CHEMISTRY LETTERS, pp. 1765-1768, 1994.

Exploratory and Mechanistic Studies of the Trimerization Reaction of Benzoylacetylenes in the Presence of a Secondary Amine

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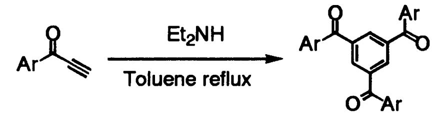
A variety of benzoylacetylenes are trimerized to give the corresponding 1,3,5-tribenzoylbenzenes when heated with a catalytic amount of diethylamine. A large amount of diethylamine gives γ-(diethylamino)propenoylbenzene at the expense of 1,3,5-tribenzoylbenzene, verifying a Michael-addition/trimerization/elimination-type mechanism for the formation of the benzene ring.

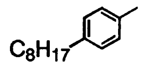
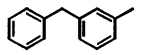
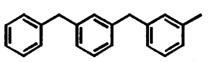
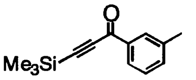
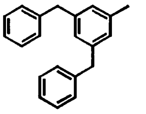
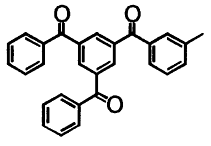
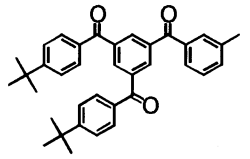
While a *m*-phenylene unit is established as a robust ferromagnetic coupling unit,[1)] a 1,3,5-benzenetriyl unit has recently been deemed superior in assembling organic free radical centers in higher concentration within a molecule and aligning those spins in parallel for the purpose of designing and constructing super-high-spin organic molecules.[2)] Thus super-high-spin hexacarbene ($S = 6$)[3)] and nonacarbene ($S = 9$)[4)] have in common a 1,3,5-benzenetriyltris(phenylcarbene) unit. Trimerization reaction of aroylacetylenes has been used as key steps in these syntheses. When a monosubstituted acetylene RC≡CH is heated with nickel or cobalt carbonyls, it gives mainly the 1,2,4-trisubstituted benzene, with lesser amount of the 1,3,5-benzene also generally obtained but little if any of the 1,2,3-isomer. Coordination of the metal with the triple bond has been considered to be involved.[6)] Since 1,3,5-regiochemistry is strictly required for the ferromagnetic coupler,[2)] an ionic reaction is preferable. In 1980, Balasubramanian et al. reported the formation of some 1,3,5-triaroylbenzenes by heating benzoylacetylenes in *N*,*N*-dimethylformamide (DMF).[7)]

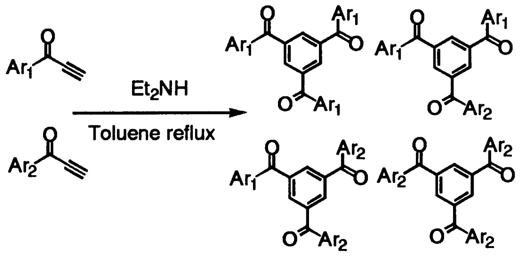
In view of the potential versatility of these reactions in the design of branched and dendritic structures for super-high-spin polyradicals and polycarbenes, we have studied these reactions in more detail and found out that a trace of diethylamine gave best results. Note that not only homotrimerization but also cross-trimerization can be performed (Table 1). Since the ethynyl group can be protected by silylation, the resulting trimerization products may be used as a second starting materials after deprotection. A synthetic strategy and a limitation of expanding these cross-conjugated π-systems to dendritic polymers has been discussed.[5)]

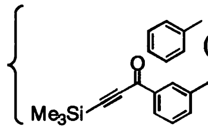
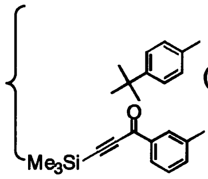
A catalytic amount of dimethylamine in DMF was considered as an effective catalyst and a mechanism similar to the one formulated in Scheme 1 had been proposed.[7)] When the secondary amine was used in a larger amount, ketoenamine was obtained indeed at the expense of the 1,3,5-tribenzoylbenzene. In this mechanism A one ketoenamine and two ethynylketone molecules form a six-membered ring from which the diethylamino group was trapped by another molecule of ethynylketone.[8)] There are two more mechanisms conceivable. They are mechanisms B and C (Scheme 2). In mechanism B the ketoenamine plays a role of the catalyst and in mechanism C the ketoenamine is in equilibrium with the ethynylketone.

Table 1. Trimerization of ethylnyl ketones

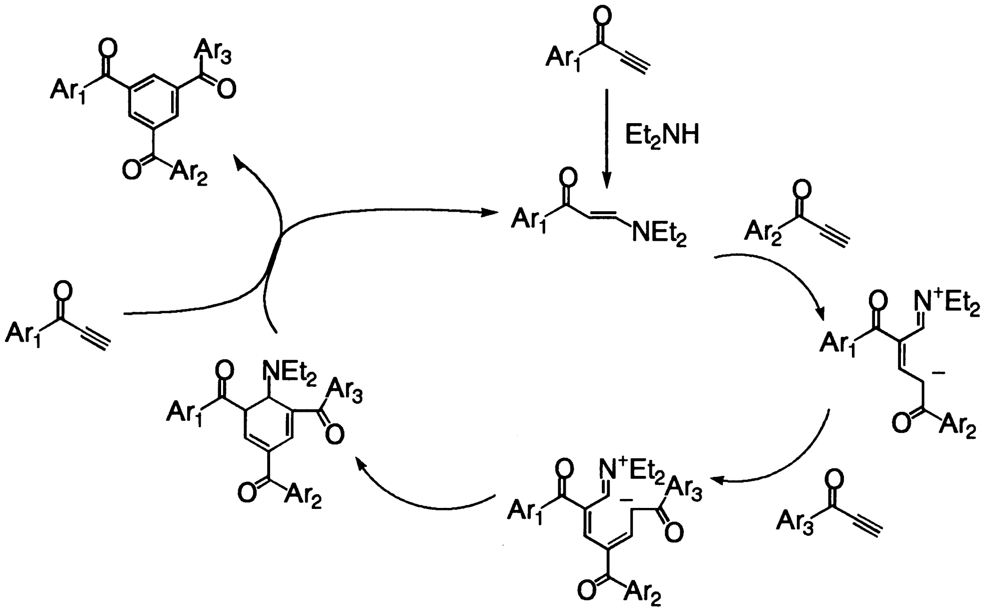


Ar	Reaction time / h	Yield / %
	22	52
	6	84
	12	84
	12	40
	40	86
	26	35
	24	65



Ar$_1$, Ar$_2$	Reaction time / h	Yield / %
 (2 eq.)	24	31*)
 (2 eq.)	12	12*)

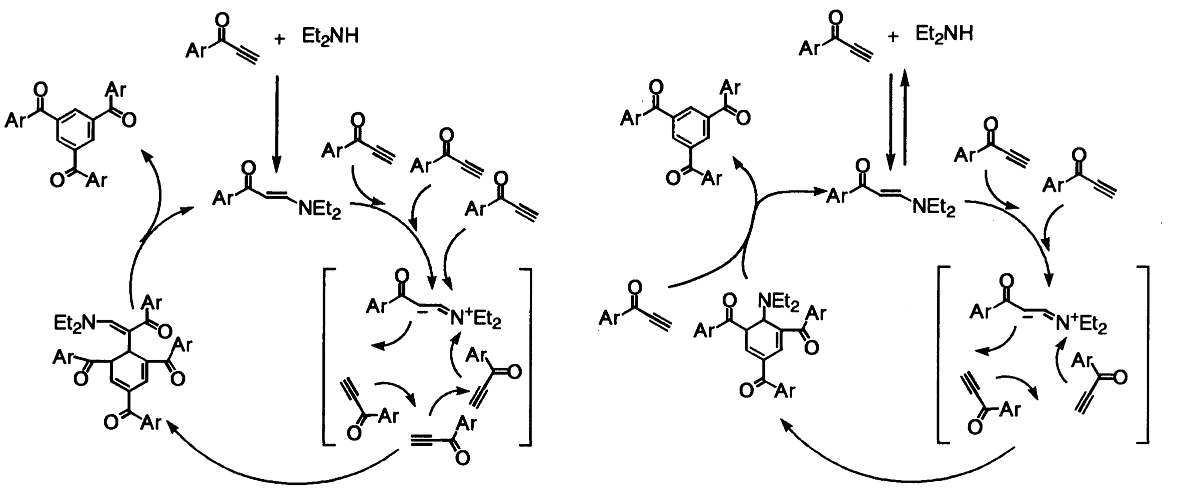
*) The yield of the main unsymmetrical product carrying one Me$_3$Si-C≡C group out of the four different products.



Mechanism A

Scheme 1.

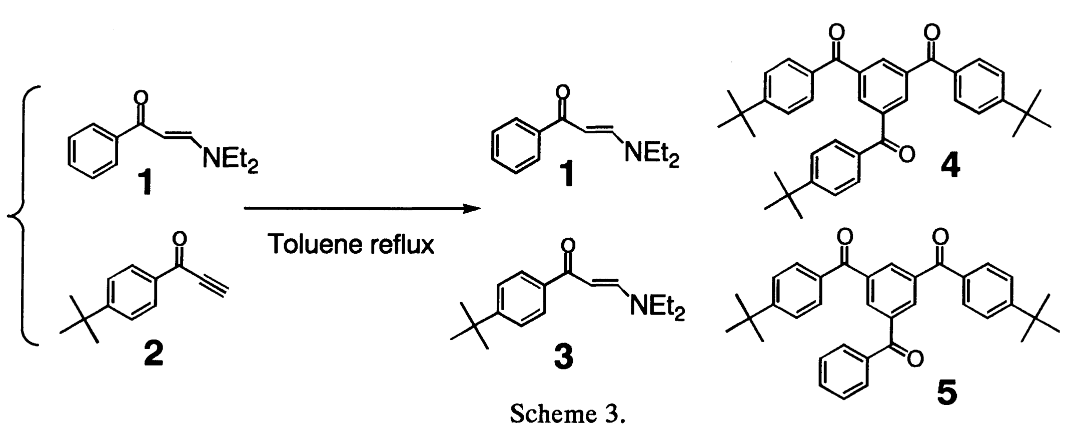
In order to discriminate among the three mechanisms, we have taken advantage of the mixed trimerization reaction. γ-(Diethylamino)propenoylbenzene **1** (90 mg, 0.44 mmol) and 4-*tert*-butylbenzoylacetylene **2** (170 mg, 0.90 mmol) were refluxed in 1 mL of toluene for 12 h, giving products **1**, **3**, **4**, and **5** (Scheme 3). The ketoenamine and triketone fractions were obtained from the reaction mixture by column chromatography on silica gel with hexane/dichloromethane (2 : 1, v/v) elution. The combined yields were 89% for **1** and **3** and 88% for **4** and **5**. The proportions of **3** to **1** and **5** to **4** were determined by ^{1}H NMR spectra of these fractions to be 1.2 and 2.5, respectively. The triketone **4** and **5** were separated by gel permeation chromatography (GPC) (8 mg of **4** and 28 mg of **5** were obtained from 50 mg of the mixture) and their structures were confirmed by ^{1}H NMR spectroscopy.9) It was found that the trimers contained no more than one phenyl group originating from **1**. Only **4**, a trimer of **2**, would have been formed in mechanism B, and the products would have been a mixture of four kinds of the trimers of all combination of benzoylacetylene and *p*-*tert*-butylbenzoylacetylene in mechanism C. From these considerations, mechanism A should be acceptable.



Mechanism B

Mechanism C

Scheme 2.



Scheme 3.

Assuming that rate determining process was the trimerization step rather than the trapping of diethylamino group by ethynylketone from trimerized six-membered ring and that the number of the molecules is large enough and the reaction rate of **1** and **3** to **2** is similar, we are able to calculate the proportion of the products by using of the recurrency formula. In mechanism A, two of **2** reacts with one **1** or **3** according to the proportion of **1** and **3**, which changes as the catalytic cycle proceeds. The calculated results showed that proportion of **3** to **1** is 0.95 and that of **5** to **4** is 2.7. These results are consistent with the proportions determined by ^{1}H NMR spectrum and GPC, further supporting mechanism A semiquantitatively.

It is concluded that a secondary amine plays a good catalytic role for the trimerization of aroylacetylene. The ketoenamine initially formed by a Michael-type reaction add to two more aroylacetylenes to ring-close to a dihydrobenzene derivative from which regeneration of the ketoenamine accompanies the aromatization. Since the reactions are ionic, the desired 1,3,5-regioselectivity is ideally kept.

This work was partially supported by a grant to N. N. from the Nishida Research Fund for Fundamental Organic Chemistry.

References

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7) K. Balasubramanian, S. Selvaraj, and P. S. Venkataramani, *Synthesis*, **1980**, 29.

8) Operationally from the product analysis alone, a mechanism consisting of unimolecular elimination of free diethylamine from the dihydrobenzene derivative and the formation of the enamine from the liberated amine with the remaining ethynylketone is indistinguishable from mechanism A.

9) Spectral data of **4**; IR (KBr) ν 2961,1653 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.36 (s, 27 H), 7.52 (d, J = 8.4 Hz, 6 H), 7.80 (d, J = 8.4 Hz, 6 H), 8.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 67.8MHz) δ 31.07, 35.21, 125.62, 130.20, 133.83, 133.85, 138.40, 157.11, 194.78.
Spectral data of **5**; IR (KBr) ν 2960, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.36 (s, 18 H), 7.49-7.54 (m, 6 H), 7.63 (t, J = 7.3 Hz, 1 H), 7.85 (d, J = 7.0 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 4 H), 8.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 31.06, 35.19, 125.62, 128.62, 130.12, 130.18, 133.19, 133.75, 133.82, 134.01, 136.53, 138.08, 138.45, 157.14, 194.68, 195.08.

(Received June 15, 1994)