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1,2,4-OXADIAZOLYL PERFLUORO-OLEFINS *

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SUMMARY

1,2,4-Oxadiazolyl perfluoro-olefins have been prepared from arylamidoxime (3-aryl-1,2,4-oxadiazol-5-yl)perfluorocarboxylates *via* the corresponding free acids and sodium salts. Attempts to homo- and co-polymerise these perfluoro-olefins by emulsion and free-radical techniques have been unsuccessful.

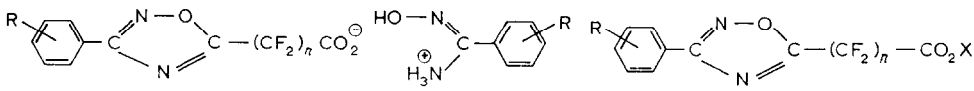
INTRODUCTION

Only a limited study has been made of heterocyclic compounds containing the perfluoroalkenyl group. Yagupol'skii and Malichenko[1] have described the syntheses and properties of 2-(trifluorovinyl)- and 2-(pentafluoropropenyl)-benzothiazoles.

It has now been found[2] that the major products of the reaction between arylamidoximes and hexafluoroglutaryl or tetrafluorosuccinyl chlorides were the arylamidoxime (3-aryl-1,2,4-oxadiazol-5-yl)perfluoro-n-butyrates or propionates. In this paper is described the preparation and characterisation of a group of 1,2,4-oxadiazolyl perfluoro-olefins derived from these carboxylates by conversion into the corresponding acids and pyrolysis of the sodium salts. Also described are some attempts to homo- and co-polymerise the olefins.

RESULTS AND DISCUSSION

The formation[2] of arylamidoxime salts (I) ($n = 3$, R = H, p-CH_3, m-CH_3; $n = 2$, R = H) from the reaction of arylamidoximes and hexafluoroglutaryl or tetrafluorosuccinyl chlorides has allowed an easy route to some 1,2,4-oxadiazolyl perfluoro-olefins, *via* the corresponding carboxylic acids.

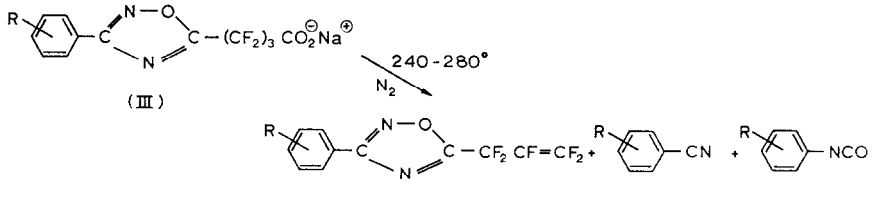


(I) (II)

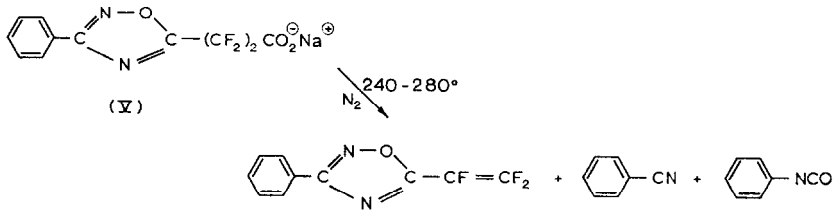
Treatment of an aqueous solution of the arylamidoxime salts (I) with an exact equivalent of sodium hydroxide, followed by extraction with ether to remove the arylamidoxime, and then acidification of the aqueous filtrate and ether extraction, gave the acids (II) (X = H) in high yield (Table 1). Their extremely hygroscopic nature made an exact analysis rather difficult. However, aniline, *o*-toluidine, isothiouronium and benzamidoxime salts were readily formed and characterised and the equivalent weights of the acids and salts obtained by potentiometric means. The infrared (IR) spectra of all the acids contained strong bands at 1780–1775 (C=O str.), at 1590 and 1510 (ring C=N) and at 1220–1120 cm^{-1} (C–F str.).

Pure, dry sodium salts (III) (R = H, *p*-CH_3, *m*-CH_3) and (V) were obtained by careful neutralisation of the corresponding acids, (II) (X = H), removing the water in a rotary film evaporator to overcome severe frothing and rigorous drying at 90° *in vacuo*. Their IR spectra showed the characteristic shift of C=O stretching frequency from 1780–1775 cm^{-1} in the un-ionised acid to 1680–1675 cm^{-1} in the ionised salt[3,4].

Thermal decomposition (200–450°) of the dry sodium salts of certain simple perfluorocarboxylic acids has given[5–9] terminal perfluoro-olefins. Controlled pyrolysis of the sodium salts (III) (R = H, *p*-CH_3, *m*-CH_3) and (V) was conducted, preferably under reduced pressure[10,11], between 240° and 280°. Unlike those from the simple sodium salts, the products (IV) (R = H, *p*-CH_3, *m*-CH_3) and (VI) were impure, containing small amounts of aryl nitriles and aryl isocyanates.



(III) (IV)



(V) (VI)

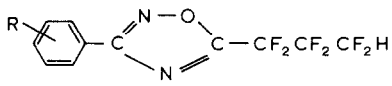
TABLE 1

4-(3-ARYL-1,2,4-OXADIAZOL-5-YL)HEXAFLUORO-n-BUTYRIC AND 3-(3-PHENYL-1,2,4-OXADIAZOL-5-YL)TETRAFLUOROPROPIONIC ACIDS AND SOME SALTS (II)*

n	R	X	Yield (%)	M.p. (°C)	Equivalent:		Analysis: Calc. %				Found %			
					Req'd.	Found	C	H	F	N	C	H	F	N
3	H	$H\overset{\oplus}{}$	91	92–93	340	336	42.4	1.8	33.5	8.2	42.8	1.9	32.5	8.2
3	H	$C_6H_5\overset{\oplus}{N}H_3$	—	105–106	433	433	49.9	3.0	26.3	9.7	49.9	3.1	26.3	9.8
3	H	$p\text{-}C_6H_4\overset{\oplus}{}$	—	139–140	447	448	50.9	3.6	25.4	9.4	50.9	3.5	25.2	9.1
3	H	$C_6H_5CH_2S(=\overset{\oplus}{N}H_2)NH_2 \cdot H_2O$	—	167–168	—	—	45.9	3.5	—	10.5	45.8	3.5	—	10.7
3	$p\text{-}CH_3$	H	87	100.5–101.5	354	356	44.1	2.3	32.2	7.9	43.7	2.5	31.4	8.2
3	$m\text{-}CH_3$	H	89	83–85	354	356	44.1	2.3	32.2	7.9	44.2	2.2	32.4	8.6
2	H	H	85	95–96	290	291	45.5	2.1	26.2	9.7	45.8	2.1	25.9	9.7

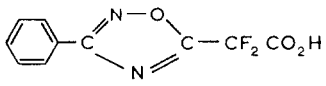
* Compounds described in the Table are new.

The aryl isocyanates, which were isolated after alkaline washing as the corresponding sym-diarylureas, may have originated from rearrangement of the arylnitrile oxide. These impurities indicated that cleavage of the 1,2,4-oxadiazole ring occurred in more than one way at the temperatures employed. Other impurities observed on pyrolysis of compounds (III) (R = H, *p*-CH_3, *m*-CH_3) were perfluoroglutarimide (traces) and the 3-(3-aryl-1,2,4-oxadiazol-5-yl)-1*H*-hexafluoropropanes (VII) which must have originated from pyrolysis of small amounts of free acids.



(VII)

The unsubstituted olefin (IV) (R = H) was isolated as the dibromide and subsequently dehalogenated to give the pure olefin; this method was not possible, however, with the methyl derivatives. Purification of olefins (IV) (R = H, *p*-CH_3) was possible by low-temperature crystallisation (−20°) from ethanol; olefin (IV) (R = *m*-CH_3) did not crystallise, and purification was accomplished by preparative scale gas–liquid chromatography (GLC). Properties are shown in Table 2. Olefin (VI) was only produced in small amounts and it was therefore isolated by preparative-scale GLC; characterisation of this compound was by mass spectrometry (MS), it having a top mass peak of *m/e* 226 (parent ion) and a consistent fragmentation pattern. The IR spectrum of 3-(3-phenyl-1,2,4-oxadiazol-5-yl)pentafluoroprop-1-ene ((IV); R = H) (Fig. 1) is typical for all of these olefins, and shows bands characteristic for perfluoroalkyl-substituted 1,2,4-oxadiazole rings and a strong band at 1780–1790 cm^{-1} due to the FC=CF_2 group[4]. The position of the double bond was confirmed by oxidation with aqueous permanganate to give the substituted difluoroacetic acid.



The ^{19}F nuclear magnetic resonance (NMR) spectra of the perfluoro-olefins (IV) (R = H, *p*-CH_3, *m*-CH_3) have been reported by Jolley and Sutcliffe[12]. Accurate chemical shifts and coupling constants have been determined at 56.44 MHz; it was found that the spectra of these olefins are identical to within ±0.2 Hz and are determined only by the presence of the ring system and not the ring substituents.

Relatively little work on the polymerisation of azoles containing vinylic or allylic side-groups has been reported; a recent review[13] has summarised the known work.

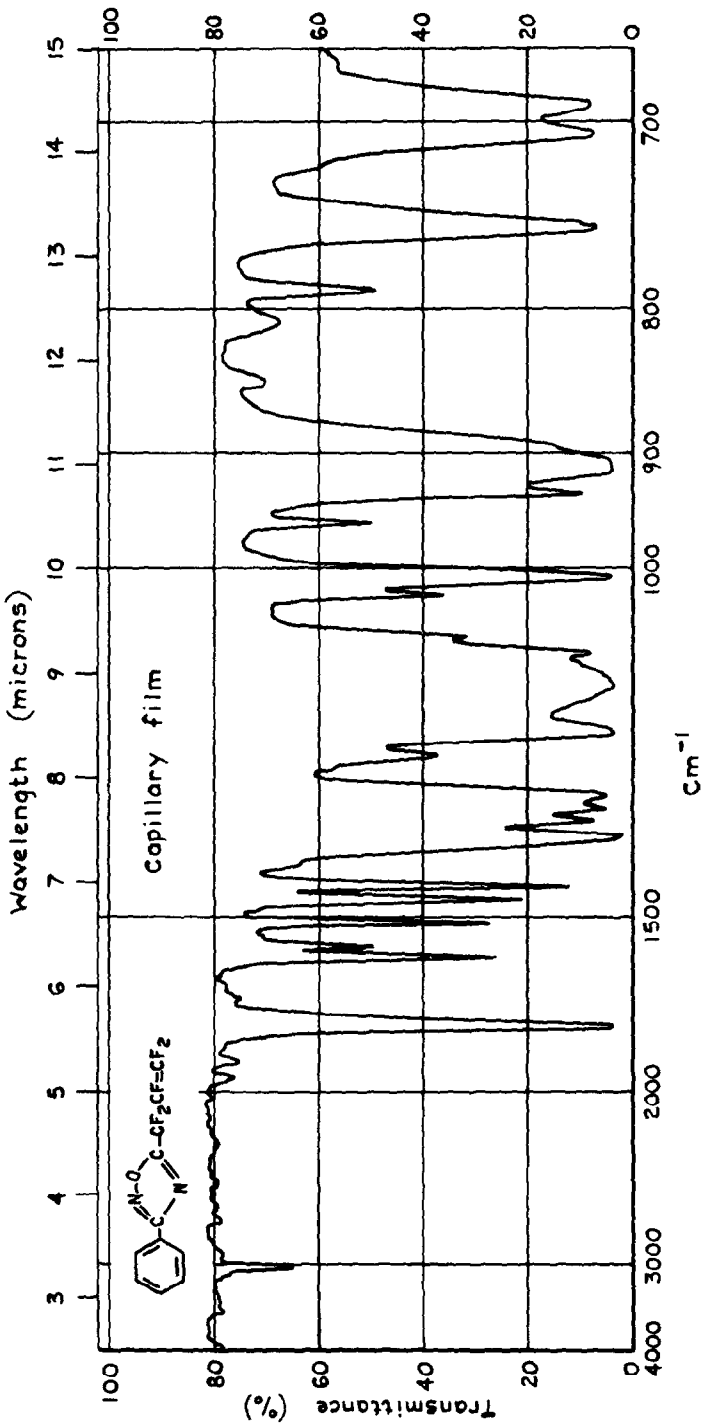


Fig. 1. The IR spectrum of 3-(3-phenyl-1,2,4-oxadiazol-5-yl)pentafluoroprop-1-ene

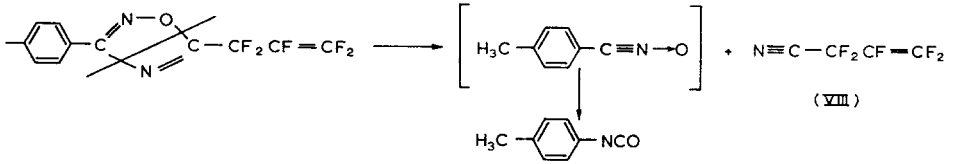
TABLE 2

1,2,4-OXADIAZOLYL PERFLUORO-OLEFINS (IV)

R	Yield %	B.p. (°C/mmHg)[a]	n_D^{20}	Analysis: Calcd. % C	H	F	N	Found % C	H	F	N
H(nc)	69	133/40	1.4680	47.8	1.8	34.4	10.2	48.0	2.2	34.7	10.1
p-CH_3(nc)	65	153/40	1.4728	49.7	2.4	32.8	—	50.0	2.4	33.1	—
m-CH_3(nc)	64	150/40	1.4708	49.7	2.4	32.8	—	49.8	2.7	32.7	—

[a] 1 mmHg = 133.3 N m^{-2}.

Attempted homopolymerisation of the 3-(3-aryl-1,2,4-oxadiazol-5-yl)pentafluoroprop-1-enes ((IV), R = H, *p*-CH_3, *m*-CH_3) in glass-lined and polytetrafluoroethylene-lined steel tubes met with very little success using emulsion or solution techniques. The *para*-tolyl compound (IV) (R = *p*-CH_3) did give a gummy material in approximately 15% yield; however, (IR) spectra indicated that polymerisation had not occurred *via* the $FC{=}CF_2$ group. *p*-Tolyl isocyanate was observed as a byproduct of the polymerisation; it may be, therefore, that the 1,2,4-oxadiazole ring was cleaving in the following way with compound (VIII) then polymerising *via* the C≡N group.



Traces only of copolymers with tetrafluoroethylene (TFE) and vinylidene fluoride (VDF) were obtained; indeed, a distinct inhibition to homopolymerisation of these two monomers seemed to occur.

The difficulties encountered in polymerising these 1,2,4-oxadiazolyl-perfluoro-olefins parallels the unsuccessful attempts[14] to polymerise 2-(trifluorovinyl)-benzothiazole by free-radical initiation in solution, or in emulsion, or by the use of Ziegler catalysts.

EXPERIMENTAL

4-(3-Phenyl-1,2,4-oxadiazol-5-yl)hexafluoro-n-butyric acid ((II); n = 3, X = H)

Benzamidoxime 4-(3-phenyl-1,2,4-oxadiazol-5-yl)hexafluoro-n-butyrate (10 g, 210 mmole), dissolved in hot water (150 ml), was titrated potentiometrically to the equivalence point (pH 8.5) with *N* NaOH (21 ml). The aqueous solution was then extracted with ether (5 × 25 ml), to remove benzamidoxime, before acidification

with 10% sulphuric acid; the oil which separated was extracted with ether (5 × 25 ml), washed with water, and dried ($MgSO_4$). Removal of the ether gave 4-(3-phenyl-1,2,4-oxadiazol-5-yl)hexafluoro-n-butyric acid ((II); $n = 3$, X = H) (nc) which was then purified by sublimation at 130–140°/0.1 mmHg (see Table 1).

The corresponding *p*- and *m*-tolyl compounds (nc) and 3-(3-phenyl-1,2,4-oxadiazol-5-yl)tetrafluoropropionic acid ((II); $n = 2$, X = H) (nc), were similarly prepared (Table 1).

Preparation of 1,2,4-oxadiazolyl perfluoro-olefins

(i) 3-(3-Phenyl-1,2,4-oxadiazol-5-yl)pentafluoroprop-1-ene ((IV); R = H)

Sodium 4-(3-phenyl-1,2,4-oxadiazol-5-yl)hexafluoro-n-butyrate ((III); R=H) (19 g, 50 mmole) was rigorously dried *in vacuo* at 90° for several hours and then anhydrously charged into a 50 ml flask. The flask was equipped with a condenser, receiver and cold-trap (−70°) and was heated in an air bath. At 210–215° the salt melted and a vacuum (5 mmHg) was applied, at 225–230° a pale-yellow coloured liquid slowly distilled and at 240° the liquid was distilling rapidly. As the distillation rate decreased, the temperature of the flask was increased, and at 275–280° a small amount of an acrid, red oil distilled and was collected separately; the (IR) spectrum showed this to be hexafluoroglutarimide.

The main distillate (11.4 g), which according to IR and GLC analysis contained benzonitrile, was dissolved in ether and the ethereal extract washed successively with 2% sodium hydroxide solution and water. The ethereal solution was dried ($MgSO_4$) and the ether removed to give a colourless oil, from which precipitated sym-diphenylurea (1.0 g), m.p. 234–235°, undepressed on admixture with an authentic sample and with the correct IR spectrum. The residual oil was distilled (113–118°/22 mmHg) giving four fractions which were shown by GLC (Silicone E 301, column temperature 150°) to consist mainly of the required olefin, together with a small yield (*ca.* 10%) of a byproduct. Precise fractional distillation (b.p. 133°/40 mmHg), followed by low-temperature crystallisation from ethanol (−20°), afforded pure 3-(3-phenyl-1,2,4-oxadiazol-5-yl)pentafluoroprop-1-ene ((IV); R = H) (nc) (Table 2).

The olefin (2.8 g, 10 mmole) was boiled under reflux with potassium permanganate (6 g) in water (30 ml) for 4 h. No residual olefin was detected and crude fluorinated acid was isolated; after two sublimations (102–103°/10^{-4} mmHg), 2-(3-phenyl-1,2,4-oxadiazol-5-yl)difluoroacetic acid (nc) was obtained, m.p. 89–90° (Found: C, 50.7; H, 1.9; F, 15.5; N, 11.4%, equiv., 238. $C_{10}H_6F_2N_2O_3$ requires C, 50.0; H, 2.5; F, 16.0; N, 11.6%, equiv., 240).

(ii) 3-[3-(p-Tolyl)-1,2,4-oxadiazol-5-yl]pentafluoroprop-1-ene ((IV); R = p-CH_3) (nc)

Compound (IV) (R = *p*-CH_3) was similarly prepared and purified by precise fractional distillation (b.p. 153°/40 mmHg), followed by low-temperature crystallisation from ethanol (−20°) (Table 2).

*(iii) 3-[3-(*m*-Tolyl)-1,2,4-oxadiazol-5-yl]pentafluoroprop-1-ene ((IV) ; R = m-CH_3) (nc)*

Compound (IV) (R = *m*-CH_3) was similarly prepared, and purified by preparative scale GLC (Silicone E 301, column temperature 200°) (Table 2). An impurity (10%) of similar retention time to the required product was observed as in preparations (i) and (ii); on this occasion it was isolated during the GLC separation and shown by IR and mass spectroscopy to be 3-[3-(*m*-tolyl)-1,2,4-oxadiazol-5-yl]-1*H*-hexafluoropropane ((VII); R = *m*-CH_3) (nc).

(iv) 2-(3-Phenyl-1,2,4-oxadiazol-5-yl)trifluoroethylene (VI) (nc)

Compound (VI) was similarly prepared and purified by preparative scale GLC (Silicone E 301, column temperature 190°).

Polymerisation studies

General

Homopolymerisations were carried out in glass tubes; copolymerisations with TFE or VDF were carried out in glass- or PTFE-lined, stainless steel bombs. Initiator systems were (A) 0.01 g $K_2S_2O_8$, 0.2 g $C_7F_{15}COONH_4$, 0.12 g $Na_2HPO_4 \cdot 12H_2O$ in 5 ml H_2O; (B) 0.01 g $K_2S_2O_8$, 0.01 g borax in 5 ml H_2O; (C) 0.001 g azo-1-cyanocyclohexane in 1.5 ml toluene; (D) 0.01 g benzoyl peroxide in 1 ml benzene.

Emulsion polymerisations

A polymerisation tube containing the pure olefin and initiator system was degassed at 0° and sealed under vacuum. The tube was then allowed to warm to room temperature and agitated at a temperature between 64 and 105° for up to 300 h. With copolymerisations, the comonomer was charged *via* a vacuum line into the polymerisation tube containing the 1,2,4-oxadiazolyl perfluoro-olefin, acetone (4.5 ml), catalyst and emulsifying agent.

Free-radical polymerisations

The 1,2,4-oxadiazolyl perfluoro-olefin and free-radical catalyst were placed in a polymerisation tube, the tube then degassed and sealed under vacuum, and heated at a temperature between 60 and 105° for up to 360 h.

(i) Olefin (IV) (R = H) (5 mmole) gave no product using initiator systems (A), (B) and (C). Copolymerisation with TFE (50 mmole) gave only PTFE (trace) using initiators (B) and (C); initiator (D) gave copolymer (IR spectrum), $T_m > 308°$, 0.3%. With VDF (50 mmole), using initiator (A) a copolymer (IR spectrum), $T_m > 312°$, 0.3%, was obtained.

(ii) Olefin (IV) (R = *p*-CH_3) (4.7 mmole) with initiator system (B) gave phenyl isocyanate and a product (14.7%) having $FC{=}CF_2$ absorptions. Copolymerisation with TFE (47 mmole) and VDF (48 mmole), using initiator system (D), gave a trace and 10%, respectively, of copolymer (IR spectrum).

(iii) Olefin (IV) (R = *m*-CH_3) (4.7 mmole), gave no product using initiator systems (B) and (C). Copolymerisation with VDF (47 mmole), using initiator (B), gave a trace of copolymer (IR spectrum).

ACKNOWLEDGEMENT

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