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REACTIONS BASED ON TETRADECAFLUOROBICYCLO-[4,4,0]-DEC-1(2),6(7)-DIENE

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SUMMARY

Depending on the proportion of nucleophile added, tetradecafluorobicyclo[4,4,0]dec-1(2),6(7)-diene (1) reacted with RXH (R=Me, Et, Ph; X=O, S) and Et_2NH forming the corresponding 2-substituted or 2,7-disubstituted dodecafluorobicyclo[4,4,0]dec-1(2),6(7)-dienes(2-10). Defluorination of the corresponding disubstituted dodecafluorobicyclo[4,4,0]dec-1(2),6(7)dienes with Mg gave 1,5-disubstituted perfluoronaphthalenes (12-14).

INDRODUCTION

Reactions of polyfluoromonocycloolefins with nucleophiles have been studied extensively. These reactions are somewhat different from the alicyclic analogues because of the ring strain. Usually vinylic substituted products were obtained in predominance. However, reactions of polyfluorobicyclic olefins with nucleophiles are not well known. Tatlow et al. reported that the reactions of dodecafluorobicyclo[3,3,0]oct-1(5)-ene and hexadecafluorobicyclo-[4,4,0]dec-1(6)-ene with nucleophiles gave mainly polysubstituted products because the olefinic bonds reformed after the addition-elimination process were even more reactive than their precursors[1]. Studies on the reactions of perfluorobicyclic compounds containing a conjugated double bond are rare. In this paper, the reaction of tetradecafluorobicyclo[4,4,0]dec-1(2),6(7)-diene (1) with nucleophiles and defluorination of the resultant products have been studied.

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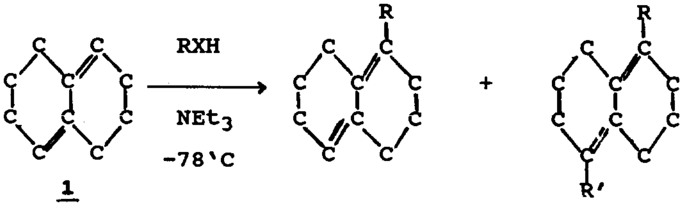
RESULTS AND DISCUSSION

Tetradecafluorobicyclo[4,4,0]dec-1(2),6(7)-diene (1) was obtained by defluorination of hexadecafluorobicyclo[4,4,0]dec-1(6)-ene with zinc powder[2]. In the presence of NR_3, the reaction of 1 with ROH, RSH and R_2NH proceeded smoothly and the mono- or di-vinylic substituted products (2-10) were formed depending on the proportion of nucleophile used (**SCHEME I**). 11 was formed from the reaction of 2 with Et_2NH. In all the cases, products arising by protonation or allylic elimination of the carbanionic intermediate were not detected.



1

2, R=EtO
3, R=Et_2N

4, R=R'=MeO
5, R=R'=EtO
6, R=R'=iso-PrO
7, R=R'=PhO
8, R=R'=EtS
9, R=R'=PhS
10, R=R'=Et_2N
11, R=EtO, R'=Et_2N

* All unmarked bonds are to fluorine.

SCHEME I.

All such products were characterized by elemental analysis, IR, UV, ^1H NMR and ^{19}F NMR (**TABLES 1-3**). Both UV and IR showed a substituted conjugated double bond[3]. Strong molecular ions were recorded by mass spectra. ^{19}F NMR revealed that only the chemical shifts at C-3 and C-8 were slightly changed in compounds 4-11 as compared with the parent 1.

These results implied that nucleophiles exclusively attacked C-2 and then C-7. In all the cases only vinylic fluorides were eliminated. The reaction was postulated to proceed as follows:

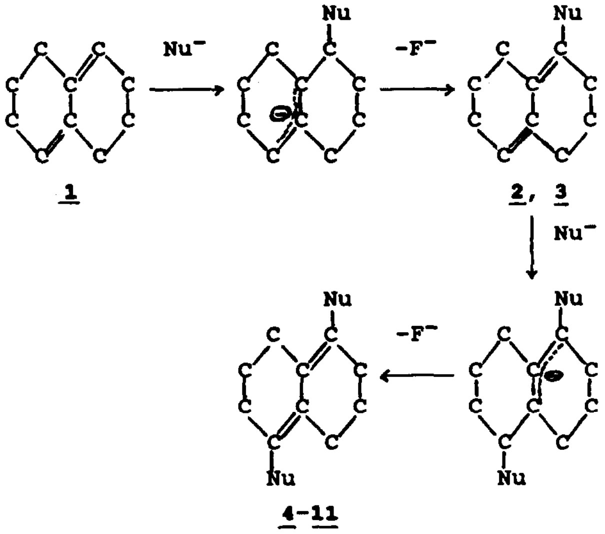


TABLE 1

Yields and Analytical Data for Compounds 2-11

Compd.	m.p. or b.p./mmHg	Yield (%)	Found/Calcd. C	Found/Calcd. H	Found/Calcd. F	Found/Calcd. N or S
2	35-45/2	61.8	34.77/34.97	1.08/1.22	59.86/59.92	
3	120-5/20	49.0	37.98/38.29	2.17/2.29	56.11/56.23	3.45/3.19
4	93.5-4.5	86.6	34.96/35.14	1.20/1.47	55.66/55.58	
5	85.5-6.5	88.2	38.21/38.37	2.13/2.30	52.61/52.03	
6	91.9-2.5	79.5	41.12/41.22	2.63/3.03	48.78/48.89	
7	171.5-2.5	85.3	49.57/49.46	1.63/1.87	42.55/42.67	
8	71.2-2.4	64.0	35.78/35.75	1.95/2.14	49.45/48.47	13.77/13.63
9	165.5-7.0	73.6	46.49/46.65	1.66/1.78	40.35/40.25	11.43/11.32
10	63.5-5.0	56.5	43.53/43.91	3.86/4.09	46.06/46.30	5.89/5.69
11	44.5-5.7	45.0	41.03/41.30	2.79/3.25	48.73/49.00	2.78/3.01

TABLE 2
IR, UV and MS of Compounds 2-11

Compd.	IR(cm^{-1})		MS	UV[a]	
	band	assign.	m/e (inten., assign.)	λ_{max}(nm)	$\varepsilon \times 10^{-4}$
2	1670w		365 (97.4, M-F-C_2H_4)	254.5	3.70
	1620s	C=C	384 (100, M-C_2H_4)		
	1140s	C-F	393 (29.2, M-F)		
			412 (53.8, M)		
3	1585vs	C=C	420 (52.9, M-F)	342.7	3.36
	1150vs	C-F	424 (100, M-CH_3)	229.4	1.61
			439 (45.4, M)		
4	1620s	C=C	81 (62.1, C_2F_3)	263.5	3.54
	1140s	C-F	305 (62.0, C_8F_{11})		
			410 (100, M)		
5	1620s	C=C	363 (38.0, M-F-2C_2H_4)	265.7	3.93
	1140s	C-F	382 (49.0, M-2C_2H_4)		
			438 (100, M)		
6	1605s	C=C	382 (100, M-2C_3H_6)	270.3	3.60
	1138s	C-F	424 (81.9, M-C_3H_6)		
			466 (13.5, M)		
7	1625s	C=C	77 (20.9, C_6H_5)	290.7	2.41
	1590s	benezene	457 (2.3, M-C_6H_5)	242.6	3.79
	1490s	ring	515 (14.5, M-F)	205.8	2.64
	1150vs	C-F	534 (100, M)		
8	1554[b]	C=C	414 (15.8, M-2C_2H_5)	378.8	3.10
	1200s	C-F	442 (11.5, M-C_2H_5)	246.1	1.19
			470 (68.4, M)		
9	1550[b]	C=C	77 (54.8, C_6H_5)	383.8	3.93
	1580m	benezene	109 (42.8, SC_6H_5)	243.5	3.35
	1470m	ring	489 (11.7, M-C_6H_5)	209.1	4.10
	1200s	C-F	566 (100, M)		
10	1560vs	C=C	463 (12.1, M-C_2H_5)	384.9	3.05
	1140vs	C-F	477 (100, M-CH_3)	225.1	1.25
			492 (47.1, M)		
11	1580vs	C=C	402 (26.4, M-F-C_3H_8)	346.4	2.14
	1150s	C-F	422 (100, M-C_3H_7)	243.0	0.78
			465 (77.5, M)		

[a] UV was measured in 95% EtOH. [b] Measured by Laser Raman Spectra.

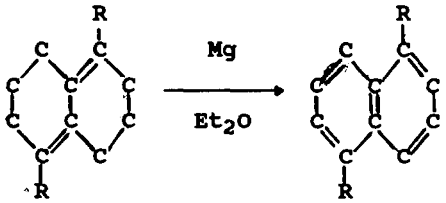
TABLE 3

^{19}F NMR and ^{1}H NMR of Compounds 2-11

Compd.	^{19}F NMR[a]							^{1}H NMR
	3	4	5	7	8	9	10	
2	41.0	61.5	48.3	48.3	41.8	61.5	41.0	1.4(CH_3), 4.4(CH_2)
3	39.0	59.7	48.0[b]	56.0	41.8	61.7	39.7	1.3(CH_3), 3.5(CH_2)
4[c]	39.4	59.3	41.0		39.4	59.3	41.0	4.3(OCH_3)
5[c]	39.0	59.7	41.0		39.0	59.7	41.0	1.3(CH_3), 4.2(CH_2O)
6[c]	38.4	60.3	40.7		38.4	60.3	40.7	1.4(CH_3), 4.6(CHO)
7[d]	38.9	60.4	40.0		38.9	60.4	40.0	6.9(C_6H_5)
8[c]	33.0	59.6	36.4		33.0	59.6	36.4	1.3(CH_3), 3.1(CH_2)
9[d]	33.1	60.7	35.4		33.1	60.7	35.4	6.8(C_6H_5)
10[c]	37.0	58.8	41.1		37.0	58.8	41.1	1.1(CH_3), 3.2(CH_2)
11[c]	38.0	59.3	41.2		41.2	61.0	40.3	1.1(CH_3), 3.2(CH_2N) 4.1(CH_2O)

[a] Except C-4 and C-9 in compounds 2-11 as well as C-5 and C-7 in compounds 2 and 3, other assignements were all tentatively made.
[b] $J_{4,5}$=22.6Hz. [c] Measured in CCl_4. [d] Measured in d-acetone.

Though defluorination of 1 with activated zinc was successful[2], attempts to synthesize 1,5-disubstituted perfluoronaphthalenes via defluorination of 2,7-disubstituted dodecafluorobicyclo[4,4,0]-dec-1(2),6(7)-dienes with activated Zn failed. Maganesium, another effective electron donor, has been used for defluorination in certain cases[3]. In fact, 2, 3 and 6 were defluorinated by Mg to give 1,5-disubstituted perfluoronaphthalenes (SCHEME II).



4, R=MeO 12, R=MeO
5, R=EtO 13, R=EtO
8, R=EtS 14, R=EtS

SCHEME II.

Defluorination of **4** with Mg was faster than of **5** . Obviously, steric hindrance retarded the defluorination process. These results could find corroboration in the case of **7**. With two big Ph groups, defluorination did not occur at all even under rather severe conditions.

TABLE 4

Analytical and Spectroscopic Data of Compounds 12-14

Compd. Data	**12**	**13**	**14**
m.p.(°C)	136-7.5	102.5-3.0	111.0-2.5
Yield(%)	83.1	74.3	46.2
Elem. Anal.	C,48.46 (48.67)[a] H,1.70 (2.04) F,37.80 (38.49)	C,51.53 (51.86) H,2.80 (3.11) F,34.85 (35.16)	C,47.11 (47.19) H,2.42 (2.83) F,31.15 (31.99) S,18.14 (17.99)
IR(cm^{-1})	2950w (C-H) 1645s and 1520m (naphthalene)	3000w (C-H) 1645s and 1520m (naphthalene)	2900w (C-H) 1625s and 1510s (naphthalene)
UV (λmax in nm)	220(ε =6.66 10^4) 288(ε =1.06 10^4) 394(ε =0.34 10^4)	220(ε =5.64 10^4) 290(ε =0.95 10^4) 394(ε =0.29 10^4)	220(ε =2.37 10^4) 324(ε =0.46 10^4)
MS	205(60.0, $M-C_3H_4FO_2$) 210(28.1,$M-2OCH_3$) 281(63.7, $M-CH_3$) 296(100, M) 297(12.6, M+1)	268(24.5,$M-2C_2H_4$) 306(5.6, M+1-F) 324(100, M) 325(18.2, M+1)	300(5.4,$M-2C_2H_4$) 338(38.5, M+1-F) 356(100, M) 357(21.1, M+1)
^1H NMR (in CCl_4)	4.1(OCH_3, s)	1.5(CH_3,t,J=7.0[b]) 4.2(OCH_2,m,J=7.0)	1.1(CH_3,t,J=7.0) 2.8(SCH_2,q,J=7.0)
^{19}F NMR (in CCl_4)	69.9(2F,d-q, J=18.8, J=3.8) 72.8(2F,d,J=20.7) 79.2(2F,d-d, J=20.7, J=18.8)	69.4(2F,d-t, J=16.9, J=6.6) 72.0(2F,d,J=22.6) 79.0(2F,d-d, J=22.6, J=16.9)	40.0(2F,d,J=22.6) 53.0(2F,d,J=18.8) 77.2(2F, d-d, J=22.6, J=18.8)

[a] The values in parentheses were calculated from the stated formula.

[b] The values of couple constants were measured in Hz.

EXPERIMENTAL

Boiling points and melting points were uncorrected. A Zeiss Specord-75 was used to record IR of samples as films or as KCl pellets. ^{1}H NMR (with chemical shifts in ppm from external TMS) and ^{19}F NMR (with chemical shifts in ppm from external TFA and positive upfield shifts) were measured at 60MHz on a Varian EM-360 Spectrometer or at 200MHz on a Varian XL-200 Spectrometer. Mass spectra were measured by a Finnigan GC-MS 4021 Mass Spectrometer. GLC analysis was performed with a 102G (Shanghai Analytical Factory) using a 3m long column packed with DNP on Chromosorb (dinonyl phthalate, 15%).

Reaction Of 1 With Nucleophiles

A slight excess of RXH (R=CH_3, C_2H_5, Ph; X=O, S) in 3ml CH_3CN was added dropwise into a solution containing 5.0g **1** (12.9mmol) and 4ml Et_3N at -78'C. The resultant mixture was then stirred at -78'C for 1-3h. After that, the temperature was allowed to come to r.t. and then the solution was poured into 30ml H_2O. The separated precipitate was washed with ice water, dried and recrystallized from methanol. The analytical and spectroscopic data of the purified samples are shown in **TABLES 1-3**.

Treated as in the previous experiments, 5.0g **1** (12.9mmol) was reacted with 0.5g EtOH(10.8mmol) in 2ml CH_3CN and 3.3g **2** was obtained. It was purified by semipreparative GLC (column temp.: 150'C)

5.0g **1** (12.9mmol) was reacted with 3ml Et_2NH at -78'C for 1h. 2.8g **3** was obtained. It was purified by column chromatography on silica gel with petroleum ether as eluent.

Defluorination of 2,7-disubstituted dodecafluorobicyclo[4,4,0]dec-1(2),6(7)-dienes With Mg

2.0g **4** (4.88mmol) in 10ml Et_2O was added dropwise within 0.5h into a suspension of 1.5g Mg in 10ml Et_2O containing some 1,2-dibromoethane. Then the mixture was refluxed for 2h. After general workup, the separated precipitate was washed with ice water and dried. 1.2g **12** (yield 83.1%) was obtained after recrystallization from Et_2O. The data of compound **12**-**14** are shown in **TABLE 4**.

ACKNOWLEDGEMENT

The UV spectra were measured by Mr. Qi Shen

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