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Nucleophilic Substitution Reactions of *N*-Alkyldi(trifluoromethane)sulfonimides. Role of the Solvent Hexamethylphosphoric Triamide

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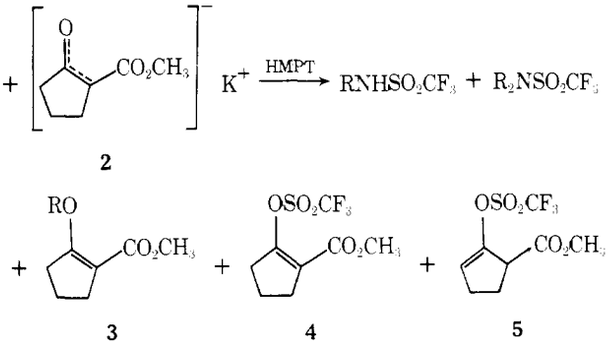
Nucleophilic substitution reactions of *N*-alkyldi(trifluoromethane)sulfonimides **1** have been reported.[1] Analogous reactions with other sulfonimides have also been investigated.[1b,2] To ascertain the synthetic utility of these reactions the alkyl group of the *N*-alkyldi(trifluoromethane)sulfonimide was varied and an assortment of nucleophiles were used.

$RN(SO_2CF_3)_2$

1a, R = n-C_6H_{13}
b, R = $C_6H_5CH_2CH_2$
c, R = $CH_3OCH_2CH_2$
d, R = $(CH_3)_2CHCH_2$
e, R = $CH_3CH_2OCOCH_2$

The results of these studies, all done using HMPT as solvent, are recorded in Tables I and II. In addition the reaction of sulfonimide **1a** with **2** afforded the products shown below. The compounds present after 233 h were n-hexyltrifluoromethanesulfonamide, *N,N*-di-n-hexyltrifluoromethanesulfonamide, **3**, **4**, and **5** in 30, 15, 39, ca. 10, and ca. 5% yield, respectively, as determined by quantitative GC analysis. Each of the products was isolated and compared with authentic material. The last two compounds were characterized by their IR, NMR, and UV spectra and elemental analysis and compared with material prepared according to the method of Stang and Dueber.[3]



These results show that nucleophilic displacements on *N*-alkyldi(trifluoromethane)sulfonimides by iodide ion to give the corresponding alkyl iodide occur in synthetically useful yields. Others have reported[1b,2b] synthetically useful displacement reactions of halide ions with *N*-alkyldi(arene)-sulfonimides.[4] Substitution reactions of sulfonimides in which alkyl iodides are presumably intermediates have also been reported.[1a,2c,f] Thus, although some reactions of sulfonimides with nucleophiles result in S–N cleavage,[2d,e,5] either by attack at sulfur or elimination,[6,7] simple nucleophilic substitution of the sulfonimide group can be achieved in many cases by a two-step sequence:[1a,2c,f] first displacement with iodide ion and then nucleophilic substitution on the alkyl iodide so obtained. An alternative to this sequence which also involves a key role for HMPT in nucleophilic substitution reactions is outlined below.

The displacements on sulfonimides were studied in HMPT because nucleophilic substitution reactions occur faster in this solvent.[8] However, it became apparent that HMPT could function as a nucleophile toward sulfonimides. Thus, NMR spectroscopy revealed that a solution of **1a** in HMPT formed salt **6a** on standing at room temperature overnight. Addition of an aqueous solution of sodium tetraphenylboron resulted in the precipitation of a crystalline salt. This salt (**6a**, X = $B(C_6H_5)_4$) was characterized spectroscopically and by elemental analysis. Similarly, **6b** was formed from **1b** in HMPT. Several other reactions illustrating the nucleophilicity of HMPT have been previously reported.[9] These salts, **6**, which are usually prepared from the corresponding alcohols,[10] are known to be useful alkylating agents.[9e,10,11] Thus reaction of **6a** with sodium cyanide in HMPT produced heptanenitrile in 72% yield, with sodiodiethyl malonate the reaction gave diethyl n-hexylmalonate in 87% yield; and with sodiomalonitrile the reaction gave the corresponding mono- and dialkylated products in 79% yield. A minor change in the procedure for reacting **1a** with sodium cyanide results in a dramatic change in the course of the reaction. If **1a** is added to sodium cyanide in HMPT rapid reaction ensues but no significant amount of heptanenitrile forms. However, if a solution of **1a** in HMPT is allowed to stand at room temperature for 18 h and then sodium cyanide is added, heptanenitrile forms in good

$ROP^+[N(CH_3)_2]_3X^-$

6a, R = n-C_6H_{13}
b, R = $C_6H_5CH_2CH_2$

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Table I. Reactions of Sulfonimides 1a–e with Nucleophiles in HMPT[a]
$RN(SO_2CF_3)_2 + M^+X^- \rightarrow RX + RNHSO_2CF_3 + R_2NSO_2CF_3$

$RN(SO_2CF_3)_2$	Registry no.	M^+X^-	RX yield, %	$RNHSO_2CF_3$ yield, %	$R_2NSO_2CF_3$ yield, %
1b	65832-17-9	KI	53	2	0
		NaCN	2	8	39
		$NaCH(CO_2CH_2CH_3)_2$[b]	11	3	25
1c	65832-18-0	KI	39	8	0
		NaCN	5	14	40
		$NaCH(CO_2CH_2CH_3)_2$	51	0	19
1d	65832-19-1	KI	76	16	0
		NaCN	2	25	19
		$NaCH(CO_2CH_2CH_3)_2$	12	10	31
1e	65832-20-4	KI	64[c]	0	0
		NaCN	10	15	0
		$NaCH(CO_2CH_2CH_3)_2$[d]	0	2	0

[a] Yields are based on quantitative GC by comparison with authentic samples. The products were identified by comparison of IR and NMR spectra and GC retention times with authentic samples. [b] Also $[CH(CO_2CH_2CH_3)_2]_2$ is formed in 16% yield. [c] Combined yield of ethyl iodoacetate and corresponding ethyl ether formed from this iodide. [d] Also $CH_3CH_2OCOCH{=}C(CO_2CH_2CH_3)_2$ is formed in 18% yield.

Table II. Reactions of *N*-*n*-Hexyltrifluoromethanesulfonimide (1a) with Nucleophiles in HMPT[a]
$RN(SO_2CF_3)_2 + M^+X^- \rightarrow RX + RNHSO_2CF_3 + R_2NSO_2CF_3$
$R = n\text{-}C_6H_{13}$

M^+X^-	RX yield, %	$RNHSO_2CF_3$ yield, %	$R_2NSO_2CF_3$ yield, %
$NaCH(COCH_3)CO_2CH_2CH_3$	ca. 30	0	
$KOCOCH_3$	0		
$NaSC_6H_5$[b]	15	23	12
NaN_3	0	52	14
$TlCH(COCH_3)_2$	46	29	25
$NaCH(CN)_2$	0	47	18
H_2O[c]	40	0	0

[a] Yields are based on quantitative GC by comparison with authentic samples. The products were identified by comparison of IR and NMR spectra and GC retention times with authentic samples. [b] Also diphenyl disulfide is formed in 50% yield. [c] Under the conditions of this reaction **6a** is formed in 40% yield and *n*-hexyl trifluoromethanesulfonate is formed in 10% yield.

yield. From the extensive work done by others on nucleophilic displacement reactions of salts **6** the formation of such salts from amines should be synthetically advantageous.

In sum nucleophilic displacement on *N*-alkyldi(trifluoromethane)sulfonimides in HMPT may involve direct displacement on carbon, direct displacement on sulfur, or displacement on carbon via solvent participation. There may well be other cases in which apparent direct displacement on carbon electrophiles in HMPT as solvent involves solvent participation. A possible example is the reduction of di(arene)sulfonimides by sodium borohydride in HMPT at 150–175 °C.[2e] We echo the warning of Anselmi et al.[9e] "that great care must be exercised in the evaluation of reactions involving catenoid transition states if carried out in HMPT".

Experimental Section

Infrared spectra were recorded on either a Perkin-Elmer Model 337 or Model 137 IR spectrophotometer. NMR spectra were measured using a 60 MHz Varian T-60 NMR spectrometer and employing tetramethylsilane as an internal standard. Ultraviolet spectra were determined using a Cary 14 UV spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E double-focusing mass spectrometer. Elemental microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were determined in open, glass capillary tubes using a Thomas-Hoover melting point apparatus or on glass cover slips using a Thermolyne microstage melting point apparatus.

Carbon tetrachloride and acetonitrile were distilled from phosphorus pentoxide, diethyl ether was distilled from sodium metal, the amines and pyridine were distilled from calcium hydride, and HMPT was distilled under vacuum from sodium metal prior to use in reactions.

Preparation of Trifluoromethanesulfonimides. The trifluoromethanesulfonimides were prepared from the corresponding sulfonamides using the method of Baumgarten et al.[5] in ethyl ether (A) or acetonitrile (B) as solvent. The trifluoromethanesulfonamides were secured using the method of Gramstad and Haszeldine,[12] but with cyclohexane used as the solvent instead of ethyl ether.

***n*-Hexyldi(trifluoromethane)sulfonimide (1a):** B (56%); bp 50 °C (0.15 mm); IR (CCl_4) 1435, 1135 cm^{-1}; NMR (CCl_4) δ 0.70–2.10 (m, 11 H, aliphatic), 3.89 (t, J = 7 Hz, 2 H, NCH_2). Anal. Calcd for $C_8H_{13}F_6NO_4S_2$: C, 26.30; H, 3.59; S, 17.55. Found: C, 26.37; H, 3.83; S, 17.58.

***n*-Hexyltrifluoromethanesulfonamide:** 79% yield; bp 83 °C (0.1 mm); IR (CCl_4) 3350, 3190, 1385, 1205 cm^{-1}; NMR (CCl_4) δ 0.80–1.75 (m, 11 H, aliphatic), 3.26 (m, 2 H, NCH_2), 5.17 (s, 1 H, NH). Anal. Calcd for $C_7H_{14}F_3NO_2S$: C, 36.05; H, 6.05; S, 13.75. Found: C, 36.06; H, 6.10; S, 13.80.

2-Phenylethyldi(trifluoromethane)sulfonimide (1b): B (61% yield); bp 84–85 °C (0.63 mm); IR (CCl_4) 1415, 1200 cm^{-1}; NMR (CCl_4) δ 3.02 (t, J = 7 Hz, 2 H, aliphatic), 4.02 (t, J = 7 Hz, 2 H, NCH_2), 7.20 (s, 5 H, aromatic). Anal. Calcd for $C_{10}H_9F_6NO_4S_2$: C, 31.17; H, 2.36; S, 16.64. Found: C, 31.20; H, 2.39; S, 16.75.

2-Phenylethyltrifluoromethanesulfonamide: (82% yield); bp 95–96 °C (0.25 mm); IR (CCl_4) 3200, 1375, 1195 cm^{-1}; NMR (CCl_4) δ 2.75 (t, J = 7 Hz, 2 H, aliphatic), 3.39 (m, 2 H, NCH_2), 5.20 (t, J = 5 Hz, 1 H), 7.12 (s, 5 H, aromatic). Anal. Calcd for $C_9H_{10}F_3NO_2S$: C, 42.69; H, 3.98; S, 12.66. Found: C, 42.78; H, 3.92; S, 12.75.

2-Methoxyethyldi(trifluoromethane)sulfonimide (1c): B (47% yield); bp 43 °C; IR (CCl_4) 1415, 1115 cm^{-1}; NMR (CCl_4) δ 3.31 (s, 3 H, CH_3O), 3.59 (t, J = 5 Hz, 2 H, OCH_2), 4.09 (t, J = 5 Hz, 2 H, NCH_2). Anal. Calcd for $C_5H_7F_6NO_5S_2$: C, 17.70; H, 2.08; S, 18.90. Found: C, 17.80; H, 2.11; S, 18.81.

2-Methoxyethyltrifluoromethanesulfonamide: 31% yield; bp 55–56 °C (0.32 mm); IR (CCl_4) 3975, 1365, 1180 cm^{-1}; NMR (CCl_4) δ 3.40 (m, 7 H), 6.00 (s, 1 H, NH). Anal. Calcd for $C_4H_8F_3NO_3S$: C, 23.19; H, 3.98; S, 15.48. Found: C, 23.14; H, 3.86; S, 15.52.

Isobutyldi(trifluoromethane)sulfonimide (1d): A (27%); bp 33–34 °C (0.55 mm); IR (CCl_4) 1420, 1120 cm^{-1}; NMR (CCl_4) δ 1.02 (d, J = 7 Hz, 6 H, Me), 2.08 (m, 1 H, CH), 3.70 (d, J = 7 Hz, 2 H, NCH_2). Anal. Calcd for $C_6H_9F_6NO_4S_2$: C, 21.37; H, 2.69; S, 19.01. Found: C, 21.43; H, 2.69; S, 19.06.

Isobutyltrifluoromethanesulfonamide: 79% yield; bp 47 °C (0.45 mm); IR (CCl_4) 3850, 3680, 1375, 1195 cm^{-1}; NMR (CCl_4) δ 0.96 (d, J = 7 Hz, 6 H, Me), 1.80 (m, 1 H, CH), 3.08 (d, J = 7 Hz, 2 H, NCH_2), 5.58 (s, 1 H, NH). Anal. Calcd for $C_5H_{10}F_3NO_2S$: C, 29.27; H, 4.91; S, 15.62. Found: C, 29.32; H, 4.87; S, 15.65.

Ethyl *N,N*-Di(trifluoromethanesulfonyl)glycinate (1e): A (34%); bp 78 °C (0.35 mm); IR (CCl_4) 1400, 1110 cm^{-1}; NMR (CCl_4) δ 1.32 (t, J = 7 Hz, 3 H, Me), 4.31 (q, J = 7 Hz, 2 H, CH_2O), 4.50 (s, 2

H, NCH_2). Anal. Calcd for $C_6H_7F_6NO_6S_2$: C, 21.50; H, 2.11. Found: C, 21.31; H, 2.34.

Ethyl *N*-trifluoromethanesulfonylglycinate: 54% yield; mp 93–94 °C; IR (CCl_4) 3950, 1195, 1140 cm^{-1}; NMR (CCl_4) δ 1.30 (t, J = 7 Hz, 3 H, Me), 3.96 (d, J = 6 Hz, 2 H, NCH_2), 4.25 (q, J = 7 Hz, 2 H, CH_2O), 5.60 (s, 1 H, NH). Anal. Calcd for $C_5H_8F_3NO_4S$: C, 25.54; H, 3.43; S, 13.63. Found: C, 25.66; H, 3.02; S, 13.72.

***N,N*-Di-*n*-hexyltrifluoromethanesulfonamide:** (23% yield); bp 109 °C (0.1 mm); IR (CCl_4) 1390, 1180; NMR (CCl_4) δ 0.80–1.80 (m, 11 H, aliphatic), 3.30 (t, J = 7 Hz, 2 H, NCH_2). Anal. Calcd for $C_{13}H_{26}F_3NO_2S$: C, 49.19; H, 8.25; S, 10.11. Found: C, 49.29; H, 8.26; S, 10.15.

Reaction of 1a with 2: A sample of **2** (0.35g, 1.9 mmol) prepared according to the method of Mayer and Alder[13] was dissolved in anhydrous HMPT (2 mL) and the solution was placed under an atmosphere of nitrogen. To this solution cooled in ice water was added a solution of **1a** (0.69 g, 1.9 mmol) dissolved in anhydrous HMPT (1.5 mL) over 1.5 h. After the addition the reaction mixture was allowed to warm to room temperature. After 233 h the reaction mixture was poured into saturated aqueous sodium bicarbonate solution (5 mL) and extracted with ethyl ether (5 × 4 mL). The combined ether extracts were washed successively with water (2 × 8 mL) and brine (2 × 8 mL) and dried over anhydrous magnesium sulfate. After removal of the solvent the residue was analyzed by quantitative GC using a 5 ft 10% Carbowax 20 M on Chromosorb W (DMCS treated) column at 120 °C. Each of the compounds in the product mixture was isolated by preparative GC and shown to be identical with authentic material. Authentic samples of **3–5** were secured as indicated below.

Authentic **3**, R = n-C_6H_{13}, was prepared from 1-bromohexane and **2** using the general method of Pond and Cargill.[14]

Preparation of 4 and 5. Following the method of Stang and Deuber[3] for the preparation of vinyl trifluoromethanesulfonates, trifluoromethanesulfonic acid anhydride[12] (3.73 g, 13.1 mmol) was rapidly added to a solution of methyl 2-ketocyclopentanecarboxylate (1.73 g, 12.0 mmol) and pyridine (1.03 g, 13.1 mmol) in carbon tetrachloride (30 mL) cooled in a −78 °C bath. The mixture was allowed to warm to room temperature and after 3 days the mixture was filtered and the solids and tars were mixed with water (40 mL) and extracted with carbon tetrachloride (5 mL). The extract and filtrate were combined, washed with water (2 × 10 mL), dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled to give a mixture of bp 53–57 °C (0.3 mm) consisting of unreacted ester and **4** and **5** (the ratio of **4** and **5** determined by GC analysis was 2.2:1). This mixture was separated by preparative GC using a 5 ft 5% SE-30 on Chromosorb W column (DMCS treated).

Vinyl trifluoromethanesulfonate (4): IR (CCl_4) 2950, 1725, 1655, 1425, 1350, 1205, 1170, 1140, 1050, 1000 cm^{-1}; NMR (CCl_4) δ 2.10 (m, 2 H), 2.78 (t, J = 7 Hz, 4 H), 3.80 (s, 3 H); UV (cyclohexane) λ_{max} (ϵ) 221 nm (12 000). Anal. Calcd for $C_8H_9F_3O_5S$: C, 35.04; H, 3.31; S, 11.69. Found: C, 35.24; H, 3.29; S, 11.62.

Vinyl trifluoromethanesulfonate (5): IR (CCl_4) 2950, 1740, 1650, 1420, 1330, 1205, 1170, 1060, 970 cm^{-1}; NMR (CCl_4) δ 2.40 (m, 5 H), 3.70 (s, 3 H), 5.80 (m, 1 H); UV (cyclohexane) λ_{max} (ϵ) 198 (4200) nm. Anal. Calcd for $C_8H_9F_3O_5S$: C, 35.04; H, 3.31; S, 11.69. Found: C, 35.19, H, 3.23; S, 11.60.

Reaction of Nucleophiles with Sulfonimides. The general procedure was to add the sulfonimide dissolved in anhydrous HMPT (1 to 2 M) to a solution of the salt (an amount equimolar to that of the sulfonimide plus 10%) dissolved in anhydrous HMPT and cooled in an ice–water bath. The solution was stirred at room temperature for 2–4 days. The mixture was then poured into water and extracted three times with ether. The combined ether extracts were washed successively with water and brine and dried over anhydrous magnesium sulfate. The solution was then analyzed by quantitative GC. In each case the product reported in Tables I and II was isolated by preparative GC and the IR and NMR spectra and GC retention times were compared with authentic samples.

Reaction of Sulfonimide 1a with HMPT. A sample of sulfonimide **1a** (0.15 g, 0.42 mmol) was dissolved in anhydrous HMPT (0.4 mL) and placed under a dry nitrogen atmosphere. An NMR spectrum of the solution was measured immediately after mixing. This spectrum showed a signal at δ 4.20 (t, J = 7 Hz, CH_2N). After 17.5 h this signal was replaced by one at δ 4.25 (m, CH_2O). After 24 h the solution was cooled in an ice–water bath and a solution of sodium tetraphenylboron (0.34 g, 1.0 mmol) dissolved in water (10 mL) was added over 5 min. A voluminous precipitate formed. After stirring with cooling for 0.5 h, the mixture was filtered to afford solid **6a**, X = $B(Ph)_4$ (0.18 g, 73%), mp 160–161 °C. After recrystallization from absolute methanol colorless needles were obtained: first crop (0.16 g), mp 169–169.5 °C; second crop (0.01 g), mp 168–168.5 °C; purified yield of 69%; IR (KBr) 3050, 2925, 1575, 1475, 1450, 1420, 1300, 1180, 1155, 1050, 1030, 995 cm^{-1}; NMR (CD_3COCD_3) δ 0.70–1.88 (m, 11 H), 2.70–2.87 (d, J = 10 Hz, 18 H), 4.23 (m, 2 H), 6.89 (m, 12 H), 7.14 (m, 8 H); spin decoupling experiments gave the following results—irradiation at δ 1.63 caused the multiplet at δ 4.23 to collapse to a doublet with J = 6 Hz. Anal. Calcd for $C_{36}H_{51}BN_3OP$: C, 74.10; H, 8.76; N, 7.23. Found: C, 73.85; H, 8.82; N, 7.30.

Reaction of Sulfonimide 1b with HMPT. A solution of sulfonimide **1b** (0.26 g, 0.67 mmol) dissolved in HMPT (0.7 mL) was stirred at room temperature for 3 days. A solution of sodium tetraphenylboron (0.38 g, 1.1 mmol) in water (10 mL) was then added over 5 min while cooling in an ice–water bath. A voluminous precipitate formed. After stirring with cooling for 0.5 h the mixture was filtered and the precipitate was washed with water to afford **6b**, X = $B(Ph)_4$ (0.22 g, 51%). Recrystallization from ethanol gave a colorless solid (although only a modest amount of solid was obtained): mp 192–194 °C; IR (KBr) 3050, 2990, 1475, 1455, 1305, 1175, 1150, 1060, 1000 cm^{-1}. Ethanol was not the best choice for a recrystallization solvent for this compound.

Reaction of 6a with Nucleophiles. These reactions were all done in a similar way. A specific example is given in detail below.

A solution of sulfonimide **1a** (0.67 mmol) dissolved in HMPT (0.6 mL) was placed under a dry nitrogen atmosphere and stirred at room temperature for 20 h. To this solution cooled in an ice–water bath was added, over 0.5 h, a solution of diethyl sodiomalonate prepared by adding diethyl malonate (0.13 g, 0.81 mmol) in HMPT (0.2 mL) to sodium hydride (0.03 g, 57% mineral oil dispersion washed with ether, 0.81 mmol) suspended in HMPT (0.2 mL) at 0 °C over 0.75 h and stirred with cooling for an additional 1 h. After stirring at room temperature for 4 days the solution was poured into water (35 mL) and extracted with ethyl ether (3 × 10 mL). The combined ether extracts were washed successively with water (10 mL) and brine (10 mL) and dried over anhydrous magnesium sulfate. The mixture was filtered, the solvent was removed, and the residual oil was analyzed by quantitative GC at 165 °C on a 5 ft 10% SE-30 on Chromosorb W (DMCS treated) column. The oil was a mixture consisting of diethyl malonate, *N,N*-di-*n*-hexyltrifluoromethanesulfonamide, and diethyl *n*-hexylmalonate (87%). Samples of each product were obtained by preparative GC and their IR and NMR spectra and GC retention times were compared with those of authentic samples.

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Registry No.—**1a**, 35920-58-2; **2**, 61114-30-5; **4**, 65832-21-5; **5**, 65832-22-6; **6a** (X = $B(Ph)_4$), 65877-70-5; **6b** (X = $B(Ph)_4$), 65898-24-0; HMPT, 680-31-9; *n*-hexyltrifluoromethanesulfonamide, 52374-19-3; 2-phenylethyltrifluoromethanesulfonamide, 36458-24-9; 2-methoxyethyltrifluoromethanesulfonamide, 65832-23-7; isobutyltrifluoromethanesulfonamide, 65832-24-8; ethyl *N*-trifluoromethanesulfonylglycinate, 65832-25-9; *N,N*-di-*n*-hexyltrifluoromethanesulfonamide, 65832-26-0.

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An Improved Synthesis of α-Methylene γ-Lactones by Electrolysis of α-Carboxy-α-phenylthiomethyl-γ-butyrolactones

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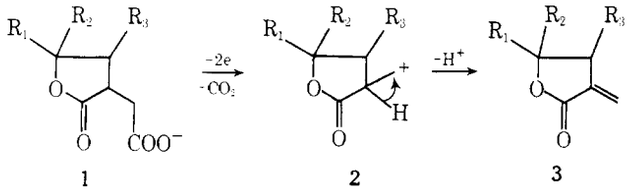
α-Methylene γ-lactone function, an important structural feature of biologically active natural products,[1] has received much attention and its synthetic attempts have been well documented in a recent publication.[2a,b] The reported methods for the preparation of α-methylene γ-lactone analogues[2] have been shown to employ largely severe conditions such as strong acids, bases, and heat in the crucial steps of the formation of the exo double bond. Recently, Ronald reported an interesting method for the preparation of *trans*-α-methylene-β,γ-tetramethylene-γ-butyrolactone from the corresponding α-carboxy-α-methylthiomethyl γ-lactone by three steps.[3] In this paper, we describe an improved one-step synthesis of α-methylene γ-lactones from α-carboxy-α-phenylthiomethyl-γ-butyrolactones, involving electrolytic elimination of both sulfenyl and carboxyl groups at room temperature.

Our preliminary challenges for the synthesis of the α-methylene γ-lactone group by electrodecarboxylation of the primary carboxylic acids **1** in pyridine–water–triethylamine (9:1:0.3 v/v)[4] at a current of 0.01–0.06 A/cm^2 (applied voltage 50–60 V) afforded **3** in 30–35% yields[5] via the intermediate **2**, indicating that the desired product **3**, which was exposed to a high applied voltage and also a high oxidation potential,[6] would undergo further anodic oxidation, causing decrease of the yield. This result suggests that the electrolysis at lower potential than that of **1** would promise a more favorable result. Besides, it is desirable that the product **3** should be removed immediately from the electrolysis solution. The advantage of allowing the anodic oxidation of the phenyl sulfide derivatives



1 2 3

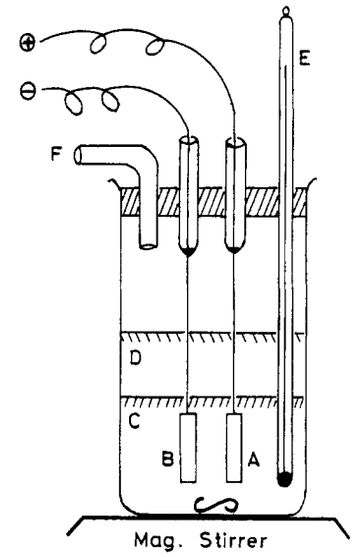
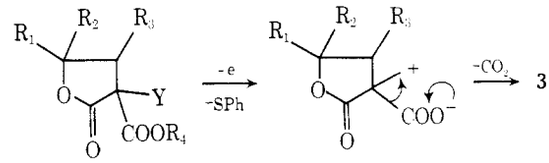


Figure 1. Electrolysis cell: (A) anode Pt plate (3 cm^2); (B) cathode Pt plate (3 cm^2); (C) aqueous phase; (D) organic phase; (E) thermometer; (F) gas lead pipe.

at the lower potential[7] rather than those of the carboxylic acids[6] led us to choose α-carboxy-α-phenylthiomethyl-γ-butyrolactone analogues **5** as a suitable compound for our synthetic purpose, since elimination of phenyl thiyl radical would be expected by one-electron oxidation on the sulfur atom of **5**,[7] affording the intermediate **7**, and subsequent loss of carbon dioxide would provide the desired **3**.



7

4, Y = H; R_4 = H
5, Y = CH_2SPh; R_4 = H
6, Y = H; R_4 = Et

Improvement of the electrolysis for the continuous extraction of the products was made by employing a two-phase system, consisting of water and organic solvents as shown in Figure 1. By this procedure, the products are expected to move from the aqueous layer to the organic layer, while the substrates are electrolyzed in the aqueous phase. Electrolysis of the ammonium salt of **5** to the desired **3** was carried out in an aqueous layer, dissolving an excess amount of triethylamine and lithium perchlorate as supporting electrolytes (Table II). The aqueous layer as depicted in Figure 1 was covered with a mixed solution of ether and benzene (3:2) as an extracting solvent. The aqueous solution was electrolyzed in an undivided beaker under a current of 16–7 mA/cm^2 with applied voltage of 3.2–3.5 V (1.3–1.5 V vs. SCE) at 38–40 °C for 4–12 h using platinum electrodes (3 cm^2). Successfully, the desired **3** was obtained only by evaporation of the extracting solvent as a sole product along with diphenyl disulfide after 40–80 Faradays/mol of electricity were passed. The electrolysis conditions of **5** as well as the yields of **3** are shown in Table II.

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were determined with a JASCO Model IRA-1 grating spectrometer. ^{1}H-NMR spectra were determined at 60 MHz with a Hitachi Model R-24 and ^{13}C-NMR spectra were determined at 25.05 MHz with a JEOL Fourier transform spectrometer, Model FX-100 with a JEC-980-16K memory computer. The chemical shift values are expressed in δ values

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