Esterification, Etherification, and Aldol Condensation Using Cathodically-Generated Organic Olate Anions

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Cathodic methods for the esterification of carboxylic acids and the etherification of phenol and benzenethiol under mild conditions were developed. The esterification was successfully carried out at room temperature by the reaction of alkylating reagents with cathodically-generated quaternary ammonium carboxylates. The etherification was similarly achieved using electrogenerated quaternary ammonium phenolate and halonitrobenzenes. A hindered phenolate anion cathodically-generated from 2,6-di-*t*-butyl-*p*-cresol remarkably promoted aldol condensation of aromatic ketones and aldehydes, and allowed subsequent Michael reaction to provide efficiently symmetrical 1,5-diketones.

Recently, there has been an increasing interest in the utilization of anionic species with onium counter cations in organic synthesis, since their reactivities are sometimes quite different from those of the anions with metal counter cations.[1] However, the preparation of the anionic species with onium counter cations from the corresponding ones with alkali metal cations is often troublesome and not practical since the use of expensive crown ethers and onium fluorides is required. Phase transfer catalysts (PTC's) enhance the nucleophilicity of anionic moieties, however, they are not always applicable owing to their instability under heating[2] and the impossibility of realizing completely dry reaction media.

Cathodic reduction of organic compounds generates anionic species with onium counter cations such as R_4N^+[3,4] and R_3S^+[4] when onium salts ($R_4N^+X^-$ and $R_3S^+X^-$) are used as supporting electrolytes. Therefore, cathodic reduction seems to be a convenient and versatile method for the generation of such active anionic species.

Therefore, as part of a broad program of the application of electrogenerated active species to organic synthesis,[3–6] cathodic esterification of carboxylic acids and etherification of phenols through S_NAr reaction were at first successfully achieved.[7]

Negatively charged species behave not only as nucleophiles but also as bases. Iversen and Lund[8] first demonstrated that an anionic species electrogenerated from azobenzene allows ylide formation from a phosphonium salt and the subsequent Wittig reaction. One (M.M.B.) of the authors named such anionic species and their precursors "electrogenerated bases (EGB's)" and "pro-bases (PB's)", respectively, and studied intensively and systematically synthetic utilization of some types of EGB's derived from azobenzene derivatives,[9,10] active olefins,[11] oxygen,[5,12–15] and carbon tetrachloride.[16] Most recently, we have found novel EGB-catalyzed polymerization of *N*-carboxy anhydrides of amino acids.[6]

Shono and Kashimura[17] have also explored the application of EGB's to organic synthesis and found that a base electrogenerated from 2-pyrrolidone possesses intriguing reactivity to promote various reactions with high selectivity. Although EGB's seem to be promising bases for organic synthesis, only a limited number of types of PB's have been reported so far.[8–17]

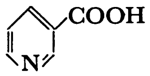
In a continuation of study on the utilization of EGB's, we have explored new ones and found that a certain type of phenolate anion also can be a useful base, that is, a hindered phenolate anion derived from 2,6-di-*t*-butyl-*p*-cresol remarkably promoted aldol condensation and allowed subsequent Michael reactions to provide efficiently symmetrical 1,5-diketones.

Results and Discussion

Cathodic Esterification of Carboxylic Acids. The esterification of carboxylic acids is an important and well-established reaction in organic synthesis. Reasonably, simple methods for the esterification under mild conditions should be required in many cases. One of the "simple methods" may be to react metal salts of carboxylic acids with alkylating reagents but this is generally "not mild" because of the high temperatures required.[18] In a previous paper,[19] one (M.M.B.) of the authors reported that quaternary ammonium salts of carboxylic acids reacted with alkyl halides to give the corresponding esters in high yields. In this method, the esterification reaction itself could proceed smoothly at room temperature, in other word, under "mild" conditions, but the preparation of either quaternary ammonium hydroxides or their carboxylates (**2**) was not very "simple". Afterword, some other methods which seemed to be mild were proposed but they were not simple because of the use of special and expensive reagents such as 1,8-diazabicyclo[5.4.0]-undec-7-ene,[20,21] 1-ethyl-2-fluoropyridinium tetrafluoroborate,[22] and alkyl chloroformates.[23]

With this in mind, a convenient method for

Table 1. Cathodic Esterification of Carboxylic Acids

RCOOH **1**	R′X	Method[a)]	Charge passed /F mol^{-1}	Yield of ester **3**[b)] /%
MeCOOH	*n*-BuCl	A	1.2	24
MeCOOH	*n*-BuBr	A	1.2	60
MeCOOH	*n*-BuI	A	1.2	25
MeCOOH	*n*-BuOTs	A	1.1	48
MeCOOH	*n*-BuCl	B	1.1	27
MeCOOH	*n*-BuBr	B	1.1	68
MeCOOH	*n*-BuI	B	1.1	96
n-PrCOOH	EtI	B	1.1	96
n-PrCOOH	EtOTs	A	1.1	70
PhCOOH	MeI	B	1.1	80
PhCOOH	EtI	B	1.1	83
PhCOOH	MeOTs	A	1.1	75
$HOOC(CH_2)_4COOH$	MeI	B	1.0	24[c)]
$HOOC(CH_2)_4COOH$	MeI	B	2.2	80[c)]
 $\underset{\underset{\text{OH}}{\vert}}{\text{PhCHCOOH}}$	EtI	B	1.1	90
$ClCH_2COOH$	MeI	B	1.1	42
MeCH=CHCOOH	MeI	B	1.0	77
HC≡CCOOH	MeI	B	1.0	58
	MeI	B	1.1	70

a) See text. b) Determined by gas chromatography. c) Dimethyl adipate.

$$\underset{\mathbf{1}}{\text{RCOOH}} \xrightarrow[\text{Et}_4\text{N}^+\text{-OTs/DMF}]{+e\ \ -1/2\text{H}_2}$$

$$\underset{\mathbf{2}}{\text{RCOO}^{-+}\text{NEt}_4} \xrightarrow[(\text{X=Halo, OTs})]{\text{R}'\text{X}} \underset{\mathbf{3}}{\text{RCOOR}'} + \text{X}^{-+}\text{NEt}_4$$

Scheme 1.

$$\text{MeCOOH} + n\text{-BuBr} \xrightarrow{+e} \text{MeCOOBu}^{n}$$

Method	Potential (V vs. SCE)	Electricity passed / F mol^{-1}	Yield / %	Current efficiency / %
A	−1.8	0.59	42	71
B	−1.5	0.83	52	71

Scheme 2.

preparing quaternary ammonium salts of carboxylic acids (**2**) by cathodic reaction and the successive one-pot esterification in a cathode chamber was developed as shown in Scheme 1.

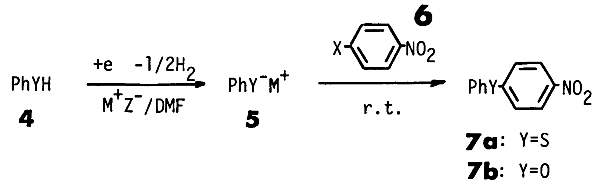
Two procedures for the esterification were employed as follows: In the presence of alkylating reagents, electrolytic reduction of carboxylic acids was carried out in DMF containing Et_4NOTs (Method A). In other method (Method B), the alkylating reagents were added to the catholyte after the electrolysis.

At first, we examined the esterification of acetic acid with butyl bromide by controlled-potential electrolysis. As shown in Scheme 2, the esterification proceeded at room temperature in both procedures to give butyl acetate. Since the amounts of electricity passed were smaller than the theoretical amount for the formation of the acetate anion because of decrease of the current during electrolysis, the yields were low although the current efficiencies were satisfactory.

Constant current electrolysis was found to improve the yield remarkably regardless of the procedures as shown in Table 1.

The yield of butyl acetate formed in Method A was greatly affected by kind of butyl halides used as alkylating reagents. The less electrophilic chloride gave a lower yield than the bromide. Although the iodide should be more electrophilic than the bromide, the former gave a lower yield. This fact is rationalized as due to a less negative reduction potential of the iodide than the bromide: It was confirmed that considerable amounts of the iodide were simultaneously reduced to the corresponding hydrocarbon. Butyl tosylate was also used in the esterification, but it did not give a higher yield than the bromide.

In order to prevent the simultaneous reduction of alkylating reagents, they were added to the catholyte after completion of the electrolysis (Method B). In the esterification of acetic acid with butyl halides by this method, the most electrophilic iodide and the least electrophilic chloride gave the highest and lowest



Scheme 3.

yields, respectively. Method B also resulted in high or reasonable yields in the esterification of other simple acids such as propionic and benzoic acids.

The esterification was successfully extended to somewhat complicated acids. It is noticeable that adipic acid gave the diester, though only 1.0 F mol^{-1} of charge was passed. When stoichiometric amounts of charge and methyl iodide for the formation of the diester were used, the yield of the diester reached to 80%. An α-hydroxy acid (mandelic acid) was also esterified in a high yield. Acids with electroreducible groups such as chloro, 1-propenyl, ethynyl, and 3-pyridyl groups could be esterified without the simultaneous reduction of their electroreducible groups.

Although Method A was inferior to Method B in yield, the former is much simpler than the latter and therefore the former may be more useful for esterification in some cases.

Shono and Kashimura have reported another excellent cathodic esterification using a base electrogenerated from 2-pyrrolidone.[17c)] However, our method is simpler and does not require the use of any electrogenerated bases.

Cathodic Etherification. Preparation of Diarylethers Using Electrogenerated Phenolate Anions. Nucleophilic aromatic substitution with phenolate anions to give diaryl ethers is also one of important reactions in organic synthesis. Recently, diarylether derivatives have found to be effective as pesticides, particulary as herbicides and certain types of such ethers are now commercially produced.[24)] However, substituents of the aromatic rings often eliminate and thus provide undesired by-products because of the high temperatures required in their synthesis. Because of this, most recently, many efforts have been made to solve such problems using PTC's.[25)] However, there are limitations to their utilization because the usual type of PTC's are sometimes consumed due to their reaction with phenolate anions under heating; therefore special thermally-stable PTC's must be employed in these cases.[2)]

These problems prompted us to attempt nucleophilic aromatic substitution using electrogenerated phenolate anion. At first, the reaction of benzenethiolate anion, an analogue of the phenolate, with halonitrobenzenes was examined. Benzenethiolate anion (**5a**) was cathodically generated from benzenethiol; subsequent reaction of the resulting **5a** with various *p*-halonitrobenzenes (**6**) was carried out in DMF at room temperature, as shown in Scheme 3.

Table 2. Preparation of Diaryl Ethers **7** from Halonitrobenzenes and Electrogenerated Benzenethiolate and Phenolate Anions

Run	**4** Y	**6** X	Supporting electrolyte[a)]	Reaction time/h	Yield of **7**[b)] /%
1	S	F	A	0.5	96
2	S	Cl	A	0.5	95
3	S	Br	A	0.5	98
4	S	Br	B	0.5	97
5	S	I	A	0.5	96
6	O	F	A	0.5	95
7	O	Cl	A	3.0	62
8	O	Cl	A	Over night	82
9	O	Br	A	0.5	75
10	O	Br	B	0.5	Trace
11	O	I	A	Over night	72
12	O	*o*-Cl	A	5.0	31[c)]

a) A=Et_4NOTs, B=$NaClO_4$. b) Isolated yield. c) *o*-Nitrophenyl phenyl ether (**7c**).

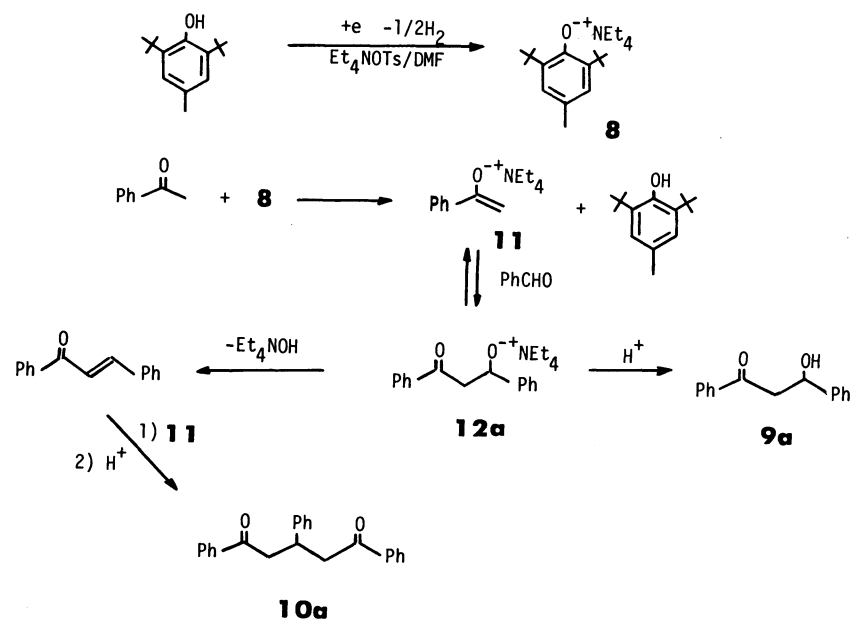
The results are summarized in Table 2.

The reaction proceeded almost quantitatively to give *p*-nitrophenyl phenyl sulfide (**7a**). This cathodic thioetherification was not affected by the kind of halogen atoms of **6** and the supporting electrolytes (M^+Z^-) probably because the benzenethiolate anion is inherently so reactive.

Next, the reaction was similarly carried out using phenol instead of benzenethiol to give *p*-nitrophenyl phenyl ether (**7b**) in good to excellent yields. In this case, the yield of **7b** depended on the kind of halogen atoms of **6**. *p*-Fluoronitrobenzene gave the best result since fluorine atom is known to be an excellent leaving group in such S_NAr reaction (Run 6). *p*-Iodonitrobenzene usually gives a poor yield in such a reaction; however, a satisfactory yield could be achieved by this cathodic method (Run 11).

Although *o*-chloronitrobenzene is sterically hindered to S_NAr reaction, the etherification proceeded to provide **7c**, though its yield was rather low (Run 12).

Furthermore, it is noticeable that the reaction was greatly affected by the cation of the supporting electrolyte as follows: The etherification did not proceed when sodium perchlorate was employed instead of Et_4NOTs as a supporting electrolyte (Run 10). This fact suggests that the nucleophilicity of quaternary ammonium salt of phenolate anion cathodically generated is much higher than that of the corresponding sodium salt.[26)] In order to comfirm the effect of a counter cation, the reaction of *p*-bromonitrobenzene with sodium phenolate prepared by the treatment of phenol with sodium hydride was



Scheme 4.

Table 3. Hindered Phenolate Anion-Promoted Aldol Condensation of Acetophenone with Benzaldehyde

Run	Reaction time/h	Reaction temp/°C	Counter cation of **8**	Yield[a)]/%	
				9a	**10a**
1	1.5	−15	Et_4N^+	39	trace
2	0.5	0	Et_4N^+	20	0
3	3.0	0	Et_4N^+	0	83
4	1.0	r.t.	Et_4N^+	0	74
5	3.0	r.t.	Et_4N^+	0	85
6[b)]	0.5	r.t.	Na^+	0	42[c)]
7[d)]	2.0	r.t.	Et_4N^+	12	16

a) Isolated yield. b) The sodium salt of **8** was prepared using sodium hydride. c) Large amounts of inseparable by-products were formed. d) A catalytic amount of **8** (0.05 equivalent) was used.

also examined under the same conditions as in the electrolysis. Expectedly, the reaction scarcely proceeded and provided only trace amounts of the desired product **7b**.

Thus, the cathodic method has an advantage as follows: The reactivity of anions can be controlled by the selection of supporting electrolytes, particularly their counter cations. It was demmonstrated here that quaternary ammonium phenolate cathodically prepared has a potential utility for the facile synthesis of *p*-nitrophenyl aryl ethers under mild conditions.

Aldol Condensation Promoted by Electrogenerated Hindered Phenolate Anion. Just like LDA, hindered phenolate anions seem to possess much lower nucleophilicity compared to ordinary phenolates. In fact, the reaction of *p*-bromonitrobenzene with the anion **8** cathodically derived from 2,6-di-*t*-butyl-*p*-cresol was found not to proceed at all. Therefore, this hindered phenolate anion seems to be one of promising candidates for EGB's.

Brown[27)] and Corey[28)] have successfully employed lithium and potassium salts of **8** for the generation of enolate anions from ketones and α-halo ketones; this allowed successive carboxylation and homologation, respectively.

These facts prompted us to investigate aldol condensations using hindered phenolate anion **8** since the reaction sought here is a typical base-promoted one.[29)] Aldol condensation of acetophenone and benzaldehyde was at first attempted under various conditions as follows: 2,6-di-*t*-butyl-*p*-cresol was reduced cathodically in DMF containing Et_4NOTs and then the catholyte was added to a mixed solution of acetophenone and benzaldehyde.

The results are summarized in Table 3.

Aldol product **9a** was found to be formed only at temperatures below 0 °C (Runs 1 and 2). When the reaction time was longer even at 0 °C, 1,5-diketone **10a** was obtained solely in a high yield (Run 3). At ambient temperature, **10a** was obtained in good yields regardless of the reaction time (Runs 4 and 5). On the other hand, the sodium salt of the phenolate anion **8** gave large amounts of various by-products together with 1,5-diketone **10** (up to 42% yield), regardless of both the reaction temperature and reaction time (Run 6). The reaction giving **10a** seems to proceed stepwise as shown in Scheme 4.

Although the aldol condensation is an efficient method for forming new carbon-carbon bonds, the product selectivity is not always satisfactory under equilibrium conditions.[30)] It is known that the intermediate keto alkoxide **12** is stabilized by six-

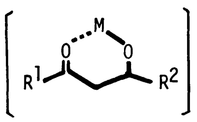
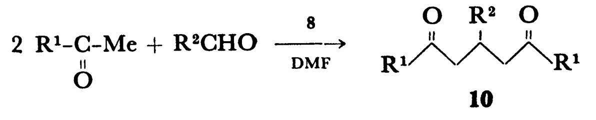
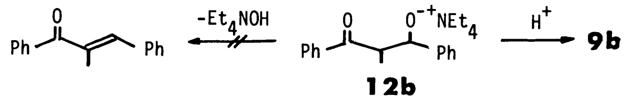


Fig. 1.

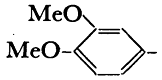


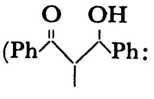
Scheme 5.



Scheme 6.

Table 4. Preparation of Symmetrical 1,5-Diketones (**10**) from acetophenones Using Electrogenerated Phenolate Anion **8**

Run	R^1	R^2	Reaction time/h	Yield of **10**[a) /%
1	Ph	Ph	3	85
2	Ph	p-$MeOC_6H_4$	Over night	59
3[b)	Ph	p-$MeOC_6H_4$	3	31[c)
4	Ph	m-$MeOC_6H_4$	3	60
5	Ph		Over night	25
6	Ph	p-ClC_6H_4	1	89
7	Ph	n-Bu	Over night	0
8	Ph	allyl	Over night	0
9	p-ClC_6H_4	Ph	3	79
10	p-MeC_6H_4	Ph	3	41
11	p-$MeOC_6H_4$	Ph	3	41
12	Ph[d)	Ph	Over night	18[e)

a) Isolated yield. b) Reaction temp = 50 °C. c) Large amounts of various by-products were formed. d) Propiophenone was used. e) The product **9b**  threo/erythro ≈ 1, ^{1}H NMR) was formed.

membered cyclic metal chelate formation (Fig. 1) in the presence of a divalent metal cation thus providing a single aldol product.[31) On the contrary, the intermediate **12** lacking such stabilization often leads to various side reactions such as retrograde aldol, poly-condensations, and enone formation followed by Michael addition; therefore inseparable mixtures of aldol products are obtained. Although a quaternary ammonium salt of the intermediate **12a** belongs to the latter case, the aldol condensation followed by dehydration and Michael addition proceeded highly selectively to provide 1,5-diketone in excellent yields in contrast to the case of the corresponding sodium salt (Run 6).

The same aldol condensation was examined by using quaternary ammonium phenolate (**5b**) instead of **8**, however the reaction became so complicated that no products could be separated probably because simultaneous nucleophilic attack of the phenolate anion to the starting compounds and/or products took place. It was also comfirmed that the reaction did not proceed smoothly with catalytic amount of **8** (Run 7).

Since the quaternary ammonium salt of hindered phenolate anion **8** was found to be an effective base for the formation of symmetrical 1,5-diketone **10**, this reaction was similarly carried out using various ketones and aldehydes (Scheme 5).

As shown in Table 4, 1,5-diketones **10** were prepared in moderate to good yields from aromatic ketones and aromatic aldehydes, whereas no products were obtained from aliphatic analogues (Runs 7 and 8). Moreover, the aldol product, keto alcohol **9b**, was obatined solely instead of 1,5-diketone from propiophenone and benzaldehyde although the yield was rather low (Run 12). This may be due to the difficulty of dehydrating the intermediate keto alkoxide **12b** (Scheme 6). It was also found that the yield of **10** was greatly affected by the substituents on the benzene rings of both ketones and aldehydes. Since the initial step of the aldol condensation reaction is abstraction of a proton from α-carbon of the ketones, the observed substituent effect was easily understood, as shown in Scheme 4.

Since the products thus obtained are known to be easily converted into pyrylium salts which possess wide utility for various organic synthesis,[32) this base-promoted reaction seems to be highly useful.

Experimental

^{1}H NMR spectra were recorded at 60 MHz on a Varian EM 360 NMR spectrometer using $CDCl_3$ and Me_4Si as solvent and internal standard, respectively. IR spectra were obtained with a Hitachi 295 infrared spectrometer. Mass spectra were obtained with a JEOL JMS-D100 mass spectrometer.

Electrolytic Procedure. An H-type electrolytic cell divided with a glass filter diaphragm was used. Platinum plates (2X3 cm) were used as cathode and anode. The catholyte was 40 cm^3 of 0.5 mol dm^{-3} Et_4NOTs or $NaClO_4$/

anhydrous DMF containing 6—10 mmol of substrates (**1**, **4**, **8**). Constant current (1.6A dm^{-2}) electrolysis was mainly carried out by passing 1.0—1.2F (1F=96480C) mol^{-1} of charge under a nitrogen atmosphere at room temperature.

Cathodic Esterification of Carboxylic Acids. Method A: Alkylating reagents (11 mmol of alkyl halides or tosylates) had been added to the catholyte containing carboxylic acids (10 mmol) before the current was turned on. After the electrolysis, the catholyte was allowed to stand for 1 h at room temperature.

Method B: Similar to Method A except that the alkylating reagents were added to the catholyte after the current had been turned off. In both methods, the catholyte was poured into water and then extracted with dichloromethane. The extract was analyzed by gas chromatography using a 2 m PEG 20M column at 100—200 °C.

Preparation of Diaryl Ethers (7) Using Electrogenerated Phenolate Anions. After the electrolysis of 6 mml of benzenethiol or phenol had been carried out by passing 1.0F mol^{-1}, the catholyte was added to a stirred solution of 5 mmol of *o*- or *p*-halonitrobenzene in 10 cm^3 of DMF. The reaction mixture was stirred at room temperature, and then the mixture was poured into water. After extraction with ether, the extracts were dried over anhydrous sodium sulfate. After removal of the solvent, the remaining residue was chromatographed on silica gel. Elution with a mixed solvent of hexane and ethyl acetate (50:1) provided pure products **7**. The products, *p*-nitrophenyl phenyl sulfide (**7a**)[33] and *p*-nitrophenyl phenyl ether (**7b**)[34] were identified by spectroscopic comparison with authentic samples.

***o*-Nitrophenyl Phenyl Ether (7c):** Yellow oil. IR (KBr): 1520 cm^{-1} (ν_{NO_2}). ^{1}H NMR δ=6.85—7.75 (m, 8H, Ar-$\underline{H}$) and 7.80—8.05 (m, 1H, Ar-$\underline{H}$). MS *m/z* 215 (M$^+$). Found: C, 66.71; H, 4.22; N, 6.18%. Calcd for $C_{12}H_9O_3N$: C, 66.97; H, 4.21; N, 6.51%.

Aldol Condensation Promoted by Electrogenerated Hindered Phenolate Anion (8). After the electrolysis had been carried out in 40 cm^3 of DMF containg 10 mmol of 2,6-di-*t*-butyl-*p*-cresol, 13.3 cm^3 of the catholyte was added to a stirred solution of 3 mmol of ketone and 3 mmol of aldehyde in 7 cm^3 of DMF under a nitrogen atmosphere. After stirring (TLC control), the reaction mixture was poured into an aqueous solution of NaCl and then extracted with ether. After drying and concentrating, the remaining residue was chromatographed on silica gel. Elution with a mixed solvent of hexane and diethyl ether (4:1) provided keto alcohol (**9**) or 1,5-pentanedione (**10**).

The products, 3-hydroxy-1,3-diphenyl-1-propanone (**9a**),[31] 1,3,5-triphenyl-1,5-pentanedione (**10a**),[31] 3-(4-methoxyphenyl)-1,5-diphenyl-1,5-pentanedione,[35] 3-(3,4-dimethoxyphenyl)-1,5-diphenyl-1,5-pentanedione,[35] 3-(4-chlorophenyl)-1,5-diphenyl-1,5-pentanedione,[35] 3-phenyl-1,5-di-*p*-tolyl-1,5-pentanedione,[36] 1,5-bis(4-methoxyphenyl)-3-phenyl-1,5-pentanedione[37] were identified by spectroscopic comparison with authentic samples.

3-(3-Methoxyphenyl)-1,5-diphenyl-1,5-pentanedione: Mp 88—90 °C. IR (KBr): 1680 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=3.15—3.50 (m, 2H, C$\underline{H}_2$), 3.65—4.35 (s, 3H, C$\underline{H}_3$O and m, 1H, C$\underline{H}$), and 6.55—8.10 (m, 14H, Ar-$\underline{H}$). MS *m/z* 358 (M$^+$). Found: C, 80.29; H, 5.97%. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19%.

1,5-Bis(4-chlorophenyl)-3-phenyl-1,5-pentanedione: Mp 125—127 °C. IR (KBr): 1690 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=3.30—3.65 (m, 4H, C$\underline{H}_2$), 3.90—4.35 (m, 1H, C$\underline{H}$), and 7.20—8.10 (m, 13H, Ar-$\underline{H}$). MS *m/z* 400 (M$^+$+4), 398 (M$^+$+2), and 396 (M$^+$). Found: C, 69.83; H, 4.83; Cl, 18.17%. Calcd for $C_{23}H_{18}O_2Cl_2$: C, 69.53; H, 4.57; Cl, 17.85%.

3-Hydroxy-2-methyl-1,3-diphenyl-1-propanone (9b): Colorless oil. IR (liquid film): 3500 (ν_{OH}) and 1670 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR δ=0.85—1.30 (d, 3H, C$\underline{H}_3$), 3.20—3.90 (m, 2H, O$\underline{H}$ and MeC$\underline{H}$), 4.77—5.13 (d, 1H, C$\underline{H}$OH), and 7.05—8.10 (m, 10H, Ar$\underline{H}$). MS *m/z* 240 (M$^+$). Found: C, 79.67; H, 6.66%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

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