Addition of Acyl and Sulfonyl Hypohalites Generated from *N*-Halogeno Amides to Alkenes: Synthesis of *trans-vic*-Halogeno Esters and their Conversion to *cis*-1,2-Diols

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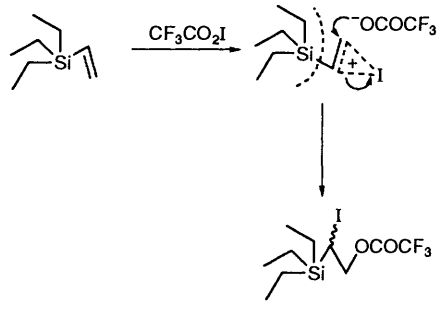
N-Iodo- and *N*-bromo-*p*-nitrobenzamide have been shown to react with various organic acids to form the respective acyl or sulfonyl hypoiodites or hypobromites. These readily add to double bonds under mild conditions to yield *trans-vic*-halogeno esters. The stereochemistry, as well as the regioselectivity, of these additions have been rationalised in terms of an intermediate iodonium or bromonium ion. Alkaline hydrolysis of adducts from cyclohexene gave good yields of *cis*-cyclohexane-1,2-diols, suggesting this methodology to be a viable alternative to the Woodward–Prévost synthesis of *cis*-1,2-diols.

trans-vic-Halogeno esters have been synthesised by the reaction of silver(I),[1-3] mercury(II)[4] or thallium(I)[5] salts of carboxylic acids and molecular halogens with alkenes. In addition, iodoacetoxylation of alkenes has been accomplished with the use of KIO_3–I_2–AcOH,[6] NIS–AcOH[7] and more recently by the Cu^{II}-promoted stereoselective iodination of alkenes.[8] The more recent interest in the use of electrophilic additions of iodonium species to alkynes,[9] as well as the use of the addition products of NBS and diphenylacetic acid to alkenes in the synthesis of *trans*-chrysanthemic acid,[10] prompted us to disclose our results on the addition of hypothalites generated from *N*-chloro-, *N*-bromo and *N*-iodo-*p*-nitrobenzamide in the presence of carboxylic and sulfonic acids to various alkenes.



Scheme 1

Results and Discussion

Some years ago, we reported a novel synthesis of trifluoroacetyl hypoiodite,[11] demonstrated its use in aromatic iodination[12] and, in a limited study, showed the reagent to add stereoselectively *anti*- to the double bond of 5α-cholest-2-ene yielding 2β-trifluoroacetoxy-3α-iodo-5α-cholestane. Similarly, cyclohexene was shown to produce *trans*-2-iodocyclohexyl trifluoroacetate.

In order to extend the scope of this addition and to further study its mechanistic aspects, an excess of cyclohexene was treated with *N*-iodo-*p*-nitrobenzamide and trifluoroacetic acid in dichloromethane. After the reaction mixture had been stirred at ambient temperature for 2 h, work-up and preparative radial TLC (PRTLC) separation gave the *vic*-iodo ester in 67% yield, based on *N*-halogeno amide (entry 1, Table 1).

An increase in the reaction temperature had a minimal effect on the isolated yield of iodo ester (71%) (entry 2), but a change in the solvent to chloroform (containing EtOH as stabiliser) and subsequent heating of the reaction mixture under reflux, resulted in an excellent yield of the *vic*-iodo ester (92%) (entry 3). Similarly, cyclopentene and cyclooctene gave modest yields of the corresponding *trans*-iodotrifluoroacetates (entries 12, 13, 16 and 17).

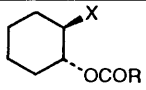
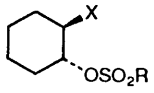
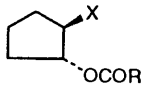
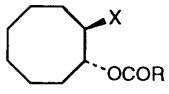
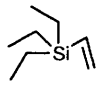
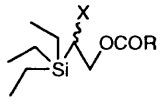
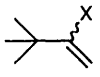
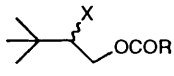
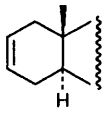
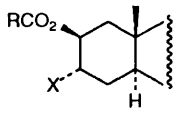
The addition with triethylvinylsilane (entries 20 and 21) proceeded regioselectively with anti-Markownikov orientation, yielding the silyl iodo ester as the only product (80%) isolated when the reaction was performed in chloroform under reflux conditions (entry 21). This regioselectivity may be attributed to hindrance by the relatively bulky triethylsilyl group of nucleophilic attack of the trifluoroacetate anion on the α-carbon of the intermediate, cyclic iodonium ion (Scheme 1). Since the carbocation at the α-carbon atom is expected to be destabilised by the silicon atom, the latter being also known to stabilise β-cations as a result of electronic effects,[13] the exclusive introduction of the trifluoroacetate moiety at the terminal carbon of the double bond is not entirely unexpected.

3,3-Dimethylbutene, similarly on reaction with the *N*-iodo amide–TFA reagent, gave the corresponding iodo ester (45 and 74%) as the sole product (entries 24 and 25). The regioselectivity in this case was attributed exclusively to steric hindrance of the bulky *tert*-butyl group to nucleophilic attack of the trifluoroacetate anion.

Treatment of 5α-cholest-2-ene with the *N*-iodo-*p*-nitrobenzamide–TFA reagent in chloroform for 2 h under reflux, gave on isolation by PRTLC, 3α-iodo-2β-trifluoroacetoxy-5α-cholestane (63%) (entry 29). In dichloromethane at ambient temperature, a lower yield of (42%) of adduct was obtained (entry 28). The stereoselective *anti*-addition of trifluoroacetyl hypoiodite was established from the 200 MHz ^{1}H NMR half-band widths of the 2 H and 3 H proton resonances at δ 4.60 (1 H, s, $W_{\frac{1}{2}}$ 6 Hz) and 5.40 (1 H, s, $W_{\frac{1}{2}}$ 6 Hz) respectively,[3,14,15] confirming our previous results.[11] This compound was spectroscopically identical with the *vic*-iodotrifluoroacetate synthesised from 5α-cholest-2-ene and trifluoroacetyl hypoiodite [generated from silver(I) trifluoroacetate and iodine].[3]

As a further extension of the scope of the reaction, *N*-bromo-*p*-nitrobenzamide was synthesised[16,17] and treated with a series of alkenes in the presence of TFA to give the corresponding *trans-vic*-bromotrifluoroacetates (entries 4, 5, 15, 18, 19, 22 and 26). As expected, the yields of the adducts obtained over the same reaction period were lower than those obtained for the corresponding iodo analogues. This is a consequence of the stronger N–Br bond, resulting in slower halogen exchange with

Table 1 Synthesis of vicinal bromo and iodo esters by the addition of acyl and sulfonyl hypohalites to various alkenes[a]

Entry no.	Alkene	Product	R	X	Yield (%)
1			CF_3	I	67[b,d]
2			CF_3	I	71[b,h]
3			CF_3	I	92[b]
4			CF_3	Br	15[b,d]
5			CF_3	Br	70[b]
6			CH_3	I	71[b]
7			p-$O_2NC_6H_4$	I	58[e]
8			$CF_3(CF_2)_2$	I	89[e]
9			CH_3	I	31[b] (40)[e]
10			p-Tolyl	I	36[b] (38)[e]
11			p-Tolyl	I	72[b]
12			CF_3	I	53[b,d]
13			CF_3	I	64[b]
14			CH_3	I	45[c,f]
15			CF_3	Br	51[b]
16			CF_3	I	20[c,d]
17			CF_3	I	51[c]
18			CF_3	Br	45[c]
19			CH_3	Br	35[c]
20			CF_3	I	56[c,d]
21			CF_3	I	80[c]
22			CF_3	Br	38[c]
23			CH_3	I	74[c]
24			CF_3	I	45[c,d]
25			CF_3	I	74[c]
26			CF_3	Br	40[b]
27			CH_3	I	38[c,g]
28			CF_3	I	42[c,d]
29			CF_3	I	63[c]

[a] Refluxing $CHCl_3$, 2 h. [b] Unoptimised yield of isolated pure product, based on *N*-halogeno amide. [c] Yield based on alkene. [d] CH_2Cl_2, ambient temperature. [e] Yield based on organic acid. [f] GC–MS analysis of the crude reaction mixture indicated cyclopentane-1,2-diol (1%) and cyclopentane iodohydrin (2%) as ancillary products.

the organic acid.[18] This phenomenon was also reflected in the inability of *N*-chloro-*p*-nitrobenzamide–TFA to react with cyclohexene, even under relatively forcing reaction conditions (48 h in refluxing $CHCl_3$). The same regioselectivity was observed for the *N*-bromo amide–TFA addition as noted for the corresponding *N*-iodoamide–TFA reagent (entries 22 and 26).

A combination of acetic acid and *N*-iodo-*p*-nitrobenzamide was also allowed to react with a series of alkenes to form the corresponding *trans-vic*-iodoacetates, through what is surmised to be the intermediacy of an acetyl hypoiodite (entries 6, 9, 14, 19, 23 and 27). These additions displayed the same regio- and stereo-selectivity as reported for this intermediate generated from KIO_3–I_2–AcOH,[19,20] NIS–AcOH,[7] silver(I) acetate and iodine,[2] or in the addition of iodine isocyanate to 3,3-dimethylbutene.[21]

The iodoacetoxylation of the *N*-iodoamide–AcOH reagent with 3,3-dimethylbutene as substrate formed a small amount (*ca.* 1%) of a rearrangement product, 1-iodo-3-methylbut-2-ene, which could be detected by GC–MS analysis. It is suggested that it is formed by methyl migration from the *tert*-butyl group to the adjacent carbon atom generating a stable tertiary carbocation, which then undergoes elimination to give the Saytzeff product.

Various carboxylic and sulfonic acids were found to add to cyclohexene in the presence of *N*-iodo-*p*-nitrobenzamide yielding *trans*-adducts in variable, isolated yields (entries 7–11). These yields, however, were not optimised. The adducts (entries 3, 9 and 11) on treatment with aqueous sodium hydroxide, gave *cis*-cyclohexane-1,2-diol in moderate to good yields (75%, 63% and 70%, respectively) suggesting this methodology to be a viable alternative to the Woodward-Prévost protocol for the synthesis of *cis*-1,2-diols.

In conclusion, the *N*-halogeno amides used are relatively stable, not obnoxious nor expensive and thus eliminate the use of expensive, potentially explosive and poisonous metal salts. An added advantage of the *N*-halogeno amides used in this study is the low solubility of the amide by-product in most organic solvents, thereby facilitating its removal in the work-up process. Separation of the halogeno esters may easily be effected by PRTLC or conventional preparative TLC.

Experimental

IR spectra were recorded on Perkin-Elmer 1600 FT-IR and 297 instruments. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer.

Preparative radial TLC (PRTLC) was performed on a Harrison Research Model 7924T Chromatotron, equipped with a glass plate (24 cm diam.) coated with a circular layer of silica gel PF_{254} (1–2 mm thick and 7 cm diam.). Mass spectra (EI) were recorded on a Hewlett-Packard Model 5985A instrument, equipped with a direct insertion probe. GC–MS were obtained using a similar instrument, equipped with a Supelco BP5 30 m capillary column. Microanalyses were performed in the microanalytical laboratories of the University of Port Elizabeth, SA. The syntheses of *tert*-butyl hypochlorite,[22,23] *N*-iodo-*p*-nitrobenzamide,[12] *N*-bromo-*p*-nitrobenzamide,[16,17] *N*-chloro-*p*-nitrobenzamide[24] and 5α-cholest-2-ene[25] have been reported previously.

Reactions of N-*Halogeno*-p-*nitrobenzamide–Carboxylic Acid with Alkenes.—General procedure.* Equivalent amounts of *N*-iodo or *N*-bromo-*p*-nitrobenzamide (8–30 mmol) and the appropriate carboxylic acid in CH_2Cl_2 (50 cm^3) were treated with the alkene (8–70 mmol) and the mixture stirred in the dark at ambient temperature for 2 h. Alternatively, the mixture was heated under reflux using either CH_2Cl_2 or $CHCl_3$ as solvent for the same period. The cold reaction mixture was filtered, washed with water (3 × 50 cm^3), 20% aq. sodium carbonate (3 × 50 cm^3), 0.1 mol dm^{-3} sodium thiosulfate (3 × 50 cm^3) and water (3 × 50 cm^3) respectively, and then dried (Na_2SO_4). The solvent was distilled off under reduced pressure to give the product, which was further purified by PRTLC using hexane–ethyl acetate (9:1) as the mobile phase. The yields of iodo esters are summarised in Table 1. Spectral and analytical data for previously unreported compounds are given below.

trans-2-*Iodocyclooctyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2930 and 1780; $\delta_H(CDCl_3)$ 1.2–2.5 (12 H, m), 4.5 (1 H, m) and 4.9 (1 H, m) (Found: C, 34.7; H, 4.4. $C_{10}H_{14}F_3IO_2$ requires C, 34.31; H, 4.03%).

trans-2-*Iodocyclopentyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2975, 2881 and 1783; $\delta_H(CDCl_3)$ 1.7–2.5 (6 H, m), 4.3 (1 H, m) and 5.5 (1 H, m); $\delta_C(CDCl_3)$ 24.31, 27.85, 31.28, 38.19 and 89.76 (Found: C, 27.1; H, 2.6. $C_7H_8F_3IO_2$ requires C, 27.29; H, 2.62%).

2-*Iodo*-2-(*triethylsilyl*)*ethyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2959, 2881 and 1784; $\delta_H(CDCl_3)$ 0.8 (6 H, q), 1.0 (9 H, t), 3.4 (1 H, t) and 4.6 (2 H, d); $\delta_C(CDCl_3)$ 5.31, 9.30, 11.08 and 72.56; *m*/*z* 353 (M^+ − 29, 1.2%), 269 (M^+ − 113, 0.1) and 225 (M^+ − 157; 0.1) (Found: C, 31.2; H, 4.9. $C_{10}H_{18}F_3IO_2Si$ requires C, 31.42; H, 4.75%).

2-*Iodo*-3,3-*dimethylbutyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 2900 and 1780; $\delta_H(CDCl_3)$ 0.9–1.5 (9 H, s), 4.2 (1 H, dd) 4.6 (1 H, dd) and 4.7 (1 H, dd); $\delta_C(CDCl_3)$ 25.26, 41.49 and 67.22; *m*/*z* 324 (M^+, 1.1%), 197 (M^+ − 127, 2.7), 211 (M^+ − 113, 7.2), 127 (17) and 83 (100).

trans-2-*Bromocyclohexyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 3030, 2947, 2866 and 1782; $\delta_H(CDCl_3)$ 1.15–2.5 (8 H, m), 4.00 (1 H, m) and 5.05 (1 H, m); $\delta_C(CDCl_3)$ 25.14, 27.24, 32.67, 37.43, 52.64, 82.08 and 98.13; *m*/*z* 195 (M^+ − Br, 12%), 162 (20), 81 (100) and 69 (CF_3, 90) (Found: C, 35.4; H, 4.1. $C_8H_{10}BrF_3O_2$ requires C, 34.93; H, 3.66%).

trans-2-*Bromocyclopentyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2977, 2878 and 1783; $\delta_H(CDCl_3)$ 1.8–2.7 (6 H, m), 4.3 (1 H, m) and 5.5 (1 H, m); $\delta_C(CDCl_3)$ 23.54, 31.29, 36.41, 53.06 and 88.01; *m*/*z* 261 (M^+, 0.1%), 181 (M^+ − 80, 2), 148 (M^+ − 113, 87) and 147 (M^+ − 114, 17).

trans-2-*Bromocyclooctyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2932, 2863 and 1780; $\delta_H(CDCl_3)$ 1.3–2.5 (12 H, m), 4.35 (1 H, ddd) and 5.4 (1 H, m); $\delta_C(CDCl_3)$ 26.54, 27.13, 27.67, 33.48, 33.73, 57.19 and 85.82; *m*/*z* 223 (M^+ − 80, 3%), 190 (M^+ − 113, 6), 109 (100) and 69 (CF_3, 99) (Found: C, 40.0; H, 5.1. $C_{10}H_{14}BrF_3O_2$ requires C, 39.62; H, 4.66%).

2-*Bromo*-3,3-*dimethylbutyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2971, 2877 and 1786; $\delta_H(CDCl_3)$ 1.2 (9 H, s), 4.05 (1 H, dd), 4.62 (1 H, dd) and 4.72 (1 H, dd); $\delta_C(CDCl_3)$ 27.63, 29.56, 37.00, 64.24 and 71.15.

2-*Bromo*-2-(*triethylsilyl*)*ethyl trifluoroacetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 2958 and 1784; $\delta_H(CDCl_3)$ 0.75 (6 H, q), 1.0 (9 H, t), 3.57 (1 H, dd), 3.75 (1 H, t) and 4.05 (2 H, m); $\delta_C(CDCl_3)$ 4.66, 9.37, 48.01, 66.75, 98.14 and 188.

2-*Iodo*-3,3-*dimethylbutyl acetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 3014, 2969, 2874 and 1734; $\delta_H(CDCl_3)$ 1.1 (9 H, s), 2.1 (3 H, s), 4.2 (1 H, dd), 4.35 (1 H, d) and 4.37 (1 H, d); $\delta_C(CDCl_3)$ 23.06, 30.85, 36.82, 50.68, 69.63 and 172.0; *m*/*z* 270 (M^+, 0.2%), 210 (M^+ − 60, 0.2) and 143 (M^+ − 127, 4) (Found: C, 35.8; H, 5.6. $C_8H_{15}IO_2$ requires C, 35.57; H, 5.60%). 1-Iodo-2,3-dimethylbut-2-ene (1%) could be detected in the GC–MS of the crude mixture, *m*/*z* 210 (M^+, 100%), 195 (M^+ − 15, 12) and 83 (M^+ − 127, 49).

2-*Iodo*-2-(*triethylsilyl*)*ethyl acetate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 3014, 2958 and 1734; $\delta_H(CDCl_3)$ 0.8 (6 H, q), 1.0 (9 H, t), 2.15 (3 H, s), 3.4 (1 H, dd), 4.30 (1 H, dd), 4.35 (2 H, m) and 4.40 (1 H, dd); $\delta_C(CDCl_3)$ 5.0 (CH_2), 9.0 (CH_2), 14.0 (CH_3), 23.0 (CH) and 69.0 (CH_2); *m*/*z* 299 (M^+ − 29, 26%), 268 (M^+ − 60, 0.2) and 201 (M^+ − 127, 4) (Found: C, 36.7; H, 6.8. $C_{10}H_{21}IO_2Si$ requires C, 36.59; H, 6.45%).

Reactions of Cyclohexene with N-*Iodo*-p-*nitrobenzamide in the Presence of Various Organic Acids.—General procedure.* Cyclohexene (2.3 g, 28.2 mmol) was added to a solution of *N*-iodo-*p*-nitrobenzamide (4.12 g, 14.11 mmol) and the organic acid (14 mmol) in CH_2Cl_2 (75 cm^3). After being stirred in the dark at ambient temperature for 16 h, the mixture was filtered, washed with 20% aq. Na_2CO_3 (3 × 50 cm^3) and water (3 × 50 cm^3). The dried organic layer (Na_2SO_4) was concentrated under reduced pressure to give the *trans-vic*-iodo ester.

trans-2-*Iodocyclohexyl heptafluorobutyrate.* (89%, based on acid); $\nu_{max}(CHCl_3)/cm^{-1}$ 3010, 2946, 2865, 1776 and 1529; $\delta_H(CDCl_3)$ 1.2–2.6 (8 H, m), 4.15 (1 H, ddd) and 5.15 (1 H, dt); $\delta_C(CDCl_3)$ 17.60, 25.04, 28.20, 29.63, 32.36 and 83.30; *m*/*z* 422 (M^+, 0.2%), 295 (M^+ − 127), 209 (M^+ − 213, 2), 127 (5) and 81 (100) (Found: C, 28.3; H, 2.6. $C_{10}H_{10}F_7IO_2$ requires C, 28.46; H, 2.39%).

trans-2-*Iodocyclohexyl methanesulfonate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 3022, 2945, 2864, 1528, 1449, 1358 and 1174; $\delta_H(CDCl_3)$ 1.2–2.5 (8 H, m), 3.15 (3 H, s), 4.15 (1 H, ddd) and 4.7 (dt); $\delta_C(CDCl_3)$ 25.10, 28.10, 32.07, 34.79, 41.27 and 86.65.

trans-2-*Iodocyclohexyl* p-*nitrobenzoate.* $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 2943, 2863, 1723 and 1606; $\delta_H(CDCl_3)$ 1.2–2.6 (8 H, m), 4.15 (1 H, ddd), 5.13 (1 H, dt), 8.25 (2 H, d) and 8.31 (2 H, d); $\delta_C(CDCl_3)$ 25.68, 29.13, 32.80, 33.72, 39.95, 80.57, 125.57 and 132.92; *m*/*z* 375 (M^+, 3.3%), 248 (M^+ − 127, 82.1), 209 (M^+ − 166, 41.4), 208 (M^+ − 167, 60.1), 167 (1.3), 150 (100) and 104 (47.2) (Found: C, 41.8; H, 4.0; N, 4.0. $C_{13}H_{14}INO_4$ requires C, 41.62; H, 3.76; N, 3.73%).

Reactions of Cyclohexyl Iodo Esters with Sodium Hydroxide.—trans-2-Iodocyclohexyl trifluoroacetate (2.82 g, 8.76 mmol) and sodium hydroxide (1.34 g, 33.75 mmol) in water (75 cm^3) were heated under reflux for 24 h. The cooled solution was then saturated with NaCl and extracted with diethyl ether (3 × 100 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give an oil, which on PRTLC separation (SiO_2, $CHCl_3$), gave starting material (710 mg, 25%) and *cis*-cyclohexane-1,2-diol (750 mg, 75%) which was identical with an authentic sample.[26]

Similarly, *trans*-2-iodocyclohexyl methanesulfonate and the corresponding toluene-*p*-sulfonate yielded 63% and 70% of the *cis*-1,2-diol respectively.

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