THE NEW CYCLOADDITION REACTIONS OF FLUORINATED 1,3,4-OXADIAZOLES

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НОВЫЕ РЕАКЦИИ ЦИКЛОПРИСОЕДИНЕНИЯ ФТОРИРОВАННЫХ 1,3,4-ОКСАДИАЗОЛОВ

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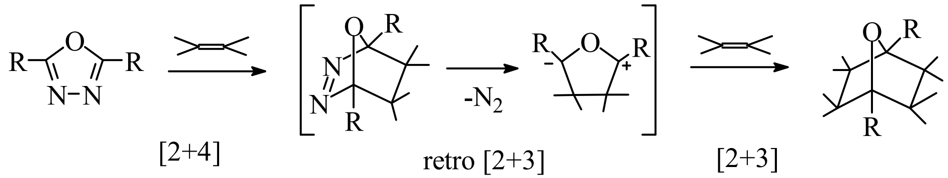
Double cycloaddition



R: CF_3, CF_2H, C_2F_5, C_3F_7, C(O)OEt

scheme 1

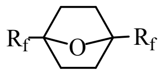
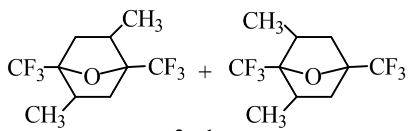
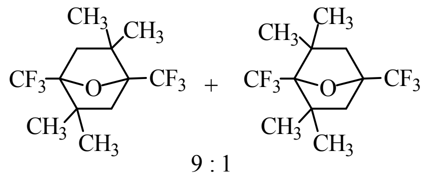
[1.] **A**: N.V. Vasiliev, Y.E. Lyashenko, A.F. Kolomietz, G.A. Sokolski, Chem. Het. Com. (engl. trans.) v.23, №4, p.470 (1987).

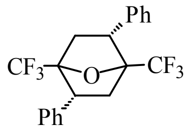
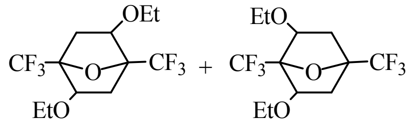
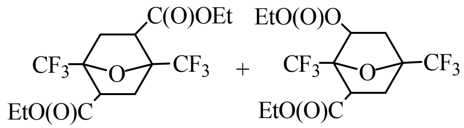
B: N.V. Vasiliev, Y.E. Lyashenko, A.E. Patalakha, G.A. Sokolski, J. Fluor. Chem., (1993), v. 65, p. 227.

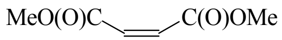
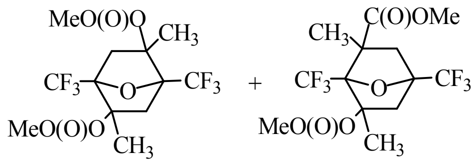
C: N.V. Vasiliev, Y.E. Lyashenko, M.V. Galahov, A.F. Kolomietz, G.A. Sokolski, Chem. Het. Com. (engl. trans.) v.26, №1, p.81 (1990).

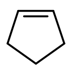
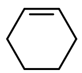
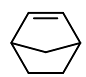
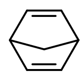
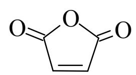
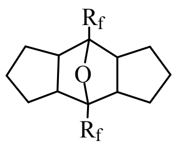
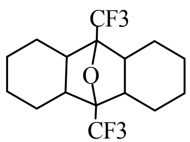
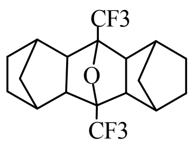
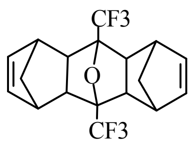
[2.] **A**: C. Seitz, H. Wassmuth, Chem.-Ztg., 112, (1988), 80.

B: F. Thalhammer, V. Wallfahrer and J. Sauer, Tetrahedron Lett., v. 29, (1988), p. 3231.

>=<:	CH_2=CH_2	CH_2=$CHCH_3$	CH_2=$C(CH_3)_2$
T, ^{0}C	180	160	180
Product		 3 : 1	 9 : 1
Yields, %	≈80	78	36

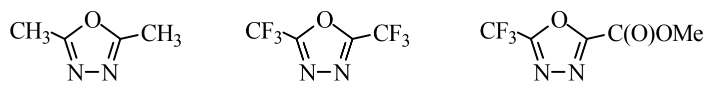
>=<:	CH_2=CHPh	CH_2=CHOEt	CH_2=CHC(O)OEt
T, ^{0}C	160	150	170
Product			
Yields, %	11	84	60

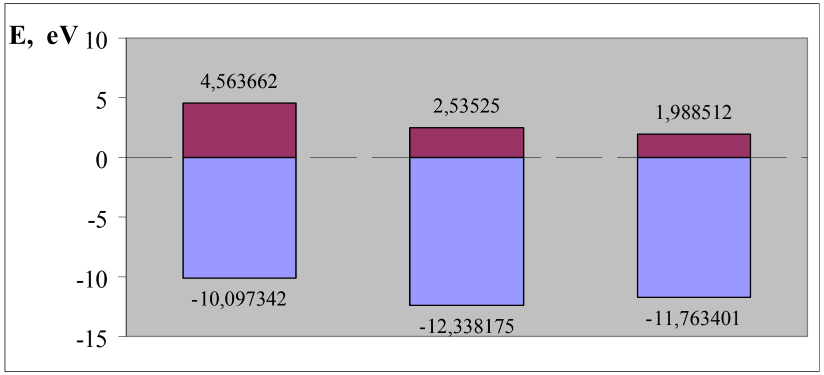
>=<:	CH_2=$C(CH_3)$C(O)OMe	
T, ^{0}C	200	-
Product		no
Yields, %	5	-

>=<:					
T, ^{0}C	180	180-200	160	160	-
Product					no
Yields, %	34	≈5	≈50	≥35	-

Энергия граничных орбиталей (G6-31*) и потенциал ионизации

HOMO and LUMO energies (G6-31*) and ionization potential

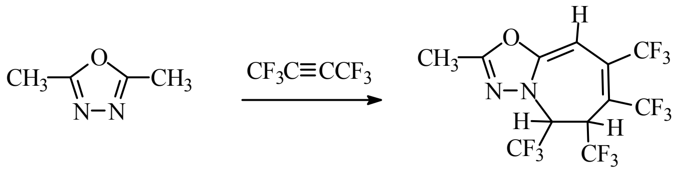




I, eV	10,32	12,08	
E_{HOMO}, eV	-10,097342	-12,338175	-11,763401
E_{LUMO}, eV	4,563662	2,53525	1,988512
ΔE	14,661004	14,873425	13,751913

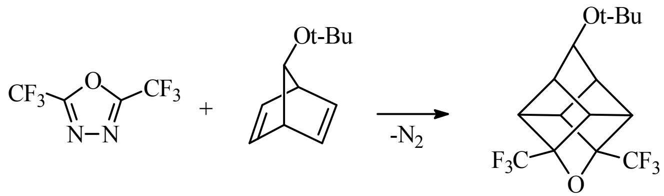
fig 1

[3.] A.V. Golyavin, N.V. Vasiliev, A.A. Rodin, A.F. Kolomietz, L.M. Reingard, Zh. Obsch. Khim., 59, (1989), 2698.



scheme 2

[4.] V.M. Koshelev, A.N. Chehlov, N.V. Vasiliev, et.al., Izv. Akad. Nauk SSSR, Ser. Khim., (1988), 744.

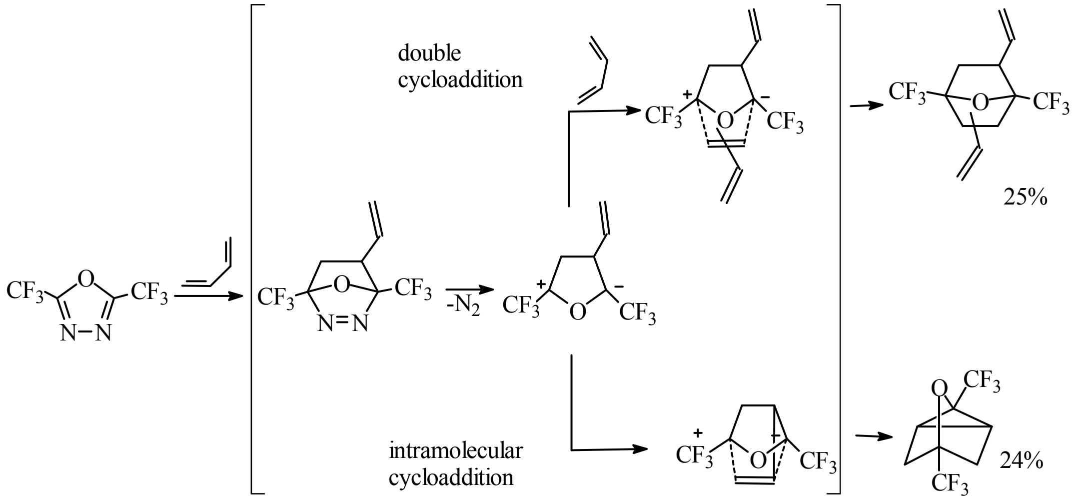


scheme 3

[5.] R.N. Warrener, G.M. Elsey, R.A. Russell, E.R. Tiekink, Tetrahedron Lett., v. 36, №29, (1995), 5275.

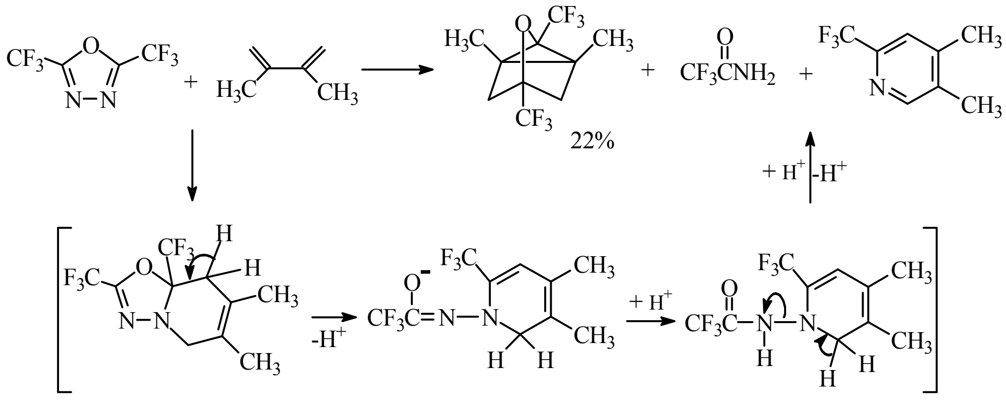
Intramolecular cycloaddition

Acyclic dienes

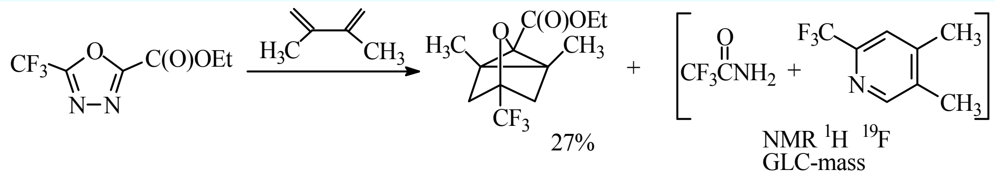


scheme 4

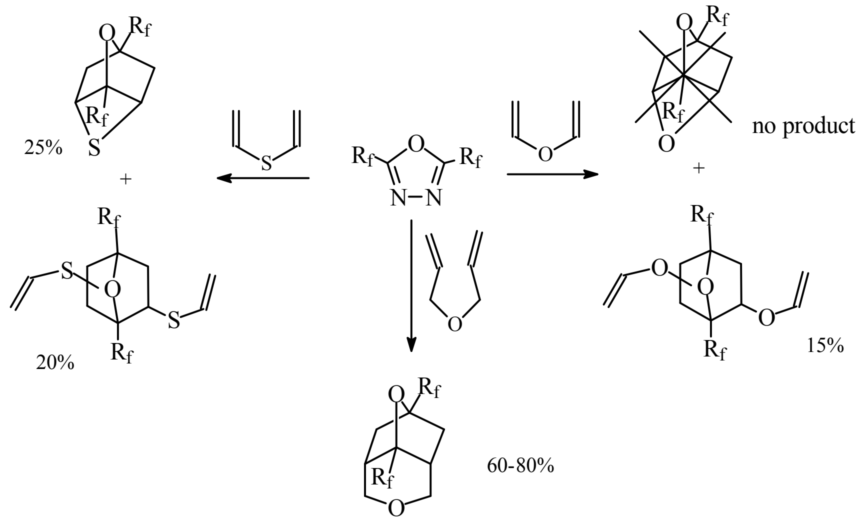
[6.] N.V. Vasiliev, D.V. Romanov, T.D. Truskanova, K.A. Lysienko, G.V. Zatonsky, Mend.Comm, 2006, in press.



scheme 5

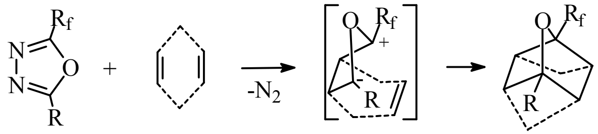


scheme 6



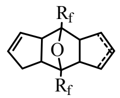
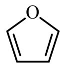
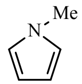
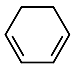
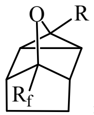
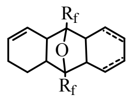
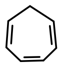
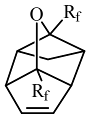
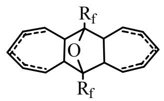
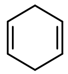
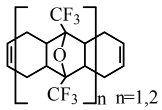
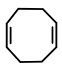
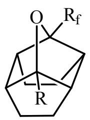
scheme 7

Cyclic dienes



R_f: CF_3, C_3F_7, CF_3

R: CF_3, C_3F_7, $CO(O)OC_2H_5$

Diene	Temperature, ^{0}C (Time, h)	Product 1:1	Product 1:2
	90-100 (4)	no	 ≥50%
	≥200	no reaction	
	≥170	no reaction	
	120-140 (30-40)	 ≈15%	 ≥40%
 *	160-180 (80-100)	 ≈60%	 ≤5%
 *	190-200 (70)	no	
 *	150 (25)	 ≈80%	no

*[6.] N.V. Vasiliev, D.V. Romanov, T.D. Truskanova, K.A. Lysienko, G.V. Zatonsky, Mend.Comm, 2006, in press.

5,7-Bis(trifluoromethyl)-6-oxatetracyclo[5.3.0.0^{2,5}.0^{4,8}]dec-9-ene

XRD analysis data

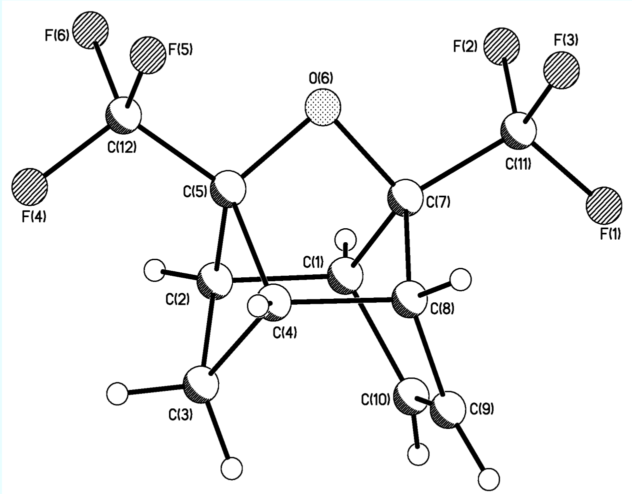


Fig. 2

The selected bond length (Å): C(1)-C(10) 1.508(2), C(1)-C(7) 1.548(2) C(1)-C(2) 1.582(2), C(2)-C(3) 1.539(2), C(2)-C(5) 1.560(2), C(3)-C(4) 1.539(2), C(4)-C(5) 1.556(2), C(4)-C(8) 1.582(2), C(5)-O(6) 1.408(2), O(6)-C(7) 1.414(2), C(7)-C(8) 1.548(2), C(8)-C(9) 1.506(2), C(9)-C(10) 1.327(3) and angle(º): C(10)-C(1)-C(7) 100.70(12), C(10)-C(1)-C(2) 113.01(13), C(7)-C(1)-C(2) 99.14(11), C(3)-C(2)-C(5) 87.29(11), C(3)-C(2)-C(1) 111.99(12), C(5)-C(2)-C(1) 99.99(11), C(4)-C(3)-C(2) 87.22(11), C(3)-C(4)-C(5) 87.42(11), C(3)-C(4)-C(8) 111.84(13), C(5)-C(4)-C(8) 99.81(11), O(6)-C(5)-C(12) 108.67(12), O(6)-C(5)-C(4) 109.86(11), C(12)-C(5)-C(4) 120.12(12), O(6)-C(5)-C(2) 109.55(11), C(12)-C(5)-C(2) 120.88(12), C(4)-C(5)-C(2) 85.89(11), C(5)-O(6)-C(7) 96.74(10), O(6)-C(7)-C(11) 106.85(12), O(6)-C(7)-C(1) 107.51(11), C(11)-C(7)-C(1) 118.19(12), O(6)-C(7)-C(8) 107.33(11), C(11)-C(7)-C(8) 118.31(13), C(1)-C(7)-C(8) 97.81(12), C(9)-C(8)-C(7) 100.88(12), C(9)-C(8)-C(4) 113.17(13)C(7)-C(8)-C(4) 99.35(11), C(10)-C(9)-C(8) 109.37(14), C(9)-C(10)-C(1) 109.65(14).