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PRELIMINARY NOTE

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

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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 $(NH_4)_2S_2O_8/HCO_2Na\cdot 2H_2O$ 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].

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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.

$$\underset{(1)}{CF_2BrCF_2Br} + \underset{(2)}{HC{\equiv}CR} \xrightarrow{(NH_4)_2S_2O_8/HCO_2Na} \underset{(3)\ (Z/E)}{CF_2BrCF_2CH{=}CHR}$$

A typical procedure is as follows: A mixture of (1) (2.60g, 10mmol), propargyl methyl ether (2e) (0.42m, 5mmol), $(NH_4)_2S_2O_8$ (2.5g, 11mmol) and $HCO_2Na{\cdot}2H_2O$ (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 $CF_2BrCF_2CH{=}CHCH_2OCH_3$ (3e). Anal. for $C_6H_7F_4OBr$: 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, $CF_2CH{=}CH$, Z-isomer), 33(s, $CF_2CH{=}CH$, E-isomer)ppm. MS m/e(fragment; relative intensity): 249(M-1, 38.1), 171(M-Br, 12.9), 91($CF_2CH{=}CHCH_2$+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 CF_2BrCF_2Br (1) to alkynes CH≡CR (2) to give adducts $CF_2BrCF_2CH{=}CHR$ (3)[a]

Entry	R	Time (h)	Conv.[b] (%)	Adduct (Z:E)	Yield[d] (%)
1	n-C_4H_9(2a)	3.5	100	32:68[c]	91.3
2	$SiMe_3$(2b)	6.5	80	61:39[b]	82
3	CH_2OH(2c)	8.5	60	16:84[b]	91
4	CH_2CH_2OH(2d)	4	100	34:66[b]	90
5	CH_2OCH_3(2e)	5	100	17:83[b,c]	87.6
6	CH_2OAc(2f)	3.5	100	21:79[b]	87.8
7	CH_2Cl(2g)	14	100	6 :94[c]	88
8	CH_2Ph(2h)	4	100	27:73[b]	88
9	CH_2NEt_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 ^{19}F 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:

$$S_2O_8^{=} + 2HCO_2^{-} \longrightarrow 2HSO_4^{-} + 2CO_2^{\mp}$$

$$(1) + CO_2^{\mp} \longrightarrow CF_2BrCF_2\cdot + Br^{-} + CO_2$$

$$\downarrow (2)$$

$$CF_2BrCF_2CH{-}\dot{C}R \xrightarrow{\text{"H"}} (3)$$

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