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SYNTHESIS OF FLUORINATED α -DIKETONES AND SOME INTERMEDIATES

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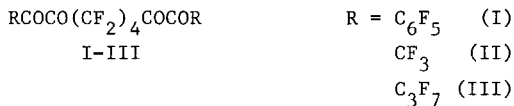
SUMMARY

Reactions of perfluoroalkylcopper compounds with α -ketoacyl chlorides were used for the synthesis of fluorinated α -diketones. Heptafluoropropylcopper prepared from copper bronze and 1-iodoheptafluoropropane reacted with benzoylformyl chloride to give heptafluoro-1-phenyl-1,2-pentanedione, with trimethylpyruvyl chloride to give 2,2-dimethyl-5,5,6,6,7,7,7-heptafluoro-3,4-heptanedione, and with 3,3,4,4,5,5,5-heptafluoro-2-ketopentanoyl chloride or oxalyl chloride to give tetradecafluoro-4,5-octanedione. Syntheses of fluorinated acetylenes, cyanohydrins, α -hydroxy acids, α -keto acids, their chlorides, and other intermediates for the syntheses of α -diketones by the above route and by other methods are described. An interesting seven-membered ring containing β -hydroxy ketone was obtained by an intramolecular aldol condensation of a fluorinated bis(methyl) ketone.

INTRODUCTION

In the previous communication [1], synthesis of 3,3,4,4,5,5,5-heptafluoro-1-phenyl-1,2-pentanedione and 3,3,4,4,5,5,6,6-octafluoro-1,8-diphenyl-1,2,7,8-octanetetronone using Grignard reactions were described. The latter compound was converted, by means of bis-amidrazone of octafluoroadipic acid, into the corresponding as-triazine polymer which showed satisfactory thermal resistance at temperatures around 260°. In order to increase the thermal stability even higher, a polymer containing no hydrogen atoms was desirable. For this purpose a perfluoro-bis- α -diketone was necessary as one of the components. Based on the commercial availability of only certain perfluorinated starting materials syntheses of the following perfluoro bis- α -diketones were attempted: perfluoro-1,8-diphenyl-

-1,2,7,8-octanetetron (I), perfluoro-2,3,8,9-decanetetron (II), and perfluoro-4,5,10,11-tetradecanetetron (III).



RESULTS AND DISCUSSION

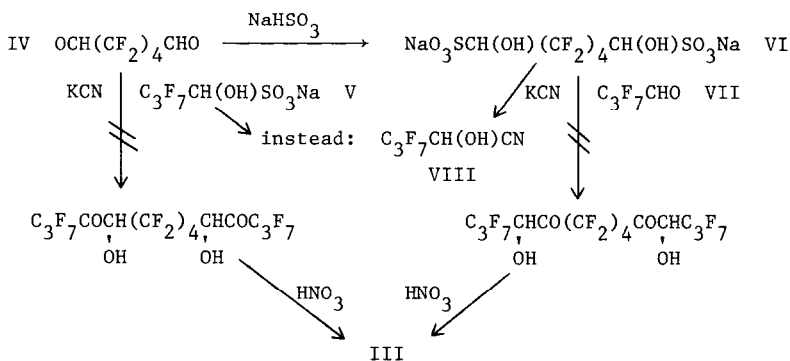
Several projects were attempted for the synthesis of perfluorobis- α -diketones I-III.

a) Claisen condensation reactions

Compound I was expected to result from selenium dioxide oxidation of $\text{C}_6\text{F}_5\text{CH}_2\text{CO}(\text{CF}_2)_4\text{COCH}_2\text{C}_6\text{F}_5$ which could be prepared via Claisen condensation of diethyl octafluoroadipate with pentafluorobenzyl cyanide, or via acylation of diethyl pentafluorophenylmalonate with octafluoroadipoyl fluoride, both followed by hydrolysis and decarboxylation. Neither of these reactions worked, both producing mixtures of condensation products in low yields. A similar failure was an attempt to prepare compound II by crossed Claisen condensation of diethyl octafluoroadipate with ethyl γ,γ,γ -trifluoropropionate. Only unreacted diethyl octafluoroadipate was recovered whether the condensation was carried out by sodium, sodium hydride, or lithium diisopropylamide.

b) Acyloin condensation reactions

After the bad experiences with aldol-type condensations for the syntheses of I and II, an attempt was made to prepare compound III by oxidation of a product of crossed acyloin condensation following the elegant method for mixed benzoin condensation described by Paciorek et al. [2].



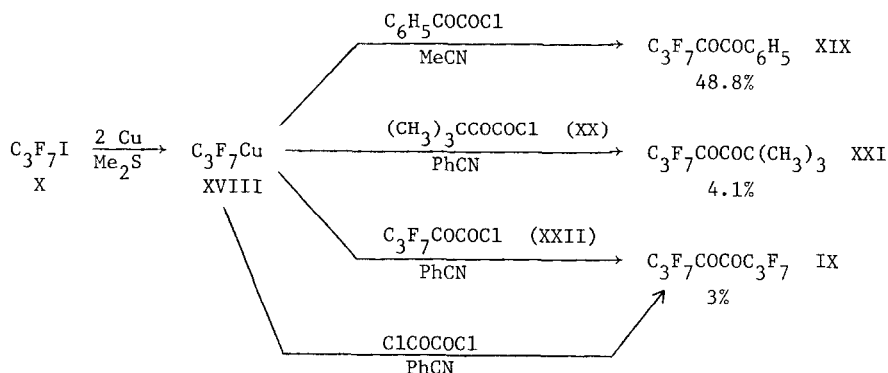
Scheme 1

By a combination of addition and elimination reactions it was possible to prepare, from acetylene and 1-iodoheptafluoropropane (X), 3,3,4,4,5,5,5-heptafluoro-1-iodopentene (XI), heptafluoropropylacetylene (XII), 4H,5-iodotetradecafluoro-4-octene (XIII), 4H,5H-tetradecafluoro-4-octene (XIV), tetradecafluoro-4-octyne (XV), and a mixture XVI of a fluorinated enol ether and acetal. Unfortunately, neither XIV nor XV gave IX on selenium dioxide oxidation, and hydrolysis of the mixture XVI followed by oxidation of the resulting ketone was not accomplished.

When the addition of 1,4-diiodooctafluorobutane (XVII) to heptafluoropropylacetylene XII, both at high temperature and under UV irradiation, failed to give perfluoro-5H,10H,4,11-diiodotetradeca-4,10-diene, an intermediate for the synthesis of III, this route was abandoned as unfeasible for the compounds III and IX.

d) Syntheses with heptafluoropropylcopper

Successful syntheses of ketones from acyl halides and perfluoroaryl-copper compounds [5] or perfluoroalkylcopper compounds [6,7] looked very promising for the preparation of fluorinated α -diketones from α -ketoacyl halides according to Scheme 3. The method was tested on four examples.



Scheme 3

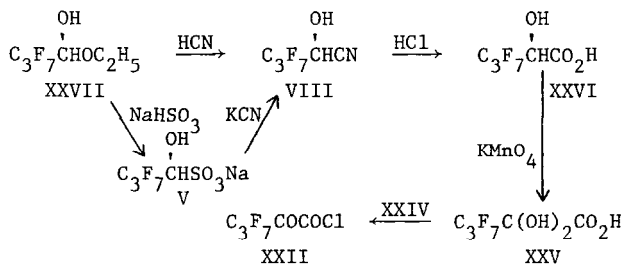
Benzoylformyl chloride and heptafluoropropylcopper (XVIII) (obtained from copper and 1-iodoheptafluoropropane (X) yielded 3,3,4,4,5,5,5-heptafluoro-1-phenyl-1,2-pentanedione (XIX) which was prepared previously by another method [1]. The reaction of XVIII with trimethylpyruvyl chloride (XX) gave a very low yield of 5,5,6,6,7,7,7-heptafluoro-2,2-dimethyl-3,4-heptanedione XXI. An analogous reaction of XVIII with heptafluoro-2-ketopentanoyl chloride XXII yielded only a trace of IX. Somewhat better

result was obtained from the reaction of XVIII with oxalyl chloride. Thus, for reasons not quite understandable, synthesis of IX via perfluoropropyl-copper proved unfeasible. Compounds used as intermediates for the syntheses shown in Scheme 3 were prepared as follows:

e) Preparation of α -keto acids and their chlorides

Trimethylpyruvyl chloride XX was obtained by distillation of trimethylpyruvic acid (XXIII) (prepared by permanganate oxidation of pinacolone) with *o*-chlorobenzoyl chloride (XXIV). This special reagent was chosen because its high boiling point allows for comfortable purification of low boiling acyl chlorides by simple distillation. It was also used for the preparation of heptafluoro-2-ketopentanoyl chloride XXII from heptafluoro-2,2-dihydropentanoic acid XXV when both the direct treatment of XXV with *o*-phthaloyl chloride as well as consecutive reactions of XXV with phosphorus pentoxide followed by phthaloyl chloride failed.

Heptafluoro-2,2-dihydropentanoic acid (XXV) was obtained by potassium permanganate oxidation of heptafluoro-2-hydroxypentanoic acid (XXVI). The latter resulted from a hydrolysis of its cyanohydrin VIII prepared from commercially available heptafluorobutylaldehyde ethyl hemiacetal XXVII (Scheme 4).



Scheme 4

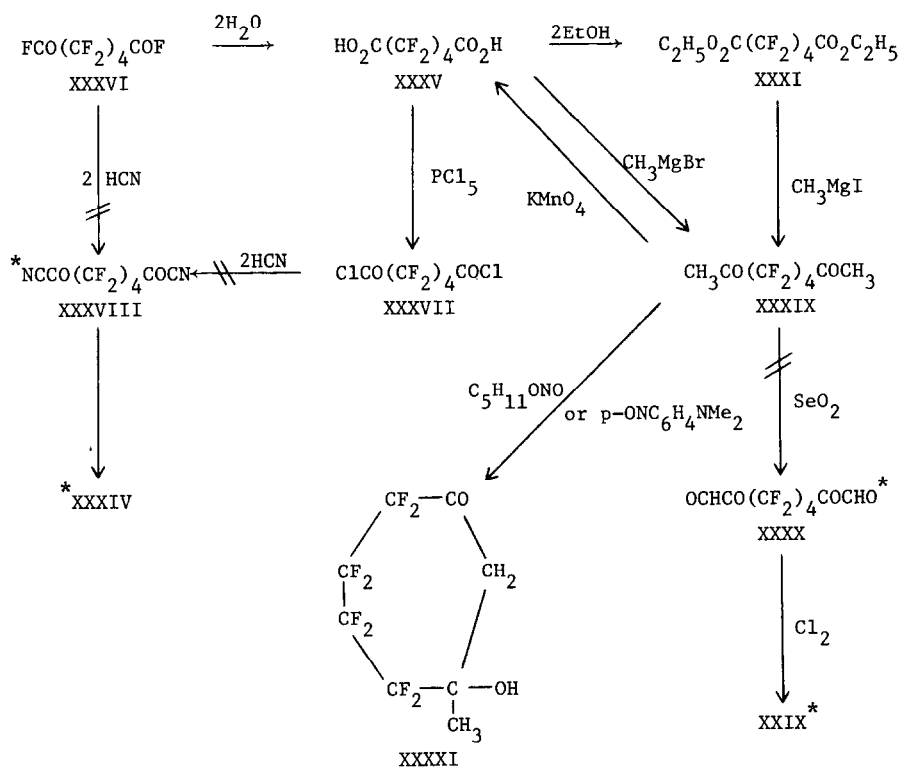
f) Attempt to synthesize octafluorotetramethylene-bis-copper

For the synthesis of III two routes involving perfluoroalkylcopper compounds were tried (Scheme 5).

Analogously to the preparation of XVIII from X (Scheme 3), 1,4-diiodooctafluorobutane XVII was treated with copper in order to prepare octafluorotetramethylene-bis-copper (XXVIII) which was expected to react with XXI to give III (Scheme 5). However, the bis-copper compound XXVIII does not seem to have been ever formed in spite of numerous attempts using

XXIX, octafluoroadipaldehyde bis-(ethyl hemiacetal) (1,6-diethoxy-1,6-dihydroxyoctafluorohexane) (XXX) obtained by reduction of diethyl octafluoroadipate (XXXI) with Vitride (sodium bis-methoxyethoxyaluminum hydride) was transformed to its bis-sodium-bisulfite adduct VI which on treatment with potassium cyanide afforded the corresponding octafluoroadipaldehyde bis-cyanohydrin (XXXII). Hydrolysis of XXXII yielded 2,7-dihydroxyoctafluorooctanedioic acid (XXXIII) which should give, on oxidation, 2,7-diketooctafluorooctanedioic acid (XXXIV). However, this step of the synthesis was not accomplished. Oxidation of XXXIII to XXXIV, tried with nitric acid, sodium dichromate, manganese dioxide, potassium permanganate, and chloranil, gave either octafluoroadipic acid (XXXV), or recovered dihydroxy acid XXXIII.

Three other methods proposed for the synthesis of the diketo acid XXXIV or its dichloride XXIX are outlined in Scheme 6.



Scheme 6

* Starred compounds were not prepared

The reaction of anhydrous hydrogen cyanide with either octafluoro-adipoyl fluoride (XXXVI) or octafluoroadipoyl chloride (XXXVII) failed to give the expected dinitrile of 2,7-diketo-octafluorooctanedioic acid (XXXVIII) which should yield the diketo acid XXXIV on hydrolysis.

For a direct synthesis of the dichloride XXIX 3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (XXXIX) was prepared as an intermediate, either by a reaction of diethyl octafluoroadipate XXXI with methylmagnesium iodide, or by treatment of octafluoroadipic acid XXXV with methylmagnesium bromide. Oxidation of XXXIX was expected to give octafluorooctane-1,8-dial-2,7-dione (XXXX) whose chlorination should afford XXIX. However, the oxidation of XXXIX by selenium dioxide failed, and an alternative oxidation using isopentyl nitrite or p-nitrosodimethylaniline yielded a product of an aldol condensation of XXXIX, 4,4,5,5,6,6,7,7-octafluoro-3-hydroxy-3-methylcycloheptanone (XXXXI). This compound was also obtained by alkali-catalyzed (but not acid-catalyzed) autocondensation of XXXIX.

Oxidation of the diketone XXXIX by potassium permanganate gave quantitatively octafluoroadipic acid XXXV. Because of the failure of obtaining the diketo acid XXXIV and its chloride XXIX, the last step of the proposed synthesis of III (Scheme 5) did not materialize.

EXPERIMENTAL

Boiling points and melting points (taken in Thomas-Hoover Unimelt apparatus) are uncorrected. Gas-liquid chromatography was carried out on Varian Aerograph 920 with thermal conductivity detector, helium as a carrier gas and a column packed with silica gel impregnated with silicone elastomer SE 30. Infrared spectra were taken on Unicam SP 1025 Infrared Spectrophotometer, NMR spectra on Varian EM 390 NMR Spectrophotometer using TMS and HFB as internal standards, unless stated otherwise. Fluorine chemical shifts downfield from HFB are positive. Coupling constants of small values were determined with an accuracy within $\pm 10\%$.

Apparatus

Photochemical addition reactions of acetylene and heptafluoropropylacetylene were carried out in heavy-wall Pyrex tubes of 18 mm diameter and 40 ml capacity. Commercial source of unfiltered UV light was used for irradiation. Thermal additions of the acetylenes were carried out in 30 or 75 ml stainless steel cylinders fitted with stainless steel swagelock valves with Teflon seats. Maximum operating pressure was 1800 psi (125 atm.).

Transfer of gaseous intermediates was carried out using a standard vacuum line. Isolation and purification of low-boiling compounds was achieved by trap-to-trap distillations. Purity of products was checked by gas-liquid chromatography.

Chemicals

Commercial chemicals, distilled, if necessary, were used throughout this work. Anhydrous ether was dried over sodium, tetrahydrofuran by distillation from lithium aluminum hydride. Fluorinated starting materials X, XXVII, XXXV and XXXVI were commercial products.

Octafluoroadipic Acid (Anhydrous) (XXXV)

Unless used as a commercial chemical, compound XXXV was prepared from commercial octafluoroadipoyl fluoride XXXVI as described previously [1].

M.p. 133.5-135°.

^{19}F NMR (CD_3COCD_3): 41.4 (1,m), 45.0 (1,m).

Octafluoroadipoyl Chloride (XXXVII)

Octafluoroadipic acid did not give XXXVII by treatment with thionyl chloride as described in the literature [9]. Phosphorus pentachloride was necessary for the preparation of XXXVII. Yield was 73.5%, b.p. 120-122°/710 mm. Lit. [9]. b.p. 131.4°/754 mm.

^{19}F NMR (CCl_4): 42.0 (1,m), 49.7 (1,m).

Diethyl Octafluoroadipate (XXXI)

Compound XXXI was prepared either by azeotropic esterification of XXXV (yield 76%), or by treatment of octafluoroadipoyl fluoride XXXVI with ethanol and pyridine (yield 89%). B.p. 110-111°/17 mm, 118-121°/23 mm. Lit. [10] b.p. 110-111°/16 mm.

^1H NMR (CCl_4): CH_3 - 1.40 (3,t,J=7 Hz); $-\text{CH}_2-$ 4.45 (2,q,J=7 Hz);

^{19}F NMR: 39.5 (1,m), 43.5 (1,m).

Octafluoroadipaldehyde bis-(ethyl hemiacetal) (XXX)

Compound XXX (claimed erroneously as octafluoroadipaldehyde dihydrate [11]) was prepared according to the literature [11] by the reduction of diethyl octafluoroadipate with Vitride. Yield was quantitative, the product partly crystalline. B.p. 101-108°/21 mm.

^1H NMR (CCl_4 , CD_3COCD_3): CH_3 - 1.37 (3,t,J=7 Hz); $-\text{CH}_2-$ 4.44 (2,q,J=7 Hz);

^{19}F NMR: complex multiplets 27-40.

Octafluoroadipaldehyde (IV)

This compound was obtained by distillation of octafluoroadipaldehyde bis-ethyl hemiacetal XXX with phosphorus pentoxide and diphenyl ether according to the literature [11]. Yield 64%, b.p. 110-114°/710 mm. Lit. [11] b.p. 122-123°. After two days at room temperature, the liquid turned to a glass.

^1H NMR (CCl_4 , CD_3COCD_3): 9.74 (m); Lit. [8] 9.47 (m).

^{19}F NMR: 37.4 (1,m), 39.7 (1,m).

3,3,4,4,5,5,5-Heptafluoro-1-iodopentene (XI)

The title compound was prepared by a modified literature procedure. Photochemical addition of 1-iodoheptafluoropropane X to acetylene at 50-55° for 113.5 hours gave XI in 54% yield, thermal addition in a glass ampul at 220° after 17 hours in 64% yield, and in a steel cylinder at 200° for 6 hours in 76% yield. B.p. 96-99°/710 mm. Lit. [12] b.p. 101.5-103°/772 mm.

An attempt to carry out the addition of X to acetylene prepared in situ from calcium carbide and a calculated amount of water in a 75 ml stainless steel cylinder by heating at 200° for 5 hours did not offer any advantage giving isolated yield of only 33%. In addition, this procedure is risky since it led to an explosion in one case, probably caused by overheating.

^1H NMR (CCl_4): =CH= 6.73 (1,m); =CHI 7.35 (1,d,J=14 Hz)

^{19}F NMR: -CF_3 80.7 (3,t,J=9 Hz); $\text{-CF}_2\text{-}$ 34.0 (2,m), -CF_2 48.4 (2,m).

1H-Heptafluoropentyne (XII) (nc)

Following a procedure for dehydroiodination of 1H,2H,1-iodo-3-trifluoromethyltetrafluorobutene [13] 16.00 g (0.05 mol) of XI gave, after a trap-to-trap distillation, 6.30 g (65.5%) of XII, b.p. 18-20°/710 mm, and 1.93 g of recovered XI. Yield 74% (based on reacted XI).

^1H NMR (CCl_4): ≡CH 2.91 (t,J=5.5 Hz);

^{19}F NMR: -CF_3 81.4 (3,t,J=10 Hz), $\text{-CF}_2\text{-}$ 61.4 (2,m,J=4 Hz),
 -CF_2 34.5 (2,t,J=5 Hz)

4H,5-Iodotetradecafluoro-4-octene (XIII) (nc)

Heptafluoropropyl acetylene XII (3.4 g, 0.0175 mol) was distilled into a 30 ml stainless steel cylinder cooled in a dry ice-acetone bath, 6.90 g (0.0233 mol) of X was added and the cylinder was closed and heated in an

oil bath at 220° for 4 hrs and 20 min. After cooling the cylinder was opened and the contents (10.30 g) fractionated at 710 mm. Systematic redistillation gave 7.05 g (82%) of XIII, b.p. 129-130°/710 mm. The compound did not give the correct elemental analysis. However, the NMR spectra are in agreement with its structure.

^1H NMR (CCl_4): 7.00 (t, J=12 Hz);

^{19}F NMR: $-\text{CF}_3$ 81.4 (3, t, J=10 Hz), 81.0 (3, t, J=10 Hz); $-\text{CF}_2$ 57.0 (2, q, J=10 Hz), 49.6 (2, m); $-\text{CF}_2-$ 38.2 (2, m), 34.2 (2, m)

4H,5H-Tetradecafluoro-4-octene (XIV)

Following with certain modifications the pattern for the preparation of 2H,3H-hexafluoro-2-butene [14] a mixture of 6.34 g (0.0129 mol) of XIII, 3 g (0.125 mol) of magnesium, 30 g (0.46 mol) of zinc dust, and 40 ml of water was stirred and heated in a water bath to 60-65° while 15 ml (0.18 mol) of concentrated hydrochloric acid was slowly added over a period of 3 hrs. The mixture was then steam distilled to give 3.16 g (67.4%) of XIV containing, according to the gas-liquid chromatography, no more than 10% of impurities.

^1H NMR (CCl_4): 6.48 (t, J=7 Hz) Lit. [14] 6.45, J=8 Hz

^{19}F NMR: $-\text{CF}_3$ 80.6 (3, t, J=9), $-\text{CF}_2$ 46.1 (2, td, J=9, J'=3), $-\text{CF}_2-$ 33.6 (2, s) Lit. [15] 81.5, 47.1, 34.5 (downfield from HFB; ϕ^* values [15] 81.5, 115.9 and 128.5, respectively).

Tetradecafluoro-4-octyne (XV) (nc)

Into a 25 ml flask surmounted by a reflux condenser connected to a dry ice trap was added 2.0 g (0.031 mol) of potassium hydroxide and 2.79 g (0.0057 mol) of XIII all at once. The mixture was refluxed for 10 min. using a free flame to give 0.74 g (36%) of a liquid, distilling at 67-80°/710 mm.

^{19}F NMR (CCl_4): $-\text{CF}_3$ 81.0 (3, t, J=8), $-\text{CF}_2-$ 58.5 (2, m), $-\text{CF}_2$ 34.8 (2, t)

4H,5-Methoxytetradecafluoro-4-octene (XVIa) (nc)

and 4H,4H-5-Dimethoxytetradecafluorooctane (XVIb)

To 1.00 g (0.00204 mol) of XIII in a 25 ml flask fitted with a stirring bar and a reflux condenser protected by a tube with potassium hydroxide, 0.55 ml (0.0022 mol) of 4N KOH in methanol was added dropwise through the reflux condenser. A white precipitate was formed immediately.

After 4 hours at room temperature 0.6 ml of water was added to dissolve the salts, and 0.63 g of a heavier liquid was separated. According to gas liquid chromatography and NMR, the crude product consisted of about 75% of XVIa, 20% of XVIb and 5% of a higher boiling impurity.

^1H NMR of XVIa: OCH_3 3.97 (3,s), $-\text{CH}=\text{}$ 5.70 (1,t,J=14.Hz)

^{19}F NMR of XVIa: $-\text{CF}_3$ 81.4, 81.0 (3,t,J=10); $-\text{CF}_2$ 55.4 (2,m), 46.1 (2,m);
 $-\text{CF}_2-$ 35.2 (2,s), 34.2 (2,s)

1,4-Diodooctafluorobutane (XVII)

The title compound was prepared according to the literature [16] from disilver octafluoroadipate and iodine in 58% yield.

^{19}F NMR (CCl_4): 103.4 (1,m), 49.8 (1,m)

Heptafluoropropylcopper (XVIII)

According to the literature and a private communication [17], 2.60 g (0.041 mol) of copper bronze was stirred with 5.92 g (0.02 mol) of 1-iodoheptafluoropropane X and 14 ml of dry dimethyl sulfide in a 50 ml flask surmounted by a reflux condenser. The mixture was kept under argon and stirred at room temperature for 22 hours and then refluxed for 8 hours. Since the reactions of XVIII with acyl chlorides were carried out in higher boiling polar solvents, dimethyl sulfide was removed from the reaction mixture by evaporation in vacuo. Part of the dimethyl sulfide remained complexed by the organocopper compound. Consequently, the recovery of the dimethyl sulfide was never complete.

3,3,4,4,5,5,5-Heptafluoro-1-phenyl-1,2-pentanedione (XIX)

To XVIII left as a residue in the flask was added, under argon, a solution of 3.40 g (0.0202 mol) of benzoylformyl chloride in 14 ml of dry acetonitrile. Gentle spontaneous warming was noticeable accompanied by precipitation of a beige cuprous chloride. The mixture was stirred for 12 hours at room temperature. Thereafter, the solvents, acetonitrile and the residual dimethyl sulfide, were evaporated at room temperature at 20-30 mm, and the residue in the flask was distilled from an oil bath into a dry ice trap at 0.05 mm and bath temperature up to 150°.

The contents of the dry ice trap - the product and acetonitrile - were redistilled under atmospheric pressure. After stripping off the aceto-

nitrile up to the temperature of 75°, the bright yellow residual diketone - 2.95 g (48.8%) - was dissolved in 10 ml of acetone and converted to its hydrate by treatment with 1.0 ml of water. Evaporation of the solvent on a Petri dish yielded the crystalline hydrate of XIX (1.61 g, 0.00503 mol) (25% overall yield), m.p. 61-64°. A mixed m.p. with an authentic sample (m.p. 67-68°) showed no depression (62-65°). Both ^1H and ^{19}F NMR spectra are in agreement with those of the hydrate prepared from benzylmagnesium chloride and heptafluorobutyric acid followed by selenium dioxide oxidation and hydration [1].

Anhydrous diketone (CCl_4): ^1H NMR: C_6H_5 o-H 7.90-8.10 (2,m), m+p-H 7.43-7.78 (3,m).

^{19}F NMR: $-\text{CF}_3$ 81.2 (3,t,J=10 Hz), $-\text{CF}_2-$ 43.4 (2,sextet,J=8 Hz), $-\text{CF}_2$ 36.3 (2,t,J=7 Hz)

Hydrate (CD_3COCD_3): ^1H NMR: C_6H_5 : o-H 8.30-8.49 (2,m), m+p-H 7.47-7.86 (3,m); OH 7.27 (s), H_2O 3.05 (s).

^{19}F NMR: $-\text{CF}_3$ 83.8 (3,t,J=12 Hz), $-\text{CF}_2-$ 45.6 (2,m), $-\text{CF}_2$ 41.0 (2,t).

Trimethylpyruvic Acid (3,3-Dimethyl-2-ketobutanoic Acid) (XXIII)

Compound XXIII was prepared by oxidation of pinacolone according to the literature [18] in a 63% yield and 93% purity. In order to remove the impurity - pivalic acid - the crude XXIII was either fractionated in vacuo in a spinning band column of about 20 theoretical plates, or purified via its semicarbazone by adding it (14.75 g) all at once to a solution of 12.72 g (0.114 mol) of semicarbazide hydrochloride and 9.32 g (0.114 mol) of sodium acetate in a minimum amount (50 ml) of water. After recrystallization from 450 ml of water 15.24 g (72%) of semicarbazone was obtained, m.p. 181-182° d. Lit. 181°d. [19], 195°d. [20].

The semicarbazone (16.69 g, 0.0892 mol) was decomposed by refluxing with 30 ml of 20% hydrochloric acid for 10 minutes. After cooling, the upper layer was separated, the aqueous layer was extracted with two 15 ml portions of ether, the ether extracts were combined with the originally separated layer, a small amount of water was separated, and the ether solution was evaporated. After storing in a freezer, 1.77 g of the unreacted semicarbazone, m.p. 182-182.5°, crystallized. It was separated by suction filtration, and the filtrate was distilled in vacuo to give 6.23 g of colorless XXIII distilling at 78-79° at 19 mm and solidifying on cooling. M.p. 18-19°. Lit. 87-89°, 90-91° [18], liq. [20] (anhyd.), 82° [21] (anhyd.), 90° [20] (hemihydrate), 125° [20] (anhyd.).

The residue in the still crystallized. It was combined with the recovered semicarbazone (1.77 g) and refluxed for 45 minutes with an equal volume of concentrated hydrochloric acid. Extraction of the mixture with two 25 ml portions of ether, evaporation of the ether extracts, and distillation afforded an additional 1.85 g of chromatographically pure XXIII, b.p. 78-80° at 19 mm. The total yield of the pure product (8.08 g) was 69.5%.

IR (neat): CO 1740, C-C 3000, OH 3200-3300 cm^{-1}

^1H NMR (CCl_4): CH_3 (9,s), -OH 9.45 (1,broad s)

Trimethylpyruvyl Chloride (3,3-Dimethyl-2-ketobutanoyl Chloride) (XX) (nc)

XXIII (7.90 g, 0.0608 mol) was mixed with 21.20 g (0.121 mol, 2 equiv.) of freshly distilled XXIV in a flask surmounted by a short (10 cm) Vigreux column, and the mixture was distilled at atmospheric pressure at 90-95° into a receiver connected to a dry ice trap fitted with a Drierite guard tube. The crude product (1 g from the dry ice trap and 6.09 g from the receiver) was redistilled at 97-105°/710 mm to give 6.15 g (68.2%) of chromatographically pure XX.

^1H NMR (CCl_4): CH_3 1.34 (s).

5,5,6,6,7,7-Heptafluoro-2,2-dimethyl-3,4-heptanedione (XXI) (nc)

In a 100 ml three-necked flask fitted with a magnetic stirring bar, a thermometer, a septum, and a reflux condenser connected to an argon cylinder, 9.41 g (0.1485 g-atom, 4 equiv.) of copper bronze was stirred under argon with 25 ml of dry dimethyl sulfide. Into the mixture, 11.0 g (0.037 mol) of X was injected all at once through the septum, and the mixture was stirred and refluxed at 37-38° for 12 hours. Approximately one-half of the solvent evaporated, and the temperature of the mixture rose to 55°. The rest of the solvent was stripped off at 30° and 30 mm and collected in a dry ice trap (5.7 g). A solution of 5.5 g (0.037 mol) of XX in 20 ml of benzonitrile was injected into the flask without producing any apparent reaction or evolution of heat. The mixture was stirred and heated at 75-85° for 1 hour.

The contents of the reaction flask were distilled at 0.1 mm up to 150° into a receiver (16.75 g, benzonitrile) and a liquid nitrogen trap (15.65 g). Redistillation of the yellow condensate from the trap gave 6.5 g of dimethyl sulfide at 35-52°, and 2.01 g of a yellow liquid distil-

ling at 85-95°. The liquid containing some unreacted XX was stirred for 30 minutes at room temperature with a 5% solution of sodium bicarbonate. The colorless heavier layer - XXI - 0.86 g, 75% pure - showed both carbonyl and hydroxyl peaks in the IR spectrum (1740 and 3450 cm^{-1} , respectively) and is most probably a mixture of the anhydrous ketone and its hydrate. B.p. 92-101°, yield 0.43 g (4.1%).

^1H NMR (CCl_4): CH_3 1.35 (s)

^{19}F : CF_3 82.1 (3,t,J=10 Hz), $-\text{CF}_2\text{CO}-$ 48.5 (2,q,J=10 Hz), $-\text{CF}_2-$ 36.6 (2,m)

3,3,4,4,5,5,5-Heptafluoro-2-hydroxypentanenitrile (VIII)

a) Anhydrous hydrogen cyanide (2.59 g, 0.096 mol) cooled to 5° was added all at once to magnetically stirred heptafluorobutyraldehyde ethyl hemiacetal XXVII (20.0 g, 0.082 mol) cooled in an ice bath. Ten drops of a saturated aqueous solution of potassium cyanide was added, the mixture was allowed to warm to room temperature and was stirred for 3 1/2 days (probably unnecessarily long). The light brown mixture was acidified with 15 drops of dichloroacetic acid to pH of 3.5 and distilled at 65-77° at 12 mm to give 13.81 g (75%) of VIII which crystallized. M.p. 25-26°.

b) XXVII (19.10 g, 0.0885 mol) was added all at once to a stirred solution of 28 g (0.27 mol) of sodium bisulfite in 42 ml of water. After 5 hours the white crystalline mush was cooled in an ice bath, filtered with suction through a large Büchner funnel (diameter 10 cm), and the crystals on the filter were washed with 10 ml of ethanol and then with 10 ml of ether to give 22.58 g (95.3%) of V. This (22.58 g, 0.0747 mol) was stirred magnetically with 68 ml of water in a 250 ml Erlenmeyer flask placed in an ice bath. At 7°, a solution of 5.62 g (0.0865 mol, 15% excess) of potassium cyanide in 22 ml of water was added all at once. The temperature rose instantaneously to 14° but dropped slowly to 6.5° after 5 minutes. After an additional 20 minutes the mixture was transferred into a separatory funnel, the heavier layer (19.5 g) was separated, the aqueous layer was twice extracted with 20 ml of ether, the ether solutions were combined with the originally separated organic layer, the solution was acidified with 1.3 ml of concentrated hydrochloric acid to pH 3.5, a small aqueous layer was separated, the ether solution was dried over magnesium sulfate, and the ether was evaporated at room temperature at 18 mm. The oily residue (17.25 g) was distilled at 68-68.5°/12 mm to give 12.72 g (75.7%) of VIII, a colorless liquid with a faint terpene-like smell. It crystallized to a white solid, m.p. 28-31°. Lit. [22] (probably in error), b.p. 62.5-64°/3 mm, m.p. 70-100°.

^1H NMR (CCl_4 , CD_3COCD_3): $-\text{CF}_2\text{CH}-\text{O}$ 5.72 (dd, $J=15$, $J'=7.5$ Hz); $-\text{OH}$
(1, broad signal centered at 6.70).

^{19}F : $-\text{CF}_3$ 83.2 (3, t, $J=10.5$ Hz), $-\text{CF}_2-$ 38.3 (2, dt, $J=6$ Hz), $-\text{CF}_2\text{CH}$
(diastereotopic F, AB spectrum), 45.8 (1, dm, $J=290$ Hz), 41.0
(1, dm, $J=290$ Hz).

Analysis: Found: 26.73% C, 1.00% H, 6.37% N. For $\text{C}_5\text{H}_2\text{F}_7\text{NO}$ (225.1)
calcd. 26.68% C, 0.90% H, 6.22% N.

3,3,4,4,5,5,5-Heptafluoro-2-hydroxypentanoic Acid (XXVI)

The cyanohydrin VIII (14.05 g, 0.0624 mol) was stirred magnetically and refluxed for 3 hours and 20 minutes with 16 ml (19 g, 0.19 mol) of concentrated hydrochloric acid in a flask immersed in an oil bath heated at 110-120°. After cooling, crystals of ammonium chloride were filtered with suction (1.42 g) and the filtrate was extracted continuously with ether. Evaporation of the ether extract at 22-25° at 15 mm gave a crystalline residue (16.22 g) which on recrystallization from 30 ml of benzene gave 9.56 g of the product, m. 72-73°, and, after evaporation of the mother liquors, an additional 3.19 g of XXVI (after recrystallization), m. 71-73°. Lit. [23] m.p. 68-69°. The combined yield was 12.75 g (83.7%). The compound sublimes at 50-60° at 12 mm and has a pleasant sweet taste.

^1H NMR (CD_3COCD_3): $-\text{CH}(\text{OH})$, 4.92 (dd, $J=20$, $J'=6$ Hz), $-\text{OH}$ 7.86 (s, broad).
 ^{19}F : $-\text{CF}_3$ 83.5 (3, dd, $J=13$, $J'=9$ Hz), $-\text{CF}_2-$ 38.4 (2, dd, $J=21$, $J'=6$ Hz),
 $-\text{CF}_2\text{CH}$ (diastereotopic F, AB spectrum), 46.9 (1, dm, $J=290$ Hz),
39.8 (1, dm, $J=290$ Hz).

Analysis: Found: 24.60% C, 1.18% H. For $\text{C}_5\text{H}_3\text{F}_7\text{O}_3$ (244.1) calcd. 24.58%
C, 1.24% H.

3,3,4,4,5,5,5-Heptafluoro-2,2-dihydroxypentanoic Acid (XXV)

The hydroxy acid XXVI (4.60 g, 0.01885 mol) was dissolved in 3.8 ml of water in a 125 ml Erlenmeyer flask fitted with a magnetic stirring bar and immersed in a bath of ice, methanol and water (temperature -10°). A solution of 1.7 g (0.0212 mol, 1.13 equiv.) of 50% aqueous sodium hydroxide in 3.8 ml of water was added followed by 15 g of crushed ice. This brought the temperature of the reaction mixture to -4°. Then 2.07 g (0.0131 mol, 0.70 equivalent, 5% excess) of potassium permanganate was added portionwise over a period of 30 minutes. The temperature of the cooling bath was -8° to -4°, inside the mixture -5° to -4°. The mixture was kept at this temperature for an additional 1.5 hours. Then the manganese dioxide was filtered with suction over an activated charcoal filter, washed thoroughly

with 15 ml of water, and the combined aqueous solutions were evaporated at 35°/10 mm. The residue (2.90 g) was dissolved in 8 ml of water, the solution was acidified with concentrated hydrochloric acid to Congo Red and extracted continuously with ether. Evaporation of the ether extract at 70°/20 mm gave 1.31 g of a crystalline residue.

The manganese dioxide cake was suspended in 50 ml of water, saturated with sulfur dioxide, and the colorless solution was extracted continuously with ether. Evaporation of the ether extract in vacuo gave an additional crop of 0.52 g of the product. The combined yield of XXV was 1.83 g (38.3%). M.p. 109–110° after sublimation at 12 mm (110–140° bath temperature) or after crystallization from 3 parts of hexane and 1 part of benzene. B.p. 175–178°/710 mm. Sweet taste similar to that of XXVI. Lit. [24] m.p. 112–113°, b.p. 92–5°/15 mm.

¹H NMR (CD₃COCD₃): OH (hydrate) 5.83, no carboxylic OH.

¹⁹F NMR: -CF₃ 83.2 (3,t,J=9.5 Hz), -CF₂ 40.0 (2,m), -CF₂- 42.6 (2,m).

Analysis: Found: 23.40, 22.67% C; 1.13%, 1.09% H. For C₅H₃F₇O₄ (260.1) calcd. 23.09% C, 1.16% H.

3,3,4,4,5,5,5-Heptafluoro-2-ketopentanoyl Chloride (XXII) (nc)

In a 25 ml distilling flask surmounted by a 10 cm long Vigreux column and a condenser connected to a dry ice trap closed by a phosphorus pentoxide drying tube, 4.78 g (0.0184 mol) of the dihydroxy acid XXV* and 12.15 g (0.0694 mol) of o-chlorobenzoyl chloride was heated with a free flame until the solid acid dissolved and a strong evolution of hydrogen chloride started. The heating was continued for about 15 minutes during which 4.0 g of a condensate was collected in the dry ice trap and 1.13 g of a liquid in a distillation receiver. Both liquids were combined and redistilled at atmospheric pressure (710 mm) to give 1.31 g (27.3%) of a colorless fuming liquid XXII distilling at 100–104°. The chloride is easily hydrolyzed in moist air to the crystalline parent dihydroxy acid XXV.

¹⁹F NMR (CD₃COCD₃): -CF₃ 83.0 (3,t,J=9.5 Hz), -CF₂CO- 44.0 (2,q,J=9 Hz),
-CF₂- 37.0 (2,m)

*The hydrate XXV, probably CF₃CF₂CF₂C(OH)₂CO₂H [24], could not be dehydrated by a vacuum sublimation. An attempt to dehydrate XXV by distillation with phosphorus pentoxide to an anhydrous anhydride resulted in a poor yield of a compound, which did not give the expected chloride XXII on treatment with phthalyl chloride.

Attempt to Synthesize Tetradecafluoro-3,4-octanedione (IX)a) From XVIII and XXII.

XVIII was prepared as described in the paragraph on the synthesis of XIX and XXI from 1.30 g (0.0205 mol) of copper bronze and 3.25 g (0.011 mol) of heptafluoropropyl iodide in 10 ml of dimethyl sulfide by refluxing the mixture for 14 hours. After stripping the solvent at 40° and 20 mm, 10 ml of benzonitrile was added followed by 1.31 g (0.005 mol) of XXII. The mixture warmed up considerably. After stirring at room temperature for 8 hours, the mixture was distilled at 0.4-0.35 mm into a dry ice trap until benzonitrile started to distil (at 40°). The contents of the dry ice trap - 1.34 g - was predominantly regenerated dimethyl sulfide with a negligible amount of a fluorinated compound whose NMR spectrum matched that of IX [3].
¹⁹F NMR (CCl₄, MeCN): -CF₃ 82.3 (3,t,J=9 Hz), -CF₂CO 43.2 (2,q,J=9 Hz),
 and -CF₂- 35.8 (2,m).

Lit. [3] 83.2, 45.7 and 38.6 (downfield from HFB).

b) *From Heptafluoropropylcopper and Oxalyl Chloride

XVIII was prepared as described from 3.00 g (0.0472 mol) of copper bronze and 6.08 g (0.0205 mol) of heptafluoropropyl iodide in 10 ml of dimethyl sulfide by refluxing the mixture for 12 hours. After stripping off the solvent at 40° at 20 mm, the residue was treated with a solution of 1.5 g (0.0118 mol) of oxalyl chloride in 8.5 ml of benzonitrile. A strongly exothermic reaction ensued accompanied by boiling of the reaction mixture, and possibly even evolution of a gas noncondensable in the dry ice trap. After stirring at room temperature for 4 hours the contents of the flask were distilled into a liquid nitrogen trap at 0.5-0.1 mm giving 5.6 ml of a yellow liquid. Redistillation at atmospheric pressure gave recovered dimethylsulfide (2.39 g) boiling at 35-70°, and an intermediate yellow distillate at 70-170° (0.46 g), a mixture which contains - according to the NMR spectra - some dimethyl sulfide, benzonitrile, and IX. Estimated yield is approximately 3%.

IR (neat): CO 1787 cm⁻¹; lit. [3] 1770 cm⁻¹.

¹⁹F NMR (neat): 82.1 (3,t), 43.3 (2,q), and 36.0 (2,m).

Lit. [3] 83.2, 45.7, 38.6 downfield from HFB.

*P. M. Hergenrother's suggestion.

Octafluoroadipaldehyde bis-Cyanohydrin (Octafluoro-2,7-dihydroxyoctane-dinitrile (XXXII) (nc)

Crude octafluoroadipaldehyde bis-(ethyl hemiacetal) XXX (15.28 g, 0.043 mol) (obtained in a quantitative yield by reduction of XXXI according to the literature [8]) was liquified by warming and added all at once to a solution of 26 g (0.25 mol) of sodium bisulfite in 39 ml of water. Ethyl alcohol (3 ml) was added to increase the miscibility, and the mixture was stirred at room temperature. After 15 hours a thixotropic mixture of the crystals of VI was filtered with suction through a Büchner funnel (10 cm diameter) and allowed to dry. Because some mother liquor stuck to the crystals higher than the theoretical yield was obtained: 22.15 g (109%).

The aldehyde-bisulfite compound VI (19.16 g, estimated 0.035 mol) was suspended in 40 ml of water and the mixture was cooled to 4° with an ice bath. A solution of 6.15 g (0.095 mol, 2.3 equiv.) of potassium cyanide in 15 ml of water was cooled to 4° and added all at once to the stirred mixture. The temperature of the mixture rose to 8°, the solid dissolved, and the color turned yellow. After stirring at 2-12° for 2.5 hours 40 ml of ether was added and the mixture was allowed to warm to room temperature. After three quarters of an hour the ether layer was separated, the aqueous layer was extracted with two 20 ml portions of ether, the combined ether solutions were acidified with 0.3 g of chloroacetic acid to pH 3.5 (to prevent reversion of the cyanohydrin to the components), and the ether was evaporated at 30° at 30 mm. The residue - 6.70 g of a viscous oil - solidified. After crystallization from benzene, 4.35 g (39.3%) of pure XXXII, m.p. 96-98°, was obtained.

¹H NMR (CD₃COCD₃): -CF₂CH 5.55 (1,dd,J=11,J'=13 Hz); -OH 7.65 (1,s,broad)
¹⁹F: -CF₂-CF₂- 42.9(m) -CF₂-CH (AB spectrum of diastereotopic fluorines.

One part overlaps the signal of -CF₂-), 42.3, 46.4 (J_{gem}=282 Hz).
 Analysis: Found: 31.08% C, 1.42% H, 48.61% F, 8.79% N. Calcd. for
 C₈H₄F₈N₂O₂ (312.1): 30.78% C, 1.29% H, 48.80% F, 8.98% N.
 Mass spectrum: 285 (M-27(HCN)).

Octafluoro-2,7-dihydroxyoctanedioic Acid (XXXIII) (nc)

A mixture of 4.00 g (0.0128 mol) of XXXII and 6 ml (7.7 g, 0.07 mol) of concentrated hydrochloric acid was stirred and refluxed in an oil bath at 130° until the solid dissolved, and an additional one half hour (2.5 hours total). After cooling the contents of the flask solidified. It was

dissolved in 20 ml of ether and enough water to dissolve the ammonium chloride. The ether layer was separated, the aqueous layer (8 ml) was extracted continuously with ether for 1 hour and the combined ether solutions were evaporated at 35° at 35 mm to give 4.60 g of crude, almost white XXXIII, m.p. 176-177°.

^1H NMR (CD_3COCD_3): $-\text{CH}(\text{OH})$ 4.89 (1, dd, $J=19, J'=5$ Hz); $-\text{OH} + \text{CO}_2\text{H}$, 7.70 (2.5, s, broad—hydrated carboxyl).

^{19}F : $-\text{CF}_2-\text{CF}_2$ 43.0 (m), $-\text{CF}_2\text{CH}(\text{OH})$ (AB spectrum of diastereotopic fluorines, one part overlapping the signal of $-\text{CF}_2-$, 41.0, 47.0 ($J_{\text{gem}}=282$ Hz)).

Analysis: Found: 27.46% C, 1.78% H, 43.38% F. Calcd. for $\text{C}_8\text{H}_6\text{F}_8\text{O}_6$ (350.1): 27.44% C, 1.73% H, 43.41% F. Mass spectrum: 350.

3,3,4,4,5,5,6,6-Octafluoro-2,7-octanedione (XXXIX) (nc)

a) From XXI and Methylmagnesium Iodide

Methylmagnesium iodide was prepared from 5.62 g (0.235 mol) of magnesium shavings, 34.0 g (0.24 mol) of methyl iodide and 120 ml of ether. This solution was slowly added over a period of 3 hours and 20 minutes to a well stirred (Teflon paddle stirrer) solution of 10.4 g (0.03 mol) of diethyl octafluoroadipate in 100 ml of ether. The reaction flask was cooled in a dry ice-acetone bath to -74° to -75° (temperature inside the flask). After the addition of the Grignard reagent has been completed, the reaction mixture was decomposed by a solution of 25 ml (0.30 mol) of concentrated hydrochloric acid in 85 ml of tetrahydrofuran added dropwise over a period of 1.5 hours to the reaction mixture cooled to -74° to -65° . The yellow-brown mixture still containing some solids was shaken up with 20 ml of water, the aqueous layer was separated and extracted with three 25 ml portions of ether. The combined ether extracts were washed with 10 ml of water, 10 ml of a saturated solution of sodium bicarbonate, 5 ml of water, dried with anhydrous magnesium sulfate, and the solvents were stripped off in a column. Distillation of the residue gave 4.94 g of crude octafluoro-2,7-octanedione, which on redistillation gave 3.36 g (39.3%) of XXXIX boiling at $75-80^\circ$ at 21 mm (96% pure according to gas-liquid chromatography).

IR (neat): F 1130-1210, CO 1762 cm^{-1}

^1H NMR (CCl_4): 2.45 (s)

^{19}F NMR: 42.8 (1, m), 41.2 (1, m).

Analysis: Found: 33.76, 33.77% C; 2.26, 2.03% H. For $\text{C}_8\text{H}_6\text{F}_8\text{O}_2$ (286.1) calcd. 33.58% C, 2.11% H.

b) From XXXV and Methylmagnesium Bromide

In a 250 ml three-necked flask fitted with a reflux condenser, an efficient paddle-type stirrer, and a dropping funnel, 4.8 g (0.20 mol) of magnesium shavings was activated by heating with a few crystals of iodine. A solution of 11.5 ml (19 g, 0.2 mol) of precooled (-5°) methyl bromide in 140 ml of ice-cooled ether was added portionwise through a dropping funnel to the magnesium over a period of 20 minutes. A vigorous reaction ensued, and when it slackened, a solution of 11.12 g (0.0384 mol) of anhydrous octafluoroadipic acid (m.p. 132-135°) in 30 ml of ether was added rapidly over 10 minutes. The exothermic reaction kept the ether boiling and resulted in precipitating a grey-white solid. The mixture was kept refluxing by heating with a water bath for an additional 1.25 hours and then allowed to stand overnight.

To the reaction mixture cooled in an ice bath a solution of 20 ml of concentrated hydrochloric acid in 17 ml of water was added dropwise. The ether layer was separated, the aqueous layer was extracted with 20 ml of ether, the combined ether solutions were washed with small amounts of water, with a saturated solution of sodium bicarbonate, with water again, and dried over anhydrous magnesium sulfate. The ether was distilled off through a 3-plate column, and the residue was distilled at atmospheric pressure to give 7.80 g (70.7%) of colorless XXXIX, b. 168-173°, identical with that prepared under a) (95% pure by gas-liquid chromatography).

4,4,5,5,6,6,7,7-Octafluoro-3-hydroxy-3-methylcycloheptanone (XXXXI) (nc)a) From XXXIX and Isopentyl nitrite

To 1.43 g (0.005 mol) of XXXIX in a 10 ml vial immersed in an ice bath were added alternately in small portions 2.50 g (0.0213 mol) of isopentyl nitrite and 1.8 ml (2.10 g, 0.021 mol) of concentrated hydrochloric acid over a period of 45 minutes. After an additional 30 minutes in the ice bath, the light yellow aqueous layer was separated, and the upper light brown layer was shaken up with 10 ml of a 5% solution of sodium hydroxide. The upper layer (1.99 g) was separated and found to be the unreacted isopentyl nitrite (80% recovered). The aqueous layer was extracted with 10 ml of ether and then acidified to Congo Red with concentrated hydrochloric acid. A small heavier layer was separated (1.15 g), the upper aqueous layer was extracted with 10 ml of dichloromethane and 10 ml of ether. The combined extracts and the original layer were dried with magnesium sulfate and distilled to give 0.73 g (51%) of XXXXI, b.p. 90-104°/22 mm (mainly 104°/22 mm) (90% pure by G.C.).

IR (neat): F 1190, CO 1766, OH 3540 (broad) cm^{-1}

^1H NMR (neat): CH_3COH 1.64, (3,s); $-\text{CH}_2-$ 3.11, 3.36 (2, AB set of diastereotopic protons, nonsym. doublets), OH 4.75 (1, broad s).

^{19}F : complex multiplet, 26-51 ppm downfield from HFB.

b) From XXXIX and p-Nitrosodimethylaniline

Following a general nitrosation procedure [25], 1.83 g (0.0064 mol) of XXXIX was added to a solution of 5.75 g (0.0384 mol, 6 equiv.) of p-nitrosodimethylaniline in 65 ml of absolute ethanol, and the mixture was stirred magnetically and refluxed for 5.5 hours. After cooling, the ethanol was stripped off at 40° and 30 mm, and the dark green residue was refluxed with 20 ml of 20% hydrochloric acid for one half hour. Thereafter, another 20 ml of 20% hydrochloric acid was added and the refluxing was continued for an additional 30 minutes. Temperature of the mixture was 90° . The black mixture was, after cooling, extracted continuously with ether for 5 hours. The brown extract was evaporated at 40° at 25 mm, and the black residue was distilled to give 0.81 g (44.2%) of a light yellow liquid XXXXI, boiling at $65-70^\circ$ at 0.45 mm.

Analysis: Found: 33.62% C, 2.19% H. For $\text{C}_8\text{H}_6\text{F}_8\text{O}_2$ (286.1) calcd. 33.55% C, 2.11% H. Mass spectrum (chemical ionization): 286.

Semicarbazone was prepared from 0.16 g of the compound, 0.13 g of semicarbazide hydrochloride, and 0.10 g of sodium acetate in a minimum amount of water. After recrystallization from water m.p. $191-193^\circ$.

Analysis: Found: 31.66, 31.50% C, 2.48, 2.38% H, 12.63, 12.66% N. For $\text{C}_9\text{H}_9\text{F}_8\text{N}_3\text{O}_2$ (343.2) calcd. 31.50% C, 2.64% H, 12.25% N.

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