The final two entries in Table I provide another example where the terminal atoms are oxygen and carbon, but with nitrogen as the center atom. Here ΔBDE is 6 for CH_3C-H=NOH, but increases to 14 when CH_3 is replaced by Ph.

To the best of our knowledge these are the first quantitative experimental results to support the conclusion drawn from theoretical calculations[4] that resonance energies in heteroallylic radicals are closely associated with the electronegativities of the atoms at the termini.

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Articles

Synthesis of Novel Perhalo 1,3-Heterodienes from *N*-Bromoperhalo-1-alkanimines

Michael I. Cook and Darryl D. DesMarteau*

H. L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-1905

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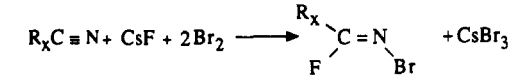
The hydrolysis of several perhalo-1-bromo-3-aza-3-alkenes ($R_xCF{=}NCF_2CF_2Br$, R_x = CF_3, C_2F_5, $ClCF_2$) affords the corresponding acid amide ($R_xCONHCF_2CF_2Br$) in excellent yield. Dehydrofluorination of the amides using active KF gives the novel 1,3-heterodienes, perhalo-1-bromo-3-aza-4-oxo-2-alkenes ($R_xCON{=}CFCF_2Br$), in high yield. Details on the synthesis and properties of the new compounds are given along with some reaction chemistry of the dienes.

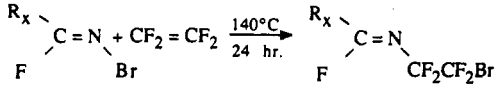
Introduction

Recently, we have reported that highly halogenated *N*-bromo-1-alkanimines ($R_xCF{=}NBr$) can be prepared in excellent yields by treatment of the corresponding perhalogenated nitrile with bromine and activated cesium fluoride.[1]



This one-step general synthesis combined with the good thermal stability of the imines has allowed us to investigate the chemistry of these compounds in some detail.

Previous studies of other *N*-halo compounds have shown that the N-X (X = Cl, Br) bond is very labile, and as a result, such compounds react quite readily under mild, thermal conditions with halogenated olefins to give 1,2-addition products.[2-5] In direct comparison, the compounds $R_xCF{=}NBr$ also undergo similar addition reactions with olefins to form perhalo-1-bromo-3-aza-3-alkenes ($R_xCF{=}NCYY'CZZ'Br$).[6] As part of this work, we have prepared a series of these addition products by treating various *N*-bromoperhalo-1-alkanimines with tetrafluoroethylene.



R_x = CF_3, C_2F_5, $ClCF_2$

The above compounds were typically prepared as indicated by heating the $R_xCF{=}NBr$ (5 mmol) and a 2-fold excess of $CF_2{=}CF_2$ in a Pyrex vessel. The products were easily separated from excess olefin and any unreacted *N*-bromo imine by vacuum-line fractionation. Although there exists the possibility of syn and anti isomerism about the C=N bond, previous NMR studies indicate that only one isomer is formed, and it is assumed on steric grounds that the observed isomer is, in each case, the one with both perhaloalkyl groups anti to each other.[6]

Further investigation of the reaction chemistry of the perhalo-*N*-alkyl-1-alkanimines, in particular their use as precursors to a series of highly halogenated 1,3-heterodienes, has been carried out, and the results of some of these studies are discussed herein.

Results and Discussion

Hydrolysis of $R_xCF{=}NCF_2CF_2Br$. Previous studies of other perhaloalkanimines have shown that they usually undergo complete or partial decomposition with H_2O at 20 °C. For example, $CF_3N{=}CF_2$ decomposes to give CO_2, NH_4F, and HF,[7] whereas $C_3F_7N{=}CF_2$ is converted to C_2F_5CN and $C_2F_5CONH_2$. With less than stoichiometric amounts of H_2O, hydrolysis is incomplete and a low yield of the corresponding isocyanate is formed.[8]

Hydrolysis of the perhalo-1-bromo-3-aza-3-alkenes in our study was carried out by shaking with an equimolar amount of H_2O at room temperature for 2–4 h. The products formed were all low-melting, white crystalline solids and were easily identified by both infrared and NMR spectroscopy as the corresponding acid amides (eq 1). The full characterization of these compounds is given

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(2) Chang, S. C.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 895.
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(8) Barr, D. A.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 3416.

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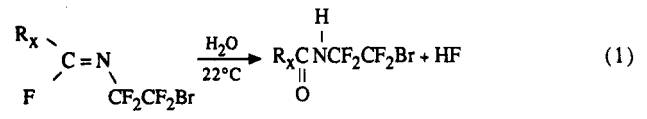
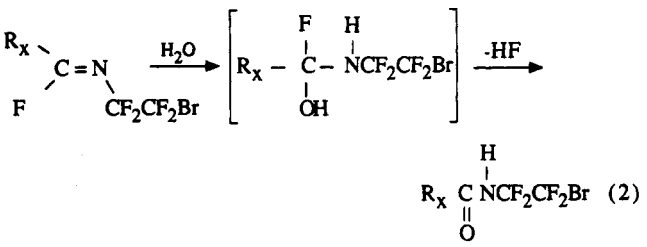
in the Experimental Section. Conceptually the formation

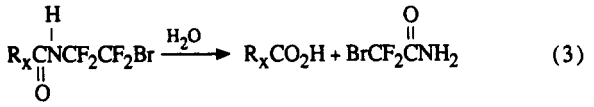


$R_X = CF_3, C_2F_5, ClCF_2$ 65 - 70%

of the amides is straightforward. Addition of H_2O to the C=N bond followed by elimination of HF gives rise to the observed products (eq 2). Due to the presence of the



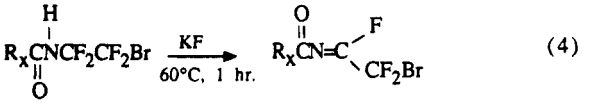
perhalo (R_x) group, the amides formed are quite stable and further decomposition to form isocyanates is not observed. However, long reaction times or the addition of excess H_2O does result in a decrease in the overall yield of the amide. The lower yield is caused by the amide undergoing further hydrolysis and decomposing to form other carboxylic derivatives (eq 3).



$R_X = CF_3, C_2F_5, ClCF_2$

While only three examples are presented here, the hydrolysis is clearly a general reaction that can be applied to the synthesis of a wide variety of amides. A large number of precursor imines are available by the addition of $R_xCF{=}NBr$ to almost any desired olefin.[6]

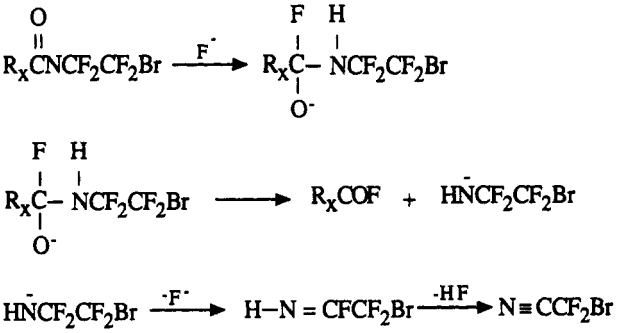
Dehydrofluorination of $R_xC(O)NHCF_2CF_2Br$. Dehydrofluorination of the amides to form perhalo-1-bromo-3-aza-4-oxo-2-alkenes (eq 4) was readily achieved by gently heating the $R_xCONHCF_2CF_2Br$ with an excess of active KF. After purification the products were isolated in ~50–60% yield. Various attempts to improve the yield



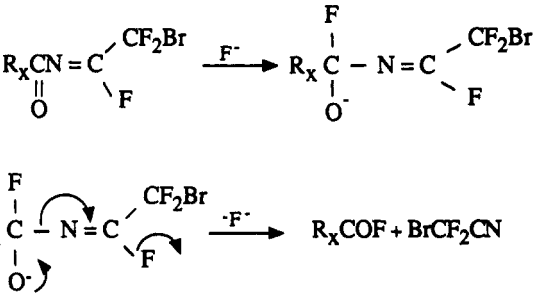
were unsuccessful, and too high a reaction temperature or prolonged exposure to the KF only resulted in the formation of the deomposition products, R_xCOF and $BrCF_2CN$. Formation of these products can occur via two possible mechanisms. First of all, apart from dehydrofluorination to form the 1,3-heterodiene, the amide can undergo nucleophilic attack by F^- at the carbonyl center, where the elimination of $BrCF_2CF_2NH^-$ accounts for the formation of R_xCOF. The nitrogen anion can then lose F^- to give the N(H) imine, which subsequently eliminates HF to give bromodifluoroacetonitrile (Scheme I).

Alternatively, once the *N*-acylimine has been formed, fluoride ion can now attack at its carbonyl center. Decomposition of the anion then formed can give rise to the observed products (Scheme II). Further experiments have shown that when the pure 1,3-heterodienes are treated with fresh KF or CsF, decomposition to the acyl fluoride and nitrile occurs quite readily, thus giving support to the

Scheme I

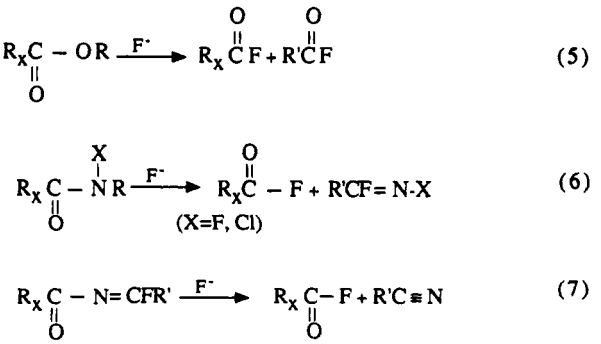


Scheme II



second mechanism. However, the first mechanism cannot be excluded on the basis of these results, and it is most likely that, during the formation of the *N*-acylimines, the decomposition products occur via both routes. These results also imply that, of the two reactive sites in these dienes (C=O, C=N), it is the carbonyl group that is the site of addition, which leads readily to subsequent cleavage.

It is noteworthy that these results provide additional examples of the instability of perhalogenated esters and their nitrogen analogues toward fluoride ion. It was first noted by Shreeve and co-workers that esters of the type $R_fCO_2CF(CF_3)_2$ were unstable in the presence of fluoride ion.[9] Subsequently it was shown that probably all halogenated esters of the type R_xCO_2R, where R contains an α-fluorine, are unstable to fluoride ion.[10] Later it was found that the nitrogen derivatives $R_xC(O)NFR$, containing an α-fluorine in the carboamide group, were similarly unstable.[11] With the current results, the generality of this reaction type is extended to *N*-chloroperhaloalkanamides (see later discussion). These three reaction types are shown in eqs 5–7 (R = halo or perhaloalkyl containing an α-fluorine on the carbon bound to O and N, R′ = alkyl, halo, or perhaloalkyl, and R_x = halo or perhaloalkyl.)



(9) DeMarco, R. A.; Couch, D. A.; Shreeve, J. M. *J. Org. Chem.* **1972**, *37*, 3332.
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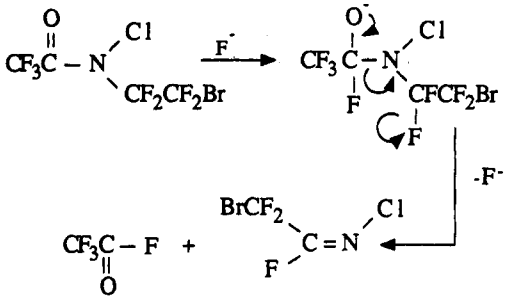
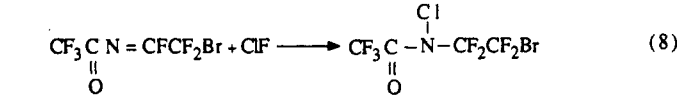
Scheme III



In eq 6, if R = CF_3 and X = F, the compounds do not undergo the indicated reaction,[12] and if X = Cl, a similar limitation when R = CF_3 is likely. However, routes to the latter compounds are not presently available. For eq 5 we predict a similar stability for X = F and R = CF_3, but the only example of this type, $CF_3C(O)OCF_3$,[13] is difficult to prepare, and its reaction with fluoride has not been carried out.

The identity of the new perhalo *N*-acylimines is strongly supported by the data given in the Experimental Section. Molecular ions MH^+ are observed for each compound in the chemical-ionization (CI) mass spectra, and each contains two strong absorptions in the infrared at ~1795 and 1765 cm^{-1} due to ν(C=O) and ν(C=N), respectively. In all cases for the $N{=}CF^BCF_2{}^CBr$ moiety, the ^{19}F NMR spectrum exhibits a doublet near δ −62 for the fluorines labeled C and a broad triplet near δ −34 for the vinylic fluorine B. The coupling constant J_{BC} has a value of 10–11 Hz. No long-range ^5J or ^6J F–F coupling was observed as has been reported for $CF_3C(O)N{=}C(CF_3)_2$.[14]

Reaction of $CF_3C(O)N{=}CFCF_2Br$ with ClF. In this paper we only touch on the reaction chemistry of these dienes. A major interest to us was the polar addition of ClF across the C=N bond and whether or not the reaction would lead readily to C—N bond cleavage, forming NCl_2 derivatives.[14] The addition of ClF yields the corresponding *N*-chloroalkanamide in almost quantitative yield (eq 8).



(8)

The completion of the reaction was readily ascertained due to the disappearance of the C=N stretching frequency at 1764 cm^{-1}, coupled with a shift of the C=O stretching frequency from 1793 to 1772 cm^{-1} in the infrared spectrum. For $CF_3C(O)N(Cl)CF_2CF_2Br$, in the ^{19}F NMR spectrum, long-range spin–spin coupling between the acyl CF_3 and NCF_2 groups is observed (^5J = 3.9 Hz).

When the above reaction was carried out with a slight excess of ClF, $CF_3C(O)N(Cl)CF_2CF_2Br$ was still the major product formed; however, small amounts of CF_3COF and $BrCF_2CF_2NCl_2$ were detected. These two products are probably formed by the further reaction of ClF with the N—C=O bond.[14]

The *N*-chloroalkanamide is thermally very stable. However, as previously mentioned, it has been shown to be unstable in the presence of fluoride ion. In the presence of CsF, $CF_3C(O)N(Cl)CF_2CF_2Br$ decomposes very rapidly to form CF_3COF and $BrCF_2CF{=}NCl$. The probable mechanism of this decomposition is outlined in Scheme III.

The ^{19}F NMR spectrum for $BrCF_2{}^ACF^B{=}NCl$ shows two peaks at δ −57.9 (d) and δ −40.6 (t) which are due to the fluorines labeled A and B, respectively. In all of the NBr and NCl imines we have previously prepared,[1,15] the vinylic fluorine usually appears in the region of δ −20 to −30 (upfield from $CFCl_3$), which we attribute to the compounds adopting the syn configuration. The shift of B to a higher field suggests that the *N*-chloroimine formed in the decomposition reaction adopts the anti configuration as indicated in Scheme III.

Conclusion

The practical use of perhaloazaalkenes to prepare a variety of secondary amides in good yield, by hydrolysis with H_2O, has been demonstrated. These compounds easily undergo dehydrofluorination using KF to afford a novel class of perhalo 1,3-heterodienes. Further studies of the reactions of these new dienes are in progress.

Experimental Section

General Methods. All work was carried out in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital indicating iron–constantan thermocouple. Molecular weights were obtained by gas density measurements.

NMR spectra were recorded with ~1% $CFCl_3$ being used as the internal reference. Mass spectra were recorded at 70 eV for electron-impact (EI) and chemical-ionization (CI, CH_4) spectra. Samples were introduced by direct gas injection.

Melting points were measured directly and boiling points determined by Siwoloboff's method[16] and are uncorrected.

Purity of new compounds was established by ^{19}F NMR. Spectra were generally free of fluorine-containing impurities or contained only trace amounts of impurities.

Reagents. KF was obtained from commercial sources and appropriately activated as previously described.[12] The compounds $CF_3CF{=}NCF_2CF_2Br$, $C_2F_5CF{=}NCF_2CF_2Br$, and $ClCF_2CF{=}N{-}CF_2CF_2Br$ were prepared by the literature method.[6] ClF was prepared by heating equimolar amounts of Cl_2 and F_2 in a Monel bomb for 18 h at 250 °C.

General Procedure for the Hydrolysis of $R_xCF{=}NCF_2CF_2Br$. $R_xCF{=}NCF_2CF_2Br$ (5.0 mmol) and H_2O (5.0 mmol) were both condensed into a 50-mL Pyrex flask fitted with a glass–Teflon stopcock. The vessel was then warmed and shaken at room temperature for 2–4 h. Trap-to-trap fractionation (−10, −96, and −196 °C) afforded the corresponding amide in the −10 °C trap, and any unreacted $R_xCF{=}NCF_2CF_2Br$ was collected in the −96 °C trap. Yields were typically 65–70%, and the compounds were characterized as follows.

$CF_3C(O)NHCF_2CF_2Br$: mp 29.5 °C; IR (gas) 3554 (w), 3460 (vs, NH), 1799 (vs, C=O), 1656 (w), 1523 (vs), 1354 (w), 1328 (w), 1260 (s), 1232 (vs), 1184 (vs), 1129 (vs), 1099 (vs), 1029 (w), 935 (vs), 792 (m), 771 (m), 723 (s), 702 (s), 645 (s), 626 (m) cm^{-1}; MS (CI, major) *m/z* 294/292 [$(M + 1)^+$, 100], 274/272 [$(M - F)^+$], 224/222 [$(M - CF_3)^+$], 212 [$(M - Br)^+$], 181/179 ($C_2F_4Br^+$), 131/129 (CF_2Br^+), (EI, major) 274/272 [$(M - F)^+$], 212 [$(M - Br)^+$], 196/194 [$(M - CF_3CO)^+$], 162 [$(M - CF_2Br)^+$, 100] 131/239 (CF_2Br^+), 119 ($C_2F_5^+$), 100 ($C_2F_4^+$), 69 (CF_3^+); ^{19}F NMR, $CF_3{}^AC(O)NHCF_2{}^BCF_2{}^CBr$ (d_6-acetone) δ_A −75.6, δ_B −94.2 (q), δ_C −67.2 (t), J_{BC} = 4.5, J_{HF^B} = 4.5 Hz; ^1H NMR δ 10.85 (br).

$CF_3CF_2C(O)NHCF_2CF_2Br$: mp 36 °C; IR (gas) 3555 (w), 3458 (s, NH), 1790 (vs, C=O), 1520 (vs), 1340 (s), 1290 (s), 1221 (vs), 1179 (s), 1135 (m), 1101 (vs), 1031 (vs), 931 (vs), 868 (w), 720 (w), 703 (m) cm^{-1}; MS (CI, major) *m/z* 344/342 [$(M + 1)^+$, 100], 324/322 [$(M - F)^+$], 276/274 [$(M - CF_3)^+$], 262 [$(M - Br)^+$], 181/179 ($C_2F_4Br^+$), (EI, major) 276/274 [$(M - CF_3)^+$], 224/222

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(13) Varetti, E. L.; Aymonino, P. J. *An. Asoc. Quim. Argent.* **1967**, *10*, 153. See ref 10.
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(16) Pavia, D. L. *Introduction to Organic Laboratory Techniques*; W. B. Saunders: Philadelphia, 1976, p 537.

[(M – C_2F_5)$^+$], 181/179 ($C_2F_4Br^+$), 119 [($C_2F_5^+$), 100], 69 (CF_3^+); ^{19}F NMR, $CF_3^ACF_2^BC(O)NHCF_2^CCF_2^DBr$ (d_6-acetone), δ_A –82.6, δ_B –122.0, δ_C –94.3 (br m), δ_D –66.7 (t), J_{CD} = 4.4 Hz; ^{1}H NMR δ 10.80.

ClCF$_2$C(O)NHCF$_2$CF$_2$Br: mp 43.5 °C; IR (gas) 3573 (w), 3458 (s, NH), 1798 (vs, C=O), 1518 (vs), 1291 (m), 1233 (m), 1170 (s), 1109 (s), 1028 (vs), 990 (m), 930 (s), 865 (w), 669 (m) cm^{-1}; MS (EI, major) m/z 274/272 [(M – Cl)$^+$], 224/222 [(M – ClCF$_2$)$^+$], 181/179 ($C_2F_4Br^+$), 131/129 (CF_2Br^+), 85/87 [($CF_2Co)^+$, 100]; ^{19}F NMR, $ClCF_2^AC(O)NHCF_2^BCF_2^CBr$ (d_6-acetone) δ_A –64.9 (s), δ_B –94.2 (br m), δ_C –66.9 (m), J_{BC} = 4.4 Hz; ^{1}H NMR δ 10.8 (br).

General Procedure for the Dehydrofluorination of R$_x$CONHCF$_2$CF$_2$Br. The amide (2.0 mmol) was condensed onto 1.0 g of KF cooled to –196 °C in a 50-mL glass reactor. The mixture was then heated at 60 °C for 1 h, after which time any volatiles were pumped off and collected in a –196 °C trap. The products were then separated from any unreacted amide by trap–trap fractionation. Yields were typically 55–60%.

CF$_3$C(O)N=CFCF$_2$Br: bp 76 °C; IR (gas) 1795 (vs, C=O), 1765 (vs, C=N), 1319 (s), 1295 (s), 1236 (vs), 1193 (vs), 1133 (vs), 1080 (vs), 942 (vs), 833 (s), 800 (w), 734 (s), 708 (s), 656 (m), 624 (s) cm^{-1}; MS (CI, major) m/z 274/272 [(M + 1)$^+$, 100], 254/252 [(M – F)$^+$], 204/202 [(M – CF_3)$^+$], 176/174 [(M – CF_3CO)$^+$], 131/129 (CF_2Br^+), (EI, major) 204/202 [(M – CF_3)$^+$], 193 [(M – Br)$^+$], 97 (CF_3CO^+), 69 [(CF_3^+), 100]; ^{19}F NMR, $CF_3^AC(O)N=CF^BCF_2^CBr$ (C_6D_6), δ_A –76.4, δ_B –34.6 (br t), δ_C –61.7 (d), J_{BC} = 11 Hz; molecular weight calcd 271.9, found 274.5.

CF$_3$CF$_2$C(O)N=CFCF$_2$Br: bp 91–93 °C; IR (gas) 1793 (s, C=O), 1764 (vs, C=N), 1336 (s), 1293 (s) 1266 (vs), 1231 (vs), 1192 (vs), 1143 (vs), 1106 (vs), 1006 (vs), 934 (s), 816 (s), 774 (w), 738 (s), 714 (m), 661 (w), 626 (m) cm^{-1}; MS (CI major) m/z 324/322 [(M + 1)$^+$, 100], 304/302 [(M – F)$^+$], 242 [(M – Br)$^+$], 204/202 [(M – C_2F_5)$^+$], 192 [(M – CF_2Br)$^+$], 147 ($C_2F_5CO^+$), 131/129 (CF_2Br^+), 119 ($C_2F_5^+$), (EI, major) 242 [(M – Br)$^+$], 204/202 [(M – C_2F_5)$^+$, 100], 69 (CF_3^+); ^{19}F NMR (C_6D_6), $CF_3^ACF_2^BC(O)N=CF^CCF_2^DBr$, δ_A –82.6, δ_B –122.4, δ_C –34.4 (br t), δ_D –61.7 (d), J_{CD} = 10 Hz; molecular weight calcd 321.9, found 318.6.

ClCF$_2$C(O)N=CFCF$_2$Br: bp 87 °C; IR (gas) 1798 (vs, C=O), 1765 (vs, C=N) 1293 (vs), 1257 (w), 1243 (w), 1171 (vs), 1128 (vs), 1086 (vs), 1052 (m), 977 (vs), 927 (s), 819 (m), 761 (m), 743 (m), 714 (w), 656 (w), 612 (m) cm^{-1}; MS (CI, major) m/z 292/290/288 [(M + 1)$^+$, 100], 291/289/287 (M$^+$), 272/270/268 [(M – F)$^+$], 204/202 [(M – $ClCF_2$)$^+$], 131/129 (CF_2Br^+), 113 ($ClCF_2CO^+$), (EI, major) 204/202 [(M – $ClCF_2$)$^+$], 87/85 [($ClCF_2^+$), 100]; ^{19}F NMR (C_6D_6), $ClCF_2^AC(O)N=CF^BCF_2^CBr$, δ_A –65.8, δ_B –34.3 (br t), δ_C –61.5 (d), J_{BC} = 10.5 Hz; molecular weight calcd 288.6, found 289.4.

Reaction of CF$_3$C(O)N(Cl)CF$_2$CF$_2$Br with CsF. $CF_3C(O)NClCF_2CF_2Br$ (0.25 mmol) was condensed onto an excess of active CsF (0.45 g) contained in a 50-mL glass reactor at –196 °C. The mixture was warmed and stirred at room temperature for 2 h. Distillation of the crude mixture afforded two major products, identified as (a) $CF_3C(O)F$ and (b) $BrCF_2CF=NCl$. For $BrCF_2CF=NCl$: IR (gas) 1687 (vs, C=N), 1348 (w), 1313 (vs), 1268 (w), 1237 (w), 1189 (vs), 1145 (s), 1113 (vs), 1030 (w), 947 (vs), 912 (m), 828 (m), 789 (s), 742 (vs), 712 (w), 648 (vs), 605 (m) cm^{-1}; MS (EI, major) m/z 211/209 (M$^+$), 192/190 [(M – F)$^+$], 132/130 [(M – Br)$^+$, 100], 131/129 (CF_2Br^+), 82/80 ($FCNCl^+$), 50 (CF_2^+); ^{19}F NMR (C_6D_6), $BrCF_2^ACF^B=NCl$, δ_A –57.9 (d), δ_B –40.6 (t), J_{AB} = 12.7 Hz.

Reaction of CF$_3$C(O)N=CFCF$_2$Br with ClF. $CF_3C(O)N=CFCF_2Br$ (0.5 mmol) and ClF (0.5 mmol) were condensed into a FEP reactor (10 mL) at –196 °C. The reactor was warmed to room temperature and left for 1 h, after which time the volatile products were separated by trap-to-trap distillation. The major product was identified as **CF$_3$C(O)NClCF$_2$CF$_2$Br**: IR (gas) 1772 (vs, C=O), 1525 (w), 1341 (s), 1240 (vs), 1186 (s), 1169 (s), 1099 (vs), 1027 (m), 1001 (m), 930 (m), 909 (m), 895 (m), 828 (s), 802 (s), 777 (vs), 724 (s), 661 (w), 627 (w) cm^{-1}; MS (EI, major) m/z 248/246 [(M – Br)$^+$], 198/196 [(M – CF_2Br)$^+$], 181/179 ($C_2F_4Br^+$), 131/129 (CF_2Br^+), 97 (CF_3CO^+), 69 [(CF_3^+), 100], 50 (CF_2^+); ^{19}F NMR (C_6D_6), $CF_3^AC(O)NClCF_2^BCF_2^CBr$, δ_A –70.7 (t), δ_B –90.6 (sex.), δ_C –63.6 (t), J_{AB} = J_{BC} = 3.9 Hz.

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Registry No. $CF_3CONH(CF_2)_2Br$, 135041-65-5; $CF_3CF_2CONH(CF_2)_2Br$, 135041-66-6; $ClCF_2CONH(CF_2)_2Br$, 135041-67-7; $Br(CF_2)_2N=CFCF_3$, 135041-68-8; $Br(CF_2)_2N=CFCF_2CF_3$, 135041-69-9; $Br(CF_2)_2N=CFCF_2Cl$, 111223-75-7; $CF_3CON=CFCF_2Br$, 135041-70-2; $CH_3CF_2CON=CFCF_2Br$, 135041-71-3; $ClCF_2CON=CFCF_2Br$, 135041-72-4; CF_3COF, 354-34-7; $ClN=CFCF_2Br$, 135041-73-5; $CF_3CONCl(CF_2)_2Br$, 135041-74-6.

Supplementary Material Available: ^{19}F NMR spectra of all new compounds (9 pages). Ordering information is given on any current masthead page.

Synthesis of β-(Trifluoromethyl)pyrroles via the Cycloaddition of Munchnones to Electron-Deficient Trifluoromethylated Olefins

Takashi Okano, Toru Uekawa, Norihito Morishima, and Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

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The 1,3-dipolar cycloaddition of munchnones (1,3-oxazolium 5-olates) to β-chloro-β-(trifluoromethyl)vinyl phenyl ketone (1) and butyl β-chloro-γ,γ,γ-trifluorocrotonate (2) gave (trifluoromethyl)pyrroles. The monocyclic munchnones **3a–c** yielded the β-(trifluoromethyl)pyrroles **7a–c** and **8a–c** regiospecifically. The bicyclic and tricyclic munchnones **9a,b** and **16a,b** reacted with 1 and 2 to give mixtures of regioisomeric fused-ring trifluoromethylated pyrroles. In all instances, the unsaturated phenone 1 was more reactive than the crotonate 2. The cycloaddition of munchnones to the former occurred with a higher degree of regioselectivity.

Because trifluoromethyl-substituted heterocycles often show biological activity, much current activity has focused on the development of methods for the regioselective synthesis of such compounds.[1] In particular, trifluoromethyl-substituted pyrroles and other five-membered heterocycles have drawn considerable attention.[1,2] However, there exist only a few reports that deal with the synthesis of β-trifluoromethyl-substituted pyrroles.[3] We

(1) For a recent review on fluorine-containing heterocyclic compounds, see: Tanaka, K. *J. Synth. Org. Chem., Jpn.* **1990**, *48*, 16 and references cited therein.

(2) For a recent review on the synthesis of pyrroles, see: Bean, G. P. *The Chemistry of Heterocyclic Compounds*; Jones, R. A., Ed.; John Wiley & Sons: New York, 1989; Vol. 48, Part 1, pp 105 and references cited therein.

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