5-Hydroxy-3,5-di-*tert*-butyl-2-furanone (4). White crystals of 4 were prepared by the method of Nishinaga:[3a] NMR δ 1.03 (s, 9 H, 5-*t*-Bu), 1.25 (s, 9 H, 3-*t*-Bu), 2.84 (1 H, OH), 6.78 (s, 1 H, olefinic).

4,5-Epoxy-6-oxo-2,4-di-*tert*-butylcyclohex-2-enone (7). The method of Grierer and Imsgard[8] was used to produce yellow-orange needles of 7 after recrystallization from petroleum ether: NMR δ 1.09 (s, 9 H, 4-*t*-Bu), 1.20 (s, 9 H, 2-*t*-Bu), 3.83 (s, 1 H), 7.09 (s, 1 H, olefinic).

3,5-Di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (9). The method described by Demmin and Rogić[11] was used to prepare 9. Recrystallization from *n*-pentane yielded colorless cubes. 9: NMR δ 1.13 (s, 9 H), 1.24 (s, 9 H), 6.12 (d, J = 2 Hz, 1 H), 6.44 (d, J = 2 Hz, 1 H).

General Procedure for Oxidations. DBC, DBQ, or DBSQ were accurately weighted into a Schlenk tube and dissolved in the appropriate solvent. The solution was either transferred via syringe to solid KO_2 or oxygen was slowly flowed over the vigorously stirred solution. Solutions to be quenched were degassed with three freeze–pump–thaw cycles, and 5% HCl was added, which destroyed any blue color which remained in solution. The solution was exposed to air, and 5% $NaHCO_3$ solution (10 mL) was added. The mixture was extracted with diethyl ether (3 × 10 mL). The combined layers were again extracted with 5% $NaHCO_3$ and the aqueous layers combined. The GC was calibrated with fresh solutions of DBQ and DBC, and the product peak areas were determined by weighing. The aqueous layer was acidified with 25 mL of 5% HCl, extracted with diethyl ether (3 × 10 mL), and dried over $MgSO_4$. If an NMR spectrum of the acidic products was to be recorded, an internal standard of *p*-dimethoxybenzene was added, the solvents were removed, and the spectra were recorded in $CDCl_3$. For GC analysis the acids were methylated with diazomethane, with excess diazomethane destroyed by acetic acid. Yields reported (Table I) are based on original reactant amounts.

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Registry No. 1, 53846-98-3; 2, 22802-86-4; 3, 53904-87-3; 4, 3807-35-0; 7, 82337-97-1; DBQ*, 82323-89-5; DBC*, 82323-90-8; NaDBSQ, 82323-91-9; 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione, 24289-60-9; *tert*-butanol-d_6, 53853-65-9; acetone-d_6, 666-52-4; 4-*tert*-butylcatechol, 98-29-3.

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Condensation of Monosubstituted Isopropylidene Malonates with Mannich Bases

Robert T. Jacobs, Allen D. Wright, and Francis X. Smith*

Department of Chemistry, King's College, Wilkes-Barre, Pennsylvania 18711

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In recent years there have been a variety of studies concerned with the chemistry of Meldrum's acid[1] (the cyclic isopropylidene ester of malonic acid). We have been particularly interested in preparative applications, where this reagent or its derivatives can be employed with advantage over acyclic malonic esters. One type of application would make use of the high acidity ($pK_a \approx 5$) of the cyclic malonates such that basic substrates could be activated toward reaction by protonation or N-acylation with concomitant formation of appreciable amounts of the enolate anion. We previously described[2] some reactions that could be explained on such a basis.

Table I. Condensation Products of Mannich Bases and Isopropylidene Malonates

compd[a]	mp, °C	recryst solvent	yield, %
1a	71–72	ether/hexane	74
1b	90–91	ether/hexane	93
1c	96–97	ether/hexane	86
2a	205–207	acetone/hexane	70
2b	205–206	acetone/hexane	66
2c	159–160	acetone/hexane	92
3a	178–179	acetone/hexane	87
3b	158–159	acetone/hexane	80
3c	157–158	acetone/hexane	66
3d	170–171	acetone/hexane	85
3e	214–215	acetone/hexane	84
3f	144–145	acetone/hexane	83
4a	102–103[b]	ether/hexane	74
4b	100–101	ether/hexane	89
4c	169–170	ether/hexane	71

[a] All compounds, except 4a which has been previously reported, were analyzed and gave satisfactory results (±0.4%) for C, H, and N where present. [b] Lit.[19] mp 105–106 °C.

We report that Mannich bases derived from acetone, ferrocene, β-naphthol, and indole readily condense with monosubstituted derivatives of Meldrum's acid in the presence of acetic anhydride. The alkylation of acyclic malonates by Mannich bases has been extensively investigated as part of a synthetic route to various substituted carboxylic acids. These reactions have usually been conducted by treating the sodium salt of the malonate with either the Mannich base or its generally more reactive quaternary salt.[3] There are a few reports of the alkylation by Mannich bases of barbituric acids,[4] 1,3-cyclohexanediones,[5] and 4-hydroxycoumarins,[6] in which the enol was heated with Mannich base, sometimes with an added base as a catalyst. When we tried heating monosubstituted Meldrum's acid derivatives with Mannich bases in neutral solvents such as benzene, 1,2-dimethoxyethane, or methanol, the reactions proceeded sluggishly, and often only moderate yields were obtained. Only upon addition of acetic anhydride did the reaction proceed readily. See Table I.

4-(Diethylamino)-2-butanone was the least reactive of the Mannich bases when subjected to reaction with the cyclic malonates in an acetic anhydride/1,2-dimethoxyethane mixture. Examination of the reaction mixture by TLC indicated that 2 days at room temperature were required for complete reaction although good product yields could also be obtained by warming at 55 °C overnight. The mechanism of these reactions may involve the generation of methyl vinyl ketone and subsequent alkylation through conjugate addition. An elimination–addition mechanism seems to be a commonly suggested pathway for alkylations by Mannich bases,[3] and it has been previously reported that isopropylidene malonates will readily undergo conjugate addition to α,β-unsaturated carbonyl compounds.[7] The conditions employed in our procedure are apparently

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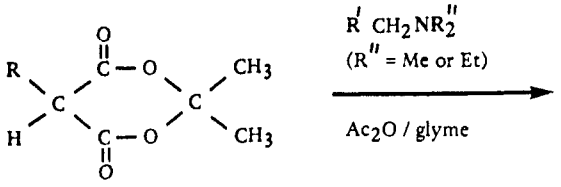
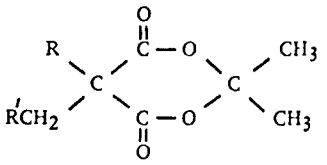
milder than those required in the base-catalyzed reaction of acyclic malonates. For example, diethyl malonate has been previously alkylated with 4-(dimethylamino)-2-butanone by treatment with sodium ethoxide/ethanol over an 8-day period with a resultant yield of 48%.[8] The products of the condensation reactions (1) hydrolyzed





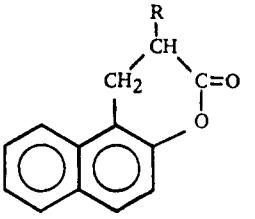
1a	R = Me	R' = CH_3COCH_2
1b	R = Et	R' = CH_3COCH_2
1c	R = Ph	R' = CH_3COCH_2
2a	R = Me	R' = Ferrocenyl
2b	E = Et	R' = Ferrocenyl
2c	R = Ph	R' = Ferrocenyl
3a	R = Me	R' = 3-Indolyl
3b	R = Et	R' = 3-Indolyl
3c	R = Ph	R' = 3-Indolyl
3d	R = $PhCH_2$	R' = 3-Indolyl
3e	R = CH_3CONH	R' = 3-Indolyl
3f	R = $PhCH_2$	R' = 3-(N-Methylindolyl)

smoothly with decarboxylation upon refluxing with concentrated hydrochloric acid, and the resultant δ-keto acids were obtained in good yield. Treatment of the products **1** with diethylamine led to a facile carbon–carbon bond cleavage, releasing the monosubstituted malonate and demonstrating the reversibility of these reactions.

In the reactions with [(dimethylamino)methyl]ferrocene, TLC indicated considerable product formation after just a few minutes at room temperature. The ease by which these condensations take place may be compared to the analogous reactions with acyclic malonates which were performed by heating the quaternary salt of the Mannich base with the sodium salt of the malonic ester for several hours.[9] The ferrocenylmethylmalonates **2** were readily hydrolyzed to the corresponding malonic acids with aqueous sodium hydroxide.

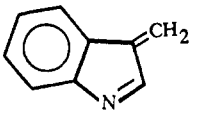
The condensation reactions with 1-[(dimethylamino)-methyl]-2-naphthol also proceeded readily producing the monodecarboxylated lactones **4** in high yield. This Mannich base was previously shown to alkylate ethoxymagnesium salts of acyclic malonates upon heating in chlorobenzene.[10] A sulfur analogue of this Mannich base was also previously reported to be reactive toward acyclic malonates under basic conditions.[11]

The monosubstituted cyclic malonates were also reactive toward gramine and its *N*-methyl derivative under the



4a R = Me
4b R = Et
4c R = Ph

general conditions. The reactions were generally complete after a few hours at room temperature, indicating that a more facile reaction occurs under these conditions than with the usual methods which employ acyclic malonates.[3] Also, this procedure is complementary to a Mannich-type condensation of three-carbon components[12,13] which employed unsubstituted Meldrum's acid, indole, and various aldehydes and which led to a useful method for the preparation of ethyl indolylpropionates, unsubstituted[13] or branched[12] β to the carbonyl. The indolylmethylmalonates also exhibited abnormal behavior upon attempts to degrade the acylal ring. Heating **3d** with piperidine resulted in a high yield of 3-(piperidinomethyl)indole rather than the expected piperidide derivative. Facile carbon–carbon bond cleavage was also observed when **3d** was treated with aqueous ethanolic sodium hydroxide at room temperature. The compound dissolved and produced 3-(ethoxymethyl)indole[14] and the anion of isopropylidene benzylmalonate. These results can be attributed to the stability of anions of Meldrum's acid derivatives and thus their tendency to be good leaving groups.[1,15,16] We felt that, at least with the sodium hydroxide treatment, the initial step in the abnormal cleavage would be deprotonation of the indolic nitrogen and the departure of the malonate anion to generate an intermediate such as **5**.[17]



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Therefore, we expected that treatment with mild base or attempted cleavage of the N-substituted derivatives should proceed in the normal fashion with opening of the acylal ring. We were able to convert malonate **3e** into *N*-acetyltryptophan through a treatment which employed aqueous sodium carbonate. The *N*-methyl derivative **3f** was converted into the corresponding malonic acid by treatment with aqueous ethanolic sodium hydroxide.

We believe the accelerating effect of the acetic anhydride is due to its direct participation in the chemical change.

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Since the reactions failed to proceed with comparable ease in methanol or in methanol/acetic acid mixtures, we would rule out the possibility of a mere solvent effect related to dielectric strength or the possibility that the reactions are catalyzed by acetic acid which is released by the anhydride. Since the products **1** can be readily cleaved by a secondary amine at room temperature, it seems reasonable that at least in these cases, the acetic anhydride can improve the yields by acting as an amine scavenger. Since we have found the ferrocenyl products **2** to be relatively stable toward secondary amines at room temperature, the rapid reactions in these cases are probably due solely to the ability of the anhydride to activate the nitrogen toward displacement.

We feel that the ease by which these reactions take place, coupled with some recent reports[18] of convenient methods of preparing monosubstituted derivatives of Meldrum's acid, make this method a useful alternative to heating the metal salts of acyclic malonates with the Mannich bases or their quaternary salts. Since the acyclic malonate, diethyl ethylmalonate, failed to condense with these Mannich bases under comparable conditions in acetic anhydride/1,2-dimethoxyethane mixtures, we conclude that the reactions reported in this article demonstrate a special reactivity of Meldrum's acid derivatives which is related to their cyclic structure.

Experimental Section

Melting points were determined on an oil bath apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. The Mannich bases, except for *N*-methylgramine which was prepared according to the literature method,[17] and isopropylidene methylmalonate were obtained from Aldrich Chemical Co.; Milwaukee, WI. Isopropylidene ethylmalonate and isopropylidene phenylmalonate were prepared by condensing the corresponding malonic acids with acetone.[20] Isopropylidene benzylmalonate was obtained by the borohydride reduction[18c] of isopropylidene benzylidenemalonate.[15,21]

General Procedure for Condensation. The monosubstituted isopropylidene malonate (10 mmol) and the Mannich base (10 mmol) were stirred in 5 mL of 1,2-dimethoxyethane, and 5 mL of acetic anhydride was added with stirring. Compounds **1a–c** were prepared by heating at 55 °C overnight. Compounds **2a–4c** were obtained after allowing the reaction mixture to stir at room temperature overnight. The product was crystallized by pouring the reaction mixture into 50 mL of ice/water and isolated by filtration. The preparation of **4a–c** should be conducted in a vented vessel since a gas is evolved.

Hydrolysis and Decarboxylation of 1a–c. The cyclic ester (1 g) was refluxed with 20 mL of concentrated hydrochloric acid overnight, and the mixture was then cooled. From **1a** there was obtained a 73% yield of α-methyl-δ-oxocaproic acid by ether extraction; semicarbazone, mp 138–139 °C (lit.[22] mp 140–141 °C). Compound **1b** gave α-ethyl-δ-oxocaproic acid by ether extraction in 80% yield; semicarbazone, mp 127–129 °C (lit.[23] mp 131–131.5 °C). Cooling the reaction mixture obtained from **1c** afforded α-phenyl-δ-oxocaproic acid as crystals: mp 69–70 °C (lit.[24] mp 69.2–70.5 °C); 95% yield.

Cleavage of 1c with Diethylamine. Isopropylidene phenyl(γ-oxobutyl)malonate (100 mg) was stirred with 2 mL of diethylamine at room temperature. Within 1 h a sizable crop of colorless crystals had separated from the solution. The following day these crystals were removed, washed with ether, and identified as the diethylammonium salt of isopropylidene phenylmalonate (73 mg, 72% yield) by comparison (IR) with a sample prepared by treating authentic isopropylidene phenylmalonate with diethylamine.

Hydrolysis and Decarboxylation of 2a–c. The cyclic esters were converted to the malonic acids by refluxing with 5% NaOH for 4 h and acidifying. The malonic acids were decarboxylated by heating on an oil bath at 160 °C under nitrogen.

From **2a** there was obtained a 66% yield of β-ferrocenyl-α-methylpropionic acid, mp 109–111 °C (lit.[9b] mp 112 °C). Compound **2b** gave β-ferrocenyl-α-ethylpropionic acid: 69% yield; mp 98–99 °C (lit.[9c] mp 82 °C). Compound **2c** afforded β-ferrocenyl-α-phenylpropionic acid: 76% yield; mp 98–99 °C (lit.[9d] mp 99 °C).

Cleavage of 3d with Sodium Hydroxide Solution. Isopropylidene benzyl[(3-indolyl)methyl]malonate (100 mg) was stirred with 1 mL of water and 1 mL of ethanol. To this mixture was added 330 mg of NaOH, and the resultant mixture was stirred at room temperature until clear (~1 h). The solution was then diluted with 3 mL of water, whereupon an oil separated. The oil was then extracted into 15 mL of ether, and the ether layer was dried (Na_2SO_4) and evaporated. The residue, identified as 3-(ethoxymethyl)indole (35 mg, 73% yield), had a melting point and IR identical with an authentic sample prepared from *N*-acetyl-3-(acetoxymethyl)indole.[14]

The aqueous layer was acidified with concentrated HCl, whereupon isopropylidene benzylmalonate separated as colorless crystals (55 mg, 85% yield). This compound had a melting point and IR identical with an authentic sample.[18c]

Cleavage of 3d with Piperidine. Isopropylidene benzyl[(3-indolyl)methyl]malonate (100 mg) was refluxed with 2 mL of piperidine for 1 h. The excess piperidine was evaporated, yielding an oil which crystallized upon the addition of 3 mL of water. The product was removed by filtration and identified as 3-(piperidinomethyl)indole: 50 mg (85% yield); mp 156–158 °C (lit.[25] mp 158–159 °C). If the above mixture was allowed to stand for 2 days without heating, most of the starting material **3d** was recovered unchanged (75 mg) along with a small amount of the 3-(piperidinomethyl)indole (4 mg).

Hydrolysis and Decarboxylation of 3e. Isopropylidene acetamido[(3-indolyl)methyl]malonate (100 mg) was refluxed under an atmosphere of nitrogen overnight with a mixture of 250 mg of sodium carbonate, 5 mL of water, and 1 mL of ethanol. The solution was filtered, acidified with hydrochloric acid, and evaporated in a hot water bath under reduced pressure. The residue was stirred with 2 mL of water, and after the mixture cooled, 55 mg of *N*-acetyltryptophan was collected by filtration and washing with water (73% yield, IR and melting point identical with those of an authentic sample).

Cleavage of 3f with Sodium Hydroxide Solution. Isopropylidene benzyl[(*N*-methylindol-3-yl)methyl]malonate (0.50 g) was stirred with a solution of 1.0 g of NaOH in 4 mL of water and 6 mL of ethanol at room temperature overnight. The solution was acidified with HCl and extracted with ether. The ether extract was diluted with hexane and allowed to slowly evaporate, whereupon 0.29 g of benzyl[(*N*-methylindol-3-yl)methyl]malonic acid deposited as crystals: 65% yield; mp 163–164 °C dec (with gas evolution). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.27; H, 5.69; N, 4.13.

Isopropylidene Acetamidomalonate. Isopropylidene phenyldiazomalonate[20] (1.00 g) was dissolved in a mixture of 15 mL of acetic acid and 15 mL of acetic anhydride. Palladium (30% on carbon, 0.10 g) was added and the mixture stirred under an atmosphere of hydrogen until the yellow color discharged (ca. 4 h). The mixture was filtered and evaporated, and 5 mL of ethanol was added to the residue. The product (0.50 g, 64% yield), which slowly crystallized, was removed by filtration and washed with ethanol. This compound was previously prepared[26] by the hydrogenation (PtO_2, $AcOH/Ac_2O$) of 5-(2,2-dimethyl-4,6-dioxo-

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1,3-dioxan-5-ylhydrazono)-2,2-dimethyl-1,3-dioxane-4,6-dione. Samples of the compound prepared by our method decomposed with gas evolution at various temperatures 10–25 °C above the reported melting point of 143 °C dec.[26] The IR spectrum was identical with that reported.

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Registry No. 1a, 82430-99-7; **1b**, 82431-00-3; **1c**, 82431-01-4; **2a**, 82431-67-2; **2b**, 82431-68-3; **2c**, 82431-69-4; **3a**, 82431-02-5; **3b**, 82431-03-6; **3c**, 82431-04-7; **3d**, 82431-05-8; **3e**, 82431-06-9; **3f**, 82431-07-0; **4a**, 21315-43-5; **4b**, 82431-08-1; **4c**, 52600-63-2; 4-(diethylamino)-2-butanone, 3299-38-5; [(dimethylamino)methyl]ferrocene, 1271-86-9; 1-[(dimethylamino)methyl]-2-naphthol, 5419-02-3; gramine, 87-52-5; *N*-methylgramine, 52972-61-9; isopropylidene methylmalonate, 3709-18-0; isopropylidene ethylmalonate, 17216-65-8; isopropylidene phenylmalonate, 15231-78-4; isopropylidene benzylmalonate, 3709-27-1; isopropylidene acetamidomalonate, 7270-66-8; isopropylidene benzylidenemalonate, 1214-54-6; α-methyl-δ-oxocaproic acid, 54248-02-1; α-methyl-δ-oxocaproic acid semicarbazone, 82431-09-2; α-ethyl-δ-oxocaproic acid, 58045-80-0; α-ethyl-δ-oxocaproic acid semicarbazone, 82431-10-5; α-phenyl-δ-oxocaproic acid, 5662-73-7; isopropylidene phenylmalonate diethylammonium, 82431-11-6; β-ferrocenyl-α-methylpropionic acid, 12093-96-8; β-ferracenyl-α-ethylpropionic acid, 36619-43-9; β-ferracenyl-α-phenylpropionic acid, 1272-82-8; 3-(ethoxymethyl)indole, 78440-77-4; 3-(piperidinomethyl)indole, 5355-42-0; *N*-acetyltryptophan, 1218-34-4; benzyl[(*N*-methylindol-3-yl)methyl]malonic acid, 82431-12-7; isopropylidene phenyldiazomalonate, 82431-13-8.

(Trifluoroacetyl)sulfur Pentafluoride

Ronald A. De Marco* and W. B. Fox

Naval Research Laboratory, Washington, DC 20375

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The synthesis of $SF_5C(O)$ derivatives has resulted in only one compound, $SF_5C(O)F$, reported[1] as a product from the photolysis of S_2F_{10} and $FC(O)C(O)F$. Our efforts in the synthesis of SF_5 derivatives has centered on developing potential precursors to $SF_5C(O)$ derivatives. We report herein a successful attempt to prepare these derivatives by proceeding through an intermediate, $SF_5CH(Br)CF_3$, isolated from the reaction of Br_2 with a previously reported[2] olefin, $SF_5CH{=}CF_2$. This olefin resists the addition of SF_5Cl or SF_5Br, and the photolytic addition of Br_2 leads to extensive cleavage of the SF_5 group, giving S_2F_{10}. However, the thermal reaction, which results in less cleavage, was found to give BrF addition rather than Br_2 addition (eq 1). The reaction is undirectional and consistently resulted in 55–60% yields of the BrF addition product when repeated in the same cylinder.

$$SF_5CH{=}CF_2 + Br_2 \xrightarrow{110\ °C} SF_5CH(Br)CF_3 + FCH(Br)CF_3 \quad (1)$$

(Trifluoroacetyl)sulfur pentafluoride can be obtained in high yield through the reaction of $SF_5CH(Br)CF_3$ with a slight excess of bis(fluorosulfuryl) peroxide ($S_2O_6F_2$, over a 1:2 ratio; eq 2). The low-volatility product FSO_3H, reported as a product in $S_2O_6F_2$ hydrogen abstraction reactions,[3-5] was not monitored, and the identification of bromine or bromine fluorosulfates was precluded by the workup procedure. The $SF_5C(O)CF_3$ is a low-melting (−112 to −111 °C) white solid, giving a colorless liquid having a boiling point of 15.6 °C and a vapor pressure curve of log $P(\text{mm}) = 7.698 - 1391.1/T$. The heat of vaporization for $SF_5C(O)CF_3$ is 6.37 kcal/mol and the Trouton constant of 22.0 eu indicates that no appreciable intermolecular association is present. In comparison to $CF_3C(O)CF_3$, having a boiling point of −27.4 °C, the boiling point of $SF_5C(O)CF_3$ appears to be abnormally high. However, this variation is consistent when compared to $CF_3C(O)F$ (bp −59 °C) and $SF_5C(O)F$ (estimated[1] bp −10 °C).

$$SF_5CH(Br)CF_3 + S_2O_6F_2 \rightarrow SF_5C(O)CF_3 + S_2O_5F_2 \quad (2)$$

Vorob'ev and co-workers[6] proposed $SF_5C(O)CF_3$ as an intermediate from the reaction of $CsSF_5$ and $CF_3C(O)Cl$ although only $CF_3C(O)F$ and SF_4 were isolated. We have found that $SF_5C(O)CF_3$ is a stable compound and does not decompose at room temperature in dry Pyrex glass during a 24-h period. Trace amounts of moisture cause extensive hydrolysis to $CF_3C(O)F$, SOF_2, and SiF_4, which is comparable to the hydrolytic sensitivity reported[1] for $SF_5C(O)F$. Thermal decomposition to $CF_3C(O)F$ and SF_4 is evident at 80 °C in dry Pyrex, but approximately 35% of the material was recovered after 16 h. The decomposition at 23 °C in prefluorinated stainless-steel vessels was much more rapid (65% after 1 h), while KF caused essentially complete decomposition in Pyrex glass vessels on warming a sample from −196 °C to room temperature.

The preparation of $SF_5C(O)CF_3$ with other oxidizing agents has been unsuccessful. We have found that $SF_5CH(Br)CF_3$ is resistant to oxidation by aqueous acidified permanganate (100 °C, 1 h), permanganate–acetone (23 °C, 24 h; 100 °C, 1 h), *m*-$ClC_6H_4CO_3H$ (23 °C, 48 h), NBS–aqueous diglyme (23 °C, 3 h), and 50% H_2O_2 (23 °C, 4 h; 95 °C, 16 h). In each case the $SF_5CH(Br)CF_3$ was quantitatively recovered and in most cases with decomposition of the oxidizing agent.

The synthesis of $SF_5C(O)CF_3$ allows a direct comparison of the chemistry of SF_5 carbonyl compounds with the synthetically useful $CF_3C(O)CF_3$. Our initial screening reactions indicate that typical addition reactions to the carbonyl function result in cleavage of the SF_5 group and subsequent formation of a $CF_3C(O)$ product. The reaction of HCN with $SF_5C(O)CF_3$, both with and without base, resulted in decomposition of the ketone, giving $CF_3C(O)F$, SF_4, SOF_2, and SiF_4. Attempts to add Me_2NH gave $CF_3C(O)NMe_2$, while CH_3OH led to the isolation of $CF_3CO_2CH_3$.

Experimental Section

Bis(fluorosulfuryl) peroxide ($S_2O_6F_2$)[7] and $SF_5CH{=}CF_2$[2] were prepared by the literature method, and Br_2 (J. T. Baker) and F_2 (Matheson Gas Products) were used as received. Gases and volatile liquids were handled in conventional Pyrex glass or stainless-steel vacuum lines, and quantities were determined by PVT measurements. Infrared spectra were taken on a Perkin-Elmer Model 567 and a Beckman Model IR 12 spectrometer. The Raman spectrum was recorded on a Jarrell-Ash Model 500 laser Raman spectrometer, and the UV spectrum was taken on a Cary 118 spectrometer. The NMR spectra[8] were taken on a JEOL

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(8) NMR chemical shifts follow the IUPAC convention of positive values being downfield and negative values being upfield from the standard.

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