

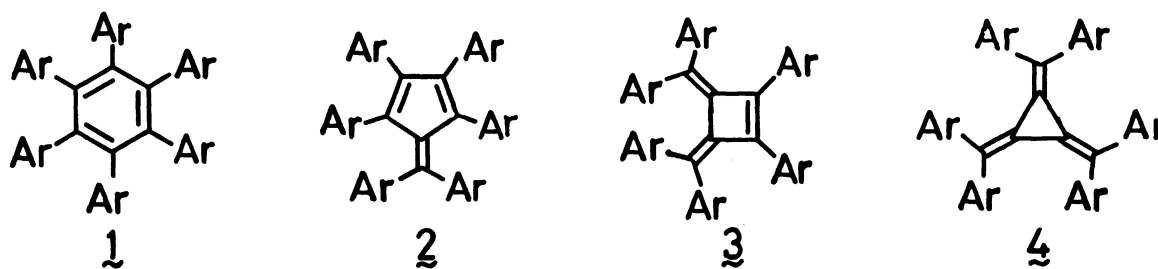
A Novel One-Step Nickel-Mediated Synthesis of C_6Ar_6 Conjugated Hydrocarbons,
Highly Substituted and Overcrowded Fulvenes and 3,4-Dimethylenecyclobutenes

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Nickel-catalyzed cyclo-oligomerization of aryl-substituted 1,1-dibromoethylenes in the presence or absence of diarylacetylenes produces 1,2,3,4,6,6-hexaarylfulvenes and/or 1,2-diaryl-3,4-bis(diarylmethylene)cyclobutenes in moderate yields, providing a new and simple method for C_6Ar_6 conjugated hydrocarbons, highly overcrowded systems.

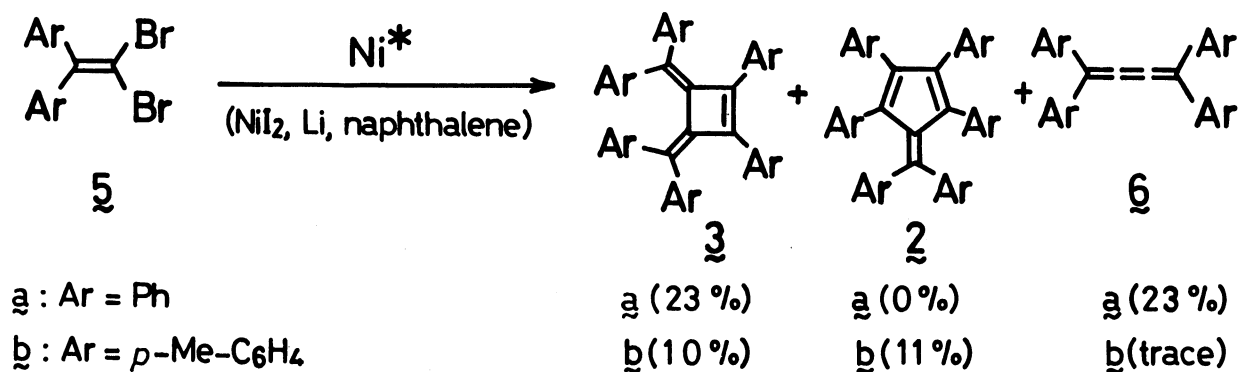
A family of C_6H_6 hydrocarbons has received considerable attention from both theorists and experimentalists.¹⁾ Although the parent C_6H_6 systems are extremely labile except for benzene, the C_6Ar_6 derivatives commonly possess the high stability. We are interested in the structure of C_6Ar_6 conjugated systems 1 - 4, because of the promising electronic interaction among their substituting benzene rings which lie parallel to one another owing to the overcrowded substitution.



Recently, we have reported the reactions of nickel and copper methylenecarbenoids to afford butatrienes and radialenes.²⁾ We now report new two pathways, in which the reaction of aryl-substituted 1,1-dibromoethylenes (5) with an active metallic nickel produces the C_6Ar_6 hydrocarbons (2 and 3), together with the corresponding butatrienes (6). In addition, the reaction of 5 with the active metallic nickel in the presence of diarylacetylenes (7) gave hexaarylfulvenes (2) in moderate yields. These reactions possess not only importance as new cyclo-trimerizations of transition metal carbenoids, but also the synthetic utility, because readily available 1,1-dibromoethylenes³⁾ can be converted into C_6Ar_6 hydrocarbons in the presence or absence of diarylacetylenes under mild conditions.

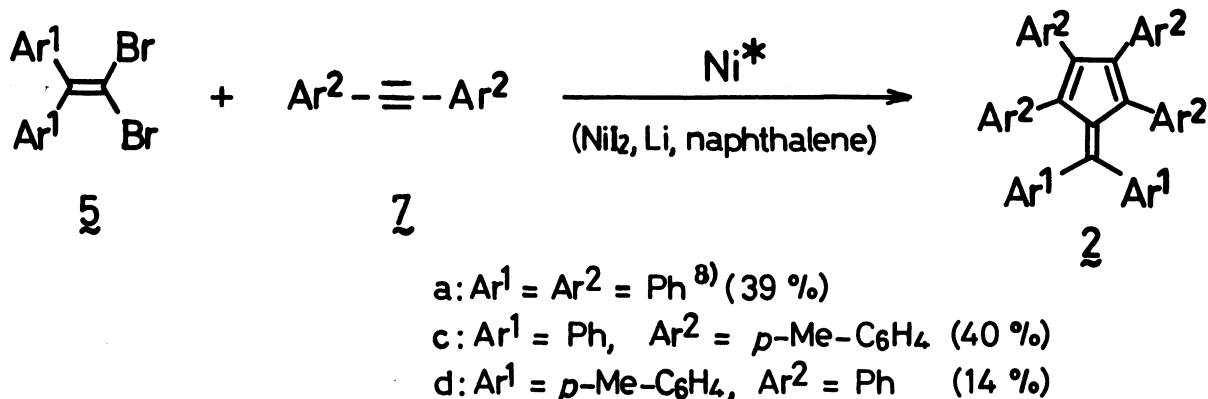
The active metallic nickel was prepared, as has been reported previously,⁴⁾ by reduction of NiI_2 with 0.9-1.0 equiv. of lithium and approximately 0.1 equiv.

of naphthalene as electron carrier in THF under sonication. As shown in Scheme 1, the reaction of 1,1-dibromo-2,2-diphenylethylene ($\underline{5a}$) with the active metallic nickel in THF under sonication at 40-50 °C for 5 h and then with mechanical stirring at 50 °C overnight gave tetraphenylbutatriene ($\underline{6a}$) as the dimer and 1,2-diphenyl-3,4-bis(diphenylmethylene)cyclobutene ($\underline{3a}$)⁵⁾ as the cyclic trimer in both 23% yields.⁶⁾ Furthermore, treatment of 1,1-dibromo-2,2-di-*p*-methylphenylethylene ($\underline{5b}$) with this metallic nickel under similar reaction conditions yields the corresponding 3,4-dimethylenecyclobutene ($\underline{3b}$) and fulvene ($\underline{2b}$) in 10% and 11% yields, respectively, with trace amount of the butatriene ($\underline{6b}$). Formation of the trimers $\underline{2}$ and $\underline{3}$ suggests that the methylidenecarbene-acetylene rearrangement occurs in these reactions to produce intermediary diarylacetylenes in the reaction media.



Scheme 1.

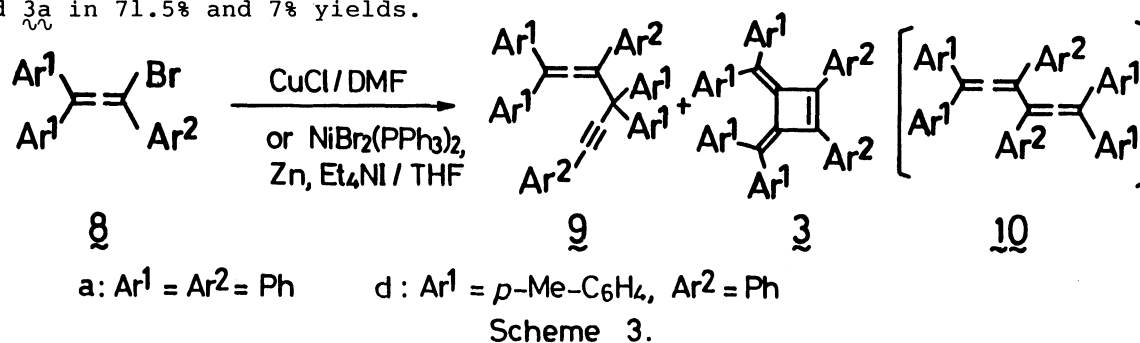
In order to obtain further insight into these cyclo-trimerizations, we carried out the reaction of 1,1-dibromoethylenes ($\underline{5}$) with the active metallic nickel in the presence of diarylacetylenes ($\underline{7}$). Treatment of $\underline{5}$ with excess amount of the metallic nickel in the presence of 2.3 equiv. of $\underline{7}$ in THF under sonication at 40-50 °C for 5 h and then with stirring at 50 °C for overnight gave the corresponding fulvenes ($\underline{2}$) as the only isolable product (Scheme 2). A remarkable feature of the active metallic nickel is the difference from that of Ni(PPh₃)₄ in the reactivity for 1,1-dibromoethylenes ($\underline{5}$) and diarylacetylenes ($\underline{7}$). Thus, treatment of equimolar amounts of $\underline{5a}$ and $\underline{7a}$ with Ni(PPh₃)₄, which was prepared in situ by reduction of NiBr₂(PPh₃)₂ with zinc,⁷⁾ in benzene at 50 °C for 24 h gave mainly tetraphenylbutatriene ($\underline{6a}$, 32%) together with small amount of the fulvene ($\underline{2a}$,



Scheme 2.

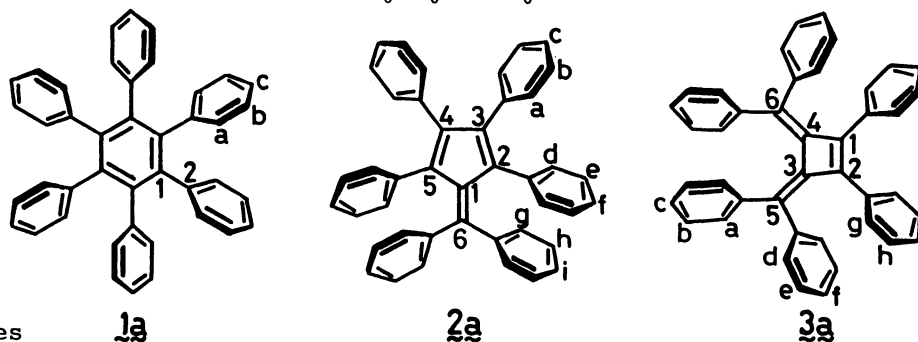
2%). This fact suggests that the metallic nickel interacts at first with diarylacetylenes ($\underline{7}$) selectively to give the nickelacyclopentadiene intermediates which reacts with 1,1-dibromoethylenes ($\underline{5}$) to result in the formation of the fulvenes ($\underline{2}$). On the other hand, $\text{Ni}(\text{PPh}_3)_4$ reacts more easily with dibromoethylenes ($\underline{5}$) than with diarylacetylenes ($\underline{7}$) to yield mainly tetraarylbutatrienes ($\underline{6}$) via the nickel methylenecarbenoid intermediate.^{2a)}

The coupling reaction of $\underline{8a}$ with CuCl in DMF was reported to give the bis-allene derivative ($\underline{10a}$).⁹⁾ Since $\underline{10}$ may be converted into $\underline{3}$ either by thermal ring closure or by transition-metal-catalyzed cyclization,¹⁰⁾ we carried out the reaction of $\underline{8d}$ with CuCl . Treatment of $\underline{8d}$ with 4 equiv. of CuCl in DMF at room temperature for 1.5 h afforded the head to tail dimer ($\underline{9d}$) in 82% yield together with 11% yield of the corresponding 3,4-dimethylenecyclobutene ($\underline{3d}$), but the formation of $\underline{10d}$ was not observed in this reaction. Therefore, we re-examined the reaction of CuCl in DMF and obtained $\underline{9a}$ ¹¹⁾ and $\underline{3a}$ ⁵⁾ in 78.5% and 10.5% yields, respectively. The reaction of $\underline{8a}$ with $\text{NiBr}_2(\text{PPh}_3)_2\text{-Zn-Et}_4\text{NI}$ in THF¹²⁾ gave also $\underline{9a}$ and $\underline{3a}$ in 71.5% and 7% yields.



The molecular models show that the compounds $\underline{1}$, $\underline{2}$ and $\underline{3}$ bear fairly rigid, propeller-like structure shown below, because aryl substituents lie parallel to one another at a distance of 3-3.5 Å. In accordance with these expectations, $^1\text{H-NMR}$ spectra of $\underline{1}$, $\underline{2}$ and $\underline{3}$ show upper-field shifts of aryl protons due to the shielding effect of the closely situated neighboring benzene rings.

Further experiments are in progress to introduce benzene rings having functional groups, in order to investigate the electronic interactions among the substituted benzene rings in $\underline{1}$, $\underline{2}$ and $\underline{3}$.



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- 6) All new compounds gave satisfactorily elemental analyses. The spectral data for the new compounds were in accordance with the structure assigned, and only selected data are cited. $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: brown needles, mp 252-255 °C; Mass (m/z) 618 (M^+); 500 MHz $^1\text{H-NMR}$ ($\text{CD}_2\text{Cl}_2\text{-CS}_2$) δ 6.76 (d, 4H, $J=8.0$ Hz, H_b), 6.70 (d, 4H, $J=8.0$, H_g), 6.57 (d, 4H, $J=8.0$, H_a), 6.50 (d, 4H, $J=8.0$, H_h), 6.46 (d, 4H, $J=8.0$, H_e), 6.44 (d, 4H, $J=8.0$, H_d), 2.17 (s, 6H, Me), 2.12 (s, 6H, Me), 2.06 (s, 6H, Me); $^{13}\text{C-NMR}$ ($\text{CD}_2\text{Cl}_2\text{-CS}_2$) δ 156.26 (C-1), 143.61 (C-3,4), 143.28 (C-6), 139.39, 138.36, 135.05, 134.77 (C-2,5), 134.64, 133.48, 133.43, 133.23, 131.25, 130.68, 127.71, 127.52, 127.49, 21.23, 21.14, 20.98; UV $\lambda_{\text{max}}^{\text{THF}}$ (log ϵ) 263 (4.55), 393.5 (4.37) nm; $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: brown needles, mp 257.5-260.0 °C; Mass (m/z) 590 (M^+); $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: brown prisms, mp 273-274.5 °C; Mass (m/z) 562 (M^+); $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: pale yellow needles, mp 245-246 °C; Mass (m/z) 534 (M^+); 500 MHz $^1\text{H-NMR}$ (CDCl_3) δ 7.03-6.96 (m, 16H), 6.84-6.78 (m, 6H), 6.73 (t, 4H, $J=8.0$, H_e), 6.55 (d, 4H, $J=8.0$, H_g); $^{13}\text{C-NMR}$ (CDCl_3) δ 154.64 (C-3,4), 141.58, 141.33, 140.28 (C-1,2), 132.94 (C-5,6), 131.69, 131.38, 129.90, 127.99, 127.10, 127.02, 126.99, 126.87, 126.73, 126.36; UV $\lambda_{\text{max}}^{\text{THF}}$ (log ϵ) 250 (4.56), 315.5 (4.65) nm; $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: pale yellow prisms, mp 258.5-259.5 °C, Mass (m/z) 618 (M^+); 500 MHz $^1\text{H-NMR}$ (CDCl_3) δ 6.85 (d, 4H, $J=8.0$, H_a), 6.81 (d, 4H, $J=8.0$, H_d), 6.72 (d, 4H, $J=8.0$, H_b), 6.63 (d, 4H, $J=8.0$, H_h), 6.50 (d, 4H, $J=8.0$, H_e), 6.42 (d, 4H, $J=8.0$, H_g), 2.20 (s, 6H, Me), 2.18 (s, 6H, Me), 2.12 (s, 6H, Me); $^{13}\text{C-NMR}$ (CDCl_3) δ 153.84 (C-3,4), 140.02 (C-1,2), 129.05 (C-5,6); UV $\lambda_{\text{max}}^{\text{THF}}$ (log ϵ) 257.5 (4.59), 321.5 (4.69); $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: pale yellow prisms, mp 234-235.5 °C, Mass (m/z) 590 (M^+); $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: colorless prisms, mp 173-174.5 °C (decomp.), Mass (m/z) 534 (M^+); $\overset{\sim}{\underset{\sim}{\text{C}}}\text{C}$: colorless prisms, mp 150.5-151 °C (decomp.).
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