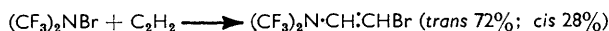


Polyfluoroalkyl Derivatives of Nitrogen. Part XXXVI.¹ Photochemical Reaction of *N*-Bromo- and *N*-Chloro-bistrifluoromethylamine with *cis*- or *trans*-But-2-ene, and the Synthesis of 1,2-Di(bistrifluoromethylamino)-difluoroethylene and 2-Bromo-1,2-difluoro-*NN*-bistrifluoromethylvinylamine

By G. L. Fleming, R. N. Haszeldine,* and A. E. Tipping, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Photochemical reactions of *N*-bromobistrifluoromethylamine with *cis*- or *trans*-but-2-ene gives the 1:1 adducts *erythro*- and *threo*-2-bromo-1-methyl-*NN*-bistrifluoromethylpropylamine in the ratios 17:83 and 77:23, respectively. The corresponding *N*-chloro-amine reactions afford the *erythro*- and *threo*- 1:1 adducts in the ratios 10:90 and 87:13, respectively. A thermal reaction of the *N*-bromo-amine with 1,2-difluoro-*NN*-bistrifluoromethylvinylamine gives 1,2-di(bistrifluoromethylamino)-2-bromo-1,2-difluoroethane in high yield, which is dehydrobrominated to give 1,2-di(bistrifluoromethylamino)difluoroethylene. The synthesis of *cis*- and *trans*-2-bromo-1,2-difluoro-*NN*-bistrifluoromethylvinylamine is described.

A NUMBER of presumed free-radical additions of *N*-bromo-²⁻⁴ and *N*-chloro-^{5,6} bistrifluoromethylamine to olefins have been reported, but the extent to which such reactions are *cis*- or *trans*-stereospecific has not been investigated. It has been observed^{7,8} however, that the similar reaction of the *N*-bromo-amine with acetylenes gives products resulting from both *cis*- and *trans*-addition, e.g.⁷



The photochemical reactions of the *N*-bromo- and *N*-chloro-amine with *cis*- and with *trans*-but-2-ene under presumed radical conditions have thus been investigated in order to determine the ratio of *trans*- to *cis*-addition. Reaction under ionic conditions gave stereospecific *trans*-addition to the olefins.⁹

In addition, the radical reaction of the *N*-bromo-amine with 1,2-difluoro-*NN*-bistrifluoromethylvinylamine has been investigated as a route to the olefin $(\text{CF}_3)_2\text{N}\cdot\text{CF}:\text{CF}\cdot\text{N}(\text{CF}_3)_2$.

But-2-enes.—Photochemical reactions at room temperature of the *N*-halogeno-amines with a slight excess of olefin gave the products shown in the Table. In all

Photochemical reaction of $(\text{CF}_3)_2\text{NX}$ (X = Cl or Br) with the but-2-enes

Olefin isomer	X	% 1:1 Adducts	Ratio of 1:1 adducts	
			<i>erythro</i>	<i>threo</i>
<i>cis</i>	Br	95	17	83
<i>trans</i>	Br	96	77	23
<i>cis</i>	Cl	99	10	90
<i>trans</i>	Cl	99	87	13

the reactions the recovered olefin was observed not to have isomerised, thus showing that the initial addition of the $(\text{CF}_3)_2\text{N}\cdot$ radical to the olefin was irreversible.

¹ Part XXXV, R. Gibbs, R. N. Haszeldine, and R. F. Simmons, *J.C.S. Perkin II*, in the press.

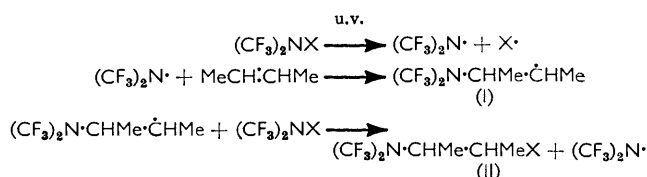
² J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

³ R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141.

⁴ E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 796.

⁵ G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

The Table shows that (i) *trans*-addition (77—90%) predominates over *cis*-addition (10—23%) of the *N*-halogeno-amine, (ii) a higher proportion of *trans*-addition



occurs with the *N*-chloro-amine than with the *N*-bromo-amine, and (iii) a slightly higher proportion of *trans*-addition occurs with *cis*-but-2-ene than with the *trans*-olefin.

Stereospecific *trans*-addition has been observed in the photochemically initiated addition of deuterium bromide to both *cis*- and *trans*-but-2-ene¹⁰ at temperatures between -60 and -78° , but at higher temperatures this stereospecificity is lost. Similarly the photochemically initiated reaction of hydrogen bromide with *cis*- or *trans*-2-bromobut-2-ene at -78° is *trans*-stereospecific,¹¹ but at room temperature the reaction is non-stereospecific and the isomers (\pm)- and *meso*-2,3-dibromobutane are formed in the approximate ratio 3:1 irrespective of the reactant olefin. The high degree of *trans*-stereospecificity of photochemical addition at room temperature in the present reactions is in contrast to this.

The predominance of *trans*-addition can be explained in terms of a fast chain-transfer reaction between the intermediate radical (I) and the *N*-halogeno-amine (because of the weak N-halogen bond) which for steric reasons occurs at the side of the molecule opposite to which initial $(\text{CF}_3)_2\text{N}\cdot$ radical addition took place.

*1,2-Difluoro-*NN*-bistrifluoromethylvinylamine*.—Thermal reaction (80°) of the *N*-bromo-amine with a small

⁶ F. S. Fawcett to E. I. Du Pont de Nemours and Co., U.S.P. 3,311,599/1967.

⁷ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096.

⁸ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1955.

⁹ M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2744.

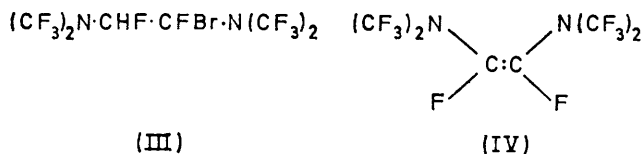
¹⁰ P. S. Skell and R. G. Allen, *J. Amer. Chem. Soc.*, 1959, **81**, 5383.

¹¹ H. L. Goering and D. W. Larsen, *J. Amer. Chem. Soc.*, 1959, **81**, 5937.

excess of the olefin $(CF_3)_2N \cdot CF : CHF$ gave the 1 : 1 adduct 1,2-di(bistrifluoromethylamino)-1-bromo-1,2-difluoroethane (III) (98%) together with appreciable amounts of unchanged reactants. The adduct was shown by n.m.r. spectroscopy to be a mixture of the *erythro*- and *threo*-forms in an approximately 1 : 1 ratio.

Dehydrobromination of the adduct mixture with powdered potassium hydroxide afforded unchanged adduct (17%) and 1,2-di(bistrifluoromethylamino)difluoroethylene (93%), formed exclusively as one isomer.

In difluoroethylenes the chemical shifts of the olefinic protons have been shown¹² to exhibit an approximately additive dependence upon the nature and position of the remaining substituents. The effect of a $(CF_3)_2N$ group on the chemical shifts of olefinic fluorine atoms may be obtained by a comparison of the chemical shifts of the olefinic fluorine atoms in the compounds $CF_2 : CF_2$ (57.7 p.p.m. relative to external trifluoroacetic acid) and $(CF_3)_2N \cdot CF : CF_2$ (F_{gem} 66.9 p.p.m.; F_{cis} 33.2 p.p.m.; F_{trans} 19.3 p.p.m.).^{13,14} Thus the expected chemical shift for the olefinic fluorine atoms in *cis*- $(CF_3)_2N \cdot CF : CF : N(CF_3)_2$ is 28.5 p.p.m. (57.7 - 38.4 + 9.2) and in *trans*- $(CF_3)_2N \cdot CF : CF : N(CF_3)_2$ is 42.4 p.p.m. (57.7 - 24.5 + 9.2). The observed chemical shift of 25.8 p.p.m. thus strongly suggests that the olefin is the sterically less favoured *cis*-isomer (IV). If this assignment is correct the reaction is in contrast to the dehydrobromination of the compound $(CF_3)_2N \cdot CH_2 \cdot CHBr \cdot N(CF_3)_2$, which gives the *trans*-isomer of the olefin $(CF_3)_2N \cdot CH : CH \cdot N(CF_3)_2$ as the exclusive product.^{4,15}

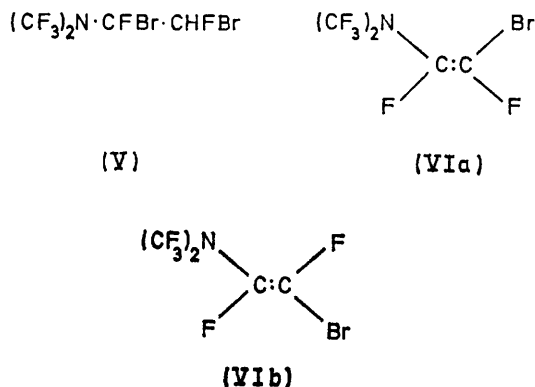


The *cis*-olefin (IV) is the expected product from an *E2* dehydrobromination of the *threo*-isomer of (III), but the *erythro*-isomer, by a similar mechanism, would afford the *trans*-isomer of (IV). The formation of only one olefin implies that one of the isomers of (III) is dehydrobrominated by a *cis*-periplanar process.

Treatment of 1,2-difluoro-*NN*-bistrifluoromethylvinylamine with bromine in daylight (24 h) gave the dibromide (V) (99%) as an approximately 1 : 1 mixture of the *erythro*- and *threo*-isomers (n.m.r.). This mixture on dehydrobromination afforded unchanged dibromide (19%) and a 1 : 1 mixture (93%) of *cis*- and *trans*-2-bromo-1,2-difluoro-*NN*-bistrifluoromethylvinylamine (VIa and b); the two olefins could not be separated on the g.l.c. columns investigated.

It has been observed¹⁴ that the compound $(CF_3)_2N \cdot CHF \cdot CFCIBr$, formed by reaction of the *N*-bromoamine with 1-chloro-1,2-difluoroethylene, is dehydrohalogenated by potassium hydroxide to afford an

approximately 1 : 1 mixture of the olefins $(CF_3)_2N \cdot CF : CBr$ (*cis*-isomer) and $(CF_3)_2N \cdot CF : CFCl$ (equal amounts of *cis*- and *trans*-isomers). The ¹⁹F n.m.r. spectra of



samples of the olefin (VIa) prepared by the two routes were identical.

EXPERIMENTAL

Techniques used were as described previously⁴ except that i.r. spectra were recorded on a Perkin-Elmer 257 instrument with sodium chloride optics, mass spectra were recorded on an A.E.I. MS/902 instrument, and g.l.c. employed Perkin-Elmer Fraktometer models 154B or 451 with columns of silicone MS550 oil or Kel-F 10 oil (30%) on Celite. *N*-Bromo-^{3,16} and *N*-chloro-³ bistrifluoromethylamine were prepared as described previously. 1,2-Difluoro-*NN*-bistrifluoromethylvinylamine was prepared by dehydrobromination of the 1 : 1 adduct formed by the reaction of the *N*-bromo-amine with *cis*-1,2-difluoroethylene.¹³

Reaction of N-Chlorobistrifluoromethylamine with Olefins.—
(a) *cis*-But-2-ene. The *N*-chloro-amine (4.50 g, 24.0 mmol) and *cis*-but-2-ene (1.49 g, 26.6 mmol), mixed in the gas phase in a Pyrex bulb (2 l) and irradiated (1 h), gave unchanged olefin (0.14 g, 2.6 mmol, 10% recovered) and a higher-boiling fraction (5.78 g, 23.8 mmol, 99%) which was separated by g.l.c. (6 m silicone at 100°) into its two components present in the ratio 10 : 90 and identified as *erythro*-2-chloro-1-methyl-*NN*-bistrifluoromethylpropylamine⁹ (0.58 g, 2.4 mmol, 10%) and *threo*-2-chloro-1-methyl-*NN*-bistrifluoromethylpropylamine (5.20 g, 21.4 mmol, 89%) (Found: C, 29.4; H, 3.5; N, 5.7%; *M*, 245. $C_6H_8ClF_6N$ requires C, 29.55; H, 3.3; N, 5.8%; *M*, 243), b.p. (Siwoloboff) 100°; main i.r. bands at 3.35w (C-H str.), 6.84m (C-H bend), 7.02m, 7.45vs, 7.64s, 7.70vs, 7.90w, 8.14s, 8.35vs, 8.70w, 9.30m, 9.68m, 10.05m and 10.37s (C-N str.), 11.70m, 12.52w, 13.54m (CF_3 def.), and 14.46m μm .

(b) *trans*-But-2-ene. The *N*-chloro-amine (5.00 g, 26.7 mmol) and *trans*-but-2-ene (1.68 g, 30.0 mmol), treated as in (a), gave unchanged olefin (0.18 g, 3.3 mmol, 11% recovered) and a higher-boiling fraction (6.44 g, 26.5 mmol, 99%) (Found: *M*, 243. Calc. for $C_6H_8ClF_6N$: *M*, 243) which was shown by g.l.c. (6 m silicone at 100°) to contain *erythro*- (5.61 g, 23.1 mmol, 86%) and *threo*-2-chloro-1-methyl-*NN*-bistrifluoromethylpropylamine (0.83 g, 3.4 mmol, 13%) in the ratio 87 : 13.

¹² M. G. Barlow, unpublished results and unpublished correlations on data from this department and from the literature.

¹³ R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 398.

¹⁴ M. G. Barlow and A. E. Tipping, unpublished results.

¹⁵ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1848.

¹⁶ H. J. Emelús and B. W. Tattershall, *Z. anorg. Chem.*, 1964, 327, 147.

Reaction of N-Bromobis(trifluoromethyl)amine with Olefins.—(a) *cis-But-2-ene*. The *N*-bromo-amine (1.67 g, 7.2 mmol) and *cis*-but-2-ene (0.52 g, 9.3 mmol), mixed in the gas phase in a Pyrex bulb (2 l) and irradiated (1 h), gave unchanged *cis*-but-2-ene (0.13 g, 2.3 mmol, 25% recovered) and a higher-boiling fraction (1.96 g, 6.8 mmol, 95%) (Found: *M*, 286. Calc. for $C_6H_8BrF_6N$: *M*, 288) which was shown by g.l.c. (6 m silicone at 150°) and n.m.r. spectroscopy to consist of *erythro*- (0.33 g, 1.2 mmol, 16%) and *threo*-2-bromo-1-methyl-*NN*-bis(trifluoromethyl)propylamine⁹ (1.63 g, 5.6 mmol, 79%) in the ratio 17 : 83.

(b) *trans-But-2-ene*. The *N*-bromo-amine (4.80 g, 20.7 mmol) and *trans*-but-2-ene (1.55 g, 27.7 mmol), treated as in (a), gave unchanged *trans*-olefin (2.70 g, 7.7 mmol, 28% recovered), contaminated with a trace of bis(trifluoromethyl)amine (i.r.), and a higher-boiling fraction (5.70 g, 19.8 mmol, 96%) (Found: *M*, 286) which was shown by g.l.c. (as above) and n.m.r. spectroscopy to consist of *erythro*- (4.41 g, 15.3 mmol, 74%) and *threo*-2-bromo-1-methyl-*NN*-bis(trifluoromethyl)propylamine (1.29 g, 4.5 mmol, 22%) in the ratio 77 : 23.

(c) 1,2-Difluoro-*NN*-bis(trifluoromethyl)vinylamine. The *N*-bromo-amine (2.50 g, 10.8 mmol) and the vinylamine (3.00 g, 13.9 mmol), sealed *in vacuo* in a Pyrex tube (300 ml) and heated at 80° (56 h), gave (i) a mixture (2.92 g, 13.2 mmol) shown by g.l.c. (4 m silicone at 20°) to consist of unchanged bromo-amine (1.16 g, 5.0 mmol, 46% recovered) and unchanged vinylamine (1.76 g, 8.2 mmol, 59% recovered) and (ii) 1,2-di(bis(trifluoromethylamino)-1-bromo-1,2-difluoroethane (2.50 g, 5.6 mmol, 98%) (Found: C, 16.4; H, 0.4; N, 6.1%; *M*, 446. $C_6HBrF_{14}N_2$ requires C, 16.1; H, 0.2; N, 6.3%; *M*, 447), b.p. (Siwoloboff) 84°; main i.r. bands at 6.87w and 6.94w (C-H bend), 7.36s, 7.50vs, 7.65s, 7.75s, 7.92s, 8.02s, 8.23s, 8.52s, 8.62m, 8.90m, 9.35m, 10.10vs (C-N str.), 10.74w, 11.92m, 12.60m, 13.45m, 13.67m, 13.95s, 14.28s, and 14.75m μ m; ^{19}F n.m.r. bands for an approximately 50 : 50 mixture of *erythro*- and *threo*- $(CF_3)_2N-CHF_2CF_2Br-N(CF_3)_2$ at -20 to -24 (complex, 12F), +31.0 (complex asymmetric multiplet, F_b) and +77.6 and +85.8 (complex, F_a) p.p.m. relative to external trifluoroacetic acid and 1H n.m.r. band at τ 3.38 (two overlapping dd); *m/e* 448 and 446 (trace, M^+), 353 and 351 (5.5%, $C_4HBrF_{11}N^+$), 264 and 262 [2.7%, $(CF_3)_2N-CFBr^+$], 234 (10%, $C_4HF_6N^+$), 202 (8.8%, $C_3F_8N^+$ or $C_5F_6N_2^+$), 184 [10%, $(CF_3)_2N-CHF^+$], 163 and 161 (2.0%, C_2HBrF_3), 146 (4.4%, $C_3HF_5N^+$), 101 (2.7%, $C_2HF_4^+$), 96 (8.8%, $CF_3N:CH^+$), 69 (100%, CF_3^+), and 31 (3.3%, CF^+).

The adduct (1.21 g, 2.7 mmol), treated with dry, powdered potassium hydroxide (ca. 5 g) *in vacuo* at room temperature (1 h) gave unchanged adduct (0.20 g, 0.45 mmol, 17% recovered) and *cis*-1,2-di(bis(trifluoromethylamino)difluoroethylene (0.77 g, 2.1 mmol, 93%) (Found: C, 20.0; N, 7.4%; *M*, 365. $C_6F_{14}N_2$ requires C, 19.7; N, 7.7%; *M*, 366), b.p. (isotenscope) 60°; i.r. bands at 4.13w, 4.63w, 5.60w, 5.72w, 5.90w, 6.38w, 7.20vs, 7.78vs, 7.90m, 8.20vs, 8.56m, 9.10m, 10.01vs and 10.30vs (C-N str.), 10.67w, 11.73s, 12.40w, 12.88w, 13.30s, and 13.70s (CF_3 def.) μ m; ^{19}F n.m.r. bands

for $[C(F_a)_3]_2N-CF_b:CF_b-N[C(F_a)_3]_2$ at -19.0 [broad t, 12F, J_{ab} 4.4 Hz] and +25.8 (complex, 2F) p.p.m. relative to external trifluoroacetic acid; *m/e* 366 (6.1%, M^+), 347 [5.8%, $(M-F)^+$], 271 (5.4%, $C_6F_6N_2^+$), 252 (5.5%, $C_6F_8N_2^+$), 183 [3.9%, $(CF_3)_2N-CF^+$], 164 (5.1%, $C_3F_8N^+$), 114 (3.0%, $C_2F_4N^+$), 69 (100%, CF_3^+), and 31 (4.3%, CF^+).

*Reaction of 1,2-Difluoro-*NN*-bis(trifluoromethyl)vinylamine with Bromine.*—The olefin (3.60 g, 16.7 mmol) and dry bromine (2.12 g, 13.2 mmol) were sealed in a Pyrex tube (300 ml) and exposed to daylight at room temperature (24 h). The excess of bromine was removed by shaking with mercury *in vacuo* to give unchanged olefin (0.99 g, 4.6 mmol, 27% recovered) and 1,2-dibromo-1,2-difluoro-*NN*-bis(trifluoromethyl)ethylamine (4.50 g, 12.0 mmol, 99%) (Found: C, 13.0; H, 0.4; N, 3.6%; *M*, 374. $C_4HBr_2F_8N$ requires C, 12.8; H, 0.3; N, 3.7%; *M*, 375), b.p. (Siwoloboff) 120°; main i.r. bands at 7.20m, 7.35s, 7.41vs, 7.64vs, 7.97s, 8.22vs, 8.51m, 8.77m, 9.10m, 10.10s (C-N str.), 10.65m, 12.04m, 13.12m, 13.70s, 13.90s, and 14.52s μ m; *m/e* 377, 375, and 373 (1%, M^+), 264 and 262 [1.7%, $(CF_3)_2N-CFBr^+$], 225, 223, and 221 (4.8%, $CHFBr-CFBr^+$), 208 and 206 (5.2%, $C_3HBrF_4N^+$), 207 and 205 (8.0%, $C_3BrF_4N^+$), 127 (7.2%, $C_3HF_4N^+$), 113 and 111 (3.4%, $CHBrF^+$), 69 (100%, CF_3^+), and 31 (10%, CF^+). The n.m.r. spectra showed the presence of approximately equal amounts of the *threo*- and *erythro*- $[C(F_a)_3]_2N-CF_bBr-CH_2CF_2Br$, with ^{19}F n.m.r. bands for the *threo*-isomer at -23.3 (dd, 6F, J_{ab} 15.5, J_{ad} 1.3 Hz), +33.7 (ddsep, F_b , J_{bd} 18.8, J_{bc} 16.6 Hz), and +71.2 (ddsep, F_a , J_{cd} 46.9 Hz) p.p.m. relative to external trifluoroacetic acid; the *erythro*-isomer showed a band at -23.45 (dd, 6F, J 16.5 and 3.4 Hz) p.p.m. with the $CFBr$ and $CHFBr$ absorptions coinciding with those for the *threo*-isomer. The 1H n.m.r. spectrum showed absorption at τ 3.22 (two overlapping dd).

*Reaction of 1,2-Dibromo-1,2-difluoro-*NN*-bis(trifluoromethyl)ethylamine with Potassium Hydroxide.*—The dibromide (2.01 g, 5.4 mmol), as a mixture of the *erythro*- and *threo*-isomers, condensed *in vacuo* on to dry, powdered potassium hydroxide (ca. 10 g) and left at room temperature (1 h), gave unchanged dibromide (0.38 g, 1.0 mmol, 19% recovered) and a 1 : 1 mixture of *cis*- and *trans*-2-bromo-1,2-difluoro-*NN*-bis(trifluoromethyl)vinylamine (1.21 g, 4.1 mmol, 93%) (Found: C, 16.5; N, 5.0%; *M*, 293. Calc. for C_4BrF_8N : C, 16.3; N, 4.8%; *M*, 294), b.p. (isotenscope) 51.3°; main i.r. bands at 5.87m ($>C:C<$ str.), 6.98m, 7.28vs, 7.45s, 7.65s, 7.80vs, 8.00s, 8.20vs, 8.39s, 9.10m, 9.40s, 9.64vs, and 10.10vs (C-N str.), 11.55vs, 12.35vs, 13.16s, 13.65s, and 14.52s μ m; ^{19}F n.m.r. bands for *trans*- $[C(F_a)_3]_2N-CF_b:CF_bBr$ at -18.9 (t, 6F), +44.2 (dsep, F_b , J_{bc} 133.7, J_{ba} 2.8 Hz), and +31.0 (dsep, F_c , J_{ca} 3.5 Hz) p.p.m. and for the *cis*-isomer¹⁴ at -19.1 (dd, 6F, J_{ab} 2.8, J_{ac} 1.7 Hz), +15.7 (dsep, F_c , J_{bc} 38.3 Hz) and +27.6 (dsep, F_b) p.p.m. relative to external trifluoroacetic acid. The mixture of olefins could not be separated on a variety of g.l.c. columns available.