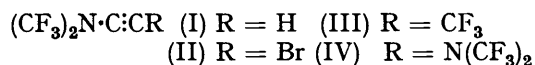


Fluorinated Acetylenes. Part VI.¹ Some Thermal and Photochemical Reactions of *N,N*-Bistrifluoromethylamino-substituted Acetylenes

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The acetylenes $(\text{CF}_3)_2\text{N}\cdot\text{C}:\text{CR}$ form mixtures of linear telomers on prolonged storage at room temperature or on heating; the ease of such telomer formation is in the order $[\text{R} = \text{H} \sim \text{Br} > \text{CF}_3 > \text{N}(\text{CF}_3)_2]$. Under photochemical conditions the acetylene ($\text{R} = \text{H}$) gives 1,3,5-tris(bistrifluoromethylamino)benzene in high yield, but under comparable conditions the acetylene $[\text{R} = \text{N}(\text{CF}_3)_2]$ affords linear telomers. The acetylene ($\text{R} = \text{CF}_3$) reacts readily with buta-1,3-diene to give the Diels–Alder adduct in high yield and the acetylene ($\text{R} = \text{H}$) reacts to give the corresponding adduct but in low yield; in contrast the acetylene ($\text{R} = \text{Br}$) gives mainly a mixture of 2 : 1 adducts of the diene and the acetylene, and the acetylene $[\text{R} = \text{N}(\text{CF}_3)_2]$ does not react under comparable conditions.

THE preparation of certain $(\text{CF}_3)_2\text{N}$ -substituted acetylenes and their reactions with free radicals, electrophiles, nucleophiles, and trifluoronitrosomethane have been reported.¹⁻⁵ We now report an investigation into photochemical and thermal reactions, alone and with buta-1,3-diene, of the acetylenes (I)–(IV).



On storage *in vacuo* at room temperature (6 months) the acetylene (I) was converted (60%) into a mixture of coloured (yellow to red) telomers consisting of a tetramer, a pentamer, and a small amount of a trimer. When heated at 250 °C (5 days) the acetylene (I) was converted (14%) into a mixture of a tetramer, and a pentamer containing small amounts of a trimer, a hexamer, and a heptamer. Similarly the bromoacetylene (II) was converted (64%) on storage *in vacuo* at room temperature (6 months) into a red multi-component telomeric oil, and the acetylene (III) was converted (20%) on storage (18 months) or on heating at 250 °C (9% in 10 days) mainly into a pale yellow trimer. In contrast the acetylene (IV) was unchanged on storage (18 months) and only converted to the extent of 2% into a pale yellow oil on heating at 250 °C (10 days). The ease of acetylene telomer formation is therefore in the order (I) \sim (II) > (III) > (IV).

It has previously been reported⁶ that phenylacetylene, when heated at 130–170 °C under nitrogen, forms a

yellow mixture of linear telomers (M 350–450). In contrast perfluorobut-2-yne, when heated under pressure at 260 or 375 °C, gives hexakis(trifluoromethyl)benzene (*ca.* 70%).⁷

Since the telomers are coloured and a mass spectral examination of those produced from the acetylenes (I) and (III) showed highest mass peaks at m/e values corresponding to $(M_2)^+$ it is suggested that the telomers are conjugated polyvinylacetylenes.

On u.v. irradiation the acetylene (I) was readily converted into a trimer (92%), which was identified as the 1,3,5-trisubstituted benzene (V) on the basis of spectral evidence [λ_{max} , 3.28 (aromatic C–H str.), 5.20 and 5.60 (1,3,5-trisubstitution pattern), 6.23 and 6.90 (aromatic ring), and 11.14 μm (C–H out of plane bending), δ_{H} –0.88 (s) p.p.m. (external benzene); δ_{F} –21.2 p.p.m. (external trifluoroacetic acid)]. In contrast the acetylene (IV) was converted (31%) into a red multi-component oil under photochemical conditions.

The photochemistry of acetylenes has been little studied, although a number of photochemical reactions of acetylenes with olefins, dienes, aromatic compounds, *etc.* have been investigated. However, irradiation of acetylene has been reported⁸ to yield a mixture of a polymer resembling cuprene, hydrogen, ethylene, vinylacetylene, diacetylene, and benzene; competing pathways involving free radical and excited acetylene molecule intermediates were proposed to account for the products.

A mixture of the acetylene (III) and buta-1,3-diene when heated at 180 °C gave the Diels–Alder adduct (VI); $\text{R} = \text{CF}_3$ (89%); the less electron-deficient acetylene (I),

⁷ H. C. Brown, H. L. Gewanter, D. M. White, and W. G. Woods, *J. Org. Chem.*, 1960, **25**, 634; J. F. Harris, jun., R. J. Harder, and G. H. Sausen, *ibid.*, p. 633; J. F. Harris, jun., U.S.P. 2,923,746/1960.

⁸ M. Zelikoff and L. M. Aschenbrand, *J. Chem. Phys.*, 1956, **24**, 1034, and references therein.

¹ Part V, J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1963.

² J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096.

³ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 411.

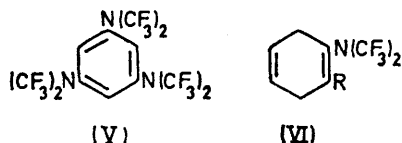
⁴ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1848.

⁵ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1955.

⁶ S. Yokomichi and M. Oiwa, *Kogyo Kagaku Zasshi*, 1963, **66**, 379.

heated similarly at 165 °C, afforded the corresponding adduct (VI; R = H) in low yield (27%), together with a small amount of an acetylene–diene 2:1 adduct and an unidentified multi-component higher-boiling oil. The acetylene (II) at 100 °C afforded a complex mixture of products including the adduct (VI; R = Br) (ca. 1%), three diene–acetylene 2:1 adducts (ca. 60%), a 1:1:1 acetylene–diene–hydrogen bromide adduct (ca. 10%), a 2:1 acetylene–hydrogen bromide adduct (ca. 5%), and a bromobis(trifluoromethyl)aminobenzene (ca. 1%). Thus considerable dehydrobromination occurred even though relatively mild conditions were used.

Reaction did not take place between the acetylene (IV) and the diene at temperatures up to 175 °C.



EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Photochemical reactions were carried out at a distance of ca. 15 cm from a Hanovia S500 medium-pressure u.v. lamp. Products were separated either by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. [Perkin-Elmer 154B or 451 Fraktometer; columns of silicone MS 550 oil (20%) on Celite]. The identities of products were established by elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 with sodium chloride optics), n.m.r. spectroscopy [Perkin-Elmer R10 operating at 56.46 MHz for ¹⁹F and 60.0 MHz for ¹H with external trifluoroacetic acid and internal tetramethylsilane as the respective references (unless stated to the contrary)], mass spectrometry (A.E.I. MS/2H or MS/902), and g.l.c.

The bistrifluoromethylamino-substituted acetylenes were prepared as described previously.^{2,3}

Reactions of NN-Bistrifluoromethylethynylamine (I).—(a) *Photochemical.* The acetylene (0.52 g, 2.93 mmol), sealed in a silica ampoule (ca. 10 cm³) *in vacuo* and irradiated (3 days), gave unchanged acetylene (0.16 g, 0.91 mmol, 31% recovered) (Found: *M*, 177. Calc. for C₄HF₆N: *M*, 177) and a higher boiling mixture (0.35 g) of a red liquid and colourless crystals. The major component of the mixture was separated by g.l.c. (2 m column at 110 °C) and identified as 1,3,5-tris(bistrifluoromethylamino)benzene (0.33 g, 0.64 mmol, 92%) (Found: C, 27.3; H, 0.8%; *M*⁺, 531. C₁₂H₃F₁₈N₃ requires, C, 27.2; H, 0.6%; *M*, 531, m.p. 53 °C; *m/e* 531 (100%, *M*⁺), 512 [62%, (*M* - F)⁺], 443 [36%, (*M* - CF₃)⁺], 355 [8%, (*M* - 2CF₃)⁺], and 69 (61%, CF₃⁺). The five minor components of the mixture with longer g.l.c. retention times were not investigated further.

(b) *Thermal.* The acetylene (0.395 g, 2.23 mmol), sealed in a Pyrex ampoule (ca. 10 cm³) *in vacuo* and heated at 250 °C (5 days), gave unchanged acetylene (0.34 g, 1.92 mmol, 86% recovered) and an orange-red, higher boiling liquid (0.056 g, 14%), which was shown by g.l.c. (2 m column at 120 °C) to contain at least five components. A g.l.c.–mass spectrometric examination of the liquid showed that it was a mixture of acetylene telomers [(CF₃)₂N·C₂H]_{*n*} in order of yield *n* = 4 > *n* = 5 ≫ *n* = 3 > *n* = 6 > *n* = 7;

the mass spectra of all the telomers showed bands corresponding to (*M_x*)⁺, (*M_x* - F)⁺, and [*M_x* - N(CF₃)₂]⁺, etc.

(c) *On storage.* A sample of the acetylene (0.395 g, 2.23 mmol), stored *in vacuo* at room temperature in a Pyrex ampoule (ca. 10 cm³), slowly changed colour during 6 months from colourless to yellow to red. Work-up gave unchanged acetylene (0.16 g, 0.89 mmol, 40% recovered) and a higher boiling red liquid (0.23 g, 99% yield) which was shown by g.l.c.–mass spectrometry to be mainly a mixture of acetylene tetramer and pentamer, together with a small amount of trimer.

(d) *With butadiene.* A mixture of the acetylene (1.98 g, 11.2 mmol) and butadiene (2.41 g, 44.6 mmol), sealed *in vacuo* in a Pyrex ampoule (ca. 300 cm³) and heated at 165 °C (5 days), gave (i) unchanged acetylene (1.76 g, 10.0 mmol, 89% recovered), (ii) unchanged butadiene (1.69 g, 31.3 mmol, 70% recovered), and (iii) a higher boiling fraction (0.76 g) which was shown by g.l.c. (2 m column at 155 °C) to consist of five components (A–E) in the ratio 10:68:5:14:3. The three major components (A, B, and D) were separated by g.l.c. (as before); component A was identified as 1-bistrifluoromethylaminocyclohexa-1,4-diene (0.076 g, 0.33 mmol, 27%) (Found: C, 41.3; H, 3.0%; *M*⁺, 231. C₈H₇F₆N requires C, 41.6; H, 3.0%; *M*, 231), b.p. (Siwoloboff) 123 °C at 735 mmHg; λ_{max}, 5.59w and 6.10w (C/C str.), 10.16s (C–N str.), and 14.03 μm (CF₃ def.); *m/e* 231 (100%, *M*⁺), 229 [25%, (*M* - H₂)⁺], 166 [71%, (CF₃)₂N·CH₂⁺], 162 [38%, (*M* - CF₃)⁺], 79 (70%, C₆H₇⁺), 78 (39%, C₆H₆⁺ and CF₃·N·CH₂⁺), 77 (84%, C₆H₅⁺ and CF₂·N·CH⁺), 69 (63%, CF₃⁺), and 67 (34%, C₆H₇⁺); τ 7.58 (4H, complex, 2CH₂), 4.76 (2H, complex, CH:CH), and 4.37 [1H, s, CH:C·N(CF₃)₂]; ¹⁹F δ -20.4(s) p.p.m.; component B was identified as 4-vinylcyclohexene by comparison of its i.r. spectrum and g.l.c. retention time with those of a pure sample, but mass spectrometry showed that it was contaminated with a small amount of an acetylene–butadiene 2:1 adduct (*m/e* 408); component D was identified as cyclo-octa-1,5-diene (i.r. and g.l.c. retention time).

A tube residue (0.16 g), washed out with diethyl ether, was shown by g.l.c. (2 m column at 175 °C) to be a complex mixture of at least twelve components; it was not examined further.

Reactions of 3,3,3-Trifluoro-NN-bistrifluoromethylprop-1-ynylamine (III).—(a) *On storage.* A sample of the acetylene (0.245 g, 1.0 mmol), stored *in vacuo* at room temperature in a Pyrex ampoule (ca. 10 cm³), slowly turned yellow during 18 months. Work-up gave unchanged acetylene (0.195 g, 0.8 mmol, 80% recovered) and a pale yellow oil (0.050 g) shown by g.l.c.–mass spectrometry to be mainly an acetylene trimer [*m/e* 735 (*M₃*)⁺] contaminated with a trace of tetramer [*m/e* 980 (*M₄*)⁺].

(b) *With butadiene.* A mixture of the acetylene (0.502 g, 2.05 mmol) and butadiene (0.210 g, 3.89 mmol), sealed *in vacuo* in a Pyrex tube (ca. 50 cm³) and heated at 180 °C (10 days), gave (i) unchanged acetylene (0.142 g, 0.58 mmol, 31% recovered), (ii) unchanged butadiene (0.068 g, 1.25 mmol, 32% recovered), and (iii) a higher boiling fraction (0.450 g) which was separated by g.l.c. (2 m column at 125 °C) into a mixture of butadiene dimers (0.061 g, 0.57 mmol) and 1-bistrifluoromethylamino-2-trifluoromethylcyclohexa-1,4-diene (0.389 g, 1.30 mmol, 89%) (Found: C, 36.3; H, 2.0; N, 4.6%; *M*⁺, 299. C₉H₆F₉N requires C, 36.2; H, 2.0; N, 4.7%; *M*, 299), b.p. (Siwoloboff) 145 °C; λ_{max}, 5.90m and 6.03w (C/C str.), 10.12s and 10.22s (C–N str.), and 14.20 μm (CF₃ def.); *m/e* 299 (94%, *M*⁺), 280 [30%, (*M* - F)⁺],

230 [34%, $M - CF_3^+$], 166 [(38%, $(CF_3)_2N \cdot CH_3^+$], 147 {87%, $[M - N(CF_3)_2]^+$ }, 114 (30%, $CF_3 \cdot N \cdot CF_3^+$), 77 (49%, $C_2HF_2N^+$ and $C_8H_8^+$), and 69 (100%, CF_3^+); τ 7.06 (4H, s, $2CH_2$) and 4.40 (2H, s, 2 vinylic H); ^{19}F δ -23.0 [6F, q, $N(CF_3)_2$, J 2.8 Hz] and -13.0 p.p.m. (3F, sept, CF_3).

(c) *Thermal*. A sample of the acetylene (0.245 g, 1.0 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 10 cm³) and heated at 250 °C (10 days), gave unchanged acetylene (0.221 g, 0.91 mmol, 91% recovered) and a higher boiling yellow liquid (0.024 g) which was shown by g.l.c.-mass spectrometry to be mainly an acetylene trimer contaminated with small amounts of tetramer and pentamer.

Reactions of Perfluoro-(1,2-bisdimethylamino)acetylene (IV).

—(a) *Thermal*. A sample of the acetylene (0.35 g, 1.07 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 10 cm³) and heated at 250 °C (10 days), gave unchanged acetylene (0.34 g, 1.05 mmol, 98% recovered) and a trace of a higher boiling yellow liquid. The acetylene was unchanged on storage *in vacuo* in a Pyrex ampoule at room temperature (18 months).

(b) *Photochemical*. The acetylene (0.548 g, 1.67 mmol), sealed *in vacuo* in a silica tube (*ca.* 10 cm³) and irradiated (10 days), gave unchanged acetylene (0.350 g, 1.07 mmol, 64% recovered) and a higher-boiling red oil (0.188 g) which was shown by g.l.c. (2 m column at 150 °C) to consist of at least six components and was not examined further.

(c) *With butadiene*. A mixture of the acetylene (0.755 g, 2.30 mmol) and butadiene (0.259 g, 4.80 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 100 cm³) and heated at 175 °C (5 days), gave unchanged acetylene (0.700 g, 2.13 mmol, 92% recovered), unchanged butadiene (0.099 g, 1.82 mmol,

38% recovered), and a higher-boiling fraction (0.150 g) consisting mainly of butadiene dimers. In a second experiment carried out at 160 °C (14 days) the acetylene and the diene were almost quantitatively recovered.

Reactions of 2-Bromo-NN-bis(trifluoromethylethynyl)amine (III).—(a) *On storage*. A sample of the acetylene (0.35 g, 1.35 mmol), stored *in vacuo* at room temperature in a Pyrex ampoule (*ca.* 10 cm³), slowly changed from a colourless liquid to a red oil during 6 months. Work-up gave unchanged acetylene (0.13 g, 0.47 mmol, 36% recovered) and a higher boiling red oil (0.22 g), which was shown by g.l.c. (2 m column at 150 °C) to be a complex mixture of at least six components and was not examined further.

(b) *With butadiene*. A mixture of the acetylene (3.46 g, 13.5 mmol) and butadiene (3.65 g, 67.5 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 300 cm³) and heated at 100 °C (5 days), gave unchanged butadiene (2.32 g, 43.0 mmol, 64% recovered) and a pale-yellow higher boiling liquid (4.41 g) which was shown by g.l.c. (2 m column at 200 °C) to consist of twelve components. A g.l.c.-mass spectrometric examination showed the presence of three 2 : 1 butadiene-acetylene adducts (*ca.* 60% of fraction) (*m/e* 365 and 363), a 1:1:1 acetylene-butadiene-hydrogen bromide adduct (*ca.* 10% of fraction) (*m/e* 393, 391, and 389), a 2:1 acetylene-hydrogen bromide adduct (*ca.* 5% of fraction) (*m/e* 596, 594, 592, and 590), small amounts of a 1:1 acetylene-diene adduct (*m/e* 311 and 309) and a bromobis(trifluoromethyl)aminobenzene (*m/e* 309 and 307), and various unidentified components.

[4/2568 Received, 9th December, 1974]