ADDITION OF FLUOROACETYLENES TO GROUP V HYDRIDES

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ABSTRACT

Compounds of the type R_2EH react readily with $CF_3C{\equiv}CCF_3$ to give $R_2EC(CF_3){=}C(CF_3)H$ (E = N, P, As), and with $CF_3C{\equiv}CH$ to give $R_2ECH{=}CHCF_3$ (E = N, As) and $R_2EC(CF_3){=}CH_2$ (E = As). The isomer distribution of the products is obtained from their n.m.r. spectra and the mechanism of the addition reaction is discussed.

INTRODUCTION

Although it was known that the fluoroacetylenes hexafluorobut-2-yne, $CF_3C{\equiv}CCF_3$ (I) and 1,1,1-trifluoropropyne $CF_3C{\equiv}CH$ (II), react with compounds such as $(C_2H_5)_2NH$ (1) and H_2S (2) to give adducts of the type $HSC(CF_3){=}C(CF_3)H$, very little information was available concerning the isomer distribution of the products. Because of our interest in the reactions of fluoroacetylenes (3, 4) and because little is known about the addition of compounds containing E—H bonds (E = N, P, As) to acetylenes, we have studied the products obtained by reacting hydrides of the type R_2EH (R = CH_3, C_6H_5, CF_3) with I and II.

Recently Stone and co-workers (5, 6) have found that I adds to transition metal hydrides to yield predominantly the *trans*-adduct, e.g.

$$(CO)_5ReH + CF_3C{\equiv}CCF_3 \rightarrow \begin{matrix} (CO)_5Re & & CF_3 \\ & \diagdown\ \diagup & \\ & C{=}C & \\ & \diagup\ \diagdown & \\ CF_3 & & H \end{matrix}$$

DISCUSSION AND RESULTS

The reactions investigated can be described by the following equations.

$$RR'EH\ (III) + CF_3C{\equiv}CCF_3\ (I) \rightarrow RR'EC(CF_3){=}C(CF_3)H\ (IV)$$
$$RR'EH\ (III) + CF_3C{\equiv}CH\ (II) \rightarrow RR'ECH{=}C(CF_3)H\ (V) + RR'EC(CF_3){=}CH_2\ (VI)$$

The products isolated from these reactions will be described first.

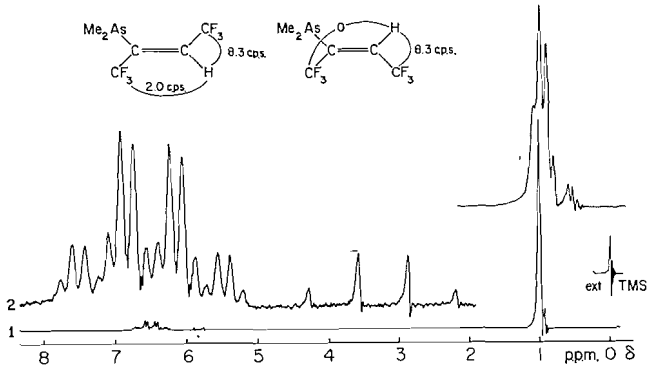


FIG. 1. ^1H n.m.r. spectrum of $(CH_3)_2AsC(CF_3){=}C(CF_3)H$.

Reaction Products

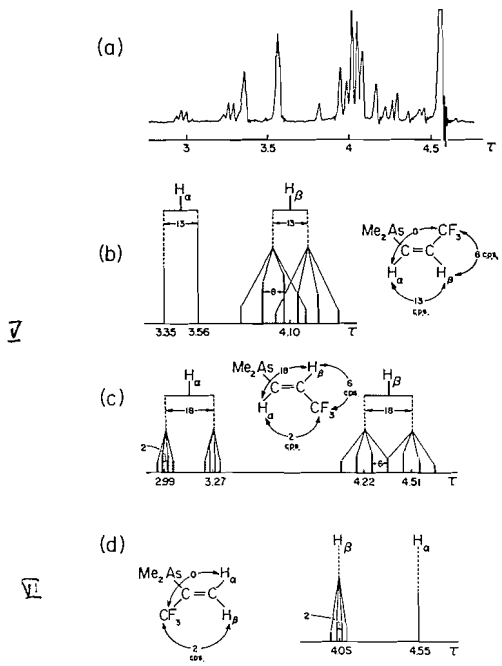
Dimethylarsine (III, R = R′ = CH_3, E = As) and I give the 1:1 adduct IV, a colorless liquid, b.p. 109–110°. The ^1H nuclear magnetic resonance (n.m.r.) spectrum of this product, before distillation, is shown in Fig. 1. The coupling constants indicated in the figure are consistent with the quartet of quartets being associated with the *trans*-isomer and the slightly higher field quartet with the *cis*-compound, the relative abundance of the two isomers being 15:1. In the high field region the areas of the two peaks are also in the ratio 15:1 indicating that they too are associated with the two isomers. These peaks which are due to the methyl groups on the arsenic atoms are split into quartets with J = 1.2 c.p.s. Splittings of this sort have been observed previously for the related compounds $(CH_3)RAsC(CF_3)=C(CF_3)Cl$ (R = CH_3, Br) (3) and $(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$. In the latter case the *cis*-compound (4) has an ill-defined quartet at 1.22 p.p.m. ($J \approx 0.5$ c.p.s.) and the *trans*-isomer a similar quartet at 1.18 p.p.m. ($J \approx 1.0$ c.p.s.). It has been suggested (3) that these splittings could be due to "through space" coupling of the arsenic methyl protons with the fluorine atoms of the geminal trifluoromethyl group since arsines of the type $(CH_3)RAsRf$, where Rf is any other type of fluorocarbon group, have only a single sharp methyl peak in their n.m.r. spectra. It is, however, possible to have the $CH_3AsC(CF_3)=$ group present without observing this splitting as in the compound $(CH_3)_2AsC(CF_3)=CHCl$ (7) where the methyl peak is split ($J \approx 1$ c.p.s.) when the arsenic atom is *cis* to the chlorine but is unsplit in the other isomer. Evidently bulky groups are necessary for splitting to occur. The ^{19}F n.m.r. spectrum of a sample of IV (R = R′ = CH_3, E = As) which was at least 90% *trans*-isomer shows two peaks. The downfield peak which consists of a doublet (J = 8.4 c.p.s.) of quartets (J = 1.9 c.p.s.) is assigned to the fluorine atoms of the $=C(CF_3)H$ group. Fig. 1 shows that $J_{CF_3\text{--}H} = 8.4$ c.p.s. and thus the 1.9 c.p.s. splitting must be due to the *trans*-CF_3 groups. These coupling constants are in agreement with those previously reported (6). The high field peak in the ^{19}F spectrum of the arsine is very broad and this is assigned to the fluorine atoms of the $(CH_3)_2AsC(CF_3)=$ group, the broadening being due to the combined effects of the weak CF_3--CF_3, CF_3--CH_3, and *cis*-CF_3--H interactions.

A predominantly *trans*-configuration is also found in the product of the reaction of methylphenylarsine (III, R = CH_3, R′ = C_6H_5, E = As) with I. The mixture of isomers of IV (R = CH_3, R′ = C_6H_5, E = As) obtained after distillation at 54° (10^{-3} mm) contained 92% *trans*-compound. This assignment can be made on the basis of the ^1H n.m.r. spectrum which is very similar to that described for the dimethylarsine adduct (IV, R = R′ = CH_3, E = As). Here again the methyl peak of each isomer has a different chemical shift and is split into a quartet by weak CF_3--CH_3 interactions. Bistrifluoromethylarsine and I give a product IV (R = R′ = CF_3, E = As) b.p. 99–100° which consists only of the *trans*-isomer as characterized by the quartet of quartets in its ^1H n.m.r. spectrum.

The product of the interaction of diphenylphosphine and I is the 1:1 adduct IV (R = R′ = C_6H_5, E = P) b.p. 127° (10^{-3} mm). The ^1H n.m.r. spectrum of this product shows the presence of aromatic and olefinic protons and the relative areas of the peaks indicate that some absorption due to the olefinic protons lies underneath the broad aromatic proton peak. The ^{31}P--H coupling for trivinylphosphine is given as 30 c.p.s. for the *trans*-hydrogen and 14 c.p.s. for the *cis* (8). Thus the diphenylphosphino compound would be expected to show some ^{31}P--H coupling also. Among the peaks associated with the olefinic protons is an isolated quartet (J = 9 c.p.s.) which shows some sign of secondary splitting and which can be assigned to a single proton or to half a proton in the group $=C(CF_3)H$ depending on

whether $J_{^{31}P\text{--}H} \simeq 0$ or $\geqslant 50$ c.p.s. The latter possibility is more likely, but the coupling can not be given more precisely because of overlap of peaks. If the trends found for the arsenic compounds are maintained for phosphorus, then the upfield position and slight secondary splittings of the quartet indicate that it is due to the *cis*-isomer. However, the secondary splitting criterion is not reliable as is seen for the nitrogen compounds described below. The area of this quartet indicates that there is a significant amount of this supposed *cis*-isomer in the mixture (ca. 40% if the ^{31}P--H coupling $\geqslant 50$ c.p.s.).

Dimethylamine and I afford the dimethylaminobutene (IV, R = R′ = CH_3, E = N) b.p. 96–97°. The initial reaction product, undistilled, consists of two isomers in the ratio 6:1 (trans:*cis*, *quod vide*), each isomer having a ^1H n.m.r. spectrum of a downfield quartet (J = 9 c.p.s., showing *slight* secondary splitting) and an upfield singlet which also shows the presence of weak coupling. By analogy with the arsenic compounds the downfield quartet is assigned to the *trans*-isomer and this is substantiated by the ^{19}F n.m.r. spectrum of the pure isomer which contains only two regions of absorption both of which show only very weak F--F coupling resulting in a broadening of the peaks. The ^{19}F spectrum of a mixture of isomers shows a quartet (J = 12.6 c.p.s.) due to the other isomer. It has been found that *trans*-CF_3--CF_3 coupling is much weaker than *cis*-CF_3--CF_3, the former having values of 1.1, 2.3 (5), and 2.5 c.p.s. (6), the latter being of the order of 11.5 c.p.s. (5). Thus in the present example the weak coupling can be assigned to the *trans*-isomer. The ^{19}F spectrum also shows the expected doublet associated with the $=C(CF_3)H$ group but unexpectedly each doublet is split into a septet presumably because of coupling with the methyl groups on the nitrogen. The slight splittings on the methyl peaks in the ^1H spectrum are a further manifestation of this interaction. This long-range coupling (J = 1.7 c.p.s.) is of similar magnitude to the 6-bond H--F coupling in *o*-fluoro-N-cyclohexyl-N-methylbenzamide (9).



V

VI

FIG. 2. Down field region of the ^1H n.m.r. spectrum of the reaction products from $(CH_3)_2AsH$ and $CF_3C{\equiv}CH$.

Trifluoropropyne (II) and dimethylarsine give a product b.p. 109–110° whose low field n.m.r. spectrum is given in Fig. 2. Analysis of this spectrum resulted in the assignments given in the figure. The assignments were based on the possibility of obtaining three isomers and the expectation that $J_{H\alpha-H\beta}$ for the *cis*-compound would be less than for the *trans*-isomer as is found in related hydrocarbon systems (10). Subsequently the pure *cis*-compound was isolated by vapor phase chromatography (v.p.c.) and converted to the *trans*-form and the n.m.r. spectra of these proved to be identical with those derived (Fig. 2). Confirmation of the *trans*-isomer comes from the infrared spectrum which shows a highly characteristic band of medium intensity at 970 cm^{-1} (11). The *cis*-isomer is transparent in this region. The iso-compound (VI, R = R′ = CH_3, E = As) has an unsplit methyl peak with the same chemical shift found for the *cis*-compound. The ratio of isomers in the original reaction product, after distillation, is *cis*:*trans*:iso = 3:3:2.

Dimethylamine and II give only the *trans*-dimethylamino derivative (V, R = R′ = CH_3, E = N) b.p. 118°. The ^1H n.m.r. spectrum is almost identical with that of the analogous *trans*-dimethylarsino compound. Confirmation of the *trans*-configuration comes from its infrared spectrum which, like the arsenic analogue, contains a strong band in the *trans* —HC=CH— "out-of-plane" bending region at 960 cm^{-1}. The H_α--H_β coupling in the *trans*-amino compound is 13 c.p.s. which is to be compared with 18 and 13 c.p.s. for the *trans*- and *cis*-arsino derivatives respectively.

Isomerization of the Products

A limited amount of information regarding isomerization of the olefinic products has been obtained in the present investigation. Thus the *cis*-isomer of 2-dimethylarsino-1,1,1,4,4,4-hexafluorobutene (IV, R = R′ = CH_3, E = As) is isomerized to the *trans*-compound on heating ($T \geqslant 140°$) although the methylphenylarsinobutene is unaffected at 140°. Isomerization of the dimethylaminobutene (IV, R = R′ = CH_3, E = N) is apparently catalyzed by oxygen since leaving a *trans*-rich mixture exposed to the air at 20° results in an increase in the *cis*-isomer content and distilling the mixture in nitrogen results in an increase in the *trans*-isomer content. (Inevitably some oxygen would be present during the distillation.) However, if a mixture of the isomers is heated in the absence of air then no isomerization takes place below 160° even though other reactions, possibly polymerization, start to become significant at the higher temperatures.

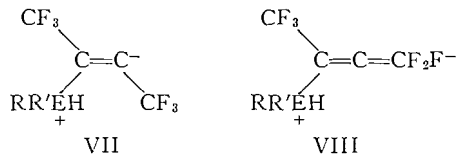
The *cis*-isomer of 1-dimethylarsino-3,3,3-trifluoropropene (V, R = R′ = CH_3, E = As) is converted to the *trans*-isomer both on ultraviolet irradiation and on heating. This provides a convenient method of obtaining the *trans*-compound since the *cis*-isomer can be isolated by v.p.c. The thermal isomerization does not take place in the absence of air below 150°, but at 175° it is almost complete after 12 days.

Mechanism of the Addition Reactions

Haszeldine (1) found that nucleophilic attack by alkoxide ion occurs readily on hexafluorobut-2-yne but less readily on 1,1,1-trifluoropropyne. Since his work was reported, a number of studies have been made on the sterochemistry of nucleophilic attack on more commonly available acetylenes which have resulted in the generalization that nucleophilic attack results in *trans*-addition (12), although a few exceptions have been noted (13). More recently *trans*-addition of alkoxide to ethynylsulfur pentafluoride to give predominantly *cis*-$SF_5CH{=}CHOCH_3$ has been found (14). Thus it seems likely that Haszeldines' products $ROC(CF_3){=}C(CF_3)H$ and $ROCH{=}CHCF_3$ will have predominantly the configuration to be expected from *trans*-addition.

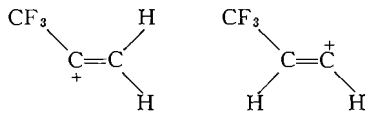
The mechanism of the addition of the compounds R_2EH to the acetylenes is less certain. In the hydrocarbon field it has been found that, in the absence of catalysts, amines add only to activated triple bonds (15, 16). It has been assumed that these additions involve nucleophilic attack by the amine (15, 16), but the geometry of the products has not been investigated.

The addition of arsines to I also appears to involve nucleophilic attack, presumably by the arsenic lone pair, since the ease of reaction of the arsines RR′AsH with I decreases in order $(CH_3)_2AsH > CH_3(C_6H_5)AsH > (CF_3)_2AsH$. This order reflects the decreasing availability of the arsenic lone pair for nucleophilic attack owing to the presence of electron-withdrawing groups on the arsenic atom (17). Similarly the reaction of dimethylamine with I probably involves nucleophilic attack. The nature of the reaction of diphenylphosphine with I is less certain because of the high proportion of what is probably the *cis*-isomer in the product. The transition state leading to *trans*-addition by nucleophilic attack can be represented by VII; hyperconjugation could result in VIII which in turn could result in some *cis*-isomer being produced, but it is difficult to see why VIII should be more stable when E = P.



VII VIII

Haszeldine found that nucleophilic attack by alkoxide on the propyne (II) leads to the formation of only $ROCH{=}CHCF_3$, no $CF_3C(OR){=}CH_2$ being produced. Dimethylamine is now found to add in a similar way to give only *trans*-$(CH_3)_2NCH{=}C(CF_3)H$ but it seems unlikely that the product arises by *cis*-addition and consequently it is believed that *trans*-addition first takes place followed by isomerization. In the corresponding arsenic system it is the *trans*-compound which is more thermodynamically stable. Dimethylarsine and II give the three isomers shown in Fig. 2. The *cis*-compound could arise from nucleophilic attack by the arsine but the amount of the *trans*-compound, which is equal to that of the *cis*, seems to be too much to have resulted from isomerization of the initially formed *cis*-isomer unless the isomerization is catalyzed by unreacted arsine. The mechanism of the formation of the iso-compound VI (R = R′ = CH_3, E = As) is also of interest since electrophilic attack by the hydrogen of the arsine should proceed through intermediates such as IX and X.



IX X

Of the two rather unlikely species X would be expected to be more stable and consequently electrophilic attack should also lead to the *cis*-isomer, Burnelle having recently calculated (18) that a *trans*-distortion of the alkyne is to be expected on the approach of an electrophile. Thus, although Haszeldine (1) found no evidence for nucleophilic attack by alkoxide at the center carbon atom of the propyne it seems likely that this is occurring in the arsine reaction. However, a concurrent free radical addition could be taking place giving rise to all three isomers.

One very important feature of these hydride addition reactions yet to be settled is the question of inter- or intra-molecular hydrogen transfer and it is hoped that competitive experiments with deuterated arsines will provide an answer.

EXPERIMENTAL

All reactions were carried out in sealed thick-walled pyrex tubes. Nuclear magnetic resonance spectra were obtained using Varian A-60 and HR-60 spectrometers and chemical shifts are reported in parts per million (p.p.m.) downfield from external tetramethylsilane (^{1}H spectra) and from external trifluoroacetic acid (^{19}F spectra). Infrared spectra were recorded using a Perkin–Elmer Model 21 instrument. Microanalyses were carried out by Dr. Alfred Bernhardt, Mulheim, Germany.

Reaction of Hexafluorobut-2-yne with Dimethylarsine

The arsine and the acetylene did not react in the gas phase at 20°. However, there was a vigorous reaction when the arsine (3.1 g) and the butyne (10.1 g) were condensed together and allowed to warm slowly to 20°. Trap-to-trap distillation gave 7.4 g of unreacted acetylene and 7.7 g of *2-dimethylarsino-1,1,1,4,4,4-hexafluorobutene* which condensed in a trap cooled to −78°. Vapor phase chromatography (dinonyl phthalate at 100°) showed the fraction to be at least 99% pure. It distilled in nitrogen at 109–110° (Found: C, 26.7; H, 2.8; As, 28.1; F, 42.3. Calcd. for $C_6H_7AsF_6$: C, 26.8; H, 2.7; As, 28.0; F, 42.6). Infrared spectrum (liquid film): 3 020(w), 2 940(w), 2 340(vw), 1 643(w), 1 430(sh,m), 1 424(m), 1 366(w), 1 331(vs), 1 257(vs), 1 160(vs), 1 140 (vs), 940(vw), 900(m), 870(sh,s), 859(s), 850(s), 722(w) cm^{-1}. Spectra (n.m.r.): ^{1}H spectrum (Fig. 1) methyl peaks at 1.03 and 0.94 p.p.m. each split into a multiplet of 4 (J = 1.2 c.p.s.), area ratio = 15.1:1. Two olefinic protons, one consisting of a quartet of quartets centered at 6.5 p.p.m. (J = 8.3 and 2.0 c.p.s.) and the other a quartet centered at 5.83 p.p.m. (J = 8.3 c.p.s.), of relative area 15.1:1. ^{19}F spectrum: two peaks of equal area at 13.6 and 11.1 p.p.m. The low field peak is a doublet (J = 8.4 c.p.s.) each doublet being further split into a quartet (J = 1.9 c.p.s .). The peak at 11.1 p.p.m. is broad being of the order of 8 c.p.s. at half height and is a multiplet of 13.

A sample of the adduct after distillation showed an isomer distribution of 95% *trans*:5% *cis*, and after 36 h at 140° even less of the *cis*-isomer remained. After 36 h at 160° the isomer composition was 98% *trans* and 2% *cis*.

The arsine (*trans*: *cis* = 95:5) and 10 ml of 10% aqueous sodium hydroxide were heated to 100° for 3 days to give 0.043 g (15% yield) of *trans*-1,1,1,4,4,4-hexafluorobutene of known infrared spectrum.

Reaction of Hexafluorobut-2-yne with Methylphenylarsine

The arsine (5.6 g) and the butyne (13.3 g) reacted slowly at 20° to give a single phase after 30 min. The less volatile product which distilled at 54° (10^{-3} mm) was identified as *2-methylphenylarsino-1,1,1,4,4,4-hexafluorobutene* (Found: C, 40.0; H, 2.9; As, 22.6; F, 34.7. Calcd. for $C_{11}H_9AsF_6$: C, 40.0; H, 2.7; As, 22.7; F, 34.6). Infrared spectrum (liquid film): 3 070(w), 2 930(vw), 2 280(vw), 1 641(w), 1 582(w), 1 485(w), 1 438(m), 1 363(w), 1 330(s), 1 283(m), 1 255(vs), 1 143(vs), 1 077(w), 1 069(vw), 1 023(w), 998(w), 870(w), 850(m), 844(m), 737(s), 721(vw), 693(s), 641(s) cm^{-1}. ^{1}H n.m.r. spectrum: two high field peaks at 1.06 and 0.93 p.p.m. of relative area 11:1, the larger one being a distorted quartet ($J \approx$ 1 c.p.s.). In the downfield region are two quartets (J = 8.5 c.p.s.) centered at 6.36 and 5.40 p.p.m. (area ratio = 11:1), each peak of the larger quartet at 6.36 p.p.m. is further split into a quartet (J = 2.0 c.p.s.). The aromatic protons appear as a complex system centered at 6.9 p.p.m. This same n.m.r. spectrum was obtained from a sample that had been heated at 140° for 3 days.

Reaction of Hexafluorobut-2-yne with Bistrifluoromethylarsine

Bistrifluoromethylarsine (2.9 g) and excess acetylene (11.0 g) did not react at 20° (2 days), and after 24 h at 130° only partial reaction had occurred. The reactants and products were then heated to 210° (24 h) to give hexafluorobut-2-yne (8.2 g) containing a little silicon tetrafluoride and fluoroform, and a fraction which condensed at −46° (5.0 g). This last fraction distilled at 99–100° in a nitrogen atmosphere and was identified as *2-bis(trifluoromethyl)arsino-1,1,1,4,4,4-hexafluorobutene*. An analytical sample was obtained by v.p.c. (dinonyl phthalate at 100°) (Found: C, 19.3; H, 0.27; As, 19.9; F, 60.5. Calcd. for C_6HAsF_{12}: C, 19.2; H, 0.27; As, 19.9; F, 60.6). Infrared spectrum (vapor): 3 100(vw), 2 302(vw), 1 793(vw), 1 649(vw), 1 385(m), 1 360(m), 1 331(vs), 1 265(vs), 1 215(s), 1 173(vs), 1 131(s), 1 099(s), 1 067(m), 1 029(m), 1 003(w), 949(vs), 887(m), 855(m), 820(vw), 735(s), 719(s) cm^{-1}. The ^{1}H spectrum consisted of a quartet of quartets centered at 6.93 p.p.m. (J = 7.5 and 1.5 c.p.s.).

Reaction of 1,1,1-Trifluoropropyne with Dimethylarsine

The propyne (6.0 g) and dimethylarsine (4.0 g) were left at 20° for 5 days. The excess alkyne was recovered by trap-to-trap distillation and the less volatile fraction was distilled in a nitrogen atmosphere to give 3.0 g of a product of formula $(CH_3)_2AsC_3F_3H_2$, b.p. 100° (Found: C, 30.2; H, 4.19; As, 37.4, F, 28.7. Calcd. for $C_5H_8AsF_3$: C, 30.0; H, 4.0; As, 37.5; F, 28.5). The ^{1}H n.m.r. spectrum of this product indicated it to be a mixture of isomers, the low field region and the assignments are shown in Fig. 2. The high field spectrum

showed peaks at 0.83 p.p.m. (*trans*) and 0.75 p.p.m. (*cis* and iso). The fraction was separated into two components by v.p.c. (dinonyl phthalate at 120°) the first being a mixture of the *trans*- and iso-compounds, the second being the *cis*-isomer. Infrared spectrum of the *cis*-isomer (vapor): 3 000(w), 2 915(w), 1 622(m), 1 424(w), 1 355(s), 1 280(vs), 1 192(vs), 1 146(vs), 1 125(vs), 892(w), 855(m), 714(m) cm^{-1}. The ^1H n.m.r. spectrum was as derived in Fig. 2 except that at high resolution $J_{H\text{--}CF_3}$ is 0.6 c.p.s. A sample of the *cis*-isomer was heated for 3 days at 110°, 3 days at 135°, and 1 day at 150° without change. However, at 175° the *trans*-isomer was slowly formed and after 12 days at this temperature almost complete isomerization had occurred. Infrared spectrum of the *trans*-isomer (vapor): 3 025(w), 2 940(w), 1 642(m), 1 435(w), 1 357(vw), 1 308(vs), 1 283(vs), 1 230(vs), 1 197(vs), 1 145(vs), 970(m), 895(w), 864(m), 722(m) cm^{-1}. The ^1H n.m.r. spectrum was as derived. A sample of the *cis*-isomer was also converted almost completely to the *trans*-compound by ultraviolet irradiation for 1 week (10 cm from 100 watt G.E. lamp).

Comparison of the infrared spectra of the *cis*- and *trans*-compounds with that of the original reaction product showed that the main bands associated with the iso-compound occur at 1 410(m), 1 220(w), 1 170(vs), 1 100(vs), 950(m) cm^{-1}.

Reaction of Hexafluorobut-2-yne with Diphenylphosphine

The phosphine (6.1 g, 32.8 mmoles) reacted immediately at 20° with hexafluorobut-2-yne (8.6 g, 53.0 mmoles) to give a viscous dark-brown material. All the butyne was consumed. The product was extracted with chloroform and distilled at 10^{-3} mm to give *2-diphenylphosphino-1,1,1,4,4,4-hexafluorobutene* b.p. 127° (Found: C, 55.1; H, 2.9; F, 32.9; P, 8.74; mol. wt. (Rast), 353. Calcd. for $C_{16}H_{11}F_6P$: C, 55.2; H, 3.2; F, 32.8; P, 8.91; mol. wt. 348). Infrared spectrum (liquid film): 3 100(w), 1 641(vw), 1 596(vw), 1 488(w), 1 445(m), 1 367(m), 1 334(m), 1 282(sh,s), 1 263(vs), 1 237(vs), 1 202(sh,s), 1 167(vs), 1 137(sh,w), 1 119(sh,w), 1 091(m), 1 072(w), 1 026(w), 1 000(w), 874(w), 841(sh,vw), 742(s), 733(sh,w), 694(s) cm^{-1}. ^1H n.m.r. spectrum: broad peak at 6.86 p.p.m. mainly due to aromatic protons, and a quartet (J = 9 c.p.s.) centered at 5.24 p.p.m. Between these lies a multiplet of 6 peaks (J = 8–9 c.p.s.) centered at 6.2 p.p.m. Both the quartet and the multiplet show secondary splittings (J = 1–2 c.p.s.).

Reaction of Dimethylamine with Hexafluorobut-2-yne

The acetylene (19.3 g) and amine (1.4 g) reacted immediately on melting. The recovered butyne weighed 13.4 g. The reaction product, which condensed in a trap cooled to −78°, distilled at 96–97° in a nitrogen atmosphere. An analytical sample of *2-dimethylamino-1,1,1,4,4,4-hexafluorobutene* was obtained by v.p.c. (dinonyl phthalate at 82°) (Found: C, 34.5; H, 3.5; N, 7.25. Calcd. for $C_6H_7F_6N$: C, 34.8; H, 3.4; N, 6.8). One small impurity was also isolated by v.p.c. from the reaction mixture and it proved to be 1,1,1,4,4,4-hexafluoropropanone (Found: C, 26.8; H, 1.31; F, 63.1. Calcd. for $C_4H_2F_6O$: C, 26.7; H, 1.12; F, 63.3. ^1H n.m.r. spectrum: quartet at 3.04 p.p.m. (J = 9 c.p.s.); infrared spectrum: carbonyl absorption at 1 790 cm^{-1}). When the reaction was done in an n.m.r. tube using excess acetylene as solvent, all the amine was used up immediately on mixing and the ^1H n.m.r. spectrum of the product showed quartets at 4.62 and 4.16 p.p.m. (J = 9.1 and 9.1 c.p.s. respectively) and slightly split methyl peaks at 2.41 and 2.24 p.p.m. The relative area of the downfield quartet to the downfield methyl peak (the *trans*-isomer) was 1:6. The other peaks are associated with the *cis*-isomer (relative area 1:6). The initial reaction product contains both isomers in the ratio of *trans*:*cis* = 6.2:1. Distillation of the isolated product mixture gave a fraction containing predominantly (>98%) the *trans*-isomer. However, if the initial reaction product is left exposed to air at 20° the proportion of *cis*-isomer increases as follows.

Time of exposure to air	*cis*:*trans*
10 min	1:6.5
25 min	1:1.9
2 days	1:1.7
12 days	1:1.6

The 1:1.6 (*cis*:*trans*) mixture was sealed and heated in the absence of air for 1 h at a variety of temperatures up to 140°. Slight darkening occurred at the higher temperatures but no change in isomer distribution was detected even though a second phase began to appear.

The infrared spectrum of the *trans*-isomer (98%) showed the following absorption bands (vapor): 2 915(m), 2 845(m), 1 710(w), 1 660(vs), 1 514(m), 1 476(m), 1 434(s), 1 310(vs), 1 274(vs), 1 239(vs), 1 195(vs), 1 156(vs), 1 127(vs), 1 069(s), 939(m), 859(s), 771(m), 730(w), 696(w), 654(s) cm^{-1}. The ^{19}F spectrum of the same sample showed a doublet (J = 9.4 c.p.s.) of septets (J = 1.7 c.p.s.) at 24.8 p.p.m. and a broad singlet at 11.4 p.p.m. Heteronuclear decoupling experiments showed that the doublet and septet splittings were due to coupling with hydrogen. Removal of hydrogen coupling still left broad fluorine peaks. The ^{19}F spectrum of a *cis–trans* mixture (ca. 1:1.5) showed a complex multiplet at 24.8 p.p.m. due to both isomers, a quartet (J = 12.6 c.p.s.) at 15.3 p.p.m. (*cis*-isomer), and a broad singlet at 11.0 p.p.m. (*trans*-isomer).

Reaction of Dimethylamine with 1,1,1-Trifluoropropyne

The amine (1.2 g) and the propyne (6.0 g) reacted violently well below room temperature. Propyne (4.1 g) was recovered and 2.1 g of a 1:1 adduct was produced. The adduct distilled with decomposition at 118° in a

nitrogen atmosphere and only 0.5 g of distillate were collected. Analysis indicated that the formula of the distillate was $(CH_3)_2NC_3H_2F_3$ (Found: C, 43.0; H, 5.7; F, 41.0; N, 10.3. Calcd. for $C_5H_8F_3N$: C, 43.2; H, 5.8; F, 41.0, N, 10.1). Infrared spectrum (vapor): 2 915(m), 2 820(w), 1 736(w), 1 660(vs), 1 488(w), 1 447(m), 1 362(s), 1 307(s), 1 258(s), 1 229(s), 1 154(sh,vw), 1 102(w), 1 076(vs), 960(s), 888(s), 845(m), 739(m), 678(s) cm^{-1}. ^1H n.m.r. spectrum peaks at 2.29 (CH_3—), 6.17 (H_α) and 3.66 (H_β) p.p.m. with $J_{CF_3\text{--}H\alpha} = 1.5$ c.p.s., $J_{H\alpha\text{--}H\beta} = 13$ c.p.s., and $J_{CF_3\text{--}H\beta} = 6.5$ c.p.s. $H_\alpha H_\beta$ are defined as in Fig. 2.

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