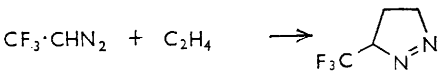
Cycloaddition Reactions of 2,2,2-Trifluorodiazoethane

By **J. H. Atherton** and **R. Fields,*** The University of Manchester Institute of Science and Technology, Sackville St., Manchester 1

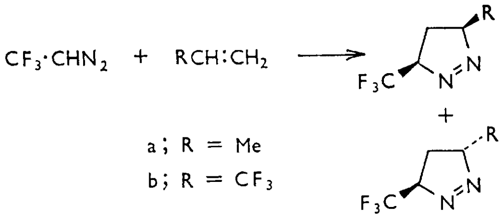
2,2,2-Trifluorodiazoethane readily forms cyclopropanes when photolysed with suitable olefins. In the absence of light, a typical 1,3-dipolar addition gives Δ^1-pyrazolines. This reaction, slow with ethylene, is retarded by alkyl substituents on the vinylic carbon, but accelerated slightly by halogens other than fluorine; a trifluoromethyl group has an accelerating effect of the same order of magnitude as an alkoxycarbonyl group.

PHOTOLYSIS of the liquid and vapour phases of 2,2,2-trifluorodiazoethane under autogenous pressure gave 3,4,5-tris(trifluoromethyl)-2-pyrazoline, together with products derived from trifluoromethylcarbene.[1] Irradiation of a mixture of the diazoethane with ethylene or cyclohexene after the reactants had been kept in the dark for three days without apparent reaction similarly gave products tentatively identified[1,2] as pyrazolines, with other products derived from the carbene. No definite reaction path for pyrazoline formation could be assigned from the evidence available, but the reaction conditions appeared to favour an excited diradical form of the diazoethane, similar to that suggested earlier[3] for the reaction of diazomethane with fluorinated olefins. Until very recently, 1,3-dipolar additions of diazo-alkanes to alkyl-olefins were regarded as impracticably slow,[4] but since this work was completed the stereospecific addition of diazomethane to *cis*- and *trans*-but-2-ene has been reported.[5] Some reactions of 2,2,2-trifluorodiazoethane with olefins and acetylenes are now reported.

Dark Reactions.—When 2,2,2-trifluorodiazoethane and a four-molar excess of ethylene were kept together in the dark at room temperature in a sealed tube, reaction was complete in 20 days, and gave 3-trifluoromethyl-1-pyrazoline in 90% yield. Under similar conditions, propene gave an 83% yield of *cis*- and *trans*-3-methyl-5-trifluoromethyl-1-pyrazolines in eleven weeks. N.m.r. studies gave the ratio (IIa) : (IIIa) as 1 : 1·3, and showed that 4-methyl-3-trifluoromethylpyrazoline, which could have been formed by the alternative mode of addition, was absent, since the chemical shifts of hydrogen atoms in the 3,5- and 4-positions of Δ^1-pyrazolines differ appreciably[6] and integration of the ^{1}H spectrum clearly showed two hydrogens in the 4-positions of both pyrazolines. The same pyrazolines were obtained (98% yield) from diazoethane and 3,3,3-trifluoropropene in a rapid dark reaction. This confirms the structural assignment, since the direction of addition to 3,3,3-trifluoropropene is established by the exclusive formation of pyrazoline (I) under these conditions with diazomethane; neither steric nor electronic factors would tend to change the direction of addition for diazoethane. The *cis*- and *trans*-isomers (IIa) and (IIIa)



(I)



(II)

(III)

a; R = Me
b; R = CF₃

---

[1] R. Fields and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 1881.

[2] R. Fields and R. N. Haszeldine, unpublished results.

[3] F. Misani, L. Speers, and A. M. Lyon, *J. Amer. Chem. Soc.*, 1956, **78**, 2801.

[4] L. Ali, unpublished results, cited in ref. 14.

[5] R. J. Crawford and L. H. Ali, *J. Amer. Chem. Soc.*, 1967, **89**, 3908.

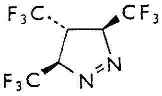
[6] (*a*) T. V. Van Auken and K. L. Rinehart, *J. Amer. Chem. Soc.*, 1962, **84**, 3736; (*b*) C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *ibid.*, 1964, **86**, 5364; 1965, **87**, 4119; (*c*) R. J. Crawford, R. J. Dummel, and A. Mishra, *ibid.*, 1965, **87**, 3023; (*d*) R. J. Crawford and A. Mishra, *ibid.*, 1965, **87**, 3768.

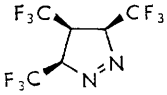
could not be separated by g.l.c. owing to isomerisation to the Δ^2-isomer; the *trans*-isomer is assumed to be the more abundant in view of the sensitivity of the reaction to steric hindrance.[7] This assumption is supported by the product ratio obtained when 2,2,2-trifluorodiazoethane reacted rapidly and quantitatively with 3,3,3-trifluoropropene to give *cis*- and *trans*-3,5-bis(trifluoromethyl)-1-pyrazolines [(IIb) and (IIIb)]. Although these, too, could not be separated, the ^{19}F n.m.r. spectrum of the mixture gave the isomer ratio 1 : 3·3, and the ^{1}H spectrum showed that the major component was the *trans*-isomer, the C-4 methylene group appearing as a ' deceptively simple ' AA′XX′ triplet. Similar triplets have been reported recently for the methylene groups of other symmetrical 3,5-di-substituted Δ^1-pyrazolines.[6b, d] The C-4 methylene of the minor component showed the ABX_2 pattern expected for the *cis*-isomer (IIIb).

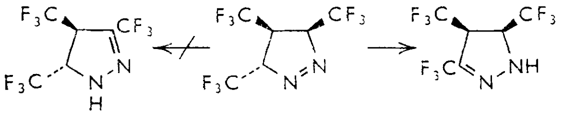
The mild conditions under which diazomethane reacted with trifluoropropene are somewhat surprising in view of the earlier report[3] that diazomethane and 3,3,3-trifluoropropene did not react ' in several hours in the dark ', but gave the Δ^2-pyrazoline after u.v. irradiation for two hours. Presumably dilution by solvent accounts to some extent for the slower reaction reported previously,[3] but the apparent photocatalysis was probably destruction of the diazomethane remaining after the dark reaction.

The enhanced reactivity of diazoethane and the reduced reactivity of 2,2,2-trifluorodiazoethane compared with diazomethane are in accord with the ground-state stability of the 1,3-dipoles.[7] It is noteworthy that while methyl substitution of the olefin results in slow additions, as expected from Huisgen's work,[7] trifluoromethyl substitution accelerates the reaction considerably. In order to check this, several olefins and alkynes containing trifluoromethyl substituents at the multiple bond were studied.

cis- and *trans*-1,1,1,4,4,4-Hexafluorobut-2-enes reacted rapidly at room temperature with trifluorodiazoethane to give different products in each case. The major product from the *trans*-isomer (87% yield) showed a doublet of septets and a doublet of quartets (intensity ratio 1 : 2) in its ^{19}F n.m.r. spectrum, consistent with either 3,*trans*-4,*cis*-5-tris(trifluoromethyl)-pyrazoline (IV) or the all-*cis*-isomer (V). The formation of isomer (V) as the only Δ^1-pyrazoline from the *trans*-olefin is extremely unlikely; the reaction with the *cis*-olefin, which would be more likely to give isomer (V), gave none of the compound obtained from the *trans*-olefin, and so isomer (V) may be excluded. The minor product, to which are attributed a broad singlet (δ_{benz} 0) in the ^{1}H n.m.r. spectrum, and N–H (3·0 μ) and C=N (6·2 μ) absorptions in the i.r. spectrum, is presumably 3,4,*trans*-5-tris(trifluoromethyl)-2-pyrazoline (VI), since this is the only Δ^2-pyrazoline which can readily be formed from isomer (IV). The major product from the *cis*-hexafluorobutene (81% yield) was 3,*cis*-4,*trans*-5-tris-(trifluoromethyl)-1-pyrazoline (VII); since the minor component was a different Δ^2-isomer, as shown by its i.r. and n.m.r. spectra, from isomer (VI) above, it must be isomer (VIII), although on steric grounds isomer (VI) would have been expected. The Δ^3-structure, which was assigned by Misani *et al.*[3] to the product from diazomethane and hexafluorobutene, is excluded in the present work by the two $CF_3{\cdot}CH$ groups in the n.m.r. spectra of the minor products. 2,2,2-Trifluorodiazoethane thus reacts stereospecifically and stereoselectively with the hexafluorobutenes, at least to the extent of 81—87%. In view of the rapidity of the reaction in the dark, the pyrazoline formed in the photochemical decomposition of the diazoethane probably takes place by this route, rather than involving excited diradical states as suggested previously,[1] followed by isomerisation to the Δ^2-pyrazoline observed. In the present work isomerisation of Δ^1-pyrazolines on irradiation, on treatment with base, exposure to air, or when heated gently, was also noted.


(IV)


(V)



(VI) (VII) (VIII)

The slow dark reactions of trifluorodiazoethane with *cis*- and *trans*-but-2-enes in each case gave products containing strong N–H absorptions (i.r.), and were thus unhelpful in the study of the stereochemistry of addition. Isomerisation of the Δ^1-pyrazolines formed by reaction of the diazoethane with dimethyl maleate or fumarate was even more troublesome, and only the Δ^2-isomer, in which the double bond is conjugated with the carbonyl group, could be isolated in either case.

Comparison of the activating effect of the trifluoromethyl group with that of the methoxycarbonyl group was obtained from reactions in which methyl propiolate and 3,3,3-trifluoropropyne competed for a deficiency of the diazoethane. The alkynes were used in preference to olefins in order to avoid the complications of isomerisation to the Δ^2-pyrazolines observed above. Russian workers have since reported that trifluorodiazoethane and methyl acrylate gave the Δ^1-pyrazoline in one experiment and the Δ^2-isomer in a second.[8] The reactivity ratio methyl propiolate : trifluoropropyne = 2·6 ± 0·5 : 1 shows that the trifluoromethyl group is almost as powerful an activating group for a 1,3-dipolarophile as the alkoxycarbonyl group, and thus considerably more powerful than the phenyl substituents studied by Huisgen.[7]

Vinylic fluorine substituents inhibited the reaction,

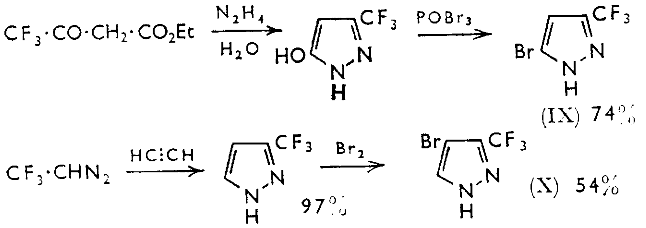
[7] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 633.

[8] B. L. Dyatkin and E. P. Mochalina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1964, 1225.

and the olefins were recovered essentially quantitatively. When silica vessels were used to avoid the known polymerisation of the diazoethane on certain glass surfaces,[1] it, too, was largely recovered. Dihydropyran, an electron-rich olefin, also failed to react.

With a reaction temperature of 100°, ethylene and the diazoethane reacted in 5 hr., but the pyrazoline yield was reduced to 45%. Nitrogen (42%) was evolved, and a small amount of trifluoromethylcyclopropane and approximately 40% of polytrifluoromethylcarbene were formed, suggesting that a carbene with lower energy than that formed photolytically (see below) is involved at this temperature.

Vinyl chloride and bromide both reacted more rapidly than ethylene with the diazoethane, but in each case the halopyrazoline underwent spontaneous dehydrohalogenation. Treatment of the pyrazole salt with base gave 3-trifluoromethylpyrazole, identical with that prepared from the diazoethane and acetylene. The yield was somewhat lower from vinyl bromide than from the chloride, and a brown tar, possibly formed by decomposition of the intermediate pyrazolenine, was also obtained. Because of the spontaneous dehydrohalogenation, the direction of addition of trifluorodiazoethane to vinyl halides could not be determined. In order to investigate the effect of halogen substitution, the addition to bromoacetylene was studied. After 6 days at room temperature this gave a mixture of 3(5)-bromo-5(3)-trifluoromethylpyrazole (IX) and the 4-bromo-3(5)-trifluoromethyl isomer (X) in 89% yield. Both isomers were synthesised independently as shown below, and the known compounds were used to calibrate the g.l.c. apparatus to give the isomer ratio (IX) : (X) = 5·3 ± 0·5 : 1.



The reaction with trifluoropropyne also gave two pyrazoles, the major product (94 ± 2%) being 3,5-bis(trifluoromethyl)pyrazole. The single absorption in its ^{19}F spectrum is in accord with other studies on symmetrical 3,5-disubstituted pyrazoles.[9] The minor product, 3(5),4-bis(trifluoromethyl)pyrazole, was unambiguously prepared from diazomethane and hexafluorobut-2-yne. The formation of the 3,4-disubstituted pyrazoles with bromoacetylene and trifluoropropyne indicates that the steric requirements are less stringent than with olefins. Presumably the acceleration by the bromine or trifluoromethyl group of the reaction giving the electronically and sterically more favourable 3,5-disubstituted product is insufficient to completely swamp that leading to the less favourable 3,4-isomers. In the faster reaction with methyl propiolate only the 3,5-isomer was detectable. Similar two-way additions to alkynes have been reported previously,[10] and addition of diazomethane to ethoxyacetylene is reported [11] to give exclusively 4-ethoxypyrazole.

The following reactivity order for olefins towards addition of trifluorodiazoethane in the dark has been established qualitatively: *cis*- and *trans*-$MeO_2C{\cdot}CH{:}CH{\cdot}CO_2Me >$ *cis*- and *trans*-$CF_3{\cdot}CH{:}CH{\cdot}CF_3 > CF_3{\cdot}CH{:}CH_2 > BrCH{:}CH_2 > ClCH{:}CH_2 > C_2H_4 > MeCH{:}CH_2 >$ *cis*- and *trans*-$MeCH{:}CHMe > CHF{:}CH_2$, $CF_2{:}CH_2$, $CF_3{\cdot}CF{:}CF_2$, dihydropyran; and for alkynes: $CF_3{\cdot}C{:}C{\cdot}CF_3 \approx MeO_2C{\cdot}C{:}CH > CF_3{\cdot}C{:}CH > BrC{:}CH > HC{:}CH$. The reaction fits the usual pattern of behaviour for a 1,3-dipolar addition, in so far as it has been reported for the substituents studied here, *i.e.*, the methoxycarbonyl group activates the 1,3-dipolarophile, and other substituents, including hydrogen, halogens, and electron-donor groups, lead to much slower reaction. It is reported [7] that ' chlorinated and fluorinated alkenes are especially poor dipolarophiles '. Although this is true for vinylic fluorine, vinyl chloride is a more reactive dipolarophile than ethylene, and the fluoroalkyl substituents lead to considerably higher reactivity. The mechanism of the activation is not altogether clear. Huisgen suggests [7] that conjugation is important, dispersing the partial charge which results from formation of one bond slightly ahead of the other. For the trifluoromethyl group, however, the dispersal can only be due to an inductive electron withdrawal, which could equally well explain the reactivity of the carbonyl substituents. The high electronegativity of fluorine, which would, on this basis, be expected to lead to high reactivity of vinyl fluoride is countered by the strong $+I_\pi$ effect of the fluorine, which prevents electron transfer to the double bond by the 1,3-dipole. The increased reactivity of vinyl chloride and bromide, in which I_π repulsion is much weaker, is in accord with this rationalisation.

Photochemical Reactions.—U.v. irradiation of 2,2,2-trifluorodiazoethane and a four-molar excess of ethylene was started as soon as the reactants had warmed to room temperature, and gave, in addition to recovered ethylene, and the usual products of decomposition of the diazo-alkane,[1] trifluoromethylcyclopropane (52%), and pyrazoline (I) (10%). The pyrazoline did not lose nitrogen under the reaction conditions, but isomerised slowly to the Δ^2-isomer. The yield of pyrazoline (I) in the present experiment is of the order expected for an uncatalysed ' dark ' reaction taking place during the irradiation. The decrease in yield compared with that reported [1] indicates the extent of the dark reaction under the conditions used previously. Further evidence

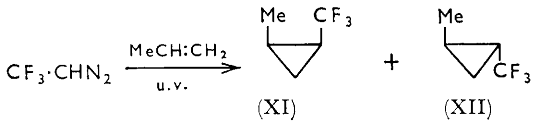
---

[9] I. L. Finar and E. F. Mooney, *Spectrochim. Acta*, 1964, **20**, 1269.

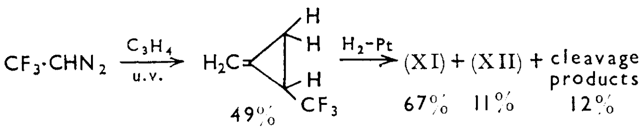
[10] E. Buchner and M. Fritsch, *Ber.*, 1893, **26**, 256; E. Buchner and W. Behagel, *ibid.*, 1894, **27**, 869; K. von Auwers and O. Ungemach, *ibid.*, 1933, **66**, 1205; R. Hüttel, J. Riedl, H. Martin, and K. Franke, *Chem. Ber.*, 1960, **93**, 1425.

[11] S. H. Groen and J. F. Arens, *Rec. Trav. chim.*, 1961, **80**, 879.

against photocatalysed pyrazoline formation is provided by the reactions with propene at room temperature and with hexafluorobutene at low temperature, neither of which showed any trace of pyrazoline. The reaction with propene gave, *inter alia*, a mixture of *trans*- (XII) and *cis*- (XI) 1-methyl-2-trifluoromethylcyclopropanes, in the ratio 54 : 46, in 68% yield. No insertion product



was identifiable (cf. ref. 12) but a minor component (3%) in the fraction of appropriate molecular weight was detected by g.l.c. The isomeric cyclopropanes were clearly distinguishable; the *cis*-isomer was prepared unambiguously by irradiation of the diazoethane in an excess of allene, to give 1-methylene-2-trifluoromethylcyclopropane (49%), followed by hydrogenation over platinum, which gave the *cis*-isomer preferentially. Although hydrogenation of 1-methyl-2-methylenecyclopropane is reported[13] to give only *cis*-dimethylcyclopropane and cleavage products, a low yield of the *trans*-isomer (XII) was also obtained.



Because of the rapidity of the competing 1,3-dipolar addition, the photochemical reaction with 3,3,3-trifluoropropene gave only a low yield (8%) of the cyclopropane fraction, which was not fully characterised. The photochemical reaction with hexafluorobut-2-ene was therefore carried out at —78°, in order to prevent interference by the ' dark ' cycloaddition. No pyrazoline at all was detectable under these conditions, showing that pyrazoline formation is not photocatalysed, and reinforcing the suggestion made above that the pyrazoline observed previously[1] in the room-temperature photolyses was due to a concurrent 1,3-dipolar ' dark ' reaction. The major product, apart from nitrogen (75%), appeared to be trifluoroacetaldazine (XIII), formed by attack of the carbene on the terminal nitrogen atom.

$$CF_3{\cdot}CHN_2 \xrightarrow{CF_3{\cdot}\dot{C}H} CF_3{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}CF_3$$

(XIII)

Presumably the olefin is inert to the electrophilic singlet state carbene which we have previously shown[12] to be the reactive species in the liquid phase.

Spectroscopic Properties.—(a) *N.m.r.* The n.m.r. spectra of ten pyrazoles are given in Table 1. The CF_3 groups in the 3,5-positions absorb in the narrow range 13·9—17·0 p.p.m. downfield from trifluoroacetic acid, whereas those in the 4-position are further downfield (21·1, 22·5 p.p.m.). These shifts appear to be sufficiently diagnostic for structural assignment, although the deshielding of the 4-substituent relative to those in the 3,5-positions is unexpected. The chemical shifts of the ^1H nuclei in the 3,5-positions in these pyrazoles are at the lower end of the range previously reported[9] for alkyl and aryl pyrazoles; apart from that in the 5-hydroxypyrazole, the shifts for the 4-position are considerably lower than those reported,[9] and although well separated from those for the 3,5-positions in Table 1, almost overlap the previously reported range. The deshielding in the present compounds is presumably due to the adjacent CF_3 groups in each case.

TABLE 1

Chemical shifts of trifluoromethyl pyrazoles

Compound: Substituent at:			Chemical shift [a]			
C-3	C-4	C-5	C-3	C-4	C-5	N–H
CF_3	H	H	−16·0	3·36	2·27	n.d.[b]
CF_3	CF_3	H	−16·4 [c]	−21·1 [c]	1·81	−1·95
CF_3	H	CF_3	−16·1	3·07	−16·1	−3·10
CF_3	CF_3	CF_3	−17·0 [d]	−22·5 [e]	−17·0 [d]	0·4
CF_3	H	Br	−16·3	3·35		−2·34
CF_3	Br	H	−16·5		2·20	−4·05
CF_3	Br	Br	−15·5			n.d.[b]
CF_3	H	CO_2Me	−15·6	2·85	6·06 [f]	−1·22
CF_3	H	OH	−15·3	4·18	−1·02 [g]	−1·02
CF_3	N_2Ph	OH	−13·9	2·5 [h]	−1·4 [g]	−2·3

[a] ^1H Shifts are τ values; ^{19}F shifts in p.p.m. to high field of interchange trifluoroacetic acid. Signals are singlets unless noted. [b] Not determined, but less than τ 0·0. [c] Quartet, $|J_{FF}|$ = 0·9 c./sec. [d] Quartet, $|J_{FF}|$ = 0·94 c./sec. [e] Septet, $|J_{FF}|$ = 0·94 c./sec. [f] CO_2Me. [g] OH. [h] N_2Ph.

The chemical shifts for the CF_3 groups in the 3 and 5-positions of six Δ^1-pyrazolines are given in Table 2.

TABLE 2

^{19}F Chemical shifts of Δ^1-pyrazolines

	Chemical shift [a]		
Compound	C-3	C-4	C-5
(I)	−5·1		
(IIa)	−5·2		
(IIIa)	−5·35		
(IIb)	−9·5		−9·5
(IIIb)	−8·8		−8·8
(IV)	−5·1	7·2	−5·1

[a] Positive signs to high field of interchange trifluoroacetic acid.

The range of shifts (—5·1 to —9·5 p.p.m.) for these positions is slightly greater than for the corresponding positions in the pyrazoles. The signals are all doublets ($|J|$ *ca.* 8 c./sec.), with, in the case of compound (IV), further splitting ($|J|$ 1·7 c./sec.) due to coupling through five bonds to the CF_3 group on the adjacent carbon atom. The only 4-CF_3 group which could be definitely assigned was 7·2 p.p.m. to high field of reference, considerably removed from the region for the 3,5-trifluoro-

---

[12] J. H. Atherton and R. Fields, *J. Chem. Soc.* (*C*), 1967, 1450.
[13] J. P. Chesick, *J. Amer. Chem. Soc.*, 1963, **85**, 2720.

methyl groups. However, the signals in the spectrum of pyrazoline (VII) at −12·2, −7·0, and +2·1 p.p.m., although not specifically assignable to the individual CF_3 groups (since each appeared as a complex multiplet) indicate that the range of chemical shifts for the 3,5-positions must be somewhat larger than that deduced from the other compounds. As expected, the ^1H spectra of the Δ^1-pyrazolines were extremely complex, and except for the signals due to the hydrogens at C-4 in compounds (IIb) and (IIIb) have not been analysed. The Δ^2-pyrazolines showed broad N–H signals. Further analysis has not been possible.

(b) *I.r.* The spectra of six Δ^1-pyrazolines all show absorption in the region 6·44—6·33 μ (1580—1552 cm.$^{-1}$) compared with the range 6·50—6·45 μ (1540—1550 cm.$^{-1}$) reported by Crawford *et al.*[14] for hydrocarbon-substituted pyrazolines and 6·37—6·31 μ (1570—1585 cm.$^{-1}$) suggested by Bellamy[15a] for the *cis*-azo-linkage. This absorption, although rather weak, is absent from the spectra of compounds free from nitrogen, and also from the spectra of the pyrazoles and Δ^2-pyrazolines (which show C=N at *ca.* 6·2 μ), and may thus be assigned to the N=N group.

The strongest band in the spectra of nine pyrazoles, seven cyclopropanes, a cyclopropene, and four open-chain compounds reported for the first time in the present work and in ref. 12 appears in the range 8·61—8·75 μ, and in view of previous assignments[16] is probably an asymmetrical stretching frequency of the CF_3 group. In the seven pyrazolines the band is at distinctly longer wavelength (8·80—8·96 μ). Other strong bands frequently occur in the regions 7·5, 7·75—7·95, and 8·1 μ, and are clearly associated with C–F vibrations, but there is rarely any absorption between 8·1 μ and $\lambda_{max.}$.

EXPERIMENTAL

Conventional vacuum-transfer techniques were used for all low-boiling materials. Hanovia U.V.S. 500 lamps and Pyrex tubes were used for all irradiations, which were started as soon as reactants reached room temperature. Products were separated by fractional condensation *in vacuo*, and by preparative g.l.c. Isomer ratios were determined by g.l.c., calibrated where possible with authentic pure samples, and by ^{19}F n.m.r. spectrometry (Perkin-Elmer R.10 spectrometer, repeated integration of CF_3-group signals) at 56·46 Mc./sec. Molecular weights were determined by Regnault's method.

Reagents.—(*a*) 2,2,2-Trifluorodiazoethane was prepared as described previously.[12]

(*b*) *Bromoacetylene.*[17] A solution of 1,2-dibromoethylene (16 g., 86 mmole), prepared by debromination[18] of *s*-tetrabromoethane, in ethanol (10 ml.) was added rapidly to a cold (0°) solution of potassium hydroxide (5 g., 90 mmole) in water (5 ml.), under nitrogen. The solution was warmed (½ hr.) to 80°, and the product was passed by way of a water condenser to a trap at −78°. Fractional condensation *in vacuo*, followed by rapid distillation at 10 mm. through a trap at −95° to remove traces of vinyl bromide, gave pure bromoacetylene (1·85 g., 20%) (Found: *M*, 105. Calc. for C_2HBr: *M*, 105).

Preparation of 3-*Trifluoromethylpyrazole.*—2,2,2-Trifluorodiazoethane (0·246 g., 2·2 mmole) and acetylene (0·232 g., 8·9 mmole) were sealed together *in vacuo* and kept at room temperature in the dark until colourless (4 weeks). Removal of the excess of acetylene (0·176 g., 76%) gave 3-*trifluoromethylpyrazole* (0·292 g., 97%) (Found: C, 35·3; H, 2·4; N, 20·4. $C_4H_3F_3N_2$ requires C, 35·3; H, 2·2; N, 20·6%), m.p. (after resublimation) 47—48°.

Preparation of other Pyrazoles and Pyrazolines.—The following compounds were prepared in the manner described above on a 2—15 mmole scale. The reactants were neat unless stated otherwise. The excess of olefin or alkyne was recovered quantitatively in each case.

(*a*) Ethylene (3 weeks) gave 3-*trifluoromethyl*-1-*pyrazoline* (90%) (Found: C, 34·7; H, 3·7; N, 20·3. $C_4H_5F_3N_2$ requires C, 34·8; H, 3·6; N, 20·3%), b.p. (Siwoloboff) 146°/777 mm.

(*b*) Propene (11 weeks) gave a mixture of *cis*- and *trans*-3-methyl-5-trifluoromethyl-1-pyrazolines (83%) (Found: C, 39·6; H, 4·6; N, 18·8. Calc. for $C_5H_7F_3N_2$: C, 39·5; H, 4·6; N, 18·4%), vap. press. 5 mm./20°.

(*c*) 3,3,3-Trifluoropropene (1 day) gave a mixture of *cis*- and *trans*-3,5-bis(trifluoromethyl)-1-pyrazolines (100%) (Found: C, 29·4; H, 2·0; N, 13·8. Calc. for $C_5H_4F_6N_2$: C, 29·1; H, 1·9; N, 13·6%) vap. press. 2 mm./20°.

(*d*) *trans*-1,1,1,4,4,4-Hexafluorobut-2-ene (<12 hr.) gave a mixture of 3,*trans*-4-*cis*,5-tris(trifluoromethyl)-1-pyrazoline (87%) and the Δ^2-isomer (13%) (Found: C, 26·6; H, 1·0; N, 10·0. Calc. for $C_6H_3F_9N_2$: C, 26·3; H, 1·1; N, 10·2%).

(*e*) *cis*-1,1,1,4,4,4-Hexafluorobut-2-ene (<12 hr.) gave a mixture of 3,*trans*-4,*trans*-5-tris(trifluoromethyl)-1-pyrazoline (81%) and the Δ^2-isomer (19%) (Found: N, 9·9%).

(*f*) Dimethyl maleate (2·30 g.) in dry ether (50 ml.) gave, after 12 hr., 3,4-*di*(*methoxycarbonyl*)-5-*trifluoromethyl*-2-*pyrazoline* (3·64 g., 90%) (Found: C, 38·0; H, 3·9%. $C_8H_9F_3N_2O_4$ requires C, 37·8; H, 3·6%), m.p. 86·5—87°. Dimethyl fumarate (12 hr.) gave an identical product (90%).

(*g*) Vinyl chloride (14 days) gave a colourless liquid which, on removal of the excess of olefin *in vacuo* at room temperature, crystallised exothermically. The solid was ground with anhydrous sodium carbonate and sublimed twice *in vacuo* to give 3(5)-trifluoromethylpyrazole (94%), identical with that prepared from acetylene above.

(*h*) Vinyl bromide (6 days) gave a colourless solution. An exothermic reaction took place when the neck of the tube was scored preparatory to opening it *in vacuo*, and a yellow solid was precipitated. Treatment as above gave 3(5)-trifluoromethylpyrazole (67%) and a tarry residue (0·1 g.).

(*i*) Vinyl fluoride (97%) was recovered after 5½ months in a Dreadnought glass tube with trifluorodiazomethane (1·165 g., 10·6 mmole). The other products were nitrogen (0·082 g., 28%), the recovered diazoethane (0·711 g., 61%), and unidentified volatile material (0·06 g.); polytrifluoromethylcarbene (0·182 g., 21%) was removed from the tube, but a considerable amount adhered firmly to the glass.

---

[14] R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Amer. Chem. Soc.*, 1966, **88**, 3959.

[15] L. J. Bellamy, 'Infrared Spectra of Complex Molecules,' Methuen, London, 1958, 2nd. edn., (*a*) p. 271; (*b*) p. 270.

[16] R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 1955, 1311.

[17] A. Sabanejeff, *J. der russ. phys.-chem. Gesellsch.*, 1885, **1**, 171; cf. *Ber.*, 1885, **18**, Referate, p. 374; J. U. Nef, *Annalen*, 1897, **298**, 355.

[18] A. Sabanejeff, *Annalen*, 1883, **216**, 251.

(*j*) Vinylidene fluoride (3·90 g., 100%), the diazoethane (1·50 g., 90%), and nitrogen (0·042 g., 5%) were recovered after 53 weeks in a silica tube. The only other product was a trace of polymeric material.

(*k*) 3,3,3-Trifluoropropyne, allowed to warm from −78° to +20° during 2 days, gave a mixture (100%) of 3,5-bis-(trifluoromethyl)pyrazole (94 ± 2% by g.l.c.) and 3(5),4-bis(trifluoromethyl)pyrazole (Found: C, 29·6; H, 1·3; N, 13·5. Calc. for $C_5H_2F_6N_2$: C, 29·4; H, 1·0; N, 13·7%), m.p. 57—60°. Trofimenko [19] reports m.p. 84° for a sample of 3,5-bis(trifluoromethyl)pyrazole prepared from the pentanedione and hydrazine.

(*l*) Bromoacetylene (6 days) gave a mixture (89%) of 4-bromo-3(5)-trifluoromethylpyrazole and 3(5)-bromo-5(3)-trifluoromethylpyrazole, shown by g.l.c. calibrated with the authentic materials (see below) to be in the ratio 1 : 5·3 (±0·5).

(*m*) Methyl propiolate (0·50 g.) in ether (2 ml.) allowed to react similarly, gave 3(5)-methoxycarbonyl-5(3)-trifluoromethylpyrazole (100%) (Found: C, 37·5; H, 2·7; N, 14·1. Calc. for $C_6H_5F_3N_2O_2$: C, 37·1; H, 2·6; N, 14·4%), m.p. 133—134° (lit.,[8] 134·5—135°), shown by n.m.r. and g.l.c. to contain no other isomer.

(*n*) Hexafluorobut-2-yne, allowed to warm from −78° to +20° overnight gave 3,4,5-*tris(trifluoromethyl)pyrazole* (97%) (Found: C, 27·0; H, 0·85; N, 10·1. $C_6HF_9N_2$ requires C, 26·5; H, 0·4; N, 10·3%), m.p. 49—53°.

Reactions (*m*) and (*n*) in particular can be explosive if the reactants are allowed to warm up too rapidly, or are insufficiently diluted.

Competition between Methyl Propiolate and 3,3,3-*Trifluoropropyne for* 2,2,2-*Trifluorodiazoethane.*—Because of the widely different boiling points of the reactants (102°/742 mm., −48°/760 mm., and 11·7°/760 mm. respectively) the reactions were carried out in ethereal solution in a sealed tube with a small (*ca.* 2 ml.) dead space. At the concentrations and temperature used, the vapour pressure of the mixture was less than 1 atmos., so that loss of trifluoropropyne from the reaction zone can be neglected. The procedure was as follows: methyl propiolate (*ca.* 0·6 g.) was degassed in a weighed tapped ampoule, the ampoule was reweighed, and ether (*ca.* 7 ml.) was added. Trifluoropropyne, equimolar with the propiolate, was condensed in at −196°, and the ampoule was warmed and shaken to ensure thorough mixing. The diazoethane (10 mole % of either alkyne) was condensed in at −196°, and the ampoule was sealed *in vacuo* at a constriction just below the tap, and shaken vigorously (8 hr.) while warming to room temperature. The ampoule was opened *in vacuo*, the excess of trifluoropropyne and some of the ether was removed, and the residual solution was examined by g.l.c. There was no detectable difference in the results at total concentrations in ether of *ca.* 50% and *ca.* 25%. The ratio of areas $C_6H_5F_3N_2O_2 : C_5H_2F_6N_2$ was 3·0 (±0·3) : 1 (8 determinations). Calibration of the g.l.c. apparatus with synthetic mixtures showed that the factor for conversion of area ratio to mole ratio was 0·88 ± 0·07 (8 determinations).

Reaction of Diazomethane with 3,3,3-*Trifluoropropene.*—3,3,3-Trifluoropropene (0·639 g., 6·65 mmole) was condensed into a trap (vol. 86 ml.) containing the diazomethane prepared by cleavage of *N*-nitroso-*N*-methyltoluene-*p*-sulphonamide [20] (5·1 g., 23·8 mmole) with sodium glycollate in n-decanol, followed by fractional condensation *in vacuo*. The trap was kept at −45° (3 hr.) in the dark; the pale yellow solution became colourless after a further ¾ hr. at 20°. Fractionation *in vacuo* gave 3-trifluoromethylpyrazoline (0·585 g., 100% based on olefin consumed), identical with that prepared above.

Reaction of Diazoethane with Trifluoropropene.—Diazoethane was prepared [21] by dropwise addition of *N*-nitroso-β-ethylaminoisobutyl methyl ketone (1·5 g., 8·7 mmole) to a stirred solution of sodium decanolate (3·9 g.) in n-decanol (25 ml.) at 30°, evacuated to <1 mm. *via* 3 traps at −78°, −95°, and −196°. Refractionation *in vacuo* gave diazoethane at −95°. 3,3,3-Trifluoropropene (0·793 g., 8·3 mmole) was condensed at −95° on to the diazoethane, and the mixture was allowed to warm to −45°. The exothermic reaction was complete in 5 min., and gave 3,3,3-trifluoropropene (0·322 g., 41%), and a mixture of *cis*- and *trans*-3-methyl-5-trifluoromethylpyrazolines (0·728 g., 98% on consumed olefin) identical with that obtained from propene and trifluorodiazoethane.

*Reaction of Diazomethane with Hexafluorobut-*2-*yne.*—A solution of diazomethane [from *N*-nitroso-β-methylaminoisobutyl methyl ketone [21] (4·0 g., 25·2 mmole)] in ether (50 ml.) was decolourised immediately on addition to hexafluorobut-2-yne (1·26 g., 7·8 mmole) in ether (50 ml.). Removal of the solvent and of the alkyne, followed by sublimation *in vacuo* gave 3(5),4-*bis(trifluoromethyl)pyrazole* (1·0 g., 63% based on initial alkyne) (Found: C, 29·6; H, 1·1; N, 13·8. $C_5H_2F_6N_2$ requires C, 29·4; H, 1·0; N, 13·7%), m.p. 121—123°.

Preparation of 3(5)-*Bromo*-5(3)-*trifluoromethylpyrazole.*—Hydrazine hydrate (3·0 g., 60 mmole) and ethyl 3,3,3-trifluoroacetoacetate [22] (11·0 g., 60 mmole) were heated [23] at 100° (2 hr.) cooled, and the product was recrystallised to give 3(5)-hydroxy-5(3)-trifluoromethylpyrazole (6·4 g., 70%) (Found: C, 31·4; H, 2·0; N, 18·6. Calc. for $C_4H_3F_3N_2O$: C, 31·6; H, 2·0; N, 18·4%), m.p. 214—217° (lit.,[23] m.p. 210—212°), which gave a 4-*benzeneazo-derivative* (71%) (Found: C, 47·15; H, 2·55; N, 21·9. $C_{10}H_7F_3N_4O$ requires C, 46·9; H, 2·7; N, 21·9%), m.p. 190—192° on treatment with phenyldiazonium chloride.

3(5)-Hydroxy-5(3)-trifluoromethylpyrazole (1·52 g., 10 mmole) and phosphorus oxybromide (4·3 g., 15 mmole), kept *in vacuo* at 120° (27 hr.), then cooled and carefully treated with water, gave 3(5)-*bromo*-5(3)-*trifluoromethylpyrazole* (1·6 g., 74%) (Found: C, 22·0; H, 0·9; N, 13·3. $C_4H_2BrF_3N_2$ requires C, 22·3; H, 0·9; N, 13·0%), m.p. 72—76°, after sublimation *in vacuo*. Phosphorus tribromide was an ineffective brominating agent, as Michaelis [24] found for other pyrazolones.

Bromination of 3(5)-*Trifluoromethylpyrazole.*—(*a*) 3(5)-Trifluoromethylpyrazole (0·44 g., 3·2 mmole) was kept with bromine (0·55 g., 3·4 mmole) and anhydrous sodium acetate (0·25 g.) in carbon tetrachloride (5 ml.) at room temperature (15 hr.). G.l.c. showed the presence of the original pyrazole (18%); the mixture was evaporated to dryness, the solid was dissolved in the minimum of boiling water, and cooled, and the resulting suspension was heated gently with bromine (0·1 g.). The solid deposited was

---

[19] S. Trofimenko, *J. Amer. Chem. Soc.*, 1967, **89**, 3165.

[20] Th. J. de Boer and H. J. Backer, *Org. Synth.*, Coll. Vol. IV, 1963, p. 943.

[21] E. C. S. Jones and J. Kenner, *J. Chem. Soc.*, 1933, 363.

[22] A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Amer. Chem. Soc.*, 1947, **67**, 1819.

[23] G. deStevens, A. Halamandaris, P. Wenk, and L. Dorfman, *J. Amer. Chem. Soc.*, 1959, **81**, 6292.

[24] A. Michaelis and H. Behn, *Ber.*, 1900, **33**, 2595.

recrystallised from water to give 4-*bromo*-3(5)-*trifluoromethylpyrazole* (0·40 g., 58%) (Found: C, 22·6; H, 1·1; N, 13·0%), m.p. 112°; g.l.c. showed that none of the dibromo-compound was present.

(*b*) Bromine (0·41 g., 2·6 mmole) was added in two portions to 3(5)-trifluoromethylpyrazole (0·17 g., 1·25 mmole) and sodium acetate (0·5 g.) in water (5 ml.) the mixture being heated on a steam-bath until colourless. Extraction with ether, evaporation of the solvent, sublimation of the residue *in vacuo*, and recrystallisation (water) gave 3(5),4-*dibromo*-5(3)-*trifluoromethylpyrazole* (0·28 g. 76%) (Found: C, 16·2; H, 0·6; N, 9·45. $C_4HBr_2F_3N_2$ requires C, 16·4; H, 0·3; N, 9·5%), m.p. 99·5—100°.

Irradiation of 2,2,2-*Trifluorodiazoethane*.—(*a*) *With an excess of ethylene*. 2,2,2-Trifluorodiazoethane (2·03 g., 18·5 mmole) and ethylene (2·00 g., 71·5 mmole), irradiated (20 hr.) gave (i) nitrogen (0·464 g., 90%), (ii) a mixture of trifluoroethylene (0·20 g., 13%) and ethylene (1·68 g., 84%), (iii) a mixture of *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0·24 g., 16%) and trifluoromethylcyclopropane (1·06 g., 52%), and (iv) a fraction (0·35 g.) containing mainly 3-trifluoromethyl-1-pyrazoline (0·25 g., 10%). The cyclopropane was purified by g.l.c. (Found: C, 43·5; H, 4·6%; *M*, 110. Calc. for $C_4H_5F_3$: C, 43·6; H, 4·6%; *M*, 110.) Its ^{19}F n.m.r. spectrum was a doublet (δ_{TFA} −8·24 p.p.m., $|J_{FH}|$ 6·8 c./sec.); the ^{1}H spectrum was a multiplet (δ_{Benz} +5·48 p.p.m., CH·CF$_3$) and a complex 4-hydrogen pattern (δ_{Benz} 6·12—6·24 p.p.m.).

(*b*) *With an excess of propene*. The diazoalkane (1·96 g., 17·8 mmole) and propene (3·00 g., 71·4 mmole) (19 hr.) gave nitrogen (0·47 g., 95%), a mixture (2·84 g.) (Found: *M*, 45·1) consisting mainly of propene, together with some trifluoroethylene and *trans*-hexafluorobut-2-ene, and a second mixture (1·58 g.) (Found: *M*, 124) shown by g.l.c. to consist (>95%) of two components (54 : 46). These were separated to give : (a) the major component 1-*methyl*-trans-2-*trifluoromethylcyclopropane* (0·81 g., 37%) (Found: C, 48·5; H, 5·35%; *M*, 124. $C_5H_7F_3$ requires C, 48·4; H, 5·65%; *M*, 124), b.p. (isoteniscope) 37·8° ± 0·3°, L_V = 7·03 kcal. mole^{-1}, Trouton's constant = 22·6 cal. deg.$^{-1}$ mole^{-1}; its ^{19}F n.m.r. spectrum was a doublet (δ_{TFA} −10·4 p.p.m., $|J_{HF}|$ 6·55 c./sec.) and the ^{1}H spectrum was complex; and (b) 1-*methyl*-cis-2-*trifluoromethylcyclopropane* (0·69 g., 31%) (Found: C, 48·5; H, 5·5%; *M*, 124), b.p. 44·6° ± 0·2°, L_V = 7·30 kcal. mole^{-1}, Trouton's constant 23·1 cal. deg.$^{-1}$ mole^{-1}; its ^{19}F n.m.r. spectrum was a doublet [δ_{TFA} −17·6 p.p.m., $|J_{FH}|$ = 8·4 c./sec. with further splitting (*ca.* 1 c./sec.)], and the ^{1}H spectrum was complex.

(*c*) *With an excess of allene*. The diazoalkane (1·79 g., 16·3 mmole) and allene (5·20 g., 130 mmole) (8 hr.) gave nitrogen (0·41 g., 91%), a mixture (5·20 g.) consisting mainly of allene, with some hexafluorobutene and possibly trifluoroethylene, and 1-*methylene*-2-*trifluoromethylcyclopropane* (0·98 g., 49%) (Found: C, 49·4; H, 4·2%; *M*, 121. $C_5H_5F_3$ requires C, 49·2; H, 4·1%; *M*, 122), b.p. 40·5° ± 0·3°, L_V = 7·05 kcal. mole^{-1}, Trouton's constant = 22·5 cal. deg.$^{-1}$ mole^{-1}, purified by g.l.c. The ^{19}F n.m.r. spectrum was a doublet (δ_{TFA} = −9·5 p.p.m., $|J_{FH}|$ = 6·55 c./sec.) and the ^{1}H spectrum showed multiplets at δ_{Benz} +1·35, +4·9, and +5·45 p.p.m. in the ratio 2 : 1 : 2.

The methylenecyclopropane (0·158 g., 1·29 mmole) in glacial acetic acid (1 ml.) was treated with hydrogen (55 cm.) and Adams catalyst (0·024 g.). Hydrogen (1·16 mmole, 90%) was absorbed (5 min.) and fractionation gave a mixture (0·144 g., 91%) shown by g.l.c., ^{19}F n.m.r. and i.r. to contain cyclopropane (XI) (67%), (XII) (11%), and two unknown materials (total 12%).

(*d*) *In the liquid phase with* trans-1,1,1,4,4,4-*hexafluorobut*-2-*ene*. The diazoethane (0·78 g., 7·1 mmole) and the butene (4·68 g., 28·6 mmole) were irradiated (50 ml. Pyrex tube) through a clear Dewar vessel containing solid CO$_2$–methylated spirit at −78° (24 hr.), to give nitrogen (0·15 g., 75%), a small amount of trifluoroethylene (<0·3 mmole), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (4·95 g., 106%), contaminated with *ca.* 3% of the *cis*-isomer, and a mixture (0·186 g., 1·0 mmole) (Found: *M*, 192. Calc. for $C_4H_2F_6N_2$: *M*, 192). The ^{19}F n.m.r. of this mixture showed major absorptions at δ_{CFCl_3} +63·4 p.p.m. (t, $|J| \approx 4$ c./sec., 19%), 70·6 p.p.m. (d, $|J|$ = 4 c./sec., 9%), +71·6 p.p.m. (d, $|J|$ = 3·8 c./sec., 56%) and 73 p.p.m. (d, $|J| \approx 5$ c./sec., 6%) and several smaller absorptions. The complex ^{1}H spectrum showed a quartet (δ_{Benz} −0·7 p.p.m. $|J| \approx 4$ c./sec., 42%) whose shift is consistent with the aldazine structure,[25] and several broad absorptions. The i.r. spectrum showed weak absorptions at 6·0 μ, again consistent [15b] with the azine structure.

Thermal Reaction of 2,2,2-*Trifluorodiazoethane with Ethylene*.—The diazoethane (0·251 g., 2·3 mmole) and ethylene (0·245 g., 8·7 mmole), kept at 100° (5 hr.) gave nitrogen (0·027 g., 42%), trifluoromethylcyclopropane (0·008 g., 3%), hexafluorobut-2-ene (0·007 g., 4%), 3-trifluoromethyl-1-pyrazoline (0·141 g., 45%), and solid material, mainly polytrifluoromethylcarbene (*ca.* 0·08 g., 40%).

We are grateful to the S.R.C. for a studentship (to J. H. A.).

[7/1637 *Received, December* 14*th*, 1967]

---

[25] E. Arnal, J. Elguero, R. Jacquier, C. Marzin, and J. Wylde, *Bull. Soc. chim. France*, 1965, 877.