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PRELIMINARY NOTE

Addition of 1,2-Dibromotetrafluoroethane to Alkynes by means of a Redox System

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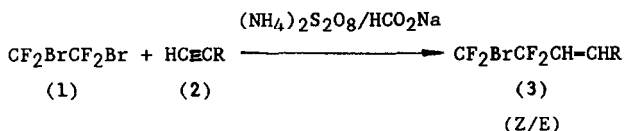
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SUMMARY

The addition of 1,2-dibromotetrafluoroethane (1) to various terminal alkynes (2a - 2j) was performed in DMF with a redox system $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{HCO}_2\text{Na}\cdot 2\text{H}_2\text{O}$ at 40°C. The products (3) were 1:1 adducts reductively debrominated under the reaction conditions, with the E isomers in predominance, and were obtained in excellent yields (82 - 93%).

Polyfluoroalkylation of carbon-carbon multiple bonds is effected by photolysis, pyrolysis, electrolysis, free radical initiators or transition-metal complexes as catalysts [1]. Though redox systems have been used extensively in the telomerization and polymerization of fluorine-containing monomers [2], few additions of polyhalofluoroalkanes to multiple bonds initiated by redox systems are known. Burton *et al* found that copper chloride - ethanolamine could catalyze the addition of polyfluoroalkyl iodides or bromides to alkenes in t-butanol, but no addition adducts could be obtained when such a redox system was applied to the polyfluoroalkylation of simple alkynes [3].

In recent years our work [4] shows that redox systems are very effective in such additions. Here the addition of 1,2-dibromotetrafluoroethane (1) to alkynes (2) initiated by the ammonium peroxydisulfate - sodium formate redox couple is reported. Such an addition reaction can be performed under mild conditions and it offers a simple and effective method for the synthesis of many organofluorine compounds containing various active functional groups.




A typical procedure is as follows: A mixture of (1) (2.60g, 10mmol), propargyl methyl ether (2e) (0.42m, 5mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2.5g, 11mmol) and $\text{HCO}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (1.0g, 10mmol) in 20ml DMF was stirred at 40°C for 5h. Then the mixture was poured into water and extracted with ether. The extract was washed and dried. Distillation under reduced pressure gave 1.31g (87.6% yield) of $\text{CF}_2\text{BrCF}_2\text{CH=CHCH}_2\text{OCH}_3$ (3e). Anal. for $\text{C}_6\text{H}_7\text{F}_4\text{OBr}$: Calcd: C, 28.71; H, 2.81; F, 30.27. Found: C, 28.78; H, 2.67; F, 30.53. IR(film): 1680(m, CH=CH) cm^{-1} . ^1H NMR(net, TMS as external standard): 5.8-6.8(m, 2H, CH=CH), 4.0-4.4(m, 2H, CH_2), 3.50(s, 3H, OCH_3)ppm. ^{19}F NMR(net, TFA as external standard and positive for upfield shifts): -10(s, 2F, CF_2Br), 30(s, $\text{CF}_2\text{CH=CH}$, Z-isomer), 33(s, $\text{CF}_2\text{CH=CH}$, E-isomer)ppm. MS m/e(fragment); relative intensity): 249(M-1, 38.1), 171(M-Br, 12.9), 91($\text{CF}_2\text{CH=CHCH}_2+1$, 22.52), 45(CH_2OCH_3 , 100).

As shown in Table 1, by controlling the molar ratio of the reactants, 1:1 adducts (3), reductively debrominated, were obtained in excellent yields with the E-isomers in predominance. In most cases, the reaction was completed within a few hours. If the hydroxyl group in propargyl alcohol (Entry 3) was pro-

TABLE 1

Addition of $\text{CF}_2\text{BrCF}_2\text{Br}$ (1) to alkynes $\text{CH}\equiv\text{CR}$ (2) to give adducts $\text{CF}_2\text{BrCF}_2\text{CH}-\text{CHR}$ (3)^a

| Entry | R | Time (h) | Conv. ^b (%) | Adduct (Z:E) | Yield ^d (%) |
|-------|--|----------------|---------------------------|----------------------|---------------------------|
| 1 | n-C ₄ H ₉ (2a) | 3.5 | 100 | 32:68 ^c | 91.3 |
| 2 | SiMe ₃ (2b) | 6.5 | 80 | 61:39 ^b | 82 |
| 3 | CH ₂ OH (2c) | 8.5 | 60 | 16:84 ^b | 91 |
| 4 | CH ₂ CH ₂ OH (2d) | 4 | 100 | 34:66 ^b | 90 |
| 5 | CH ₂ OCH ₃ (2e) | 5 | 100 | 17:83 ^{b,c} | 87.6 |
| 6 | CH ₂ OAc (2f) | 3.5 | 100 | 21:79 ^b | 87.8 |
| 7 | CH ₂ Cl (2g) | 14 | 100 | 6:94 ^c | 88 |
| 8 | CH ₂ Ph (2h) | 4 | 100 | 27:73 ^b | 88 |
| 9 | CH ₂ NEt ₂ (2i) | — ^e | — | — | — |
| 10 | CH ₂ -  (2j) | 3 | 100 | 35:65 ^c | 86 |

^a The structure was confirmed by spectra and elemental analysis.

^b Determined by ¹⁹F NMR.

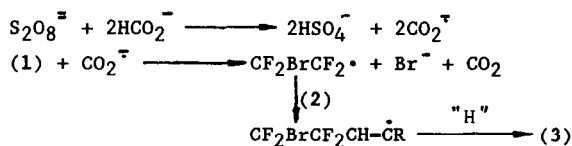
^c Determined by GC.

^d Isolated yield based on alkynes.

^e Polymeric substance was obtained.

tected as in entries 5-6, the conversion could be markedly improved. Thus this method affords a convenient approach to the synthesis of many fluorine-containing synthons.

The reaction is likely to proceed through the following mechanism:



- 1 See references cited in: C. P. Andrieux, L. Gelis,
M. Medebielle, J. Pinson and J.-M. Saveant, J. Am. Chem.
Soc., 112 (1990) 3509.
- 2 A. Battais, B. Boutevin, Y. Pietrasanta, R. Bertocchio and
A. Lantz, J. Fluorine Chem., 42 (1989) 215.
- 3 D. J. Burton and L. J. Kehoe, J. Org. Chem., 35 (1970) 1339
Idem., ibid., 36 (1971) 2596.
- 4 C. M. Hu and F. L. Qing, Tetrahedron Lett., 31 (1990) 1307.