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# Reaction between triphenylphosphine, diaroylacetylenes and arylidenemalononitriles: a novel and simple synthesis of 3-aroyl-2,5-diaryl-2,4-cyclopentadiene-1,1-dicarbonitriles

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## Abstract

A novel and simple synthesis of 3-aroyl-2,5-diaryl-2,4-cyclopentadiene-1,1-dicarbonitriles is described. The reactive 1:1 zwitterionic intermediate, formed by the addition of triphenylphosphine to diaroylacetylenes, was trapped by arylidenemalononitriles to produce the title compounds under mild reaction conditions in fairly good yields.

*Keywords:* Triphenylphosphine; Diaroylacetylenes; Arylidenemalononitriles; 3-Aroyl-2,5-diaryl-2,4-cyclopentadiene-1,1-dicarbonitriles

Cyclopentadienes (Cps) are highly useful synthetic intermediates. Considerable attention has been focused on the synthesis of substituted Cps as units for the construction of fused ring systems via inter- and intramolecular Diels–Alder reactions, as ligands in coordination chemistry and as homogeneous catalysis for olefin polymerization.[1]

Several methods have been reported for the direct preparation of substituted Cps including [3+2] annulation of allylidenetriphenylphosphoranes with 1,2-diacylethylenes,[2] reaction between isocyanides, dimethyl acetylenedicarboxylate, and electrophilic styrenes,[3] Pt(II)- or Au(I)-catalyzed cyclization of 1,2,4-trienes,[4] acid catalyzed cyclization of 1,4-pentadien-3-ols,[5] Pd-mediated cyclization of 1,5-hexadien-3-ols,[6] reaction of 1,1-dibromo-2-vinylcyclopropanes with methyllithium,[7] cycloaddition of α,β-unsaturated Fisher carbene complexes with alkynes or alkenes,[8] electrophilic allylation of enolizable 1,3-dicarbonyl compounds and successive acid catalyzed cyclizations,[9] insertion of aroyl cyanides or acid chlorides with zirconacyclopentenes,[10] reaction of zirconacyclopentadienes with a one-carbon unit building block such as aldehydes, propynoates, acyl halides or 1,1-dihalides,[11] and reaction of 1,4-dilithio-1,3-dienes with carboxylic acid derivatives, aldehydes, or ketones.[12]

As part of our current studies on the design of new routes for the preparation of interesting organic compounds,[13] we report herein a novel synthesis of polysubstituted Cps using simple starting materials. Thus, a mixture of triphenylphosphine, a diaroylacetylene **1**, and an arylidenemalononitrile **2** underwent a smooth reaction in dry dichloromethane at ambient temperature to afford 3-aroyl-2,5-diaryl-2,4-cyclopentadiene-1,1-dicarbonitriles **3a**–**h** in 60–72% yields (Scheme 1).

The reactions were carried out by first mixing triphenylphosphine and arylidenemalononitrile **2** in dry $CH_2Cl_2$. Then, a solution of the acetylenic compound **1** in dry $CH_2Cl_2$ was added to the reaction mixture. The reaction proceeded spontaneously at ambient temperature and was completed within an hour. TLC and $^1H$ NMR analysis of the reaction mixtures clearly indicated the formation of the functionalized Cps **3** in fairly good yields.[14]

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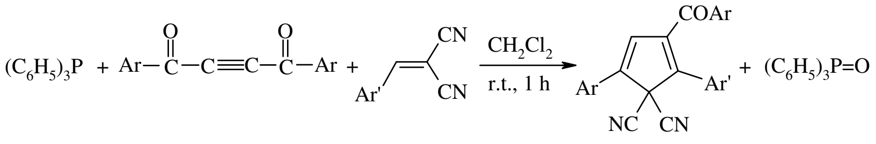


**1** **2** **3**

| 3 | Ar | Ar' | % Yield |
|---|---|---|---|
| **a** | $C_6H_5$ | $C_6H_5$ | 71 |
| **b** | $C_6H_5$ | 4-$CH_3C_6H_4$ | 72 |
| **c** | $C_6H_5$ | 4-$CH_3OC_6H_4$ | 70 |
| **d** | $C_6H_5$ | 4-$ClC_6H_4$ | 65 |
| **e** | $C_6H_5$ | 4-$FC_6H_4$ | 69 |
| **f** | $C_6H_5$ | 4-$CH_3C_6H_4$ | 66 |
| **g** | 2,5-$(CH_3)_2C_6H_3$ | $C_6H_5$ | 62 |
| **h** | 4-$CH_3C_6H_4$ | $C_6H_5$ | 60 |

Scheme 1.

The structures of the isolated Cps **3a–h** were confirmed by IR, $^1$H, and $^{13}$C NMR spectroscopy, mass spectrometry, and elemental analysis. The IR spectrum of **3a** showed absorptions at 2249 and 1647 cm$^{-1}$ indicating the presence of a nitrile and a conjugated ketone, respectively. The mass spectrum of **3a** displayed the molecular ion ($M^+$) peak at *m*/*z* 372. The fragmentation pattern exhibited characteristic peaks with the appropriate *m*/*z* values consistent with the structure of the isolated product. The $^1$H NMR spectrum of **3a** exhibited a single sharp resonance ($\delta$ 7.23 ppm) arising from the CH of the Cp ring, along with characteristic signals with appropriate chemical shifts and coupling constants for the 15 H atoms of the three phenyl substituents. The $^1$H decoupled $^{13}$C NMR spectrum of **3a** showed three signals readily recognized as arising from the 1,1-disubstituted quaternary carbon atom of the Cp ring ($\delta$ 45.79 ppm), 2 equiv nitrile substituents ($\delta$ 111.55 ppm) and a carbonyl group ($\delta$ 192.05 ppm) as well as 16 distinct resonances in agreement with the proposed structure.[14] Single-crystal X-ray analysis conclusively confirmed the structure of these compounds. An ORTEP diagram of **3a** is shown in Figure 1.[15]

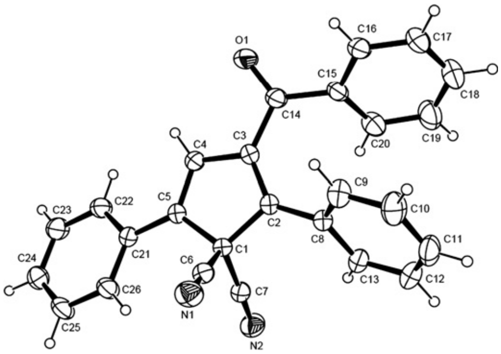
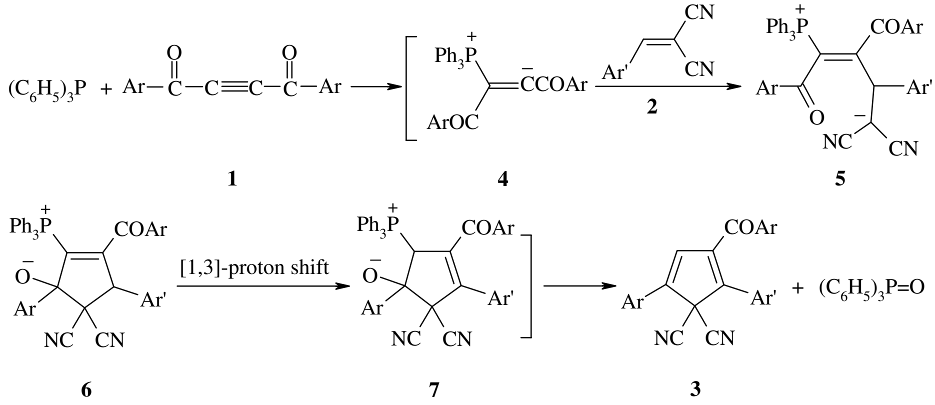


Fig. 1. X-ray structure of **3a**, with 50% probability displacement ellipsoids, H atoms with arbitrary radii.

A mechanistic rationalization for this reaction is provided in Scheme 2. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[16–19] it is reasonable to assume that zwitterion **4** formed from the initial addition of triphenylphosphine to the electron-deficient acetylenic compound **1** is trapped by the electrophilic styrene **2** leading to 1:1:1 adduct **5**, which undergoes intramolecular cyclization to betaine **6**. This betaine can undergo a [1,3]-proton shift to form a new betaine **7** from which triphenylphosphine oxide is removed to afford the product 3-aroyl-2,5-diaryl-2,4-cyclopentadiene-1,1-dicarbonitriles **3**.



Scheme 2.

In summary, we have succeeded in synthesizing 1,1,2,3,5-pentasubstituted cyclopentadienes of potential synthetic interest via a novel reaction between diaroylacetylenes and arylidenemalononitriles in the presence of triphenylphosphine. Good yields of the products, relatively short reaction times, and use of simple starting materials are the main advantages of this method. The reactions were performed under neutral and mild conditions, and the starting materials and reagents can be mixed without any activation or modification. The highly substituted Cps prepared in the present study may find useful applications in synthetic organic chemistry.

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14. The procedure for the preparation of 3-benzoyl-2,5-diphenyl-2,4-cyclopentadiene-1,1-dicarbonitrile **3a** is described as an example. To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 mmol) and benzylidenemalononitrile (0.154 g, 1 mmol) in dry $CH_2Cl_2$ (6 mL) was added dropwise a solution of dibenzoylacetylene (0.234 g, 1 mmol) in dry $CH_2Cl_2$ (2 mL) at −5 °C over 4 min. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. The solvent was removed and the solid residue was purified by column chromatography using *n*-hexane–EtOAc (3:1) as eluent. The solvent was removed and the residue was recrystallized from 1:1 *n*-hexane–EtOAc to afford **3a** as pale yellow crystals, mp 153 °C, yield 0.26 g, 71%. IR (KBr) ($\nu_{max}/cm^{-1}$): 2249 (CN), 1647 (C=O), 1620, 1600, 1564, 1491, 1443, 1358, 1240, 1076, 982, 868, 766, 734, 692. EI-MS, *m*/*z* (%): 372 ($M^+$, 70), 345 (M-HCN, 54), 277 (9), 240 (10), 172 (7), 159 (8), 105 ($C_6H_5CO^+$, 100), 77 ($C_6H_5^+$, 61), 51 (9). Anal. Calcd for $C_{26}H_{16}N_2O$ (372.43): C, 83.85; H, 4.33; N, 7.52. Found: C, 83.7; H, 4.3; N, 7.4. $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ 7.23 (1H, s, CH), 7.29–7.33 (3H, m, 3CH), 7.38 (2H, dd, $J = 7.9$ Hz and $J = 7.9$ Hz, 2CH), 7.46 (1H, t, $J = 7.4$ Hz, CH), 7.50–7.54 (3H, m, 3CH), 7.56 (2H, dd, $J = 7.3$ Hz and $J = 1.5$ Hz, 2CH), 7.79 (2H, dd, $J = 7.3$ Hz and $J = 1.3$ Hz, 2CH), 7.84 (2H, dd, $J = 7.2$ Hz and $J = 1.0$ Hz, 2CH). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta$ 45.79 ($C(CN)_2$), 111.55 (CN), 125.90, 128.56, 128.86 and 129.08 (4CH), 129.34 (C), 129.47 and 129.54 (2CH), 129.59 (C), 130.13, 130.35, 132.32 and 134.35 (4CH), 134.96, 140.60, 141.38 and 144.13 (4C), 192.05 (C=O).
15. *Selected X-ray crystallographic data for compound* **3a**: $C_{26}H_{16}N_2O$, triclinic, space group = $P\bar{1}$ (No. 2), $a = 9.1144(14)$ Å, $b = 9.8798(11)$ Å, $c = 11.0952(12)$ Å, $\alpha = 93.889(13)°$, $\beta = 91.678(2)°$, $\gamma = 96.691(2)°$, $V = 989.32(10)$ Å, $T = 295(2)$ K, $Z = 2$, $D_{calcd} = 1.25\ g\ cm^{-3}$, $\mu = 0.077\ mm^{-1}$, 2641 observed reflections, final $R_1 = 0.053$, $wR_2 = 0.116$ and for all data $R_1 = 0.086$, $wR_2 = 0.135$. CCDC 662538 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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