4-Chloro-3-(ethoxycarbonyl)-6-methyl-2-pyrone (III). A 26-g (0.2-mol) sample of diisopropylethylamine is added dropwise with stirring to 40 g (0.2 mol) of 3-(ethoxycarbonyl)-4-hydroxy-6-methyl-2-pyrone in 150 g of phosphorus oxychloride. The mixture is heated at 110 °C with stirring for 5–6 h and is then concentrated as well as possible under vacuum on a rotary evaporator. The residue is extracted three times with 300 mL of ether. The ether is removed on a rotary evaporator. The residue is heated in 250 mL of refluxing petroleum ether (90–100 °C) and decanted while hot. The product (mp 85–86 °C, 32 g) crystallizes. ^{1}H NMR ($CDCl_3$): δ 1.32 (t, 3 H), 2.22 (s, 3 H), 4.30 (q, 2 H), 6.08 (s, 1 H). IR (KBr): 3080, 2980 (w), 1725 (s), 1625 (m), 1550 (m), 1320, 1240 and 1110 (m). MS, *m/e* calcd for $C_9H_9ClO_4$ 218.0159/216.0189, M^+ 218.0135 (14), 216.0163 (39), 188 (25), 175 (15), 173 (42), 172 (14), 171 (100), 162 (15), 160 (29), 147 (13), 146 (12), 144 (38), 129 (13), 118 (13), 116 (35), 51 (18).

3-(Ethoxycarbonyl)-6-methyl-4-phenoxy-2-pyrone (IV). A 10.3-g (0.11-mol) sample of phenol (p.a. grade) and 15 g (0.12 mol) of dry triethylamine in 50 mL of dichloromethane are added with cooling to 22 g (0.1 mol) of III in 100 mL of dichloromethane, and the mixture is stirred at room temperature overnight (about 12 h). Dichloromethane is removed under vacuum on a rotary evaporator, 200 mL of ether is added, and the flask is shaken vigorously. Triethylammonium chloride is removed by filtration with suction, the ether phase is concentrated under vacuum on a rotary evaporator, about 70 mL of propan-2-ol is added to the residue, and the mixture is placed in a refrigerator. The crude product is collected by filtration. Recrystallization from petroleum ether (90–100 °C) gives 19.2 g, 70% of the product. Mp 104–106 °C. ^{1}H NMR: δ 1.28 (t, 3 H), 2.20 (s, 3 H), 4.28 (q, 2 H), 5.65 (s, 1 H), 6.90–7.55 (tot, 5 H). IR (KBr): 3080 (w), 2990 (w), 1720 (s), 1645 (w), 1565 (m), 1380 (m), 1230 (m), 1070 (m). MS, *m/e* calcd for $C_{15}H_{14}O_5$ 274.0841, M^+ 274.0842 (70), 246 (25), 243 (40), 230 (20), 229 (95), 193 (33), 174 (24), 162 (25), 161 (31), 151 (28), 139 (49), 125 (23), 113 (26), 94 (95), 77 (27), 51 (100).

3-Methyl-1*H*,10*H*-pyrano[4,3-*b*][1]benzopyran-1,10-dione (V). From IV and Concentrated Sulfuric Acid. A 5.0-g sample of IV is heated for 45 min in 30 mL of concentrated sulfuric acid at 100 °C, and then it is poured on ice and filtered. Two recrystallizations from acetic acid give an almost colorless product, yield 3.0 g (72%). Mp 264–266 °C, darkens at 210–230 °C.

From IV and Polyphosphoric Acid. A 1.0-g sample of IV is heated for 30 min in 25 g of polyphosphoric acid and is then poured on ice and filtered. Recrystallization from acetic acid gives 0.52 g (63%) of V. ^{1}H NMR ($CDCl_3$ + TFA): δ 2.50 (s, 3 H), 6.68 (s, 1 H), 7.45–8.48 (tot, 4 H). IR (KBr): 3050 (w), 1720 (s), 1620 (s), 1440 (s), 1170 and 1140 (m). MS, *m/e* calcd for $C_{13}H_8O_4$ 228.0422, M^+ 228.0416 (79), 219 (17), 214 (14), 213 (100), 151 (11), 121 (45), 113 (11).

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Registry No. Ia, 110014-13-6; Ib, 110014-14-7; IIa, 58152-49-1; IIb, 92189-06-5; III, 110014-15-8; IV, 110014-16-9; V, 110014-17-0; phenol, 108-95-2.

Electrolytic Transformation of Fluoroorganic Compounds. 2.[1] Generation and Alkylation of a Stable (Trifluoromethyl)malonic Ester Enolate Using an Electrogenerated Base

Toshio Fuchigami* and Yuuki Nakagawa

Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan

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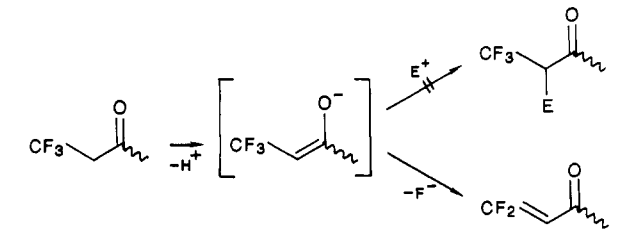
Recently, a number of new synthetic methodologies using trifluoromethyl building blocks have been developed to prepare biologically active compounds bearing a trifluoromethyl group.[2]

Although enolates are versatile building blocks, very few studies reported the use of α-CF_3 enolates because of their instability. These enolates are known to undergo extremely facile defluorination prior to trapping, as indicated in Scheme I.[3-6] The generation of α-CF_3 enolates under conditions where defluorination does not occur remains to be achieved.

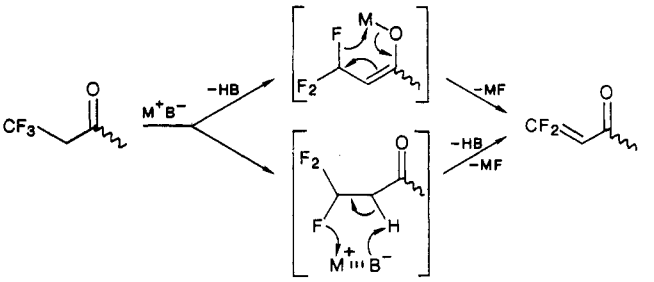
As shown in Scheme II, it is reasonable to assume that the defluorination is assisted by the countercation M^+ of the base used to generate the enolate. Indeed, countercations (M^+) with a strong affinity for the fluorine atom seem to accelerate the defluorination.[3,6] Therefore, it could be anticipated that the use of countercations with a weak affinity for the fluorine atom, such as, for example, quaternary ammonium, phosphonium, and tertiary sulfonium cations, would impede the defluorination reaction.

On the basis of these premises and our continuous interest in organic synthesis using electrogenerated bases (EGBs),[7-10] we have attempted the generation of an α-CF_3

Scheme I



Scheme II



Scheme III

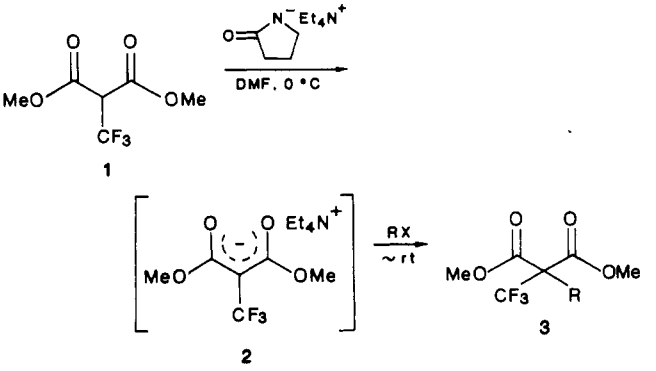


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Table I. α-Alkylation of Dimethyl (Trifluoromethyl)malonate (1)

entry	RX	product	yield,[a] %
1	MeI	**3a**	80 (60)[b]
2	*n*-BuI	**3b**	39 (0)
3	$PhCH_2Br$	**3c**	63 (45)[c]
4	p-$NO_2C_6H_4CH_2Br$	**3d**	70
5	p-$NO_2C_6H_4CH_2Cl$	**3d**	31
6	CH_2=$CHCH_2Br$	**3e**	70 (47)[c]

[a] Figures in parentheses show yields obtained by use of CsF as a base.[6] [b] Reacted at room temperature overnight. [c] Reacted with 2.5 equiv of halides at 70–75 °C.

ester enolate by using EGB with a quaternary ammonium cation.

We report herein successful generation of a stable enolate **2** derived from (trifluoromethyl)malonate **1**, which is a useful starting material for various trifluoromethylated aliphatic and heterocyclic compounds,[11] and its efficient alkylation with alkyl halides (Scheme III).

The enolate **2** was generated by treatment of **1** with electrogenerated α-pyrrolidone anion[8,12] with tetraethylammonium as the countercation. When the reaction mixture was quenched with deuteriated trifluoroacetic acid, α-deuterio **1** [65% deuterium content (determined by NMR) 30 min after the generation of **2** at 0 °C] could be recovered in 88% yield. In contrast, **1** was recovered in extremely low yield when α-pyrrolidone anion with sodium as the countercation was used as a base.

Thus, as expected, the enolate **2** with a quaternary ammonium countercation would appear stable. Most recently, Smart et al. also reported extremely stable perfluoroalkyl carbanion salts with tris(dimethylamino)sulfonium cation (TAS).[14]

As shown in Table I, the electrogenerated enolate **2** reacted smoothly with various alkyl halides to provide the corresponding alkylated malonates **3** without any defluorination in good to reasonable yields.

Ishikawa and Yokozawa reported the successful alkylation of **1** in the presence of a large excess of CsF.[6] However, as indicated in Table I, their alkylation procedure is very sensitive to the reactivity of the alkyl halides. Methyl iodide can alkylate **1** at room temperature, whereas the alkylation with slightly less reactive benzyl and allyl bromides requires higher temperatures (Table I, entries 3 and 6). Furthermore, long-chain alkyl halides such as butyl iodide do not give any alkylated products (entry 2).[15]

In contrast, our method requires milder conditions and is less dependent upon the reactivity of the alkylating reagents.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a Hitachi R-24B NMR spectrometer using $CDCl_3$ and Me_4Si as solvent and internal standard, respectively. ^{19}F NMR spectra were recorded at 60 MHz on a Hitachi R-24F NMR spectrometer using CF_3COOH as external standard. IR spectra were obtained with a Hitachi 295 infrared spectrometer. Mass spectra were obtained with a JEOL JMS-D100 mass spectrometer.

General Procedure for α-Alkylation of Dimethyl (Trifluoromethyl)malonate (1). Using an undivided cell equipped with two platinum electrodes, cathodic reduction of α-pyrrolidone (4 mmol) was carried out in 8 mL of DMF containing Et_4NOTs (1.2 M) at room temperature under a nitrogen atmosphere. After 1.2 faradays mol^{-1} of electricity was passed at 0.58 A dm^{-2} of current density,[16] an aliquot (2.4 mL) of the catholyte was added dropwise to a stirred solution of **1** (1 mmol) in 1 mL of DMF at 0 °C under a nitrogen atmosphere. After the resultant mixture was stirred for 0.5 h at 0 °C, alkyl halide (1.2 mmol) was added, and the mixture was allowed to stand overnight. After addition of water to the reaction mixture, the resulting solution was extracted repeatedly with ether. The extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of ether under reduced pressure, the residue was chromatographed on silica gel. Elution with hexane–AcOEt (8:1) provided alkylated products **3**.

The products other than **3b** and **3d** were identified by spectroscopic comparison with the authentic samples.[6]

Dimethyl butyl(trifluoromethyl)malonate (3b): ^1H NMR, δ 0.67–1.57 (m, 7 H, C_3H_7), 1.93–2.30 (m, 2 H, CH_2), 3.79 (s, 6 H, OCH_3); ^{19}F NMR, δ −11.5 (s); IR, 1772 cm^{-1} ($\nu_{C=O}$); MS, m/e 228 ($M^+ - C_2H_4$), 226 ($M^+ - C_2H_6$), 200 ($M^+ - CH_3CH_2CH$=CH_2), 159 ($M^+ - C_2H_4CF_3$). Anal. Calcd for $C_{10}H_{15}F_3O_4$: C, 46.88; H, 5.90. Found: C, 46.64; H, 5.92.

Dimethyl (*p*-nitrobenzyl)(trifluoromethyl)malonate (3d): mp 62–63 °C; ^1H NMR, δ 3.62 (s, 2 H, CH_2), 3.82 (s, 6 H, OCH_3), 7.23–8.08 (m, 4 H, C_6H_4); ^{19}F NMR, δ −12.8 (s); IR, 1775 cm^{-1} ($\nu_{C=O}$); MS, m/e 335 (M^+), 226 ($M^+ - CF_3$), 136 (p-$NO_2C_6H_4CH_2^+$). Anal. Calcd for $C_{13}H_{12}NF_3O_6$: C, 46.56; H, 3.61. Found: C, 46.30; H, 3.88.

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Registry No. **1**, 5838-00-6; **1**-α-*d*, 110315-68-9; **3a**, 86311-85-5; **3b**, 110315-66-7; **3c**, 86311-86-6; **3d**, 110315-67-8; **3e**, 86317-58-0; MeI, 74-88-4; BuI, 542-69-8; $PhCH_2Br$, 100-39-0; p-$NO_2C_6H_4CH_2Br$, 100-11-8; p-$NO_2C_6H_4CH_2Cl$, 100-14-1; H_2C=$CHCH_2Br$, 106-95-6; α-pyrrolidone, 616-45-5; α-pyrrolidone(1^-)·tetraethylammonium, 39510-70-8.

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Electrochemical Oxidation of the 2,3-Diphenylindole System. Elucidation of the Coupling Position and Analogous Behavior for the N-Substituted System

Graham T. Cheek* and Robert F. Nelson[1]

Chemistry Department, Stop 9b, U.S. Naval Academy, Annapolis, Maryland 21402

James M. Bobbitt and Paul M. Scola

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268

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In our previous investigations, we studied the electrochemical oxidation of 2,3-diphenylindole (**1**) and reported

