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PHOTOCHEMICAL ADDITION OF PERFLUORO-n-BUTYL IODIDE TO ALKYNES AND OLEFINS

MOHAMMAD H. HABIBI§ and THOMAS E. MALLOUK

Department of Chemistry and Biochemistry, The University of Texas
at Austin, Austin, Texas 78712 (USA)

SUMMARY

Perfluoro-n-butyl iodide reacts photochemically with alkynes and other unsaturated organic compounds to give the corresponding adducts in quantitative yields. The kinetics of addition were studied by ^{19}F-NMR, and indicated that the reaction involves a free radical mechanism.

INTRODUCTION

Organofluorine compounds have unique properties [1], and they are widely used as medicines, pesticides, dyes and surfactants. Incorporation of a perfluoroalkyl group at a particular position in an organic compound is especially important, since it may give rise to physical or biochemical properties which cannot be achieved by means of non-fluorine containing functional groups. The addition of perfluoroalkyl iodides to double and triple bonds is a versatile and selective route to these compounds. This reaction can be driven by light [2], heating [2], radical initiators [3], metal complexes [4-6], triethylborane [7], sodium dithionates [8,9], and by other methods [10,11].

The kinetics of the perfluoroalkyl iodide addition reaction have been studied recently by electrochemical methods [12], and the mechanism is now well understood. It involves first the generation of perfluoroalkyl radicals, followed by a two-step radical chain. As the course of the reaction is essentially independent of the initiation step, the photochemical method seems especially attractive since it requires no chemical initiators and therefore simplifies the purification of the final

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§On sabbatical leave from the Department of Chemistry, University of Esfahan, Esfahan 81745 (Iran).

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product. Although Haszeldine and coworkers studied the photochemical reactions of CF_3I with olefins in detail more than 40 years ago [2], they reported only two cases of photochemically driven reactions of CF_3I with alkynes [13]. In that work, photolysis of *vapor phase* CH_3I and propyne derivatives gave addition products in yields of 38-86%. In this paper we show that photochemical initiation of the reaction of a perfluoroalkyl iodide, C_4F_9I, with *liquid phase* acetylenic compounds in the absence of solvent or free radical initiators is an extremely convenient synthetic method, affording addition products in essentially quantitative yield.

RESULTS AND DISCUSSION

Perfluoro-n-butyl iodide reacted with terminal alkynes photochemically to form 1:1 adducts in quantitative yields. The yields and reaction conditions are shown in Table 1.

$$C_4F_9I + H\text{-}C{\equiv}C\text{-}(CH_2)_nCH_3 \xrightarrow{h\nu,\ 25\ ^{o}C} C_4F_9CH{=}CI(CH_2)_nCH_3$$

1, n=3 → **2**, n=3

3, n=4 → **4**, n=4

The photochemical reaction of alkynols with F-n butyl iodide gave the corresponding adducts:

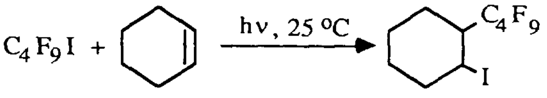
$$C_4F_9I + H\text{-}C{\equiv}CCH_2OH \xrightarrow{h\nu,\ 25\ ^{o}C} C_4F_9CH{=}CICH_2OH$$

5 → **6**

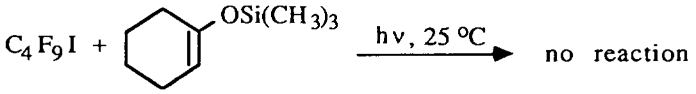
$$C_4F_9I + H\text{-}C{\equiv}C\text{-}C(CH_3)_2OH \xrightarrow{h\nu,\ 25\ ^{o}C} C_4F_9CH{=}CIC(CH_3)_2OH$$

7 → **8**

The reaction could also be applied to olefins such as cyclopentene and cyclohexene (**9**), but the addition reaction did not occur with the corresponding substituted olefins such as trimethylsiloxycyclopentene or trimethylsiloxycyclohexene (**11**).



9 **10**



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Perfluoro-n-butyl iodide was reacted photochemically with propargyl benzensulfonate (**12**) to give the corresponding adduct **13**.

$$\underset{\mathbf{12}}{C_4F_9I + HC{\equiv}C\text{-}CH_2SO_3C_6H_5} \xrightarrow{h\nu,\ 25\ ^{o}C} \underset{13}{C_4F_9CH{=}CI\text{-}CH_2SO_3C_6H_5}$$

Similarly, photochemical addition of C_4F_9I to propargyl chloride gave **15** in pure form:

$$\underset{\mathbf{14}}{C_4F_9I + HC{\equiv}C\text{-}CH_2Cl} \xrightarrow{h\nu,\ 25\ ^{o}C} \underset{\mathbf{15}}{C_4F_9CH{=}CI\text{-}CH_2Cl}$$

In all cases of photochemical C_4F_9I addition to terminal acetylenes, it is the CH carbon which is the site of perfluoroalkyl radical addition. Attack at the terminal carbon gives initially a vinyl radical which is stabilized both on steric and electronic grounds, relative to the radical which would be formed by attack at the $\equiv\underline{C}\text{-}CH_2$ carbon. Similar selectivity was observed by Haszeldine [14] in the reactions of trifluoromethyl radical with olefins $R\text{-}CH{=}CH_2$, $CF_2{=}CClF$, and $CF_3{=}CFCF_2$.

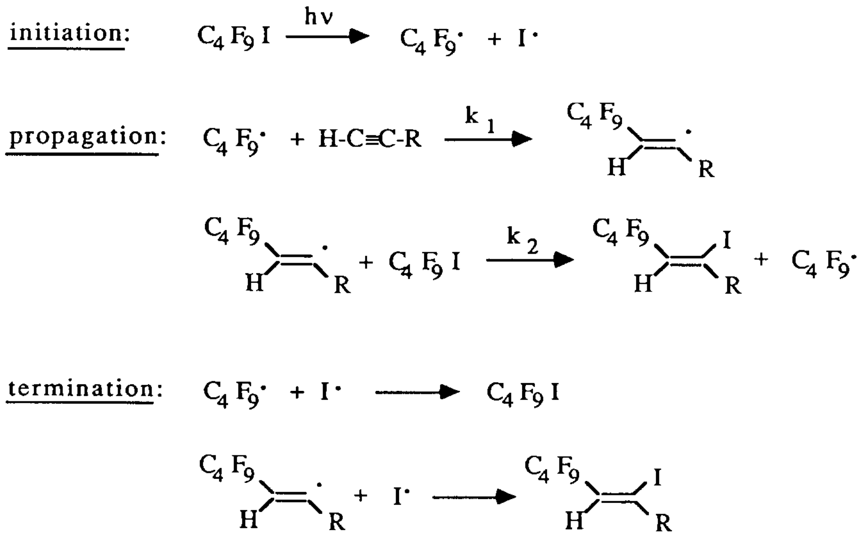
TABLE 1

Photochemical reactions of C_4F_9I with unsaturated compounds

Compound	Reaction time(h)	Product	Yield(%)
1	1.5	**2**	98 *cis*
3	1.5	**4**	96 *cis*
5	5.0	**6**	98(41% *cis*, 57% *trans*)
7	12.0	**8**	98 *cis*
9	3.0	**10**	97 (53% *cis*, 44% *trans*)
12	32.0	**13**	95 (60% *cis*, 35% *trans*)
14	8.0	**15**	97 (34% *cis*, 53% *trans*)

The reaction is also quite stereoselective in some cases, giving the pure *cis* isomer in reactions of aliphatic acetylenes **1** and **3**, and branched alkynol **7**. Substitution at the β-position by electron withdrawing groups such as OH, Cl, and p-toluenesulfonate (**5**, **14**, and **12**, respectively) results in a mixture of *cis* and *trans* addition products.

The kinetics of a representative addition reaction were studied by ^{19}F-NMR. The progress of the reaction of **5** with C_4F_9I was monitored by the decrease in the CF_2(a) NMR peak area (at -61 ppm) in the starting material $CF_3(d)CF_2(c)CF_2(b)CF_2(a)I$, compared to the CF_2(a) peak area of the adduct **6** (at -107.4 ppm). The percent conversion of C_4F_9I to the adduct was measured as a function of the amount of C_4F_9I at ratios of **5** to C_4F_9I between 33 and 100. The results are consistent with a chain reaction mechanism like that proposed previously [12] for a similar electrochemically initiated radical addition:



The dependence of reaction rate on the concentrations of C_4F_9I and **5** can be derived by means of a steady-state approximation, assuming that during the propagation steps there is a constant, low total concentration of radicals C^o. If the first propagation step is significantly faster than the second one, then C^o will equal the concentration of vinylic radicals, $[R_fHC{=}CR\cdot]$. If the second step is faster, then C^o will be equal to $[C_4F_9\cdot]$. Following the analysis of Calas et al. [12], we can write:

rate = d[**6**]/dt = $k_2[R_fHC{=}CR\cdot][C_4F_9I]$

for $k_1[5] << k_2[C_4F_9I]$, $C^o = [C_4F_9\cdot]$, and rate = $k_1C^o[5]$
for $k_1[5] >> k_2[C_4F_9I]$, $C^o = [R_fHC{=}CR\cdot]$, and rate = $k_2C^o[C_4F_9I]$.

Figure 1 shows the percent conversion vs. time for mole ratios (**5** to C_4F_9I) of 100, 50, and 33. The slopes of these lines are proportional to rate/[C_4F_9I] at a given concentration of C_4F_9I. These slopes are plotted against the initial amount of C_4F_9I in the inset.

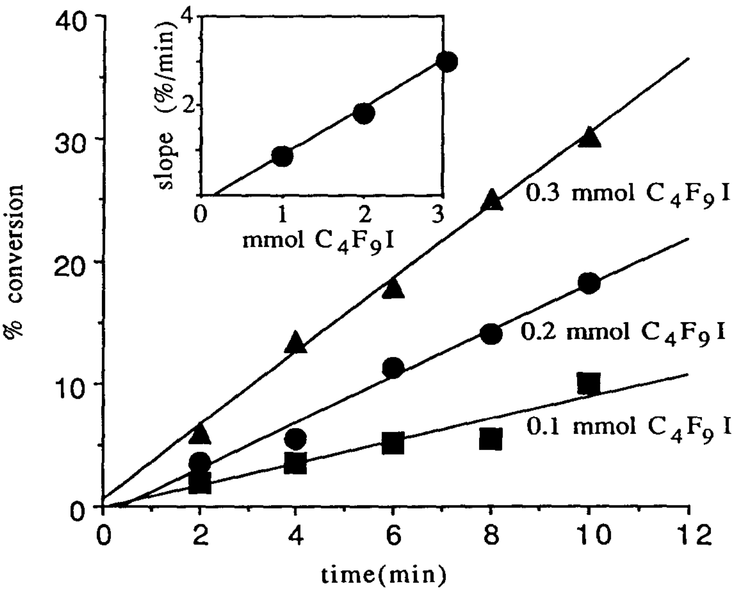


Fig.1. Percent conversion of C_4F_9I to **6** as a function of the amount of C_4F_9I added. 10 mmol of **5** was used, with 0.1, 0.2, and 0.3 mmol C_4F_9I. Inset shows the linear relation between slope (% conversion/min) and [C_4F_9I].

In Fig.1, the slope increases linearly with [C_4F_9I], and so the reaction rate, which is defined as d[**6**]/dt, increases with the *square* of the C_4F_9I concentration. It should be noted as well that the steady-state concentration of radicals, C^o, will increase linearly with [C_4F_9I], since in this concentration regime, where the absorbance is low, the amount of light absorbed is directly proportional to [C_4F_9I]. Therefore, the kinetic data are consistent with the radical mechanism for the case where $k_1[5] >> k_2[C_4F_9I]$, since rate = $k_2C^o[C_4F_9I]$ = constant x $[C_4F_9I]^2$.

For a similar reaction, initiated electrochemically in DMF solution, the k_2/k_1 ratio was found to be ca. 270 by means of cyclic voltammetry [12]. The linear dependence of rate/C^o on [C_4F_9I] shows that in the present case the k_2/k_1 ratio must be at least a factor of 10 smaller, since even at a concentration ratio ([5]/[C_4F_9I]) = 33, the reaction is in the regime where $k_1[5] >> k_2[C_4F_9I]$. If we assume that the second propagation step is diffusion controlled, then we would expect it to be significantly slower under the reaction conditions reported here (i.e., in neat 5, which is considerably more viscous than DMF).

EXPERIMENTAL

^{19}F-NMR spectra were recorded on a Varian EM-390 spectrometer at 84.67 MHz using $CFCl_3$ as an external standard and C_6F_6 as an internal standard. ^{19}F chemical shifts are reported in ppm upfield from $CFCl_3$. ^{1}H-NMR spectra were recorded on a Varian EM-390 using TMS as an external standard. Mass spectra were obtained on a GC-MS, Varian-3400 Gas Chromatograph with a Finnigan Mat-700 Ion Trap Detector. Perfluorobutyl iodide and other starting materials were purchased from Aldrich Chemical Co. and used as received.

In a typical reaction, 5 mmol of the organic substrate was loaded into a 10-mm diameter borosilicate glass tube with 5 mmol of perfluorobutyl iodide. The mixture was stirred and illuminated at ambient temperature using a 200 watt mercury-xenon lamp. The products were identified by ^{1}H and ^{19}F-NMR, and by mass spectra. Analytical data are given below:

2: ^{1}H NMR ($CDCl_3$); 6.3 (t, 1H) J_{FH}=15 Hz, 2.8 (t, 2H), 2.3 (m, 2H), 1.7 (m, 2H), 1.1 (t, 3H). ^{19}F NMR ($CDCl_3$); -83.0 (3F,CF_3), -106.9 (2F, CF_2(a)), -125.7 (2F,CF_2(b)), -127.7 (2F, CF_2(c). m/e: 428 (M), 427 (M-1), 301 (M-I).

4: ^{1}H NMR ($CDCl_3$); 6.2 (t, 1H) J_{FH}=15 Hz, 2.8 (t, 2H), 2.2 (m, 2H), 1.7 (m, 2H), 1.5 (m, 2H), 1.2 (t, 3H). ^{19}F NMR ($CDCl_3$); -83.0 (3F,CF_3), -106.3 (2F,CF_2(a)), -125.6 (2F, CF_2(b)), -127.3 (2F, CF_2(c)). m/e: 442 (M), 441 (M-1), 315 (M-I).

6: ^{1}H NMR ($CDCl_3$); 6.5 (t, 1H) J_{FH}=15 Hz, 4.8 (d, 2H), 2.3 (t, 1H). ^{19}F NMR ($CDCl_3$); -83.2 (3F, CF_3), -107.4 (2F, CF_2(a)), -126.0 (2F, CF_2(b)), -128.6 (2F, CF_2(c)). m/e : 402 (M), 401 (M-1), 275 (M-I).

8: ^{1}H NMR ($CDCl_3$); 6.8 (t, 1H) J_{FH}= 15Hz, 2.7 (s, 1H), 1.5 (s, 1H). ^{19}F NMR ($CDCl_3$); -82.0 (3F, CF_3), -110 (2F, CF_2(a)), -126.0 (2F, CF_2(b)), -128.3 (2F, CF_2(c)). m/e : 430 (M), 429 (M-1), 303 (M-I).

10: ^{1}H NMR (CCl_4); *cis*: 4.6 (m, 1H) J_{FH}=15 Hz, 1.8 (m, 9H), *trans:* 4.8 (m, 1H), 1.8 (m, 9H). ^{19}F NMR; *cis:* -78.4 (3F, CF_3), -119.1 (2F, CF_2(a)), -120.7 (2F, CF_2(b)), -124.2 (2F, CF_2(c)); *trans:* -78.4 (3F, CF_3), -116.0 (2F, CF_2(a)), -119.3 (2F, CF_2(b)), -124.1 (2F, CF_2(c)). m/e : 428 (M), 427 (M-1), 301 (M-I).

13: ^{1}H NMR ($CDCl_3$); *cis:* 5.6-5.9 (5H, C_6H_5), 2.7 (2H, CH_2), 0.75(1H, CH), *trans:* 5.6-5.9 (5H, C_6H_5), 2.7 (2H, CH_2), 0.10 (1H, CH). ^{19}F NMR; *cis:* -83.4 (3F, CF_3), -111.7 (2F, CF_2(a)), -126.7 (2F, CF_2(b)), -128.0 (2F, CF_2(c)), *trans:* -83.4 (3F, CF_3), -108.5 (2F, CF_2(a)), -126.7 (2F, CF_2(b)), -128.0 (2F, CF_2(c)). m/e: 542 (M), 541 (M), 415 (M-I).

15: ^{1}H NMR ($CDCl_3$); *cis:* 6.8 (t, 1H) J_{FH}= 15Hz, 4.3 (s, 2H), *trans:* 7.2 (t, 2H), 4.3 (s, 2H). ^{19}F NMR; *cis:* -81.9 (3F, CF_3), -107.7 (2F, CF_2(a)), -126.2 (2F, CF_2(b)), -127.9 (2F, CF_2(c)), *trans:* -81.9 (3F, CF_3), -110.6 (2F, CF_2(a)), -125.5 (2F, CF_2(b)), -127.9 (2F, CF_2(c)). m/e : 422 (M), 420 (M-2).

Typical procedure for kinetic measurements

Kinetic measurements were carried out with radiation from a 200-W mercury-xenon lamp with stirring in five 10 mm diameter borosilicate glass tubes, each of which contained 10 mmol 5 and the appropriate quantity of C_4F_9I. 10µL C_6F_6 was added as an internal standard and ^{19}F NMR spectra were run at two minute intervals.

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REFERENCES

1 (a) R. Filler and Y. Kobayashi, Biological Aspects of Fluorine Chemistry Kodansha, Tokyo (1982); (b) R. E. Banks, Organofluorine Chemicals and their Industrial Applications, Ellis Horwood, Chichester (1979).

2 (a) R. N. Haszeldine, J. Chem. Soc., (1949) 2856; (1950) 3037; (1951) 588; (b) W.O. Godtfredsen and S. Vangedal, Acta. Chem. Scand., 15 (1961) 1786; (c) W. A. Sheppard and C. M. Sharts, Organic Fluorine Chemistry, Benjamin, Elmsford, NY, (1969).

3 M. O. Brace, J. Org. Chem., 27 (1962) 3027; 3033.

4 T. Fuchikami and I. Ojima, Tetrahedron Lett., 25 (1984) 303.

5 K. V. Werner, J. Fluorine Chem., 28 (1985) 229.

6 Q. Y. Chen and Z. Y. Yang, J. Fluorine Chem., 39 (1988) 217.

7 Y. Takeyama, Y. Zchinose, K. Oshima and K. Utimoto, Tetrahedron Lett., 30 (1989) 3159.

8 W. Y. Huang, W. Wang and B. N. Huang, Acta Chim. Sinica, (English Edn), (1986) 178.

9 W. Y. Huang and J. L. Chen, Acta Chim. Sinica, 46 (1988) 669.

10 M. H. Habibi and L. C. Sams, J. Fluorine Chem., 21 (1982) 287.

11 M. H. Habibi and L. C. Sams, J. Fluorine Chem., 18 (1981) 277.

12 P. Calas, C. Amatore, L. Gomez, and A. Commeyras, J. Fluorine Che 49 (1990) 247.

13 K. Leedham and R. N. Haszeldine, J. Chem. Soc.,(1954) 1634.

14 R. N. Haszeldine, J. Chem. Soc., (1953) 3565.