L.R.G. and W.M.H. Valuable suggestions by Professor Vincent J. Traynelis (West Virginia University) regarding this manuscript are gratefully acknowledged. This work was supported by a grant from the Alfred P. Sloan Foundation to Williams College. A portion of this work (W.J.M.) was supported by Grant RR 00356 from the Biotechnology Resources Branch of the National Institutes of Health.

Registry No.—**8**, 21883-34-1; **10**, 53608-48-3; **11**, 19490-90-5; **14**, 53608-50-7; diphenyl-2-pyridylmethane, 3678-72-6; diphenyl-2-pyridylmethyl chloride, 53608-51-8; *N*-chlorosuccinimide, 128-09-6; acetic anhydride, 108-24-7; 1,4-diazabicyclo[2.2.2]octane, 280-57-9.

References and Notes

(1) (a) Presented at the 6th Northeast Regional Meeting of the American Chemical Society in Burlington, Vt., Aug 1974. (b) Part VI: C. W. Koch, R. M. Milberg, R. J. Katt, J. H. Markgraf, and P. M. Wege, *J. Heterocycl. Chem.*, **11**, 475 (1974).

(2) Based in part on the Honors theses of S.R.B., 1973, and G.G.S., 1964, Williams College.

(3) M. Katada, *J. Pharm. Soc. Jap.*, **67**, 51 (1947); *Chem Abstr.*, **45**, 9536*d* (1951).

(4) G. Kobayashi and S. Furukawa, *Pharm. Bull.*, **1**, 347 (1953); *Chem. Abstr.*, **49**, 10948*e* (1955).

(5) V. Boeckelheide and W. J. Linn, *J. Amer. Chem. Soc.*, **76**, 1286 (1954).

(6) O. H. Bullitt and J. T. Maynard, *J. Amer. Chem. Soc.*, **76**, 1370 (1954).

(7) V. J. Traynelis, "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1969, pp 1–42.

(8) E. Ochiai, "Aromatic Amine Oxides," Elsevier, Amsterdam, 1967, pp 290–302, 310–325.

(9) See ref 7 (pp 23–31) for a detailed discussion of this pathway.

(10) S. Fujii and H. Kobatake, *J. Org. Chem.*, **37**, 2635 (1972).

(11) J. Schnekenburger, *Arch. Pharm. (Weinheim)*, **306**, 360 (1973).

(12) J. H. Markgraf, H. B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *J. Amer. Chem. Soc.*, **85**, 958 (1963).

(13) S. Oae, S. Tamagaki, T. Negoro, and S. Kozuka, *Tetrahedron*, **26**, 4051 (1970).

(14) V. J. Traynelis and P. L. Pacini, *J. Amer. Chem. Soc.*, **86**, 4917 (1964).

(15) C. W. Muth and R. S. Darlak, *J. Org. Chem.*, **30**, 1909 (1965).

(16) These values are percentages of the isotopic species representing the total molecular ion. For unlabeled **10** the relative abundance of M^+ was 3%; the base peak was *m/e* 259. For unlabeled **11** the molecular ion was the base peak.

(17) G. Aksnes, D. Aksnes, and P. Albriktsen, *Acta Chem. Scand.*, **20**, 1325 (1966).

(18) C. W. Muth, R. S. Darlak, M. L. DeMatte, and G. F. Chovanec, *J. Org. Chem.*, **33**, 2762 (1968).

(19) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968).

(20) (a) V. J. Traynelis and R. F. Martello, *J. Amer. Chem. Soc.*, **80**, 6590 (1958); (b) *ibid.*, **82**, 2744 (1960); (c) V. J. Traynelis and A. I. Gallagher, *ibid.*, **87**, 5710 (1965).

(21) A. Deegan and F. L. Rose, *J. Chem. Soc. C*, 2756 (1971).

(22) A. E. Tschitschibabin and S. W. Benewolenskaja, *Ber.*, **61**, 547 (1928).

Acetylenedicarbonyl Fluoride. I. Its Physical Properties and Reaction with Nucleophilic Reagents

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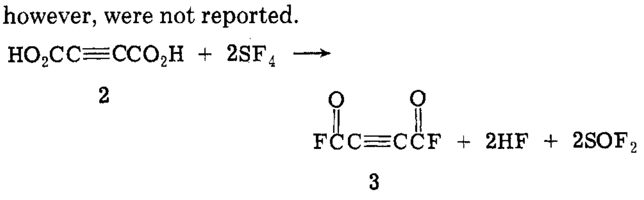
Acetylenedicarbonyl fluoride (**3**) has been prepared by (a) reaction of SF_4 with the monopotassium salt of acetylenedicarboxylic acid and (b) by reaction of phenylsulfur trifluoride with acetylenedicarboxylic acid. The physical and spectral properties including a mass spectral analysis of **3** have been determined. The diacyl fluoride reacts with alcohols, phenols, and aliphatic primary and secondary amines to give the respective esters and diamides in good yield. With ethanethiol and **3**, a mixture of α-ethylthiofumaroyl and maleoyl fluorides, is produced.

The properties and reactions of acetylenedicarbonyl halides have not been reported. Only two disclosures on their synthesis have been documented. The synthesis in low yield of acetylenedicarbonyl chloride (**1**) by a Diels–Alder displacement reaction involving maleic anhydride was reported in 1938.[2] Attempts to prepare **1** from acetylenedicarboxylic acid (**2**) or its salts by more direct routes[4a] give only addition products and tars.[3a,4b,c] Acetylenedicarbonyl fluoride (**3**) has been prepared by the controlled fluorination of **2** with SF_4.[5] Its properties and experimental details, however, were not reported.



$$\underset{\mathbf{2}}{HO_2CC{\equiv}CCO_2H} + 2SF_4 \longrightarrow \underset{\mathbf{3}}{F\overset{O}{\overset{\|}{C}}C{\equiv}C\overset{O}{\overset{\|}{C}}F} + 2HF + 2SOF_2$$

The diacyl halides of **2** are potentially reactive intermediates for the preparation of acetylenic compounds which cannot be conventionally prepared from **2** or its diesters. Acetylenedicarbonyl fluoride has been prepared by two additional routes[6] in moderate to good yields. We report here on these modified routes as well as a survey of its physical properties and reactions with alcohols, phenols, a thiol, and amines.

Synthesis

The fluorination of the monopotassium salt of **2** (**4**) in dimethylcyclohexane with SF_4 at 60° for 15 hr produced **3** in yields ranging from 48 to 70%, depending upon the purity of the SF_4 employed. The substitution of **2** by **4** alleviated the problem of having excess HF which is always a potential source of side reactions in the product mixture. The HF produced in the fluorination is thus scavenged by the KF generated. Alternatively, **3** could be prepared in the laboratory and in glass equipment from **2** and phenylsulfur trifluoride[7] in 1,2-dibromoethane[8] at 10°. The latter preparation required a catalytic amount of HF to initiate the fluorination as evidenced by a short induction period at the onset of the phenylsulfur trifluoride addition. The yield of **3** using this route was *ca.* 50%.

$$\underset{\mathbf{4}}{HO_2CC{\equiv}CCO_2K} + SF_4 \longrightarrow \mathbf{3} + KHF_2 + 2SOF_2$$

$$\mathbf{2} + 2C_6H_5SF_3 \longrightarrow \mathbf{3} + 2C_6H_5SOF + 2HF$$

Physical Properties of 3

Acetylenedicarbonyl fluoride has a bp of 46° and a fp of −51° (DTA). From −15 to 41° the vapor pressure obeyed the relation $\log P_{\mathrm{Torr}} = -(1688 \pm 41)/T°\ \mathrm{K} + 8.19 \pm 0.16$

Table I
Mass Spectrum of Acetylenedicarbonyl Fluoride (70 eV)

m/e	Assigned ion$^+$	Intensity
118	$FCOC{\equiv}CCOF$	52.1
99	$FCOC{\equiv}CCO$	6.0
90	$FCOC{\equiv}CF$	32.8
71	$FCOC{\equiv}C$	100.0
62	$FC{\equiv}CF$	38.4
52	$COC{\equiv}C$	20.7
47	COF	22.7
43	$C{\equiv}CF$	15.4
31	CF	19.9
28	CO	13.9
24	C_2	24.8
19	F	1.4
12	C	17.5

which gave $\Delta H_v = 7.72 \pm 0.27$ kcal mol^{-1} and $\Delta S_v = 22.5$ cal mol^{-1} deg^{-1}.

The mass spectrum of **3** has not been reported and is given in Table I. The base peak ion is $FCOC{\equiv}C^+ \rightleftharpoons {}^+O{=}C{\equiv}CF$ (m/e 71) resulting from the facile loss of COF^+. Fragment ions of $FCOC{\equiv}CF^{\cdot +}$ (m/e 90) and $FC\ CF^{\cdot +}$ (m/e 62) appear to be generated by carbon–carbon bond cleavage with elimination of CO followed by a skeletal migration of a fluorine atom. The ease to which this occurs is associated with the presence of the acetylenic linkage which may be ionized by electron removal followed by migration of the fluorine atom to the electron deficient site.[9] An additional striking feature of the fragmentation pattern of **3** is the large relative abundance of the C_2 ion (m/e 24) compared to that produced in the mass spectral fragmentation pattern of acetylenic esters and diesters.[9] The large intensity of the C_2 ion suggested that thermolysis or photolysis of **3** might generate the ion in the gas phase. Our attempts to generate the C_2 ion using flash photolysis, however, were unsuccessful. Scheme I summarizes the mass spectral fragmentation and rearrangement mode of **3**.

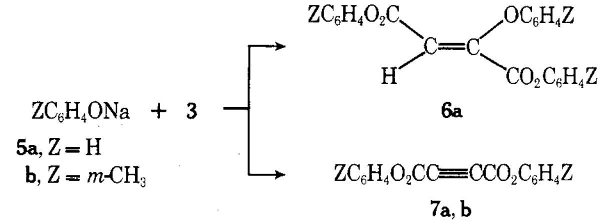
Scheme I

$$\begin{tikzcd}
{[FCOC\equiv CCOF]^{\cdot +}} \arrow[r, "-CO"] \arrow[dd, "-COF"] & {[FCOC\equiv CF]^{\cdot +}} \arrow[r, "-CO"] & {[FC\equiv CF]^{\cdot +}} \\
 & m/e\ 90\ (32\%) & m/e\ 62\ (38\%) \\
{[FCOC\equiv C]^{\cdot +}} \arrow[r, "-F"] & {[O\equiv CC\equiv C]^{\cdot +}} \arrow[r, "-CO"] & {[C\equiv C]^{\cdot +}} \\
 & m/e\ 52\ (21\%) & m/e\ 25\ (25\%)
\end{tikzcd}$$

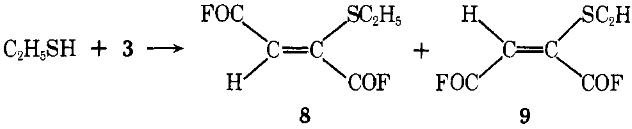
Having a center of symmetry about the acetylenic bond, **3** exhibits little absorption in the infrared spectrum. Raman analysis of **3** displayed strong absorptions for the acyl carbonyl and triple bond at 1824 and 2262 cm^{-1}, respectively. The ^{19}F nmr spectrum of **3** in methylene chloride displayed a sharp singlet at δ 49.4 and was shifted only to δ 50.5 when cooled to −90°. The ^{13}C satellite spectrum (see Experimental Section) yielded a fluorine–fluorine coupling of 1.8 Hz similar to an analogous four-bond coupling in perfluoro-2-butyne of 2.2 Hz.[10]

Reactions of 3

With Alcohols and Phenols. Acetylenedicarbonyl fluoride acylates alcohols under neutral conditions with negligible addition to the acetylenic bond to yield the corresponding diesters. For example, the diallyl[11] and dipropargyl[12] esters were obtained in 81 and 80% yield, respectively. Attempts to acylate phenols under similar conditions were unsuccessful, but addition of **3** to sodium phenoxide in dioxane at 15° produced a 3:1 adduct, diphenyl phenoxyfumarate (**6a**). The undesired addition of phenoxide ion to the triple bond was minimized by carrying out the addition of **3** to a suspension of **5** in fluorotrichloromethane at 0°. The insoluble diphenyl acetylenedicarboxylate (**7a**) could then be filtered and purified.



With Thiols. Treatment of a neat mixture of ethanethiol and NaF at 10° with **3** gave an exclusive mixture of only α-ethylthiofumaroyl (**8**) and maleoyl fluorides (**9**). The infrared spectrum of the mixture exhibited strong absorptions at 1842 and 1802 cm^{-1} (COF). The ^1H nmr spectrum of the mixture displayed two nonequivalent ethyl groups. The vinyl proton in **9** appeared as a doublet of doublets resulting from geminal ($J_{H-F} = 4.5$ Hz) and trans ($J_{H-F} = 1.3$ Hz) coupling with the acyl fluorides.[13] The olefinic proton in **8** appeared as a doublet.



With Amines. In general, activated acetylenic derivatives add primary and secondary amines exothermically to yield imino or enamino derived products.[14] Attempts to prepare di- or tetrasubstituted acetylenedicarboxylic amides from dimethyl acetylenedicarboxylate and aliphatic amines have met with little success. An earlier report[15] described the synthesis of *N,N,N′,N′*-tetraethylacetylenedicarboxamide (**10a**) from dimethyl acetylenedicarboxylate and diethylamine. Later work[16] established the compound to be the addition product, dimethyl α-diethylaminomaleate, rather than **10a**. Acetylenedicarboxamide[17] has been prepared from dimethyl acetylenedicarboxylate and aqueous ammonia at −10°.

Recently, a novel synthesis of new disubstituted and tetrasubstituted acetylenic diamides (**10**) was reported[18] starting from dibromofumaryl chloride followed by amination and dehalogenation (Scheme II). Similar acetylenic diamides (**10**) can also be prepared by controlled addition of primary and secondary amines to **3** in methylene chloride at 0°. The yields of these alicyclic and cyclic diamides **10** (Table II) ranged from 40 to 70%. Addition products appear also to be formed, but their isolation has not been attempted. The diamides are easily separated from these colored side products by column chromatography. Their properties are summarized in Table II. The infrared spectra of **10** showed the characteristic amide carbonyl at 1630–1650

Scheme II

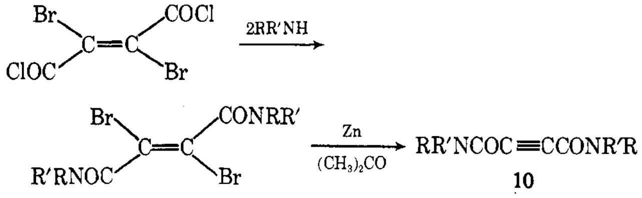
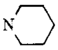
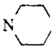


Table II
Properties of Acetylenic Diamides (10)[a,b]

Compd	R	R'	Yield[c]	Mp, °C	ν(C=O), cm^{-1} [d]	ν(C≡C), cm^{-1} [e]
a	C_2H_5	C_2H_5	40	65	1642	
b	H	n-C_3H_7	67	151–153	1637	2238
c	H	i-C_3H_7	48	189–190	1642	2244
d	H	Allyl	45	103–104	1637	2246
e	n-C_4H_9	n-C_4H_9		Oil	1645	
f	H	C_6H_{11}	72	244–245	1634	2234
g	H	$CH_2C_6H_5$	45	204–205	1631	2245
h	H	1-Adamantyl	67	263–274	1645	2246
i	R,R' = 		43	98–99	1664	2237
j	R,R' = 		64	145–147	1656	2230
k	R,R' = 		40	118–119	1626	2232

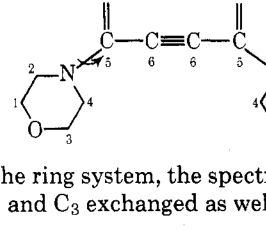
[a] Satisfactory analytical data were reported for all new compounds listed in the table. Compounds **10k** and **10f** had a ±0.7 deviation in the carbon analysis. [b] The ^1H nmr spectra of **10a–k** were measured in either $CDCl_3$ or DMSO-d_6 and displayed absorptions, coupling constants, and multiplicities consistent with the assigned structures. [c] Isolated yield. [d] Nujol mull. [e] Neat powder

Table III
^{13}C Nmr Spectrum of 10j in Methylene Chloride

δ, ppm	Assignment
−171.9	C_5
−101.4	C_6
−87.6	C_1 or C_3
−87.2	C_3 or C_1
−68.2	C_4
−63.0	C_2

cm^{-1} and Raman analysis displayed a strong absorption for the symmetric triple bond at 2232–2246 cm^{-1} (Table II). The pnmr spectra (Table II, footnote *b*) of the *N,N'*-disubstituted derivatives exhibited proton coupling through nitrogen with the adjacent methylene or methine proton. In **10b** the proton absorption of the α-methylene group appeared as a quartet arising from coupling through nitrogen in addition to the β-methylene hydrogens (*i.e.*, $J_{HN-H} \sim J_{H-H}$). In **10d** the amido hydrogen appeared as a triplet with J = 5.5 Hz resulting from α-methylene coupling. The tetrasubstituted derivatives of **10** displayed nonequivalence of the *N,N*-dialkyl group typical of disubstituted amides.

The cyclic diamides displayed complex pnmr spectra with the exception of **10j**. The pnmr of **10j** displayed two singlets of 1:1 intensity at δ 3.82 and 3.90 for the α- and β-methylene protons. No additional splitting was observed down to −64°, and the doublet coalesced in DMSO-d_6 at 90° to a singlet at δ 3.88. The ^{13}C nmr spectrum of **10j** exhibited six peaks. Their assignments and chemical shifts are summarized in Table III. Because of hindered rotation around the C–N bond, C_1 and C_3, and C_2 and C_4, are nonequivalent. In the other rotational isomer, because of the symmetry of the ring system, the spectrum is exactly reproduced with C_1 and C_3 exchanged as well as C_2 and C_4. Since the ring is symmetric along the C–N bond, only one type of carbonyl carbon and acetylenic carbon is observed. The two singlets observed arise by accidental degeneracy of the C_1 and C_2 hydrogens. The chemical shifts of the C_1 and C_3 hydrogens, which are chemically equivalent, will have different chemical shifts because of restricted rotation around the C–N bond. Similarly, the chemical shifts and the C_2 and C_4 hydrogens are different. This coupled with the accidental degeneracy of the chemical shifts of hydrogen in C_1 and C_2 and also on C_3 and C_4 result in the observed two-line pattern in the proton spectrum.



Experimental Section

All melting points are uncorrected. Chemical shifts are expressed in δ, parts per million, downfield from an internal standard of TMS. The ^{13}C nmr spectrum of **10j** was recorded on a Bruker Scientific, In HFX-90 multinuclear magnetic resonance spectrometer operating at 22.6 MHz using CH_3I as an external reference.

Materials. All solvents including methylene chloride, dioxane, fluorotrichloromethane, 1,2-dibromoethane, and dimethylcyclohexane (isomeric mixture) were dried over molecular sieves (Type 4A). SilicAR CC7, 100–200 mesh, was obtained from Mallinckrodt Co. The amines used in the preparation of the acetylenic diamides were all commercially available and used without further purification.

The preparation of acetylenedicarbonyl fluoride (**3**) has already been described.[6] Analysis of the ^{13}C satellite coupling in the ^{19}F spectrum of **3** in carbon tetrachloride showed a set of doublets with $J_{^{13}C-F}$ = 324 Hz and a second set of doublets with $J_{^{13}C-F}$ = 115 Hz. Analysis of these couplings gave J_{F-F} = 1.8 Hz.

Diallyl Acetylenedicarboxylate. A mixture of 4.9 g (0.085 mol) of allyl alcohol and 4 g of NaF in 40 ml of dry benzene was treated dropwise with 2.0 g (0.017 mol) of **3** in 10 ml of dry benzene at 15°. After stirring for 20 hr, the mixture was filtered and benzene removed under vacuum. Residual benzene and allyl alcohol were removed at 25° at 0.001 Torr yielding 2.7 g (81%) of diallyl acetylenedicarboxylate:[11] bp 77–79° (0.4 Torr); ir (neat) 1754^{-1} (C=O), 1647 (C≡C), and 1250 cm^{-1} (CO).

Dipropargyl Acetylenedicarboxylate. A mixture of 4.8 g (0.085 mol) of propargyl alcohol and 4 g of NaF in 40 ml of dry benzene was treated dropwise with a solution of 2 g (0.017 mol) of **3** in 10 ml of dry benzene at 15°. After stirring 18 hr at 25°, the solids were filtered and the solvent and propargyl alcohol removed under vacuum. Fractional distillation yielded 2.2 g (80%) of dipropargyl acetylenedicarboxylate:[12] bp 95° (0.4 Torr); ir (neat) 3322 (HC≡C), 2155 (C≡C), 1742 (C=O), and 1250 cm^{-1} (CO).

Diphenyl Phenoxyfumarate (6a). A solution of 2 g (17 mmol) of **3** in 20 ml of dioxane was added dropwise to a mixture of 3.9 g (34 mmol) of sodium phenoxide[19] in 100 ml of dioxane at 15°. The mixture was stirred 2 hr and filtered. After removal of solvent *in vacuo,* the residue was chromatographed on 90 g of silica gel with 1:1 benzene–carbon tetrachloride to yield 1.7 g (28%) of pure **6b:** mp 137–138°; ir (Nujol) 1770 and 1727 cm^{-1} (C=O); nmr (DMSO) δ 5.69 (s, CH=C, 1 H), and singlet multiplet for aromatic protons.

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.39; H, 4.44. Found: C, 72.82; H, 4.38.

Diphenyl Acetylenedicarboxylate (7a). A suspension of 4.0 g (3.4 mmol) of sodium phenoxide[19] in 50 ml of fluorotrichloromethane was treated dropwise at −15° with a solution of 2.0 g (17 mmol) of **3** in 15 ml of fluorotrichloromethane. After 2 hr, the mixture was warmed to 25° and filtered. The solids were stirred 3 hr at 25° with 50 ml of fluorotrichloromethane followed by filtration. Removal of solvent from the filtrate yielded an oil whose infrared spectrum indicated a mixture of phenol and the 3:1 adduct **6.** The fluorotrichloromethane insolubles were extracted with benzene producing a tan solid on removal of the benzene. Recrystallization from ethanol yielded 2.2 g (50%) of pure (**7a**): mp 149–150°; ir (KBr) 1733 (C=C), 1587 cm^{-1} (C=C); nmr ($CDCl_3$), multiplet for the aromatic protons.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.08; H, 3.88.

Di-*m*-tolyl Acetylenedicarboxylate (7b). A solution of 1.0 g (8.5 mmol) of **3** in 15 ml of 1,1,2-trichlorotrifluoroethane was added dropwise to a stirred suspension of 2.2 g (17 mmol) of sodium *m*-cresoxide[19] in 50 ml of 1,1,2-trichlorotrifluoroethane at 0°. After 4 hr, the mixture was warmed to 25° and filtered. The solid was extracted with benzene (200 ml) to yield 1.3 g (52%) of **7b:** mp

85–86° (ethanol); ir (Nujol), 1727 (C=O), 1220 cm^{-1} (CO); uv (isoöctane) sh 245 (ϵ 5320) and sh 225 nm (ϵ 6880); nmr ($CDCl_3$) δ 2.38 (s, CH_3, 6 H), 7.2–7.4 (m, phenyl, 8 H).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 480. Found: C, 73.22; H, 5.07.

Ethanethiol with 3. A solution of 2.0 g (17 mmol) of **3** in 10 ml of dry benzene was added dropwise to a stirred mixture of 3.1 g (50 mmol) of ethanethiol and 4 g of NaF in 40 ml of benzene at 10°. After 18 hr at 10°, the mixture was filtered followed by removal of benzene and excess thiol under vacuum. Distillation of the orange residue yielded a light yellow liquid: bp 49–56° (0.9 Torr). The infrared spectrum of the distillate indicated a mixture of α-ethylthiofumaroyl and -maleoyl fluorides: ir (neat) 1842 and 1802 (COF), 1572 cm^{-1} (C=C); nmr ($CDCl_3$), α-ethylthiofumaroyl fluoride, δ 1.37 (t, CH_3, 3 H), 3.08 (q, $-CH_2S-$, 2 H), 6.52 (doublet, J_{H-F} = 4.5 Hz, HC=C, 1 H), and α-ethylthiomaleoyl fluoride, δ 1.45 (t, CH_3, 3 H), 3.17 (q, $-CH_2-$, 2 H) (doublet of doublets, J_{H-F} = 4.5 Hz; J_{H-H} (trans) = 1.3 Hz, HC=C, 1 H).

General Method for the Preparation of Acetylenic Diamides 10. A mixture of 26 mmol of **3** and 6 g of NaF in 75 ml of dry methylene chloride was treated dropwise at 0° with 102 mmol of the primary or secondary alkyl amine in 30 ml of dry methylene chloride. After 0.5 hr, the mixture was warmed to 25° and filtered. The volatiles were removed on a rotary evaporator to yield dark semisolid residues. These residues were chromatographed on SilicAR CC-7 employing a chloroform–carbon tetrachloride mixture as the eluent. The products, which eluted first, were then recrystallized from either chloroform, acetone, or a chloroform–hexane mixture and vacuum dried over P_2O_5 at 25° to yield analytically pure samples. In the case of **10f,g** the products precipitated from solution during the addition. In these cases the filter cake was washed with water (400 ml) and air dried prior to recystallization.

***N,N'*-Dicyclohexylacetylenedicarboxamide. Aqueous Method.** An Osterizer blender was charged with 3.64 g (33.4 mmol) of cyclohexylamine, 250 ml of distilled water, and 13.3 ml of 10% NaOH (33.4 mmol). The blender was started, and a solution of 3.0 g (16.7 mmol) of **3** in 125 ml of dry carbon tetrachloride was added in one portion. The mixture was stirred vigorously for 10 min and filtered. The yield of **10f** by this method was 2.3 g (50%) after recrystallization.

Registry No.—3, 675-75-2; **5a,** 139-02-6; **5b,** 4549-72-8; **6a,** 53683-88-8; **7a,** 53683-89-9; **7b,** 53683-90-2; **8,** 53683-91-3; **9,** 53683-92-4; **10a,** 25883-23-2; **10b,** 29453-12-1; **10c,** 53683-93-5; **10d,** 53683-94-6; **10e,** 29606-11-9; **10f,** 53683-95-7; **10g,** 53683-96-8; **10h,** 53683-97-9; **10i,** 29453-10-9; **10j,** 53683-98-0; **10k,** 25883-25-4; diallyl acetylenedicarboxylate, 14447-07-5; allyl alcohol, 107-18-6; dipropargyl acetylenedicarboxylate 3154-91-4; propargyl alcohol, 107-19-7; ethanethiol, 75-08-1; diethylamine, 109-89-7; propylamine, 107-10-8; isopropylamine, 75-31-0; allylamine, 107-11-9; dibutylamine, 111-92-2; cyclohexylamine, 108-91-8; benzylamine, 100-46-9; 1-adamantylamine, 768-94-5; piperidine, 110-89-4; morpholine, 110-91-8; pyrrolidine, 123-75-1.

References and Notes

(1) Contribution No. 2187.

(2) O. Diek and W. E. Thiele, *Chem. Ber.*, **71B**, 1175 (1938); attempts to repeat this reaction sequence have not been successful.[3]

(3) (a) R. N. McDonald and R. A. Kruegler, *J. Org. Chem.*, **28**, 254 (1963); (b) F. D. Marsh, Central Research Department, E. I. du Pont de Nemours and Co., Inc., private communication.

(4) (a) S. Patai, Ed., "The Chemistry of Acyl Halides," Interscience, New York, N.Y., 1972; (b) O. Diels and W. E. Thiele, *Chem. Ber.*, **71B**, 1173 (1938); (c) F. E. Herkes, private communication.

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

(6) F. E. Herkes and H. E. Simmons, *Synthesis*, **3**, 166 (1973).

(7) W. A. Sheppard, *Org. Syn.*, **44**, 82 (1964).

(8) 1,2-Dibromoethane (bp 131°) was employed as the solvent to provide a large boiling point differential. Any inert solvent of comparable boiling point would also be suitable.

(9) J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll, and S. O. Lawesson, *Tetrahedron*, **23**, 305 (1967).

(10) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

(11) C. D. Heaton and C. R. Nollar, *J. Amer. Chem. Soc.*, **71**, 2948 (1949); authors report 70% esterification yield with H_2SO_4 catalyst.

(12) J. Randell, B. W. Brodman, A. Hirshfeld, and E. D. Bergmann, *J. Phys. Chem.*, **69**, 928 (1969); authors report 4% esterification yield without catalyst.

(13) T. P. Vasileff and D. F. Koster, *J. Org. Chem.*, **35**, 246 (1970).

(14) H. G. Viehe, Ed., "The Chemistry of Acetylenes," Marcel Dekker, New York, N.Y., 1969, pp 286–299.

(15) C. Vassiliades and H. Capatos, *C. R. Acad. Sci.*, **194**, 1830 (1932).

(16) R. J. Alaimo and D. G. Farnum, *Can. J. Chem.*, **43**, 700 (1965).

(17) A. J. Saggiomo, *J. Org. Chem.*, **22**, 1171 (1957).

(18) K. E. Schulte, J. Ruisch, and K. Coen, *Chim. Ther.*, **5**, 72 (1970); K. Coen, H. Moellmann, J. Reisch, and K. E. Schulte, *Arzneim.-Forsch.*, **19**, 1761 (1969).

(19) W. R. Boehme, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 492.

Acetylenedicarbonyl Fluoride. II. Its Reaction with Arylamines to Yield Isomaleimides, Maleimides, and α-Phenylimino- and α-Phenylaminofuramides

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Contrary to expectation, acetylenedicarbonyl fluoride, **2**, had been found to react with aniline and substituted anilines under strict nonacid conditions to yield 1-arylamino-4-arylimino-α-crotonolactones (*i.e.*, isomaleimides), **3**. Under acidic conditions, the isomeric 1-arylaminomaleimides, **4**, are formed. The configuration of **3** was deduced chemically by mild reduction of **3a** (R = H) with sodium borohydride to give 2-anilino-1-hydroxy-4-phenylimino-2,5-dihydrofuran, **9**, which in turn could be reoxidized back to **3a** with MnO_2. Similarly, the reduction of **4a** (R = H) yielded 4-anilino-5-hydroxy-2-pyrrolin-2-one, **10**. With excess aniline and **2**, the only product isolated was the 3:1 adduct, *N,N*-diphenyl-*N*-phenyliminofuramide, **13**. The imino isomer, **13**, was found to tautomerize slowly in DMSO at 50° producing the isolatable enamino derivative, **16**. The isomerization was observed to be irreversible and catalyzed by acid. The physical and spectral properties of **3** and **4** are summarized as well as the pnmr data for all the compounds described.

Several reports on the synthesis of *N,N'*-diphenylacetylenedicarboxamide (**1**) have recently appeared. Schulte,[2a] *et al.*, obtained **1** by addition of phenyl isocyanate to acetylenedimagnesium iodide. A later report by Dehmlow[2b] described the formation of **1**, based on infrared data, by photolysis of diethoxycyclobutenedione in an aniline–ether mixture. With the reported[3,4] synthesis of acetylenedicarbonyl fluoride (**2**) there appeared to be an additional and more general route to **1** and other acetylenic dianilids.

The condensation of primary and secondary aliphatic and alicyclic amines with **2** was observed[3] to yield the corresponding acetylenic diamides with minimal addition of