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SOME POLYFLUORINATED ENYNES

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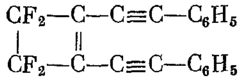
In 1960 by the reactions of the sodium derivatives of ethynylbenzene and 1-hexyne with tetrafluoroethylene fluorinated enynes were obtained which consisted in the products of the symmetrical replacement of two fluorine atoms in tetrafluoroethylene by phenylethynyl or 1-hexynyl groups, $R-C\equiv C-CF=CF-C\equiv C-R$ [1]. We have shown that the analogous reactions with chlorotrifluoroethylene, hexafluoropropene, and perfluoroisobutene lead to the monosubstituted products (I)-(III), which are formed as a result of the replacement of the terminal vinyl fluorine atom. In the case of hexafluorocyclobutene the disubstituted product (IV) is formed.

$$CFCl=CF-C\equiv C-C_6H_5 \qquad (I)$$

$$CF_3CF=CF-C\equiv C-C_6H_5 \qquad (II)$$

$$(CF_3)_2C=CF-C\equiv C-C_6H_5 \qquad (III)$$



$$\begin{array}{l} CF_2-C-C\equiv C-C_6H_5 \\ \ \ | \qquad \| \\ CF_2-C-C\equiv C-C_6H_5 \end{array}$$

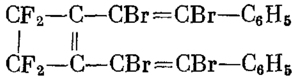
(IV)

It was of interest to compare the activities of the double and triple bonds of substances of this type. In the IR spectra the fluorine-weighted double bond and the triple bond absorb at 1670-1700 and 2210-2220 cm^{-1} respectively. Our investigations showed that in polyfluorinated enynes considerable exaltation of molecular refraction is observed (2-6 units); it is at its highest in 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne. The comparative evaluation of the activities of the double and triple bonds in these substances was carried out on the basis of the results of their reactions with bromine and with diazomethane. Experiment showed that in the main the triple bond is brominated with formation of the dibromides (V)-(VIII).

$$CFCl=CF-CBr=CBr-C_6H_5 \qquad (V)$$

$$CF_3CF=CF-CBr=CBr-C_6H_5 \qquad (VI)$$

$$(CF_3)_2C=CF-CBr=CBr-C_6H_5 \qquad (VII)$$



$$\begin{array}{l} CF_2-C-CBr=CBr-C_6H_5 \\ \ \ | \qquad \| \\ CF_2-C-CBr=CBr-C_6H_5 \end{array}$$

(VIII)

In the IR spectra of the dibromides the double bond frequency at about 1700 cm^{-1} (fluorine at a double bond) is preserved, the triple bond disappears, and a new frequency characteristic for a $>C=C<$ bond conjugated with a benzene nucleus appears. Further bromination is achieved only on exposure to UV radiation, and in the case of (V) and (VI) it leads to the tetrabromides (IX) and (X).

$$CFClBr-CFBr-CBr=CBr-C_6H_5 \qquad (IX)$$

$$CF_3CFBr-CFBr-CBr=CBr-C_6H_5 \qquad (X)$$

Their structures follow from the disappearance of the IR band at about 1700 cm^{-1} and the retention of the double bond frequency at about 1590 cm^{-1}. (VII) does not form a tetrabromide, which is in keeping with the behavior of isobutene toward bromine. It is evident that the donation of electron density from the bromine-substituted double bond is unable to make up the deficiency in the perfluoroisobutenyl group. The activities of the double and triple bonds in the polyfluoro enynes investigated were also compared for the case of the reaction of 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne with the nucleophilic reagent diazomethane. Experiment shows that unsubstituted perfluoroisobutene reacts readily with diazomethane with formation of a pyrazoline.

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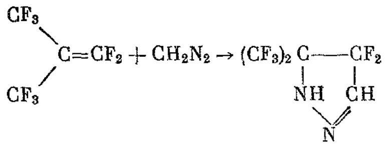
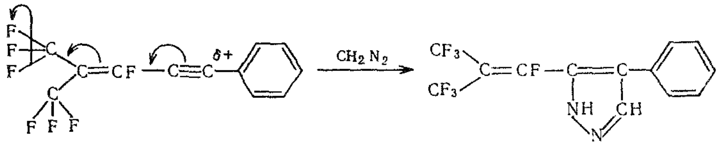


It was therefore impossible to guess the result of the reaction of 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne with diazomethane. It was found that it reacts with ethereal diazomethane at room temperature with formation of 4-phenyl-5-perfluoroisobutenylpyrazole. The structure of this was proved by the IR spectrum, which contains no frequency in the region of 2200 cm^{-1}, but contains an absorption band at about 1700 cm^{-1} characteristic for a fluorine-weighted double bond.



The triple bond therefore proved to be the more active, evidently because of the strong conjugation in the molecule of 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne. This view is confirmed by the fact that 3,4,5,5,5-pentafluoro-1-phenyl-3-penten-1-yne and 1-chloro-1,2-difluoro-4-phenyl-1-buten-3-yne do not react with diazomethane.

EXPERIMENTAL

Preparation of 3,4,5,5,5-Pentafluoro-1-phenyl-3-penten-1-yne (II), 3,5,5,5-Tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne (III), and Tetrafluoro-1,2-bisphenylethynylcyclobutene (IV). A four-necked flask fitted with stirrer, reflux condenser, and tube for the passage of gas was charged with a suspension of phenylethynylsodium in dry ether prepared from 0.1 mole of sodium wire and 0.1 mole of ethynylbenzene, and with vigorous stirring 0.1 mole of the perfluoro olefin was passed in at room temperature. The reaction mixture was left overnight at room temperature. The precipitate of sodium fluoride was filtered off and washed several times with dry ether. From the ethereal solution the polyfluorophenylpentenyne was isolated by distillation. Tetrafluoro-1,2-bisphenylethynylcyclobutene was isolated by crystallization from ethanol. The physical constants and analyses of the compounds obtained are given in Table 1. The yield was calculated on the amount of the perfluoro olefin that reacted.

Preparation of 1-Chloro-1,2-difluoro-4-phenyl-1-buten-3-yne (I). A 250-ml metal ampule was charged with a suspension of phenylethynylsodium in dry ether, prepared from 0.2 mole of sodium wire and 0.2 mole of ethynyl benzene, and also 0.3-0.4 mole of chlorotrifluoroethylene. The metal ampule was heated for 6 h at 80°. The pressure was then released, and the precipitate of sodium fluoride was filtered off and washed several times with ether. By distillation we isolated (I). The physical properties and results of analysis are given in Table 1.

Preparation of α,β-Dibromostyryl Polyfluoroalkenes. The polyfluoro enyne was brominated with bromine in chloroform solution with cooling with ice water. The yields of the dibromides were quantitative. The physical constants and analyses are given in Table 2.

Bromination of α,β-Dibromostyryl Polyfluoroalkenes. A mixture of 0.1 mole of the α,β-dibromostyryl polyfluoroalkene and 0.1 mole of bromine in chloroform was exposed to UV radiation for 10 h. The tetrabromide was isolated by distillation. Physical constants and analyses are given in Table 2.

Reaction of Diazomethane with Perfluoroisobutene. Liquid perfluoroisobutene was added to ethereal diazomethane at –30°. The temperature was gradually brought to that of the room. By distillation we isolated 4,4-difluoro-5,5-bistrifluoromethyl-2-pyrazoline, b.p. 103-104°, m.p. 28-29°; n_D^{30} 1.335; d_4^{30} 1.599. Yield 71%. Found %: C 25.05; H 0.80; F 62.91; N 11.62. $C_5H_2N_2F_8$. Calculated %: C 24.79; H 0.82; F 62.81; N 11.57.

Reaction of Diazomethane with 3,5,5,5-Tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne. 0.05 mole of 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-

TABLE 1

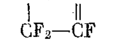
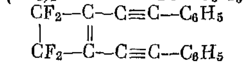
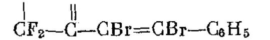
Cpd. No.	Perfluoro olefin	Polyfluoro enyne	Yield, %	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found				Calculated			
							MR	C, %	H, %	F, %	*MR*	C, %	H, %	F, %
I	$CFCl{=}CF_2$	$CFCl{=}CF-C{\equiv}C-C_6H_5$	80	87 (6)	1,5560	1,2512	51,04	60,52	2,25	20,52	47,45	60,45	2,51	19,14
II	$CF_3CF{=}CF_2$	$CF_3CF{=}CF-C{\equiv}C-C_6H_5$	80	78 (8)	1,4900	1,2740	51,84	56,90	2,16	41,29	47,64	57,32	2,15	40,98
III	$(CF_3)_2C{=}CF_2$	$(CF_3)_2C{=}CF-C{\equiv}C-C_6H_5$	60	85 (10)	1,4815	1,3620	58,96	50,74	2,06	46,86	52,54	51,06	1,77	47,16
IV	 $\begin{array}{l}CF_2-CF\\ \mid\qquad \parallel\\ CF_2-CF\end{array}$	 $\begin{array}{l}CF_2-C-C{\equiv}C-C_6H_5\\ \mid\qquad \parallel\\ CF_2-C-C{\equiv}C-C_6H_5\end{array}$	10	M.p. 58	—	—	—	73,46	3,01	23,43	—	73,62	3,06	23,31

TABLE 2

Cpd. No.	α, β-Dibromostyryl polyfluoro-alkenes and -alkanes	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found						Calculated					
					MR	C, %	H, %	F, %	Cl, %	Br, %	*MR*	C, %	H, %	F, %	Cl, %	Br, %
V	$CFCl{=}CF-CBr{=}CBr-C_6H_5$	124 (4)	1,5880	1,8340	65,77	33,54	1,32	10,23	—	43,9	64,51	33,47	1,39	10,60	—	44,63
VI	$CF_3CF{=}CF-CBr{=}CBr-C_6H_5$	103 (4)	1,5225	1,7945	66,66	33,52	1,25	24,38	—	40,67	64,70	33,67	1,27	24,23	—	40,81
VII	$(CF_3)_2C{=}CF-CBr{=}CBr-C_6H_5$	114 (9)	1,4940	1,7750	72,4	33,49	1,22	29,40	—	35,10	69,53	32,58	1,13	30,09	—	36,20
VIII	 $\begin{array}{l}CF_2-C-CBr{=}CBr-C_6H_5\\ \mid\qquad \parallel\\ CF_2-C-CBr{=}CBr-C_6H_5\end{array}$	M.p. 219	—	—	—	37,16	1,58	12,00	—	49,81	—	37,15	1,54	11,76	—	49,53
IX	$CFClBr-CFBr-CBr{=}CBr-C_6H_5$	152 (0,04)	1,6230	—	—	23,64	1,08	7,91	6,70	61,77	—	23,14	0,96	7,33	6,84	61,71
X	$CF_3CFBr-CFBr-CBr{=}CBr-C_6H_5$	162 (5)	1,5690	—	—	23,70	1,01	18,52	—	58,69	—	23,91	0,90	17,20	—	57,57

1-yne was added gradually to ethereal diazomethane at 5-10°. The reaction mixture was left at room temperature overnight. Ether was vacuum-distilled off. The product, 4-phenyl-5-perfluoroisobutenylpyrazole, had m.p. 129-131° (chloroform, benzene). Yield 61%. Found %: C 48.11; H 2.17; F 40.94; N 8.88. $C_{13}H_7F_7N_2$. Calculated %: C 48.14; H 2.16; F 41.05; N 8.64.

CONCLUSIONS

1. The following polyfluoro enynes were prepared: 3,4,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne, 3,4,5,5,5-pentafluoro-1-phenyl-3-penten-1-yne, 1-chloro-1,2-difluoro-4-phenyl-1-buten-3-yne, and tetrafluoro-1,2-bisphenylethynylcyclobutene.

2. Bromine in chloroform solution adds only at the triple bond of the enynes with formation of the corresponding dibromides. The further bromination of the dienes can be effected under UV irradiation, and the fluorine-substituted, not the bromine-substituted, double bond takes up the bromine. Only one molecule of bromine will add to 3,4,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne.

3. With diazomethane perfluoroisobutene forms 4,4-difluoro-5,5-bistrifluoromethyl-2-pyrazoline, and diazomethane added to 3,5,5,5-tetrafluoro-1-phenyl-4-(trifluoromethyl)-3-penten-1-yne with formation of 4-phenyl-5-perfluoroisobutenylpyrazoline.

LITERATURE CITED

1. D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, J. Amer. Chem. Soc., 82, 19, 5116 (1960).