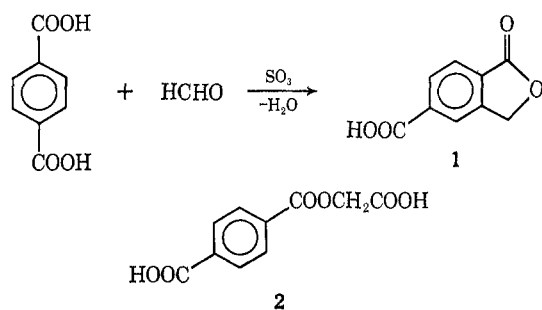


group under dehydrating conditions, a rapid loss of water would occur to produce a phthalide moiety. However, in the few reported instances of negatively substituted benzoic acids or benzoic acid itself undergoing reaction with formaldehyde, more vigorous conditions were required and only intermolecular condensation products were isolated. Thus benzoic acid reacted with formaldehyde in sulfuric acid to give 3,3'-dicarboxydiphenylmethane,⁵ and isophthalic acid provided 3,3',-5,5'-tetracarboxydiphenylmethane.⁶

We wish to report the condensation of terephthalic acid with formaldehyde in sulfur trioxide media, a process which produces 5-carboxyphthalide (1) cleanly and in excellent yield. The reaction is generally free of by-product formation over a fairly wide range of reaction conditions, although terephthaloyloxyacetic acid (2) has been identified (as its dimethyl ester) from reaction in the presence of excess formaldehyde and from reaction media containing <20% SO₃. Prior routes to 1 involved several-step processes or reduction of trimellitic anhydride, which provides a mixture of the 5- and 6-carboxyphthalides which are difficult to separate.⁷ This synthesis of 1 is believed to represent the first reported substitution of terephthalic acid with an electron-deficient carbon species.



Experimental Section

A Beckman IR-5A infrared spectrophotometer, Varian A-60 nmr spectrometer and 21-110B Consolidated Electronics mass spectrometer were used for spectral determinations. Gravimetric analysis utilized a Du Pont 950 Thermogravimetric Analyser. Carbon-hydrogen analyses were done by Galbraith Laboratories, Knoxville, Tenn. An F & M 5750 research chromatograph was used with a 12 ft \times 0.25 in. 10% UCW 98 on an acid-washed Chromosorb W DMCS-treated column for analysis of esters.

5-Carboxyphthalide (1).—Sulfur trioxide (180 ml, 4.3 mol of "Sulfan B") was slowly added to terephthalic acid (200 g, 1.2 mol), with stirring, and formaldehyde (48 g, 1.6 mol of "Trioxane") added (exothermic). The resultant slurry was heated to 120–130° for 2 hr. The reaction was accompanied by a color change after the excess sulfur trioxide distilled off. After cooling, the mixture was poured into ice water (4 l.) and crude product received by filtration. The filter cake was slurried with water, partially neutralized with NaOH to remove residual sulfuric acid, filtered, and washed again, to give 192.3 g of pink solids, mp 285–290°. Chloroform extraction of the filtrates gave an additional 6.0 g of product (93% yield). The acid can be recrystallized from acetic acid or 50% aqueous dimethyl sulfoxide to provide purified 5-carboxyphthalide, mp 290–294° (literature value,⁸ 283–284°). Esterification with methanol-BF₃ gave 5-carbomethoxyphthalide, mp 166–167°, which exhibited ir bands at 5.70 (phthalide C=O) and 5.80 μ (carboxyl C=O); nmr

(CDCl₃, 60 MHz) δ 8.08 (m, 3), 5.37 (s, 2, OCH₂), 3.98 (s, 3, OCH₃); mass spectrum (70 eV) *m/e* 192 (parent peak). Both the ester and phthalide linkages were cleaved under basic conditions, in accord with the literature.⁹

Anal. Calcd for C₁₀H₈O₄: C, 62.48; H, 4.20. Found: C, 63.57; H, 4.21; sapon equiv 96.05.

Esterification with ethanol-BF₃ gave 5-carbomethoxyphthalide, mp 147.5–148°.

Anal. Calcd for C₁₁H₁₀O₄: C, 64.05; H, 4.89. Found: C, 64.11; H, 4.86.

2-Hydroxymethylterephthalic Acid.—Acidification of the solution received from saponification of 5-carbomethoxyphthalide gave 2-hydroxymethylterephthalic acid, isolated by filtration and drying [85° (20 mm)]. It gave no phthalide C=O absorption at 5.70 μ in the ir.

Anal. Calcd for C₉H₈O₅: C, 55.10; H, 4.08. Found: C, 54.70, 54.88; H, 4.15, 4.18. Differential gravimetric analysis indicated loss of water at 200° (Calcd weight loss for -H₂O: 9.20%. Found: 10.21%) and melting at 296° (5-carboxyphthalide).

Terephthaloyloxyacetic Acid Dimethyl Ester (2).—Terephthalic acid (0.83 g, 5 mmol), formaldehyde (0.90 g, 30 mmol, "Trioxane"), and 5.0 ml of 98% sulfuric acid were sealed in a glass tube and heated to 150° for 2 hr. The tube was chilled and opened; the contents were poured into methanol (100 ml), concentrated, poured into water (700 ml), and extracted into dichloromethane. In this way, 0.71 g of esters was received, shown by gas chromatography to contain 83.2% dimethyl terephthalate, 1.1% 5-carbomethoxyphthalide, and 15.7% a third component, by peak areas. The unknown was trapped from the eluent gases and identified as dimethyl terephthaloyloxyacetic acid: nmr (CCl₄, 60 MHz) δ 3.80 (s, 3, OCH₃), 3.97 (s, 3, OCH₃), 4.82 (s, 2, CH₂), 8.13 (s, 4).

Anal. Calcd for C₁₂H₁₂O₆: C, 57.14; H, 4.80. Found: C, 56.78; H, 4.76.

Registry No.—Terephthalic acid, 100-21-0; formaldehyde, 50-00-0; 2-hydroxymethylterephthalic acid, 23405-34-7; 1 methyl ester, 23405-32-5; 1 ethyl ester, 23405-31-4; 2 dimethyl ester, 23405-33-6.

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Novel Fluorine-Containing β -Diketone Chelating Agents¹

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Increasing interest in volatile chelating agents² (or volatile metal chelates derived therefrom) for separations of metals by distillation or gas chromatography, for ultratrace analysis of metals or metal mixtures, for vapor deposition, for use as solvent extraction reagents, and for use as reagents that react directly with metals or oxides to form chelates has prompted the synthesis and examination of two new β -diketones. These ligands are 1,1,1,2,2,6,6,6-octafluoro-3,5-

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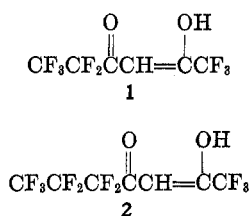
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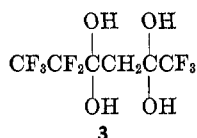
(1) This work was supported in part by Aerospace Research Laboratory In-House Independent Laboratory Research Funds, and by Contract AF 33(615)-1093.

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hexanedione (1) and 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione (2), enol forms of which are shown below.



These compounds were prepared by Claisen condensation of trifluoroacetone with the required perfluoro ester using sodium methoxide.^{3,4} Advantage was taken of the formation of a sparingly water-soluble hydrate of 1 (3) to effect its purification, which could



not be accomplished easily by distillation when ether or xylene was used as a solvent owing to azeotrope formation. The β -diketone was subsequently regenerated from 3 by treatment with phosphorus pentoxide and was distilled. The existence of a stable hydrate of 1 is not surprising since the analogous dihydrate of hexafluoroacetylacetone [H(hfa)] has been reported.⁵ The infrared spectrum of 3 exhibits a strong OH absorption band at $\sim 3 \mu$, no absorption in the carbonyl region at $\sim 6 \mu$, and increased absorption at 11.0μ . The spectrum of H(hfa) dihydrate possesses quite similar features.

Synthesis of 2 was effected conveniently in a hexane medium. After acidification of the reaction mixture and separation of the phases, the hexane phase was shaken with aqueous sodium acetate to remove the ligand from the hexane. The β -diketone was then purified in the usual manner⁴ by precipitation of its copper chelate and regeneration of the β -diketone from the chelate with concentrated sulfuric acid.

A white solid appeared in 2 stored at -25° . This material was isolated and air-dried. Its infrared spectrum permits identification of the material as a hydrate of 2 (strong OH⁻ absorption band at $\sim 3 \mu$, no carbonyl absorption band at $\sim 6 \mu$, strong absorption band at 11μ). When a mixture of 1 ml of 2 and 0.20 ml of water was cooled to -25° , all of the material solidified to a homogeneous white solid. An infrared spectrum of this solid material was identical with that of the solid material isolated from free β -diketone. On warming to room temperature, the solid melted with decomposition to 2 plus water. From these observations, then, it appears that 2 does indeed form a hydrate, but that the reaction occurs below room temperature, and that the hydrate is unstable at room temperature. The relatively poor tendency of 2 to form a hydrate as compared with H(hfa) and 1 may account, in part, for its greatly increased ability to extract divalent metals from aqueous solution as discussed below.

Nmr data on the compounds indicated that both 1 and 2 exist essentially 100% in the enol form. There was no measurable peak in the δ 3.6–4.1 region where methylene protons of the keto form of β -diketones would be expected to appear.

Infrared spectra of both compounds exhibited carbonyl absorption bands at 5.95 (w) and 6.17 (m) μ , which are similar in position and intensity to those for H(hfa) [5.92 (w) and 6.15 (m) μ]. The spectra also contain broad, strong absorption bands in the 7–9- μ CF region, and medium intensity absorption bands at $\sim 12.2 \mu$. The latter absorption band diminishes greatly upon hydrate formation, as is also the case with H(hfa).

The zirconium and hafnium chelates of 2 were prepared by direct reaction of the ligand with the anhydrous tetrachloride. It is interesting to note that despite molecular weights of 1319 and 1407, respectively, both chelates are liquids and can be distilled (Zr, 65–70°, 0.001–0.05 mm; Hf, 70°, 0.01 mm). The chromium(III) chelates of 1 and 2, and the iron(III) chelate of 2 are also liquids at room temperature.

The solvent extraction properties of 1 and 2 have been examined and compared with 1,1,1-trifluoro-2,4-pentanedione [H(tfa)] and H(hfa).⁶ In benzene or chloroform 2 ($\sim 0.1 M$) was able to extract 97% zinc or 98.7% cobalt(II) in 10 min from an equal volume of water at pH 5–6 provided the initial metal ion concentration was 0.001 M or less. The order of effectiveness of the reagents for the extraction of zinc or cobalt was found to be 2 > 1 \gg H(tfa) > H(hfa). Increasing ability of these ligands to extract divalent metals with increasing fluorocarbon chain length may be related to the decreasing tendency of the ligands toward hydrate formation. Ligand hydrate formation would be expected to result in decreased solvent extraction ability because the metal ion would be in competition with water for the ligand.

Ultraviolet absorption measurements on $10^{-4} M$ aqueous solutions of 2 at pH 4.7 and 8.0 after 0, 1, 2, 5, and 7 days revealed logarithmically decreasing absorbance values at 308 nm (enolate ion) with time. The rate of decrease was faster at pH 4.7 than at pH 8.0. The half-life values were 45.6 and 67.2 hr, respectively.

Increasing instability of 2 with decreasing pH is opposite to the behavior of H(tfa) observed by Stokely.⁷ Aqueous solutions of this ligand were stable at pH 7 and below, but decomposed rapidly at pH 9 or 10 with half-lives of ~ 3 and 2 hr, respectively.

Compounds 1 and 2 possess extremely irritating odors. Inhalation of small quantities is followed by a persistent bitter taste. Consequently, these compounds should be handled only in a hood.

Experimental Section

1,1,1,2,2,6,6,6-Octafluoro-3,5-hexanedione (1).—Ethyl pentafluoropropionate (Pierce Chemical Co., 250 g, 1.30 mol) was added dropwise with good stirring to a slurry of xylene (500 ml) and sodium methoxide (78 g, 1.45 mol) in a 2-l. flask fitted with a Dry Ice condenser. Trifluoroacetone (Pierce Chemical Co., 141 g, 1.25 mol) was added to the vigorously stirred solution; the temperature was maintained at 35–40° with an ice bath. The

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solution was allowed to stand overnight at room temperature. Dilute H_2SO_4 (650 ml, 6 *N*) was added slowly with stirring to the reaction mixture; the temperature was maintained at 20° or below with an ice bath. During the addition of the acid the color changed from amber to bright yellow to white. The mixture appeared to be an emulsion. By adding 5 ml of concentrated H_2SO_4 and shaking, the emulsion was broken and a white solid was observed. The solid was removed by vacuum filtration yielding 166 g of crude material (mp 84–87.5°).

The two phases in the filtrate were separated; the aqueous one was xylene extracted three times (150 ml each). These extracts were combined with the organic layer. The combined extracts were washed first with 200 ml of water and then with 200 ml of saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and distilled on a Todd 42-in. Vigreux column, yielding 73 g of material boiling at 68–125°. Water (25 ml) was added to the distillate and the mixture was allowed to stand overnight. The resulting crystals were filtered and dried: yield, 40 g. The total yield of **3** was 206 g (56%). A small portion of the compound was purified by sublimation at 85°, mp 60–61°.

Anal. Calcd for $\text{C}_6\text{H}_6\text{O}_4\text{F}_8$: C, 24.50; H, 2.06; F, 51.68. Found: C, 24.31; H, 1.94; F, 51.49.

A portion (50 g) of **3** was placed in a 500-ml erlenmeyer flask and ~50 g of P_{10} was added with stirring in 10–15-g portions. Gummy semisolids resulted and liquid **1** was released. The remaining **3** was dehydrated. All liquid product was decanted, combined, and twice distilled, yielding 77.5 g (53%) of **1**: bp 85–86° (atm); n_D^{25} 1.3260; d_4^{25} 1.538; nmr (downfield from tetramethylsilane, internal) δ 12.9 (s, 1, enol OH), 6.49 (s, 1, CH=C); nmr (fluorine resonance upfield from trifluoroacetic acid, external) δ +48.4 (m, 2, $J = 1$ Hz, CF_3CF_2), +6.9 (t, 3, $J = 1$ Hz, CF_3CF_2), +0.9 (s, 3, CCF_3).

Anal. Calcd for $\text{C}_6\text{H}_6\text{O}_2\text{F}_8$: C, 27.92; H, 0.78; F, 58.90. Found: C, 27.71; H, 0.78; F, 59.06.

1,1,1,2,2,3,3,3,7,7,7-Decafluoro-4,6-heptanedione (2).—Sodium methoxide (78 g, 1.45 mol) was suspended in 478 ml of hexane with vigorous stirring. Ethyl heptafluorobutyrate (Pierce Chemical Co., 323 g, 1.33 mol) was added to the flask from a dropping funnel over a 30-min period with vigorous stirring. After an additional 30-min stirring almost all of the sodium methoxide was dissolved. Following the addition of the ester, 172 g, 1.53 mol, of trifluoroacetone was added dropwise over a 1-hr period. The solution was allowed to stand overnight. During addition of the ester and the ketone, a Dry Ice condenser was connected to the flask to prevent the escape of volatile materials.

Two phases were apparent after standing overnight. The mixture was acidified with 500 ml of 6 *N* H_2SO_4 with vigorous swirling in an ice bath. The two phases were separated in a 2-l. separatory funnel. The aqueous phase was washed twice with 100-ml portions of hexane, and the hexane extracts were added to the original hexane phase. The hexane phase was extracted five times with 200-ml portions of aqueous sodium acetate (260 g/l.). The third extraction produced a third phase (on the bottom) of a dark yellow–orange color. The first three aqueous extracts were added with vigorous stirring to a solution of 126 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 750 ml of water. A green precipitate formed as the extracts were added to the copper sulfate solution. This precipitate was collected on a Büchner funnel, washed sparingly with ice–water, and air-dried overnight.

The solid (331 g) was powdered and placed in a 2-l. flask and cooled in an ice bath. Cold concentrated H_2SO_4 was added in three 50-ml portions to the copper chelate, resulting in a green liquid with white solids. The liquid was distilled through a glass helices-packed column. The forecut (cloudy) consisted of material(s) boiling up to 100°. After the forecut was taken, the distillation was stopped, and the condenser was rinsed with acetone to remove white solids and was air-dried. The distillation was then continued. The principal cut (214 g) boiled between 100 and 104°.

After storage for 5 days at –25°, white solid material was observed in the product. This was removed by filtration. The filtrate was redistilled yielding 166 g (40%) of **2**: bp 103–104° (atm); n_D^{25} 1.3243; d_4^{25} 1.592; nmr (downfield from tetramethylsilane, internal) δ 13.3 (s, 1, enol), 6.50 (s, 1, CH=C); nmr (fluorine resonance upfield from trifluoroacetic acid, external) δ +50.8 (m, 2, $J \cong 1$ Hz, $\text{CF}_3\text{CF}_2\text{CF}_2$), +45.8 (m, 2, $J = 9$ Hz, $\text{CF}_3\text{CF}_2\text{CF}_2$), +4.6 (t, 3, $J = 9$ Hz, $\text{CF}_3\text{CF}_2\text{CF}_2$), +0.7 (s, 3, CCF_3).

Anal. Calcd for $\text{C}_7\text{H}_2\text{O}_2\text{F}_{10}$: C, 27.29; H, 0.65; F, 61.67. Found: C, 27.07; H, 0.70; F, 61.78.

Registry No.—**1** (keto form), 20825-07-4; **2** (keto form), 20583-66-8; **3**, 23405-28-9.

Carbanions in Dimethyl Sulfoxide. II.¹ Dimerization During the Base-Catalyzed Disproportionation of 1,4-Dihydronaphthalene

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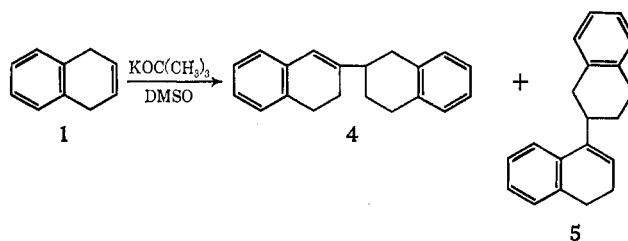
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Recently the base-catalyzed disproportionation of cyclohexadiene to give benzene and cyclohexene was reported.² Disproportionation was effected with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) and went equally well for the 1,3- or 1,4-dienes, which readily isomerize in base.^{2,3}

In our investigation of DMSO and 1,4-dihydronaphthalene, we observed a similar disproportionation that gave naphthalene and tetralin (**3**) in the $\text{KOC}(\text{CH}_3)_3$ -DMSO system at 25°. In contrast, however, the disproportionation accounted for only 37% of the reaction product. The main reaction was a dihydronaphthalene–anion addition to afford a 58% yield of a crystalline dimer **4** (Scheme I) that analyzed for $\text{C}_{20}\text{H}_{20}$

SCHEME I



with a molecular ion at m/e 260.1565 (theory 260.1565). The nmr spectrum showed the presence of eight aromatic protons (singlet at δ 7.00), eleven aliphatic protons in a broad multiplet at δ 1.60–3.00, and one unsplit olefinic proton that is assigned as being conjugated at δ 6.22. Evidence that the two ring systems are joined at the 2,2' positions is obtained from the dehydrogenation product. When **4** is heated in the presence of palladium on charcoal, 2,2'-binaphthyl is obtained as the only product.

Two other dimers (**5** and **6**), isomeric with **4** ($\text{C}_{20}\text{H}_{20}$), were also found but in much smaller amounts. Compound **5** (5% yield) has an nmr spectrum showing an unsymmetrical aromatic multiplet at δ 6.75–7.38 within which is a sharp singlet at δ 6.96 (8 H), an olefinic triplet (1 H) centered at δ 5.81 ($J = 4.3$ Hz), and a

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