Thermolysis of Dicyclopentadienylmethyl Alcohols. A Novel Synthesis of Fulvenes

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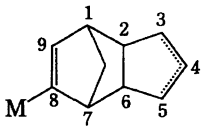
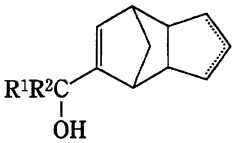
(Received July 22, 1994)

Thermolyses of isomeric mixtures of dicyclopentadienylmethyl alcohols were obtained by reactions of the corresponding isomeric mixture of metallodicyclopentadiene with aldehydes and ketones at 300 °C by a flow method. These thermolyses give by cycloreversion the corresponding isomeric mixtures of cyclopentadienylmethyl alcohols. These mixtures in turn furnish the corresponding fulvenes upon treatment with bases. At higher temperatures, the thermolyses regenerate starting ketones, probably by retro-ene reaction of the cycloreversed alcohols.

Recently, we have reported that isomeric mixtures of 8-substituted dicyclopentadienes (tricyclo-[6.2.1.$0^{2,6}$]deca-3,8-dienes) can be preparatively obtained through the corresponding metallodicyclopentadienes **1**. These were generated either by direct metallation (potassiation) of dicyclopentadiene with the base complex BuLi–*t*-BuOK or by halogen-lithium exchange, with BuLi, of an isomeric mixture of bromodicyclopentadiene. This was obtained through the potassiation and subsequent treatment with 1,2-dibromoethane.[1] An advantage of this new method for the functionalization of dicyclopentadiene is that we can use a variety of electrophiles for the reaction of **1**. When aldehydes and ketones are used as electrophiles, dicyclopentadienylmethyl alcohols **2** are obtained in good yields.[1] In view of the ready thermal cycloreversion of dicyclopentadienes,[2] thermolysis of **2** should form cyclopentadienylmethyl alcohols **3**, and either spontaneous dehydration under the thermolytic conditions or base treatment of **3** would produce fulvenes **4**. Fulvenes are usually prepared by condensation of cyclopentadienyl anions with aldehydes and ketones.[3] One of us has recently developed an effective modification of this method using amides, organolithium compounds, and cyclopentadiene as starting materials.[4] However, these methods still suffer limitations of scope, because cyclopentadienyl anion is an aromatic species and hence has rather weak reactivities towards ketones. Because vinyl metals **1** have much higher reactivities towards carbonyl compounds than cyclopentadienyl anion, the thermolytic transformation of **2** to fulvenes would provide, if successful, a valuable way of fulvene synthesis (Chart 1). We here report the results of thermolytic reactions of **2** and base-induced dehydration of the resulting alcohols **3**.



1a, M=K
b, M=Li

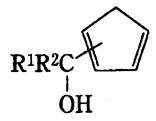


2a, $R^1=R^2$=Ph
b, $R^1=R^2$=*p*-MeC_6H_4
c, $R^1=R^2$=*p*-$MeOC_6H_4$
d, $R^1=R^2$=*p*-ClC_6H_4
e, $R^1=R^2$=2-thienyl
f, $R^1=CH_3$, R^2=Ph
g, R^1=H, R^2=Ph
h, R^1-R^2=-$(CH_2)_5$-

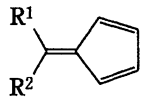
Chart 1.

Results and Discussion

Since 6,6-diphenylfulvene **4a** is thermally a rather stable compound for a fulvene,[3] cycloreversion of benzophenone-adduct **2a** in solutions was first examined. Heating of **2a** at 180 °C in *o*-dichlorobenzene yielded a complex mixture, with no formation of **4a**. Heating of **2a** in hexamethylphosphoric triamide or heating of admixture of **2a** with alumina under reduced pressure gave **4a**, but in poor yields (23 or 17% yields with some recovery of **2a**). The best result was obtained by use of quinoline as solvent: heating of **2a** in quinoline at 180 °C for 3 h furnished **4a** in 86% yield (Chart 2). Similar results were also obtained for the synthesis of



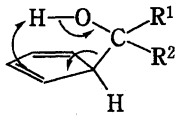
3a - h



4a - h

$R^1R^2C{=}O$

5a - h



6

Chart 2.

di(*p*-tolyl)fulvene **4b**, di(*p*-anisyl)fulvene **4c**, and di(*p*-chlorophenyl)fulvene **4d** in 85, 61, and 92% yield, respectively. Presumably, the basic property of quinoline assisted the dehydration of **3a** via a cyclopentadienyl anion. This condition, however, did not work well for the synthesis of thermally less stable 6-phenylfulvene and 5-cyclohexylidene-1,3-cyclopentadiene from **2g** and **2h**, indicating a severe limitation in scope. Therefore, thermolysis of **2** by a flow method was examined next. Poor volatility and thermal lability of **2** precluded use of the method of flash vacuum pyrolysis.

Table 1 summarizes the results of thermolysis. Here benzene solutions of **2a**—**h** were passed through a hot zone of about 300 °C under nitrogen flow. The following features are to be noted: (1) cycloreversed alcohols **3** and ketones **5** are major products; (2) fulvenes **4** are obtained, but in poor yields; (3) use of quinoline as solvent for **2a** does not improve the yield of **4a** appreciably, and (4) at the higher temperature of 350 °C, the yield of benzophenone from **2a** sharply increases. The further thermal fission of **3** to ketones **5** (and cyclopentadiene) at 350 °C is explicable in terms of retro-ene reaction, as shown mechanistically in formula 6. Thus, the cycloreversion of **2** to **3** and the retro-ene reaction of **3** to **5** take place competitively at about 300 to 350 °C,

Table 1. Thermolysis of Alcohols **2a**—**h** by Flow Method[a)]

Compound	Temp	Products/%			Recovery
	°C	**3**	**4**	**5**	%
2a	250	29	9	29	5
	300	52	6	26	3
	300[b)]	23	12	31	3
	350	0	4	70	0
2b	300	24	11	26	4
2c	300	39	19	4	5
2d	300	41	4	38	6
2e	300	14	6	39	9
2f	280	32	11	27	4
2g	300	25	1	18	45
2h	300	51	6	Trace	10

a) Benzene was used as solvent unless otherwise noted.
b) Quinoline was used as solvent.

with preference for the latter reaction at higher temperatures.

Alcohols **3** correspond to the aldol-type intermediates in the condensation of cyclopentadienyl anion with ketones. These intermediates have not been isolated in the condensation reactions; therefore, behaviors of **3** towards bases are of interest. Which is the preferred reaction, dehydration to fulvenes **4** or dissociation to ketones **5** and cyclopentadienyl anion ? Table 2 tells us that reactions of alcohols **3a**—**f** with bases give mainly fulvenes **4a**—**f**, along with small amounts of ketones **5a**—**f**. But the dehydration proceeds poorly for monophenyl compound **3g** and cyclohexyl compound **3h**. The more easily base-induced dehydration of **3a**—**f** may reflect the higher thermodynamic stability of diarylfulvenes **4a**—**f**, compared to those of a monoarylfulvene **4g** and a dialkylfulvene **4h**.

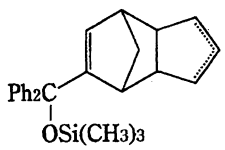
In order to improve the yield of fulvenes, a modification of the reaction was examined. Protection of the hydroxyl group of **3** would suppress the retro-ene reaction improving the yield of **3**. Addition of chlorotrimethylsilane to a reaction of **1b** and benzophenone gave trimethylsilyl ether **7** in 70% yield. Thermolysis of **7** at 350 °C and subsequent treatment of crude product **8** with *t*-BuOK in THF afforded **4a** in 49% yield (Chart 3). Although this modification suppressed the retro ene-reaction (cf. the results for **2a** in Table 1), the overall yield of **4a** was not improved appreciably.

To conclude, fulvene derivatives can be obtained by thermolyses of hydroxymethyldicyclopentadiene and subsequent base treatment of the resulting isomeric

Table 2. Reactions of Alcohols **3a**—**h** with Bases

Compound	Base/Solvent	Temp	Time	Products/%	
		°C	h	**4**	**5**
3a	DBU/THF	R.T.	24	90	5
	DBU/C_6H_6		24	60	7[a)]
		80	1	85	9
	KOH/EtOH	0	3	75	7
	KOBu-*t*/THF	0	3	60	8
3b	DBU/THF	R.T.	24	74	20
3c				71	26
3d				65	14
3e				57	—[b,c)]
3f				60	6
3g				27	6
3h				23	—[c)]

a) 31% recovery. b) 21% recovery. c) Ketone was not isolated.



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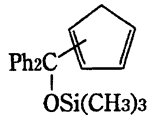

8

Chart 3.

mixtures of cyclopentadienylmethanols, although the yields are not necessarily higher than those obtained by the condensation method.

Experimental

Melting points are not corrected. ^{1}H NMR spectra were recorded on a JEOL FX-100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. IR spectra were obtained on a Hitachi 215 spectrometer, and mass spectra were measured on a Hitachi M-80B. The microanalysis was performed at the Advanced Instrumentation Center for Chemical Analysis, Ehime University.

Tetrahydrofuran (THF) was freshly distilled from sodium metal using diphenylketyl as indicator. BuLi was purchased in hexane solution and used as such.

Preparation of an Isomeric Mixture of 8-(Diphenylhydroxymethyl)dicyclopentadienes 2a as a Typical Procedure. To a solution of an isomeric mixture of bromodicyclopentadiene (1.60 g, 7.58 mmol) in THF (4 mL) was added dropwise some hexane solution of BuLi (1.6 M, 4.2 mL, 6.82 mmol, 1 M=1 mol dm^{-3}) over a few minutes using a syringe at −55 °C under nitrogen atmosphere. After 30 min, a solution of benzophenone (1.657 g, 9.09 mmol) in THF (0.7 mL) was added and this mixture was stirred for 30 min at room temperature. Drops of brine (20 mL) were added. The mixture was extracted with ether (2×20 mL), and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane : AcOEt= 60 : 1) to afford **2a** (1.95 g, 91% yield base on BuLi used) as a colorless solid, mp 68—72 °C.

Compound **2a** is also obtained more directly from dicyclopentadiene through potassiation with the base complex BuLi–*t*-BuOK in somewhat lower yield. Bromodicyclopentadiene is a convenient stock precursor because of its easy lithiation with BuLi.

2a: IR (CCl_4) 3626, 1490, 1327, 1169, 1012, 700 cm^{-1}; ^{1}H NMR δ=1.22—2.46 (5H, m), 2.52—3.10 (3H, m), 3.12—3.41 (1H, m), 5.35—5.47 (1H, m), 5.67—5.85 (2H, m), 7.06—7.56 (10H, m); MS *m/z* 314 (M^+). Found: C, 87.85; H, 7.04%. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05%.

2b: (75% yield); colorless oil; IR (CCl_4) 3558, 1449, 1325, 1165, 1016 cm^{-1}; ^{1}H NMR δ=1.34—2.50 (5H, m), 2.26, 2.29, 2.32 (6H, each s), 2.77—3.04 (3H, m), 3.14—3.38 (1H, m), 5.18—5.83 (3H, m), 6.78—7.43 (8H, m). Found: *m/z* 342.1970. Calcd for $C_{25}H_{26}O$: M, 342.1981.

2c: (67% yield); colorless solid, mp 131—134 °C; IR (CH_2Cl_2) 3574, 1260, 1179, 1038, 830 cm^{-1}; ^{1}H NMR δ= 1.32—2.67 (5H, m), 2.71—3.04 (3H, m), 3.14—3.45 (1H, m), 3.75, 3.80, 3.81 (6H, each s), 5.16—5.88 (3H, m), 6.62—7.50 (8H, m); MS *m/z* 374 (M^+). Found: C, 79.87; H, 7.07%. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00%.

2d: (80% yield); colorless solid, mp 61—64 °C; IR (CCl_4) 3590, 1095, 1013, 747, 714 cm^{-1}; ^{1}H NMR δ=1.20—2.45 (5H, m), 2.59—2.97 (3H, m), 3.18—3.50 (1H, m), 5.15—5.86 (3H, m), 6.95—7.53 (8H, m). Found: *m/z* 382.0913. Calcd for $C_{23}H_{20}OCl_2$: M, 382.0890.

2e: (94% yield); colorless oil; IR (CCl_4) 3558, 1312, 1249, 1046, 697 cm^{-1}; ^{1}H NMR δ=1.25—2.50 (5H, m), 2.63—3.10 (3H, m), 3.18—3.51 (1H, m), 5.40—5.90 (3H, m), 6.69—7.19 (4H, m), 7.20—7.37 (2H, m). Found: *m/z* 326.0801. Calcd for $C_{19}H_{18}OS_2$: M, 326.0798.

2f: (60% yield); colorless solid, mp 85—88 °C; IR (CCl_4) 3430, 1327, 1165, 1058, 913, 697 cm^{-1}; ^{1}H NMR δ=1.21—2.41 (5H, m), 1.55 (3H, s), 2.52—2.99 (3H, m), 3.03—3.35 (1H, m), 5.30—5.95 (3H, m), 7.05—7.50 (5H, m); MS *m/z* 252 (M^+). Found: C, 85.28; H, 8.03%. Calcd for $C_{18}H_{20}O$: C, 85.67, H, 7.99%.

2g: (91% yield); colorless oil; IR (CCl_4) 3626, 1450, 1437, 1188, 1012, 700 cm^{-1}; ^{1}H NMR δ=1.20—2.46 (5H, m), 2.52—3.10 (3H, m), 3.12—3.41 (1H, m), 4.94—5.34 (1H, m), 5.34—5.89 (3H, m), 7.12—7.45 (5H, m); MS *m/z* 238 (M^+). Found: C, 85.41; H, 7.97%. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61%.

2h: (51% yield); colorless oil; IR (CCl_4) 3400, 1447, 1262, 1150, 965 cm^{-1}; ^{1}H NMR δ=1.08—2.42 (15H, m), 2.61—3.06 (3H, m), 3.16—3.44 (1H, m), 5.42—5.86 (3H, m). Found: *m/z* 230.1664. Calcd for $C_{16}H_{22}O$: M, 230.1669.

Thermolysis of 2a in Quinoline. A solution of **2a** (0.076 g, 0.24 mmol) in quinoline (2 mL) was heated at 180 °C under nitrogen atmosphere for 3 h. The mixture was poured into cold 4 M HCl (15 mL) and then was extracted with ether (2×10 mL). The ether extract was washed with saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluted with hexane) to afforded **4a** (0.048 g, 86%, mp 81—82 °C, lit,[4] 82 °C).

Thermolysis of 2a by Flow Method as a Typical Procedure. An electric furnace (inside: 23×330 mm), a quartz tube (12×450 mm) packed with Pyrex glass tips, a pressure equalizing dropping funnel with nitrogen inlet, and a receiver with nitrogen outlet are set up vertically. The receiver is cooled in an ice-bath. A solution of **2a** (0.320 g, 1.02 mmol) in benzene (9 mL) was dropped over 90 s into the quartz tube heated at 300 °C under nitrogen flow of about 60 mL min^{-1}. Immediately after completion of the dropping, benzene (5 mL) was dropped in to wash the pyrolysate out. The benzene solution in the receiver was concentrated under reduced pressure, and the residue was chromatographed on silica gel (hexane : AcOEt=60 : 1, then 20 : 1) to afford, in the order of elution: **4a** (0.014 g, 6%), unreacted **2a** (0.010 g, 3%), benzophenone (0.048 g, 26%), and **3a** (0.132 g, 52%). The results with **2b**—**h** are given in Table 1. Alcohols **3a**—**h** were always obtained as mixtures of position isomers.

3a: Colorless solid, mp 128—131 °C; IR (KBr) 3440, 1447, 1010, 893, 750, 699 cm^{-1}; ^{1}H NMR δ=2.62, 2.64 (1H, each s), 3.04 (2H, s-like), 5.95, 6.10 (1H, each m), 6.39 (1H, s-like), 6.45 (1H, s-like), 7.37 (10H, m). Found: *m/z* 248.1204. Calcd for $C_{18}H_{16}O$: M, 248.1200.

3b: Colorless oil; IR (CCl_4) 3386, 1181, 1157, 1021, 910 cm^{-1}; ^{1}H NMR δ=2.32 (7H, s-like), 3.01 (2H, s-like), 5.87—6.14 (1H, m), 6.32—6.50 (2H, m), 6.87—7.36 (8H, m). Found: *m/z* 276.1505. Calcd for $C_{20}H_{20}O$: M, 276.1512.

3c: Colorless oil: IR (CH_2Cl_2) 3280, 1179, 1020, 921, 835 cm^{-1}; ^{1}H NMR δ=3.03 (2H, bs), 3.77 (1H, s), 3.86 (6H, s), 5.66—5.98 (1H, m), 6.18—6.50 (2H, m), 6.75—7.20 (8H, m). Found: *m/z* 308.1395. Calcd for $C_{20}H_{20}O_3$: M, 308.1411.

3d: Colorless oil; IR (CCl_4) 3400, 1241, 1097, 1013, 897, 694 cm^{-1}; ^{1}H NMR δ=2.67 (1H, bs), 2.97, 3.04 (2H, each bs), 5.86—6.12 (1H, m), 6.30—6.54 (2H, m), 7.26 (8H, bs). Found: *m/z* 316.0463. Calcd for $C_{18}H_{14}OCl_2$: M, 316.0505.

3e: Colorless oil; IR (neat) 3340, 1036, 954, 900, 786, 765 cm^{-1}; ^1H NMR δ=3.06 (3H, m), 6.20—6.65 (3H, m), 6.75—7.04 (4H, m), 7.10—7.35 (2H, m). Found: *m/z* 260.0329. Calcd for $C_{14}H_{12}OS_2$: M, 260.0343.

3f: Colorless oil; IR (neat) 3350, 1163, 899, 763, 698 cm^{-1}; ^1H NMR δ=1.79 (3H, s), 2.28 (1H, bs), 2.89, 3.01 (2H, each bs), 6.15—6.48 (3H, m), 7.08—7.51 (5H, m). Found: *m/z* 186.1040. Calcd for $C_{13}H_{14}O$: M, 186.1043.

3g: Colorless oil; IR (CCl_4) 3612, 3350, 1175, 1020, 900, 700 cm^{-1}; ^1H NMR δ=2.59—3.03 (3H, m), 4.80—5.15 (1H, m), 5.51 (1H, bs), 6.11—6.49 (2H, m), 7.27 (5H, bs). Found: *m/z* 172.0878. Calcd for $C_{12}H_{12}O$: M, 172.0887.

3h: Colorless oil; IR (CCl_4) 3610, 3400, 1260, 1035, 955, 900 cm^{-1}; ^1H NMR δ=1.05—1.92 (10H, m), 2.16 (1H, m), 2.97 (2H, m), 5.48 (1H, bs), 6.12—6.70 (2H, m). Found: *m/z* 164.1181. Calcd for $C_{11}H_{16}O$: M, 164.1199.

Reaction of 3a with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) Giving Fulvenes 5a as a Typical Procedure. DBU (0.18 mL, 1.20 mmol) was added to a solution of **3a** (0.100 g, 0.40 mmol) in THF (3 mL) and the mixture was stirred at room temperature for 24 h. The mixture was poured into cold 1 M HCl (10 mL) and extracted with ether (3×10 mL). The combined ether extract was washed with saturated $NaHCO_3$ and brine, and then dried over $MgSO_4$. Ether was removed, and the residue was chromatographed on silica gel (hexane, then hexane : AcOEt=20 : 1) to afford **4a** (0.084 g, 90%) and unreacted **3a** (0.005 g, 5%). The results with **3b—h** are listed in Table 2. All the fulvenes here obtained are known compounds and were identified by comparison of spectral data with those of authentic samples prepared by a condensation method.[3,6]

Trimethylsilyl Ether 7. To a solution of an isomeric mixture of bromodicyclopentadiene (0.80 g, 3.79 mmol) in THF (2 mL) was added dropwise some hexane solution of BuLi (1.6 M, 2.1 mL, 3.41 mmol) over a few minutes using a syringe at −55 °C under nitrogen atmosphere. After 30 min, a solution of benzophenone (0.829 g, 4.55 mmol) in THF (0.5 mL) was added; then the mixture was stirred at the same temperature for 10 min. To the mixture was added chlorotrimethylsilane (0.7 mL, 5.50 mmol), and the resulting solution was stirred for 30 min at room temperature. Drops of brine (15 mL) were added. The mixture was extracted with ether (2×15 mL), and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane) to afford **7** (0.92 g, 70% yield base on BuLi used) as a colorless oil: IR (neat) 1253, 1063, 841, 758, 704 cm^{-1}; ^1H NMR δ=−0.19 (9H, s), 1.23—2.41 (4H, m), 2.59—2.99 (3H, m), 3.00—3.45 (1H, m), 4.70—4.86, 5.19—5.80 (3H, m), 7.12—7.49 (10H, m). Found: *m/z* 386.2071. Calcd for $C_{26}H_{30}OSi$: M, 386.2065.

Thermolysis and Subsequent Base Treatment of 7. The experimental apparatus was used as described above. A solution of **7** (0.313 g, 0.081 mmol) in benzene (9 mL) was dropped over 90 s into the quartz tube heated at 350 °C under nitrogen flow of about 60 mL min^{-1}. Immediately after completion of the dropping, benzene (5 mL) was dropped in to wash the pyrolysate out. The benzene solution in the receiver was concentrated under reduced pressure, and the residue was chromatographed on silica gel (hexane) to afford a mixture of **8** and **4a** (0.158 g) as a reddish yellow oil. Compounds **8** and **4a** have a similar R_f value on TLC (hexane), so the compounds were used without further purification. *t*-BuOK (0.111 g, 0.989 mmol) was added to a solution of a mixture of **8** and **4a** (0.158 g) in THF (4 mL) at 0 °C. After stirring for 3.5 h at 0 °C, brine (15 mL) was added and the mixture was extracted with ether (3×15 mL). The combined ether extract was washed with brine, and dried over $MgSO_4$. Ether was removed, and the residue was chromatographed on silica gel (hexane) to afford **4a** (0.092 g, 49%).

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