3,4-Dimethoxybenzylurethane (*Veratrylamine Urethane*) (**7**). Veratrole (3.46 grams, 25 mmol) and methylene diurethane (4.72 grams, 25 mmol) afforded 1.2 grams (20%) of a colorless oil, bp 163–7° (0.035 mm), which solidified to a white solid, mp 49–50°C (ether/pet ether), ir 3400 cm^{-1}, 1700 cm^{-1}; nmr δ 1.16 (*t*, 3, $J = 7$ Hz); 4.02 (*q*, 2, $J = 7$ Hz), 3.70 (*s*, 6), 4.15 (*d*, 2, $J = 6$ Hz), 5.45 (*b*, NH), 6.67 (*bs*, 3). *Anal.* Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.86. Found: C, 59.74; H, 7.18; N, 5.98.

Urethane **7** was prepared independently from veratrylamine and ethylchlorocarbonate and was converted to *N*-methyl veratrylamine hydrochloride, mp 201–3°C [reported 202–4° (*5*)].

α-Phenyl-3,4-dimethylbenzylurethane (**8**). Veratrole (3 grams, 22 mmol) and phenyl methylene diurethane (5.85 grams, 22 mmol) afforded 2.35 grams (37%) of white solid, mp 98.5–99.5° (90% ethanol). Ir 3450 cm^{-1}, 1700 cm^{-1}; nmr δ 7.15 (*s*, 5); 6.67 (*s*, 3), 5.81 (*d*, one, $J = 9$ Hz), 5.22 (*d* broad, one, $J = 9$ Hz), 4.08 (*q*, 2, $J = 7.5$ Hz), 3.76 (*s*, 3), 3.73 (*s*, 3), 1.2 (*t*, 3, $J = 7.5$ Hz). *Anal.* Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.68; H, 6.52; N, 4.54.

α-Acetyl-3,4-dimethoxybenzylurethane (**9**). Veratrole (4.0 grams, 29 mmol) and α-acetyl-1,1-diurethane (6.75 grams, 29 mmol) afforded, after elution from florisil with 50/50 ether/pet ether, 3.71 grams (46%) of a white solid, mp 80–1°C (ether). Ir 3375 cm^{-1}, 1700 cm^{-1} broad; nmr δ 6.78 (*s*, 5), 6.26 (*d*, one, $J = 6$ Hz), 5.23 (*d*, one $J = 6$ Hz), 4.0 (*q*, 2, $J = 7$ Hz), 3.77 (*s*, 6), 2.08 (*s*, 3), 1.15 (*t*, 3, $J =$ Hz). *Anal.* Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98. Found: C, 59.82; H, 6.84; N, 5.06.

REFERENCES

(1) Bianci, G., *Gazz Chim Ital.*, **42**, 1, 499 (1912); *CA* **6**, 2418 (1912).

(2) Cava, M., Wilkins, C., *Chem. Ind.*, 1422 (1964).

(3) Cava, M., Wilkins, C., Dalton, D., Bessho, K., *J. Org. Chem.*, **30**, 3772 (1965).

(4) Frydman, B., Reil, S., Valasinas, A., Frydman, R., Rapoport, H., *J. Amer. Chem. Soc.*, **93**, 2738 (1971).

(5) Grethe, G., Lee, H., Uskokovic, M., Brossi, A., *J. Org. Chem.*, **33**, 491 (1968).

(6) Gutsche, C., Johnson, H., *J. Amer. Chem. Soc.*, **77**, 109 (1955).

(7) Harter, H., Liisberg, S., *Acta Chem. Scand.*, **22**, 2685 (1968).

(8) Hobson, J. D., Riddell, W. D., *Chem. Commun.*, **1968**, 1180.

(9) Merten, R., Müller G., *Angew. Chem.*, **74**, 866 (1962).

(10) Merten, R., Müller, G., *Chem. Ber.*, **97**, 682 (1964).

(11) Merten, R., Müller, G., Kritzler, H., Wagner, K., Holtschmidt, H., Belg. Patent 627,280 (1963); *CA*, **60**, 10598e (1964).

(12) Quan, M. P., Karns, T. K. B., Quin, L. D., *Chem. Ind.*, 1553 (1964).

(13) Wilkins, C., *Tetrahedron Lett.*, **1965**, p 4817.

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Esterification and Addition Reactions of Perfluoroacryloyl Chloride

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Perfluoroacryloyl chloride was prepared from the acid using phosphorus pentachloride, and 3-chloro-2,3,3-trifluoropropionyl chloride was obtained as an unexpected by-product. 2,2-Difluoro-2-nitroethyl perfluoroacrylate was prepared using triethylamine and aluminum chloride. The physical properties and stereochemistry of the compounds are described.

Our interest in the synthesis of energetic monomers led to development of a synthesis for 2,2-difluoro-2-nitroethanol and its acrylate ester (*6*). This work was extended to include the preparation of 2,2-difluoro-2-nitroethyl perfluoroacrylate, IV. During the course of this work, some unusual addition reactions of hydrogen chloride and difluoronitroethanol to the perfluoroacryloyl group were observed. We now report the ester synthesis and a stereochemical analysis of the adducts.

The direct esterification of perfluoroacrylic acid, I, with difluoronitroethanol by conventional methods proved difficult; consequently, the esterification of perfluoroacryloyl chloride, II was investigated. To obtain the chloride, I was first prepared using a modification of Knunyants' procedure which involved the treatment of $CF_2 = CFMgI$ with carbon dioxide followed by acidification (*3*). The synthesis of II in 75% yield by the reaction of I with phosphorus pentachloride was reported by Gruz et al. (*3*), but the reaction conditions were not described. As a result several exploratory reactions were carried out to find optimum conditions for the preparation of II. When I was treated with an equimolar amount of phosphorus pentachloride at ambient temperature, II (10%) and 3-chloro-2,3,3-trifluoropropionyl chloride, III (40%), resulted, Reaction 1.

$$\underset{\text{I}}{CF_2 = CFCO_2H} + PCl_5 \rightarrow \underset{\text{II}}{CF_2 = CFCOCl} + \underset{\text{III}}{ClCF_2CHFCOCl} \quad (1)$$

The formation of III by the addition of hydrogen chloride to II was unusual when one considers the mild conditions used. Although several examples of nucleophilic and hydrogen halide addition to the double bond of the perfluoroacryloyl group have been reported (*1*, *3*, *7*, *9*, *10*), hydrogen halide additions usually require high temperatures and pressures. The structure of III was confirmed and differentiated from its other possible positional isomer, 2-chloro-2,3,3-trifluoropropionyl chloride, by proton and fluorine nmr spectral analyses. The best procedure developed for preparation of II was the dropwise addition of a benzoyl chloride solution of I to a slurry of phosphorus pentachloride in benzoyl chloride at 7 mm Hg. With use of this technique, II was removed from the reaction vessel as formed and was obtained in 60% yield with a 10% yield of III. Those reactions in which the pressure was allowed to rise to 15-20 mm showed a considerable increase in the yield of III.

The esterification of II with 2,2-difluoro-2-nitroethanol to obtain 2,2-difluoro-2-nitroethyl perfluoroacrylate, IV, was carried out by two different methods. First, II was treated with difluoronitroethanol at −35° to −40°C in the presence of triethylamine. IV was obtained in 8% yield, and a by-

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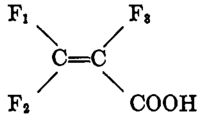
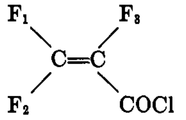
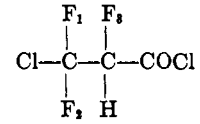
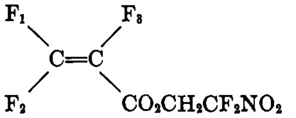
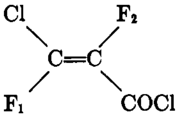
Table I. Nmr Data for Fluoronitro Compounds

Compound	Structure	Atom	Chemical shift, φ^*/τ	Splitting[a] pattern	Coupling constants, Hz
I		F_1	8.6/	2d	$J_{F_{1,3}}$ = 35, $J_{F_{1,2}}$ = 25
		F_2	95.0/	2d	$J_{F_{2,3}}$ = 116, $J_{F_{1,2}}$ = 25
		F_3	178.0/	2d	$J_{F_{2,}}$ = 116, $J_{F_{1,3}}$ = 37
II		F_1	76.0/	2d	$J_{F_{1,3}}$ = 42, $J_{F_{1,2}}$ = 8.6
		F_2	86.7/	2d	$J_{F_{2,3}}$ = 117, $J_{F_{1,2}}$ = 8.6
		F_3	168.0/	2d	$J_{F_{2,3}}$ = 117, $J_{F_{1,3}}$ = 44
III	 $\mathrm{Cl{-}CF_1F_2{-}CF_3H{-}COCl}$	F_1 & F_2	61.5/	q	$J_{F_{1,2,3}}$ = 75
		F_3	177.0/	2t	J_{HF_3} = 46, $J_{F_{1,3}}$ = 15
		H	/5.0	4d	$J_{F_{1,2}}$ = 15, J_{HF_3} = 46
IV		F_1	78.5/	2d	$J_{F_{1,3}}$ = 37, $J_{F_{1,2}}$ = 8.0
		F_2	90.0/	2d	$J_{F_{2,3}}$ = 117, $J_{F_{1,2}}$ = 8.0
		F_3	180.0/	2d	$J_{F_{2,3}}$ = 117, $J_{F_{1,3}}$ = 37
		CF_2	91.5/	t	J = 7
		CH_2	/5.2	t	J = 10
V	$NO_2CF_2CH_2OCF_2CFHCOCl$	OCF_2	62.0/	m	
		CF_2NO_2	92.5/	bs	
		CHF	220.0/	2t	J_{HF} = 43
		CH_2	/5.2	t	
		CHF	/5.0	m	
VI		F_1	143.0/	d	$J_{F_{1,2}}$ = 142
		F_2	86.0/	d	$J_{F_{1,2}}$ = 142

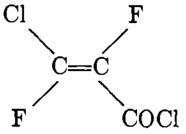
[a] s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, b = broad.

product, 3-(2,2-difluoro-2-nitroethoxy)-2,3,3-trifluoropropionyl chloride, V, was isolated in 7% yield, Reaction 2. V resulted from the addition of difluoronitroethanol to II.

$$\text{II} + HOCH_2CF_2NO_2 \xrightarrow{N(Et)_3} \underset{\text{IV}}{F_2C = CFCOOCH_2CF_2NO_2} + \underset{\text{V}}{O_2NCF_2CH_2OCF_2CFHCOCl} \quad (2)$$

To improve the yield of IV, a second esterification method was employed. Catalysis by aluminum chloride has been effective when electronegatively substituted alcohols are esterified (*4*, *5*). Therefore, difluoronitroethanol in chloroform was treated with an equimolar amount of aluminum chloride to give a solution of the dichloroaluminate of the alcohol. This solution was allowed to react with II to produce mainly 3-chloro-*trans*-2,2-difluoroacryloyl chloride, VI, Reaction 3, and small amounts of IV and V.

$$\text{II} + Cl_2AlOCH_2CF_2NO_2 \rightarrow$$



VI

$$+ \text{IV} + \text{V} \quad (3)$$

These results indicate that under the above conditions the fluorine trans to the acid chloride group is more susceptible to chlorine substitution than is the acid chloride group toward esterification. The nmr data for compounds I–VI are recorded in Table I.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Elemental analyses were determined by Stanford University Microanalytical Laboratory. Nmr analyses were performed on a Varian HA-100 spectrometer. ^1H chemical shifts are given in τ units relative to tetramethylsilane, and ^{19}F chemical shifts are given in φ^* units (*2*) relative to fluorotrichloromethane. Infrared spectra were run on a Perkin-Elmer 137 Infracord spectrophotometer. In ir designations, s = strong, m = medium, w = weak, and b = broad. Glpc analyses were run on an F&M Model 500 gas chromatograph; the column was 4 ft × $^1/_4$ in.-stainless steel packed with silicone gum rubber on Chromosorb P, 30–60 mesh.

CAUTION: The fluoro and nitro compounds described in this paper possess varying degrees of toxicity, and therefore, should be handled with care. Although no hazardous incidents occurred during the present work, difluoronitroethanol and perfluoroacryloyl chloride may cause painful burns when brought into contact with the skin.

Perfluoroacryloyl Chloride, II. To a rapidly stirring mixture of 30.0 grams (0.143 mole) of phosphorus pentachloride in 25 ml of benzoyl chloride under 7 mm Hg pressure was added a solution of 13.2 grams (0.105 mole) of I in 20 ml of benzoyl chloride at such a rate that the hydrogen chloride liberated from the reaction mixture did not appreciably increase the pressure. Under these conditions II was removed from the reaction mixture as it formed, through a 50-cm vertical condenser connected to two receivers in series at −75°C. The crude reaction product consisted of II, III, phosphorus oxychloride, and benzoyl chloride. Fractional distillation of the mixture through a 5-cm column gave 8.6 grams (60%) of II: bp 54-58°C (760 mm); [lit. (*8*) bp 49-51°C (760 mm)]; ir (gas) 1680 (s, C = 0), 1660 (m, C = C), 1300 and 1350 cm^{-1} (s, CF).

2,2-Difluoro-2-nitroethyl Perfluoroacrylate, IV. 2,2-Difluoro-2-nitroethanol (3.4 grams, 0.026 mole) and triethylamine (2.72 grams, 0.027 mole) in 40 ml of ether were added over 40 min to a solution of II (3.9 grams, 0.026 mole) in 100 ml of ether at −35° to −40°C. The triethylamine hydrochloride was filtered, and the filtrate was evaporated at 18 mm leaving 1.0 gram of liquid material. Fractional distillation gave 0.5 gram (7.9%) of IV: bp 65°C (10 mm) and 0.4 gram (7%) V, containing approximately 10% of IV: ir (neat) 2935 (w, CH), 1750 (s, C = 0), 1000 (m, NO_2), 1300-1400 cm^{-1} (bs, CF).

Anal. Calcd. for $C_5H_2F_5NO_4$: C, 25.6; H, 0.9; N, 6.0. Found: C, 24.7; H, 1.0; N, 5.6.

Reaction of Perfluoroacryloyl Chloride with 2,2-Difluoro-2-nitroethanol and Aluminum Chloride Catalyst. Aluminum chloride (0.26 gram, 0.002 mole) was added to a solution of 2,2-difluoro-2-nitroethanol (0.25 gram, 0.002 mole) in 0.5 gram of chloroform. Hydrogen chloride evolved, and after 1 hr the aluminum chloride had dissolved. To the solution was then added II (0.3 gram, 0.002 mole), and the mixture was allowed to stir for 18 hr. The mixture was washed with 1 ml of cold concentrated hydrochloric acid, dried over magnesium sulfate, filtered, and analyzed by glpc. The major fraction (Peak A) was VI: ir (gas) 1700 (s, C = 0) 1690 (w, C = 0), 1250-1300 cm^{-1} (bs, CF).

Anal. Calcd. for $C_3Cl_2F_2O$: C, 22.4; Cl, 44.0. Found: C, 22.4; Cl, 39.8.

Peak B was 40% of Peak A and was identified as IV. Peak C was 40% of Peak A and was identified as V: IR (neat) 2920 (w, CH), 1800 (s, C═O), 1600 (s, C—NO_2), 1100-1200 cm^{-1} (bs, CF).

Anal. Calcd. for $C_5H_3ClF_5NO_4$: C, 22.2; H, 1.1; Cl, 13.1; N, 5.6. Found: C, 21.5; H, 1.3; Cl, 15.6; N, 4.3.

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LITERATURE CITED

(1) Brice, T. J., Lazerte, J. D., Hals, L. J., Pearlson, W. H., *J. Amer. Chem. Soc.*, **75**, 2698 (1953).
(2) Filipovich, G., Tiers, G. V. D., *J. Phys. Chem.*, **63**, 761 (1959).
(3) Gruz, B. E., Sterlin, R. I., Yagupol'skii, L. M. *Zh. Obshch. Khim.* **34** (12), 4122 (1964); see *CA* **62**, 16225*g* (1965); also *J. Gen. Chem. USSR*, **34** (12), 1487 (1964).
(4) Hill, M. E., *J. Amer. Chem. Soc.*, **75**, 3020 (1953).
(5) Hill, M. E., *ibid.*, **76**, 2329 (1954).
(6) Hill, M. E., Ross, L. O., *J. Org. Chem.*, **32**, 2595 (1967).
(7) Knunyants, I. L., Shokina, V. V., Kuleshova, W. D., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.* (9), 1693 (1960); see *CA* **55**, 9254*g* (1961); also *Bull. Akad. Sci. USSR* (9), 1568 (1960).
(8) Knunyants, I. L., Sterlin, R. N., Yatsenko, R. D., Pinkina, L. N., *Ivz. Akad. Nauk SSSR, Otd. Khim. Nauk.* (11), 1345 (1958); see *CA* **53**, 6987g (1959); also *Bull. Akad. Sci. USSR*, (11), 1297 (1958).
(9) Koshar, R. J., Simmons, T. C., Hoffmann, F. W., *J. Amer. Chem. Soc.*, **79**, 1741 (1957).
(10) Lazerte, J. D., Koshar, R. J., *ibid.*, **77**, 910 (1955).

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