Thermolysis of *N*-[2,2,2-Trifluoro-1-(tritylazo)ethylidene]anilines and Related Azo-Compounds

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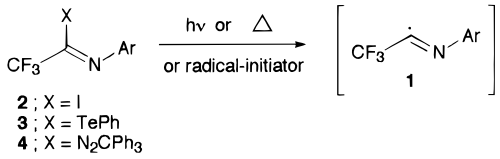
N-[2,2,2-Trifluoro-1-(tritylazo)ethylidene]anilines and the related 2,2-difluoromethyl azo-, 2,2,3,3,4,4,4-heptafluoropropyl azo-, and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoroheptyl azo-compounds (**4**) were synthesized and subjected to thermolysis in toluene. The rate constants of the thermolysis of **4** were in the order of 10^{-4} s^{-1} at 55 °C. The rates were correlated with Hammett's σ constants of *N*-aryl substituents with ρ value of −0.6. The difluoromethyl azo- (**4g**), heptafluoropropyl azo- (**4h**) and pentadecafluoroheptyl azo-compounds (**4i**) decomposed slightly faster than the trifluoromethyl azo-compound (**4a**).

Introduction

Recently, the generation and utilization of reactive radical intermediates have been well investigated.[1] Imidoyl radicals are promising intermediates for nitrogen heterocycles. The imidoyl radicals first reported by Saegusa and Ito[2] are generated by several methods such as addition of trialkyltin radicals and alkyl radicals to isocyanates[2] and thiocyanates,[3] hydrogen abstraction from imines,[4] and photochemical homolysis of selenoimidates.[5] We have reported syntheses of 2-trifluoromethylated indole and quinoline derivatives *via* *N*-aryl-2,2,2-trifluoroacetimidoyl radicals **1**.[6] These radicals are highly reactive to both electron-rich and electron-deficient alkenes and alkynes and thus widely applicable intermediates for trifluoromethylated nitrogen heterocycles. The radicals **1** were generated by the tin-radical-promoted homolysis of carbon−iodine bond of iodides **2**,[6] by the photolysis of **2**[6] and tellurides **3**.[7] However, these methods involved the disadvantages of low product-selectivity[6] and long reaction times.[7] Recently, we have reported thermal generation of **1** from the azo-compounds *N*-[2,2,2-trifluoro-1-(tritylazo)ethylidene]anilines (**4a**, **4b**, **4d**, and **4f**) and their synthetic utilization.[6] Elucidation of the relationship between the thermal reactivity and structures of these and the related azo-compounds will provide insights into the feasibility of the thermal reaction for conventional syntheses of trifluoromethylated nitrogen heterocycles.

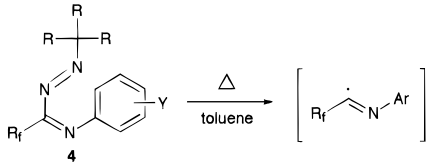
We have synthesized the related azo-compounds **4** where substituents (Y) on *N*-aryl group, perfluoroalkyl group (R_f) on imino carbon, and substituent R on *tert*-carbon attached to the azo nitrogen atom were systematically changed, and we have examined kinetics of their thermal decompositions.

Scheme 1



2 ; X = I
3 ; X = TePh
4 ; X = N_2CPh_3

Scheme 2



4

Compd	R_f	Y	R
4a	CF_3	*p*-OMe	Ph
4b	CF_3	*p*-Me	Ph
4c	CF_3	H	Ph
4d	CF_3	*p*-Cl	Ph
4e	CF_3	*m*-Cl	Ph
4f	CF_3	*p*-NO_2	Ph
4g	CHF_2	*p*-OMe	Ph
4h	C_3F_7	*p*-OMe	Ph
4i	C_7F_{15}	*p*-OMe	Ph
4j	CF_3	*p*-OMe	CH_3

Results and Discussion

Preparations. Azo-compounds **4a**−**i** were prepared in three steps[6] starting from the corresponding imidoyl chlorides **5**[8] as shown in Scheme 3. The reaction of **5** with hydrazine monohydrate in aqueous acetonitrile afforded **7** almost quantitatively and none of the corresponding amides formed by hydrolysis of **5**. When R_f was difluoromethyl and pentadecafluoroheptyl group, the hydrazides (**7g** and **7i**) and the tritylhydrazides (**8g** and **8i**) were not purified because of their instability on silica-gel column. All of the tritylazo-compounds **4** are stable crystals, except for **4i**, and can be stored in the refrigerator. Pentadecafluoroheptylazo-compound **4i** is an un-

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(2) Saegusa, T.; Ito, Y.; Yasuda, N.; Hotaka, T. *J. Org. Chem.* **1970**, *35*, 4238. Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1991**, *113*, 2127. Bachi, M. D.; Denenmark, D. *J. Org. Chem.* **1990**, *55*, 3442.

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(6) Dan-oh, Y.; Matta, H.; Uemura, J.; Watanabe, H.; Uneyama, K. *Bull. Chem. Soc. Jpn.* **1995**, *65*, 1497.

(7) Ueda, Y.; Watanabe, H.; Uemura, J.; Uneyama, K. *Tetrahedron Lett.* **1993**, *34*, 7933. Photolysis of **2** and **3** requires mostly 3−5 days for completion.

(8) Tamura, K.; Mizukami, H.; Maeda, K.; Watanabe, H.; Uneyama, K. *J. Org. Chem.* **1993**, *58*, 32.

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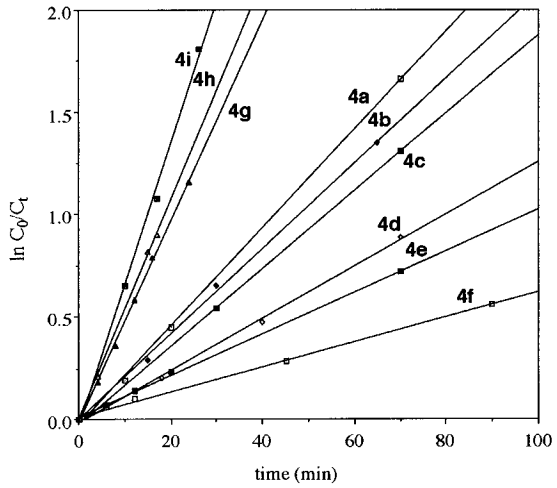
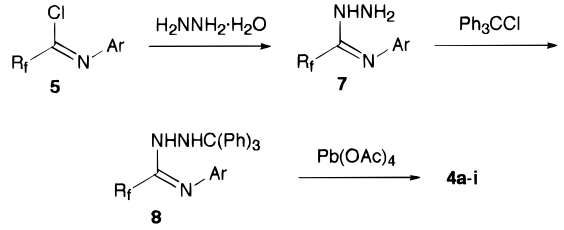
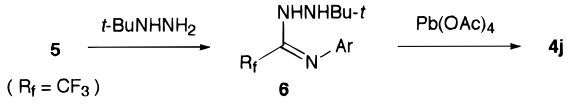


Figure 1. Decomposition of **4a**−**i** in toluene at 55 °C.

Scheme 3



Scheme 4



stable liquid. The *tert*-butylazo-compound **4j** was prepared *via* the route of (**5** → **6** → **4j**) shown in Scheme 4.

Kinetics of Thermal Decomposition. Seltzer *et al.* reported that thermal decomposition of symmetrical azo-compounds is first-order and follows a two-bond scission mechanism.[9] On the other hand, Benson and O'Neal reported that the decomposition of unsymmetrical azo-compounds is not always first-order and may be one-bond scission mechanism.[10] An ^{15}N CIDNP and radical trapping studies of unsymmetric diazenes supported the one-bond cleavage decomposition mechanism.[11]

Kinetics of the decomposition of these fluorinated tritylazo-compounds **4** were followed by analyzing the ^{19}F NMR intensity of R_f group of **4** relative to that of the internal standard 1,4-bis(trifluoromethyl)benzene. Plots of ln C_0/C_t (C_t; ^{19}F NMR intensity of the starting substrates **4**) *versus* time gave straight lines as shown in Figure 1, suggesting the first-order. The rate of **4d** in *n*-octyl alcohol was almost same as that in toluene, suggesting the homolytic cleavage of carbon−nitrogen bonds in **4**. The rate constants of **4** in toluene are summarized in Table 1.

Table 1. Rate Constants and Relative Rate for Thermolysis of Azo-Compounds[a,b]

compd	R_f	Y	10^4 k (s^{-1})	rel rate
4a	CF_3	*p*-OMe	4.0	1.3
4b	CF_3	*p*-Me	3.5	1.1
4c	CF_3	H	3.2	1.0
4d	CF_3	*p*-Cl	2.1	0.7
4e	CF_3	*m*-Cl	1.7	0.5
4f	CF_3	*p*-NO_2	1.0	0.3
4g	CHF_2	*p*-OMe	8.2	2.6
4h	C_3F_7	*p*-OMe	9.0	2.8
4i	C_7F_{15}	*p*-OMe	11	3.4

[a] Determined by ^{19}F NMR intensity of R_f of **4a**−**i** relative to internal standard 1,4-bis(trifluoromethyl)benzene. [b] The thermolysis temperature = 55.01 ± 0.02 °C.

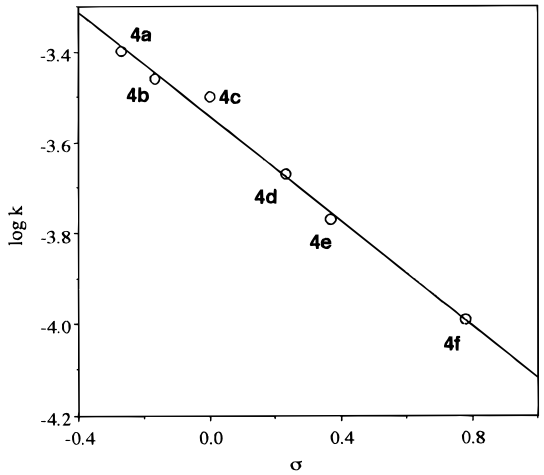


Figure 2. Plots of log *k* vs σ constants. The σ constants were taken from Hansch, C.; Leo, A.; Taft, W. A. *Chem. Rev.* **1991**, *91*, 165.

The azo-compounds **4a**−**f** decomposed cleanly at 55 °C in toluene with the rate constants of 10^{-4} s^{-1}, which were close to those of substituted (arylazo)triphenylmethanes.[11] On the other hand, *tert*-butylazo-compound **4j** decomposed much more slowly than tritylazo-compounds **4a**−**f** with a rate constant of 10^{-5} s^{-1} at 145 °C in toluene.[12] The relative rate of decomposition of tritylazo-compounds **4a**−**f** to *tert*-butylazo-compound **4j** was estimated to be about 10^6 at 55 °C. This result suggests that breaking of the bond between azo nitrogen and *tert*-carbon of trityl group occurs preferentially in the transition state.

An electronic effect of substituent on the *N*-aryl group was observed in the reaction of substituted *N*-arylazo-compounds as summarized in the Table 1. An electron-donating group enhanced the rate and an electron-withdrawing group retarded it. Plot of relative rates (log *k*) *versus* Hammett's σ constants gave a straight line with the reaction constant (ρ) of −0.6 (r = 0.99) as shown in Figure 2.

Cohen reported a good correlation of the rates of thermolysis of meta-substituted (phenylazo)triphenylmethanes with Hammett's σ constants (ρ value of −0.85),[13] but poor correlation for para-substituents.[14] The ρ (−0.6) value for the decomposition of **4** is comparatively large as compared with −0.85 for substituted (arylazo)triphenylmethanes[11] even though the azo double bond (N=N) and *N*-aryl moiety in **4** are separated by imino double

(9) Seltzer, S. *J. Am. Chem. Soc.* **1961**, *83*, 2625. Seltzer, S. *J. Am. Chem. Soc.* **1963**, *85*, 14. Ruchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. Seltzer, S.; Dunne, F. T. *J. Am. Chem. Soc.* **1965**, *87*, 2628.

(10) Benson, S. W.; O'Neal, H. E. *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.* **1970**, *21*, 31.

(11) The same type of bond cleavage was clarified by ^{13}C and ^{15}N CIDNP experiments of substituted (phenylazo)triphenylmethanes. Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920.

(12) The reaction of **4j** was conducted in a sealed tube at 145 °C.

(13) Solomon, S.; Wang, C. H.; Cohen, S. G. *J. Am. Chem. Soc.* **1957**, *79*, 4104.

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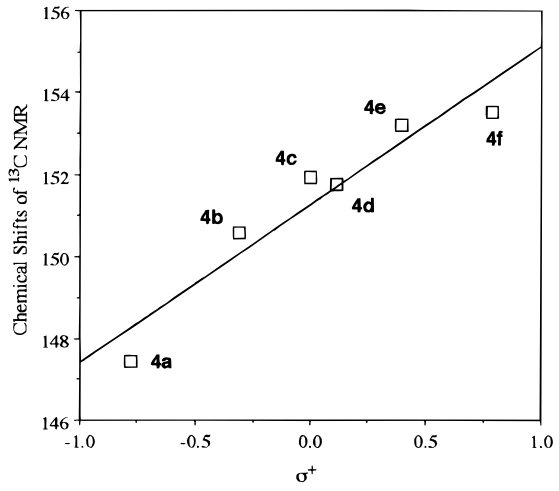

Figure 3. Relation between ^{13}C NMR chemical shifts of imino carbon of azo-compounds **4a**−**f** and Brown−Okamoto σ^+ constants. The σ^+ constants were taken from Hansch, C.; Leo, A.; Taft, W. A. *Chem. Rev.* **1991**, *91*, 165.

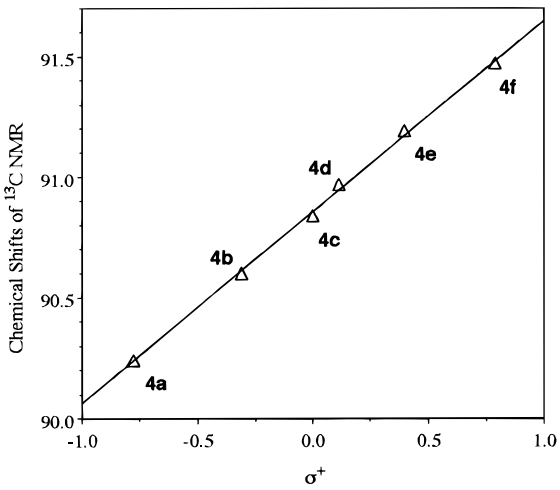

Figure 4. Relation between ^{13}C NMR chemical shifts of trityl-carbon of azo-compounds **4a**−**f** and Brown−Okamoto's σ^+ constants.

bond (C═N). This fact suggests that the electronic effect of substituent on the *N*-aryl ring is transmitted to the bond between imino carbon and azo nitrogen and even to the bond between trityl carbon and azo nitrogen. This is also supported by the observations that ^{13}C NMR chemical shifts of both the imino carbon and trityl carbon of **4** are correlated with Brown−Okamoto's σ^+ constants as illustrated in Figure 3 and Figure 4.[15] Difluoromethyl azo−compound **4g** was 2.0 fold as reactive as trifluoromethyl azo-compound **4a**, suggesting the less electronegative substituent enhanced the rate. It is interesting that replacement of CF_3 group with C_3F_7 or C_7F_{15} group led to rate enhancement presumably because the steric bulkiness of the perfluoroalkyl group (C_3F_7, and C_7F_{15}) would instabilize the ground state of **4i** and **4j**.

Experimental Section

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured using TMS for ^{1}H and C_6F_6 for ^{19}F NMR as internal standards and $CDCl_3$ as the solvent. The boiling points and melting points were uncorrected.

The compounds **4**, **7**, and **8** were prepared by the methods described,[6] and the spectral data of **4a**,**b**,**d**,**f**, **7a**,**b**,**d**,**f**, and **8a**,**b**,**d**,**f** were described previously.[6]

Trifluoroacetohydrazide *N*-Phenylimide (7c). Yield: 99%; a white solid; mp 39−40 °C; IR ($CHCl_3$) 3428, 3308, 1604, 1498, 1440, 1356, 1298 cm^{-1}; ^{1}H NMR δ 5.51 (br, 3H), 6.64−6.71 (m, 2H), 6.95−7.03 (m, 1H), 7.25−7.35 (m, 2H); ^{19}F NMR δ 90.85 (s, 3F). Anal. Calcd for $C_8H_8F_3N_3$: C, 47.30; H, 3.97; N, 20.68%. Found: C, 47.29; H, 4.05; N, 20.51%.

Trifluoroacetohydrazide *N*-(*m*-Chlorophenyl)imide (7e). Yield: 98%; a yellow oil; IR (neat) 3416, 3304, 1600, 1498, 1480, 1426, 1350, 1286, 1268 cm^{-1}; ^{1}H NMR δ 5.48 (br, 3H), 6.54 (m, 1H), 6.65 (dd, J_1 = 2.2 Hz, J_2 = 2.2 Hz, 1H), 6.95 (m, 1H), 7.20 (dd, J_1 = 8.1 Hz, J_2 = 8.1 Hz, 1H); ^{19}F NMR δ 90.90 (s, 3F). Anal. Calcd for $C_8H_7ClF_3N_3$: C, 40.44; H, 2.97; N, 17.68%. Found: C, 40.66; H, 6.91; N, 17.39%.

2,2,3,3,4,4,4-Heptafluorobutanohydrazide *N*-(*p*-Methoxyphenyl)imide (7h). Yield: 95%; a white solid; mp 114−115 °C; IR (Nujol) 3424, 3268, 1634, 1512, 1244, 1198, 1182, 1148, 1114, 1032 cm^{-1}; ^{1}H NMR δ 3.77 (s, 3H), 5.45 (br, 2H), 5.64 (br, 1H), 6.63 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H); ^{19}F NMR δ 36.01 (br, 2F), 46.15 (br, 2F), 81.58 (t, J = 9.7 Hz, 3F). Anal. Calcd for $C_{11}H_{10}F_7N_3O$: C, 39.65; H, 3.02; N, 12.61%. Found: C, 39.87; H, 3.20; N, 12.33%.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanohydrazide *N*-(*p*-Methoxyphenyl)imide (7i). Yield: 62%; a white solid; mp 130−132 °C; IR ($CHCl_3$) 3440, 3320, 1644, 1612, 1502, 1466, 1444 cm^{-1}; ^{1}H NMR δ 2.41 (br, 2H), 3.78 (s, 3H), 6.65 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H); ^{19}F NMR δ 35.61 (br, 2F), 39.02 (br, 2F), 39.71 (br, 2F), 40.46 (br, 2F), 40.54 (br, 2F), 47.03 (br, 2F), 80.98 (t, J = 9.8 Hz, 3F). Anal. Calcd for $C_{15}H_{10}F_{15}N_3O$: C, 33.79; H, 1.89; N, 7.88%. Found: C, 33.84; H, 1.81; N, 7.74%.

Trifluoroaceto-*N*^{2}-tritylhydrazide *N*-Phenylimide (8c). Yield: 83%; a white solid; mp 138−139 °C; IR ($CHCl_3$) 3428, 3288, 1602, 1494, 1446, 1352, 1296 cm^{-1}; ^{1}H NMR δ 5.50 (br, 1H), 6.07 (br, 1H), 6.59−6.66 (m, 2H), 6.95−7.03 (m, 1H), 7.15−7.31 (m, 17H); ^{19}F NMR δ 91.69 (s, 3F). Anal. Calcd for $C_{27}H_{22}F_3N_3$: C, 72.80; H, 4.98; N, 9.43%. Found: C, 72.66; H, 5.23; N, 9.31%.

Trifluoroaceto-*N*^{2}-tritylhydrazide *N*-(*m*-Chlorophenyl)-imide (8e). Yield: 85%; a white solid; mp 137−138 °C; IR ($CHCl_3$) 3424, 1598, 1492, 1448, 1344 cm^{-1}; ^{1}H NMR δ 5.49 (br, 1H), 6.16 (br, 1H), 6.49 (m, 1H), 6.69 (dd, J_1 = 2.2 Hz, J_2 = 2.2 Hz, 1H), 6.97 (m, 1H), 7.13−7.32 (m, 16H); ^{19}F NMR δ 91.69 (s, 3F). Anal. Calcd for $C_{27}H_{21}ClF_3N_3$: C, 67.57; H, 4.41; N, 8.76%. Found: C, 67.63; H, 4.52; N, 8.37%.

2,2,3,3,4,4,4-Heptafluorobutano-*N*^{2}-tritylhydrazide *N*-(*p*-Methoxyphenyl)imide (8h). Yield: 96%; a yellow solid; mp 84−85 °C; IR (Nujol) 3416, 3308, 1600, 1512, 1492, 1352, 1276, 1226, 1198, 1140, 1108, 1044, cm^{-1}; ^{1}H NMR δ 3.76 (s, 3H), 5.73 (br, 1H), 6.59 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 7.12−7.30 (m, 16H); ^{19}F NMR δ 36.20 (t, J = 15.8 Hz, 2F), 47.63 (m, 2F), 81.66 (t, J = 9.8 Hz, 3F). Anal. Calcd for $C_{30}H_{24}F_7N_3O$: C, 62.61; H, 4.20; N, 7.30%. Found: C, 62.73; H, 4.36; N, 7.31%.

Preparation of Trifluoroaceto-*N*^{2}-*tert*-butylhydrazide *N*-(*p*-Methoxyphenyl)imide (6j). Into a solution of *N*-(*p*-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (3.80 mmol) in CH_3CN (7 mL) were added *tert*-butylhydrazine (0.430 g, 3.80 mmol) and Et_3N (1.06 mL, 7.59 mmol), and the mixture was stirred at room temperature for a few minutes. The mixture was extracted with AcOEt. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was recrystallized from hexane to give **6j**: yield: 71%; a brown solid; mp 59−60 °C; IR ($CHCl_3$) 3428, 3296, 1626, 1594, 1504, 1466, 1366, 1352, 1302, 1286 cm^{-1}; ^{1}H NMR δ 1.17 (s, 9H), 3.78 (s, 3H), 5.26 (br, 2H), 6.56−6.61 (m, 2H), 6.80−6.84 (m, 2H); ^{19}F NMR δ 91.96 (s, 3F). Anal. Calcd for $C_{13}H_{18}F_3N_3O$: C, 53.97; H, 6.27; N, 14.52%. Found: C, 54.02; H, 6.37; N, 14.25%.

***N*-[2,2,2-Trifluoro-1-(tritylazo)ethylidene]aniline (4c).** Yield: 78%; a red solid; IR ($CHCl_3$) 1686, 1596, 1584, 1490, 1446, 1302 cm^{-1}; ^{1}H NMR δ 6.75−7.32 (m, 20H); ^{19}F NMR δ

(15) The ^{13}C NMR chemical shifts of the imino carbon of imidoyl chlorides **5** (R_f = CF_3) are correlated well with Brown−Okamoto σ^+ constants.[8]

93.73 (s, 3F). Anal. Calcd for $C_{27}H_{20}F_3N_3$: C, 73.13; H, 4.55; N, 9.48%. Found: C, 73.25; H, 4.55; N, 9.54%.

3-Chloro-*N*-[2,2,2-trifluoro-1-(tritylazo)ethylidene]-aniline (4e). Yield: 88%; a red solid; IR ($CHCl_3$) 1686, 1590, 1490, 1470, 1446, 1376 cm^{-1}; ^1H NMR δ 6.59−6.70 (m, 1H), 6.83−6.94 (m, 6H), 7.01−7.08 (m, 2H), 7.18−7.33 (m, 10H); ^{19}F NMR δ 93.49 (s, 3F). Anal. Calcd for $C_{27}H_{19}ClF_3N_3$: C, 67.86; H, 4.01; N, 8.79%. Found: C, 68.07; H, 4.07; N, 8.63%.

***N*-[2,2-Difluoro-1-(tritylazo)ethylidene]-*p*-anisidine (4g).** Yield: 36% from imidoyl chloride **5g**; a red solid; IR (Nujol) 1592, 1572, 1506, 1488, 1300, 1258 cm^{-1}; ^1H NMR δ 3.78 (s, 3H), 6.65 (t, J = 53.6 Hz, 1H), 6.58−6.66 (m, 2H), 6.89−6.97 (m, 2H), 7.00−7.11 (m, 5H), 7.25−7.35 (m, 10H); ^{19}F NMR δ 39.36 (d, J = 53.6 Hz, 2F). Anal. Calcd for $C_{28}H_{23}F_2N_3O$: C, 73.83; H, 5.09; N, 9.22%. Found: C, 74.03; H, 5.21; N, 9.30%.

***N*-[2,2,3,3,4,4,4-Heptafluoro-1-(tritylazo)butylidene]-*p*-anisidine (4h).** Yield: 98%; a red solid; IR ($CHCl_3$) 1668, 1588, 1496, 1466, 1446, 1348 cm^{-1}; ^1H NMR δ 3.74 (s, 3H), 6.58 (d, J = 9.1 Hz, 2H), 6.79 (d, J = 9.1 Hz, 2H), 6.92−7.00 (m, 5H), 7.22−7.30 (m, 10H); ^{19}F NMR δ 36.89 (s, 2F), 49.15−49.29 (m, 2F), 81.81 (t, J = 9.2 Hz, 3F). Anal. Calcd for $C_{30}H_{22}F_7N_3O$: C, 62.83; H, 3.87; N, 7.33%. Found: C, 62.74; H, 3.94; N, 7.19%.

***N*-[2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-(tritylazo)octylidene]-*p*-anisidine (4i).** Yield: 54% from imidoyl chloride **5i**; a red liquid; IR (Nujol) 1662, 1586, 1506, 1448, 1246 cm^{-1}; ^1H NMR δ 3.74 (s, 3H), 6.59 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 6.94−6.99 (m, 5H), 7.23−7.28 (m, 10H); ^{19}F NMR δ 36.07 (br, 2F), 39.61 (br, 2F), 40.32 (br, 2F), 41.53 (br, 2F), 41.96 (br, 2F), 50.86 (t, J = 13.0 Hz, 2F), 81.44 (t, J = 9.7 Hz, 3F). Anal. Calcd for $C_{34}H_{22}F_{15}N_3O$: C, 52.79; H, 2.87; N, 5.43%. Found: C, 53.16; H, 3.24; N, 4.98%.

***N*-[2,2,2-Trifluoro-1-(*tert*-butylazo)ethylidene]-*p*-anisidine (4j).** The *tert*-butylhydrazide **6j** was oxidized under the same conditions for the tritylhydrazides. Yield: 88%; a red solid; IR (neat) 1672, 1598, 1506, 1464, 1444, 1366, 1294, 1254, 1152, 1082, 1032 cm^{-1}; ^1H NMR δ 1.28 (s, 9H), 3.81 (s, 3H), 6.80−6.89 (m, 2H), 7.03−7.12 (m, 2H); ^{19}F NMR δ 93.92 (s, 3F). Anal. Calcd for $C_{13}H_{16}F_3N_3O$: C, 54.35; H, 5.61; N, 14.63%. Found: C, 54.40; H, 5.62; N, 14.75%.

Kinetics. The two-necked round bottom flask (10 mL) containing 2.0 mL of toluene solution of **4** was settled in a water bath. Each 0.2 mL of the sample solution were taken out by a syringe. The concentrations of the sample **4** and 1,4-bis(trifluoromethyl)benzene as an internal standard were 3.80 $\times$ 10^{-2} M and 1.27 $\times$ 10^{-3} M in toluene, respectively. The water bath temperature was maintained at 55 °C within ±0.02 °C. The rates of decomposition of the azo-compounds **4a**−**f** and **4j** were determined by measuring the relative intensity of ^{19}F NMR signals of trifluoromethyl group observed at around δ 95 to the internal standard 1,4-bis(trifluoromethyl)-benzene (δ 99, singlet) and those of difluoromethyl-compound (**4g**) by measuring the relative intensity of difluoromethyl group (δ 39, doublet). The ^{19}F NMR intensities of fluorine atoms on C-2 carbon of heptafluoropropyl azo- and pentadecafluoroheptyl azo-compounds (**4h** and **4i**) which were separated by the signals of products, were employed for analyzing the decomposition rates.

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