but a negligible amount of polymer formed even after refluxing overnight. Addition of 0.25 g of sodium methoxide caused polymer to form rapidly. After refluxing overnight the solution was filtered and 9.9 g of dried polymer recovered.

Dehalogenation of Bromodifluoroacetyl Chloride in Benzaldehyde.—A mixture of 12 g of amalgamated zinc and 50 ml of benzaldehyde was stirred at 0 to −10° while 10 ml (20 g, 0.1 mole) of bromodifluoroacetyl chloride was added dropwise. Volatile material was then evaporated into a Dry Ice trap under vacuum while the pot was heated with boiling water. Redistillation of material in the trap gave 1.5 g of difluorostyrene, bp 78° (100 mm), $n^{25}D$ 1.4855. The infrared spectrum agreed with that of a known sample.[15]

Registry No.—1 (X = Cl), 15080-17-8; 1 (X = Br), 15080-18-9; **2,** 15156-62-4; **3,** 433-53-4; **4,** 15156-63-5; difluoroketene, 683-54-5; methyl trifluorovinyl ether, 3823-94-7; methyl trifluorovinyl ether dibromide, 15080-20-3; bromodifluoroacetyl chloride, 3832-48-2; bromodifluoroacetyl bromide, 1796-12-9; methyl bromodifluoroacetate, 683-98-7; α,α-difluoro-β,β-dimethyl-β-hydroxypropionic acid, 15080-23-6.

(15) J. L. Anderson, U. S. Patent 2,733,278 (1956); *Chem. Abstr.*, **50**, 15575 (1956).

Fluorinated Acetylenic Alcohols and Derived Allenes

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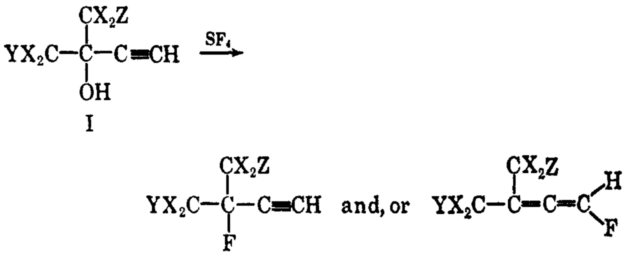
Acetylenic alcohols derived from several haloacetones were converted into novel fluorinated allenes by treatment with sulfur tetrafluoride. In some cases the corresponding fluorinated acetylenes were also formed by replacement of the hydroxyl group by fluorine and in one instance the fluorinated acetylene was the sole product. Two of the allenes were thermally rearranged to the corresponding butadienes. The mechanism of the reaction is discussed and the spectroscopic properties of the new compounds are reported.

As part of a general program of the reactions and derivatives of hexafluoroacetone and related compounds[1] the preparation of haloalkylacetylenes (II) was attempted by treatment of the corresponding acetylenic alcohols (I) with sulfur tetrafluoride.



$$YX_2C-C(CX_2Z)(OH)-C\equiv CH \xrightarrow{SF_4}$$

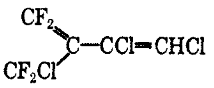
I

$$YX_2C-CF(CX_2Z)-C\equiv CH \quad \text{and, or} \quad YX_2C-C(CX_2Z)=C=C(H)F$$

II III

a, X = Y = Z = F d, X = Y = F; Z = H
b, X = Y = F; Z = Cl e, X = F; Y = Z = H
c, X = F; Y = Z = Cl f, X = F; Y = Cl; Z = H

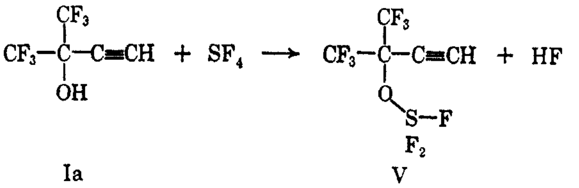
Alcohols Ia and Ic have been known for some time.[2,3] The remainder are new compounds. The use of SF_4 for the smooth replacement of hydroxyl by fluorine in other types of alcohols has been reported by England.[4] It was found in the present study, however, that the type II product was formed in only minor yield from alcohols Id, e, and f, and not at all from alcohols Ia, b, and c. The major (or sole) product in all of these cases was the corresponding allene III. It is noteworthy that the reaction proceeds easily even at room temperature or below, even though this type of alcohol, as pointed out by Simmons and Wiley[3] in the case of Ic, is unusually inert toward acidic reagents which normally afford replacement of the hydroxyl group. The only exception observed by these authors was the reaction of Ic with phosphorus pentachloride, which resulted in the formation of the 1,3-butadiene (IV). It is probable that the formation of IV from Ic is related to the chemistry described in the present paper.



$$CF_2=C(CF_2Cl)-CCl=CHCl$$

IV

While the mechanism of the reaction resulting in allene formation has not been investigated, it is possible to postulate a reasonable pathway. It is suggested that the first stage is interaction of the alcohol and sulfur tetrafluoride. This is derived from a mechanism which has been suggested for the reaction of SF_4 with carbonyl groups in the presence of a suitable Lewis acid.[5] In our mechanism it is possible to make use of the fact that SF_4 itself is known to be a weak Lewis acid[6] and we might therefore postulate that first it forms a complex in which oxygen is the donor. The complex would then lose HF to form the intermediate V. However, in view of the strongly acidic nature of such fluorinated alcohols,[7] it is more likely that there is formed initially a strong hydrogen bond between the hydroxyl proton and a fluorine atom of SF_4. This would pave the way for electron donation by oxygen to sulfur, with subsequent elimination of HF to form V. The net result is shown in eq 1. This intermediate (V) can then rearrange by an



$$CF_3-C(CF_3)(OH)-C\equiv CH + SF_4 \longrightarrow CF_3-C(CF_3)(O-SF_3)-C\equiv CH + HF \quad (1)$$

Ia V

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[1] This is paper XIII in the series on perhalo ketones and their derivatives. For paper XII, see *J. Org. Chem.*, **31**, 3174 (1966). Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill. Sept 1967.

[2] I. L. Knunyants, C. Ch'ing-yun, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. 4, 686 (1960).

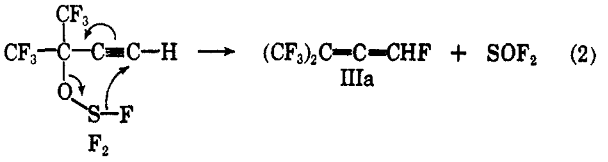
[3] H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

[4] D. C. England, U. S. Patent 3,236,894 (1966).

[5] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[6] E. L. Muetterties, W. D. Phillips, and W. C. Smith, U. S. Patent 2,897,055 (1959).

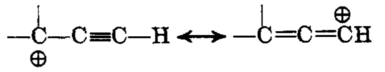
[7] I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 923 (1964).



$$\mathrm{CF_3-\underset{O-SF_2}{\overset{CF_3}{C}}-C{\equiv}C-H \longrightarrow \underset{IIIa}{(CF_3)_2C{=}C{=}CHF} + SOF_2} \quad (2)$$

V

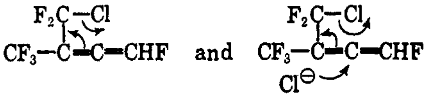
intramolecular (SNi) pathway to an allene (eq 2). Such an occurrence would be facilitated by the strong electron-withdrawing influence of the two CF_3 groups. This causes the oxygen-bearing carbon to assume a positive character, which in turn attracts the π electrons of the triple bond and results in the terminal carbon being susceptible to nucleophilic attack by the fluorine. Analogous SNi mechanisms have been proposed for the formation of allenes from unhalogenated tertiary acetylenic alcohols and thionyl chloride.[8] The absence of any acetylenic product is also a point in favor of an intramolecular rearrangement since there is no reason why an intermolecular process would be expected to result in a single product. In such an SN1 reaction the intermediate carbonium ion would be resonance stabilized (eq 3) and theoretically both possible structures could appear in the products.



$$-\underset{\oplus}{\overset{|}{C}}-C\equiv C-H \longleftrightarrow -\overset{|}{C}=C=\overset{\oplus}{C}H \quad (3)$$

More convincingly, the fact that these alcohols can be distilled through hot concentrated sulfuric acid without structural change indicates that the carbonium ion species is not readily formed and would not be expected to be present under the mild conditions of the present reaction.

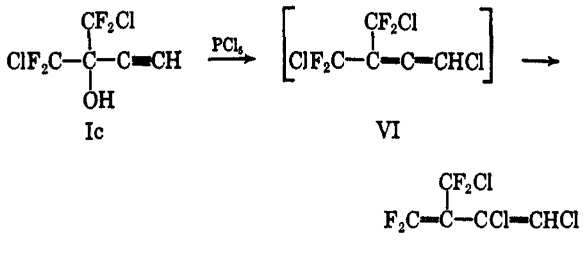
Alcohols Ib and c, by similar reactions, gave allenes IIIb and c. Again no acetylenic products were observed and a similar SNi mechanism is presumed to operate. However, it was noted that these latter allenes underwent a further, facile rearrangement and formed halogenated 1,3-butadienes on warming to 60°. This change, which was essentially quantitative, also occurred when the samples were stored at room temperature for several months; it could be accelerated by the addition of aqueous hydrochloric acid. These changes, which occur fastest with IIIb, may be represented by



$$\mathrm{CF_3-\overset{F_2C-Cl}{C}{=}C{=}CHF \quad and \quad CF_3-\overset{F_2C-Cl}{C}{=}C{=}CHF \quad Cl^{\ominus}}$$

Isomerism of this nature was not observed when IIIa was held at room temperature.

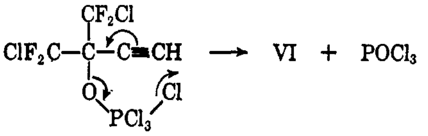
These results render highly probable the proposal by Simmons and Wiley[3] that an allene VI is intermediate in the conversion of carbinol Ic to diene IV by the action of phosphorus pentachloride (eq 4).



$$\mathrm{ClF_2C-\underset{OH}{\overset{CF_2Cl}{C}}-C{\equiv}CH \xrightarrow{PCl_5} \left[ClF_2C-\overset{CF_2Cl}{C}{=}C{=}CHCl\right] \longrightarrow F_2C{=}\overset{CF_2Cl}{C}-CCl{=}CHCl} \quad (4)$$

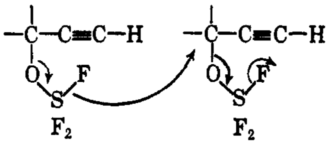
Ic VI IV

We regard this reaction to involve, as its first step, formation of a phosphorus compound of type VII (eq 5) rather than "direct attack of phosphorus pentachloride on the terminal acetylenic carbon atom," as previously proposed.[3] Owing to the high reaction temperature necessary (50°), the allene then would rearrange immediately to the observed 1,3-butadiene. When the alcohols Id, e, and f were subjected to similar treatment with SF_4 an allene III again resulted, but was now accompanied by some of the corresponding acetylenic product, II. Although it is possible to account for these results by invoking an SN1 mechanism this again seems unlikely since the alcohols are not affected by treatment with hot, concentrated sulfuric acid. It is more plausible to consider that two competitive reactions are taking place. Since there are no longer two trifluoromethyl groups attached to the hydroxyl-bearing carbon the positive character of the proton bearing acetylenic carbon is considerably reduced. Thus, the intramolecular production of the allene is slower; a slower intermolecular displacement may be able to compete.

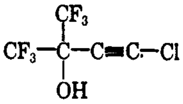


$$\mathrm{ClF_2C-\underset{O-PCl_3-Cl}{\overset{CF_2Cl}{C}}-C{\equiv}CH \longrightarrow VI + POCl_3} \quad (5)$$

VII

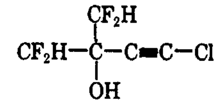


Similar results were obtained when the alcohols were modified by the replacement of the acetylenic proton by chlorine. Thus in the alcohol[9] VIII the influence of the two trifluoromethyl groups is countered sufficiently by the presence of the chlorine atom that the acetylenic isomer predominates in the products X and XI. When alcohol IX was treated with sulfur tetra-



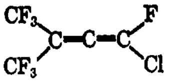
$$\mathrm{CF_3-\underset{OH}{\overset{CF_3}{C}}-C{\equiv}C-Cl}$$

VIII

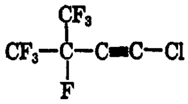


$$\mathrm{CF_2H-\underset{OH}{\overset{CF_2H}{C}}-C{\equiv}C-Cl}$$

IX

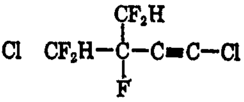


X



$$\mathrm{CF_3-\underset{F}{\overset{CF_3}{C}}-C{\equiv}C-Cl}$$

XI



$$\mathrm{CF_2H-\underset{F}{\overset{CF_2H}{C}}-C{\equiv}C-Cl}$$

XII

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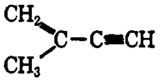
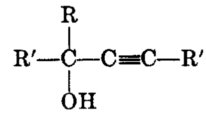
[8] (a) Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.* 24 (1959). (b) S. R. Landor, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society 1965, p 164. (c) The reaction of $(CH_3)_2C(OH)C{\equiv}CH$ with SF_4 does not, however, result in any allene formation. This explosively vigorous reaction resulted only in the following compounds.

$(CH_3)_2CFC{\equiv}CH$



[9] The α-chloro alcohols were prepared by the method of H. G. Viehe, *Ber.* 92, 1950 (1959); U. S. Patent 3,053,911 (1962).

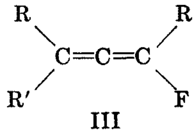
TABLE I
PHYSICAL DATA FOR ACETYLENIC ALCOHOLS


$R'\text{—}C(R)(OH)\text{—}C{\equiv}C\text{—}R''$

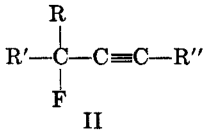
Compd	R	R′	R″	Yield, %, based on ketone	Bp °C	$n^{25}D$	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl
Ia	CF_3	CF_3	H	75.4	77[a]	1.3064						
Ib	CF_3	CF_2Cl	H	59.8	107	1.3530	28.80	0.97		28.70	1.11	
Ic	CF_2Cl	CF_2Cl	H	68.9	139[b]	1.3939						
Id	CF_3	CF_2H	H	67.4	97.5	1.3334	34.46	1.74		34.17	1.81	
Ie	CF_2H	CF_2H	H	67.8	122.5	1.3634	38.47	2.58		38.45	2.61	
If	CF_2Cl	CF_2H	H	46.7	131	1.3801	31.52	1.59	18.61	31.49	1.69	18.76
VIII	CF_3	CF_3	Cl	83.4	104	1.3473	26.51	0.45	15.65	26.65	0.70	15.35
IX	CF_2H	CF_2H	Cl	64.4	142	1.3965	31.52	1.59	18.61	31.76	1.54	18.36

[a] Lit.[2] gives bp 77.5–78.5°; $n^{20}D$ 1.3205. [b] Lit.[3] gives bp 41–42° (16 mm); $n^{25}D$ 1.3940.

TABLE II
PRODUCTS OF SF_4 REACTION


III

or


$R'\text{—}C(R)(F)\text{—}C{\equiv}C\text{—}R''$

II

Products	R	R′	R″	Yield, %, based on alcohol	% allene	% acetylene	Bp, °C	$n^{25}D$	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl
IIIa	CF_3	CF_3	H	45.0	100	0	34	<1.3	30.94	0.52	68.52[a]	30.60	0.57	68.40[a]
IIIb	CF_3	CF_2Cl	H	30.4	100	0	62		28.53	0.48	16.84	28.57	0.59	16.59
IIIc	CF_2Cl	CF_2Cl	H	57.5	100	0	98 38 (57 mm)	1.3747	26.65	0.44	31.42	26.19	0.55	31.13
IIId + IId	CF_3	CF_2H	H	36.2	90	10	62[b]		34.10	1.15		33.87[b]	1.30	
IIIe + IIe	CF_2H	CF_2H	H	57.8	55	45	32 (40 mm)[c]		37.98	1.91		37.74[c]	1.95	
IIIf + IIf	CF_2Cl	CF_2H	H	51.4	50	50	42 (108 mm)[b]		31.20	1.05	18.42	30.97[b]	1.27	18.49
X + XI	CF_3	CF_3	Cl	43.0	30	70	50[b]		26.28		15.52	26.31[b]		15.35
XII	CF_2H	CF_2H	Cl	83.7	0	100	33 (63 mm)	1.3576	31.19	1.05	18.42	31.15	1.20	18.43

[a] % F. [b] Isomeric mixture. [c] Allene data. Structure of isomer based on spectroscopic evidence.

fluoride the only product observed was the acetylene XII.

The physical constants of the alcohols are shown in Table I. Analytical data are presented where appropriate. The products obtained by the action of sulfur tetrafluoride on the alcohols are listed in Table II.

The infrared spectra of all the compounds discussed are typical and will not be described in detail. The acetylenic alcohols generally exhibited two O—H stretching vibrations of medium intensity at 3660 and 3500 cm^{-1}. The acetylenic proton, when present, appeared at 3344 (C—H stretch) and the C≡C stretch was a weak band between 2155 and 2146 cm^{-1}. The α-chloroacetylenes were characterized by a strong C≡C stretching vibration between 2262 and 2237 cm^{-1}. The other bands of the spectra were characteristic of the various substituted methyl groups. In the allenes studied the C=C=C stretching vibration appeared as a weak to medium band between 2028 and 2004 cm^{-1}. For perfluorotetramethyl allene a value of 2025 cm^{-1} has been reported.[10]

The 1,3-butadienes which resulted from the isomerism of IIIb and c showed typical C=C stretching vibrations at 1739 ($C{=}CF_2$) and 1675 cm^{-1} (C=CHF). The former band was also observed in IV.[3] The structure of the conjugated product was confirmed by examination of the nmr spectra. The proton nmr curve of the alcohols showed single lines for the O—H and ≡C—H protons at about δ 3.2 and 2.75, respectively (δ, parts per million from tetramethylsilane as internal standard). The data obtained from the curves of the reaction products are shown in Table III. F^{19} spectra were also obtained from some of these materials, using trichlorofluoromethane as an internal standard (δ scale; parts per million from CCl_3F). The allenes exhibited first-order spectra with characteristic shifts and coupling constants. Thus the fluorine atom in the allene structure C=C=C(F)H always appeared between 155 and 160 ppm and exhibited a typical coupling of about 77 Hz with the geminal proton. In the corresponding 1,3-butadiene the coupling constant remained unchanged but the fluorine atom now resonates further downfield at 112.5 ppm, owing to the deshielding effect of the vinyl chlorine atom. A similar but stronger effect of a geminal chlorine is observed in the allene structure C=C=C(F)Cl where the fluorine atom has a chemical shift of 92.1 ppm. The geminal coupling constants and those of the 1,3-butadiene reported in Table III are in accord with those previously determined.[11]

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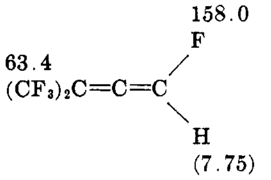
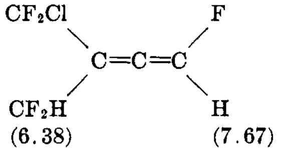
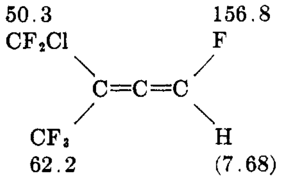
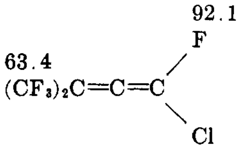
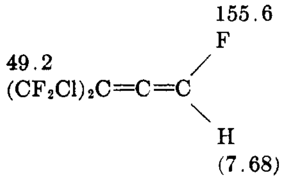
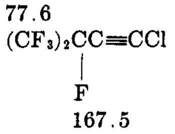
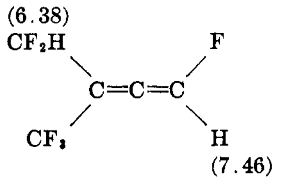
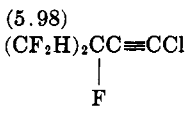
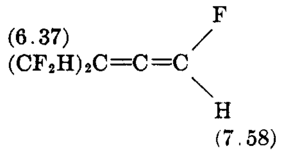
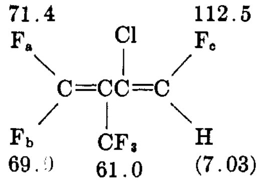
(10) Y. A. Cheburkov, Y. E. Aronov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 582 (1966).

(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Ltd., Oxford, 1966, Chapter 11.

Table III

Nuclear Magnetic Resonance Data

Compd and chemical shift,[a] ppm	Coupling constants	*J*, Hz	Compd and chemical shift, ppm	Coupling constants	*J*, Hz
	CFH *gem* CF_3-CF CF_3-CH	77 5.4 1.2		CFH *gem* CF_2H-CF CF_2-H	78 3 55
	CFH *gem* CF_2-CF CF_3-CF CF_2-CH CF_3-CH	76.6 5.8 5.5 1.2 1.1		CF_3-CF	3.5
	CFH *gem* CF_2-CF CF_2-CH	77 5.8 1.1	 77.6 $(CF_3)_2\underset{\displaystyle F}{\underset{\vert}{C}}C{\equiv}CCl$ 167.5	CF_3-CF	10.0
	CFH *gem* CF_2H-CF CF_2-H	80 3 55	 (5.98) $(CF_2H)_2\underset{\displaystyle F}{\underset{\vert}{C}}C{\equiv}CCl$	CF_2-H CF-H	55 5.6
	CFH *gem* CF_2H-CF CF_2-H	77 3 55		CFH *gem* F_aF_c F_bF_c F_aF_b CF_3 F_c CF_3 F_b CF_3 F_a	77 1.9 2.8 5.1 0.7 21.1 10.3

[a] F^{19} and H^1 chemical shifts are reported on the δ scale, using internal references of $CFCl_3$ and $(CH_3)_4Si$, respectively. H^1 chemical shifts are indicated by parentheses.

Experimental Section

The perhalo ketones are products of the Industrial Chemicals Division, Allied Chemical Corp. The other ketones were purchased from the Hynes Chemical Research Corp., Durham, N. C. Sulfur tetrafluoride was purchased from the Matheson Co.

Halogenated Acetylenic Alcohols (I).—The alcohols were made following the procedure of Knunyants,[2] by addition of the appropriate ketone to a solution of ethynyl magnesium bromide[12] in tetrahydrofuran solution. The free alcohols were obtained from the unavoidable THF-alcohol azeotropes by addition of the azeotropes to concentrated sulfuric acid maintained at 90–95° and under a sufficient vacuum to cause the alcohols to distil out of the mixture. By utilization of this technique excessive decomposition of the THF by the hot acid was avoided and maximum yields of the alcohols were obtained.

In a typical procedure, ethynyl magnesium bromide was prepared from ethyl magnesium bromide, in turn prepared from ethyl bromide (60 g, 0.55 mole) and magnesium (12 g, 0.5 g-atom) in dry tetrahydrofuran (THF) (300 ml) according to the instructions of Jones, *et al.*[12] The Grignard solution so obtained was cooled to −8° and hexafluoroacetone (66.2 g, 0.4 mole) was passed in over a 2.5-hr period. The mixture was stirred overnight at room temperature and then hydrolyzed with 10% aqueous HCl (200 ml). The excess solvent was distilled from the organic layer, leaving a THF–alcohol azeotrope, from which the free alcohol was obtained by addition of the azeotrope to hot, concentrated sulfuric acid, as described above.

α-Chloroalkynyl Alcohols. VIII and IX.—These were made by the method of Viehe.[9] Typically, a 1.7 *M* solution of methyllithium in diethyl ether was added to 200 ml of anhydrous ether. The quantity of methyllithium present was 22 g (1.0 mole). *cis*-Dichloroethylene (48.5 g, 0.5 mole) was added at 0–5° to this solution, with continuous cooling and stirring under a nitrogen atmosphere. The mixture so produced was allowed to warm to room temperature (23–25°) and stirred for 1.5 hr. Hexafluoroacetone (83 g, 0.5 mole) was passed into the mixture at ambient temperature over a 1.5-hr period. After stirring an additional hour, the pale brown mixture was cooled to −60° and the alcohol liberated by the addition of saturated ammonium chloride solution. The organic layer was recovered and washed with 2 *N* HCl, brine, and dried over calcium sulfate. The excess ether was removed by distillation and the free alcohol obtained by treatment of the residual azeotrope with concentrated sulfuric acid as already described.

Reaction of the Alcohols with SF_4.—1,1,1-Trifluoro-2-trifluoromethyl-3-butyn-2-ol (20 g, 0.104 mole) was placed in a 300-ml, stainless steel pressure reactor. The reactor was then closed, cooled to −78°, and evacuated and sulfur tetrafluoride

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[12] L. Skattebøl, E. R. H. Jones, and M. C. Whiting, *Org. Syn.*, **39**, 56 (1959).

(11.25 g, 0.104 mole) was introduced through a vacuum manifold system. The reactor was then set aside and allowed to stand overnight at ambient temperature. At the end of this period (about 16 hr), the excess pressure in the reactor was released and the liquid contents were slurried with sodium fluoride, filtered, and distilled. There was obtained 9.0 g of a water-white liquid, bp 34°, which was shown to be 1,1,1,4-tetrafluoro-2-trifluoromethyl-2,3-butadiene.

This procedure was used to prepare all the compounds listed in Table II.[13]

Registry No.—Ia, 646-72-0; Ib, 15052-50-3; Ic, 5714-47-6; Id, 15052-52-5; Ie, 15052-53-6; If, 15052-54-7; IId, 15052-55-8; IIe, 15052-56-9; IIf, 15052-57-0; IIIa, 15052-58-1; IIIb, 15052-59-2; IIIc, 15052-60-5; IIId, 15052-61-6; IIIe, 15052-62-7; IIIf, 15052-63-8; VIII, 15052-64-9; IX, 15052-65-0; X, 15052-66-1; XI, 15052-67-2; XII, 15052-68-3; $F_2C{=}C(CF_3)CCl{=}CFH$, 15052-69-4.

Acknowledgment.—We are grateful to Dr. B. B. Stewart, Dr. R. Ettinger, and Mr. R. J. Tepper for assistance with the nmr spectra, and to Professor Jerrold Meinwald for helpful discussions of the theoretical aspects of the work.

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[13] NOTE ADDED IN PROOF:—C. Woolf and B. Lichstein, Central Research Laboratory, Allied Chemical Corp., have noted a reaction similar to that described in this paper.

$$(F_3C)_2C(OH)CH{=}CH_2 \xrightarrow{SF_4} (F_3C)_2C{=}CHCH_2F$$

Notes

Azuleno[1,8-*bc*]thiapyran and Azuleno[1,8-*cd*]azepine[1]

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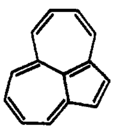
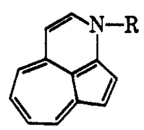
There has been much interest recently in heterocyclic analogs of nonbenzenoid aromatic hydrocarbons. Both π-excessive[2] and π-equivalent[3] heteroanalogs of azulene have been reported.

We have been interested in new heterocycles which are iso-π-electronic with the interesting, nonbenzenoid aromatic hydrocarbon cyclopenta[*e,f*]heptalene (I)[4] prepared by Hafner and Schneider. The first π-excessive[5] heteroanalog of I to be prepared[6] was 1H-cyclohepta[*d,e*]-1-pyrindine (II). Its absorption spectra were found to be quite similar to those of I.

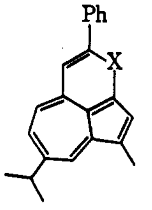
In this paper we wish to report the syntheses of two new heteroanalogs of I. Two derivatives, III and IV, of the azuleno[1,8-*bc*]thiapyran structure have been prepared. A nitrogen heterocycle obtained during the synthesis of III has been identified as 1,3-diphenyl-7-isopropyl-9-methylazuleno[1,8-*cd*]azepine (V). Compound V is the first π-equivalent[7] heteroanalog of I to be reported.



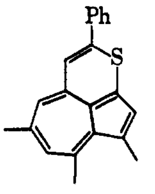
I



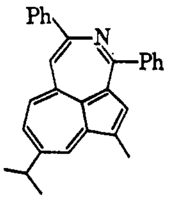
II



III, X = S
XV, X = N



IV



V

Azuleno[1,8-*bc*]thiapyran.—Guaiazulene (1,4-dimethyl-7-isopropylazulene) was selected initially as the starting material since it had the desired structural features. That is, a functional group can be introduced at the 4-methyl carbon *via* base-induced condensation reactions,[8] and electrophilic substitution, which can occur only at the 3 position, can be used to introduce a sulfur-containing functional group at that position.

The sodium salt of guaiazulene VI, generated[8] by the reaction of guaiazulene with sodium N-methylanilide was treated with benzonitrile to give, after acid hydrolysis, 7-isopropyl-1-methyl-4-phenacylazulene (VII), mp 116–117°, in 58% yield. This ketone had a carbonyl band at 5.90 μ in the infrared, and showed a λ_{max} of 608 mμ in the visible region. Treatment of VII with thiocyanogen[9] gave a 92% yield of the 3-thiocyano derivative VIII. This derivative had a band at 4.64 μ ascribed to the –SCN group,[10] as well as the carbonyl band at 5.88 μ, in its infrared spectrum and a visible λ_{max} at 583 mμ. When VIII was treated with zinc and acetic acid, the thiocyano

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[1] (a) Supported in part by a grant (GP-250) from the National Science Foundation. (b) Previously reported as a communication to *Tetrahedron Letters*, No. 23, 1877 (1965).

[2] (a) A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *J. Am. Chem. Soc.*, **85**, 3448 (1963). (b) G. V. Boyd and F. W. Clark, *J. Chem. Soc.*, 859 (1966). (c) R. Mayer, J. Franke, V. Horak, I. Hanker, and R. Zharadnik, *Tetrahedron Letters*, 289 (1961).

[3] T. Nozoe, in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 7; K. Hafner and M. Kreuder, *Angew. Chem.*, **73**, 657, (1961).

[4] K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

[5] A. Albert, "Heterocyclic Chemistry. An Introduction," Oxford University Press, Inc., Essential Books Division, New York, N. Y., 1959.

[6] L. L. Replogle, *J. Am. Chem. Soc.*, **86**, 3137 (1964).

[7] See ref. 2a; *cf.* footnote 9.

[8] K. Hafner, H. Pelster, and H. Patzelt, *Ann.*, **650**, 80 (1961).

[9] A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

[10] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 28.