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A New Method for the Preparation of Michael Adducts and Cyclic Enones Using Lithium Chloride–Hexamethylphosphoramide System[1)]

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A new procedure using lithium chloride in hexamethylphosphoramide was found to be useful for the synthesis of Michael-type adducts and cyclic enones. Selectivity for the two products could be controlled by altering the reaction temperature employed. The urea-type solvents were also examined instead of hexamethylphosphoramide.

Key words lithium chloride; hexamethylphosphoramide; decarboxylation; [2C+4C] annulation; enone; Michael-type reaction

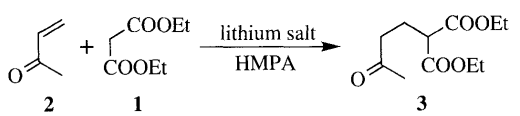
Carbon–carbon bond formation reactions are most important in synthetic organic chemistry, and Michael-type addition and Robinson annulation have been very frequently used. The latter is often employed for effecting six-membered ring formation by condensation of cyclohexanones with methyl vinyl ketone or its equivalents.[2)] In general, [2C+4C] annulation reactions giving cyclic enones are carried out under basic or acidic conditions, but neutral conditions for Michael-type additions have been proposed in recent years, because the addition under the conventional drastic conditions (basic or acidic) is accompanied by side reactions that decrease the yields of the desired products.[3)] Nevertheless, few studies on cyclic enone formation reactions have appeared in the literature. In this paper, we report a new procedure for both Michael-type reaction and decarboxylative cyclic enone synthesis using a lithium chloride–aprotic solvent system.

Lithium salts coupled with a solvent are efficient reagents for various reactions, such as the Michael-type reaction, decarboxylation, alkylation, *etc.*[3e,4)] In the course of our investigation on annulation reactions, we examined the Michael-type reaction using malonic acid diethyl ester (**1**) and 3-buten-2-one (**2**) in the presence of several lithium salts [lithium fluoride (LiF), lithium chloride (LiCl), lithium bromide (LiBr), lithium iodide (LiI)] in hexamethylphosphoramide (HMPA) at 90 °C to find the best conditions. The reactions controlled by LiCl, LiBr, and LiI gave 2-(3-oxobutyl)malonic acid diethyl ester (**3**) as shown in Table 1. The results indicated that LiCl (entry 3) was the best catalyst among these lithium salts for the Michael-type reaction. Various pairs of Michael donors [malonic acid diethyl ester (**1**), 2-oxocyclopentanecarboxylic acid ethyl ester (**4**), 2-oxocyclohexanecarboxylic acid ethyl ester (**5**), 2-oxocycloheptanecarboxylic acid ethyl ester (**6**), 3-oxobutyric acid ethyl ester (**7**), 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**8**), 3-oxo-3-phenylpropionic acid ethyl ester (**9**), ethanethiol (**10**), and benzenethiol (**11**)] and acceptors [3-buten-2-one (**2**), 1-penten-3-one (**12**), 2-cyclohexen-1-one (**13**), 4-phenyl-3-buten-2-one (**14**), and 1,4-benzoquinone (**15**)] were treated with LiCl in HMPA at 25—120 °C to confirm the utility of this procedure. The resulting adducts (**3**, **16**—**32**) and their yields are shown in Table 2. The yields of the adducts were moderate to good except for those of 2,3′-dioxobicyclohexyl-1-carboxylic acid ethyl ester (**26**) and 3-(ethylthio)cyclohexanone (**29**). The steric hindrance between the acceptor (**13**) and the donor (**5**) resulted in a low yield of **26** at 90 °C. A similar compound, 2-oxo-1-(3-oxocyclohexyl)cyclopentanecarboxylic acid ethyl ester (**25**) was obtained in a better yield at 120 °C. The reaction of ethanethiol (**10**) and 2-cyclohexen-1-one (**13**) was performed under lower temperature at 25 °C due to the low boiling point of **10**, affording **29** in low yield.

It was found that some of these pairs gave cyclic enones directly at higher temperature. Heating of the reaction mixture at 160 °C gave the cyclic compounds (**33**—**38**) from the pairs using the β-ketoesters (**4**—**7**, **9**) as the Michael donors and the acyclic α,β-unsaturated ketones (**2**, **12**) as the Michael acceptors as shown in Table 3. These enones were the results of both decarboxylation and intramolecular aldol condensation of the Michael adducts. It should be emphasized that the overall yield of compound **34** based on **2** is the best so far reported.[5)] The reaction of compound **8** with 3-buten-2-one (**2**) gave no enone compound owing to the inactivity of the conjugated ketone of the Michael adduct. The low yield of compound **37** could be attributed to the similar character of the ketone group.

The utility of *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU; IUPAC name: 1,3-dimethyltetrahydro-2(1*H*)-pyrimidinone) (**39**) has been reported as a cosolvent for highly reactive nucleophiles. It has been shown that the urea (**39**) has similar effects to HMPA in diverse types of reactions.[6)] In this study, DMPU (**39**) and its analogs, 1,3-dimethyl-2-imidazolidinone (DMI) (**40**) and 1,1,3,3-tetramethylurea (TMU) (**41**), were applied as solvents in several reactions instead of HMPA (Tables 2 and 3). The

Table 1. Yields of 2-(3-Oxobutyl)malonic Acid Diethyl Ester (**3**) in the Reaction Promoted by Lithium Salt in HMPA



2 **1** **3**

Entry	Lithium salt	Yield (%)
1	LiF	0
2	LiCl	84
3	LiBr	81
4	LiI	50

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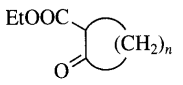
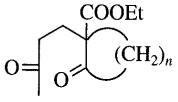
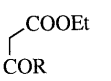
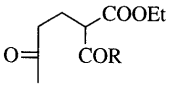
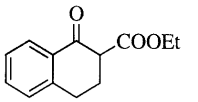
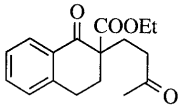
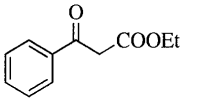
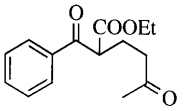
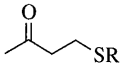
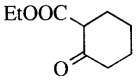
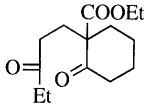
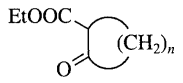
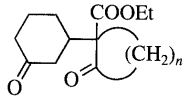
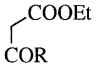
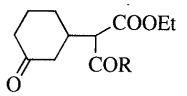
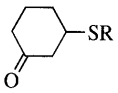
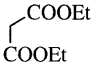
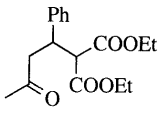
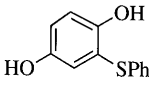
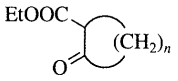
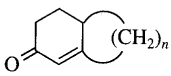
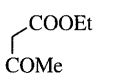
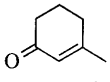
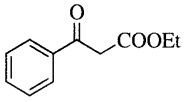
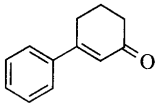
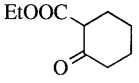
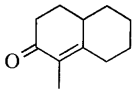
Table 2. LiCl-Promoted Michael Reaction in HMPA

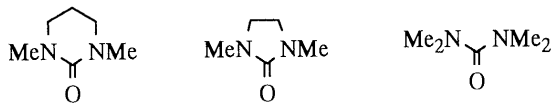
Donor		Acceptor	Product		Temp. (°C)	Time (h)	Yield (%)
	**4** ($n=3$)	**2**		**16** ($n=3$)	90	1	83
	5 ($n=4$)	**2**		**17** ($n=4$)	90	2	90 (86[b])
	6 ($n=5$)	**2**		**18** ($n=5$)	90	2	65
	**1** (R=OEt)	**2**		**3** (R=OEt)	90	1	84 (85,[a] 72,[b] 66[c])
	7 (R=Me)	**2**		**19** (R=Me)	90	1	76 (76,[a] 75,[b] 80[c])
	**8**	**2**		**20**	90	2	99
	**9**	**2**		**21**	90	1	92
RSH	**10** (R=Et)	**2**		**22** (R=Et)	25	18	66
	11 (R=Ph)	**2**		**23** (R=Ph)	90	1	91
	**5**	**12**		**24**	90	1	86
	**4** ($n=3$)	**13**		**25** ($n=3$)	120	2	60
	5 ($n=4$)	**13**		**26** ($n=4$)	90	2	29
	**1** (R=OEt)	**13**		**27** (R=OEt)	90	3	82
	7 (R=Me)	**13**		**28** (R=Me)	90	7	62
RSH	**10** (R=Et)	**13**		**29** (R=Et)	25	18	43
	11 (R=Ph)	**13**		**30** (R=Ph)	90	1	80
	**1**	**14**		**31**	90	8	60
PhSH	**11**	**15**		**32**	25	18	77

a) In DMPU. *b*) In DMI. *c*) In TMU.

Table 3. LiCl-Promoted Cyclic Enone Synthesis in HMPA

Donor		Acceptor	Product		Temp. (°C)	Time (h)	Yield (%)
	**4** ($n=3$)	**2**		**33** ($n=3$)	160	2	65
	5 ($n=4$)	**2**		**34** ($n=4$)	160	2	77 (85[b])
	6 ($n=5$)	**2**		**35** ($n=5$)	160	2	50
	**7**	**2**		**36**	160	2	73 (56,[a] 52,[b] 55[c])
	**9**	**2**		**37**	160	1	21
	**5**	**12**		**38**	160	6	66

a) In DMPU. *b*) In DMI. *c*) In TMU.



39 40 41

Chart 1

yields of the products were similar to those of the reactions in the case of HMPA except in the case of compound **3** using TMU and compound **36**.

In conclusion, LiCl in HMPA is one of the best mediators to obtain Michael adducts in terms of both practical operation and yield. Cyclic enones can be obtained from the same reaction system in one pot using β-ketoester and α,β-unsaturated acyclic ketones. The selectivity for the products, the Michael adducts or the cyclic enones, depends on the reaction temperature employed. Several ureas, such as DMPU, DMI, and TMU, can be used as solvents in this reaction system as alternatives to HMPA.

Experimental

IR spectra were recorded on a Hitachi 270-30 infrared spectrometer. ^{1}H-NMR spectra were recorded with a JEOL JNM-PMX 60si spectrometer (60 MHz) using tetramethylsilane as an internal standard. Melting points were measured on a Yanaco model MP micro melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX300 mass spectrometer. LiCl and other lithium salts were dried at 150 °C under reduced pressure for 15 min. All organic extracts were dried over anhydrous $MgSO_4$.

2-(3-Oxobutyl)malonic Acid Diethyl Ester (3)[3a,7] Malonic acid diethyl ester (**1**) (10 mmol) was added to a mixture of LiCl (10 mmol) and HMPA (5 ml) at room temperature. The reaction mixture was stirred for 15 min, then 3-buten-2-one (**2**) (10 mmol) was added. Stirring was continued for 1 h at 90 °C. The reaction mixture was poured into water and the product was extracted with Et_2O. The organic extract was washed with brine, dried, and evaporated. The residual oil was distilled under reduced pressure to give **3** (1.93 g, 84%) as a colorless oil. The same reaction was performed using LiF, LiBr, and LiI instead of LiCl, and the yields of **3** were 0%, 81%, and 50%, respectively. bp 135—140 °C (2 mmHg). IR (neat): 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (6H, t, J=7 Hz, $-COOCH_2C\underline{H}_3 \times 2$), 2.13 (3H, s, $-COCH_3$), 2.0—2.73 (4H, m, $CH_3COC\underline{H}_2C\underline{H}_2-$), 3.40 (1H, t, J=6 Hz, $-C\underline{H}(COOCH_2CH_3)_2$), 4.17 (4H, q, J=7 Hz, $-COOC\underline{H}_2CH_3 \times 2$). HRMS: Calcd for $C_{11}H_{18}O_5$ (230.1155). Found: m/z 230.1158 (M^+). The same compound **3** was obtained when LiCl was used in DMPU, DMI, and TMU instead of HMPA. The yields of **3** were 85%, 72%, and 66%, respectively.

2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylic Acid Ethyl Ester (16)[8] Compound **16** was obtained from 2-oxocyclopentanecarboxylic acid ethyl ester (**4**) and **2** in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 83% yield, a colorless oil, bp 137—139 °C (2 mmHg). IR (neat): 1752, 1726 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.22 (3H, t, J=6 Hz, $-COOCH_2C\underline{H}_3$), 1.7—2.7 (m), 2.10 (3H, s, $-COCH_3$), 4.13 (2H, q, J=6 Hz, $-COOC\underline{H}_2CH_3$). HRMS: Calcd for $C_{12}H_{18}O_4$ (226.1205). Found: m/z 226.118 (M^+).

2-Oxo-1-(3-oxobutyl)cyclohexanecarboxylic Acid Ethyl Ester (17)[9] Compound **17** was obtained from 2-oxocyclohexanecarboxylic acid ethyl ester (**5**) and **2** in the same manner as described for **3** using LiCl/HMPA for 2 h at 90 °C, 90% yield, a colorless oil, bp 142—145 °C (2 mmHg). IR (neat): 1725, 1708 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23 (3H, t, J=6 Hz, $-CH_2C\underline{H}_3$), 1.5—2.7 (m), 2.11 (3H, s, $-COCH_3$), 4.20 (2H, q, J=6 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{13}H_{20}O_4$ (240.1362). Found: m/z 240.1353 (M^+). The same compound **17** was obtained in 86% yield by using DMPU instead of HMPA.

2-Oxo-1-(3-oxobutyl)cycloheptanecarboxylic Acid Ethyl Ester (18)[10] Compound **18** was obtained from 2-oxocycloheptanecarboxylic acid ethyl ester (**6**) and **2** in the same manner as described for **3** using LiCl/HMPA for 2 h at 90 °C, 65% yield, a colorless oil, bp 135—140 °C (1 mmHg). IR (neat): 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.28 (3H, t, $-CH_2C\underline{H}_3$), 1.40—2.8 (m), 2.13 (3H, s, $-COCH_3$), 4.18 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{14}H_{22}O_4$ (254.1518). Found: m/z 254.1490 (M^+).

2-Acetyl-5-oxohexanoic Acid Ethyl Ester (19)[7b] Compound **19** was obtained from 3-oxobutyric acid ethyl ester (**7**) and **2** in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 76% yield, a colorless oil, bp 115—118 °C (3 mmHg). IR (neat): 1735, 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, t, J=6 Hz, $-CH_2C\underline{H}_3$), 1.87–2.70 (m), 2.13 (3H, s, $-COCH_3$), 2.23 (3H, s, $-COC\underline{H}_3$), 3.50 (1H, t, J=6 Hz, $-C\underline{H}COOCH_2CH_3$), 4.20 (2H, q, J=6 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{10}H_{16}O_4$ (200.1049). Found: m/z 200.1054 (M^+). The same compound **19** was obtained when LiCl was used in DMPU, DMI, and TMU instead of HMPA. The yields of **19** were 76%, 75%, and 80%, respectively.

1-Oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylic Acid Ethyl Ester (20) Compound **20** was obtained from 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**8**) and **2** in the same manner as described for **3** using LiCl/HMPA for 2 h at 90 °C, 99% yield, a colorless oil, bp 206—212 °C (2 mmHg). IR (neat): 1724, 1692, 1604 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 2.0—3.0 (m), 2.15 (3H, s, $-COCH_3$), 4.19 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$), 7.03—8.10 (4H, m, aromatic protons). HRMS: Calcd for $C_{17}H_{20}O_4$ (288.1362). Found: m/z 288.1355 (M^+). *Anal.* Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.53; H, 7.00.

2-Benzoyl-5-oxohexanoic Acid Ethyl Ester (21)[7b] Compound **21** was obtained from 3-oxo-3-phenylpropionic acid ethyl ester (**9**) and **2** in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 92% yield, a colorless oil, bp 201—203 °C (1 mmHg). IR (neat): 1740, 1720, 1690, 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 2.0—2.8 (m), 2.18 (3H, s, $-COCH_3$), 4.10 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$), 4.40 (1H, t, J=6 Hz, $-C\underline{H}COCH_3$), 7.17—8.20 (5H, m, aromatic protons). HRMS: Calcd for $C_{15}H_{18}O_4$ (262.1205). Found: m/z 262.1201 (M^+).

4-(Ethylthio)butan-2-one (22)[11] Compound **22** was obtained from ethanethiol (**10**) and **2** in the same manner as described for **3** using LiCl/HMPA for 18 h at 25 °C, 66% yield, a colorless oil, bp 118—120 °C (17 mmHg). IR (neat): 1708 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (3H, t, J=7 Hz, $-SCH_2C\underline{H}_3$), 2.07 (3H, s, $-COCH_3$) 2.55 (2H, q, J=7 Hz, $-SC\underline{H}_2CH_3$). 2.70 (4H, br s, $-CH_2CH_2-$). HRMS: Calcd for $C_6H_{12}OS$ (132.0609). Found: m/z 132.0609 (M^+).

4-(Phenylthio)butan-2-one (23)[12] Compound **23** was obtained from benzenethiol (**11**) and **2** in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 91% yield, a colorless oil, bp 173—175 °C (17 mmHg). IR (neat): 1715, 1590 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.07 (3H, s, $-COCH_3$), 2.56—3.30 (4H, m, $-CH_2CH_2-$), 7.27 (5H, s, aromatic protons). HRMS: Calcd for $C_{10}H_{12}OS$ (180.0609). Found: m/z 180.0612 (M^+).

2-Oxo-1-(3-oxopentyl)cyclohexanecarboxylic Acid Ethyl Ester (24) Compound **24** was obtained from 2-oxocyclohexanecarboxylic acid ethyl ester (**5**) and pent-1-en-3-one (**12**) in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 86% yield, a pale yellow oil, bp 146—149 °C (3 mmHg). IR (neat): 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.02 (3H, t, J=7 Hz, $-COCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $-OCH_2C\underline{H}_3$), 1.3—3.0 (m), 4.15 (2H, q, J=7 Hz, $-OC\underline{H}_2CH_3$). MS m/z: 254 (M^+). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.82; H, 8.60.

2-Oxo-1-(3-oxocyclohexyl)cyclopentanecarboxylic Acid Ethyl Ester (25) Compound **25** was obtained from 2-oxocyclopentanecarboxylic acid ethyl ester (**4**) and cyclohex-2-enone (**13**) in the same manner as described for **3** using LiCl/HMPA for 2 h at 120 °C, 60% yield, a pale yellow oil, bp 166—168 °C (2 mmHg). IR (neat): 1740, 1714 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 1.50—2.83 (15H, m), 4.14 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{14}H_{20}O_4$ (252.1362). Found: m/z 252.1372 (M^+). *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.51; H, 7.85.

2,3′-Dioxobicyclohexyl-1-carboxylic Acid Ethyl Ester (26) Compound **26** was obtained from 2-oxocyclohexanecarboxylic acid ethyl ester (**5**) and **13** in the same manner as described for **3** using LiCl/HMPA for 2 h at 90 °C, 29% yield, a pale yellow oil, bp 173—176 °C (2 mmHg). IR (neat): 1740, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 1.2—2.2 (m), 4.21 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{15}H_{22}O_4$ (266.1513). Found: m/z 266.1513 (M^+). *Anal.* Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.35; H, 8.06.

2-(3-Oxocyclohexyl)malonic Acid Diethyl Ester (27)[13] Compound **27** was obtained from **1** and **13** in the same manner as described for **3** using LiCl/HMPA for 3 h at 90 °C, 82% yield, a colorless oil, bp 155—158 °C

(2 mmHg). IR (neat): 1740, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, t, J=7 Hz, $-CH_2C\underline{H}_3 \times 2$), 1.3—2.7 (m), 3.30 (1H, d, J=8 Hz, $-C\underline{H}(COOCH_2CH_3)_2$), 4.18 (4H, q, J=7 Hz, $-C\underline{H}_2CH_3 \times 2$). HRMS: Calcd for $C_{13}H_{20}O_5$ (256.1311). Found: m/z 256.1317 (M^+).

3-Oxo-2-(3-oxocyclohexyl)butyric Acid Ethyl Ester (28)[14] Compound **28** was obtained from **7** and **13** in the same manner as described for **3** using LiCl/HMPA for 7 h at 90 °C, 62% yield, a pale yellow oil, bp 148—151 °C (2 mmHg). IR (neat): 1740, 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 1.50—2.67 (m), 2.22 (3H, s, $-COCH_3$), 3.42 (1H, d, J=8 Hz, $-C\underline{H}COCH_3$), 4.18 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_{12}H_{18}O_4$ (226.1205). Found: m/z 226.1208 (M^+).

3-(Ethylthio)cyclohexanone (29)[15] Compound **29** was obtained from **10** and **13** in the same manner as described for **3** using LiCl/HMPA for 18 h at 25 °C, 43% yield, a pale yellow oil, bp 145—150 °C (17 mmHg). IR (neat): 1706 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23 (3H, t, J=7 Hz, $-CH_2C\underline{H}_3$), 1.5—3.4 (m), 2.57 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$). HRMS: Calcd for $C_8H_{14}OS$ (158.0765). Found: m/z 158.0748 (M^+).

3-(Phenylthio)cyclohexanone (30)[16] Compound **30** was obtained from **11** and **13** in the same manner as described for **3** using LiCl/HMPA for 1 h at 90 °C, 80% yield, a pale yellow oil, bp 155—158 °C (2 mmHg). IR (neat): 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.50—2.90 (9H, m), 3.10—3.68, (1H, m, C$\underline{H}$SPh), 7.23 (5H, m, aromatic protons). HRMS: Calcd for $C_{12}H_{14}OS$ (206.0765). Found: m/z 206.0766 (M^+).

2-(3-Oxo-1-phenylbutyl)malonic Acid Diethyl Ester (31)[17] Compound **31** was obtained from **1** and 4-phenyl-1-but-3-en-2-one (**14**) in the same manner as described for **3** using LiCl/HMPA for 8 h at 90 °C, 60% yield, a pale yellow oil, bp 179—182 °C (2 mmHg). IR (neat): 1732 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.00 and 1.40 (6H, each t, J=7 Hz, $-CH_2C\underline{H}_3 \times 2$), 1.96 (3H, s, $-COCH_3$), 2.90 (2H, d, $-C\underline{H}_2COCH_3$), 3.57—4.32 (6H, m, $-C\underline{H}_2CH_3 \times 2$, $-C\underline{H}(Ph)C\underline{H}(COOC_2H_5)_2$), 7.15 (5H, br s, aromatic protons). HRMS: Calcd for $C_{17}H_{22}O_5$ (306.1468). Found: m/z 306.1447 (M^+).

2-(Phenylthio)-1,4-benzenediol (32)[18] Compound **32** was obtained from **11** and 1,4-benzoquinone (**15**) in the same manner as described for **3** using LiCl/HMPA for 18 h at 25 °C, 77% yield, pale yellow crystals, mp 89—90 °C. IR (neat): 3610, 1622 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.34 (1H, br s, –OH), 6.15 (1H, br s, –OH), 6.84—7.60 (8H, m, aromatic protons). HRMS: Calcd for $C_{12}H_{10}O_2S$ (218.0402). Found: m/z 218.0408 (M^+).

4,4a,5,6,7,8-Hexahydro-3*H*-naphthalen-2-one (34)[19] 2-Oxocyclohexanecarboxylic acid ethyl ester (**5**) (10 mmol) was added to a solution of LiCl (210 mg) in HMPA (5 ml) at room temperature. The mixture was stirred for 15 min, then **2** (10 mmol) was added, and stirring was continued for 2 h at 160 °C. The reaction mixture was poured into water and the product was extracted with Et_2O. The organic extract was washed with brine, dried, and evaporated *in vacuo*. The residual oil was distilled under reduced pressure to give **34** (1.15 g, 77%) as a pale yellow oil, bp 116—120 °C (2 mmHg). IR (neat): 1676 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.34—2.43 (m), 5.78 (1H, br s, olefinic proton). ^{13}C-NMR ($CDCl_3$) δ: 25.57, 26.95, 29.17, 34.45, 35.57, 36.52, 37.92, 124.29, 167.59, 200.29. HRMS: Calcd for $C_{10}H_{14}O$ (150.1045). Found: m/z 150.1067 (M^+). The same compound **34** was obtained in 85% yield under similar reaction conditions when DMI was used instead of HMPA.

1,2,3,6,7,7a-Hexahydroinden-5-one (33)[19] Compound **33** was obtained from **4** and **2** in the same manner as described for **34** using HMPA in 65% yield as a pale yellow oil, bp 88—90 °C (1 mmHg). IR (neat): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.83—3.0 (11H, m), 5.88 (1H, br s, olefinic proton). ^{13}C-NMR ($CDCl_3$) δ: 23.89, 29.28, 31.87, 32.82, 37.48, 43.13, 122.23, 175.53, 199.86. HRMS: Calcd for $C_9H_{12}O$ (136.0888). Found: m/z 136.0902 (M^+).

3,4,4a,5,6,7,8,9-Octahydrobenzocyclohepten-2-one (35)[20] Compound **35** was obtained from **6** and **2** in the same manner as described for **34** using HMPA in 50% yield as a pale yellow oil, bp 121—122 °C (1.5 mmHg). IR (neat): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.33—2.77 (15H, m), 5.83 (1H, br s, olefinic proton). HRMS: Calcd for $C_{11}H_{16}O$ (164.1201). Found: m/z 164.1225 (M^+).

3-Methyl-2-cyclohexen-1-one (36)[21] Compound **36** was obtained from **7** and **2** in the same manner as described for **34** using HMPA in 73% yield as a pale yellow oil, bp 102—105 °C. IR (neat): 1671 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.95 (3H, s, $-CH_3$), 2.00—2.60 (6H, m), 5.87 (1H, br s, olefinic proton). HRMS: Calcd for $C_7H_{10}O$ (110.0732). Found: m/z 110.0732 (M^+). The same compound **34** was obtained in 56%, 52%, and 55% yield under similar reaction conditions when DMPU, DMI, and TMU, respectively, were used instead of HMPA.

3-Phenyl-2-cyclohexen-1-one (37)[22] Compound **37** was obtained from **9** and **2** in the same manner as described for **34** using HMPA for 1 h at 160 °C in 21% yield as pale yellow crystals, mp 64—65 °C. IR ($CHCl_3$): 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.78—2.88 (6H, m), 7.31 (1H, s, olefinic proton), 7.38 (5H, m, aromatic protons). HRMS: Calcd for $C_{12}H_{12}O$ (172.0888). Found: m/z 172.0891 (M^+).

4,4a,5,6,7,8-Hexahydro-1-methyl-3*H*-naphthalen-2-one (38)[23] Compound **38** was obtained from **5** and **12** in the same manner as described for **34** using HMPA for 6 h at 160 °C in 66% yield as a pale yellow oil, bp 109—112 °C (1 mmHg). IR (neat): 1668 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.77 (3H, s, $-CH_3$), 1.1—3.1 (m). HRMS: Calcd for $C_{11}H_{10}O$ (164.1201). Found: m/z 164.1193 (M^+).

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