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シクロペンタ［*cd*］アズレンの合成

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Synthesis of Cyclopenta [*cd*] azulenes

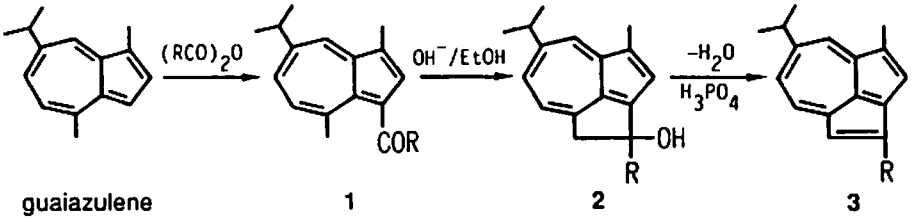
Kouichi SATOH*, Isao AWATA**, and Isao OGURA**

Abstract

3-Perfluoroacylguaiazulenes were treated with ethanolic alkaline to give 1', 2'-dihydrocyclopenta [*cd*] azulene-2'-ols, followed by dehydration with phosphoric acid to result 2'-perfluoroalkylcyclopenta [*cd*] azulenes, correspondingly, and the fundamental frame-work of these fluorinated hydrocarbons was assumed to be azulene and ethylenic double bond structures on the base of ^{1}H-NMR study.

1. Introduction

In the previous communication[1], Satoh and Ogura have reported that 3-trifluoroacetylguaiazulene (**1a**)[2] was converted into a tricyclic alcohol (**2a**) with ethanolic alkaline. We now report that 2'-perfluoroalkylcyclopenta [*cd*] azulene easily obatined from 3-perfluoroacylguaiazulene through the alcohol.



guaiazulene　　1　　2　　3

		Yield (%)		
	R	1	2	3
a	CF_3	68	34	23
b	C_2F_5	94	59	97
c	C_3F_7	87	52	–

Fig.1 Synthesis of cyclopenta[*cd*]azulenes from gutazulene

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2. Results and Discussion

3-pentafluoropropionylguaiazulene (**1b**) and 3-heptabutyronylguaiazulene (**1c**) were prepared from guaiazulene and pentafluoropropionic anhydride, and heptafluorobutyric anhydride in 94 and 87% yields, respectively. With ethanolic alkaline, **1b** was converted into the homologue **2a** ; 2'-pentafluoroethyl-5-isopropyl-2'-hydroxy-1',2'-dihydrocyclopenta [*cd*] azulene (**2b**) in 59% yield. And in the same manner, **1c** gave **2c** in 52% yield.

Then **2a** and **2b** were dehydrated with 85% phosphoric acid to provide 2'-trifluoromethyl-and 2'-pentafluoroethyl-5-isopropyl-3-methylcyclopenta [*cd*] azulenes (**3a**) and (**3b**) as red oil in 23 and 97% yields, respectively, and both products were purified as TNB complex[3], but in the same reaction of **2c**, a reddish oily product was so unstable that it was impossible to identify even as a TNB complex. Mass spectrometric molecular weight was determined to be 276 for **3a** and 326 for **3b** just as expected.

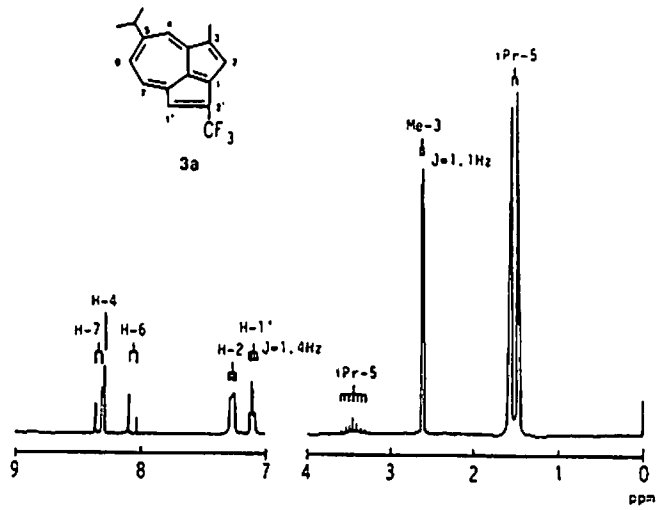

Fig.2 ^{1}H-NMR spectrum of cyclopenta[*cd*]azulene (**3a**)

Furthermore, some supplemental but remarkable phenomena, supporting their structure elucidation and suggesting a presence of 3-perfluoroalkylazulene structure and of an ethylenic double bond in the molecule, were disclosed in their ^{1}H-NMR spectra (Fig.2 and Table 1). By means of H-F or H-H spin decoupling treatment, it become to be obvious that **3a**'s δ 7.09 (quartet) and **3b**'s δ 7.25 (triplet) were due to proton (s) at C-1' or Me-1 splitted by H-F through space coupling with fluorine atoms in the adjacent substituent, and pairs of **3a**'s δ 7.15 (quartet) and 2.57 (doublet), and of **3b**'s δ 7.26 (quartet) and 2.58 (doublet) were owing

to H-H long range coupling between H-2 and methyl protons at C-1. Though the latter was observed generally in the system of $H_3C-C=C-H$ (*Z* form), but never with guaiazulene or its derivatives, so far as examined.

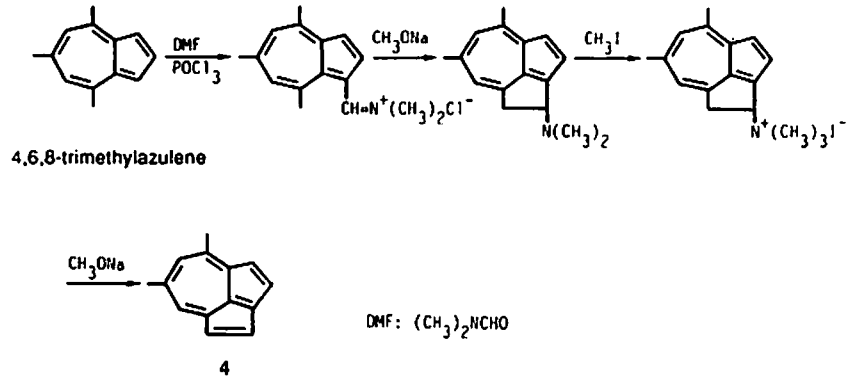

Fig.3 Synthesis of Cyclopenta[*cd*]azulenes by Hafner and Schneider[4]

Hafner and Schneider[4] reported on a synthesis of a cyclopenta[*cd*]azulene (**4**) from 4,6,8-trimethylazulene under anhydrous condition (Fig.3), and on its reactivity, especially of a double bond in any one of five membered rings which were highly strained. It is that the most reactive site of **3** should be the C_2-C_3 [5] segment because it is a ethylenic double bond located out of azulenoid system.

Table 1. ^{1}H-NMR spectral data [a,b]

Compound	H-2 ($J_{H-2,F}$)	Me-3 ($J_{Me-3,H-2}$)	H-4	H-6 ($J_{H-6,H-7}$)	H-7	Others
2a	7.37	2.60	8.01	7.41[d] (10.2)	6.85[d]	2.49 (OH), 3.26[d] and 4.01[d] (CH_2, J_{CH_2} = 17.4)
2b	7.50	2.63	8.13	7.53[d] (12.0)	6.97[d]	2.59 (OH), 3.67[d] and 4.26[d] (CH_2, J_{CH_2} = 18.0)
2c	7.49	2.64	8.07	7.51[d] (8.0)	6.98[d]	2.59 (OH), 3.67[d] and 4.26[d] (CH_2, J_{CH_2} = 18.0)
3a[c]	7.25[s]	2.57[d] (1.4)	8.26	8.04[d] (9.7)	8.29[d]	7.09[s] (H-1', $J_{H-1',F}$ = 1.4)
3b[c]	7.26[s]	2.58[d] (1.4)	8.29	8.07[d] (9.3)	8.33[d]	7.09[s] (H-1', $J_{H-1',F}$ = 1.4)

a) in $CDCl_3$ at 200MHz.

b) isopropyl group's signals of all products : δ 1.34-1.51[d] and 3.05[sept].

c) TNB complex.

3. Experimental

3.1 Preparation of 3-perfluoroacylguaiazulene (1b) and (1c).

Both **1b** and **1c** were prepared in the same manner as **1a**[2]. **1b**: brown prisms (hexane); mp 80.0-81.0°C[5]; IR (nujol) 1654 cm^{-1} (C = O); ^{1}H-NMR ($CDCl_3$) δ: 2.60 (3H, s, Me-1), 2.86 (3H, s, Me-4), 7.53 (1H, d, J = 10.8Hz, H-7), 7.71 (1H, dd, J = 2.3 and 10.8Hz, H-6), 8.09 (1H, t, J = 2.6Hz, H-2), 8.33 (1H, d, J = 2.3Hz, H-4), MS m/z 344 (M^+), 225 ($M^+-C_2F_5$); *Anal.* Calcd for $C_{18}H_{17}F_5O$: F, 27.58%; Found: F, 27.27%. **1c**: brown needles (hexane); mp 35.4 – 36.4°C; IR (nujol) 1666 cm^{-1} (C = O), ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, Me-1), 2.69 (3H, s, Me-4), 7.49 (1H, d, J = 10.8Hz, H-7), 7.66 (1H, dd, J = 2.3 and 10.8Hz, H-6), 7.99 (1H, t, J = 2.7Hz, H-2), 8.25 (1H, d, J = 2.3Hz, H-4), MS m/z 394 (M^+), 225 ($M^+-C_3F_7$); *Anal.* Calcd for $C_{19}H_{17}F_7O$: F, 33.72%; Found: F, 31.47%.

3.2 Ring closure of 1b and 1c.

A mixture of **1b** (6.9 g, 20 mmol), 50 ml of ethanol, and 10 ml of 10% aqueous NaOH was refluxed for 0.5 h. The reaction mixture was flooded with water and extracted with ether, followed by 60-80 mesh silica-gel column chromatography (eluted with ether) to give **2b** as blue oil (4.1g). **2b**: IR (nujol) 3600-3400 cm^{-1} (OH); MS m/z 344 (M^+), 326 (M^+-H_2O); 225 ($M^+-C_2F_5$); *Anal.* Calcd for $C_{18}H_{17}F_5O$: F, 27.58%; Found: F, 25.35%. **2c**: blue prisms (hexane); dec. 77.0°C; IR (nujol) 3575 – 3442cm^{-1} (OH); MS m/z 394 (M^+), 376 (M^+-H_2O); 225 ($M^+-C_3F_7$); *Anal.* Calcd for $C_{19}H_{17}F_7O$: F, 33.7%; Found: F, 32.0%.

3.3 Dehydration of 2a and 2b with phosphoric acid.

A solution of **2a** (1.4 g, 85 mmol) in 100 ml of ether was shaken with 100 ml of 85% phosphoric acid for 0.5 h. The reaction mixture was poured into 800 ml of ice cooled water and extracted with ether, followed by chromatography as above (eluted with hexane) to give **3a** as red oil (0.32 g). TNB of **3a** was recrystallized from EtOH to brown needles; mp 109.0 – 110.5°C; ^{13}C-NMR ($CDCl_3$) δ: 118.3 (quart, J = 9.9Hz, C-1'), 127.9 (C-5), 131.2 (C-8), 132.0 (C-6), 132.9 (C-2), MS m/z 276 (M^+), 207 (M^+-CF_3); *Anal.* Calcd for $C_{23}H_{16}F_3N_3O_6$: F, 11.64%; Found: F, 11.11%. **3b**: red oil; TNB: brown needles (EtOH); mp 106.0-107.0°C; MS m/z 326 (M^+); *Anal.* Calcd for $C_{24}H_{16}F_5N_3O_6$: F, 17.61%; Found: F, 15.32%.

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3) 1,3,5-Trinitrobenzene complex.
4) K. Hafner, J. Schneider, *Ann.*, **624**, 37 (1959).
5) C_2 and C_3 are meaning of C-2 and C-3, respectively.
6) The melting points are uncorrected.