

Contribution No. 321  
The Central Research Laboratories  
Minnesota Mining and Manufacturing Company

## Difluorodiazirine. V. Difluoromethyl Esters and Ethers

Ronald A. Mitsch and Jerry E. Robertson

The preparation of difluoromethyl esters and ethers by the photolytic reaction of difluorodiazirine with acids and alcohols, respectively, is described. Difluoromethyl benzoate is converted, under mild conditions, to methyl benzoate, benzamide and benzamide by reaction with methanol, ammonium hydroxide and aniline, respectively. The difluoromethyl esters are activated to nucleophilic reaction by virtue of the  $\alpha$ -fluorine substitution.

### INTRODUCTION

The reactions of difluorocarbene, generated by photolysis or pyrolysis of difluorodiazirine (I) with olefins (2,3) and free radical-type reagents (4) have been the subject of previous publications.

As part of the continuing investigation into the chemistry of difluorodiazirine, the present paper reports the synthesis of difluoromethyl esters and ethers by the direct reaction of difluorocarbene with acids and alcohols, respectively.

Previously, difluoromethyl ethers have been synthesized by the basic hydrolysis of difluoromethane derivatives in the presence of excess alkoxide. In this manner, the preparation of methyl (5), ethyl (6), and isopropyl (7) difluoromethyl ethers and the hydrolytic instability of this class of compounds, has been described. Utilizing the reaction of 1,1,2-trichlorodimethyl ether with a mixture of antimony trifluoride and antimony pentachloride, Sokol'skii and Dmitriev (8) report the preparation of other difluoromethyl ethers.

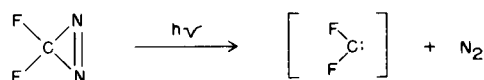
As a class of compounds, the difluoromethyl esters have received even less attention. The only difluoromethyl ester of a carboxylic acid which has been described in the literature, difluoromethyl difluoroacetate, was prepared by Yarovenko and coworkers (9) while studying the reaction of mercury difluoroacetate with iodine. More recently, the electrochemical fluorination of methyl sulfates and sulfonates has been reported to yield difluoromethyl fluorosulfonate (10) and difluoromethylmethyl sulfate (10d). Difluoromethyl sulfates have also been prepared by the reaction of difluoromethyl ethers with sulfur trioxide (8).

### RESULTS AND DISCUSSION

#### Difluoromethyl esters.

Difluorodiazirine (I) is known to be stable in strong acids in the absence of ultraviolet light (1). Thus, I is recovered unchanged after several months in solution in trifluoroacetic acid at room temperature.

However, under the influence of ultraviolet irradiation, the reported (1-4) photochemical decomposition involving the formation of the electrophilic difluorocarbene and nitrogen is realized.

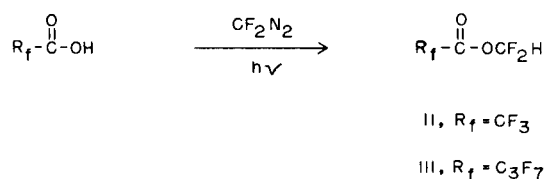


I

The ability of difluorocarbene to combine with nucleophilic reagents has been demonstrated by earlier investigations in the field (5-7). We will report here that difluorocarbene reacts with carboxylic and sulfonic acids, presumably in a concerted manner, to give the corresponding difluoromethyl esters.

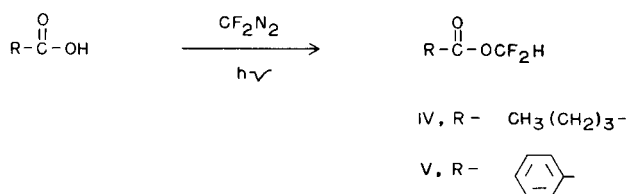
In general, the syntheses of the difluoromethyl esters described in the present paper were carried out by the photolysis of the liquid phase of a mixture of I in a 2-5 molar excess of the acid. The area above the liquid was protected from the ultraviolet light by wrapping that portion of the ampoule with aluminum foil. Because of the greater volatility of the resulting difluoromethyl ester product, preliminary separation of the reaction mixture by fractional distillation-condensation techniques affords an ester of at least 90-95% purity.

In this manner, difluoromethyl trifluoroacetate (II) and difluoromethyl heptafluorobutyrate (III) were synthesized in 75 and 50 percent yields, respectively. After final purification by vapor phase chromatography, the structures of II and III were confirmed



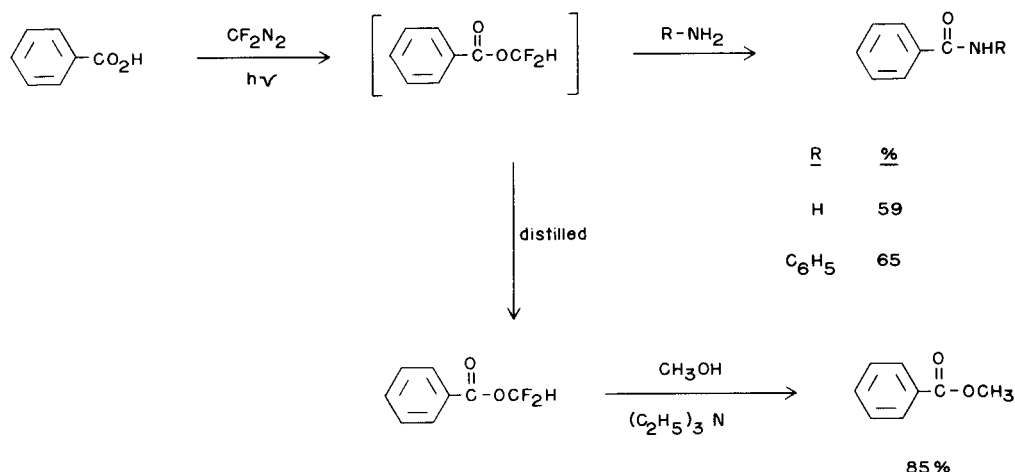
by elemental and spectral analyses. In the fluorine nuclear magnetic resonance spectra of II and III (Table II), the  $-\text{CF}_2\text{H}$  groups appear as doublets at  $91.9 \phi^*$  ( $J = 68.3 \text{ c/s}$ ) and  $91.8 \phi^*$  ( $J = 68.6 \text{ c/s}$ ), respectively, due to spin-spin coupling with the hydrogen atom. As a result of similar couplings, the proton spectrum of II and III exhibit triplets at  $2.89 \tau$  ( $J = 68.8 \text{ c/s}$ ) and  $2.87 \tau$  ( $J = 68.6 \text{ c/s}$ ),

The reactions of difluorocarbene with valeric and benzoic acids were carried out in dichloromethane solvent. In both cases, the stirred solvent portion of the reaction mixture containing two molar equivalents of the acid was irradiated. Purification of IV



and V was accomplished by vapor phase chromatography at  $75^\circ$  and  $125^\circ$ , respectively. Confirmation of the structures of these difluoromethyl esters was by elemental and spectral analyses. The fluorine n.m.r. spectra of IV and V show the expected doublets at  $92.7 \phi^*$  ( $J = 70.8 \text{ c/s}$ ) and  $91.9 \phi^*$  ( $J = 70.7 \text{ c/s}$ ), respectively, due to the difluoromethyl moiety. The proton absorption of the  $-\text{CF}_2\text{H}$  groups also show the expected triplets due to the spin-spin couplings with the two fluorine atoms.

The convenience of preparation of V and the properties of benzoate derivatives suggested that the reactions of difluoromethyl benzoate be investigated to determine if the difluoromethyl esters, as a class, exhibit activated reactivity to nucleophilic attack by virtue of the electron withdrawing fluorine substitution. Difluoromethyl benzoate was generated *in situ* by photolysis of a 2:1 molar mixture of difluorodiazirine and benzoic acid in chloroform. Infrared examination of a portion of the chloroform solution revealed virtually complete esterification.



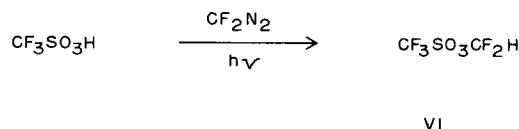
The chloroform solution was filtered, diluted with additional chloroform and used as such for the preparation of benzamide and benzanilide.

The formation of benzamide and benzanilide was executed for two steps, without isolation of the intermediate ester and including only pure product, in yields of 59 and 65%, by reaction with concentrated ammonium hydroxide at room temperature and aniline at reflux, respectively.

The methyl ester was generated in 85% yield by treating distilled difluoromethyl benzoate (V) with methanol and triethylamine in refluxing chloroform.

Based on a quantitative experiment, the activated ester, V, appears stable in water or aqueous dimethoxyethane at room and reflux temperature for several minutes but was rapidly saponified by dilute base at the reflux temperature.

In a manner analogous to the reactions with trifluoroacetic acid and heptafluorobutyric acid, difluorodiazirine (I) was allowed to react with trifluoromethylsulfonic acid under photolytic conditions without solvent. Difluoromethyl trifluoromethylsulfonate (VI) was obtained in a 71 percent yield after vapor phase chromatographic separation.



The fluorine nuclear magnetic resonance absorption of the  $-\text{CF}_2\text{H}$  group in VI appears at  $82.9 \phi^*$ . The structure of this peak is a double quadruplet with J values of 68.5 and 3.2 c/s, respectively. In the proton magnetic resonance spectrum, the carbon-hydrogen absorption shows the expected triplet structure ( $J = 68.5 \text{ c/s}$ ) at  $3.16 \tau$ .

As illustrated by esters II-VI, the most characteristic spectral feature which is useful for the identification of this class of compounds is the

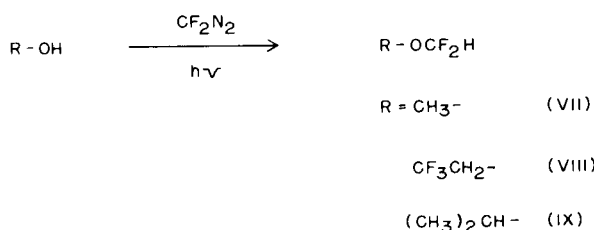
nuclear magnetic resonance absorption due to the  $-\text{CF}_2\text{H}$  group. As previously mentioned, the difluoromethyl group appears as a doublet due to spin-spin coupling with the hydrogen and as a result of similar couplings, the fine structure of the proton spectrum is that of a triplet.

#### Difluoromethyl Ethers.

Previous disclosures (5-7) have described the syntheses of difluoromethyl ethers involving the basic hydrolysis of haloforms as a source of difluorocarbene. Inherent in this technique are side reactions leading to orthoformates, thereby requiring a somewhat more difficult separation procedure.

In the present work, difluoromethyl ethers are obtained in 95-98% purity by simple trap-to-trap distillation of the product mixture resulting from photolysis of difluorodiazirine and excess alcohol. Although vapor phase reactions were utilized primarily in this work because of the experimental simplicity, photolysis of the liquid phase mixtures of difluorodiazirine and the nucleophilic coreactant in an inert solvent should be equally effective.

The difluoromethyl ethers from methanol and isopropyl alcohol were obtained by gas phase reactions while the corresponding ether from 2,2,2-trifluoroethanol was synthesized in a liquid phase photolysis because of the solubility of difluorodiazirine in the alcohol. After final purification by vapor phase



chromatography, the structures of the difluoromethyl ethers VII (69%), VIII (51%), and IX (83%) were established by elemental and spectral analyses. As in the case of the difluoromethyl esters, the fluorine and proton nuclear magnetic resonance spectra (Table II) of the ethers are definitive for establishing the presence of the  $-\text{CF}_2\text{H}$  moiety.

Since the rate of reaction of difluorocarbene with the compounds under investigation should be related to their nucleophilic reactivity, a competition experiment was carried out in which difluorocarbene was generated in the presence of two alcohols having substantially different electron availability at the oxygen atom. A gaseous mixture of difluorodiazirine and four molar equivalents of methanol and trifluoroethanol was irradiated overnight at room temperature. Only one difluoromethyl ether product, difluoromethylmethyl ether (VII) resulting from reaction of difluorocarbene with the more nucleophilic alcohol,

was detected and isolated by vapor phase chromatography.

As a class, difluoromethyl ethers have been reported to be hydrolytically unstable (5-7). In general, this difficulty was also observed in the present work. Analytical samples of VII which were stored in  $\text{CFCl}_3$  at room temperature were completely decomposed via HF elimination after several weeks. On the other hand, VII was stored for several weeks in a gas bulb with an equimolar quantity of water without showing any evidence of hydrolysis by infrared examination. Difluoromethyl isopropyl ether (IX), however, was even more unstable than VII. Liquid or gaseous samples of IX in glass bulbs which had been flamed-out under vacuum were observed to form appreciable quantities of isopropyl formate upon standing overnight at room temperature.

#### EXPERIMENTAL

##### General.

Chromatographic analyses were performed with a Model 154-D Perkin-Elmer Vapor Fractometer, utilizing fluorocarbon type stationary phases. In most cases, the preparative separations were obtained at 25° using a 1/2" o.d. tube two meters long and packed with 33% KF-8126 (14) oil on Celite. The high boiling esters, IV and V, were purified at 75° and 125°, respectively, on a 1/4" o.d. tube 3.5 meters long and packed with 33% Kel-F 90 grease on Celite.

Fluorine and proton nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc; internal standards of  $\text{CFCl}_3$  and  $(\text{CH}_3)_4\text{Si}$  were used for the determination of shielding values. The shielding values are reported in phi ( $\Phi^*$ ) (11) and tau ( $\tau$ ) (12) units for fluorine and proton, respectively, at dilutions of about 20-30 percent.

##### Preparation of Difluoromethyl Ethers and Esters.

In general, the volatility of the nucleophilic reagent to be reacted with difluorodiazirine determined the experimental procedures utilized in this work.

a. Procedure (a) employing liquid phase photolysis of a mixture of difluorodiazirine and excess coreactant (See Table I for molar ratios) was utilized for the preparation of II, III, VI and VIII. The nucleophilic reagent was weighed into a glass ampoule and degassed at liquid nitrogen temperature. Difluorodiazirine was then condensed into the ampoule and the ampoule sealed. After warming to room temperature and covering the top portion of the ampoule with aluminum foil, the liquid mixture was irradiated overnight with a General Electric BH-6 ultraviolet lamp fitted with a Corning No. 5840 filter. Preliminary separation of the difluoromethyl ester or ether from the reaction mixture was effected by simple fractional distillation-condensation techniques. Preparative vapor phase chromatography was employed for the final purification. The reported yields (Table I) represent the quantity of pure product which was separated from the reaction mixture by vapor phase chromatographic trapping techniques.

b. Procedure (b) employing gas phase photolysis of a mixture of difluorodiazirine and the alcohol was utilized for the preparation of difluoromethyl ethers VII and IX (see Table I for molar ratios). The reactants were condensed into a one liter glass storage bulb at liquid nitrogen temperature by suitable gas transfer techniques. After degassing and warming to room temperature, the mixture was irradiated overnight with a General Electric BH-6 ultraviolet lamp fitted with a Corning No. 5840 filter. As in procedure (a), preliminary fractional distillation-condensation and vapor phase chromatography were employed to separate the reaction mixture into its pure components.

c. Procedure (c) was used in the preparation of the higher boiling esters IV and V. The acid was weighed into a glass ampoule containing a stirring bar and fitted with a Fischer-Porter Teflon valve. Either chloroform or dichloromethane solvent was then added and the vapor portion of the ampoule covered with aluminum foil. The ampoule was degassed at liquid nitrogen temperature and the difluorodiazirine added by condensation. After warming to room temperature, the mixture was stirred and irradiated overnight with the General Electric BH-6 lamp. Preliminary separation, using appropriately cooled traps on a vacuum system, was followed by vapor phase chromatography.

TABLE I  
Difluoromethyl Esters and Ethers

Reactant	Molar Ratio (a)	Product	Yield, %	Analyses, %	
				Calcd.	Found
$\text{CF}_3\text{CO}_2\text{H}$	5	$\text{CF}_3\text{CO}_2\text{CF}_2\text{H}$ (II)	75	C, 22.0 F, 57.9	C, 21.7 F, 58.4
$\text{C}_3\text{F}_7\text{CO}_2\text{H}$	2	$\text{C}_3\text{F}_7\text{CO}_2\text{CF}_2\text{H}$ (III)	50	C, 22.7 F, 64.8	C, 22.1 F, 64.6
$\text{C}_4\text{H}_9\text{CO}_2\text{H}$	2	$\text{C}_4\text{H}_9\text{CO}_2\text{CF}_2\text{H}$ (IV)	88	C, 47.4 F, 25.0	C, 47.4 F, 25.3
$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	2	$\text{C}_6\text{H}_5\text{CO}_2\text{CF}_2\text{H}$ (V)	75	C, 55.8 F, 22.1	C, 55.6 F, 22.2
$\text{CF}_3\text{SO}_3\text{H}$	4.5	$\text{CF}_3\text{SO}_3\text{CF}_2\text{H}$ (VI)	71	C, 12.0 F, 47.5	C, 12.0 F, 47.4
$\text{CH}_3\text{OH}$	4	$\text{CH}_3\text{OCF}_2\text{H}$ (VII)	69	C, 29.3 F, 46.4	C, 29.1 F, 46.9
$\text{CF}_3\text{CH}_2\text{OH}$	5	$\text{CF}_3\text{CH}_2\text{OCF}_2\text{H}$ (VIII)	51	C, 24.0 F, 63.3	C, 23.4 F, 62.5
$(\text{CH}_3)_2\text{CHOH}$	2.5	$(\text{CH}_3)_2\text{CHOCF}_2\text{H}$ (IX)	83	(b)	

(a) Molar Ratio = moles of reactant/moles of  $\text{CF}_2\text{N}_2$ . (b) Hine (7) has reported the synthesis, infrared absorption spectrum, and elemental analyses for IX. Elemental analyses were not obtained in the present work since our spectral data are identical to that reported in the literature cited above.

TABLE II  
Nuclear Magnetic Resonance Spectra

Compound	Group	Position	Structure-Coupling (13)
$\text{CF}_3\text{CO}_2\text{CF}_2\text{H}$ (II)	$\text{CF}_3$	76.2 $\phi^*$	s
	$\text{CF}_2$	91.9 $\phi^*$	d, J = 68.2 c/s
	CH	2.89 $\tau$	t, J = 68.8 c/s
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2\text{CF}_2\text{H}$ (III)	$\text{CF}_3$	81.4 $\phi^*$	t, J = 8.8 c/s
	$\text{CF}_2$ (a)	127.3 $\phi^*$	s
	$\text{CF}_2$ (b)	120.2 $\phi^*$	q, J = 8.8 c/s
	$\text{CF}_2$ (c)	91.8 $\phi^*$	d, J = 68.6 c/s
	CH	2.87 $\tau$	t, J = 68.6 c/s
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CF}_2\text{H}$ (IV)	$\text{CF}_2$	92.7 $\phi^*$	d, J = 70.8 c/s
	CH	3.00 $\tau$	t, J = 70.8 c/s
	$\text{CH}_3$	9.03 $\tau$	t
	$\text{CH}_2$ (a)	~8.43 $\tau$	m
	$\text{CH}_2$ (b)	7.58 $\tau$	t
$\text{C}_6\text{H}_5\text{CO}_2\text{CF}_2\text{H}$ (V)	$\text{CF}_2$	91.9 $\phi^*$	d, J = 70.7 c/s
	CH	2.76 $\tau$	t, J = 70.7 c/s
	$\text{C}_6\text{H}_5$	~ { 1.98 $\tau$ 2.51 $\tau$	
$\text{CF}_3\text{SO}_3\text{CF}_2\text{H}$ (VI)	$\text{CF}_3$	75.5 $\phi^*$	t, J = 3.2 c/s
	$\text{CF}_2$	82.9 $\phi^*$	d-q, J = 68.5, 3.2 c/s
	CH	3.16 $\tau$	t, J = 68.5 c/s

TABLE II (Continued)

CH <sub>3</sub> OCF <sub>2</sub> H (VII)	CF <sub>2</sub>	88.2 $\phi^*$	d, J = 74.4 c/s
	CH	3.92 $\tau$	t, J = 74.4 c/s
	CH <sub>3</sub>	6.49 $\tau$	s
CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> H (VIII)	CF <sub>3</sub>	75.6 $\phi^*$	t-t, J = 8.0, 2.0 c/s
	CF <sub>2</sub>	87.1 $\phi^*$	d-q, J = 72.0, 2.0 c/s
	CH	3.72 $\tau$	t, J = 72.0 c/s
	CH <sub>2</sub>	5.83 $\tau$	q, J = 8.0 c/s
(CH <sub>3</sub> ) <sub>2</sub> CHOCF <sub>2</sub> H (IX)	CF <sub>2</sub>	82.2 $\phi^*$	d, J = 75.4 c/s
	CH	3.91 $\tau$	t, J = 75.4 c/s
	CH <sub>3</sub>	8.74 $\tau$	d, complex

TABLE III

Vapor Phase Chromatography Results

Compound	T <sub>R</sub> (a)	Compound	T <sub>R</sub>
CF <sub>3</sub> CO <sub>2</sub> CF <sub>2</sub> H (II)	30.0	CH <sub>3</sub> OCF <sub>2</sub> H (VII)	19.7
C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> CF <sub>2</sub> H (III)	174	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> H (VIII)	45.6
C <sub>4</sub> H <sub>9</sub> CO <sub>2</sub> CF <sub>2</sub> H (IV)	28.9 (b)	(CH <sub>3</sub> ) <sub>2</sub> CHOCF <sub>2</sub> H (IX)	139.
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CF <sub>2</sub> H (V)	225 (b)		
CF <sub>3</sub> SO <sub>3</sub> CF <sub>2</sub> H (VI)	107		

$$(a) T_R = \text{relative retention time} = \frac{T_{\text{compound}} - T_{\text{air}}}{T_{\text{CFC}_3} - T_{\text{air}}} \times 100.$$

(b) Bromobenzene was utilized as the reference in place of CFC<sub>3</sub>.

#### Difluoromethyl Benzoate.

A solution of 2.4 g. (0.020 mole) benzoic acid and 2.0 g. (0.0257 mole) difluorodiazirine in 16 ml. chloroform was irradiated as described in procedure (c). Infrared evaluation revealed that roughly 50% esterification had occurred when all of the diazirine had been photolyzed. Distillation through a short path apparatus afforded 1.4 g. (41%) of sweet-smelling product, b.p. 75°/15 mm.

*Anal.* Calcd. for C<sub>8</sub>H<sub>6</sub>F<sub>2</sub>O<sub>2</sub>: C, 55.8; F, 22.1. Found: C, 56.2; F, 21.8.

#### Hydrolysis of Difluoromethyl Benzoate.

A solution of 0.0517 g. (0.3 × 10<sup>-3</sup> mole) of difluoromethyl benzoate in 4 ml. of 3:1 1,2-dimethoxyethane-water was heated at reflux for 15 minutes, cooled, diluted with 10 ml. of water, and extracted twice with chloroform. The combined organic layers were dried over sodium sulfate and an infrared spectrum was recorded. The presence of a 5.62  $\mu$  absorption and the virtual absence of several absorptions characteristic of benzoic acid suggested that little or no hydrolysis occurred.

A 0.0550 g. (0.32 × 10<sup>-3</sup> mole) sample of V was stirred with 3 ml. of 2:1 1,2-dimethoxyethane - 1.0 N aqueous sodium hydroxide at reflux temperature for 20 min., cooled, diluted with 10 ml. of water, acidified with concentrated hydrochloric acid to pH 2, and extracted three times with chloroform. The combined organic layers were dried over sodium sulfate and concentrated to dryness to afford 0.0257 g. (66%) of benzoic acid as shown by melting point (120-121°) and failure to depress the melting point of authentic material after admixture.

#### Methyl Benzoate.

A solution of 0.34 g. (0.0020 mole) of difluoromethyl benzoate, 0.61 g. (0.0060 mole) of triethylamine and 0.42 g. (0.010 mole) of methanol in 5 ml. of chloroform was refluxed and stirred for 1.5 hours, cooled, extracted once with water, dried over sodium sulfate, and concentrated to 0.23 g. (85%) of essentially pure methyl benzoate as demonstrated by its infrared spectrum.

#### Difluoromethyl Benzoate.

A solution of 1.57 g. (0.0128 mole) benzoic acid and 2.0 g. (0.0257 mole) difluorodiazirine in 11 ml. of chloroform was irradiated as previously described, filtered to remove a small amount of brown residue, and diluted to 15.0 ml. A 1.0 ml. portion was used for infrared analysis which revealed virtually complete esterification.

#### Benzamide.

A 7.0 ml. (0.0060 mole) portion of the above chloroform solution containing V and 1.0 ml. of concentrated ammonium hydroxide were stirred at room temperature for 4 hours. The combined organic layers from three chloroform extractions were dried over sodium sulfate and diluted progressively with hexane to afford two crops of pure benzamide, 0.38 g. (52%), m.p. 125.5-127.5° and 0.05 g. (7%), m.p. 125-127°. Yields are calculated for two steps.

#### Benzanilide.

A 7.0 ml. (0.0060 mole) portion of the chloroform solution and 2.33 g. (0.0240 mole) aniline were stirred at reflux temperature for 3.0 hours, then cooled. The mixture was partitioned between water and additional chloroform. The separated organic layer was dried over sodium sulfate and diluted with hexane to afford two crops of benzanilide, 0.72 g. (61%), m.p. 161.5-162°, and 0.05 g. (4%), m.p. 155-160°. Evaporation of the mother liquors to dryness gave an additional 0.08 g. (7%) of crude product, m.p. 152-156°. Yields are for two steps.

#### Acknowledgments.

The authors are indebted to Mr. D. P. Babb and Mr. D. L. Wood for technical assistance, Dr. J. J. McBrady and Mr. R. A. Meiklejohn for infrared and nuclear magnetic resonance measurements and interpretation and Mr. B. W. Nippoldt and Mr. P. B. Olson for various analytical determinations.

This research was supported in part by the Advanced Research Projects Agency under contract NOrd 18688, and was monitored by the Bureau of Naval Weapons.

#### REFERENCES

- (1) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).
- (2) R. A. Mitsch, *ibid.*, **1**, 271 (1964).
- (3) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965).
- (4) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 233 (1964).
- (5) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957).
- (6) A. L. Henne and M. A. Smook, *ibid.*, **72**, 4378 (1950).
- (7a) J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957). (b) J. Hine and K. Tanabe, *ibid.*, **80**, 3002 (1958).
- (8) G. A. Sokol'skii and M. A. Dmitriev, *J. Gen. Chem., USSR*, **31**, 2561 (1961).
- (9) N. N. Yarovenko, M. A. Raksha, V. N. Shemanina, and A. S. Vasilyeva, *ibid.*, **27**, 2305 (1957).
- (10a) G. A. Sokol'skii and M. A. Dmitriev, *J. Gen. Chem., USSR*, **31**, 648 (1961). (b) *Ibid.*, **31**, 1023 (1961). (c) *Ibid.*, **31**, 1026 (1961). (d) *Ibid.*, **31**, 1540 (1961).
- (11) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).
- (12) G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).
- (13) s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; d-q, double quadruplet; t-t, triple triplet.
- (14) Minnesota Mining and Manufacturing Company, Kel-F 8126 oil; a chlorotrifluoroethylene tetramer.

Received March 31, 1965

St. Paul, Minnesota 55119