

NOVEL COPPER(I) CHLORIDE-ASSISTED COUPLING REACTION OF 1-CHLORO-1-ARYLOYL-3,3-DIARYLALLENE  
TO AFFORD 3,7-DIOXA-2,6-DIARYL-4,8-BIS(DIARYLMETHYLENE)BICYCLO[3.3.0]OCTA-1,5-DIENE  
AND 1,1,4,4-TETRAARYL-3,6-DIARYLOYLHEXA-1,2-DIENE-5-YNE, AND THERMAL  
CYCLIZATION OF THE LATTER TO A FULVENE

Fumio Toda,\* Masataka Yamamoto, Koichi Tanaka  
Department of Industrial Chemistry, Faculty of Engineering,  
Ehime University, Matsuyama 790, Japan

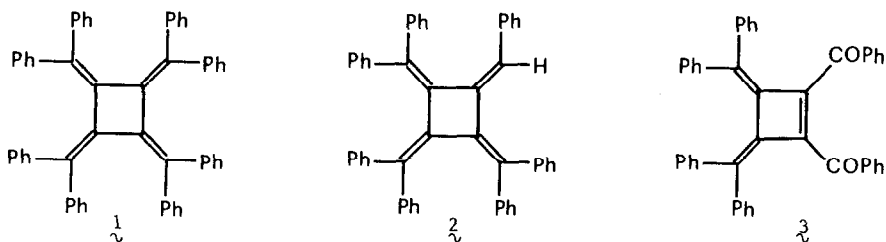
Thomas C.W. Mak\*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

*Abstract:* A novel CuCl-assisted coupling reaction of 1-chloro-1-aryloyl-3,3-diaryllallene ( $\zeta$ ) and two new thermal cyclization reactions of 1,1,4,4-tetraaryl-3,6-diaryloylhexa-1,2-diene-5-yne ( $\eta$ ) are described.

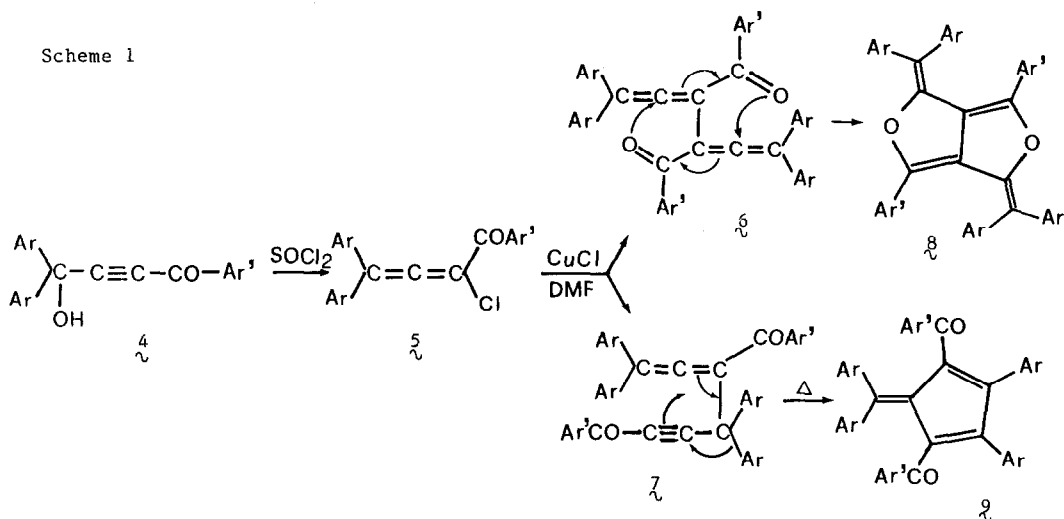
Octaphenyltetradialene ( $\lambda$ ) is an interesting compound because it is shaped like a four-leaved propeller, each blade comprising a pair of similarly-oriented phenyl rings, between which  $\pi$ -interaction becomes possible. Although heptaphenyltetradialene ( $\mu$ ) has been prepared<sup>1</sup> and characterized by X-ray crystallography,<sup>2</sup> synthesis of  $\lambda$  has not yet been accomplished. In one synthetic plan, the addition of phenylmagnesium halide (2 mol. eq.) to 3,4-dibenzoyl-1,2-bis(diphenylmethylene)cyclobutene ( $\nu$ ) followed by elimination of two hydroxyl groups might be expected to give  $\lambda$ . Accordingly we tried to prepare precursor  $\nu$  via coupling of haloallene<sup>3</sup> ( $\xi$ ) followed by thermal cyclization of the coupling product ( $\eta$ ).

Coupling of  $\xi$  (prepared by treating  $\zeta$  with  $\text{SOCl}_2$ ), however, gave a highly reactive new ring system  $\theta$  (probably via  $\phi$ ) and a cross-coupling product  $\eta$  (Scheme 1). Thermal cyclization of  $\eta$  to fulvenes  $\rho$  and of  $\eta$  to  $\sigma$  (Scheme 3) were also found. We now report these findings.



When  $\xi$  was treated with CuCl in DMF at room temperature under  $\text{N}_2$ ,<sup>3</sup> an exothermic reaction occurred and 3,7-dioxa-2,6-diphenyl-4,8-bis(diphenylmethylene)bicyclo[3.3.0]octa-1,5-diene ( $\theta$ , 39%, red needles) and 1,1,4,4-tetraphenyl-3,6-dibenzoylhexa-1,2-diene-5-yne ( $\eta$ , 47%, colorless needles) were obtained. By the same procedure,  $\xi$  yielded similar reaction products (Table 1). Notably  $\xi$  gave only  $\theta$  but not  $\eta$ , probably because of steric crowding around the two diaryl-substituted carbon atoms.  $\theta$  is highly reactive, very sensitive

Scheme 1



to acid, and gradually decomposed by light. For example, treatment of **8a** with dil. HCl immediately gave a diketone [95%, colorless needles, mp 198 °C, IR (Nujol mull) 1660  $\text{cm}^{-1}$ , UV (in  $\text{CHCl}_3$ ; nm,  $\epsilon$  in parentheses) 252(22200), 288(10700),  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ )  $\delta$  5.23 and 5.46 (each s, 1H, CH), 7.5–6.5 (m, 30H, Ph),  $^{13}\text{C-NMR}$   $\delta$  49.14 and 62.82 (each d, CH), 191.2 and 195.4 (each s, CO)]; of the two possible structures, **11'** and **11**, the latter was tentatively assigned on the basis of the similarity of its UV absorption band at 288 nm to that of cinnamaldehyde [289(25100)]. A plausible mechanism of the formation of **11** is shown in Scheme 2. Benzoyl peroxide-catalyzed ethanol addition to **8** also occurs easily. For instance, treatment of **8a** with EtOH in  $\text{CHCl}_3$  in the presence of benzoyl peroxide at room temperature afforded **12** [80%, colorless needles, mp 198–200 °C, UV 282(22300), and 342(7400)]. The steric course of this 1,2-addition reaction has not been established. However, similar treatment of **8d** resulted in *cis* 1,4-addition of EtOH to give **13** [56%, yellow prisms, mp 268–271 °C, UV 278(14800), 375(23800)], whose structure (Fig. 1) has been elucidated by X-ray crystallography.<sup>4</sup> Although the UV absorption bands of **13** are comparable to those of (*E*)-1,1,6,6-tetraphenylhexa-1,3,5-triene [254(51000), 375(124000)],<sup>5</sup> the  $\epsilon$ -values are much smaller. This may be ascribed to larger deviation from co-planarity of the 2,4-dimethylphenyl

Fig. 1. Perspective view of **13** with atom numbering.

Selected bond distances ( $\sigma \sim 0.01 \text{ \AA}$ ) and torsion angles ( $\sigma \sim 1^\circ$ ):

O(1)–1 1.42 Å, O(2)–4 1.39 Å; O(1)–6 1.48 Å, O(2)–5 1.45 Å; O(3)–6 1.40 Å, O(4)–5 1.39 Å; 1–2 1.47 Å, 3–4 1.42 Å; 2–5 1.53 Å, 3–6 1.51 Å; 1–19 1.32 Å, 4–36 1.35 Å; 2–3 1.35 Å.

1–2–5–O(4)  $-76^\circ$ , 4–3–6–O(3)  $-76^\circ$ ; 1–2–5–13  $51^\circ$ , 4–3–6–7  $50^\circ$ ; 2–5–13–18  $45^\circ$ , 3–6–7–8  $47^\circ$ ;

2–1–19–20  $14^\circ$ , 3–4–36–37  $8^\circ$ ; 2–1–19–28  $-170^\circ$ ,

3–4–36–45  $178^\circ$ ; 1–19–20–21  $56^\circ$ , 4–36–37–38  $68^\circ$ ;

1–19–28–33  $59^\circ$ , 4–36–45–50  $62^\circ$ .

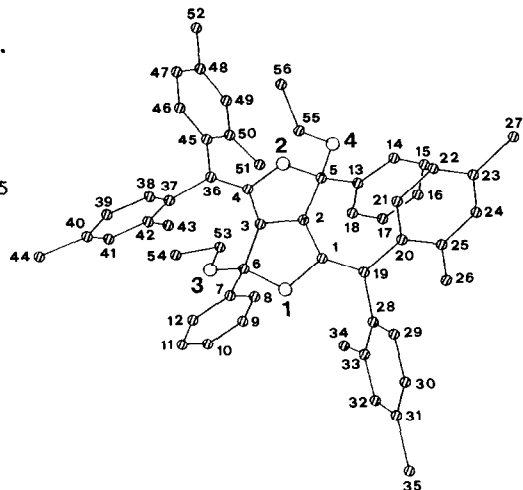





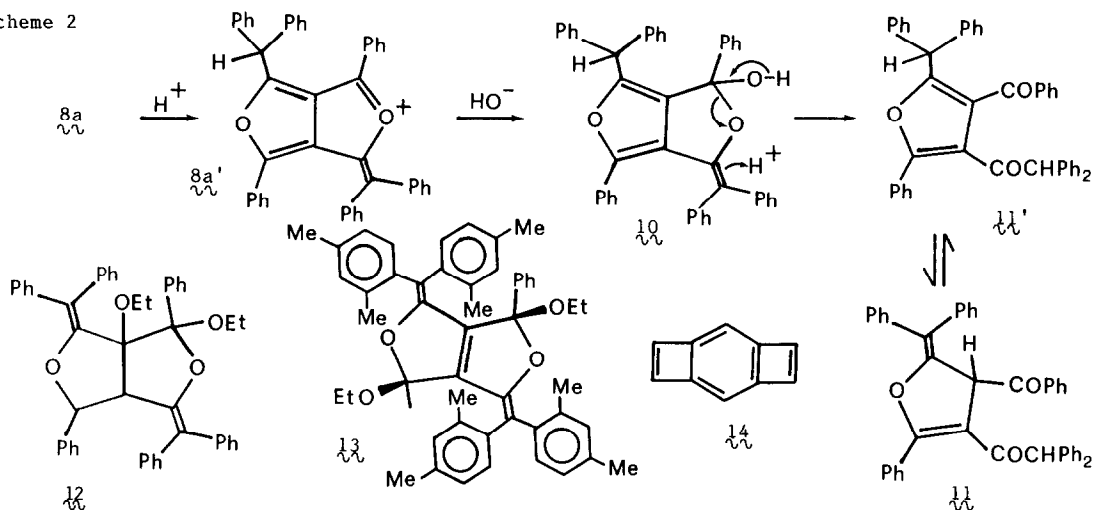


Table 1. Yields(%), melting points(°C), and UV spectra(nm,  $\epsilon \times 10^{-2}$ ) of coupling products of  $\mathfrak{5}$ 

Haloallene	Yield	$\mathfrak{8}$ mp	UV	Yield	$\mathfrak{7}$ mp	UV
$\mathfrak{a}$ : Ar = Ph; Ar' = Ph	39	>300	297 (497) 536 (210)	47	158-160	247 (323) 262 (354)
$\mathfrak{b}$ : Ar = Ph; Ar' = Me 	36	>300	304 (245) 540 (123)	33	152-153	250 (177) 260 (200)
$\mathfrak{c}$ : Ar = Ph; Ar' = Cl 	17	273-275	305 (191) 546 (116)	21	155-156	250 (192) 266 (226)
$\mathfrak{d}$ : Ar = Me  ; Ar' = Ph	26	258-262	304 (306) 506 (148)			
$\mathfrak{e}$ : Ar <sub>2</sub> =  ; Ar' = Ph	39	278-281	256 (524) 325 (407) 570 (224) 604 (283)	22	not clear	253 (456) 260 (531) 302 (140) 316 (147)
$\mathfrak{f}$ : Ar <sub>2</sub> =  ; Ar' = Ph	38	>300	267 (561) 326 (305) 575 (154) 612 (208)	29	not clear	250 (402) 267 (611) 302 (280) 313 (224)

Scheme 2



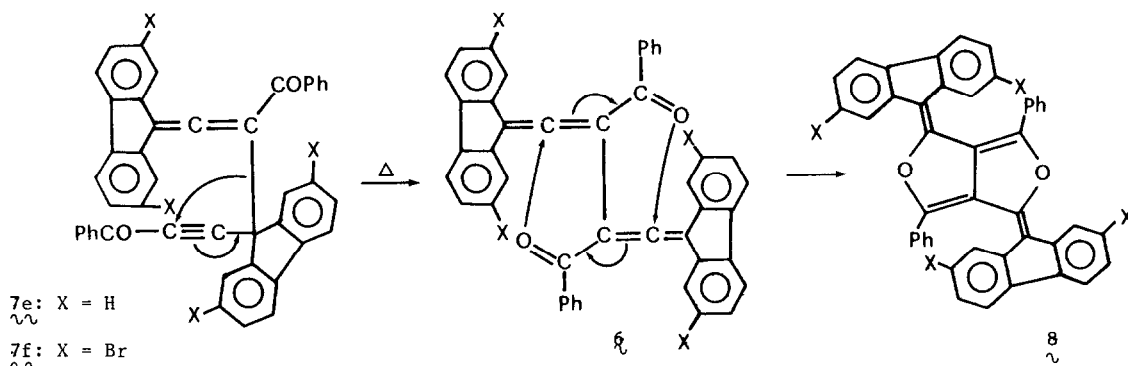
rings with the triene moiety, and the observed configuration (Fig. 1) presumably persists in solution.

Treatment of  $\mathfrak{8a}$  with  $\text{CuCl}_2$  in  $\text{CHCl}_3$ -EtOH at room temperature for 30 min gave  $\mathfrak{12}$  in 60% yield. Similar high reactivity to benzoyl peroxide<sup>6</sup> and metal salt<sup>7</sup> has been observed for the antiaromatic system benzodicyclobutadiene ( $\mathfrak{14}$ ).<sup>8</sup> However, the reason for the high reactivity of  $\mathfrak{8}$  is not clear.

Two new thermal reactions of  $\mathfrak{7}$  were found. Heating of  $\mathfrak{7a}$ ,  $\mathfrak{7b}$ , and  $\mathfrak{7c}$  in toluene under reflux for 30 min afforded 2,5-diaryloyl-3,4,6,6-tetraarylfulvene,  $\mathfrak{9a}$  [85%, red prisms, mp 294-296 °C, UV 256(36500), 294(17200), 394(23500)],  $\mathfrak{9b}$  [93%, red prisms, mp 265-166 °C, UV 264(24700), 296(10800), 394(20000)], and  $\mathfrak{9c}$  [79%, red prisms, mp 275-276 °C, UV 258(21200), 296(10800), 395(13900)],

respectively. The symmetric nature of the fulvene products was established by NMR; for example, **9b** showed a single  $\text{CH}_3$  signal at  $\delta$  2.23. This thermal cyclization is accompanied by aryl group migration (Scheme 1). Similar treatment of **7e-f** (in which aryl migration is prohibited) gave the corresponding cyclization products, **8e-f**, in almost quantitative yields. This novel  $8\pi$ -electron thermal cyclization reaction may be rationalized by assuming the formation of diallene intermediate **6** (Scheme 3).

Scheme 3



#### References and Notes

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4. **X-Ray Analysis.**  $\text{C}_{56}\text{H}_{56}\text{O}_4$ , MW = 793.05, monoclinic, space group  $\text{P2}_1/\text{a}$ ,  $a = 19.253(4)$ ,  $b = 9.697(3)$ ,  $c = 25.889(5)$  Å,  $\beta = 104.35(2)^\circ$ ,  $V = 4683(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.125$ ,  $D_m$  (floatation in  $\text{KI}/\text{H}_2\text{O}$ ) = 1.14 g cm<sup>-3</sup>, Mo-K $\alpha$  radiation (graphite-monochromatized),  $\lambda = 0.71069$  Å,  $\mu = 0.64$  cm<sup>-1</sup>. 3344 independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $2\theta_{\text{max}} = 45^\circ$ ] were measured on a Nicolet R3m diffractometer using  $\omega$ - $2\theta$  scans. The structure was solved by direct methods. The phenyl rings were treated as rigid groups (hexagons of edge 1.395 Å), and the remaining C and O atoms varied anisotropically. One  $\text{o-CH}_3$  group is two-fold disordered in a 2:1 ratio. Aromatic and methylene H atoms were geometrically generated (C-H fixed at 0.96 Å) and included in structure factor calculations with assigned isotropic thermal parameters. Final  $R$  for 299 variables is 0.141. Atomic coordinates and molecular dimensions have been deposited with the Cambridge Crystallographic Data Centre, and anisotropic thermal parameters and structure factors with the British Library Lending Division.
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(Received in Japan 25 September 1984)