

Preliminary communication

**On the preparation of tris(tribenzylideneacetylaceton)-
 tripalladium: a correction**

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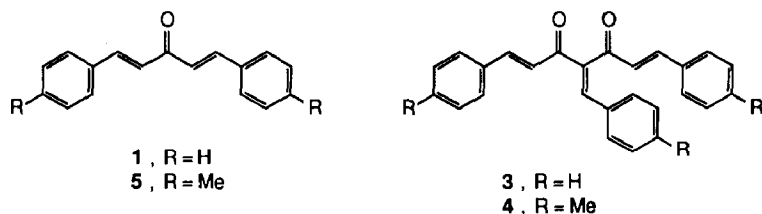
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Abstract

The aldol condensation of acetylaceton with benzaldehyde in the presence of sodium hydroxide yields exclusively dibenzylideneaceton (dba), and no tribenzylideneacetylaceton (tbaa) as reported for the synthesis of the complex $\text{Pd}_3(\text{tbaa})_3\text{CHCl}_3$.

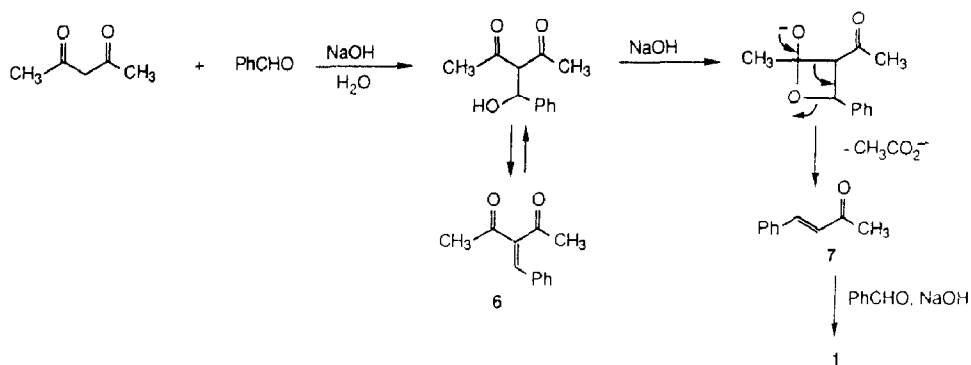
Palladium(0) complexes containing dibenzylideneaceton (dba) (1) [2*–4*] as a ligand are of interest both as catalysts and pre-catalysts in a variety of useful organic transformations [5] and in the synthesis of other palladium complexes [6]. In



1974 the preparation of the new complex $\text{Pd}_3(\text{tbaa})_3\text{CHCl}_3$ (2), containing the ligand tribenzylideneacetylaceton (tbaa) (3) was reported [1], by a procedure analogous to the one used in the synthesis of $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ [3a]. This complex was claimed to be an excellent source of weakly ligated palladium(0), and readily gave rise to new complexes by exchange reactions [1,7]. Complex 2 has been used as a catalyst in the cotrimerization of olefins [8] and in the palladium catalyzed reaction of vinyl epoxides with C–H acidic reagents [9]. Recently, a report described the syntheses of the *p*-methyl analog of 3 (4, ttaa) and the corresponding palladium complex, $\text{Pd}_3(\text{ttaa})_3$ [10].

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* Reference numbers with asterisks indicate notes in the list of references.



Scheme 1

The synthesis of ligand **3** calls for the aldol condensation of acetylacetone with benzaldehyde (3.6 equiv.) in 60% aqueous ethanol, with an excess sodium hydroxide (8.25 equiv) [1]. In our hands, the reaction proceeded as reported to yield a yellow solid, m.p. 109–110°C (lit. [1] 112–113°C). However, much to our surprise, spectroscopic data for this substance did not correspond with **3**, but rather with the well known dba (**1**) [11*]. No tbaa (**3**) was ever observed in the ^1H NMR of the crude reaction mixtures when the aldol condensation was carried out under a variety of conditions. Similarly, the reaction of acetylacetone and *p*-tolualdehyde gave **5** [12*] in 72% yield, instead of the reported **4** [10]. Reaction of dba (**1**) with PdCl_2 under the conditions reported for the synthesis of **2** [1] gave rise to the known complex $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ [13*].

We have now succeeded in developing an authentic synthesis of tbaa (**3**). Reaction of acetylacetone and benzaldehyde (3.5 equiv.) in benzene in the presence of piperidine (0.1 equiv.) at 23°C for 12 h, and at reflux with continuous removal of water (Dean–Stark) for 28 h, afforded **3** in 53% yield [14*]. Diketone **3** could also be synthesized, although less efficiently, by the reaction of 1,7-diphenylhepta-1,6-diene-3,5-dione [15] with benzaldehyde (piperidine, benzene, reflux, $-\text{H}_2\text{O}$) in 48% yield. However, no palladium complex could be isolated after heating **3** with PdCl_2 in the presence of NaOAc [16*].

The anomalous condensation leading to **1** instead of the expected **3** in the presence of sodium hydroxide can be explained by the mechanism proposed [17] for the reaction of acetylacetone with reactive aldehydes under anhydrous conditions (Scheme 1).

In accordance with this mechanism, 3-benzylideneacetylacetone (**6**) [18], a likely intermediate in the condensation, reacted at 20°C with benzaldehyde (NaOH , aqueous ethanol, 2 h) to afford dba (**1**) in 73% yield. In the absence of added aldehyde, benzalacetone **7** was formed as the major product, along with **1** (2/1 ratio, 48%).

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- 11 **1** was obtained in 81% yield; lit. m.p. 110–111°C (Merck Index 2977, 10th edit.), IR (KBr) and UV (THF) spectra of **1** agree with the data reported for **3** by Ishi [6].
- 12 (a) m.p. 175–176°C; lit. [12b] 175–177°C; (b) N.J. De Stefano, D.K. Johnson, R.M. Lane, L.M. Venanti, *Helv. Chim. Acta*, 59 (1986) 2674.
- 13 m.p. 127–128°C (dec), lit. [2] 122–124°C. A m.p. 132–135°C (dec) was reported for **2** [6].
- 14 After evaporation of the solvent, the crude mixture was chromatographed (flash silica gel column, 2/3 EtOAc/hexanes) to give crude **3** in 63% yield. Recrystallization from EtOAc/hexanes (23°C to –20°C) gave pure **3**, m.p. 106–107°C. TLC (5/1 hexane/EtOAc) *R_f* 0.25 (dba, same eluent, *R_f* 0.40); IR (KBr) 1660, 1640, 1610, 1585, 1575, 1445, 1450, 1325, 965 cm⁻¹; (CHCl₃) 1660, 1635, 1610, 1575, 1325, 1120, 970 cm⁻¹; UV (THF) 310 (strong), 228 (weak); ¹H NMR (CDCl₃, 270 MHz) δ 7.90 (s, 1 H), 7.82 (d, *J* 15.6 Hz, 1 H), 7.60–7.57 (m, 2 H), 7.53 (partially overlapping d, *J* 16.3 Hz, 1 H), 7.51–7.32 (m, 13 H), 7.14 (d, *J* 15.5 Hz, 1 H), 6.89 (d, *J* 16.2 Hz, 1 H); ¹³C NMR (CDCl₃, 68 MHz) δ 196.92, 187.15, 146.22, 144.82, 141.20, 140.74, 134.75, 134.26, 133.57, 130.70, 130.46, 130.16, 130.08, 128.75, 128.66, 128.43, 127.44, 122.39 (two C signal overlap); LRMS *m/z* 364 (*M*⁺, 5.4), 336 (3.1), 276 (12.1), 273 (16.6), 260 (6.2), 233 (19), 206 (18.1), 202 (19.4), 131 (100), 103 (83.1). Anal. Found: C, 85.51; H, 5.58. C₂₆H₂₀O₂ calcd.: C, 85.69; H, 5.53%.
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