REACTIONS OF COORDINATED CYCLIC POLYOLEFINS *.
REGIO- AND STEREO-SPECIFIC CYCLOADDITIONS OF KETENES AND TRICARBONYL(η^4-POLYENE)IRON COMPLEXES. STRUCTURAL EVIDENCE FOR A CONCERTED 2 + 2 MECHANISM

ZEEV GOLDSCHMIDT *, SHLOMO ANTEBI, DRORA COHEN,

Department of Chemistry, Bar-Ilan University, Ramat Gan 52100 (Israel)

and ISRAEL GOLDBERG

Department of Chemistry, Tel Aviv University, Ramat Aviv 69978 (Israel)

(Received April 24th, 1984)

Summary

The cycloaddition of ketenes $R^1R^2C=C=O$ ($R^1 = Me$, $R^2 = Ph$; $R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = p\text{-tolyl}$) (III) and tricarbonyl(η^4-cycloheptatriene)iron (II) at room temperature gave regiospecifically the cyclobutanones IV, in which the carbonyl is bonded to the uncoordinated terminal of the conjugated triene. Tricarbonyl(η^4-cyclooctatetraene)iron, VI, similarly reacts with dipenylketene to give the regio-isomeric cyclobutanone VIII. Single crystal X-ray analysis of tricarbonyl[(η-2,3,4,5)-9-methyl-9-phenylbicyclo[5.2.0]nonan-2,4-dien-8-one]iron (IVa) confirmed the presence of the phenyl group at the *endo* position, providing a stereochemical evidence for a concerted $2s + 2a$ cycloaddition mechanism. The adducts IV undergo cyclobutanone ring cleavage catalyzed by acid to give the isomeric ketones VII. The diaryl adducts (IVb and IVc) rearrange thermally to the σ,π-allylic complexes IX, which may also be obtained directly upon heating cycloheptatriene complex II and the diarylketenes.

Introduction

Ketenes possess a unique property among uniparticulate electrophiles [2] in their capability to undergo perispecifically 2 + 2 cycloaddition reactions with alkenes [3]. Nonpolar ketenes react with electron rich alkenes (eq. 1) and with conjugated olefins (eq. 2) to give regiospecifically the cyclobutanones in which the functional group resides at the β-position to the carbonyl group. When the ketene is unsymmetrically
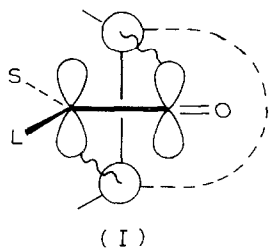
---

(1)

(2)
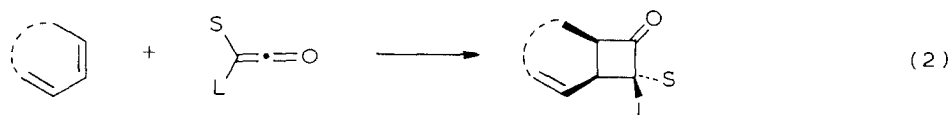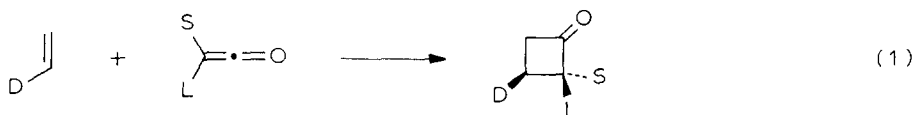
D = donor
S = small, L = large

substituted a stereospecific cycloaddition is observed whereby the bulkier group (L) assumes the more crowded position. Reactions with cyclic alkenes thus lead to the isomer in which the large group (L) appears at the *endo* position (2). These and


(I)

further kinetic [4] and theoretical [5] data are consistent with a concerted $\pi 2s + \pi 2a$ cycloaddition mechanism [5a] involving a perpendicular transition state (I) in which the ketene plays the role of the antarafacial π component and the small group (S) is oriented inward.

Donor-substituted alkenes which can greatly stabilize a positive charge may react with ketenes with the loss of stereo- and peri-specificity, presumably in a stepwise reaction pathway involving a bipolar intermediate [6.5c]. Of particular interest are the reactions of metal bonded unsaturated systems with ketenes. Wojcicki et al. [7] have shown that diphenylketene (DPK) among other heterocumulenes cycloadds to 2-alkynylmetal complexes in a 3 + 2 fashion, presumably via a bipolar η^2-olefinmetal intermediate [8] (eq. 3). A similar bipolar intermediate has been recently suggested

(3)

(4)
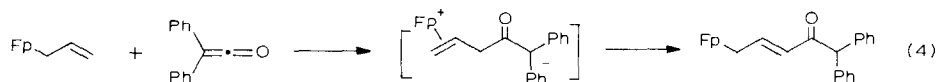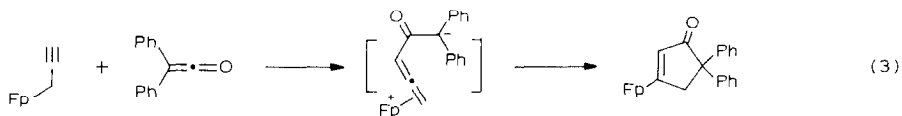
Fp = $(\eta^5-C_5H_5)Fe(CO)_2$

by Rosenblum [9] for the acylation of $(\eta^1$-allyl)Fp (Fp = $\eta^5-C_5H_5Fe(CO)_2$) with ketenes (eq. 4). We, however, have previously reported [10] that the peripheral

$$M = Fe(CO)_3$$

a R = Ph, R' = Me
b R = R' = Ph
c R = Ph(p-tolyl)
   R = p-tolyl(Ph)
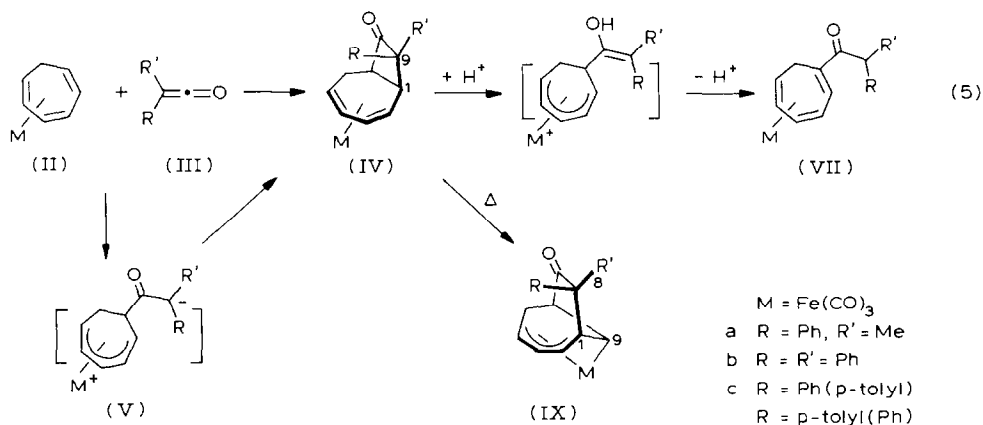
double bond of tricarbonyl(cycloheptatriene)iron (II) reacts with DPK (IIIb) in the usual $2 + 2$ fashion to give cyclobutanone IVb (eq. 5). Since the (diene)Fe(CO)$_3$ group is known to be very effective at stabilizing a positive charge [11], it was of interest to verify whether this cycloaddition is stepwise, via zwitterion V, or concerted.

In this paper we present the results of our study on the reaction of (η^4-cycloheptatriene)Fe(CO)$_3$ (II) and (η^4-cyclooctatetraene)Fe(CO)$_3$ (VI) with arylketenes III, and provide stereochemical evidence for a concerted $2 + 2$ cycloaddition mechanism. We also describe herein the thermal and catalyzed rearrangements of the resulting cyclobutanones. Some aspects of this work have been briefly communicated previously [10,12].

Results and Discussion

When a mixture of methylphenylketene (IIIa) and tricarbonyl(cycloheptatriene)-iron (II) in benzene was kept for 1 month at room temperature, a single 1/1 adduct was isolated by flash chromatography on a Florisil column in 38% yield. The analytical and spectroscopical data are consistent with the structure of cyclobutanone complex IVa. The IR spectrum showed a strong absorption band at 1765 cm^{-1} of the cyclobutanone carbonyl and two ligand carbonyl bands at 1965 and 2005 (broad) cm^{-1}. The Raman spectrum in the solid state confirmed the presence of an Fe(CO)$_3$ group by displaying three characteristic carbonyl stretching vibrations at 1958, 1980 and 2034 cm^{-1} [13].

The ^{1}H NMR spectrum of IVa revealed the presence of only one stereoisomer whose methyl singlet appeared at δ 1.68 ppm. The η^4-diene moiety displayed at high field two resonances of the outer protons, H(2) and H(5) at 2.66 and 2.98 ppm, and a pair of low field signals of the inner protons, H(3) and H(4), at 4.50 and 4.98 ppm. The methylene protons at δ 2.06 (H(6x)) and 2.50 (H(6n)) were distinguished by the large geminal coupling constant J 17 Hz, leaving two high field resonances at δ 2.98 and 3.57 for the bridgehead protons H(1) and H(7), and an aromatic five protons signal at δ 7.3 ppm.

The ^{13}C NMR spectrum of IVa confirmed the presence of a single stereoisomer by a methyl signal at δ 27.9 ppm. The nonaromatic carbon resonances are typical of

the complexed bicyclo[5.2.0]nona-2,4-dien-8-one system [10] and appear at δ 22.7 (C(6)), 40.8 (C(1)), 50.7 (C(7)), 58.3 (C(2)), 59.4 (C(5)), 71.8 (C(9)), 87.1 (C(4) and 90.0 (C(3)) ppm. The ligand and ring carbonyls appeared at δ 210.8 and 212.2 ppm.

Similarly prepared and characterized were the 2 + 2 adducts IVb and IVc obtained by the reaction of complex II with diphenyl- (IIIb) and phenyltolyl-ketene (IIIc). The latter constitutes an inseparable mixture of stereoisomers. Care must be

(VI)   (III)   (VIII)
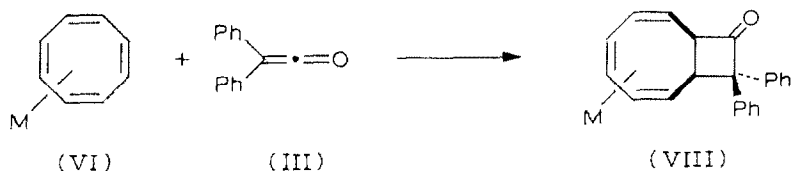
taken not to leave the cyclobutanones IV on the chromatographic column for extended times or else they will undergo ring cleavage to the corresponding ketones VII, presumably via an acid catalyzed isomerization [12].

Diphenylketene (IIIb) also reacts with η^4-cyclooctatetraene complex VI in refluxing benzene to give adduct VIII, whose spectroscopic features resemble those of the corresponding cycloheptatriene cycloadducts (see Experimental Section), (eq. 6).

Cyclobutanone IVa remains stable when heated in toluene to 80°C. Higher temperatures cause a slow decomposition of IVa with the formation of the cycloheptatriene complex II (detected by TLC), as a result of thermal cycloreversion. In contrast, the diarylcyclobutanones IVb and IVc rearrange upon heating in refluxing benzene to the corresponding σ,π-allylic complexes IXb [10] and IXc (as a mixture of isomers). The rearrangement is accompanied by some cycloversion as indicated by the formation of small amounts of complex II. Alternatively, IXb and IXc, but not IXa, could be directly obtained from II and the corresponding ketenes when the reaction was carried out at 80°C. Isomers IX, formally obtained by a 3 + 2 cycloaddition of the diarylketenes and II are readily characterized by their NMR spectra. Specifically, we note the typical high field absorption of H(9) at δ 1.99 ppm (CDCl$_3$) and the corresponding C(9) resonance at δ 22.1 ppm [10,14]. The detailed spectroscopic data are given in the Experimental Section.

In order to verify the regio- and stereo-chemistry of the 2 + 2 adducts, a single crystal X-ray analysis of IVa was carried out, which unequivocally established that the carbonyl group was bonded to C(6) of the starting complex II and that the more bulky phenyl group at C(9) of IVa is *endo* (Fig. 1).

Crystal structure analyses of IVa *

X-ray diffraction data were measured on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator, employing Mo-K_α radiation (λ 0.71069 Å). The unit-cell dimensions were determined from 2θ measurements of 20 carefully centered reflections and refined by the method of least-squares. Intensity data were collected in the ω–2θ mode with a scan width of $0.8 + 0.3 \tan \theta$ out to $2\theta = 54°$. The scan rate varied according to the detected intensity between 1.2 and 4° min^{-1}. In addition to corrections for background, variable measuring time and the Lorentz-

---

* The atom numbering in this section is as shown in Fig. 1

polarization factor, the intensities were modified by $(1.0 - \alpha)^{-1}$ to account for the slow deterioration of the crystals (the maximum value of α was 0.06) which was almost proportional to the time. Because of the small size of the analyzed crystals absorption corrections were not considered necessary.

Crystal data: $C_{19}H_{16}FeO_4$, $M_r = 364.2$, monoclinic, a 12.701(6), b 6.570(2), c 21.048(4) Å, β 106.46(3)°, V 1684.4 Å^3, $Z = 4$, d_c 1.436 g cm^{-3}, $F(000) = 752$, space group $P2_1/n$.

The structure was solved by a combination of direct methods (MULTAN 80) and Fourier techniques. Refinement was carred out by full-matrix least-squares calculations including the atomic coordinates and anisotropic thermal parameters of the nonhydrogen atoms. Most of the hydrogen atoms were located directly from electron
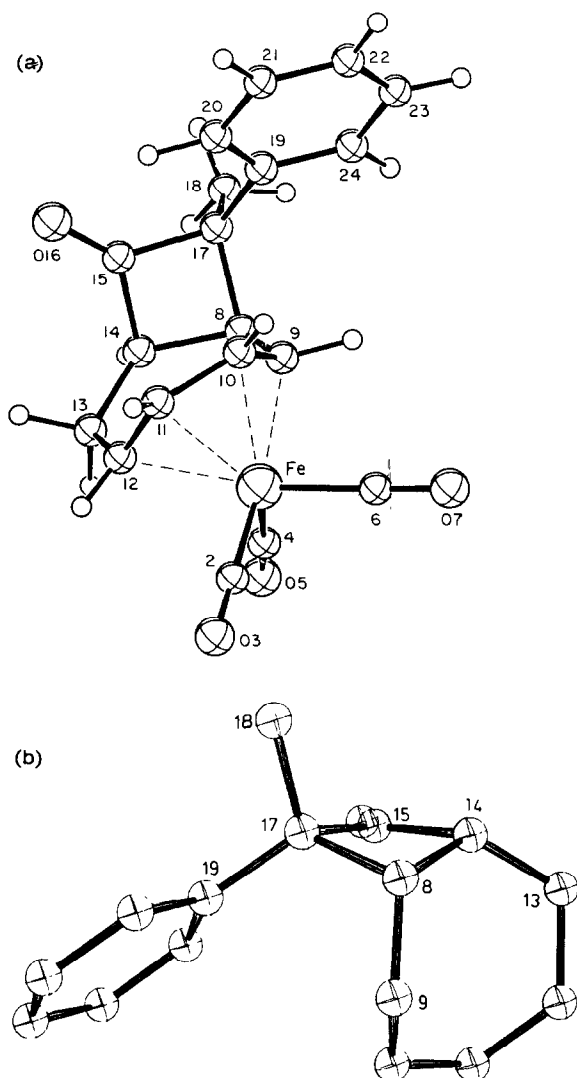

Fig. 1. Stereoscopic views of cyclobutanone complex IVa. (a) Top view, including hydrogens. (b) Side view, $Fe(CO)_3$ and hydrogens omitted.

density difference maps; hydrogens of the phenyl ring, which exhibit a relatively high thermal motion, were introduced in calculated positions. The hydrogen atoms were assigned isotropic temperature factors, but their atomic parameters were not refined except for a partial adjustment of the coordinates at an intermediate state with low order data below $\sin\theta/\lambda$ 0.50 Å. The final discrepancy index at the end of the refinement was $R = 0.035$ for 2856 unique observations above threshold of 3σ. The final difference Fourier maps showed no indications of incorrectly placed or missing atoms; diffraction ripples (ranging from -0.4 to $+0.4$ eÅ^{-3}) appeared only

TABLE 1

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF COMPOUND IVa [a]

Atom	x	y	z	$U_{eq}/U(\text{Å}^2)$
Fe(1)	5324(1)	1097(1)	1612(1)	362
C(2)	6752(2)	1285(4)	2016(1)	549
O(3)	7569(2)	1392(3)	2279(1)	863
C(4)	4912(2)	−641(3)	2144(1)	437
O(5)	4640(2)	−1643(3)	2508(1)	686
C(6)	5552(2)	−530(4)	990(1)	575
O(7)	5661(2)	−1616(4)	583(1)	929
C(8)	2753(2)	1702(3)	1275(1)	366
C(9)	3723(2)	1592(3)	998(1)	375
C(10)	4440(2)	3227(3)	969(1)	390
C(11)	5050(2)	4184(3)	1545(1)	408
C(12)	4975(2)	3545(3)	2178(1)	390
C(13)	3963(2)	3432(3)	2412(1)	412
C(14)	2884(2)	3050(3)	1901(1)	371
C(15)	2305(2)	4725(4)	1437(1)	416
O(16)	2276(2)	6532(3)	1495(1)	665
C(17)	1849(2)	3248(4)	867(1)	397
C(18)	691(2)	2597(5)	873(1)	628
C(19)	1878(2)	3831(4)	176(1)	471
C(20)	2259(2)	5687(5)	39(1)	649
C(21)	2310(3)	6166(6)	−597(2)	920
C(22)	1959(3)	4797(9)	−1095(2)	1083
C(23)	1586(3)	2934(8)	−970(2)	1011
C(24)	1543(3)	2436(5)	−039(1)	750
H(8)	252	19	131	50
H(9)	355	64	56	50
H(10)	461	365	56	50
H(11)	566	519	152	50
H(12)	563	390	255	50
H(13A)	392	485	266	50
H(13B)	405	236	282	50
H(14)	234	254	216	50
H(18A)	48	130	67	60
H(18B)	10	361	71	60
H(18C)	64	232	133	60
H(20)	258	674	42	70
H(21)	262	760	−69	70
H(22)	201	516	−154	70
H(23)	130	182	−131	70
H(24)	126	104	−27	70

[a] For nonhydrogen atoms U_{eq} represents the equivalent value of the anisotropic Debey–Waller factor.

in the vicinity of Fe. The refined atomic parameters are listed in Table 1. Bond lengths and bond angles are given in Table 2. Figure 1 shows two perspective views of the molecular structure of IVa which emphasize the twisted conformations of the seven and four membered rings.

The coordinated cycloheptadiene ring has essentially a boat conformation, which resembles that of cycloheptatriene (X) [15], with C(14) of IVa comprising the boat's
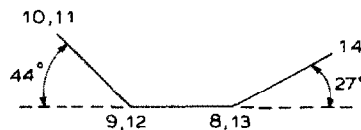
(X)

prow instead of the methylene group of X. The slightly twisted (ca. 4°) central plane defined by C(8), C(9), C(12) and C(13) and the plane containing the four coordinated carbons C(9)–C(12) intersect with an average dihedral angle of ca. 44° (XII)
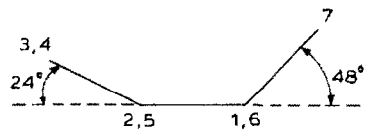
(XI)   (XII)

TABLE 1a

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF COMPOUND IVa

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Fe(1)	337(2)	386(2)	379(2)	65(1)	70(1)	128(1)
C(2)	455(14)	564(15)	639(16)	116(12)	134(12)	174(12)
O(3)	389(11)	942(17)	1166(20)	67(11)	205(13)	69(12)
C(4)	462(13)	383(12)	467(13)	11(10)	13(10)	133(11)
O(5)	880(15)	563(11)	678(12)	−128(11)	123(9)	321(12)
C(6)	629(16)	587(15)	553(15)	252(13)	112(12)	239(13)
O(7)	1232(22)	944(16)	706(14)	465(16)	−72(12)	430(15)
C(8)	354(11)	355(10)	377(11)	−33(9)	−14(8)	85(9)
C(9)	398(11)	390(11)	331(10)	57(9)	−33(8)	95(9)
C(10)	390(11)	453(11)	· 355(11)	110(10)	111(9)	154(9)
C(11)	374(11)	359(11)	515(13)	16(9)	65(9)	167(10)
C(12)	363(11)	394(12)	385(11)	−29(9)	5(9)	62(9)
C(13)	462(12)	466(12)	318(10)	−15(10)	−39(9)	127(9)
C(14)	384(11)	406(11)	356(11)	−5(9)	16(9)	160(9)
C(15)	397(12)	455(12)	436(12)	57(10)	7(10)	182(10)
O(16)	850(14)	456(10)	687(12)	144(10)	−40(9)	217(11)
C(17)	319(10)	473(12)	395(11)	19(10)	32(9)	96(9)
C(18)	331(13)	900(21)	647(17)	−47(13)	43(16)	130(12)
C(19)	322(11)	690(16)	376(11)	96(11)	58(11)	60(9)
C(20)	607(17)	778(20)	578(16)	65(15)	209(15)	193(14)
C(21)	840(24)	1273(33)	730(22)	189(23)	485(23)	358(20)
C(22)	773(25)	1969(50)	561(21)	358(31)	460(28)	276(19)
C(23)	791(24)	1749(43)	420(17)	128(29)	−192(23)	52(17)
C(24)	672(19)	1018(24)	502(16)	−0(18)	−93(16)	72(14)

The anisotropic temperature factor takes the form $\exp[-2\pi^2(U^{11}h^2(a^*)^2 + \ldots 2U^{12}hka^*b^* + \ldots)]$

as compared to the 24° found for the respective angle of fold in cycloheptatriene (XI). On the other hand the average dihedral angle between the central plane of IVa and plane C(8) C(14) C(13) is 27°, significantly smaller than the corresponding folding angle of 48° observed in cycloheptatriene.

In accord with earlier structural studies of diene-Fe(CO)₃ complexes [16], coordination about the iron atom is roughly square pyramidal. The two butadiene double bonds and the pair of ligand carbonyls C(2)O(3) and C(6)O(7) define the basal plane of the pyramid, and the third C(4)O(5) carbonyl is positioned at the apex. This carbonyl arrangement around the metal atom is reflected in the Raman Spectrum of IVa by the C(4)O(5) vibrational stretching band at 2034 cm^{-1} and by the symmetrical and asymmetrical vibrational modes of the pair of basal carbonyls at 1958 and 1980 cm^{-1} [13].

The conformation of the four membered cyclobutanone ring is puckered (Fig. 2).

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) IN COMPOUND IVa

| Fe(1)–C(2)	1 776(2)	C(11)–C(12)	1 425(3)
Fe(1)–C(4)	1.778(2)	C(12)–C(13)	1.504(4)
Fe(1)–C(6)	1.776(3)	C(13)–C(14)	1 503(3)
Fe(1)–C(9)	2.102(2)	C(14)–C(15)	1.516(3)
Fe(1)–C(10)	2.047(2)	C(15)–O(16)	1.195(3)
Fe(1)–C(11)	2.056(2)	C(15)–C(17)	1.524(3)
Fe(1)–C(12)	2.121(2)	C(17)–C(18)	1.535(4)
C(2)–O(3)	1.142(3)	C(17)–C(19)	1.515(3)
C(4)–O(5)	1.135(3)	C(19)–C(20)	1 372(4)
C(6)–O(7)	1.153(4)	C(19)–C(24)	1.377(4)
C(8)–C(9)	1.507(3)	C(20)–C(21)	1.394(5)
C(8)–C(14)	1.556(3)	C(21)–C(22)	1.357(6)
C(8)–C(17)	1.590(3)	C(22)–C(23)	1 365(8)
C(9)–C(10)	1.421(3)	C(23)–C(24)	1.404(5)
C(10)–C(11)	1.391(3)		
C(4)–Fe(1)–C(2)	100.7(1)	C(8)–C(14)–C(15)	87.3(1)
C(6)–Fe(1)–C(2)	92.1(1)	C(13)–C(14)–C(8)	123 9(2)
C(6)–Fe(1)–C(4)	102 5(1)	C(13)–C(14)–C(15)	121.1(2)
C(10)–Fe(1)–C(2)	124.2(1)	C(14)–C(15)–O(16)	132 8(2)
C(10)–Fe(1)–C(4)	130.7(1)	C(14)–C(15)–C(17)	93.0(2)
C(10)–Fe(1)–C(6)	95.6(1)	C(17)–C(15)–O(16)	134.2(2)
C(11)–Fe(1)–C(2)	95.4(1)	C(8)–C(17)–C(18)	111.4(2)
C(11)–Fe(1)–C(4)	127.0(1)	C(8)–C(17)–C(19)	118.0(2)
C(11)–Fe(1)–C(6)	127.1(1)	C(15)–C(17)–C(8)	85.8(2)
Fe(1)–C(2)–O(3)	179.3(3)	C(15)–C(17)–C(18)	108.8(2)
Fe(1)–C(4)–O(5)	175.5(2)	C(15)–C(17)–C(19)	119.2(2)
Fe(1)–C(6)–O(7)	177 4(3)	C(19)–C(17)–C(18)	111.2(2)
C(14)–C(8)–C(9)	116.9(2)	C(17)–C(19)–C(20)	122.2(2)
C(17)–C(8)–C(9)	111.5(2)	C(17)–C(19)–C(24)	119.2(2)
C(17)–C(8)–C(14)	88.9(2)	C(24)–C(19)–C(20)	118.6(3)
C(8)–C(9)–C(10)	125.8(2)	C(19)–C(20)–C(21)	121.2(3)
C(9)–C(10)–C(11)	120.6(2)	C(20)–C(21)–C(22)	119.8(4)
C(10)–C(11)–C(12)	120.9(2)	C(21)–C(22)–C(23)	120.1(4)
C(11)–C(12)–C(13)	127.6(2)	C(22)–C(23)–C(24)	120 2(4)
C(12)–C(13)–C(14)	117.7(2)	C(23)–C(24)–C(19)	120.0(3)
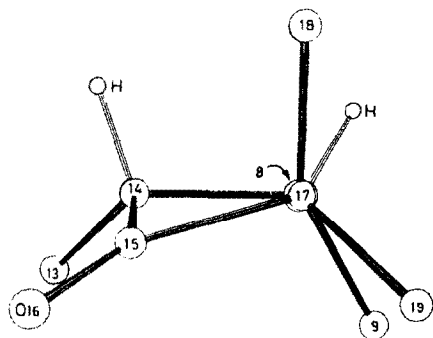
Fig. 2. View of the cyclobutanone ring of IVa along C(17)–C(8) bond. Prominent dihedral angles include C(8)–C(14)–C(17)–C(15), 24.55° (puckering angle); C(9)–C(8)–C(17)–C(19), 19.03°; C(14)–C(8)–C(17)–C(15), 16.63°; C(14)–C(8)–C(17)–C(18), 91.92°; C(18)–C(17)–C(8)–H(8), 27.74°; H(8)–C(8)–C(14)–H(14), 30.44°; carbonyl endo tilt, 2.54°.

The dihedral angle of pucker 24.6° is within the average range of regular cyclo-butanones [17]. Of the two possible bent conformations of the cyclobutane ring the one with the *endo* phenyl group in the less crowded equatorial position is obviously preferred (Fig. 2). This also causes a folding of the carbonyl group toward the *endo*-side of the bicyclic system. These results are fully consistent with those recently obtained by the rigorous conformational analysis of bicyclo[3.2.0]heptanone deriva-tives [18] and related systems [19].

The C(8)–C(17) bond distance 1.590 Å is considerably longer than the expected 1.55 Å of regular C–C bonds in cyclobutane systems [17]. Anomalously long cyclobutane C–C bonds were previously observed in the centrosymmetric dimer of stilbene (2.585 Å) [20] and in the highly strained bicyclo[2.1.0]pentane (1.622 Å) [21]. It is thus not surprising that this bond is relatively easily cleaved upon either thermal or catalyzed reactions [10,12].

Conclusions

Formation of a single stereoisomeric cyclobutanone (IVa) in the reaction of cycloheptatriene complex II and methylphenylketene (IIIa) implies a highly ordered transition state for the 2 + 2 cycloaddition. The observation that the more bulky phenyl group is found at the endo position strongly suggests an orthogonal approach of the two interacting double bonds of II and IIIa as required for a concerted $\pi 2s + \pi 2a$ thermal cycloaddition [5a] where the ketene reacts in an antarafacial manner. The sterically most favorable orientation of the ketene in the orthogonal transition state is the one in which the carbonyl group is placed over the cyclohep-tatriene ring with the smaller methyl group pointing toward the interacting double bond as shown in Fig. 3. The regiospecific ring closure to cyclobutanone will ultimately lead to the observed stereoisomer in which the larger phenyl group is endo oriented.

The analysis of the present 2 + 2 cycloadditions according to the frontier molecu-lar orbital theory as formulated by Houk [5c,22] suggests the $[2s^0 + 1s^K]$ interaction of the complex HOMO and the ketene LUMO (Fig. 3a), and the simultaneous $[2s^0 + 2a^K]$ interaction involving the complex LUMO and ketene HOMO (Fig. 3b).
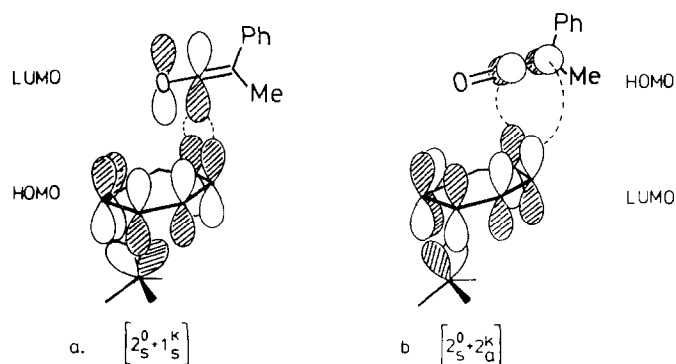
Fig. 3. HOMO-LUMO interactions of $(\eta^4$-$C_7H_8)Fe(CO)_3$ (II) and methylphenylketene (III). (a) $2s^0 + 1s^K$ interaction, (b) $2s^0 + 2a^K$ interaction.

The (diene)Fe(CO)₃ moiety being an electron donor group [23] facilitates the reaction by increasing the energy of the olefin HOMO and also directs the regiospecific bonding of the central sp carbon of the ketene toward C(6) of complex II, where the larger orbital coefficient is expected [22].

It may thus be concluded that unlike the (η^1-allyl)iron complexes which react with ketenes and other heterocumulenes [7,9] in a stepwise bipolar mechanism, the analogous (η^4-triene)iron complexes react with ketenes in a concerted manner.

The rearrangement of the diaryl cyclobutanones IV to the σ,π-allylic isomers IX may also proceed concertedly. This however can not be supported by stereochemical evidence from this work since unfortunately IVa did not rearrange thermally nor could we separate stereoisomers IVc. We are at present investigating this rearrangement with other structural isomers in order to confirm our previous assumptions [10,12].

Experimental

General. ¹H NMR spectra were recorded on Varian Model EM-360A and HA-100 spectrometers. ¹³C NMR spectra were recorded on a Varian CFT-20 spectrometer, with TMS as internal standard. IR spectra were recorded on a Perkin–Elmer Model 257 spectrometer. Mass spectra were determined with a GS/MS Finnigan Model 4000 spectrometer. Elemental analyses were determined in the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

Tricarbonyl[(η-2,3,4,5)-endo-9-phenyl-9-methyl-bicyclo[5.2.0]nona-2,4-dien-8-one]iron (IVa)

A solution of methylphenylketene (IIIa) [24] (0.89 g, 6.7 mmol) and cycloheptatriene complex II [25] (1.22 g , 5.3 mmol) in dry benzene (40 ml) was kept at room temperature for 1 month. The solvent was removed in vacuum and the residue was flash chromatographed on a Florisil column, first with hexane to elute excess II, then with 1/1 hexane/toluene to elute IVa. Recrystallization from CH_2Cl_2/hexane gave yellow prisms (0.5 g, 38% yield) m.p. 135–136°C. IR ($CHCl_3$): 2005 (br), 1965 (ligand CO) and 1765 cm⁻¹ (cyclobutanone CO). Raman (solid): 2034, 1980 and

1958 cm^{-1}; MS: m/e 364 (M), 336, 308, 280 and 224. Anal.: Found C, 62.85; H, 4.26. $C_{19}H_{16}FeO_4$ calcd.: C, 62.66, H, 4.43%. ^1H NMR (CDCl$_3$): δ 1.68 (3H, s), 2.06 (1H, ddd, J 17, 9 and 3 Hz), 2.50 (1H, dd, J 17 and 5 Hz), 2.66 (1H, dd, J 8 and 4.5 Hz), 2.98 (2H, m), 3.57 (1H, dd, J 10 and 9 Hz), 4.50 (1H dd, J 8 and 5 Hz), 4.98 (1H, dd, J 7 and 5 Hz), 7.3 (5H, m) ppm. ^{13}C NMR (CDCl$_3$): δ 22.7 (C(6), t, J 129 Hz), 27.9 (Me(9), q, J 129 Hz), 40.8 (C(1), d, J 140 Hz), 50.7 (C(7), d, J 130 Hz), 58.3 (C(2), d, J 152 Hz), 59.4 (C(5), d, J 145 Hz), 71.8 (C(9), s), 87.1 (C(4), d, J 169 Hz), 90.0 (C(3), d, J 167 Hz), 126.6, 127.1 128.1, 140.6 (aromatic), 210.7, 211.9 (ligand and ring carbonyls) ppm.

Tricarbonyl[(η-2,3,4,5)-9,9-diphenyl-bicyclo[5.2.0]nona-2,4-dien-8-one]iron (IVb) [10]

A solution of diphenylketene (IIIb) [26] (1.27 g, 6.6 mmol) and complex II (1.02 g, 4.4 mmol) in dry benzene (20 ml) was kept at room temperature for 1 week. The solvent was removed in vacuum and the residual oil triturated with hexane to give a yellow precipitate, which was recrystallized from CH_2Cl_2/hexane to give yellow prisms of IVb (0.46 g, 25% yield), m.p. 136–138°C. IR (CHCl$_3$): 2060 (br), 1980 and 1775 cm^{-1}. Anal.: Found C, 67.51; H, 431. $C_{24}H_{18}FeO_4$ calcd.: C, 67.62; H, 4.26% ^1II NMR (CDCl$_3$): δ 1.99 (1H, ddd, J 18, 9 and 2.5 Hz), 2.48 (1H, dd, J 18 and 5.5 Hz), 2.72 (1H, dd, J 8 and 4.5), 2.99 (1H, m), 3.35 (1H, dd, J 10 and 9 Hz), 3.83 (1H, dd, J 10 and 4.5 Hz), 4.70 (1H, dd, J 8 and 5 Hz), 5.10 (1H, dd, J 8 and 5 Hz), 7.3 (10H, m) ppm. ^{13}C NMR (CDCl$_3$): δ 22.62, 38.81, 52.43, 58.18, 59.14, 80.26, 87.22, 90.31, 126.47, 126.70, 127.20, 127.99, 128.17, 128.98, 208.09 and 210.76 ppm.

Tricarbonyl[(η-2,3,4,5)-9-phenyl-9-(4-tolyl)-bicyclo[5.2.0]nona-2,4-dien-8-one]iron (IVc)

This was similarly obtained as a mixture of stereoisomers by treatment of phenyltolylketene (IIIc) [27,26] with complex II, in 18% yield, m.p. 128–130°C (CH$_2$Cl$_2$/hexane). IR (CHCl$_3$): 2030 (Br), 1970 and 1765 cm^{-1}; MS: m/e 440 (M), 412, 384, 356, 300. Anal.: Found C, 68.49; H, 4.56. $C_{25}H_{20}FeO_4$ calcd.: C, 68.20; H, 4.58%. ^1H NMR (CDCl$_3$): 1.95 (1H, ddd, J 18, 8 and 3 Hz) 2.26 and 2.29 (3H, 2x s), 2.42 (1H, dd, 18 and 5 Hz), 2.70 (1H, dd, J 5 and 4 Hz), 2.98 (1H, m), 3.32 (1H, dd, J 10 and 8 Hz), 3.79 (1H, dd, J 10 and 5 Hz), 4.70 (1H, m), 5.09 (1H, dd, J 7 and 5 Hz), 7.3 (9H, m) ppm. ^{13}C NMR (CDCl$_3$): 20.94 and 20.82 (2 × Me), 22.54, 38.83, 52.25, 58.23, 59.27, 79.90 and 80.08 (2 × C(9)), 87.77 and 87.82 (2 × C(4)), 90.21, 126.29, 126.53, 127.02, 127.85, 128.18, 128.90, 129.58, 136.11, 136.85, 137.46, 138.91, 140.64, 141.97, 208.13 and 210.76 ppm.

Tricarbonyl[(η-2,3,4,5)-10,10-diphenyl-bicyclo[6.2.0]deca-2,4,6-trien-9-one]iron (VIII)

A solution of cyclooctatetraene complex VI [28] (3.05 g, 12.5 mmol) and diphenylketene (7.3 g, 37.6 mmol) in dry benzene (100 ml) was refluxed for 5 days. The solvent was removed in vacuum and the residue chromatographed on a Florisil column, using hexane to elute excess VI and 1/1 hexane/toluene to elute the cycloadduct VIII. Recrystallization from CH_2Cl_2/hexane gave bright yellow needles (0.70 g, 13% yield), m.p. 162°C (dec.). IR (CHCl$_3$): 2040 (br), 1990 and 1790 cm^{-1}; MS: m/e 410 ($M-CO$), 382, 354, 298. Anal.: Found C, 68.47, H, 3.89. $C_{25}H_{18}FeO_4$ calcd.: C, 68.57; H, 4.14%. ^1H NMR (CDCl$_3$): δ 3.39 (2H, m), 3.74 (1H, dd, J 12 and 8 Hz), 4.03 (1H, dd, J 10 and 9 Hz), 4.84 (1H, dd, J 8 and 5 Hz), 5.33 (1H, dd, J

8 and 5 Hz), 6.07 (1H, dd, J 9 and 7 Hz), 6.64 (1H, t, J 9 Hz), 7.2 (10H, m) ppm. ^{13}C NMR (CDCl$_3$): δ 43.34, 52.00 (C(1), C(8)), 69.70, 72.14 (C(2), C(5)), 92.04, 95.03, 125.99, 127.25, 127.63, 128.66, 129.14, 130.61, 133.00, 138.18, 139.41, 208.85, 210.02 ppm.

Tricarbonyl[1-[(η-1,2,3,4)-1,3,5-cycloheptatrien-6-yl]-2,2-diphenylethanone]iron (VIIb) [12]

Cyclobutanone complex IVb was absorbed on a Florisil column in a 1/1 hexane/toluene mixture. Elution after 10 h with the same solvent afforded the ketone VIIb in 80% yield from CH$_2$Cl/hexane. Yellow needles, m.p. 159–161°C. IR (Nujol): 2020, 1975, 1955 and 1640 cm^{-1}; MS: m/e 398 (M − CO). Anal.: Found C, 67.39; H, 4.51. C$_{24}$H$_{18}$FeO$_4$ calcd.: C, 67.62; H, 4.26%. ^{1}H NMR (CDCl$_3$): δ 2.35 (1H, dd, J 22 and 3 Hz), 2.81 (1H, dd, J 22 and 3 Hz), 2.99 (1H, t, J 8 Hz), 3.49 (1H, m), 5.34 (2H, m), 5.61 (1H, s), 7.18 (11H, m) ppm. ^{13}C NMR (CDCl$_3$): δ 29.05 (C(7), t, J 131 Hz), 53.76 and 60.48 (C(1) and C(4), 2 × d, J 135 HZ), 57.30 (C(2'), d, J 127 Hz), 88.92, 94.23 (C(2) and C(3), 2 × d, J 167 and 171 Hz), 126.83, 128.53, 128.84, 129.08, 139.83 (C(6), s), 144.53 (C(5), d, J 154 Hz), 197.38, 209.94 ppm.

Tricarbonyl[1-[(η-1,2,3,4)-1,3,5-cycloheptatrien-6-yl]-2-phenylpropanone]iron (VIIa)

This was similarly obtained from IVa as yellow prismatic crystals (from CH$_2$Cl$_2$/hexane), m.p. 111°C. IR (CDCl$_3$): 2035 (br), 1995 and 1645 cm^{-1}, MS: m/e 336 (M − CO), 308, 280, 224. Anal.: Found C, 62.41; H, 4.64. C$_{19}$H$_{16}$FeO$_4$ calcd.: C, 62.66; H, 4.43%. ^{1}H NMR (CDCl$_3$) δ 1.35 (3H, d, J 6.5 Hz), 2.28 (1H, dd, J 21 and 2.5 Hz), 2.79 (1H, dd, J 22 and 5 Hz), 3.03 (1H, dd, J 10 and 8 Hz), 3.50 (1H, m), 4.30 (1H, q, J 6.5 Hz), 5.32 (2H, m) 7.2 (6H, m) ppm.

Tricarbonyl[(η-2,3,4,9)-8,8-diphenyl-bicyclo[4.2.1]nona-3-en-7-one-2,9-diyl]iron (IXb)

A solution of cyclobutanone complex IVb (0.25 g, 1.29 mmol) in benzene (5 ml) was refluxed for 3 h. Removal of solvent in vacuo and chromatography on Florisil gave IXb (0.1 g, 40% yield), m.p. 155–156°C (from hexane). IR (CDCl$_3$): 2060 (br), 1975 and 1725 cm^{-1}. Anal.: Found C, 67.57; H, 4.27. C$_{24}$H$_{18}$FeO$_4$ calcd.: C, 67.63; H, 4.23%. ^{1}H NMR (C$_6$D$_6$): δ 1.66 (1H, dd, J 8 and 9 Hz), 2.02 (1H, bt, J 10 and 9 Hz), 2.39 (1H, ddd, J 16, 10 and 3.5 Hz), 2.69 (1H, bd, J 16 Hz), 3.35 (2H, m), 3.71 (2H, m), 7.3 (10H, m) ppm. ^{13}C NMR (CDCl$_3$): δ 22.1, (C(9)), 40.5 (C(5)), 49.6 (C(6)), 55.6 (C(1)), 66.4 and 72.3 (C(2), C(4)), 69.0 (C(8)), 99.9 (C(3)), 126.4, 127.3, 127.9, 129.9, 139.0, 139.6 (aromatic), 208.1, 212.8, 213.3, 214.1 (ligand and ring CO) ppm.

Tricarbonyl[(η-2,3,4,9)-8-phenyl-8-(4-tolyl)-bicyclo[4.2.1]nona-3-en-7-one-2,9-diyl]iron (IXc). (Mixture of stereoisomers)

A solution of phenylmethylketene (IIIc) (2.0 g, 9.6 mmol) and complex II (2.23 g, 9.6 mmol) in dry benzene (40 ml) was heated to 80°C for 4 days. The solvent was removed in vacuo and the residue chromatographed on a Florisil column, using 1/1 hexane/toluene as eluent. Recrystallization from CH$_2$Cl$_2$/hexane gave yellow crystals (0.42 g, 21% yield), m.p. 153–155°C. IR (CHCl$_3$): 2040, 1975 and 1720 cm^{-1}, MS: m/e 440 (M), 412, 384, 356, 300. Anal.: Found C, 68.18; H, 4.53. C$_{25}$H$_{20}$FeO$_4$ calcd.: C, 68.20; H, 4.58%. ^{1}H NMR: δ 1.99 (1H, m), 2.29 and 2.31 (3H, 2 × s), 2.52 (1H, m) 2.86 (2H, m), 4.61 (1H, bd, J 9 Hz), 4.04 (2H, m), 4.22 (1H, m), 7.1 (9H, m) ppm.

Acknowledgement

References

1 Z. Goldschmidt and S. Antebi, J. Organomet. Chem., 260 (1984) 105.
2 L.A. Paquette, G.R. Allen Jr. and M.J. Broadhurst, J. Am. Chem. Soc., 93 (1971) 4503.
3 Reviews: R.W. Holder, J. Chem. Educ., 53 (1976) 81; L. Ghosez and M.J. O'Donell, in A.P. Marchand and R.E. Lehr (Eds.), Pericyclic Reactions, Academic Press, 1977, Vol. III, p. 79.
4 R. Huisgen and L.A. Feiler and G. Binsch, Chem. Ber., 102 (1969) 3460; J.E. Baldwin and J.A. Kapecki, J. Am. Chem. Soc., 92 (1970) 4868; C.J. Collins, B.M. Benjamin and G.W. Kabalka, J. Am. Chem. Soc., 100 (1978) 2570.
5 (a) R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press, New York, 1970, p. 163; (b) R. Sustmann, A. Ansmann and F. Vahrenholt, J. Am. Chem. Soc., 94 (1972) 8099; (c) K.N. Houk, Acc. Chem. Res., 8 (1975) 361.
6 G.A. Berchthold, G.R. Harvey and G.E. Wilson, Jr., J. Org. Chem., 30 (1965) 2642; P. Otto, L.A. Feiler and R. Huisgen, Angew. Chem., Int. Ed. Eng. 7 (1968) 737; P.R. Brook and K. Hunt, J. Chem. Soc., Chem. Comm., (1974) 989; D. Becker and N.C. Brodsky, ibid., (1978) 237.
7 L.S. Chen, D.W. Lichtenberg, P.W. Robinson, Y. Yamamoto and A. Wojcicki, Inorg. Chim. Acta, 25 (1977) 165.
8 M. Rosenblum, Acc. Chem. Res. 7 (1974) 122; P.B. Bell and A. Wojcicki, Inorg. Chem., 20 (1981) 1585.
9 A. Bucheister, P. Klemarczyk and M. Rosenblum, Organometallics, 1 (1982) 1679.
10 Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271.
11 J.E. Mahler and R. Pettit, J. Am. Chem. Soc., 85 (1963) 3955; M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, J. Chem. Soc. A, (1967) 240; R. Hoffman and P. Hofmann, J. Am. Chem. Soc., 98 (1976) 598; A.J. Pearson, Transition Met. Chem., 6 (1981) 67.
12 Z. Goldschmidt and S. Antebi, J. Organomet. Chem., 206 (1981) C1.
13 P.S. Braterman, Struct. Bonding, 26 (1976) 1; S.F.A. Kettle, Top. Current Chem., 71 (1977) 111.
14 M. Green, S. Heathcock and D.C. Wood, J. Chem. Soc., Dalton Trans. (1973) 1564.
15 R.E. Paris and A. Tulinsky, J. Am. Chem. Soc., 88 (1966) 4583.
16 F.H. Herbstein and M.G. Reisner, Acta Cryst., B, 33 (1977) 3304.
17 R.M. Moriarty, Topics Stereochem., 8 (1974) 271.
18 M. Rey, S.M. Roberts, A.S. Dreiding, A. Roussel, H. Vanlierde, S. Toppet and L. Ghosez, Helv. Chim. Acta, 65 (1982) 703.
19 K.B. Becker, M.K. Hohermuth and G. Rihs, Helv. Chim. Acta, 65 (1982) 235.
20 J.D. Dunitz, Acta Cryst., 2 (1949) 1.
21 R.J. Bohn and Y.-H Tai, J. Am. Chem. Soc., 92 (1970) 6447.
22 K.N. Houk, in A.P. Marchand and R.E. Lehr, (Eds.), Pericyclic Reactions, Academic Press, 1977, Vol. II, p. 181.
23 J.M. Landesberg and L. Katz, J. Organomet. chem., 33 (1971) C15; D. Stierle, E.R. Biehl and P.C. Reeves, J. Organomet. Chem., 72 (1974) 221; J.A. Connor, L.M.R. Derrick, M.B. Hall, J.H. Hillier, M.F. Guest, B.R. Higginson and O.R. Lloyd, Mol. Phys., 28 (1974) 1193; M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
24 G. Quinkert and P. Jacobs, Chem. Ber., 107 (1974) 2473.
25 H.A. Bockmeulen and A.W. Parkins, J. Chem. Soc., Dalton Trans., (1981) 262; M. Brookhart, K. Karel and L.E. Nance, J. Organomet. Chem., 140 (1977) 203.
26 L.I. Smith and H.H. Hoehn, Org. Syn. Coll. Vol. 3 (1955) 356.
27 H.H. Hatt, A. Pilgrim and W.J. Hurran, J. Chem. Soc., (1936) 93.
28 T.A. Manuel and F.G.A. Stone, J. Am. Chem. Soc., 82 (1960) 366.