DIELS–ALDER REACTIONS OF CYCLOPENTADIENE WITH SEVERAL FERROCENYL- AND η^6-PHENYLTRICARBONYLCHROMIUM ANALOGUES OF CHALCONE. CATALYTIC EFFECT OF SiO_2

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Received July 24, 1995
Accepted October 24, 1995

The Diels–Alder reaction of cyclopentadiene with eight electron deficient dienophiles was studied. The reaction was performed at room temperature using silica gel as an inorganic support, without solvent. Only one of the two possible Diels–Alder adducts was isolated in moderate to good yield. The structure of products with *endo*-oriented electron-withdrawing group was proved by ^{1}H NMR spectrum and in one case (**9b**) by X-ray analysis.

Key words: Diels–Alder reaction; Solid support; Chalcone.

Recently we reported[1] the results of the Diels–Alder (D–A) reaction of dienophiles such as acryloylferrocene (**1**), 4-ferrocenyl-3-buten-2-one (**2**), cinnamoylferrocene (**3**), 3-ferrocenyl-1-phenyl-2-propenone (**4**), chalcone (**5**), 1-(η^6-phenyltricarbonylchromium)-3-phenyl-2-propenone (**6**), 1-phenyl-3-(η^6-phenyltricarbonylchromium)-2-propenone (**7**) and 2-nitrovinylferrocene (**8**) with 1,3-diphenylisobenzofuran under various conditions. The compounds **1**–**8** gave the expected adducts only when silica gel or montmorillonite KSF were used as reaction medium. The enones **1**, **2**, **4** and **8** also reacted under aluminium chloride catalysis, though the isolated products had not the structure typical for D–A adducts. Since our results with solid supports were very good, we decided to examine the D–A reaction of the above-mentioned compounds with cyclopentadiene on silica gel. This support is frequently used for D–A reactions of various dienes with aliphatic enones[2–4]. The objective of this work was to examine if similar effect of silica gel will be also observed in D–A reactions of less reactive dienes such as cyclopentadiene or cyclohexadiene.

In our preliminary experiments, cyclohexadiene did not react with the chosen dienophiles[1]. Since it is known that cyclopentadiene is much more reactive than cyclohexa-

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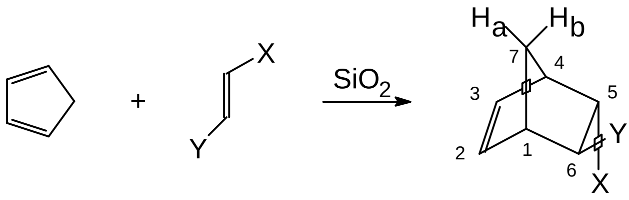
diene[5], we decided to examine the former as the reactant. Adsorption of the dienophile and cyclopentadiene (molar ratio 1 : 40) on silica gel, followed by standing of the reaction mixture at room temperature, was the procedure of choice. The Diels–Alder reaction proceeded as given in Scheme 1 and the results achieved are summarized in

TABLE I
Reaction times and yields of SiO_2-mediated D–A reactions of cyclopentadiene with dienophiles **1**–**8**

Experiment	Dienophile	Reaction time, h	Product	Yield, %
1	**1**	44.5	**9a**	37
2	**2**	43.5	**9b**	68
3	**3**	47.5	**9c**	51
4	**4**	44.0	**9d**	65
5	**5**	45.0	**9e**	60
6	**6**	24.0	**9f**	50
7	**7**	24.0	**9g**	71
8	**8**	45.0	**9h**	51



1-8 **9a-9h**

	X	Y
1, 9a	COFc	H
2, 9b	$COCH_3$	Fc
3, 9c	COFc	Ph
4, 9d	COPh	Fc

	X	Y
5, 9e	COPh	Ph
6, 9f	COAr	Ph
7, 9g	COPh	Ar
8, 9h	NO_2	Fc

Fc = $(C_5H_4)Fe(C_5H_5)$, Ar = $(C_6H_5)Cr(CO)_3$

SCHEME 1

Table I. It follows from the results that the D–A reaction of cyclopentadiene with dienophiles **1**–**8** proceeded easily under very mild conditions.

The catalytic effectiveness of silica gel was confirmed by an experiment conducted without this solid support. In the absence of silica gel, the reaction of cyclopentadiene with cinnamoylferrocene (**3**) gave the expected product in only 3.3% yield, even when the reaction time was prolonged to 50 h.

In all cases only a single product was isolated. The steric relation of the groups X and Y to the CH_2-bridge in the bicyclic products was determined by HH COSY technique for the product **9h**. The mutual relation of the groups X and Y was invariably *trans* because all the enones used had *trans*-configuration. Two multiplets at 1.64 and 3.21 ppm with J = 2.7 Hz belonged to H-7a and H-6, respectively. This long-range coupling is frequently observed when the bonds between two protons are w-shaped. To hold a w-shape of the (7-Ha)–(7-C)–(1-C)–(6-C)–(6-H) bonds, the X group must be *endo*- and the group Y *exo*-oriented. The typical coupling constants for such steric orientation of neighbouring groups are 2.5–5.0 Hz, the observed J(*endo*,*exo*) = 3.8 Hz.

TABLE II
Crystal data and parameters for compound **9b**

Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	10.541(1)
b, Å	7.520(1)
c, Å	19.371(2)
β, °	90.73(1)
V, Å^3	1 535.4(5)
Z	4
D_{calc}, g cm^{-3}	1.385
Radiation, Å	graphite monochromated MoKα
Wavelength, Å	0.70926
θ range for data collection, °	3–25
Number of variables	190
Number of reflections measured	3 014
Number of reflections with $I > 2\sigma(I)$	1 301
R	0.030
R_w	0.034
Weighting scheme	$1/\sigma^2(\lvert F_o \rvert)$
Max. residual electron density, e Å^{-3}	0.488

Analogously, the same structure has been assumed for all the obtained D–A adducts and was checked by X-ray analysis of compound **9b**. The main crystallographic parameters are listed in Tables II–IV. The structure was solved by a combination of the heavy atom and direct methods using the program system DIRDIF92 (ref.[6]) and is presented in Fig. 1.

EXPERIMENTAL

^{1}H NMR spectra (δ, ppm; *J*, Hz) of the samples were recorded in $CDCl_3$ or CD_3COCD_3 on a Varian VXR 300 spectrometer (300 MHz) with tetramethylsilane as internal standard. Melting points were measured on a Kofler hot plate apparatus and are uncorrected. Solvents were purified according to the published methods. Silica gel was used without drying.

General Procedure for Diels–Alder Reactions on SiO_2

The dienophile **1–8** (0.39 mmol) was dissolved in dichloromethane (20–25 ml) in a 100 ml round-bottomed flask and SiO_2 (2.00 g; 100–160 mesh) was added. The solvent was evaporated under reduced pressure and freshly distilled cyclopentadiene (15.8 mmol, 1.29 ml) was dropped on the dry solid support with the adsorbed dienophile. The flask was immediately stoppered and the reaction mixture was allowed to stand with occasional shaking. After the reaction was finished, the flask was opened, the unreacted cyclopentadiene was partly evaporated on the air (several minutes) and the reaction mixture was chromatographed on SiO_2 (gradient from isohexane to isohexane–ethyl acetate 9 : 1).

5-Ferrocenoylbicyclo[2.2.1]hept-2-ene (**9a**), m.p. 104–105 °C. For $C_{18}H_{18}FeO$ (306.2) calculated: 70.61% C, 5.93% H, 18.24% Fe; found: 70.82% C, 5.99% H, 18.53% Fe. ^{1}H NMR ($CDCl_3$): 1.44 q, 2 H, *J* = 8.1 (2 × H-6); 1.59 d, 1 H, *J* = 8.3 (H-7a); 1.92 t, 1 H, *J* = 9.0 (H-7b); 2.94 br s, 1 H and 3.24 br s, 1 H (H-1 and H-4); 3.47 br s, 1 H (H-5); 4.23 s, 5 H (C_5H_5); 4.51 br s, 2 H (C_5H_4); 4.85 br s, 2 H (C_5H_4); 5.90 br s, 1 H and 6.18 br s, 1 H (H-2 and H-3).

5-Acetyl-6-ferrocenylbicyclo[2.2.1]hept-2-ene (**9b**), m.p. 106.5–108 °C. For $C_{19}H_{20}FeO$ (320.2) calculated: 71.27% C, 6.30% H, 17.44% Fe; found: 71.67% C, 6.45% H, 17.71% Fe. ^{1}H NMR ($CDCl_3$): 1.54 d, 1 H, *J* = 8.3 (H-7a); 1.80 d, 1 H, *J* = 8.0 (H-7b); 2.17 s, 3 H (CH_3); 2.82 d, 3 H,

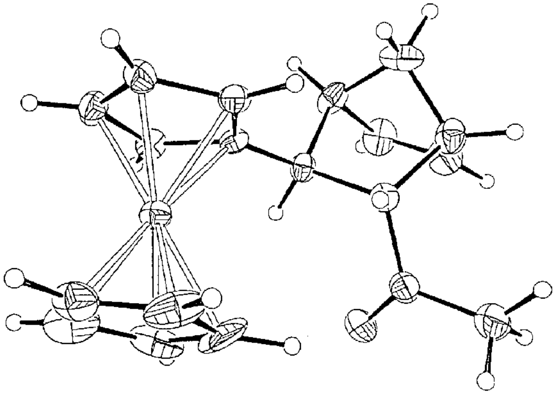


FIG. 1
Structure of compound **9b**

J = 8.2 and 3.23 br s, 1 H (H-1, H-4, H-5, H-6); 4.14–4.25 m, 4 H (C_5H_4); 4.20 s, 5 H (C_5H_5); 5.87 dd, 1 H, J_1 = 5.5, J_2 = 1.0; 6.35 dd, 1 H, J_1 = 5.6, J_2 = 2.7 (H-2, H-3).

5-Ferrocenoyl-6-phenylbicyclo[2.2.1]hept-2-ene (**9c**), m.p. 157–160 °C. For $C_{24}H_{22}FeO$ (382.3) calculated: 75.41% C, 5.80% H, 14.61% Fe; found: 75.82% C, 5.88% H, 14.73% Fe. ^{1}H NMR ($CDCl_3$): 1.49 d, 1 H, J = 8.1 (H-7a); 1.62 d, 1 H, J = 8.2 (H-7b); 1.99 t, 1 H, J = 7.4; 3.08 m, 1 H and 3.33 m, 1 H and 3.52 m, 1 H (H-1, H-4, H-5, H-6); 4.01 s, 2 H (C_5H_5); 4.08 s, 3 H (C_5H_5); 4.50 br s, 2 H (C_5H_4); 4.79 m, 2 H (C_5H_4); 5.95 dd, 1 H, J_1 = 5.6, J_2 = 2.5; 6.46 dd, 1 H, J_1 = 5.6, J_2 = 3.2 (H-2, H-3); 7.21–7.32 m, 5 H (C_6H_5).

5-Benzoyl-6-ferrocenylbicyclo[2.2.1]hept-2-ene (**9d**), m.p. 166–169 °C. For $C_{24}H_{22}FeO$ (382.3) calculated: 75.41% C, 5.80% H, 14.61% Fe; found: 75.31% C, 5.84% H, 14.81% Fe. ^{1}H NMR ($CDCl_3$): 1.56 d, 1 H, J = 8.5 (H-7a); 1.95 d, 1 H, J = 8.1 (H-7b); 2.88 br s, 1 H and 3.09 br s, 1 H and 3.23 br s, 1 H and 3.69 br s, 1 H (H-1, H-4, H-5, H-6); 4.12 s, 5 H (C_5H_5); 4.10–4.31 m, 4 H (C_5H_4); 5.73 dd, 1 H, J_1 = 5.7, J_2 = 2.5; 6.43 dd, 1 H, J_1 = 5.7, J_2 = 2.8 (H-2, H-3); 7.48 t, 2 H, J = 7.5 (*m*-C_6H_5); 7.57 t, 1 H, J = 7.4 (*p*-C_6H_5); 7.99 d, 2 H, J = 7.5 (*o*-C_6H_5).

5-Benzoyl-6-phenylbicyclo[2.2.1]hept-2-ene (**9e**), m.p. 78.5–80.5 °C. For $C_{20}H_{18}O$ (274.4) calculated: 87.56% C, 6.61% H; found: 87.53% C, 6.73% H. ^{1}H NMR ($CDCl_3$): 1.65 dq, 1 H, J_1 = 8.5, J_2 = 1.8 (H-7a); 2.03 dt, 1 H, J_1 = 8.5, J_2 = 1.5 (H-7b); 3.12 m, 1 H, J = 1.6; 3.34 m, 1 H, J = 1.6 (H-1, H-4);

TABLE III
Bond lengths for compound **9b**

Atoms	Bond length, Å	Atoms	Bond length, Å
Fe(1)–C(12)	2.055(4)	C(5)–C(6)	1.471(8)
Fe(1)–C(13)	2.041(5)	C(5)–C(9)	1.528(8)
Fe(1)–C(14)	2.043(5)	C(6)–C(7)	1.303(8)
Fe(1)–C(15)	2.040(5)	C(7)–C(8)	1.516(8)
Fe(1)–C(16)	2.041(5)	C(8)–C(9)	1.540(8)
Fe(1)–C(17)	2.007(7)	C(10)–C(11)	1.476(8)
Fe(1)–C(18)	2.027(6)	C(12)–C(13)	1.420(6)
Fe(1)–C(19)	2.037(6)	C(12)–C(16)	1.416(6)
Fe(1)–C(20)	2.043(6)	C(13)–C(14)	1.418(7)
Fe(1)–C(21)	2.028(7)	C(14)–C(15)	1.392(7)
O(2)–C(10)	1.190(6)	C(15)–C(16)	1.433(6)
C(3)–C(4)	1.542(6)	C(17)–C(18)	1.40(1)
C(3)–C(8)	1.585(7)	C(17)–C(21)	1.37(1)
C(3)–C(12)	1.507(6)	C(18)–C(19)	1.338(9)
C(3)–C(5)	1.582(7)	C(19)–C(20)	1.377(9)
C(4)–C(10)	1.513(7)	C(20)–C(21)	1.39(1)

3.48 dd, 1 H, J_1 = 5.0, J_2 = 1.8 (H-6); 3.91 dd, 1 H, J_1 = 5.0, J_2 = 3.4 (H-5); 5.87 dd, 1 H, J_1 = 5.6, J_2 = 2.8; 6.46 dd, 1 H, J_1 = 5.7, J_2 = 3.2 (H-2, H-3); 7.17–7.29 m, 5 H (C_6H_5CH); 7.43 tt, 2 H, J_1 = 7.3, J_2 = 1.4 (*m*-C_6H_5CO); 7.53 tt, 1 H, J_1 = 7.3, J_2 = 1.4 (*p*-C_6H_5CO); 7.93 dt, 2 H, J_1 = 7.1, J_2 = 1.4 (*o*-C_6H_5CO).

5-(η^6-Benzoyltricarbonylchromium)-6-phenylbicyclo[2.2.1]hept-2-ene (**9f**), m.p. 117–119 °C. For $C_{23}H_{18}CrO_4$ (410.4) calculated: 67.31% C, 4.42% H; found: 67.57% C, 4.46% H. ^{1}H NMR (CD_3COCD_3): 1.61 dq, 1 H, J_1 = 8.5, J_2 = 1.8 (H-7a); 2.03 d, 1 H, J = 9.0 (H-7b); 3.10 br s, 1 H (H-1 or H-4); 3.42 dd, 1 H, J_1 = 5.1, J_2 = 1.9 (H-6); 3.54 br s, 1 H (H-1 or H-4); 3.84 dd, 1 H, J_1 = 5.0, J_2 = 3.4 (H-5); 5.64 dt, 2 H, J_1 = 6.4, J_2 = 1.6 (CO-*m*-$C_6H_5Cr(CO)_3$); 5.98 dd, 1 H, J_1 = 5.6, J_2 = 2.8 (H-2 or H-3); 6.04 tt, 1 H, J_1 = 5.3, J_2 = 1.0 (CO-*p*-$C_6H_5Cr(CO)_3$); 6.49 dd, 1 H, J_1 = 5.7, J_2 = 3.2 (H-2 or H-3); 6.54 dd, 2 H, J_1 = 7.0, J_2 = 1.0 (CO-*o*-$C_6H_5Cr(CO)_3$); 7.19–7.35 m, 5 H (C_6H_5).

5-Benzoyl-6-(η^6-phenyltricarbonylchromium)bicyclo[2.2.1]hept-2-ene (**9g**), m.p. 138–141 °C. For $C_{23}H_{18}CrO_4$ (410.4) calculated: 67.31% C, 4.42% H; found: 67.54% C, 4.47% H. ^{1}H NMR (CD_3COCD_3): 1.64 dt, 2 H, J_1 = 56.3, J_2 = 10.3 (2 × H-7); 3.05 br s, 1 H and 3.17–3.55 m, 2 H (H-1, H-4, H-5); 4.10 br s, 1 H (H-6); 5.55–5.77 m, 5 H ($C_6H_5Cr(CO)_3$); 6.23 br s, 1 H and 6.65 br s, 1 H (H-2, H-3); 7.55 m, 2 H (CO-*m*-C_6H_5); 7.63 d, 1 H, J = 7.1 (CO-*p*-C_6H_5); 8.10 m, 2 H (CO-*o*-C_6H_5).

6-Ferrocenyl-5-nitrobicyclo[2.2.1]hept-2-ene (**9h**), m.p. 115–117 °C. For $C_{17}H_{17}FeNO_2$ (323.2) calculated: 63.18% C, 5.30% H, 17.28% Fe, 4.33% N; found: 63.53% C, 5.33% H, 17.71% Fe, 4.24% N. ^{1}H NMR ($CDCl_3$): 1.64 dq, 1 H, J_1 = 9.3, J_2 = 1.8, J(7a,6) = 2.7 (H-7a); 1.78 dt, 1 H, J_1 = 9.3, J_2 = 1.5 (H-7b); 2.87 m, 1 H, J_1 = 2.5, J_2 = 1.6 (H-1 or H-4); 3.21 dd, 1 H, J_1(*endo,exo*) = 3.8,

TABLE IV
Selected bond angles of compound **9b**

Atoms	Bond angle, °	Atoms	Bond angle, °
C(8)–C(3)–C(4)	102.3(4)	C(4(–C(10)–O(2)	123.2(5)
C(12)–C(3)–C(4)	115.3(4)	C(11)–C(10)–O(2)	121.6(6)
C(12)–C(3)–C(8)	111.7(4)	C(11)–C(10)–C(4)	115.2(5)
C(5)–C(4)–C(3)	103.2(4)	C(13)–C(12)–C(3)	124.1(4)
C(10)–C(4)–C(3)	115.9(4)	C(16)–C(12)–C(3)	129.5(4)
C(10)–C(4)–C(5)	112.5(4)	C(16)–C(12)–C(13)	106.2(4)
C(6)–C(5)–C(4)	106.2(5)	C(14)–C(13)–C(12)	109.4(5)
C(9)–C(5)–C(4)	100.3(4)	C(15)–C(14)–C(13)	107.8(4)
C(9)–C(5)–C(6)	100.7(5)	C(16)–C(15)–C(14)	108.0(4)
C(7)–C(6)–C(5)	107.9(5)	C(15)–C(!6)–C(12)	108.7(4)
C(8)–C(7)–C(6)	108.6(5)	C(21)–C(17)–C(18)	108.3(7)
C(7)–C(8)–C(3)	104.2(5)	C(19)–C(18)–C(17)	108.1(7)
C(9)–C(8)–C(3)	100.7(4)	C(20)–C(19)–C(18)	108.9(7)
C(9)–C(8)–C(7)	98.9(4)	C(21)–C(20)–C(19)	108.1(7)
C(8)–C(9)–C(5)	93.8(4)	C(20)–C(21)–C(17)	106.6(7)

J(7a,6) = 2.7 (H-6); 3.52 m, 1 H, *J* = 1.7 (H-4 or H-1); 4.12 s, 5 H (C_5H_5); 4.18 s, 4 H (C_5H_4); 4.92 t, 1 H, *J*(*endo*,*exo*) = 3.8 (H-5); 6.02 dd, 1 H, J_1 = 5.7, J_2 = 2.7; 6.57 dd, 1 H, J_1 = 5.7, J_2 = 3.1 (H-2, H-3).

Our thanks are due to Drs N. Pronayova and M. Alfoldi for the ^{1}*H NMR measurements and to Dr E. Grieplova and her staff for the microanalyses. The financial support by Ministry of Education and Science of Slovak Republic (Grant No. 1/1442/94) is gratefully acknowledged.*

REFERENCES

1. Prokesova M., Solcaniova E., Toma S.: J. Org. Chem., in press.
2. Hudlicky M.: J. Org. Chem. *39*, 3460 (1974).
3. Proust S. M., Ridley D. D.: Aust. J. Chem. *37*, 1677 (1984).
4. Veselovsky V. V., Gybin A. S., Lozanova A. V., Moiseenkov A. M., Smit W. A., Caple R.: Tetrahedron Lett. *29*, 175 (1988).
5. Schatz J., Sauer J.: Tetrahedron Lett. *35*, 4767 (1994).
6. Beurskens P. T., Admiraal G., Beurskens G., Bosman W. P., Garcia-Granda S., Gould R. O., Smits J. M. M., Smykalla C.: *The DIRDIF Program System. Technical Report.* University of Nijmegen, Nijmegen 1992.