

Experimental Section¹¹

Ketones.—Ethyl 3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate (11)¹² and ethyl benzoylacetate¹³ were synthesized as described in the literature. The ethyl acetoacetate was a redistilled commercial product.

Nitroso Ketones.—The general procedure of Barltrop and co-workers¹⁴ using isoamyl nitrite and hydrogen chloride with the ketone was followed. A minor variation in the present work was the use of tetrahydrofuran as the solvent instead of ethyl ether. Ethyl nitrosoacetoacetate (9) (29–43%) showed bp 122–125° (2.6–3.0 mm), n_D^{25} 1.4562 (lit.¹⁵ n_D^{25} 1.4557); ethyl nitrosobenzoylacetate (6), mp 119–120° (lit.¹⁶ 120–121°).

The nitrosation of ethyl 3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate (11) led to a product (3) in high yield (95% calcd for the nitroso derivative) which was found by tlc (SilicAR TLC-7G, 5% methanol–95% chloroform) to be a ca. 1:1 mixture of two components. When the slower moving component was allowed to stand in ethyl acetate for 18 hr, it was found that two components having the same R_f values as those in the original mixture were again present. The isolation of the component with the higher R_f by fraction crystallization was unsuccessful, but the component with the lower R_f was obtained from ether in this way. The crystalline white solid melted at 146–148° dec.

Anal. Calcd for $C_{14}H_{18}N_2O_6$: C, 54.18; H, 5.84; N, 9.02. Found: C, 54.03; H, 5.72; N, 8.96.

The ir (KBr) for the higher R_f fraction showed absorption bands at 2.99 (pyrrole NH), 5.74 (side chain ester C=O), 5.95 (ring ester C=O), 6.18 (keto C=O), 8.28 μ (nitroso dimer),^{10d} the lower R_f fraction, 2.87 (oximino OH), 3.07 (pyrrole NH), 5.74 (side chain ester C=O), 5.91 (ring ester C=O), 6.21 (keto C=O), 6.68 μ (oximino C=N).¹⁷

Ethyl 2-Amino-3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate Hydrochloride (2).—A solution of 3.1 g of the mixture 3 obtained from the nitrosation of ethyl 3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate in 50 ml of 95% ethyl alcohol and 1.67 ml of 6 *N* hydrochloric acid was shaken with 0.3 g of 5% palladium-on-charcoal catalyst in an atmosphere of hydrogen (initial pressure 42 psig) in a Burgess-Parr hydrogenator. Hydrogenation stopped with the uptake of 41% of the amount of hydrogen calculated for the nitroso derivative. Removal of the catalyst followed by crystallization of the solid product from a mixture of absolute ethanol and ethyl ether, containing hydrogen chloride, gave the amine hydrochloride 2. When heated this compound starts to decompose at ca. 188°.

Anal. Calcd for $C_{14}H_{21}ClN_2O_6$: C, 50.52; H, 6.26; N, 8.41. Found: C, 50.37; H, 6.19; N, 8.59.

2-(2,4-Diethoxycarbonyl-5-methylpyrrol-3-yl)-3,5-dimethyl-4-ethoxycarbonylpyrrole (4).—Following the literature description for the synthesis of Knorr's pyrrole,⁹ a solution of 5.0 g of ethyl 2-nitroso-3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate (11) and 2.1 g of ethyl acetoacetate in 100 ml of glacial acetic acid was treated with 5.0 g of zinc dust. The mixture was stirred and heated to 70° for 50 min, and the crude product was isolated as described in the literature reference. Column chromatography of the crude reaction product (SilicAR CC-7, ethyl acetate–hexane, 1:1), decolorization of the chromatograph fraction with Norit in 95% ethyl alcohol, and crystallization from the same solvent gave 0.40 g (6%) of the bipyrrole (4), mp 168.0–168.5°. The nmr spectrum for this compound shows the following: ethyl CH_3 , δ 1.25 (pentuplet, relative intensity 9); ring CH_3 , 2.04, 2.49, 2.53 (singlets, 3 each); ethyl CH_2 , 4.23 (multiplet, 6); pyrrole NH, 8.65, 9.91 (broad singlets, 1 each).

(11) Melting points were determined with a Fisher-Johns apparatus and are uncorrected; ir spectra, Beckman IR-5; nmr spectrum, Varian HA-100, in $CDCl_3$ using the TMS lock signal; vpc, Model A-100-C and A-700 Aerographs, Wilkens Instrument Co., using columns from the same company. Elemental analyses are by the Berkeley Analytical Laboratory.

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(14) J. A. Barltrop, A. J. Johnson, and C. D. Meakins, *J. Chem. Soc.*, 181 (1951).

(15) M. M. Joullie, S. Nasfay, and L. Rypstat, *J. Org. Chem.*, **21**, 1358 (1956).

(16) L. Wolff and A. A. Hall, *Ber.*, **36**, 3612 (1903).

(17) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 97.

Anal. Calcd for $C_{20}H_{26}N_2O_6$: C, 61.52; H, 6.71; N, 7.17. Found: C, 61.31; H, 6.69; N, 7.30.

2,4-Diethoxycarbonyl-5-methyl-3-phenylpyrrole (7).—Essentially the procedure used for the synthesis of the bipyrrole was followed using 2.2 g of ethyl nitrosobenzoylacetate, 1.3 g of ethyl acetoacetate, 30 ml of glacial acetic acid, and 2.0 g of zinc dust. The reaction mixture was held at 100–110° for 45 min in this synthesis. The product, mp 124–126°, isolated directly from the reaction mixture, weighed 2.0 g (67%). A sample recrystallized from cyclohexane–benzene and three times from 95% ethyl alcohol melted at 127.0–128.0° (lit.¹⁸ 117–119°).

Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.87; H, 6.43; N, 4.59.

Denitrosation of Nitroso Ketones. (a) **Ethyl Nitrosoacetoacetate (9).**—Fifty grams of zinc dust was added portionwise to a stirred solution of 12.3 g of the nitroso derivative in 200 ml of glacial acetic acid. During this period the temperature was held to a maximum of 70° and, after all of the zinc had been added, the mixture was stirred and refluxed for 1 hr. The reaction system was maintained in an atmosphere of argon during the entire operation. The white solid that separated, 2.4 g (13%), when the reaction mixture was poured into water, was shown to be 2,4-dimethyl-3,5-diethoxycarbonylpyrrole (10) by its mp 132–134° (lit.⁹ 136–137°) and a comparison of its infrared spectrum with that of an authentic sample. The aqueous phase from which 10 had separated was neutralized with sodium bicarbonate and extracted with ether. After drying the extract with magnesium sulfate and evaporating the solvent, an oil remained. This was shown by vpc analysis (Carbowax 20M) to contain ethyl acetoacetate (1) (3.9%).

(b) **Ethyl Nitrosobenzoylacetate (6).**—A mixture of 1.1 g of the nitroso compound and 0.65 g of ethyl acetoacetate in 45 ml of glacial acetic acid was treated with 15.3 g of zinc dust as in the preceding experiment. However, in this case the reaction mixture was held at 70° for 10 min after addition of all of the zinc and was not heated further. Also, the reaction was conducted in an atmosphere of helium. The work-up was the same as in the above example and 0.76 g of an oil was obtained. Vpc analysis (diethylene glycol succinate) showed the presence of four components. Ethyl cinnamate (8), the major component, and ethyl acetoacetate were identified by "spiking." The cinnamate ester was also isolated and identified by comparison of its ir spectrum with that of an authentic sample.

(c) **Ethyl 2-Nitroso-3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate (3).**—The reaction was carried out as in the above example using 5.0 g of 3, 2.1 g of ethyl acetoacetate, 100 ml of glacial acetic acid, and 13.5 g of zinc dust. A reaction temperature of 100–110° was used. The bulk of the solvent was evaporated at reduced pressure, the remaining acetic acid was neutralized with aqueous sodium bicarbonate, and the crude product was extracted with ethyl ether. Column chromatography (SilicAR CC-7, ethyl acetate–hexane) yielded 4.17 g (92%) of ethyl 3-oxo-3-(3,5-dimethyl-4-ethoxycarbonylpyrrol-2-yl)propanoate (11), mp 143° (lit.¹² 140.5–142°), having an ir spectrum identical with that of an authentic sample.

Registry No.—2, 24744-71-6; 3, 24744-72-7; 4, 24744-73-8; 7, 3651-13-6; 9, 24744-75-0.

(18) S. Cusmano and V. Sprio, *Gazz. Chim. Ital.*, **82**, 567 (1952); *Chem. Abstr.*, **48**, 3960e (1954).

Selective Photocoupling of Perfluorodiacyl Fluorides

R. A. MITSCH, P. H. OGDEN, AND A. H. STOSKOPF

Contribution No. 562 from the Central Research Laboratories, 3M Co., St. Paul, Minnesota 55119

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Photolysis of monofunctional perfluoroacyl fluorides has been described as a route to nonfunctional fluorocarbons¹ and fluorocarbon ethers.² However, irradiation

(1) J. F. Harris, Jr., *J. Org. Chem.*, **30**, 2182 (1965).

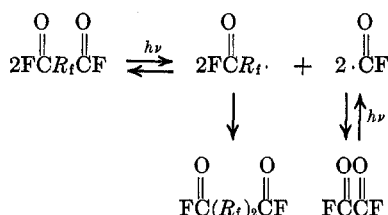
(2) British Patent 1,038,365; German Patent 1,249,247.

TABLE I
PHOTOLYSIS OF PERFLUORODIACYL FLUORIDES

Diacyl fluoride	Product	Conversion (yield, %)
OFC(CF ₂) ₃ CFO	OFC(CF ₂) ₆ CFO ^a	78 (62)
OFC(CF ₂) ₆ CFO	OFC(CF ₂) ₁₂ CFO	76 (41)
OFCCF ₂ CF ₂ OCF ₂ CF ₂ CFO	OFC(CF ₂ CF ₂ OCF ₂ CF ₂) ₂ CFO	72 (62)
OFC(CF ₂ CF ₂ OCF ₂ CF ₂) ₂ CFO	OFC(CF ₂ CF ₂ OCF ₂ CF ₂) ₄ CFO ^b	53 (41)
OFCCF ₂ OCF ₂ CFO	OFC(CF ₂ OCF ₂) ₂ CFO	52 (35)

^a An 11% yield of OFC(CF₂)₉CFO was also isolated. ^b Photolysis carried out at reduced pressure (100 mm).

tion of perfluoroglutaryl fluoride produced an inseparable, solid reaction product presumed to be a mixture of long-chain polyacyl fluorides.¹ It is the object of this paper to describe a technique wherein fluorocarbon diacyl fluorides are photolyzed under controlled conditions to produce good yields of higher molecular weight diacyl fluorides. As will be shown, further telomerization and other side reactions are substantially avoided by controlling the residence time of the desired products in the photolysis zone. Since oxalyl fluoride is known to generate the fluoroformyl radical on photolysis, it is also important to remove the volatile by-products so that fluoroformyl radical recombination is minimized and maximum photolytic efficiency maintained.



These requirements can be achieved conveniently in a continuous process by utilizing the apparatus shown in Figure 1 which relies upon differences in volatility between the starting materials and the products. The technique affords good yields of the desired products and is readily adaptable to the conversion of pound quantities of starting diacyl fluorides.

The process consists of refluxing a fluorocarbon diacyl fluoride, with or without a suitable codistilling solvent, into the photoreactor zone where the liquid phase is photolyzed and then returned to the flask. During the course of the reaction, the higher diacyl fluoride produced, hereinafter referred to as "dimer," is returned to the flask and remains therein while the starting material continues to reflux and is recycled to the photolysis chamber. In general, the residence time is determined empirically and the return tube leading from the photolysis chamber to the Vigreux column is made with appropriate dimensions to accomplish the desired residence time. It is necessary to increase gradually the temperature of the flask in order to ensure vaporization of the progressively decreasing amount of starting material. Thus, the extent of reaction can be followed by monitoring the pot temperature or more exactly by vapor phase chromatographic analysis of aliquots withdrawn from the flask. The uncondensed by-products of the reaction, primarily oxalyl fluoride and minor amounts of carbonyl fluoride and carbon dioxide, are removed effectively from the system by volatilization.

The conversions to linear, dimer products (50–80%) indicate that the predominant reaction is radical–radical combination. Other than those derived from the

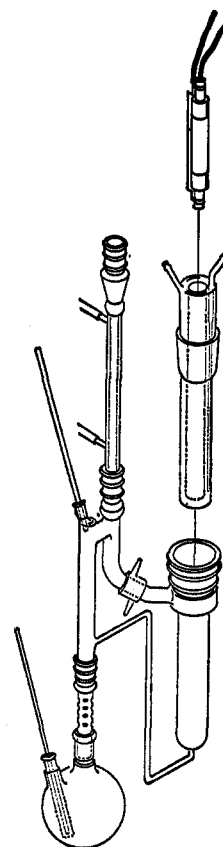


Figure 1.—Photodimerization reactor.

fluoroformyl radical, the by-products of the reaction are generally higher boiling materials which are probably branched and result from the addition of perfluoroalkyl radicals to the oxygen of an acyl fluoride group.^{1,3}

In all but one example, the reactions shown in Table I were carried out at atmospheric pressure since the volatilities of the starting fluorocarbon diacyl fluorides were sufficient to permit convenient vaporization. Since the photoreactor zone had a holdup volume of about 40 cc, codistilling inert fluorocarbon solvents were used in reactions employing limited amounts of starting materials. The use of fluorocarbon solvents in the photodimerization of perfluorodiacyl fluorides resulted in up to 97% conversions of starting material into dimerized products. The good conversions to the desired products and minimal amounts of higher homologs attest to the effectiveness of using volatility differences to control residence time in the photolysis zone.

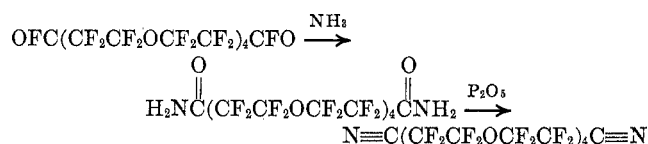
It was difficult to achieve a satisfactory yield of OFC(CF₂OCF₂)₂CFO from the photolysis of OFCCF₂-

(3) The nature of the high boiling products has been studied in detail and will be reported in a forthcoming paper by Dr. J. R. Throckmorton.

OCF₂CFO because of condenser losses. The condenser was required to return starting material (bp 38°) to the system yet not condense oxalyl fluoride by-product (bp 6°). Satisfactory yields were obtained only with careful temperature control while employing four 15-watt, low-pressure ultraviolet lamps rather than a 450-watt medium-pressure unit. A low yield of OFC(CF₂-OCF₂)₂CFO was also obtained.

It was found convenient to carry out the photolysis of OFC(CF₂CF₂OCF₂CF₂)₂CFO under reduced pressure to effect adequate boil-up rates of the starting material. The use of vacuum also facilitated the removal of the low boiling uncondensed by-products, *e.g.*, oxalyl fluoride, and as a consequence, substantially reduced the required photolysis time necessary to achieve good conversions. Conventional pressure-reducing means were connected to the top of the condenser and, to ensure a smooth operation under reduced pressure, a ballast or vacuum surge chamber was incorporated into the system. A vacuum of 100 mm was achieved easily and although the boil-up rate was somewhat less than in other reactions; the preparation of OFC(CF₂-CF₂OCF₂CF₂)₄CFO proceeded smoothly.

Two derivatives of the above diacyl fluoride were also prepared in the course of this investigation. Reaction with ammonia in ether afforded the diamide. Dehydration of the diamide to the corresponding perfluoroether dinitrile was accomplished by coating an



etheral solution of the diamide on P₂O₅, evaporating the ether and heating the resulting P₂O₅-amide mixture to 220°. The yield of dinitrile for the two steps was 63%.

Experimental Section

Infrared spectra were measured on a Perkin-Elmer Model 21 double beam instrument using NaCl plates. The vpc unit used for monitoring the reactions was an F & M Model 500 gas chromatograph employing a 12 ft × 3/8 in. column packed with 33% FS-1265 (fluorosilicone) on Chrome P. Nuclear magnetic resonance measurements were made with a Varian V-4300-2 instrument operating at 40.0 Mc and utilizing an internal standard of CFCl₃ for the determination of chemical shifts. The values reported in Table II are ϕ^* values⁴ at a dilution of 10–25%. Trifluoroacetic acid is ϕ^* 76.5 on this scale.

Diacyl fluoride starting materials were prepared from the corresponding diacyl chlorides by treatment with potassium fluoride.

General Photolysis Procedure.—All of the reactions were carried out in essentially the same manner, using the apparatus shown in Figure 1 or larger variations thereof.

The perfluorodiacyl fluoride starting material was heated with magnetic stirring in the flask until it refluxed vigorously through the Vigreux column. The vapors were condensed in the upright condenser and dripped into the photoreactor zone. The photoreactor consisted of a water-cooled 7 60–50 jointed quartz immersion cell (20 × 80 × 2 mm), a photolysis chamber with a hold-up volume of about 40 cc, a wound 36 in. length of 1/8 in. polytetrafluoroethylene cord placed as a distributor in the top of the cell, and a Hanovia 450-watt ultraviolet immersion lamp. Aluminum foil was wrapped around the reactor to act as a reflector. The photolyzed reaction mixture was carried from the bottom of the photoreactor into the Vigreux column from which the unreacted starting material was vaporized and recycled while the higher

boiling products remained in the flask. The process was continuously carried out in this manner at atmospheric pressure, the heating bath being maintained about 50° higher than the pot temperature to facilitate boiling. After the reaction was complete, the liquids in the flask and photoreactor were combined and separated by distillation.

Photolysis of OFC(CF₂)₂CFO.—A sample of perfluoroglutaryl fluoride (236 g, 0.97 mol) was placed in a 250-cc flask containing a magnetic stirring bar and the flask attached to the photoreactor as shown in Figure 1. At reflux, the initial pot and head temperatures were 48 and 43°, respectively. After 68 hr of photolysis, the pot temperature had risen to 109° and the head temperature to 46°. Distillation of the product mixture afforded 118 g (78% conversion, 62% yield) of perfluorooctanedioyl fluoride, bp 70° (155 mm), identified by spectral comparisons with an authentic sample. Perfluoroundecanedioyl fluoride, amounting to 19.2 g (14% conversion, 11% yield), was obtained as a higher boiling fraction, bp 89° (30 mm).

Photolysis of OFC(CF₂)₈CFO.—In this experiment, 110.4 g (0.28 mol) of perfluorooctanedioyl fluoride was photolyzed in a similar manner. The flask (60 cc) was heated overnight to maintain 110° material flowing through the photolysis chamber. When the pot temperature reached 170°, the reaction was terminated and the contents of the flask and photolysis chamber were combined. Distillation of the combined liquid yielded 50 g of starting material in the forecut [bp 70° (155 mm)], 15 g of an intermediate cut, and 40 g (76% conversion, 41% yield) of the desired perfluorotetradecanedioyl fluoride, OFC(CF₂)₁₂CFO, bp 110–113° (20 mm). The structure was confirmed by ¹⁹F nuclear magnetic resonance and infrared spectroscopy.

Hydrolysis of the diacyl fluoride yielded perfluorotetradecanedioic acid, HO₂C(CF₂)₁₂CO₂H, a colorless solid, mp 185–188° (lit.⁵ mp 191–193°).

Anal. Calcd for C₁₄F₂₄H₂O₄: C, 24.35; F, 66.1; H, 0.3; mol wt, 690; neutral equiv, 345. Found: C, 24.5; F, 64.9; H, 0.5; mol wt, 649; neutral equiv, 328.

Photolysis of OFCCF₂CF₂OCF₂CF₂CFO.—Following the procedure outlined above, 1250 g (4.03 mol) of perfluorooxydipropionyl fluoride,⁶ OFCCF₂CF₂OCF₂CF₂CFO, was heated in a flask, previously purged with nitrogen, to maintain a steady flow of condensate through the photolysis chamber. Reaction was continued for 100 hr at which time the pot temperature was 146.5° and the head temperature was 88°. Distillation of the combined flask and photolysis chamber contents produced 78 g of unreacted starting material and 658 g (72% conversion, 62.5% yield) of the desired product, OFC(CF₂CF₂OCF₂CF₂)₂CFO, bp 88° (100 mm). The structure was confirmed by ¹⁹F nuclear magnetic resonance and infrared and mass spectroscopy.

After reaction of the diacyl fluoride with excess methanol in the presence of sodium fluoride, distillation afforded the corresponding dimethyl ester, CH₃O₂C(CF₂CF₂OCF₂CF₂)₂CO₂CH₃, bp 98° (2 mm).

Anal. Calcd for C₁₂F₁₆H₆O₆: C, 26.1; F, 55.3. Found: C, 26.1; F, 55.3.

Photolysis of OFC(CF₂CF₂OCF₂CF₂)₂CFO.—A sample of OFC(CF₂CF₂OCF₂CF₂)₂CFO (167.7 g, 0.318 mol) was placed in the reactor shown in Figure 1. The apparatus was modified by connecting a 1-l. ballast or surge chamber to the top of the condenser through vacuum tubing in order to carry out the process under a reduced pressure (100 mm). The flask was heated to about 90° and the head temperature was maintained at about 79°. During 5 hr of photolysis, the pot temperature was raised to about 190° to maintain constant boil-up. The liquid contents of the flask and photolysis chamber were combined and distilled to yield 40.4 g (in three fractions) of the starting material and 61.5 g (53% conversion, 41% yield) of the desired product, OFC(CF₂CF₂OCF₂CF₂)₄CFO, bp 87–90° (0.9 mm). The structure was confirmed by ¹⁹F nuclear magnetic resonance, infrared and mass spectroscopy and elemental analysis.

Anal. Calcd for C₁₈F₂₄O₆: C, 22.6; F, 67.4. Found: C, 22.7; F, 67.0.

Reaction of the diacyl fluoride (191 g, 0.199 mol) with excess ammonia in diethyl ether afforded 161 g (85%) of the diamide after filtration to remove NH₄F and evaporation of the ether filtrate.

(5) I. L. Knunyants, C. Y. Li, and V. V. Shokina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1462 (1961).

(6) British Patent 858,671; V. Ya Kazakov, R. A. Dzerzhinskoy, V. I. Tsimbalist, and E. A. Shishkin, *Zh. Obshch. Khim.*, **36**, 1807 (1966).

(4) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

TABLE II
¹⁹F NUCLEAR MAGNETIC RESONANCE SPECTRA

Formula	Registry no.	Group	δ^*
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{CF}_2 \text{CFO}$	678-78-4	CFO	-24.1
$\text{OFC} \overset{\text{a}}{\text{CF}_2} (\overset{\text{b}}{\text{CF}_2})_4 \text{CF}_2 \text{CFO}$	24647-09-4	CF_2 (a)	118.2
		CF_2 (b)	123.7
		CFO	-24.2
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} (\overset{\text{c}}{\text{CF}_2})_6 \text{CF}_2 \text{CF}_2 \text{CFO}$	24647-10-7	CF_2 (a)	118.1
		CF_2 (b)	122.1
		CFO	-24.0
$\text{HO}_2 \overset{\text{a}}{\text{CCF}_2} \overset{\text{b}}{\text{CF}_2} (\overset{\text{c}}{\text{CF}_2})_8 \text{CF}_2 \text{CF}_2 \text{CO}_2 \text{H}$	24647-11-8	CF_2 (a)	118.4
		CF_2 (b)	122.4
		CF_2 (c)	121.7
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} (\overset{\text{c}}{\text{CF}_2})_8 \text{CF}_2 \text{CF}_2 \text{CFO}$	24647-12-9	CF_2 (a)	118.8
		CF_2 (b)	122.6
		CF_2 (c)	121.6
$\text{HO}_2 \overset{\text{a}}{\text{CCF}_2} \overset{\text{b}}{\text{CF}_2} (\overset{\text{c}}{\text{CF}_2})_8 \text{CF}_2 \text{CF}_2 \text{CO}_2 \text{H}$	2822-93-7	CFO	-24.0
		CF_2 (a)	118.6
		CF_2 (b)	122.7
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \text{CF}_2 \text{CFO}$	1428-40-6	CF_2 (c)	121.9
		CF_2 (a)	119.2
		CF_2 (b)	122.9
$(\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \overset{\text{c}}{\text{CF}_2} \overset{\text{d}}{\text{CF}_2})_2$	24647-14-1	CF_2 (c)	121.8
		CFO	-23.6
		CF_2 (a)	121.6
$(\text{CH}_3 \text{O}_2 \overset{\text{a}}{\text{CCF}_2} \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \overset{\text{c}}{\text{CF}_2} \overset{\text{d}}{\text{CF}_2})_2$	24689-55-2	CF_2 (b)	85.7
		CF_2 (c)	83.3
		CF_2 (d)	125.9
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{O} [\overset{\text{c}}{\text{CF}_2} \overset{\text{d}}{\text{CF}_2} \text{CF}_2 \text{CF}_2 \text{O}]_3 \text{CF}_2 \text{CF}_2 \text{CFO}$	24647-15-2	CF_2 (a)	122.2
		CF_2 (b)	85.7
		CF_2 (c)	83.3
$\text{H}_2 \text{NC} \overset{\text{O}}{\parallel} \text{CF}_2 \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{O} (\overset{\text{c}}{\text{CF}_2} \overset{\text{d}}{\text{CF}_2} \text{CF}_2 \text{CF}_2 \text{O})_5 \text{CF}_2 \overset{\text{O}}{\parallel} \text{CF}_2 \text{CNH}_2$	24647-16-3	CF_2 (d)	125.9
		CF_2 (a)	121.2
		CF_2 (b)	85.4
$\text{NCC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{O} (\overset{\text{c}}{\text{CF}_2} \overset{\text{d}}{\text{CF}_2} \text{CF}_2 \text{CF}_2 \text{O})_5 \text{CF}_2 \text{CF}_2 \text{CN}$	23790-63-8	CF_2 (c)	83.0
		CF_2 (d)	83.2
		CF_2 (a)	109.0
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \text{OCF}_2 \text{CFO}$	21297-64-3	CF_2 (b)	87.3
		CF_2 (c)	83.5
		CF_2 (d)	126.0
$\text{OFC} \overset{\text{a}}{\text{CF}_2} \text{OCF}_2 \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \text{CFO}$	24647-19-6	CFO	-13.3
		CF_2 (a)	76.7
		CF_2 (b)	77.0
$\text{CH}_3 \text{O}_2 \overset{\text{a}}{\text{CCF}_2} \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \text{CF}_2 \text{OCF}_2 \text{CO}_2 \text{CH}_3$	24647-20-9	CF_2 (b)	88.2
		CF_2 (a)	77.9
		CF_2 (b)	88.8
$(\text{OFC} \overset{\text{a}}{\text{CF}_2} \overset{\text{b}}{\text{CF}_2} \text{OCF}_2 \overset{\text{c}}{\text{CF}_2})_2 \text{O}$	24689-56-3	CFO	-13.2
		CF_2 (a)	77.2
		CF_2 (b)	88.5
		CF_2 (c)	88.8

The diamide (161 g, 0.169 mol) was dissolved in 500 cc of ether and poured onto 100 g of P_2O_5 . The slurry was dried in a rotating evaporator and heated to 220° for 2 hr. Upon application of a vacuum to the flask, the colorless liquid dinitrile distilled into the collection flask. Redistillation afforded 144.5 g (75%) of $\text{N}\equiv\text{C}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_4\text{C}\equiv\text{N}$, bp 125° (10 mm). The infrared spectrum shows the nitrile absorption at 4.42μ .

Photolysis of $\text{OFC}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_2\text{CFO}$ in Solvent.—A mixture of 944 g (1.79 mol) of $\text{OFC}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_2\text{CFO}$ and

408 g of perfluorotributylamine solvent was photolyzed following the general procedure outlined above, using a 1-l. flask and reduced pressure (100 mm). The initial pot and head temperatures were 97° and 91° , respectively. After 54 hr of photolysis, the temperatures had risen to 136° and 113° , respectively. Distillation of the combined flask and photolysis chamber contents produced a forecut containing unreacted starting material and solvent and a 413.2 g fraction (48.1% yield) of the desired product, $\text{OFC}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_4\text{CFO}$.

Photolysis of OFCCF₂OCF₂CFO.⁷—A mixture of 390 g (1.85 mol) of perfluorooxydiacetyl fluoride, bp 38°, and 2197 g of FC-78⁸ were photolyzed in a larger unit than that described above. Ultraviolet light was supplied by four 15-watt low-pressure mercury lamps (2537 Å). The reactor temperature was maintained at about 30° during the 10 days of the run. The yield of OFC(CF₂OCF₂)₂CFO, bp 82°, was 101 g (52% conversion).

Reaction of the diacetyl fluoride with methanol at 0° in the presence of excess sodium fluoride produced the corresponding dimethyl ester, CH₃O₂C(CF₂OCF₂)₂CO₂CH₃, bp 123.5° (50 mm).

Anal. Calcd for C₅F₈H₆O₆: C, 27.5; F, 43.5; H, 1.7; mol wt, 350. Found: C, 27.5; F, 43.6; H, 1.8; mol wt, 339 (in acetone).

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(7) The authors are indebted to Dr. W. B. Isaacson and Dr. S. T. Ting for carrying out this experiment in a wiped-film photoreactor. The description of this new photoreactor has been published in *Ind. Eng. Chem., Fundam.*, **9**, 171 (1970).

(8) A perfluorocarbon inert liquid, bp 50–52°, sold by the 3M Company, St. Paul, Minn.

The Synthesis of 2,5-Dialkoxy-1,4-diphosponiacyclohexane Salts¹

KEITH C. HANSEN² AND CONNIE H. WRIGHT

Department of Chemistry, Lamar State College of
Technology, Beaumont, Texas 77705

ADAM M. AGUIAR, CARY J. MORROW,³
AND R. M. TURKEL

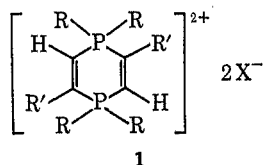
Department of Chemistry, Newcomb College,
Tulane University, New Orleans, Louisiana 70118

NORMAN S. BHACCA

Department of Chemistry, Louisiana State
University, Baton Rouge, Louisiana 70803

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A new organophosphorus heterocycle, 1,4-diphosponiacyclohexadiene-2,5 (1), of both theoretical and biological interest has been reported recently.^{4–9}



(1) Taken in part from the dissertation of K. C. Hansen, Tulane University, 1967.

(2) NASA Fellow at Tulane University, 1964–1967.

(3) NASA Fellow, 1966–1967; NDEA Fellow, 1967–1969; NSF Fellow, 1969–1970.

(4) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *J. Amer. Chem. Soc.*, **89**, 3087 (1967).

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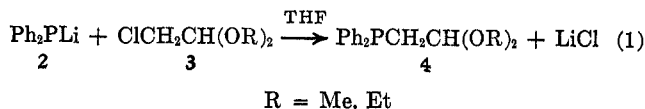
(6) A. M. Aguiar, J. R. S. Ireland, G. W. Prejean, J. P. John, and C. J. Morrow, *J. Org. Chem.*, **34**, 2681 (1969).

(7) A. M. Aguiar, J. R. Ireland, C. J. Morrow, J. P. John, and G. W. Prejean, *ibid.*, **34**, 2684 (1969).

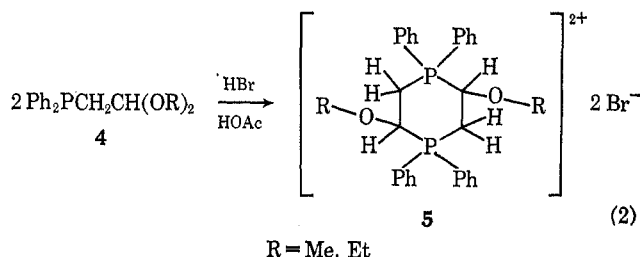
(8) A. M. Aguiar, G. W. Prejean, J. R. S. Ireland, and C. J. Morrow, *ibid.*, **34**, 4024 (1969).

(9) R. Majeste and L. M. Trefonas, *J. Heterocycl. Chem.*, **6**, 269 (1969).

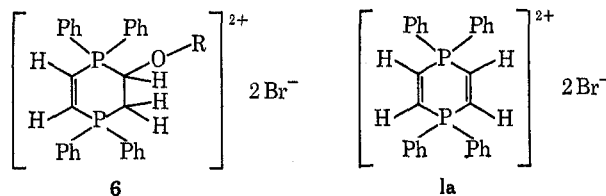
In an attempt at developing a new synthetic route to this system, we have found that a tetrahydrofuran solution of lithium diphenylphosphide (2) reacts with the dimethyl and diethyl acetals of chloroacetaldehyde (3) to give the corresponding acetal of diphenylphosphinoacetaldehyde (4) (eq 1).



Upon reaction of 4 with hydrogen bromide in boiling glacial acetic acid, the new 2,5-dialkoxy-1,4-diphosponiacyclohexane dibromide (5) could be isolated (eq 2).

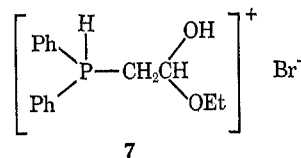


No mono- (6) or di- (1a) unsaturated heterocycles were isolated.



It is surprising that under these conditions no 1a is isolated since this could occur *via* the aldehyde, the acetylene, or even the dealcoholization of 5. Dealcoholization of isolated 5 to 1a was attempted employing boron trifluoride etherate with no success. At present the stability of 5 to Lewis acids is not clear. It may involve interaction of the unshared pair of electrons on the oxygen with the positive phosphorus.

The possibility that the compound which we have designated 5b is actually the hemiacetal phosphine hydro-



bromide (7) has been eliminated by ir spectrophotometry. The ir spectrum of 5b contains no band between 2000 and 2500 cm⁻¹. It has been shown that phosphine hydrobromides exhibit a fairly intense peak in this region.⁶ Furthermore, there was no change in the nmr spectrum of a CDCl₃ solution of 5b upon treatment with D₂O. It is known that the proton of a phosphine hydrobromide undergoes rapid exchange with D₂O under these conditions.⁶

The structure of compound 5b was unequivocally determined with the aid of its 100-MHz spectrum. The complex downfield nmr pattern centered at 7.90 ppm