67.5 (t), 128.5 (d), 129.8 (d), 134.7 (d), 138.8 (s), 196.0 (s); IR (cm^{-1}) 3010, 2920, 2900, 1700, 1300, 1160, 700. Anal. Calcd for $C_9H_{10}SO_3$: C, 54.53; H, 5.08. Found: C, 54.76; H, 5.01.

1-Cyclohexyl-2-(phenylsulfonyl)ethanone: recrystallized yield from CCl_4 63%; mp 83-84 °C. ^1H NMR ($CDCl_3$), ppm: 1.1-2.0 (m, 10 H), 2.6 (m, 1 H), 4.3 (s, 2 H), 7.5-8.1 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 25.2 (t), 25.6 (t), 27.8 (t), 51.5 (d), 64.6 (t), 128.3 (d), 129.2 (d), 134.1 (d), 139.0 (s), 201.2 (s). IR (cm^{-1}) 3010, 2990, 2960, 1680, 1420, 1275, 1140, 1110, 730, 660. Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.43; H, 6.69; S, 12.29.

1-Phenyl-2-(phenylsulfonyl)ethanone: recrystallized yield from CCl_4 63%; mp 90-91 °C (lit.[14] mp 93-94 °C). ^1H NMR ($CDCl_3$), ppm: 4.7 (s, 2 H), 7.6-7.9 (m, 10 H). ^{13}C NMR ($CDCl_3$), ppm: 63.4 (t), 128.6 (d), 128.9 (d), 129.2 (d), 129.3 (d), 134.2 (d), 134.4 (s), 135.7 (d), 138.7 (s), 187.9 (s). IR (cm^{-1}) 3040, 3000, 2880, 1690, 1330, 1160, 755, 695. Anal. Calcd for $C_{14}H_{12}SO_3$: C, 64.60; H, 4.65. Found: C, 64.24; H, 4.77.

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Selective C-Alkylation of β-Diketones[1]

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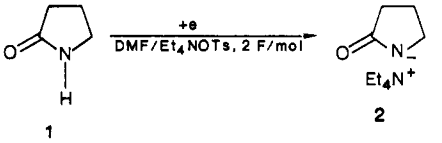
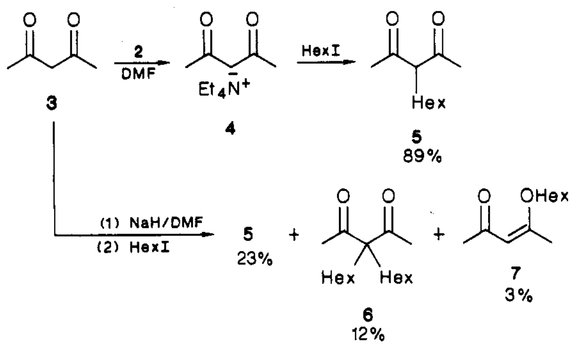
The C-monoalkylation of β-diketones are not always selectively achievable by using usual bases[2-5] since some undesirable side reactions such as O-alkylation,[6] dialkylation,[7] and cleavage of β-diketones may take place together with the C-monoalkylation. Although a method using thallium enolates has been reported,[8] it is suggested to be effective for only methylation.[9] Tetraalkylammonium enolates of β-diketones have also been shown to be useful to overcome such difficulty; however, the preparation[10] of these enolates under anhydrous conditions is not necessarily easy.

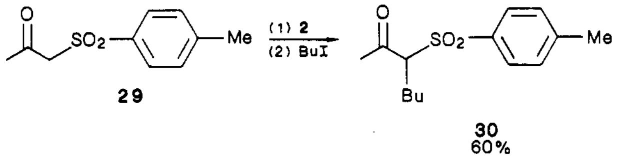
We have previously reported[11-13] that the electroreduction of 2-pyrrolidone (1) in DMF using Et_4NOTs as a supporting electrolyte yielded the corresponding anionic species 2 having tetraethylammonium cation (Et_4N^+) as a counterion.



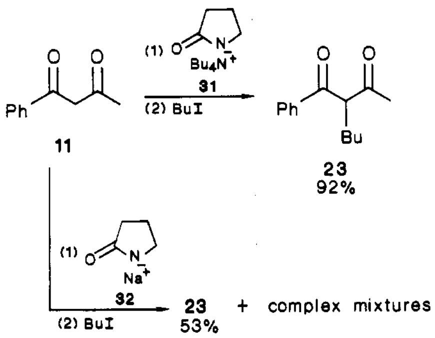
Scheme I



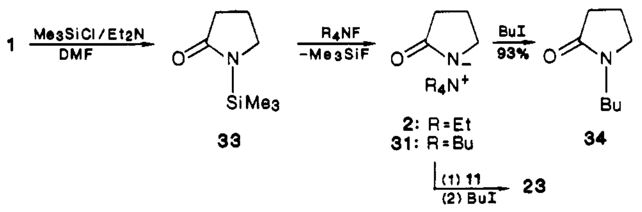
Scheme II



Scheme III



Scheme IV



In this paper, we wish to report that the reaction of 2 with β-diketones gave the corresponding tetraethylammonium enolates under anhydrous conditions and the reaction of these enolates with alkyl halides led to the selective C-monoalkylation of β-diketones.

As shown in Scheme I, the addition of a solution of 2 in DMF to a DMF solution of 2,4-pentanedione (3) at room temperature followed by the trapping of the resulting ammonium enolate 4 with hexyl iodide gave the corresponding C-alkylated product 5 in excellent yield, whereas the alkylation of 3 using NaH as a base gave a mixture of

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Table I. Alkylation of β-Diketones

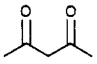
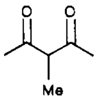
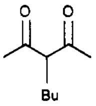
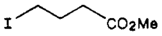
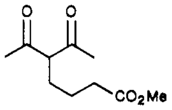
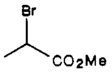
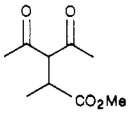
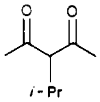
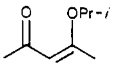
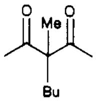
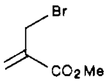
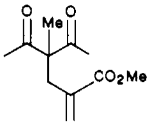
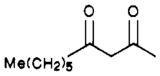
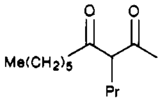
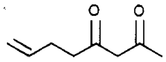
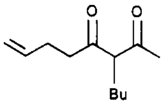
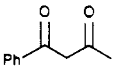
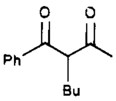
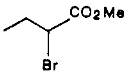
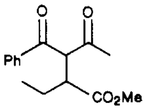
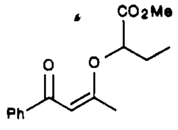
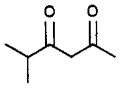
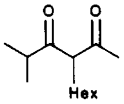
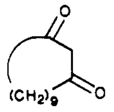
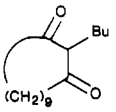
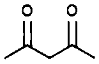
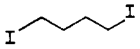
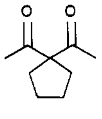
run	β-diketone	alkyl halide	product	yield, %[a]
1	 **3**	MeI	 **8**	92
2	3	BuI	 **14**	89
3	3		 **15**	78
4	3		 **16**	94
5	3	*i*-PrI	 **17**	68
			 **18**	21
6	8	BuI	 **19**	91
7	8		 **20**	93
8	 **9**	PrI	 **21**	89
9	 **10**	BuI	 **22**	84
10	 **11**	BuI	 **23**	91
11	11		 **24**	70

Table I (Continued)

run	β-diketone	alkyl halide	product	yield, %[a]
			 25	13
12	 12	HexI	 26	90
13	 13	BuI	 27	87
14	 3		 28	64

[a] Isolated yields.

diketones 5, 6, and O-alkylated product 7 in rather poor total yields.

As the other examples are summarized in Table I, this new method is applicable to the selective C-monoalkylation of a variety of β-diketones (3, 9–13). Although the alkylation of β-diketones 3 and 11 with secondary alkyl halides (runs 5 and 11) gave the corresponding O-alkylated products 18 and 25 in some extents as the side products, the other side reactions such as dialkylation and cleavage of β-diketones were not observed. The introduction of two different alkyl groups into β-diketone 3 has also been found to be possible in two steps. For examples, the methylation of 3 to 8 (run 1, Table I) and further alkylation of 8 (runs 6 and 7, Table I) using 2 as a base afforded the corresponding β-diketones 19 and 20 in high yields. In addition, it seems interesting that the reaction of 3 with a dihalide (run 14) using 3 equiv of 2 led to the formation of a cyclic β-diketone 29 in one step.

Moreover, this new method is also applicable to the C-alkylation of β-keto sulfone 29 to 30 in good yield (Scheme II), while the selective alkylation of 29 using usual bases is not always easy.

In these reactions, the fact that the countercation of 2-pyrrolidone anion is tetraalkylammonium ion is important to get the high selectivity. As shown in Scheme III, for example, the alkylation of acetylacetophenone (11) using 2-pyrrolidone anion 31 prepared by the electroreduction of 1 in DMF in the presence of Bu_4NBF_4 gave the corresponding C-alkylated product 23 in good yield, whereas the use of chemically prepared sodium salt 32 was not effective to the selective C-monoalkylation of 11.

In the next place, we have investigated the preparation of 2 and 31 by the conventional chemical method to confirm that 2 and 31 are formed indeed by electroreduction of 1 in the presence of Et_4NOTs or Bu_4NBF_4 in DMF and they are really effective to accomplish the selective alkylation. The preparation of 2 and 31 by the chemical method (Scheme IV) was attained by the transformation of 1 to *N*-(trimethylsilyl)pyrrolidone (33) followed by the treatment of 33 with Et_4NF or Bu_4NF in DMF. The formation of pyrrolidone anion by this chemical method was proved by the fact that the addition of BuI into the DMF solution gave *N*-butylpyrrolidone (34) in 93% yield. It is also highly reasonable that the countercation of this chemically prepared pyrrolidone anion is tetraalkylammonium ion. The fact that alkylation of 11 using the chemically prepared 2 and 31 selectively yielded 23 in 90% and 92% yields, respectively, strongly suggests that the pyrrolidone anion having tetraalkylammonium cation as the countercation is really effective for the selective alkylation and the electroreduction of 1 in the presence of tetraalkylammonium salts really yields 2 and 31 which are the same as those chemically prepared.

The chemical method is, however, more inconvenient than the electroreductive method from the standpoint of organic synthesis.

Experimental Section

Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. Proton nuclear magnetic resonance spectra (^1H NMR) were measured on a Varian Associates EM-390 spectrometer with chemical shifts given in parts per million (δ) downfield from tetramethylsilane as an internal standard. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University.

Materials. 2,4-Pentanedione 3 was commercially available. β-Diketones 9–13[14,15] and β-keto sulfone 29[16] were prepared by the known methods.

Preparation of a DMF Solution of 2. A solution of 2-pyrrolidone 1 (15 mmol) in 20 mL of DMF containing Et_4NOTs (15 mmol) as a supporting electrolyte was put into a cathodic chamber of an electrolysis cell equipped with a platinum electrode (2 × 2 cm) and a glass filter diaphragm. The anodic solution was 15 mL of DMF containing Et_4NOTs (10 mmol). The preparation of a DMF solution of 2 was accomplished by passing 2 F/mol of

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[15] Eistert, B.; Schank, K. *Chem. Ber.* **1966**, *99*, 1414.

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electricity through the cell at room temperature under the conditions of constant current[17] (0.2 A).

Alkylation of β-Diketones. Into a solution of a β-diketone (10 mmol) in 5 mL of DMF was added a solution of **2** (15 mmol), and the solution was stirred for 15 min at room temperature. To this solution was added 15 mmol of an alkyl halide, and the reaction mixture was stirred for 30 min at room temperature. The mixture was then poured into an aqueous solution (100 mL) of NH_4Cl and extracted with ether. The alkylation of **3** to form **28** was accomplished by the addition of **3** (10 mmol) into a solution of **2** (30 mmol) in DMF (40 mL) followed by the addition of 1,4-diiodobutane (15 mmol). All the products were isolated by silica gel column with a mixed solvent of hexane and ethyl acetate (10:1) and identified by spectroscopic comparison with the authentic samples (**5–8**, **14**, **17**, and **18**) prepared by the known methods[6,7] and/or elemental and spectroscopic analyses (**15**, **16**, and **19–28**).

15: IR (neat) 1740, 1700, 1200 cm^{-1}; NMR ($CDCl_3$) δ 1.15–2.00 (m, 4 H), 2.13 (s, 6 H), 2.00–2.60 (m, 2 H), 3.40–3.65 (m, 1 H), 3.65 (s, 3 H). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.69; H, 8.11.

16: IR (neat) 1740, 1700, 1115 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (d, 3 H, *J* = 9.5 Hz), 2.25 (s, 6 H), 3.13–3.50 (m, 1 H), 3.67 (s, 3 H), 4.05 (d, 1 H, *J* = 10.5 Hz). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.98; H, 7.42.

19: IR (neat) 1720, 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.67–1.10 (m, 3 H, *J* = 6 Hz), 0.90–2.10 (m, 6 H), 1.35 (s, 3 H), 2.10 (s, 6 H). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.22; H, 10.75.

20: IR (neat) 1720, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (s, 3 H), 2.16 (s, 6 H), 2.97 (s, 2 H), 3.73 (s, 3 H), 5.59 (s, 1 H), 6.26 (s, 1 H). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.01; H, 7.48.

21: IR (neat) 1735, 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.77–1.10 (m, 6 H), 1.10–2.00 (m, 12 H), 2.17 (s, 3 H), 2.48 (t, 2 H, *J* = 5 Hz), 3.64 (t, 1 H, *J* = 5 Hz). Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.32; H, 11.26.

22: IR (neat) 3020, 1735, 1705, 1000, 920 cm^{-1}; NMR ($CDCl_3$) δ 0.74–1.10 (m, 3 H), 1.10–2.00 (m, 6 H), 2.07 (s, 3 H), 2.00–2.60 (m, 4 H), 3.47 (t, 1 H, *J* = 6 Hz), 4.76–5.20 (m, 2 H), 5.20–6.20 (m, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.19; H, 10.20.

23: IR (neat) 1720, 1675, 1180, 1000 cm^{-1}; NMR ($CDCl_3$) δ 0.60–1.10 (m, 3 H), 1.00–1.60 (m, 4 H), 1.60–2.05 (m, 2 H), 2.17 (s, 3 H), 4.48 (t, 1 H, *J* = 7 Hz), 7.30–8.40 (m, 5 H). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.22; H, 8.13.

24: IR (neat) 1730, 1675, 1170, 770, 695 cm^{-1}; NMR ($CDCl_3$) δ 0.82 and 0.93 (t, 3 H, *J* = 7.5 Hz), 1.10–1.93 (m, 2 H), 2.10 and 2.13 (s, 3 H), 3.27–3.60 (m, 1 H), 3.60 and 3.70 (s, 3 H), 4.90 and 5.05 (d, 1 H, *J* = 12 Hz), 7.30–8.20 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.70; H, 6.75.

25: IR (neat) 1750, 1660, 1190, 880 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (t, 3 H, *J* = 7.5 Hz), 1.73–2.20 (m, 2 H), 2.45 (s, 3 H), 3.70 (s, 3 H), 4.53 (t, 1 H, *J* = 7.5 Hz), 6.03 (s, 1 H), 7.30–7.90 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.52; H, 7.18.

26: IR (neat) 1735, 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.80–2.00 (m, 19 H), 2.15 (s, 3 H), 2.40–3.10 (m, 1 H), 3.80 (t, 1 H, *J* = 6.4 Hz). Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.25; H, 11.52.

27: IR (neat) 1690 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (t, 3 H, *J* = Hz), 0.90–2.10 (m, 18 H), 2.30 (t, 4 H, *J* = 6 Hz), 3.63 (t, 1 H, *J* = 6.5 Hz). Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.99; H, 10.92.

28: IR (neat) 1720, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.45–1.75 (m, 4 H), 1.80–2.35 (m, 4 H), 2.10 (s, 6 H). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.95; H, 9.00.

Alkylation of 3 Using NaH. A solution of **3** (10 mmol) in DMF (10 mL) was added into a DMF (10 mL) suspension of NaH (12 mmol), and the mixture was stirred for 1 h at room temperature. Into this solution was added hexyl iodide, and the reaction mixture was stirred for 1 h at room temperature. After the usual workup, the product **5–7** were isolated by silica gel column (hexane/EtOAc = 10:1) and identified by the spectroscopic comparison with authentic samples (**5–7**) prepared by the usual method.[6]

Alkylation of β-Keto Sulfone 29. The alkylation of **29** yielding **30** was carried out under the similar reaction conditions to those for β-diketones, and the structure of **30** was determined by spectroscopic and elemental analyses.

30: IR (neat) 3050, 1725, 1320, 1150, 820 cm^{-1}; NMR ($CDCl_3$) δ 0.70–1.09 (m, 3 H), 1.10–2.05 (m, 6 H), 2.40 (s, 3 H), 2.50 (s, 3 H), 3.95 (dd, 1 H, *J* = 6 and 8 Hz), 7.35–7.95 (m, 4 H). Anal. Calcd for $C_{14}H_{20}SO_3$: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.41; H, 7.69; S, 11.88.

Alkylation of 11 Using 31 or 32 as a Base. Preparation of a DMF solutin of **31** was carried out under the similar reaction conditions to the electroreductive preparation of **2** using Bu_4NBF_4 as a supporting electrolyte.

Preparation of a DMF solution of **32** was accomplished by the addition of **1** (12 mmol) into a suspension of NaH (12 mmol) in 20 mL of DMF at room temperature.

The alkylation of **11** giving **23** using these bases (**31** or **32**) was carried out similarly to those described above.

Preparation of 2 and 31 by Chemical Method. (Trimethylsilyl)pyrrolidone **33** was prepared by the reaction of **1** with trimethylsilyl chloride in the presence of triethylamine.[18] Into a solution of Et_4NF or Bu_4NF (10 mmol) in 15 mL of DMF was added a solution of **33** (10 mmol) in 5 mL of DMF at room temperature, trimethylsilyl fluoride was removed (89.5% of the theoretical amount) under reduced pressure (20 mmHg). the addition of BuI (10 mmol) into the thus prepared solution followed by the usual workup gave **34**[19] in 93% yield. This solution of **2** or **31** was used for the alkylation of **11** under similar reaction conditions described above.

Registry No. **2**, 39510-70-8; **3**, 123-54-6; **5**, 64122-32-3; **6**, 112114-41-7; **7**, 112114-42-8; **8**, 815-57-6; **9**, 13329-78-7; **10**, 10151-22-1; **11**, 93-91-4; **12**, 7307-03-1; **13**, 6498-49-3; **14**, 1540-36-9; **15**, 112114-43-9; **16**, 112114-44-0; **17**, 1540-38-1; **18**, 1540-25-6; **19**, 112114-45-1; **20**, 112114-46-2; **21**, 112114-47-3; **22**, 112114-48-4; **23**, 10225-39-5; **24**, 112114-49-5; **25**, 112114-50-8; **26**, 112114-51-9; **27**, 112114-52-0; **28**, 69994-30-5; **29**, 5366-49-4; **30**, 112114-53-1; **31**, 39510-72-0; **32**, 3195-95-7; **33**, 14468-90-7; **34**, 3470-98-2; BuI, 542-69-8; $BrCH_2C(=CH_2)CO_2Me$, 4224-69-5; PrI, 107-08-4; $H_3CCH_2CHBrCO_2Me$, 3196-15-4; $H_3C(CH_2)_5I$, 638-45-9; $I(CH_2)_4I$, 628-21-7; MeI, 74-88-4; $I(CH_2)_3CO_2Me$, 14273-85-9; $H_3CCHBrCO_2Me$, 5445-17-0; *i*-PrI, 75-30-9.

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(17) Cathode potential was −2.2 to −2.4 V vs SCE.

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