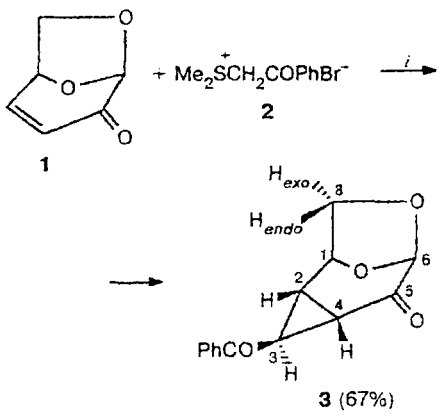

i. Et_3N, EtOH, 40—50 °C, 10 min

It is of special interest that not only the two centers, which were initially present in a molecule of **1** (C(2) and C(4)), but also the center present in salt **2** (C(3)) have the defined absolute configurations in compound **3**. The configurations of the atoms of the cyclopropanic fragment of compound **3** were established from the ^1H NMR spectrum. The three-membered cycle is closed from the side opposite to the anhydro bridge ("from the bottom"), as indicated by the value of the coupling constant $J_{1,2}$ = 1.5 Hz.[4] As follows from the values of the coupling constants $J_{2,3} = J_{3,4}$ = 4.1 Hz and $J_{2,4}$ = 7.8 Hz, the H(3) proton is in the *trans*-position to the H(2) and H(4) atoms (as is known, in cyclopropanes the coupling constants of *cis*-protons are greater than those of *trans*-protons).

(1*S*,2*S*,3*S*,4*S*,6*R*)-3-Benzoyl-7,9-dioxatricyclo[4.2.1.$0^{2,4}$]-nonan-5-one (3), m.p. 119—120 °C (EtOH). ^1H NMR (300 MHz, acetone-d_6), δ: 2.27 (ddd, 1 H, H(2), J = 7.8, 4.1, 1.5 Hz); 2.36 (br.dd, 1 H, H(4), J = 7.8, 4.1 Hz); 3.63 (t, 1 H, H(3), J = 4.1 Hz); 3.88 (dd, 1 H, H_{exo}(8), J = 7.1, 4.7 Hz); 4.17 (d, 1 H, H_{endo}(8), J = 7.1 Hz); 4.98 (s, 1 H, H(6)); 5.11 (br.d, 1 H, H(1), J = 4.7 Hz); 7.56 (t, 2 H); 7.67 (t, 1 H); 8.10 (d, 2 H) (all Ph). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 25.41 (C(2)); 27.23, 30.07 (C(3) and C(4)); 69.08 (C(8)), 71.66 (C(1)); 100.13 (C(6)); 129.24, 129.84, 134.65, 137.44 (all C_{Ph}); 195.56, 196.04 (C(5) and COPh).

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(Alk-1-ynyl)fluorocarbenes — a new class of carbenic intermediates: generation from 3-substituted 1,1,3-tribromo-1-fluoropropanes by treatment with bases and cycloaddition to alkenes

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We have previously suggested new methods for generating (alk-1-ynyl)chloro- and (alk-1-ynyl)bromocarbenes from the corresponding 1,1-dihaloalk-2-ynes[1—5] and 3-substituted 1,1,1,3-tetrahalopropanes by the action of bases.[6] Therefore, it was of interest to evaluate the possibility of preparing unknown (alk-1-ynyl)fluorocarbenes by a similar approach, since the introduction of fluorine into polyhalomethanes (alkanes) makes their dehydrohalogenation substantially difficult and, in some cases, completely rules out the generation of fluorocarbenes by this method.[7]

For this purpose, we studied the action of bases on 1,1,3-tribromo-3-organyl-1-fluoropropanes **1**. As it turned out (Scheme 1), the reaction with Bu^tOK in hexane at 20 °C (method *i*) or with KOH in the presence of benzyltriethylammonium chloride in CH_2Cl_2 at 20 °C

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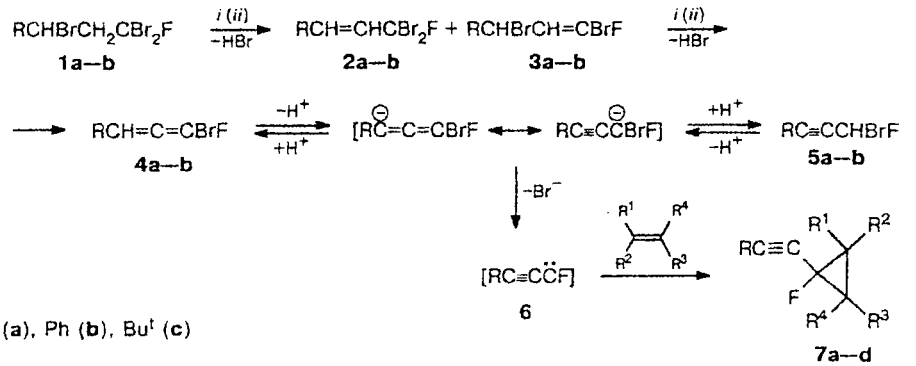
Scheme 1



Reagents and conditions: *i.* Bu^{t}OK, hexane, 20 °C; *ii.* KOH, $PhCH_2N^+Et_3Cl^-$ (cat.), CH_2Cl_2, 20—40 °C

7a: $R^1 = R^2 = Me$, $R^3 = R^4 = H$, $R = Bu^n$;
7b: $R^1 = R^2 = R^3 = R^4 = Me$, $R = Ph$;
7c: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$, $R = Bu^n$;
7d: $R^1 = R^4 = H$, R^2, $R^3 = (CH_2)_4$, $R = Ph$

(method *ii*) is accompanied by the elimination of three HBr molecules to form the previously unknown (alk-1-ynyl)fluorocarbenes **6**, which are easily trapped by a threefold molar excess of olefin yielding the corresponding 1-(alk-1-ynyl)-1-fluorocyclopropanes **7a—d** in 41—70% yields.

The following experimental data indicate that the reaction proceeds *via* the route presented in Scheme 1. When 1,1,3-tribromo-1-fluoroheptane **1a** was treated with an equimolar amount of Bu^{t}OK in the absence of olefin, the reaction mixture contained along with the starting halide **1a** (*E*)-1,1-dibromo-1-fluorohept-2-ene (**2a**) and *E*- and *Z*-isomers of trihalide **3a** in the 1 : 1.8 : 0.9 : 0.75 ratio, respectively. The further reaction of the resulting mixture with Bu^{t}OK leads to the formation of allene **4a** and alkyne **5a**.

The structures of compounds **2a**, **3a**, **4a**, and **5a** and cyclopropanes **7a—d** were proved by the data of the ^{1}H, ^{13}C, and ^{19}F NMR spectra (200 MHz for ^{1}H, 50 MHz for ^{13}C, and 188 MHz for ^{19}F; $CDCl_3$) and GC-MS (EI, 70 eV).

2,2-Dimethyl-1-(hex-1-ynyl)-1-fluorocyclopropane (7a) was obtained in 41% yield from tetrahalide **1a** and isobutene by method *i*.

^{1}H NMR, δ: 0.73 (dd, 1 H, CH_2 *cyclo*-C_3H_2, J = 6.5 Hz, J_{HF} = 7.8 Hz); 0.91 (t, 3 H, CH_3, Bu^n, J = 7.4 Hz); 0.94 (dd, 1 H, CH_2, *cyclo*-C_3H_2, J = 6.5 Hz, J_{HF} = 18.3 Hz); 1.15 (d, 3 H, CH_3, J_{HF} = 2.3 Hz); 1.21 (d, 3 H, CH_3, J_{HF} = 2.0 Hz); 1.25—1.60 (m, 4 H, 2 CH_2, Bu^n); 2.28 (dt, 2 H, $CH_2C\equiv$, J = 6.7 Hz, J_{HF} = 6.7 Hz). ^{13}C NMR, δ: 13.6 (CH_3, Bu^n); 18.6 (CH_2, Bu^n); 19.0 (d, $(\underline{C}H_3)_2C$, J = 10 Hz); 21.9 (CH_2, Bu^n); 22.6 ($(\underline{C}H_3)_2C$); 23.3 (d, $\underline{C}Me_2$, *cyclo*-C_3H_2, J = 12 Hz); 26.7 (d, CH_2, *cyclo*-C_3H_2, J = 12 Hz); 30.6 ($\underline{C}H_2C\equiv$); 75.7 (d, $\underline{C}CF$, J = 31 Hz); 76.2 (d, $\underline{C}F$, J = 208 Hz); 89.3 (d, $\underline{C}\equiv CCF$, J = 10 Hz). ^{19}F NMR, δ ($CFCl_3$): −181.6. Found (%): C, 78.61; H, 10.25. $C_{11}H_{17}F$. Calculated (%): C, 78.52; H, 10.18.

2,2,3,3-Tetramethyl-1-(phenylethynyl)-1-fluorocyclopropane (7b) was obtained in 49% yield from tetrahalide **1b** and tetramethylethylene by method *i*.

^{1}H NMR, δ: 1.21 and 1.22 (both s, 12 H, 4 Me); 7.30—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 15.5 (d, 2 Me, J = 9 Hz); 19.0 (2 Me); 27.7 (d, 2 $\underline{C}Me_2$, J = 12 Hz); 80.3 (d, CF, J = 215 Hz); 83.5 (d, $\equiv\underline{C}CF$, J = 33 Hz); 89.8 (d, $Ph\underline{C}\equiv$, J = 10 Hz); 122.6 (d, C-1, Ph, J = 3 Hz); 128.2, 128.4, 131.6 (Ph). ^{19}F NMR, δ ($CFCl_3$): −191.9. MS (*m/z*): 216 $[M]^+$. Found (%): C, 83.22; H, 7.85. $C_{15}H_{17}F$. Calculated (%): C, 83.29; H, 7.92.

1-(Hex-1-ynyl)-2-phenyl-1-fluorocyclopropane (7c) was obtained in 50% yield from tetrahalide **1a** and styrene by method *ii* (isomer ratio *cis*-(Ph, F) : *trans*-(Ph, F) = 3.5 : 1).

cis-(Ph, F)-Isomer. ^{1}H NMR, δ: 0.76 (t, 3 H, CH_3, J = 7.3 Hz); 1.00—1.80 (m, 6 H, 2 CH_2, Bu^n and CH_2, *cyclo*-C_3H_3); 2.07 (dt, 2 H, $CH_2C\equiv$, J = 6.8 Hz, J_{HF} = 6.8 Hz); 2.68 (ddd, 1 H, CH, *cyclo*-C_3H_3, J = 8.6 Hz, J = 17.7 Hz, J = 6.2 Hz); 7.10—7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 13.4 (CH_3); 18.4 (d, CH_2, Bu^n, J = 2.5 Hz); 20.2 (d, CH_2, *cyclo*-C_3H_3, J = 14 Hz); 21.6 (CH_2, Bu^n); 30.0 (d, CH, *cyclo*-C_3H_3, J = 11 Hz); 30.2 (CH_2, Bu^n); 73.7 (d, CF, J = 213 Hz); 74.2 (d, $\equiv\underline{C}CF$, J = 30 Hz); 91.4 (d, $\equiv\underline{C}CH_2$, J = 10 Hz); 126.6, 128.0, 128.1 (Ph); 136.2 (C-1, Ph). *trans*-(Ph, F)-Isomer. ^{1}H NMR, δ: 0.91 (t, 3 H, CH_3, J = 7.3 Hz); 1.00—1.80 (m, 6 H, 2 CH_2, Bu^n and CH_2, *cyclo*-C_2H_3); 2.26 (dt, 2 H, $CH_2C\equiv$, J = 6.8 Hz, J_{HF} = 6.8 Hz); 2.41 (ddd, 1 H, CH, *cyclo*-C_2H_3, J = 2.5 Hz, J = 8.5 Hz, J = 11 Hz); 7.10—7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 13.6 (CH_3); 18.6 (d, CH_2, Bu^n, J = 3 Hz); 19.6 (d, CH_2, *cyclo*-C_3H_3, J =14 Hz); 22.0 (CH_2, Bu^n); 30.5 (CH_2, Bu^n); 30.8 (d, CH, *cyclo*-C_3H_3, J = 11 Hz); 70.6 (d, CF, J = 213 Hz);

77.4 (d, ≡CCF, J = 32 Hz); 87.8 (d, ≡CCH$_2$, J = 9 Hz); 126.8, 128.2, 128.5 (Ph); 134.7 (C-1, Ph).

MS (m/z): 216 [M]$^+$. Found (%): C, 83.38; H, 8.01. $C_{15}H_{17}F$. Calculated (%): C, 83.29; H, 7.92.

7-Fluoro-7-(phenylethynyl)bicyclo[4.2.0]heptane (7d) was obtained in 69% yield from tetrahalide **1b** and cyclohexene by method *ii* (isomer ratio *endo*-F : *exo*-F = 4.5 : 1).

^{1}H NMR, δ: 1.20—2.10 (m, 12 H, 4 CH$_2$ and 2 CH); 7.30—7.60 (m, 5 H, Ph). *endo*-(F)-Isomer. ^{13}C NMR, δ: 19.0 (2 CH$_2$); 20.8 (d, 2 CH$_2$, J = 3 Hz); 22.4 (d, 2 CH, J = 14 Hz); 76.9 (d, CF, J = 208 Hz); 82.6 (d, ≡CCF, J = 30 Hz); 93.4 (d, ≡CCH$_2$, J = 10 Hz); 122.3 (d, C-1, Ph, J = 3 Hz); 128.4, 128.7, 131.6 (Ph). ^{19}F NMR, δ ($CFCl_3$): −163.6. *exo*-(F)-Isomer. Partial ^{13}C NMR spectrum, δ: 17.7 (d, 2 CH$_2$, J = 3 Hz); 21.3 (d, 2 CH, J = 14 Hz); 21.4 (d, 2 CH$_2$, J = 2 Hz); 128.3, 128.5, 131.7 (Ph). ^{19}F NMR, δ ($CFCl_3$): −199.7. Found (%): C, 83.92; H, 7.15. $C_{15}H_{15}F$. Calculated (%): C, 84.08; H, 7.06.

gem-(Alk-1-ynyl)fluorocyclopropanes obtained by the addition of (alk-1-ynyl)fluorocarbenes to olefins are of great interest as probable physiologically active compounds and synthons in organic syntheses.

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Allylzinc bromide: reductive *trans*-1,3-diallylation of isoquinoline and intramolecular cyclization of 2,4-dizinc derivative

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Pyrrole, isoquinoline, and pyridines treated successively with triallylborane and alcohol undergo reductive *trans*-α,α′-diallylation.[1,2] These stereospecific reactions accompanied by the destruction of aromatic system of the corresponding heterocyclic systems occur under mild conditions (20—100 °C) and are not complicated by side processes. The only disadvantage of these reactions is the necessity to obtain triallyborane. The latter is an accessible reagent but easily oxidized and hydrolyzed in air, and work with it requires certain skills. Therefore, we started to search for more convenient routes for reductive α,α′-diallylation of nitrogen heterocycles.

In this report, we present the first results of studying the transformations of isoquinoline under the action of

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