Tetrahedron Letters, Vol. 33, No. 47, pp. 7201-7204, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

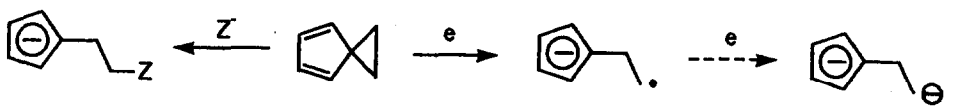
Synthesis and Alkali Metal Reduction of 1,1-Diarylspiro[2.4]hepta-4,6-dienes. Generation of Homopentafulvene Dianions

Takeshi Kawase, Hiroyuki Kurata, Shin-ichi Fujino, Tatsuya Ekinaka, and Masaji Oda*
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

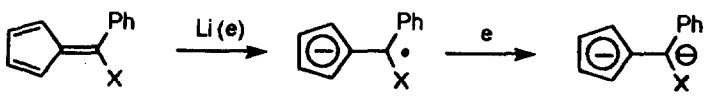
Abstract: Reaction of 6,6-diarylfulvene dianions with dichloromethane yields 1,1-diarylspiro[2.4]hepta-4,6-dienes, and reduction of the diphenylspiroheptadiene with lithium metal or lithium naphthalene cleanly generates a novel homopentafulvene dianion.

Spiro[2.4]hepta-4,6-diene **1** undergoes either ring opening to cyclopentadienyl anions **2** or metallation on the cyclopropane ring upon treatment with bases, which provides useful synthetic tools in organic and organometallic chemistry.[1,2] In similar fashion, reduction of **1** with sodium in liquid ammonia yields ethylcyclopentadienyl anion, where the intermediacy of the radical anion **3** has been postulated.[3] If further electronic reduction of **3** is possible under the reducing condition, the dianion **4** (homopentafulvene dianion) would result from **1**. However, no generation of **4** has been described yet. This may be due to either too high reactivity (hence too short lifetime) or a high reduction potential of **3**.

We have recently reported the synthesis of the pentafulvene dianions **7** by alkali metal reduction of the pentafulvenes **5**; among them diphenyl compound **7a** was a substantially stable dianion to be first characterized spectroscopically.[4] Stabilization of the intermediate radical anion **6** by the phenyl groups plays an important role for the clean generation of **7a**. Accordingly, introduction of diaryl groups at the C-1 position of **1** should enable a clean formation of the derivatives of **4** upon electronic reduction.



2 **1** **3** **4**

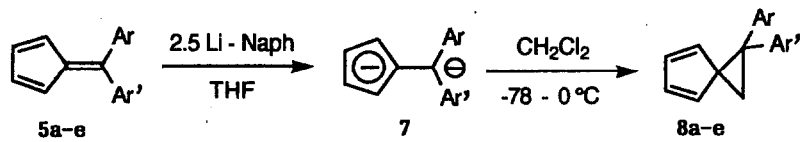


5 **6** **7**: X = Ph (**7a**), NMe_2

Although a number of spiro[2.4]heptadienes have been synthesized in several ways, no 1,1-diaryl derivatives **8** have been described.[3,5] The pentafulvene dianion **7** turned out to be good precursors for the synthesis of 1,1-diarylspiro[2.4]hepta-4,6-dienes **8**, because the C-6 position is more reactive than the cyclopentadienyl part

toward electrophiles.[4] We now report the synthesis of **8**, generation of homopentafulvene dianions from **8**, and some properties of them.

The reduction of 6,6-diphenylfulvene **5a** with lithium naphthalene (2.5 equiv.) in THF at -78 °C for 20 min affords a solution of the dianion **7a**. Addition of dichloromethane (3.0 equiv.) to this solution at -78 °C and stirring the solution at 0 °C for 3 h furnished 1,1-diphenylspiro[2.4]hepta-4,6-diene **8a**[6] in 82% yield.[5] The reaction is applicable for the synthesis of other diarylspiroheptadienes such as **8b-e**[6] in moderate to good yields (Table 1).



5a-e **7** **8a-e**

Table 1. Synthesis of 1,1-diarylspiro[2.4]hepta-4,6-dienes 8 from 6,6-diarylfulvenes 5.

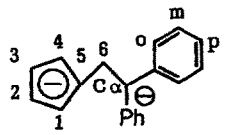
Starting fulvene	Ar	Ar'	Spirodiene[a]	Product Yield/%	Mp °C
5a	C_6H_5	C_6H_5	**8a**	82	52.5-53
5b	p-C_6H_4-OCH_3	p-C_6H_4-OCH_3	**8b**	95	72-73
5c	p-C_6H_4-Cl	p-C_6H_4-Cl	**8c**	53	121-122
5d	C_6H_5	p-C_6H_4-OCH_3	**8d**	56	73-74
5e	C_6H_5	2-pyridyl	**8e**	20	oil

[a] Selected spectral data are given in ref. 6.

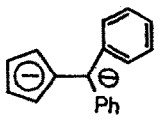
The treatment of **8a** with lithium powder in THF at room temperature under sonication cleanly afforded the dianion **10a** in red solution, probably through the radical anion **9a**. With lithium naphthalene, the reduction proceeded rapidly even at -78 °C by virtue of the homogeneous reaction. The ^1H and ^{13}C NMR data (Table 2) are consistent with the dianion structure of **10a**. The chemical shift of the phenyl ortho protons of **10a** (δ 7.05) lies between those of **7a** (δ 7.25)[4] and diphenylmethyl anion **11** (δ 6.51)[7] to indicate the presence of considerable anisotropic effect by the aromatic cyclopentadienyl part though somewhat weaker than that in **7a**.

The oxidation of **10a** with copper(II) chloride regenerated **8a** (70%), whereas the quenching with water gave an isomeric mixture of the cyclopentadiene derivative **12**[6] (98%). Like **7a**, the diphenylmethyl anion part of **10a** is more reactive than the cyclopentadienyl part toward electrophiles, providing **10a** with synthetic utility. The reaction of **10a** with dichloromethane (4.0 equiv.) at 0 °C followed by quenching with water afforded the chloromethyl compound **14** (60%).[6] The intermediate **13** was reluctant to intramolecular cyclization even around room temperature probably for steric reasons. With 1,2-dichloroethane, however, **10a** underwent sequential nucleophilic reactions yielding the spiro[4.4]nonadiene **15** (28%),[6] thus presenting a new synthetic method for

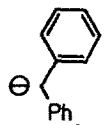
Table 2. ^{1}H and ^{13}C NMR data of **10a**[a,b] compared with those of **7a**[a,c] and diphenylmethylanion **11**[d] (δ ppm).



10a



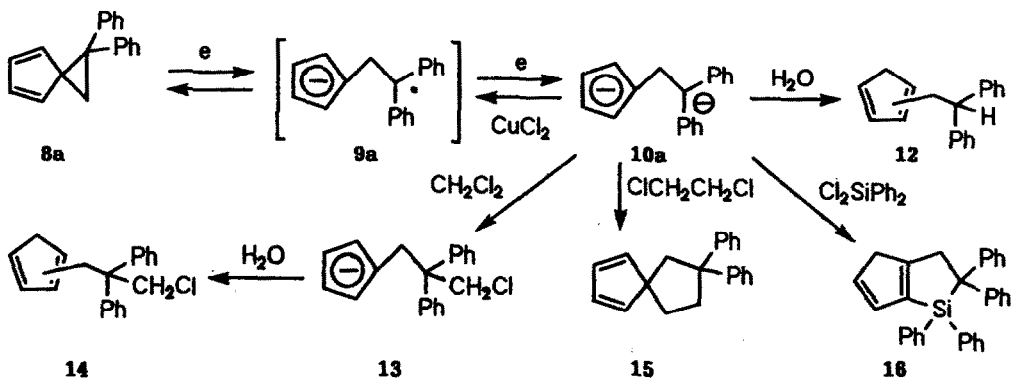
7a



11

Position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	5.73	103.86	5.92	100.60	——	——
2	5.62	102.20	5.56	99.25	——	——
3	5.62	102.20	5.56	99.25	——	——
4	5.73	103.86	5.92	100.60	——	——
5	——	125.47	——	127.88	——	——
6	3.48	33.25	——		——	——
C_α	——	85.14	——	81.30	——	78.5
ipso	——	146.79	——	148.94	——	147.4
ortho	7.05	117.25	7.25	121.18	6.51	117.5
meta	6.49	128.40	6.39	127.94	6.54	128.1
para	5.54	107.78	5.67	109.67	5.65	107.1

[a] ^{1}H at 270 MHz and ^{13}C at 67.5 MHz in THF-d_8. [b] ^{1}H-^{1}H coupling constants: $J_{1,2} = J_{1,3} = 2.64$ Hz, $J_{o,m} = 7.59$ Hz, $J_{m,p} = 6.93$ Hz. [c] ref. 4. [d] ref. 7.

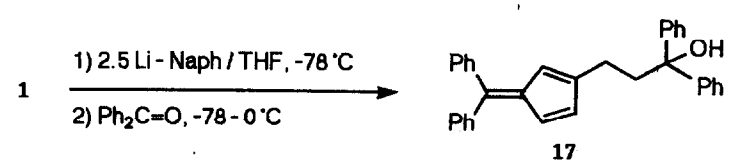


8a **9a** **10a** **12**

14 **13** **15** **16**

spiro[4.4]nona-1,3-dienes. On the other hand, **10a** furnished the novel tetrahydrosilapentalene **16** (31%)[6] upon reaction with dichlorodiphenylsilane.

In the light of these results, we reexamined alkali metal reduction of the parent spiroheptadiene **1**. Addition of **1** to a THF solution of lithium naphthalene (2.5 equiv.) at -78 °C followed by addition of benzophenone (4.3 equiv.) and warming the mixture up to room temperature gave rise to the pentafulvene derivative **17** (33%), where two molecules of benzophenone took part in.[8] This result suggests the intermediate formation of the dianion **4** under the reducing condition even if not cleanly.



17

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture, Japan.

References and Notes

1. Kauffmann,T.; Bisling,M.; Konig,R.; Rensing,A.; Steinseifer,F. *Chem. Ber.*, **1985**, 118, 4517 and references cited therein.
2. Eilbracht,P.; Dahler,P.; Mayser,U.; Henkes,E. *Chem. Ber.*, **1980**, 113, 1033; Eilbracht,P.; Totzauer,W. *ibid.*, **1982**, 115, 1669; Slawin,A.M.Z.; Williams,D.J.; Ramsden,J.A.; White,C. *J. Chem. Soc., Dalton Trans*, **1988**, 2491; Kettenbach,R.T.; Butenschoen,H. *New J. Chem.*, **1990**, 14, 599; Lhemkuhl,H.; Naeser,J.; Mehler,G.; Keil,T.; Danourski,F.; Benn,R.; Mynott,R.; Schroth,G.; Krueger,C.; Betz,P. *Chem. Ber.*, **1991**, 124, 441.
3. Alder,K.; Ache,H.J.; Flock,F.H. *Chem. Ber.*, **1960**, 93, 1888.
4. Kawase,T.; Fujino,S.; Oda,M. *Chem. Lett.*, **1990**, 1683.
5. Wilcox,C.F.Jr.; Craig,R.R. *J. Am. Chem. Soc.*, **1961**, 83, 3866; Amaro,A.; Grohmann, K. *ibid.*, **1975**, 97, 3830; Kosman,D.; Stock,L.M. *J. Org. Chem.*, **1975**, 40, 2255; Moss,R.A.; Young,C.M.; Perez,L.A.; Krogh-Jespersen,K. *J. Am. Chem. Soc.*, **1981**, 103, 2413; Antczak,K.; Kingston,J.F.; Fallis,A.G. *Tetrahedron Lett.*, **1984**, 25, 2077.
6. NMR data of selected compounds (270 or 67.5 MHz, in $CDCl_3$); **8a**: ^1H δ 2.53 (2H, s), 5.87 (2H, m), 6.43 (2H, m), 7.10-7.27 (6H, m), 7.37-7.43 (4H, m), ^{13}C δ 23.23, 48.16, 48.77, 126.82, 128.27, 128.96, 129.34, 137.84, 144.26; **8c**: ^1H δ 2.46 (2H, s), 5.81 (2H, m), 6.44 (2H, m), 7.21 (4H, d, J=8.7 Hz), 7.30 (4H, d, J=8.7 Hz); **8e**: ^1H δ 2.47 (1H, d, J=4.0 Hz), 3.22 (1H, d, J=4.0 Hz), 5.87 (1H, dt, J= 5.3, 1.7 Hz), 6.02 (1H, dt, J=5.3, 1.7 Hz), 6.42 (2H, m), 7.06 (1H, ddd, J=7.9, 5.0, 1.0 Hz), 7.13 (1H, dd, J=7.9, 1.0 Hz), 7.20-7.50 (6H, m), 8.55 (1H, dd, J=5.0, 1.8, 1.0 Hz); **14**: 1.35:1 mixture of two isomers; ^1H (aliphatic protons) δ 2.10 (0.85H, d, J=1.4 Hz), 2.84 (1.15H, t, J=1.2 Hz), 3.36 (1.15H, s), 3.41 (0.85H, s), 4.17 (1.15-H, s), 4.19 (0.85H, s); **15**: mp 81-83 °C; ^1H δ 1.97 (2H, t, J=6.9 Hz), 2.67 (2H, t, J=6.9 Hz), 2.67 (2H, s), 6.11 (4H, br.s), 7.22-7.35 (10H, m); **16**: 6:1 mixture of two isomers; ^1H (major isomer) δ 3.19 (2H, t, J=1.5 Hz), 3.74 (2H, t, J=2.8 Hz), 6.77 (1H, dt, J=5.1, 1.5 Hz), 6.94-7.35 (11H, m); **17**: orange oil, ^1H δ 1.54 (1H, s, OH), 2.46 (2H, m), 2.57 (2H, m), 5.98 (1H, m), 6.28 (1H, dd, J=5.2, 2.0 Hz), 6.48 (1H, dd, J=5.2, 1.7 Hz), 7.17-7.49 (20H, m).
7. Waack,R.; Doran,M.A.; Baker,E.B.; Olah,G.A. *J. Am. Chem. Soc.*, **1966**, 88, 1272; Takahashi,K.; Kondo,Y.; Asami,R. *Org. Mag. Reson.*, **1974**, 6, 580.
8. Cram,D.J.; van Duuren,B.L. *J. Am. Chem. Soc.*, **1955**, 77, 3576; Semmelhack,M.F.; Foos,J.S.; Katz,S. *ibid.*, **1973**, 95, 7325.

(Received in Japan 20 July 1992)