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PERISELECTIVE CYCLOADDITION OF TRICARBONYLIRON COMPLEXES OF 7-MEMBERED RING UNSATURATED COMPOUNDS WITH DICHLOROCARBENE

MASKING EFFECT OF TRICARBONYLIRON GROUP AND REACTIVITY OF CYCLOADDUCTS

TAKASHI ISHIZU, KAZUNOBU HARANO, NORIYUKI HORI,
MASAMI YASUDA and KEN KANEMATSU*
Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi,
Higashiku, Fukuoka 812, Japan

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Abstract—Dichlorocarbene (DCC) showed significant differences of periselectivity in reactions between 7-membered ring unsaturated compounds with masking and without masking by the tricarbonyliron group. Tricarbonyl[N-(ethoxycarbonyl)-azepine]iron (7) and tricarbonyl(cycloheptatriene)iron (8) gave tricarbonyl[N-(ethoxycarbonyl)-2,3-homoazepine]iron derivative (9) and tricarbonyl(2,3-homocycloheptatriene)iron derivative (10). Oxidative degradation of these adducts (9 and 10) with trimethylamine N-oxide afforded N-(ethoxycarbonyl)-2,3-homoazepine derivative (11) and 2,3-homocycloheptatriene derivative (12). By contrast, treatment of 2 equivalents of *o*-chloranil with these adducts (9 and 10) gave two types of novel spiroadducts (13a and 13b), (14a and 14b), respectively. The structure of adduct 13a was fully established by X-ray analysis.

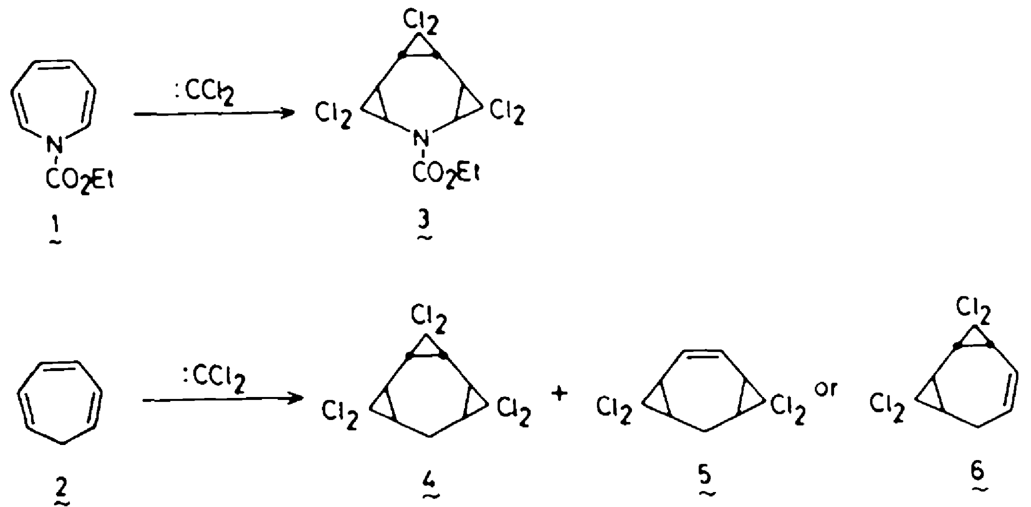
The pericyclic syntheses are very valuable for the stereo-, regio- and periselective controls. Especially during the past decade, the thermal pericyclic reactions of conjugated medium-ring polyenes have aroused considerable interest, and much effort has been made to establish their capability for cycloaddition. Previously Sasaki *et al.*[1] reported that addition of DCC in aqueous medium to medium-membered ring unsaturated compounds proceeded in a highly stereospecific manner. Thus, N-(ethoxycarbonyl)-azepine (1) and cycloheptatriene (2) reacted with DCC to give all-*trans*-σ-tris(homoazepine) derivative 3, and all-*trans*-σ-tris(homocycloheptatriene) derivative 4 and σ-bis(homocycloheptatriene) derivative 5 or 6, respectively (Scheme 1).

Recent synthetic studies by us have shown that coordination of medium-membered ring unsaturated compounds such as N-(ethoxycarbonyl)-azepine (1), cycloheptatriene (2), 8-azaheptafulvene, and tropone to a tricarbonyliron group can lead to significant changes in periselectivities and reaction patterns towards electrophilic reagents such as 2-oxyallyl cation[2] and 1,2,4,5-tetrazine.[3]

This paper deals with the role of tricarbonyliron complexes of these 7-membered ring unsaturated compounds in the cycloaddition reactions with an electron-deficient DCC.

RESULTS AND DISCUSSION

DCC addition to tricarbonyliron complexes of 7-membered ring unsaturated compounds. The reaction of



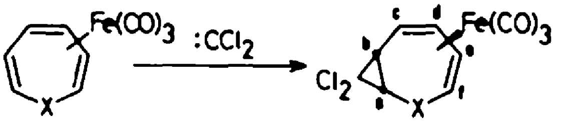
Scheme 1

tricarbonyl[N-(ethoxycarbonyl)-azepine]iron (7) with excess of DCC prepared from chloroform in the presence of aqueous sodium hydroxide-benzene with triethylbenzylammonium chloride as a catalyst afforded tricarbonyl[N-(ethoxycarbonyl)-2,3-homoazepine]iron derivative (9) in 73% yield (Scheme 2).

The structure of the adduct 9 was assigned on the basis of spectroscopic data. The mass spectrum showed ions at *m/e* 388 (M^+), 360 (M^+-CO), 332 (M^+-2CO), and 304 (M^+-3CO) and the IR spectrum exhibited a urethane CO band at 1705 cm^{-1} in addition to tricarbonyliron bands at 1990 cm^{-1} and 2085 cm^{-1}. These spectral data suggested the formation of a 1:1 adduct which consisted of a tricarbonyliron group. In the ^1H NMR spectrum, the methine protons H_a and H_b displayed characteristic signals at 3.14 ppm and 2.03 ppm as a doublet and double doublet, respectively.

Similarly, the reaction of tricarbonyl(cycloheptatriene)iron (8) with excess of DCC under the same conditions afforded tricarbonyl(2,3-homocycloheptatriene)iron derivative (10) in 56% (Scheme 2).

These reactions were expected to give *anti*-adducts, wherein the dichlorocyclopropane ring is oriented *anti* to the tricarbonyliron group, which might be due to the steric hindrance between them.



7 X=NCO$_2$Et
8 X=CH$_2$

9 X=NCO$_2$Et
10 X=CH$_2$

Scheme 2

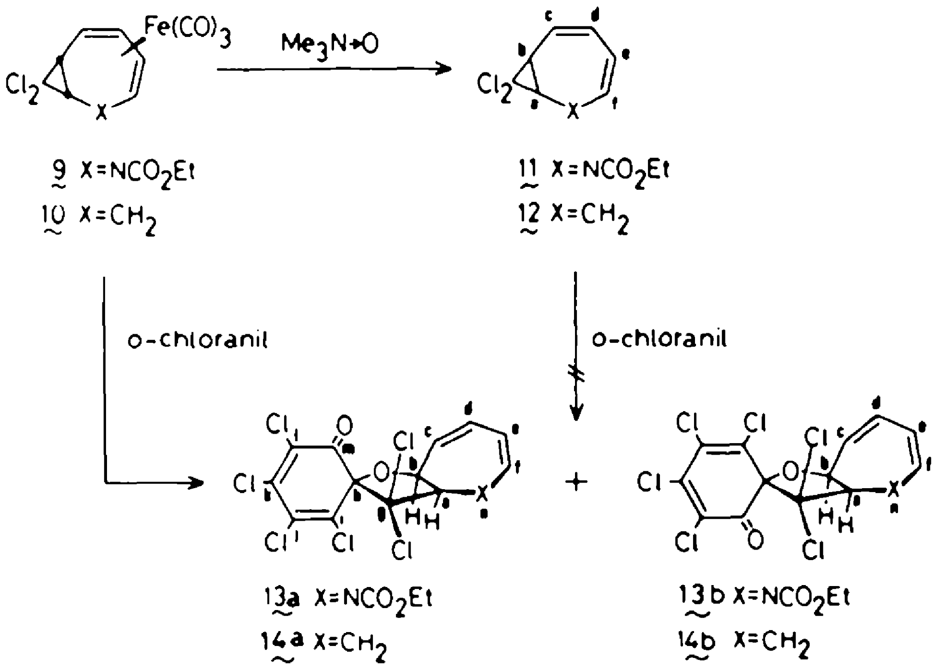
It is interesting that the generation of DCC by various catalytic methods gave the following products. Tricarbonyl(cycloheptatriene)iron (8) reacted with DCC, produced by the reaction of chloroform with a suspension of potassium t-butoxide in heptane, to give a 1:1 adduct (10) but in a low yield.[4] On the other hand, when cycloheptatriene (2) was allowed to react with haloform in the presence of potassium carbonate and 18-crown-6 at 140°, the reaction afforded 1-halobenzocyclobutene in a low yield via the intermediate of 2,3-homocycloheptatriene derivative.[5] However, the tricarbonyliron complexes under these reaction conditions failed to react with DCC. As described above, 7-membered ring unsaturated compounds reacted with DCC by the phase transfer method to afford the bishomo- or trishomo-compounds. From these results, it is pointed out that the coordinated 7-membered unsaturated compounds reacted with DCC by this catalytic method to proceed periselectivity at the C_2–C_3 position in moderate yield.

Oxidative degradation of tricarbonyliron complexes of 2,3-homo-7-membered ring unsaturated compound derivatives with trimethylamine N-oxide

Tricarbonyl[N-(ethoxycarbonyl)-2,3-homoazepine]iron (9) was oxidized with trimethylamine N-oxide to give N-(ethoxycarbonyl)-2,3-homoazepine derivative (11) in 92% yield (Scheme 3). The IR spectrum of adduct 11 did not show the absorption of a tricarbonyliron group. The ^1H NMR spectrum exhibited characteristic signals of two methine protons H_a and H_b at 3.62 ppm and 2.54 ppm as a doublet and double doublet, respectively.

Similar treatment of tricarbonyl(2,3-homocycloheptatriene)iron (10) with trimethylamine N-oxide gave 2,3-homocycloheptatriene derivative (12) in 68% yield (Scheme 3).

Cycloaddition of tricarbonyliron complexes of 2,3-homo-7-membered ring unsaturated compound deriva-



9 X=NCO$_2$Et
10 X=CH$_2$

11 X=NCO$_2$Et
12 X=CH$_2$

13a X=NCO$_2$Et
14a X=CH$_2$

13b X=NCO$_2$Et
14b X=CH$_2$

Scheme 3

ties with o-chloranil and removing tricarbonyliron group. Tricarbonyl[N - (ethoxycarbonyl) - 2,3 - homoazepine]iron derivative (**9**) was allowed to react with 2 equivalents of o-chloranil to give a mixture of stereoisomers (**13a** and **13b**) in total yield of 71% (ratio 1.5:1).

The mass spectrum of the adduct **13a** showed a molecular ion peak at *m/e* 494 (M^+). In the ^1H NMR spectrum, the methine protons H_a and H_b displayed signals at 6.42 ppm and 4.47 ppm as a doublet and doublet of double doublet, respectively. These spectral data were very similar to that of adduct **13b**. However, the IR spectrum of adduct **13a** exhibited urethane and dienone absorptions at 1730 cm^{-1}, while one of adduct **13b** exhibited urethane absorption at 1725 cm^{-1} and dienone absorption at 1710 cm^{-1}.

From these spectroscopic data, the three alternative structures **15**, **16** and **13a**, and their stereoisomers are possible (Chart 1).

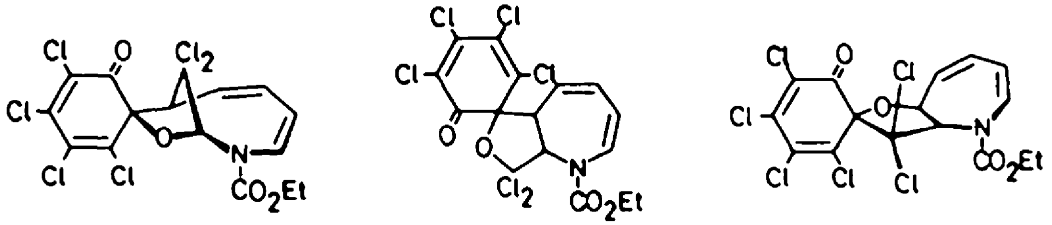
It is unreasonable that there should be five protons in the olefinic field in the ^1H NMR spectrum and only one CO absorption in the IR spectrum.

As described above it was too high field for dienone. Thus, a single crystal X-ray study was undertaken to provide direct proof of structure for the product **13a**.

The crystal structure was solved by the direct method.* Refinement to an R factor of 4.48% was obtained by the method of least-squares on 1563 nonzero structure factors.

The configuration of the molecule with the numbering sequence in this paper is illustrated in Fig. 1, where each nonhydrogen atom is represented as an ellipsoid with 20% probability.

The molecule consists of the cyclohexadienone, the tetrahydrofuran, and the azepine ring. The former two rings are joined through a spiro-C atom ($C_{17}(C_b)$), wherein the dienone carbonyl group and urethane group are on opposite sides (*anti*) with respect to the tetrahydrofuran ring system (Fig. 1). The bond lengths of 1.579 Å for C_{sp^3}–C_{sp^3} bond ($C_{13}(C_a)$–$C_{17}(C_b)$) and 1.549 Å for C_{sp^3}–C_{sp^2} bond ($C_{17}(C_b)$–$C_{18}(C_c)$) are considerably longer than the normal values and these may be due to spiro-C atom strains.* The tetrachlorodiene moiety is roughly planar and the torsion angle of O_{19}–$C_{18}(C_c)$–$C_{20}(C_d)$–$C_{22}(C_e)$ is 155.1°. These facts indicate that the enone CO does not fully conjugate with the diene, which is compatible with the IR absorption band at 1730 cm^{-1} considerably higher than those of unstrained groups. This may be due to the large steric repulsion between Cl_{14} and O_{19} (Cl_{14}–O_{19} 3.08 Å). The UV absorption band



15 **16** **13a**

Chart 1

Table 1 Interatomic distances (Å) and their estimated standard deviations of adduct (13a)

C(1)-C(2)	1.412 (14)	C(13)-Cl(15)	1.769 (7)
C(2)-O(3)	1.447 (10)	C(13)-C(17)	1.579 (9)
O(3)-C(4)	1.336 (9)	O(16)-C(17)	1.397 (8)
C(4)-O(5)	1.197 (9)	C(17)-C(18)	1.549 (10)
C(4)-N(6)	1.417 (10)	C(17)-C(26)	1.524 (9)
N(6)-C(7)	1.420 (10)	C(18)-O(19)	1.191 (9)
N(6)-C(12)	1.441 (9)	C(18)-C(20)	1.473 (10)
C(7)-C(8)	1.317 (11)	C(20)-Cl(21)	1.738 (7)
C(8)-C(9)	1.428 (11)	C(20)-C(22)	1.322 (10)
C(9)-C(10)	1.322 (11)	C(22)-Cl(23)	1.711 (7)
C(10)-C(11)	1.501 (11)	C(22)-C(24)	1.468 (9)
C(11)-C(12)	1.516 (10)	C(24)-Cl(25)	1.710 (7)
C(11)-O(16)	1.449 (9)	C(24)-C(26)	1.303 (9)
C(12)-C(13)	1.520 (9)	C(26)-Cl(27)	1.729 (7)
C(13)-Cl(14)	1.787 (7)		

Table 2 Interatomic angles (deg) with estimated standard deviations of adduct (13a)

C(1)-C(2)-O(3)	107.4 (8)	Cl(15)-C(13)-C(17)	113.4 (5)
C(2)-O(3)-C(4)	116.2 (6)	C(11)-O(16)-C(17)	112.2 (5)
O(3)-C(4)-O(5)	125.1 (7)	C(13)-C(17)-O(16)	106.1 (5)
O(3)-C(4)-N(6)	110.8 (6)	C(13)-C(17)-C(18)	110.7 (5)
O(5)-C(4)-N(6)	124.1 (7)	C(13)-C(17)-C(26)	112.4 (5)
C(4)-N(6)-C(7)	114.7 (6)	O(16)-C(17)-C(18)	108.4 (5)
C(4)-N(6)-C(12)	119.9 (6)	O(16)-C(17)-C(26)	109.8 (5)
C(7)-N(6)-C(12)	125.4 (6)	C(18)-C(17)-C(26)	109.4 (5)
N(6)-C(7)-C(8)	128.4 (7)	C(17)-C(18)-O(19)	121.6 (6)
C(7)-C(8)-C(9)	131.8 (8)	C(17)-C(18)-C(20)	114.8 (6)
C(8)-C(9)-C(10)	129.6 (8)	O(19)-C(18)-C(20)	123.6 (7)
C(9)-C(10)-C(11)	126.4 (7)	C(18)-C(20)-Cl(21)	114.5 (5)
C(10)-C(11)-C(12)	121.1 (6)	C(18)-C(20)-C(22)	121.8 (6)
C(10)-C(11)-O(16)	108.8 (6)	Cl(21)-C(20)-C(22)	123.1 (6)
C(12)-C(11)-O(16)	101.3 (5)	C(20)-C(22)-Cl(23)	120.7 (5)
N(6)-C(12)-C(11)	120.0 (6)	C(20)-C(22)-C(24)	120.7 (6)
N(6)-C(12)-C(13)	116.8 (5)	Cl(23)-C(22)-C(24)	118.6 (5)
C(11)-C(12)-C(13)	104.1 (5)	C(22)-C(24)-Cl(25)	116.9 (5)
C(12)-C(13)-Cl(14)	112.1 (5)	C(22)-C(24)-C(26)	120.1 (6)
C(12)-C(13)-Cl(15)	112.5 (5)	Cl(25)-C(24)-C(26)	122.8 (5)
C(12)-C(13)-C(17)	100.5 (5)	C(17)-C(26)-C(24)	123.9 (6)
Cl(14)-C(13)-Cl(15)	106.3 (4)	C(17)-C(26)-Cl(27)	115.4 (5)
Cl(14)-C(13)-C(17)	112.3 (5)	C(24)-C(26)-Cl(27)	120.6 (5)

of dienone is also affected by this effect. The compound **13a** exhibited n → π* absorption band at 340 nm which is 10 nm lower than that of stereoisomer **13b**, wherein the dienone CO group and urethane group are on the same side (*syn*) with respect to the tetrahydrofuran ring system.

The molecular model analysis of the stereoisomer of **13a** based on this X-ray study indicates that the steric repulsion between Cl_{14}-----O_{16} may not be so serious that it prevents coplanarity of the enone system. The N_a–$C_{12}(C_a)$ distance of 1.441 Å is shorter than those observed in the cycloadducts of N-(ethoxycarbonyl)-azepine (**1**) and cyclopentadienones (*ca* 1.47 Å).[8] The bond angle of N_a–$C_{12}(C_a)$–$C_{11}(C_b)$ expands to 120.0°. The facts suggest that C_{12} (C_a) C atom has a somewhat sp^2 character. The low field shifts of ^1H NMR signal of $H_{12}(H_a)$ (6.42 ppm in C_6D_6) and ^{13}C NMR signal of $C_{12}(C_a)$ (64.9 ppm) may be effected by these structural features in addition to the inductive effect of β-dichloro substituents.[9] The dihedral angle of $H_{10}(H_c)$–$C_{10}(C_c)$–$C_{11}(C_b)$–$H_{11}(H_b)$ is 59.9°, which is consistent with ^1H NMR result.

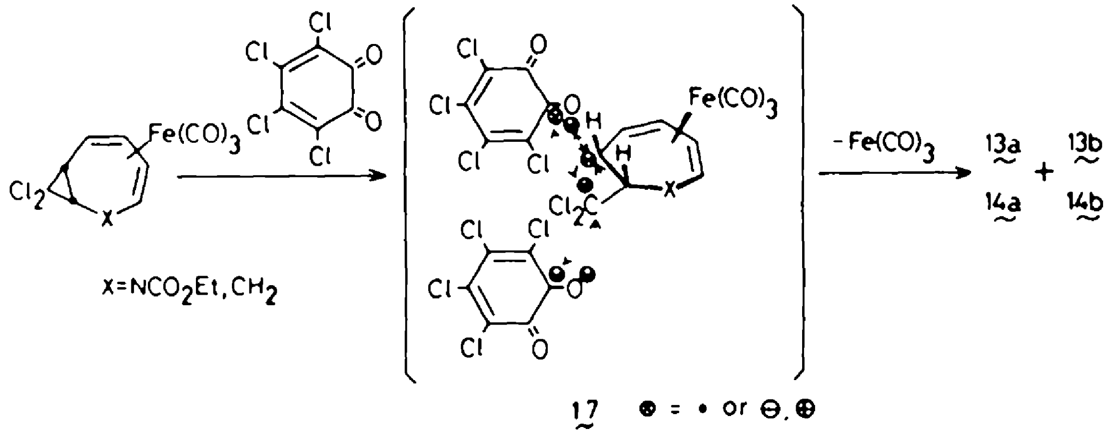
Tricarbonyl(2,3-homocycloheptatriene)iron derivative (**10**) was likewise reacted with 2 equivalents of *o*-choranil to afford a mixture of stereoisomers (**14a** and **14b**) in total yield of 46% (ratio 1 1 4).

By contrast, N-(ethoxycarbonyl)-2,3-homoazepine derivative (**11**) and 2,3-homocycloheptatriene derivative (**12**) were inert to this reagent.

Since the addition of compounds **9** and **10** with *o*-chloranil were the symmetry-forbidden [2σ + 2π] type, cycloadditions were expected to proceed via zwitterion or biradical intermediate (**17**), and oxidised with *o*-chloranil to give **13** and **14** (Scheme 4).

On the other hand, Saito *et al*[10] recently reported that N-ethoxycarbonyl)-azepine (**1**) with *o*-chloranil afforded a [6π + 4π] cycloadduct as a major product in addition to two [4π + 2π] cycloadducts, which were of the symmetry-allowed type adducts.

Another possible mechanism involved initially formed



Scheme 4

Table 3 Atomic parameters and estimated standard deviations of the adduct (13a)

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
C1	-999(8)	4671(9)	6504(9)	764(107)	1639(100)	1783(99)	544(80)	-713(77)	-698(81)
C2	-539(7)	5263(7)	7430(7)	427(85)	1166(68)	1003(58)	369(57)	-99(50)	-135(50)
O3	406(4)	4740(4)	7900(4)	290(46)	880(35)	682(28)	96(29)	29(25)	-230(24)
C4	924(6)	5159(5)	8833(5)	565(76)	707(43)	525(37)	-94(43)	256(37)	-81(31)
O5	641(4)	5896(3)	9325(4)	691(52)	692(30)	872(33)	37(30)	216(30)	268(25)
N6	1872(4)	4623(4)	9157(4)	356(53)	661(32)	440(27)	-41(31)	98(26)	-100(23)
C7	2405(6)	4929(5)	10227(5)	525(74)	919(51)	479(37)	-141(46)	142(36)	232(34)
C8	3119(6)	4424(6)	10893(5)	543(76)	1188(62)	391(35)	-144(52)	55(36)	-157(36)
C9	3639(6)	3476(6)	10738(5)	555(78)	1073(58)	449(36)	5(50)	93(37)	126(36)
C10	3492(6)	2808(5)	9889(5)	557(73)	767(46)	464(35)	-45(43)	32(35)	188(31)
C11	2644(6)	2843(4)	8904(5)	425(69)	617(39)	444(33)	-81(39)	155(33)	79(22)
C12	2231(5)	3850(4)	8407(4)	202(64)	520(34)	408(30)	-81(34)	92(29)	-12(24)
C13	3046(5)	4173(4)	7609(4)	379(68)	443(32)	387(31)	65(34)	79(31)	-5(23)
CL14	4138(2)	4819(1)	8363(1)	452(19)	612(9)	516(9)	-188(10)	104(9)	-89(7)
CL15	2523(2)	5016(1)	6516(1)	629(20)	477(8)	520(8)	98(9)	115(9)	117(7)
O16	3040(4)	2376(3)	7904(3)	576(46)	442(22)	501(23)	-26(24)	117(22)	93(18)
C17	3367(5)	3101(4)	7134(4)	241(64)	456(32)	426(31)	-43(32)	57(30)	41(24)
C18	4580(5)	3021(4)	7129(4)	354(68)	578(37)	412(32)	11(36)	-9(31)	-35(26)
O19	5125(4)	2723(4)	7950(3)	487(49)	1064(37)	475(25)	221(32)	-75(24)	65(24)
C20	4993(5)	3371(4)	6059(4)	386(21)	461(19)	437(11)	2(15)	46(10)	-9(12)
CL21	6335(2)	3636(2)	6191(2)	327(65)	1448(39)	632(29)	-57(37)	51(29)	-139(25)
C22	4418(5)	3345(4)	5064(4)	245(22)	677(18)	321(9)	116(15)	91(10)	-7(10)
CL23	4945(2)	3687(2)	3823(1)	563(64)	1394(37)	444(29)	-79(34)	143(28)	102(25)
C24	3306(5)	3038(4)	4996(4)	103(20)	622(13)	352(8)	44(12)	-61(9)	-46(8)
CL25	2692(2)	2811(2)	3652(1)	560(20)	976(12)	422(11)	-4(12)	-133(10)	-96(9)
C26	2849(5)	2891(4)	5935(4)	381(67)	427(32)	431(31)	-1(33)	36(31)	-8(24)
CL27	1554(2)	2507(2)	5867(2)	394(67)	872(33)	736(32)	-195(34)	41(31)	-126(24)

[a] The values have been multiplied by 10^4. The temperature factor is in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*)]$.

Table 4. Hydrogen atomic parameters and their estimated standard deviations[a] of the adduct (13a)

ATOM	X	Y	Z	B
H1-1	-173(6)	500(6)	609(6)	11.6(2.5)
H1-2	-44(6)	459(6)	586(7)	11.9(2.6)
H1-3	-117(6)	390(6)	682(7)	12.1(2.6)
H2-1	-112(6)	533(5)	808(6)	8.7(2.0)
H2-2	-36(5)	606(5)	717(5)	8.7(2.0)
H7	211(5)	570(4)	1046(5)	5.9(1.5)
H8	543(5)	494(5)	1158(5)	6.6(1.6)
H9	428(5)	318(4)	1148(5)	6.6(1.6)
H10	380(5)	201(4)	1000(5)	5.8(1.5)
H11	202(4)	230(4)	915(4)	4.9(1.4)
H12	154(4)	365(4)	779(4)	3.9(1.2)

[a] The values have been multiplied by 10^3.

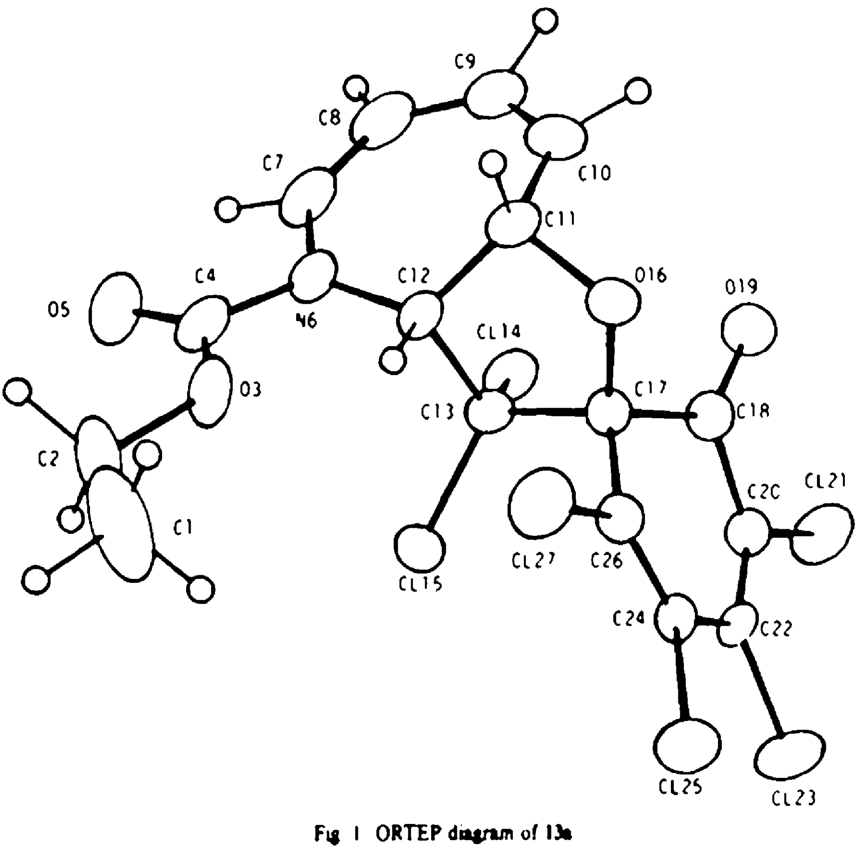


Fig. 1. ORTEP diagram of **13a**

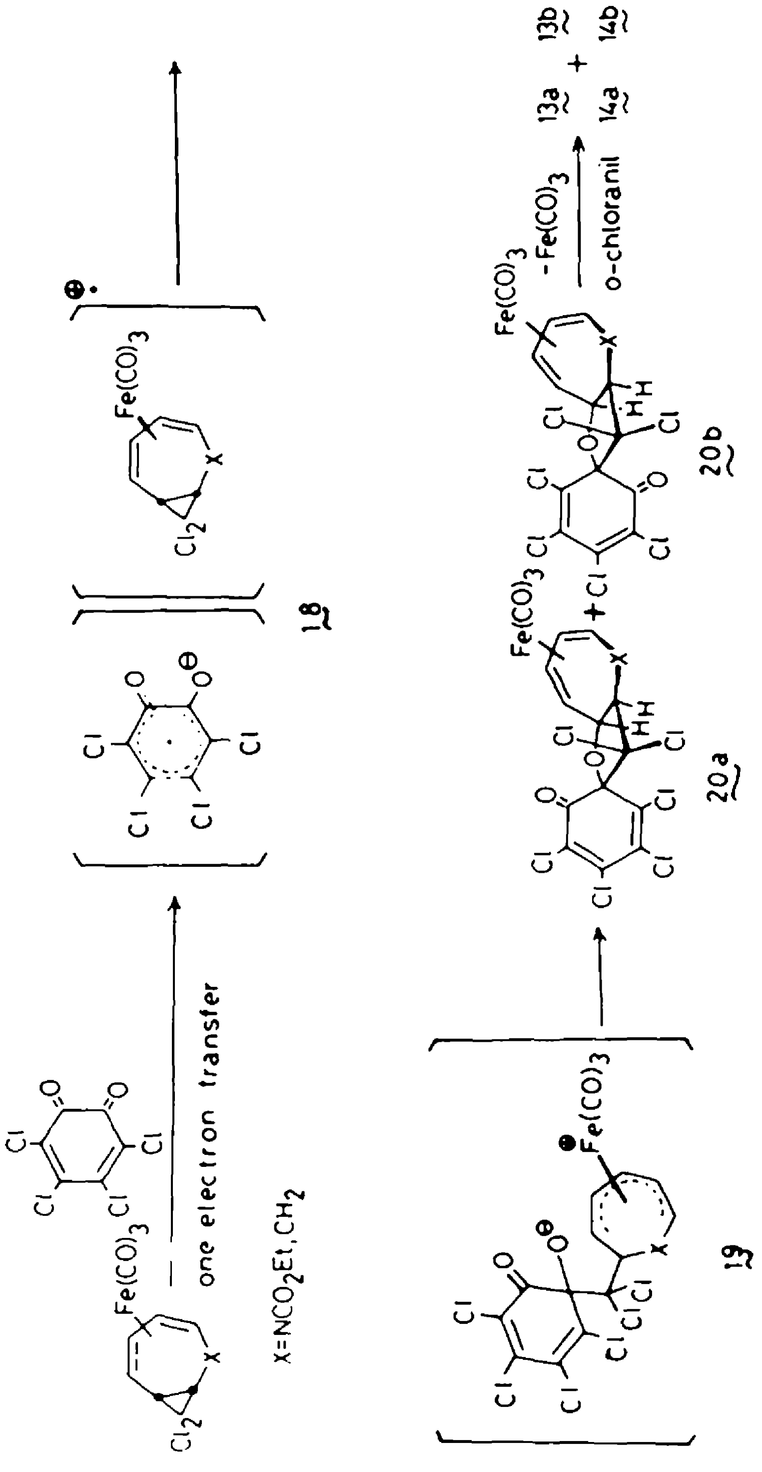
radical ions (**18**), which were formed by one electron transfer,[11] produced zwitterion intermediate (**19**), followed by nucleophilic addition to give **20a** and **20b**, and further oxidation with *o*-chloranil to give **13** and **14**, respectively (Scheme 5).

EXPERIMENTAL

M.ps were measured with a Yanagimoto micro m.p. apparatus and uncorrected. ^1H NMR spectra were taken with a JEOL PS-100 spectrometer with Me_4Si as an internal standard; chemical shifts are expressed in δ values. ^{13}C NMR spectra recorded on a JEOL FX-100 with Me_4Si as an internal standard. IR spectra were taken with a JASCO DS-701G IR spectrophotometer. The UV spectra were determined with a Hitachi ESP-3T spectrometer. Mass spectra were obtained with a JEOL-01SG double-focusing spectrometer operating at an ionizing potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200°.

Reaction of tricarbonyl[N-(ethoxycarbonyl)-azepine]iron (**7**) *with DCC*. A mixture of 50% (w/w) NaOHaq (6.6 ml), benzene (4 ml), triethylbenzylammonium chloride (0.013 g), and **7** (1.00 g, 3.28 mmol) was vigorously stirred at room temp. Stirring was continued, and $CHCl_3$ (5.3 ml, 65.5 mmol) was added slowly during 30 min. The mixture was vigorously stirred for 1.5 hr. The brown slurry was poured into water (16 ml), and the mixture was extracted with CH_2Cl_2.

The extract was dried over Na_2SO_4 and evaporated *in vacuo*. The residue was chromatographed on a column of silica gel with benzene—n-hexane (3:1) as an eluent to give **9** (0.929 g, 73%). The product was recrystallized from n-hexane to give pale yellow crystals, m.p. 113–114°, mass spectrum *m/e* 388 (M^+), 360 (M^+ -


Fe(CO)3
Cl2
X
Cl
O
one electron transfer
X=NCO2Et,CH2
18
19
20a
20b
H
-Fe(CO)3
o-chloranil
13a
13b
14a
14b
+

Scheme 5

CO), 332 (M$^+$-2CO) and 304 (M$^+$-3CO). IR (CHCl$_3$) 1705 (NCO), 1990 (Fe(CO)$_3$) and 2085 (Fe(CO)$_3$) cm^{-1}. ^{1}H NMR (C$_6$D$_6$) δ 0.99 (t, 3H, CH$_3$, $J_{CH_3-CH_2}$ = 7.0 Hz), 2.03 (dd, 1H, H$_b$, J_{ab} = 11.5 Hz, J_{bc} = 7.5 Hz), 2.48 (dd, 1H, H$_c$, J_{ce} = 7.5 Hz), 3.14 (d, 1H, H$_a$), 3.7–4.5 (m, 4H, H$_d$, H$_e$ and CH$_2$), 5.26 (bd, 1H, H$_f$, J_{ef} = 6.5 Hz) (Found: C, 40.30; H, 2.87; N, 3.52. Calc for C$_{13}$H$_{11}$O$_5$NCl$_2$Fe: C, 40.24; H, 2.86; N, 3.61%).

Reaction of tricarbonyl(cycloheptatriene)iron (8) *with DCC.* A mixture of 50% (w/w) NaOHaq (14 ml), benzene (4 ml), triethylbenzylammonium chloride (0.028 g), and tricarbonyl-(cycloheptatriene)iron (1.618 g, 6.97 mmol) was vigorously stirred at room temp. The stirring was continued, and CHCl$_3$ (4.5 ml, 55.8 mmol) was added slowly during 30 min. The same workup gave the residue, which was chromatographed on a column of silica gel with n-hexane as an eluent to give MeOH 10 (1.240 g, 56%).

The product was recrystallized from MeOH to give pale yellow crystals. m.p. 62–64° (lit.[4] 64–66°).

Oxidative degradation of tricarbonyl[N-(*ethoxycarbonyl*)-2,3-*homoazepine*]*iron derivative* 9 *with trimethylamine* N-*oxide.* A mixture of 9 (0.400 g, 1.03 mmol) and trimethylamine N-oxide (1.500 g, 20.6 mmol) in dry benzene (10 ml) was refluxed for 30 min.

The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was passed through a short column of silica gel with benzene as an eluent to give a colorless oil 11 (0.234 g, 92%). b.p. 135°/3 mm Hg. IR (neat) 1730 (NCO) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 1.38 (t, 3H, CH$_3$, $J_{CH_3-CH_2}$ = 7.0 Hz), 2.54 (dd, 1H, H$_b$, J_{ab} = 8.0 Hz, J_{bc} = 3.0 Hz), 3.62 (d, 1H, H$_a$), 4.1–4.5 (m, 2H, CH$_2$), 4.9–5.2 (m, 1H, H$_c$), 5.8–6.1 (m, 2H, H$_e$ and H$_d$), 6.82 (d, 1H, H$_f$, J_{ef} = 10.5 Hz), exact mass 247.01578 (Calc 247.01577).

Oxidative degradation of tricarbonyl(2,3-*homocycloheptatriene*)*iron derivative* (10) *with trimethylamine* N-*oxide.* A mixture of 10 (0.272 g, 0.863 mmol) and trimethylamine N-oxide (1.295 g, 17.3 mmol) in dry benzene (6 ml) was refluxed for 40 min. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was passed through a short column of a silica gel with n-hexane as an eluent to give a colorless oil 12 (0.102 g, 68%). b.p. 47°/3 mm Hg (lit.[12] 35.5°/0.5 mm Hg).

Reaction of tricarbonyl[N-(*ethoxycarbonyl*)-2,3-*homoazepine*]*iron derivative* (9) *with o-chloranil.* To a soln of *o*-chloranil (0.635 g, 2.58 mmol) in dry CH$_2$Cl$_2$ (5 ml), a soln of 9 (0.500 g, 1.29 mmol) in the same solvent (5 ml) was added dropwise at room temp, and stirred for 1 hr. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was chromatographed on a column of silica gel with benzene-n-hexane (5:1) as an eluent to give a mixture of the two products (0.450 g, 71%). The mixture was separated by preparative-TLC (silica gel, benzene-n-hexane (2:1)) to give yellow crystals of 13a (0.240 g, 42%) and orange crystals of 13b (0.160 g, 28%), and these were recrystallized from n-hexane.

Compound 13a. m.p. 143–145°, mass spectrum *m/e* 494 (M$^+$). IR (CHCl$_3$) 1730 (NCO and CO) cm^{-1}. UV (EtOH) λ_{max} (log ε) 260 (4.10) and 340 nm (3.45). ^{1}H NMR (C$_6$D$_6$) δ 0.85 (t, 3H, CH$_3$, $J_{CH_3-CH_2}$ = 7.0 Hz), 3.88 (q, 2H, CH$_2$), 4.47 (ddd, 1H, H$_b$, J_{ab} = 8.0 Hz, J_{bc} = 2.5 Hz, and J_{bd} = 2.5 Hz), 4.71 (dd, 1H, H$_e$, J_{ae} = 8.0 Hz and J_{ef} = 10.5 Hz), 5.51 (ddd, 1H, H$_d$, J_{cd} = 12.0 Hz), 6.14 (dd, 1H, H$_c$), 6.42 (d, 1H, H$_a$), 6.93 (d, 1H, H$_f$). ^{13}C NMR (CDCl$_3$) δ 14.3 (q, CH$_3$), 64.3 (t, CH$_2$), 64.9 (d, C$_a$), 75.0 (d, C$_b$), 89.3 (s, C$_h$), 96.9 (s, C$_g$), 106.2 (d, C$_f$), 121.7, 127.8 and 129.6 (d, C$_c$, C$_d$ and C$_e$), 137.0 and 142.7 (each s, each 2C, C$_i$–C$_l$), 154.3 (s, NCO), 190.6 (s, CO) (Found: C, 38.89; H, 2.25; N, 2.81. Calc for C$_{16}$H$_{11}$O$_5$NCl$_4$: C, 38.90; H, 2.24; N, 2.84%).

Compound 13b. m.p. 137–139°, mass spectrum *m/e* 494 (M$^+$). IR (CHCl$_3$) 1710 (CO) and 1725 (NCO) cm^{-1}. UV (EtOH) λ_{max} (log ε) 255–270 plateau (3.95) and 350 nm (3.28). ^{1}H NMR (C$_6$D$_6$) δ 0.89 (t, 3H, CH$_3$, $J_{CH_3-CH_2}$ = 7.0 Hz), 3.88 (q, 2H, CH$_2$), 4.5–5.0 (m, 2H, H$_b$ and H$_e$), 5.4–5.9 (m, 2H, H$_c$ and H$_d$), 6.64 (d, 1H, H$_a$, J_{ab} = 8.0 Hz), 6.98 (d, 1H, H$_f$, J_{ef} = 10.5 Hz) (Found: C, 39.24; H, 2.38; N, 2.76. Calc for C$_{16}$H$_{11}$O$_5$NCl$_4$: C, 38.90; H, 2.24; N, 2.84%).

Reaction of tricarbonyl(cycloheptatriene)iron derivative (10) *with o-chloranil.* To a soln of *o*-chloranil (0.935 g, 38.0 mmol) in dry CH$_2$Cl$_2$ (9 ml), a soln of 10 (0.600 g, 1.90 mmol) in the same solvent (9 ml) was added dropwise at room temp and stirred for 1 hr. The mixture was filtered and the filtrate evaporated *in vacuo*. The residue was chromatographed on a column of silica gel with benzene—n-hexane (3:7) to give two products 14a (0.154 g, 19%) and 14b (0.212 g, 27%). They were recrystallized from n-hexane to give pale yellow crystals.

Compound 14a. m.p. 125–126°, mass spectrum *m/e* 421 (M$^+$). IR (CHCl$_3$) 1725 (CO) cm^{-1}, UV (EtOH) λ_{max} (log ε) 229 (4.22) and 337 nm (3.48). ^{1}H NMR (CDCl$_3$) δ 2.0–2.5 (m, 1H, H$_n$), 2.73 (ddd, 1H, H$_{n'}$, $J_{an'}$ = 12.0 Hz, $J_{fn'}$ = 4.5 Hz, and $J_{nn'}$ = 12.0 Hz), 3.81 (ddd, 1H, H$_a$, J_{ab} = 9.5 Hz, J_{an} = 6.0 Hz), 5.0–5.3 (m, 1H, H$_b$), 5.7–6.6 (m, 4H, H$_c$, H$_d$, H$_e$, and H$_f$) (Found: C, 39.93; H, 1.95. Calc for C$_{14}$H$_8$O$_3$Cl$_4$: C, 39.95; H, 1.91%).

Compound 14b. m.p. 115–117°, mass spectrum *m/e* 421 (M$^+$). IR (CHCl$_3$) 1705 (CO) cm^{-1}. UV (EtOH) λ_{max} (log ε) 232 (4.13) and 348 nm (3.36). ^{1}H NMR (CDCl$_3$) δ 2.1–2.4 (m, 1H, H$_n$), 2.65 (ddd, 1H, H$_{n'}$, $J_{an'}$ = 12.5 Hz, $J_{fn'}$ = 4.5 Hz, and $J_{nn'}$ = 12.5 Hz), 3.65 (ddd, 1H, H$_a$, J_{ab} = 10.0 Hz, J_{an} = 4.5 Hz), 5.1–5.4 (m, 1H, H$_b$), 5.7–6.4 (m, 4H, H$_c$, H$_d$, H$_e$, and H$_f$) (Found: C, 39.96; H, 1.91. Calc for C$_{14}$H$_8$O$_3$Cl$_4$: C, 39.95; H, 1.91%).

X-ray crystallographic study of compound (13a). Suitable single crystals of 13a were obtained by slow crystallization from a MeOH-benzene soln. A crystal of 13a with approximate dimensions 0.4 × 0.35 × 0.45 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimensions were approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex P$\bar{1}$ four-circle diffractometer equipped with a graphite monochrometor and using Mo *Kα* radiation.

Fifteen reflections were used in the least-squares refinement of the lattice parameters and orientation matrix. The cell parameters obtained were a = 12.741 (6), b = 13.114 (6), c = 11.660 (5) Å, β = 95.44 (3)°, V = 1939 (1) Å^3, D_m (KI + H$_2$O) = 1.677, D_x = 1.692 g cm^{-3}. Statistical Wilson analysis of the data indicated a centrosymmetric distribution of intensities. Systematic absences for the h0l reflection with h + l = 2n + 1 and for the 0k0 reflections with k = 2n + 1 are consisted with the space group $P2_1/n$.

Intensity data were collected by $\theta-2\theta$ scan to a limit of 2θ = 50° with X-ray source and monochrometor settings identical with those used for determination of the unit cell parameter. A variable scan rate from 24.0 to 4.0 min^{-1} was used. Three reflections monitored at regular intervals during the data collection, showed no significant variation in intensity.

Of 1861 independent reflections, 1563 were treated as observed ($I > 2.3\sigma(I)$). The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption. Observed structure factors were converted into normalized structure factor amplitude, $|E|$ values, by use of the scale factor and overall temperature factor from Wilson's statistics.[13] The structure was solved by the direct method by using MULTAN 78 series of programs.[14] An E map calculated with 208 signed E's ($E > 1.584$) which gave a combined figure of merit of 1.2662 revealed the positions of 21 nonhydrogen atoms. The positions of the remaining 6 atoms were located on a subsequent difference Fourier map. Nine cycles of block-diagonal least-squares of minimizing of $\Sigma(|Fo| - k|Fc|)^2$ by varying the positions and isotropic vibrational amplitudes of the nonhydrogen atoms led to R = 0.148. Twelve further cycles of least-squares refinement of atomic parameters with anisotropic vibrational amplitudes for the all nonhydrogen atoms converged to R = 0.065. A difference Fourier map calculated at stage revealed peaks of density appropriate to the H atoms with the exception of ones of the Et group. The positions of the remaining five were calculated by using the program HYCO.[14a] After adding the hydrogens, assigning their vibrational amplitudes to B(H) = B(C) + 1.0 Å^2, and refining the values with anisotropic U's for non H atoms and isotropic U's for H atoms, we obtained a final R = 0.045. In this refinement, an equal weight was applied to the structure factors. The atomic scattering factors were taken from the lit.[15]

All the calculations were performed on the FACOM M-200 computer in the computer center of Kyushu University with the Universal Crystallographic Computation Program System (UNICS II).[16]

Supplementary material available Crystallographic data including positional and thermal parameters as well as bond distance and angle calculation have been deposited with the Cambridge Crystallographic Data Centre (CCDC) in England

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