

Mechanistic and Exploratory Investigations into the Synthesis of 1,3,5-Triarylbenzenes from 1-Aryl-2-propyn-1-ones and 1,3,5-Triacetylbenzene from 4-Methoxy-3-buten-2-one by Cyclotrimerization in Hot Water in the Absence of Added Acid or Base

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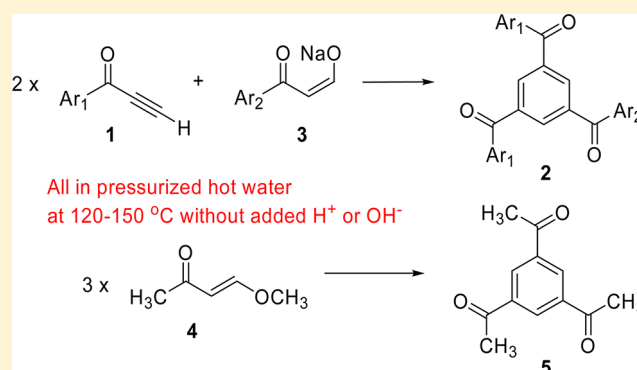
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Supporting Information

ABSTRACT: Neat 1-phenyl- and 1-(*p*-tolyl)-2-propyn-1-ones (**1** and **1'**, respectively) were heated in water without any additive at 150 °C for 2 h to give 1,3,5-tribenzoyl- and 1,3,5-tri(*p*-toluoyl)benzenes (**2** and **2'**, respectively) in 74 and 52% yields, respectively. The crossed reactions of **1** with the enolate of *p*-toluoylacetaldehyde (**3'**) and **1'** with the enolate of benzoylacetaldehyde (**3**) were carried out to give unsymmetrically substituted 1-toluoyl-3,5-dibenzoylbenzene (Ph₂Tol) and 1,3-ditoluoyl-5-benzoylbenzene (PhTol₂), respectively, corroborating the previously proposed reaction mechanism in which **3** and **3'** that are formed by rate-determining nucleophilic attack of HO⁻ on **1** and **1'** or its conjugate acids formed by subsequent protonation would serve as a common intermediate for the formation of **2**, **2'** and the acetophenone derivatives as byproducts. When 4-methoxy-3-buten-2-one (**4**) was heated in hot pure water without any additive at 150 °C for 30 min, 1,3,5-triacetylbenzene (**5**) was obtained in an isolated yield of 77% just by removing water by filtering the crystalline product from the cooled reaction mixture. The reaction did not take place in the absence of water. Slow decompositions of **5** in water set in at the temperature of 300 °C for 30 min.



INTRODUCTION

1,3,5-Triarylbenzenes serve as molecular hosts in solution as well as in the solid phase.^{1–4} They are also used as key intermediates for the synthesis of dendrimers of various functions, including superparamagnetic polycarbene^{5–7} and superelectrophilic 1,3,3-trisubstituted 2-oxindoles.⁸ Hyper-branched polymers with a high degree of branching, such as poly(aroxycarbonylphenylene)s and ferrocene-containing poly(aroylarylene)s, have been prepared.^{9,10} The physicochemical properties of the disklike molecules of medium size thus warrant further synthetic investigations. In most of these cases, the 1,3,5-triarylbenzene skeletons are constructed by base-catalyzed Michael-type cyclotrimerization of the corresponding 1-aryl-2-propyn-1-ones in the presence of organic base such as diethylamine and pyridine in organic solvents like DMF, dichloromethane, toluene, etc.^{5,11–13} Strict 1,3,5-regioselectivity maintained in these ionic addition reactions is in strong

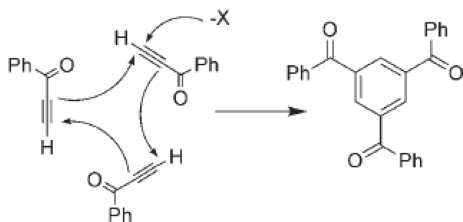
contrast to the various nickel-, cobalt- and other transition-metal-catalyzed cyclotrimerizations of monosubstituted acetylenes in which 1,2,4-trisubstituted benzenes are the main products, with lower amounts of the 1,3,5-isomers also generally obtained and little, if any, of the 1,2,3-isomers.^{14–22} Recently, we reported that 1-phenyl-2-propyn-1-one (**1**) produces 1,3,5-tribenzoylbenzene (**2**) in the absence of any added catalyst in one pot in 65% yields at 200 °C for 7 min or 74% at 150 °C for 60 min in subcritical water (Scheme 1).²³ Here again, the strict 1,3,5-trisubstitution regioselectivity was noted. When the pH of the aqueous media was raised by addition of sodium hydroxide at the start of the reaction, the initial rates of the reaction were enhanced. At higher

Special Issue: Howard Zimmerman Memorial Issue

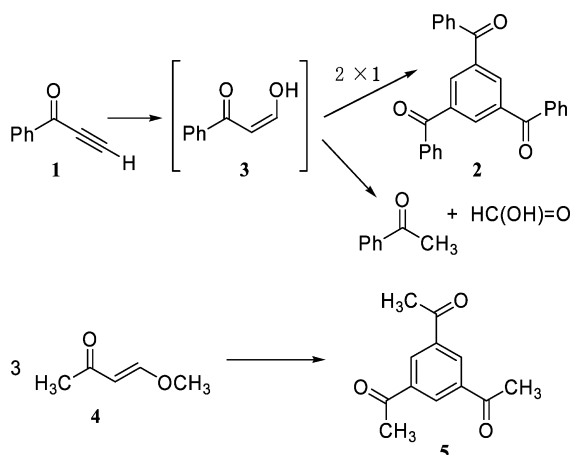
Received: September 11, 2012

Published: November 5, 2012

Scheme 1. X = NH(C₂H₅)₂ in the Previous Work^{5,11–13} and OH[−] Due to Pressurized Hot Water in This Work²³



Scheme 2. Similarity between the Two Reactions



temperatures, the yield of acetophenone increased at the expense of **2** (Scheme 2).

The dielectric constant (ϵ_r) of water decreases from 78.4 at 25 °C to ca. 35 (cf. $\epsilon_r = 33$ of methanol at room temperature)^{24–26} in pressurized hot water at 200 °C. The ion product of water ($pK_W = 14$) at 25 °C increases almost 3 orders of magnitude to $pK_W = 11.2$ at 200 °C.^{27,28} These two factors were concluded to be responsible for the success of the three consecutive Michael cycloaddition reactions in the absence of added acid or base.²³ The reaction rates increased with temperature but the yield of **2** decreased at the expense of the formation of acetophenone as a side product at higher temperatures. The enol of benzoylacetaldehyde (**3**) that was formed by rate-determining nucleophilic attack of HO[−] on **1** followed by protonation was postulated as an intermediate.²³ In view of these reaction conditions using neither organic solvents nor added acid or base and therefore consistent with the concept of green chemistry,²⁹ it seemed worthwhile to study this mechanism further by preparing the sodium salt of **3** which would then be allowed to react with 1-phenyl-2-propyn-1-one (**1**). In order to determine how many benzoyl groups in **2** are from **1** and **3** in these test reactions, it seemed appropriate to label either the benzoyl group in **1** or **3** by using the *p*-methyl substituent.

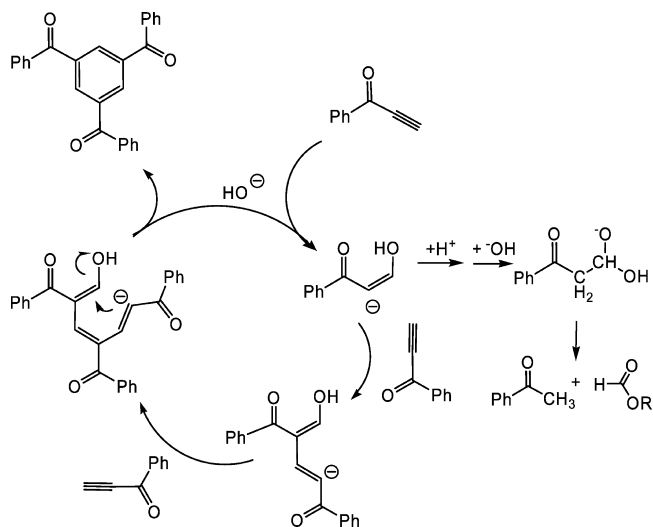
Second, 4-methoxy-3-buten-2-one (**4**) is equivalent to the methyl ether of the acetyl counterpart of **3**. We have been encouraged to examine whether **4** might be able to produce 1,3,5-triacetylbenzene (**5**) under similar conditions of pressurized hot water in the absence of any added catalyst (Scheme 2). In view of the usefulness of **5** for the synthesis of cyanine dyes,³⁰ functional dendrimers,^{31,32} phenolic molecular glasses,³³ cyclophanes,³⁴ and several ligands for transition metals,^{35–37} its synthesis by condensation of the sodium salt of acetoacetaldehyde in the presence of acetic acid in 30–38% yield was

documented in 1947 in *Organic Syntheses*, a publication of reliable synthetic procedures for fundamental organic compounds.³⁸ More recently, another procedure treating 4-methoxy-3-buten-2-one (**4**) in aqueous ethanol with acetic acid as a catalyst giving **5** in 61–64% yield at 77 °C for 48 h was described again in *Organic Syntheses*.³⁹ Both the procedures use organic solvents and acetic acid as a Brønsted acid catalyst. We have examined the latter reaction of **4** in hot water in the absence of any additive.

RESULTS AND DISCUSSION

Reactions of the Sodium Salt of the Enol of *p*-Toluylacetaldehyde (**3'**) with 1-Phenyl-2-propyn-1-one (**1**) and the Enol of Benzoylacetaldehyde (**3**) with 1-(*p*-Tolyl)-2-propyn-1-one (**1'**) in Hot Water in the Absence of Any Additive. The reaction mechanism proposed in the previous paper^{5–7,23} and summarized in Scheme 2 is elaborated in Scheme 3. According to this mechanism, the enolate of **3**

Scheme 3. Reaction Mechanism for the Formation of 1,3,5-Triarylbenzenes



should react with 1-phenyl-2-propyn-1-one (**1**). In order to determine how many benzoyl groups in **2** are from **1** and **3** in these test reactions, the aryl groups in **1** or **3** were labeled by using the *p*-methyl substituent. The results are given in Tables 1 and 2. See Tables S1 and S2 in the Supporting Information for the raw data.

Runs 1 and 6 are nothing but the reactions of neat 1-phenyl-2-propyn-1-one (**1**) and 1-(*p*-tolyl)-2-propyn-1-one (**1'**) giving 1,3,5-tribenzoyl- and tri(*p*-toluoyl)benzenes (**2** and **2'**), respectively, serving as references. The two results are almost comparable. In support of the proposed reaction mechanism, Ph₂Tol was obtained in runs 2–4 in which the highest yield was run 2. The stoichiometric amount appears not to be enough and the presence of higher concentration of **1** is favorable for the nucleophilic addition of **3'** leading to the formation of 1-toluoyl-3,5-dibenzoylbenzene (Ph₂Tol). A similar relation seems to hold for the formation of 1,3-ditoluoyl-5-benzoylbenzene (PhTol₂) from **1'** and **3** in run 7.

A larger proportion of the enolates leads to the formation of the acetophenone derivatives. Runs 5 and 10 are such extremes, showing that the enolate salts of the arylacetaldehyde cannot cyclotrimerize to form 1,3,5-triarylbenzenes.

Table 1. Production of 1,3,5-Triarylbenzenes and Acetophenones from the Reaction of 1-Benzoyl-2-propyn-1-one (1) with the Sodium Salt of *p*-Toluoaldehyde (3') at 150 °C for 2 h

run	molar ratio of the reactants 1:3'	chemical yield of the products (mol percentage) ^a					
		1,3,5-triarylbenzenes				acetophenones	
		Ph ₃ (2)	Ph ₂ Tol	PhTol ₂	Tol ₃ (2')	PhCOCH ₃	TolCOCH ₃
1	1.0:0.0	74	0	0	0	13	0
2	3.7 ₂ :1.0	27	57.0	0	0	10	11.8
3	2.0 ₃ :1.0	25	26.8	0	0	15	14
4	0.23 ₃ :1.0	4	7.3	1.6	0	41	65
5	0.0:1.0	0	0	0	0	0	69

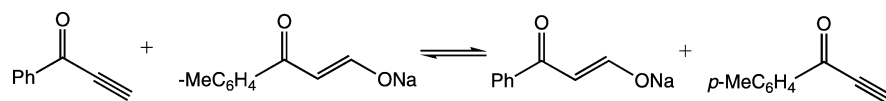
^aBased on the moles of 3' in the reactant mixture except for Ph₃ and PhCOCH₃ for which the yields are based on moles of 1.

Table 2. Production of 1,3,5-Triarylbenzenes and Acetophenones from the Reaction of 1-(*p*-Tolyl)-2-propyn-1-one (1') with the Sodium Salt of Benzoylacetaldhyde (3) at 150 °C for 2 h

run	molar ratio of the reactants 1':3	chemical yield of the products (mol percentage) ^a					
		1,3,5-triarylbenzenes				acetophenones	
		Ph ₃ (2)	Ph ₂ Tol	PhTol ₂	Tol ₃ (2')	PhCOCH ₃	TolCOCH ₃
6	1.0:0	0	0	0	52	0	17
7	3.5:1.0	0	0	32.5	34	6.6	8
8	2.0 ₃ :1.0	0	0	22.3	25	18	10
9	0.25:1.0	0	4.5	8.4	9	34	26
10	0:1.0	0	0	0	0	57	0

^aBased on the moles of 3 in the reactant mixture except for Tol₃ and TolCOCH₃ for which the yields are based on moles of 1'.

Scheme 4. Exchange Reaction of the Aryl Groups

**Table 3. Product Distributions of the Reaction of an Equal Molar Mixture of 1-Phenyl-2-propyn-1-one (1) and 1-(*p*-Tolyl)-2-propyn-1-one (1') at 150 °C for 2 h**

run	amt of starting materials (μmol) 1	chemical yield of the products (μmol)						
		1,3,5-triarylbenzenes				acetophenones		
		1'	Ph ₃ (2)	Ph ₂ Tol	PhTol ₂	Tol ₃ (2')	PhCOCH ₃	TolCOCH ₃
11	106	106	7.05	12.4	13.5	5.45	4.7	6.7

The formation of PhTol₂ in 1.6% yield in run 4 and Ph₂Tol in 4.5% yield in run 9 are observations that can immediately have no serious effect on the mechanism of the whole reactions, but they suggest necessarily the equilibration in Scheme 4.

The predominant structures with respect to the enol, enolate, and *cis*- and *trans*-forms of aroylacetaldhydes are discussed by means of their NMR spectra in various solvents. Most of them are in equilibrium with the enthalpy difference of less than a few kJ/mol and rapidly interconverting.⁴⁰ According to the Curtin–Hammett principle, the most populating species does not necessarily lead to the main product. Therefore, the presentation in this paper does not necessarily conform to the most predominant structure of aroylacetaldhydes and their derivatives.

Crossed Cyclotrimerization of 1-Phenyl-2-propyn-1-one (1) and 1-(*p*-Tolyl)-2-propyn-1-one (1') in Hot Water in the Absence of Any Additive. When an equal molar mixture of 1-phenyl-2-propyn-1-one (1) and 1-(*p*-tolyl)-2-propyn-1-one (1') was heated in hot water in the absence of any additive, the products were obtained as shown in Table 3. All of the possible combinations were produced, and there appears to be no selectivity. The molar ratio of the 1,3,5-

triarylbenzenes are distributed slightly in the direction toward the binomial coefficients of 1:3:3:1 for statistical combination. Whereas the reason for the observed trend in Table 3 is not clear, the results of the cross-reactions obtained in Tables 1 and 2 will open the door for the synthesis of the 1,3,5-triarylbenzenes having the unsymmetrical substitution pattern.

Cyclotrimerization of 4-Methoxy-3-buten-2-one (4) To Give 1,3,5-Triacetylbenzene (5) in Hot Water in the Absence of Any Additive. The results are listed in Table S3 (Supporting Information), and typical results are shown in Figure 1. The highest yield obtained by these methods was 88% in 30 min at 150 °C and 90 min at 110 °C, with values systematically higher than the isolated yield (see Table S4, Supporting Information). The variance of the yield data in these studies were dominated by the uncertainty of the manual processes and was estimated to be 5%. The reaction product 5 appeared to decompose slightly in water at 150–300 °C. For example, the recovered yield of 5 at 300 °C in water decreased from 80.4 to 79.3 and 72.2% for 30, 50, and 100 min, respectively. In the absence of water at 150 and 200 °C for 30 min, starting material 4 was recovered unchanged with a small amount of 4,4-dimethoxy-2-butanone detected.

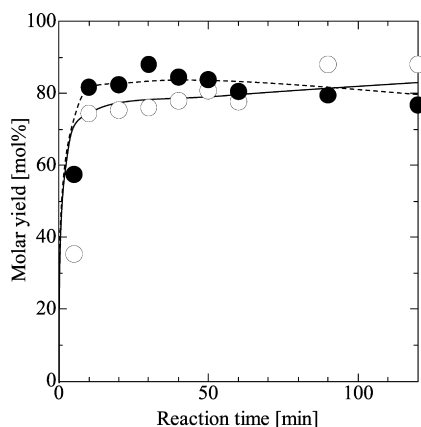
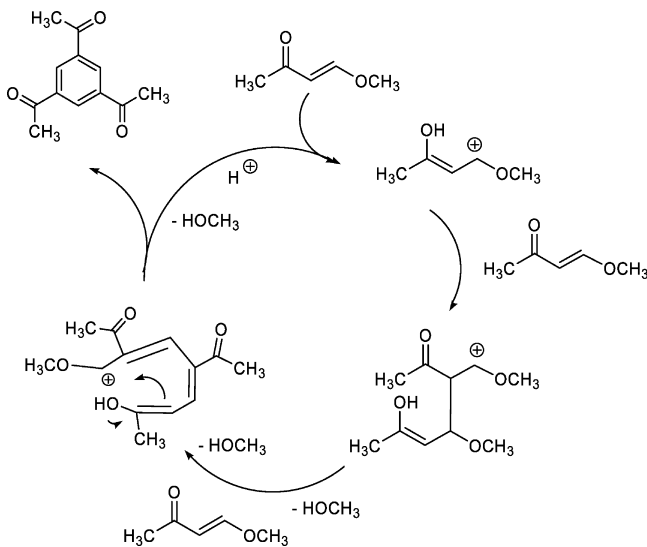


Figure 1. Temporal variation of the yield of product **5** at 110 °C (○) and 150 °C (●).

It is suggested from all of the above results that a series of cationic aldol condensations are operating. In the enol formed by protonation at the carbonyl oxygen, the positive charge on carbon 4 is stabilized by the electron-donating methoxy group and serve as an electrophile for the second molecule of **4**. Methanol may be eliminated here or later. The older *Organic Syntheses* method employs the heating of sodium salt of acetoacetaldehyde in the presence of acetic acid at 50 °C giving **5** in 30–38% yield.³⁸ Pivaloylacetaldehyde gave 1,3,5-tripivaloylbenzene in 30% yield when warmed in acetic acid.⁴¹ Therefore, the mechanism depicted in Scheme 5 is tentatively proposed; the elimination of methanol may take place at any stage.

Scheme 5. Tentative Mechanism for the Formation of 1,3,5-Triacetylbenzene (5) from 4-Methoxy-3-buten-2-one (4)



In general, we have to take the following factors into account for the organic reactions in water at high temperature under high pressure:

(1) The density of water decreases with temperature and reaches to 0.32 g/cm³ at the critical point of 374.15 °C and 22.12 MPa. The hydrogen bonding among the water molecules that is responsible for the polarization of water is disrupted, and as a result, the dielectric constant (ϵ_r) of water decreases from

78.4 at 25 °C to ca. 35 in the pressurized hot water at 200 °C (cf. $\epsilon_r = 33$ of methanol at room temperature).^{7,8}

(2) The ionic dissociation of water is endothermic and therefore increases with temperature according to Le Chatelier's principle. However, as the dielectric constant decreases with temperature as described in (1), a maximum value appears at 250–265 °C under the conditions of saturated vapor pressure.^{9,10} Its value of $pK_w = 11.2$ is almost 3 orders of magnitude greater than $pK_w = 14$ at 25 °C.

(3) The solubility of organic compounds in water increases with temperature. The trend is pronounced for those carrying hydrophilic substituent such as OH and >C=O.

(4) In 1980, Breslow and co-workers reported that the Diels–Alder reactions of cyclopentadiene with butenone proceeded 730 times faster in water than in isooctane and ascribed the phenomenon to the hydrophobic interaction in water.^{42,43} The aggregation energy density of organic molecules in water is due to the hydrogen-bonded structure of water and decreases with increasing temperature. It disappears at critical point of water and therefore can be disregarded for the reactions at higher temperature.

(5) The rate enhancement of organic reactions in pressurized hot water is interpreted to some extent in terms of the elevated temperature. According to the Arrhenius equation, a given reaction with the activation energy of ca. 100 kJ/mol is accelerated about thousand times from 100 to 200 °C.

Whereas the size of the reaction was limited by the reaction vessels used (Figure S1, Supporting Information), it could readily be expanded by employing larger size reactors. The reaction environment is at subcritical temperature and the inside pressure of the batch reactor is estimated to be ca. 1.6 MPa at 200 °C. It must not be difficult to find a commercially available pressure bottle (an autoclave) of the inner volume of 100–1000 mL. Furthermore, it has been a definite improvement in flow reactors of recent date using water under sub- and supercritical conditions in some laboratories.

CONCLUSIONS

When heated alone in water without any additive at 150 °C for 2 h, 1-phenyl- and 1-(*p*-tolyl)-2-propyn-1-ones (**1** and **1'**, respectively) gave 1,3,5-tribenzoyl- and 1,3,5-tri(*p*-toluoyl)-benzenes (**2** and **2'**, respectively) in 74 and 52% yields, respectively. The cross-reactions of **1** with the enolate of *p*-toluoylacetaldehyde (**3'**) on the one hand and **1'** with the enolate of benzoylacetaldehyde (**3**) on the other gave 1,3,5-triaroylbenzenes, Ph₂Tol and PhTol₂, that lack a trigonally symmetric substitution pattern. These results not only corroborate the previously proposed reaction mechanism in which the enolates formed by rate-determining nucleophilic attack of HO[−] on **1** and **1'** or its conjugate acids formed by subsequent protonation would serve as a common intermediate for the formation of **2**, **2'** and the acetophenone derivatives, but also opened the possibility of new logical method for the production of unsymmetrically substituted 1,3,5-triaroylbenzenes. Similarly, 4-methoxy-3-buten-2-one (**4**) gave 1,3,5-triacetylbenzene (**5**) in hot water in the absence of added acid or base. Whereas the reaction mechanism remains speculative, a considerably higher isolated yield of **5** in pure water than that of the procedure described in *Organic Syntheses*³⁹ appears simply sufficient to inclusion of our finding here. All of the reactions described in water without any added acid or base in this paper are ascribed to the reduced dielectric constant of water at higher temperatures and the increased ion

product of water and conform to the 12 criteria of green chemistry in a number of points.²⁹

EXPERIMENTAL SECTION

Starting Materials. Preparation of 1-aryl-2-propyn-1-ones is described in the previous paper.²³ Sodium enolate of benzoylacetaldhyde (3) was prepared by the condensation of acetophenone and ethyl formate by the action of sodium methoxide in dry diethyl ether according to the literature.^{44,45} The sodium enolate of *p*-toluoylacetaldhyde (3') was prepared similarly.

Commercially available 4-methoxy-3-buten-2-one (4) of chemical purity greater than 90% was used without further purification. Ultrapure water with a specific resistivity greater than 18.2 MΩ and TOC less than 20 ppb was obtained by passing tap water through an ultrapure water purification system. Other chemicals and solvents when necessary were commercially available and used as received.

General Experimental Methods. The reactions were performed in batch reactors (Figure S1, Supporting Information) fabricated out of a 1/2-in. tube (diameter of 12.7 mm, wall thickness of 2.1 mm) fitted with two 1/2-in. caps both of grade 316 stainless steel. The effective inner volumes of ca. 2.1 and 10 cm³ were used for the preparation of triarylbenzenes and 1,3,5-triacetylbenzene, respectively. Prior to its use in experiments, the reactor was loaded with 2% aqueous hydrogen peroxide and conditioned for 1 h at 370 °C to remove any lubricants/oils that might remain from the manufacture of the Swagelok parts and possible catalytic metal sites on the inner-wall, unless otherwise stated. The reactor was cleaned with acetone and dried prior to repeated safe use of ca. 5 times. The internal pressure was subjected to the gas-liquid equilibrium of water and estimated to be 0.48 MPa at 150 °C.

Preparation of 1,3,5-Triarylbenzene. The crossed reactions: 1-phenyl-2-propyn-1-one (1) with sodium enolate of *p*-toluoylacetaldhyde (3') and 1-(*p*-tolyl)-2-propyn-1-one (1') with sodium enolate of benzoylacetaldhyde (3) were mixed in pure water in molar ratios of 0:1:400–4:1:400. After the mixture was purged with a stream of argon, the sealed reactor was immersed in an oil bath preheated at 150 °C for 120 min. The reactor was cooled by immersing it in cold water to stop the reaction. The cap was carefully opened, and the contents of the reactor were washed with dichloromethane. The organic layer was analyzed by means of GC/MS and ¹H NMR. Quantitative analyses were performed by ¹H NMR with 1,3,5-triacetylbenzene as an internal standard. Separation of the reaction mixtures was performed by preparative gel permeation chromatography on a couple of columns of exclusion size limits of MW 1000 and 5000 (in reference to the molecular weight of the standard polystyrenes), in series using CHCl₃ as an elution solvent. Both had a column volume of i.d. 20 mm × 600 mm. After removal of the acetophenone fractions, the triarylbenzene fractions were subjected to repeated recycling of ca. 35 times until effective separation was obtained.

1,3-Dibenzoyl-5-(*p*-toluoyl)benzene (Ph₂Tol). NMR (400 MHz, CDCl₃): δ 8.38 (t, *J* = 1.2 Hz, 1H), 8.37 (d, *J* = 1.2 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 4H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H) (see Figure S3a, Supporting Information, for a chart). MS: 404 (parent peak), 119 (base peak), 105, 91, 77 (see Figure S2, Supporting Information).

5-Benzoyl-1,3-di(*p*-toluoyl)benzene (PhTol₂). NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 1.2 Hz, 2H), 8.37 (t, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 4H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 4H), 2.45 (s, 6H) (see Figure S3b, Supporting Information, for a chart). MS: 418 (parent peak), 119 (base peak), 105, 91, 77 (see Figure S2, Supporting Information).

Strong base peaks of *m/z* = 105 and 119 were observed for 1,3,5-tribenzoylbenzene (Ph₃) and 1,3,5-tri(*p*-toluoyl)benzene (Tol₃) corresponding to the ions PhCO and CH₃C₆H₄CO, respectively. In Ph₂Tol and PhTol₂, both the 105 and 119 peaks were observed in appropriate relative strength.

Preparation of 1,3,5-Triacetylbenzene. 4-Methoxy-3-buten-2-one (4) (0.1033 g) and water (1.8036 g) in a molar ratio of 1:200 were

introduced into the reaction vessel, and the contents were purged with a stream of argon. The capped vessel was immersed in an oil bath at 150 °C. After 30 min, heating was discontinued by removing the reactor from the heat bath and immersing it promptly in cold water. The reactor heat-up time was on the order of 30 s, which was generally short compared with the reaction times employed. After cooling, the crystalline solid product was flushed out of the reaction vessel with water and collected on a membrane filter as pale yellow needles (0.0567 g, mp 164–165 °C).³⁵ The reactions at elevated temperature in water followed by crystallization during the cooling process may have had an effect similar to recrystallization from hot water.

Additionally, the effects of reaction temperatures and duration of the reactions were studied in the ranges 100–400 °C and 10–120 min. A metal salt bath preheated at 200–400 °C was used when needed. In these studies, the reaction products were extracted with dichloromethane, and an aliquot (1 μL) was injected into a column of a gas chromatograph–mass spectrometer and developed with He gas with a flow rate of 0.55 mL/min. The amounts of 5 produced were determined accurately by reference to added 1-pentanol as an internal standard and on the basis of calibration curves obtained independently for the pure samples.

ASSOCIATED CONTENT

Supporting Information

Experimental details concerning raw yield data; NMR and MS spectra of new compounds Ph₂Tol and PhTol₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Prof. Soichiro Watanabe of Toho University for his permission and advice on the use and separation of the reaction mixture using preparative gel permeation chromatography. This research was supported in part by a Grant from the Ministry of Education, Culture, Sports, Science and Technology to promote multidisciplinary research projects.

DEDICATION

Dedicated to the memory of Professor Howard E. Zimmerman.

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