+3CH₂+2CO)], 113 [M⁺-(H+3CH₂+3CO)], 99 [M⁺-
(H+4CH₂+3CO)], 85[M⁺-(H+5CH₂+3CO)+], 72[M⁺-
(6CH₂+3CO)].

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References