# Synthesis of 3-(4-Cyclopentene-1,3-dione-2-ylidene)-6-(diphenyl-methylene)cyclohexadienes as Novel p-Quinodimethanes Stabilized by Antiaromaticity of Cyclopentadienone

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Title compounds, whose polarization is decreased by antiaroma-ticity of cyclopentadienone, have been synthesized through a novel Rh(II)-catalyzed arylation of cyclic 2-diazo-1,3-diones.

p-Quinodimethanes (3,6-dimethylene-1,4-cyclohexadienes) are intriguing mole-cules from both synthetic and physicochemical points of view. Simple p-quinodi-methanes, especially the parent compound $\underset{\sim}{1}$, are highly reactive species and have been used for the synthesis of [2.2]-paracyclophanes.[1] 7,7,8,8-Tetracyano-p-quinodimethanes ($\underset{\sim}{2}$) and the related compounds show high electron affinity and have been extensively studied as electron acceptors for electron-conducting charge-transfer complexes.[2] These properties are greatly due to the tendency of central six-membered ring to attain aromatic benzene structure. Because of this tendency, when substituents are introduced unsymmetrically at the terminal methylene carbons (i.e. X $\neq$ Y in $\underset{\sim}{A}$-$\underset{\sim}{C}$), polarization of the molecules is amplified by favorable reso-nance contribution of the dipolar structure $\underset{\sim}{C}$. The amplification is so effective that such a molecule as $\underset{\sim}{3}$[3] reversibly oligomerizes in solutions, preventing its isolation.[4] If a cyclic conjugated system that forms a 4π electron antiaromatic system in the dipolar structure $\underset{\sim}{C}$ constitutes one of the terminals, it will coun-teract polarization and in consequence contribute to stabilization of the molecule. We here describe the facile synthesis of such kind of molecules, the title com-pounds, involving a novel Rh(II)-catalyzed arylation of cyclic 2-diazo-1,3-diones.

$\underset{\sim}{1}$: X=Y=H

$\underset{\sim}{2}$: X=Y=CN

$\underset{\sim}{3}$: X=CN, CY$_2$=cycloheptatri-enylidene
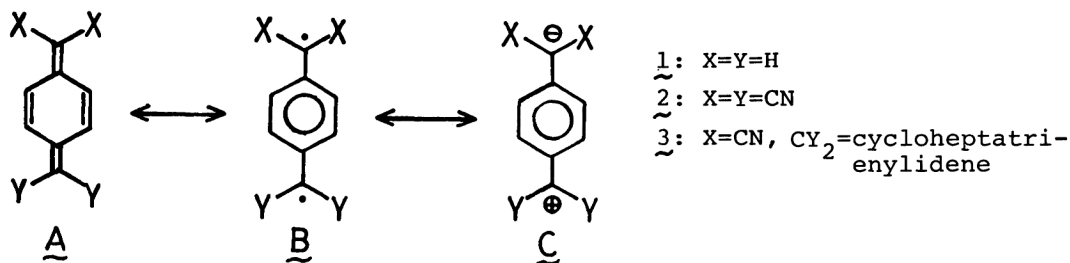
As a key reaction for the construction of carbon skeleton of the title com-pounds, we have found an effective 2-arylation of cyclic 1,3-diones through Rh(II)-catalyzed reaction of 2-diazo-1,3-diones with benzenoid aromatic compounds.[5] For example, when a benzene solution of 2-diazoindane-1,3-dione ($\underset{\sim}{4}$) was heated at reflux for 1.5 h in the presence of a catalytic amount of $Rh_2(OAc)_4$, nitrogen was

evolved smoothly and 2-phenylindane-1,3-dione (5) was obtained in 81% yield. This arylation reaction was also successful for other electron-rich benzene derivatives with predominant para-orientation.[6]

Similar reaction of ethoxytriphenylmethane (6) with 4 afforded only the para-substituted product 7, probably owing to steric effects, in 76% yield after chromatography on silica gel. The results with several 2-diazo-1,3-diones are given in Table 1, where the isolated products varies in type depending on the properties of 1,3-dione moieties:[7] the quinodimethane 15, an elimination product, was obtained from the diazodiketone 8; the triphenylcarbinols 11 and 12, hydrolyzed products, from 9 and 10, respectively after chromatographic purification.[8] While the diketoether 7 exists preferably in the keto-form as 5 does because of anti-aromatic property of indenone, 11 and 12 take the enol-forms which are responsible for the ready hydrolysis by stabilizing the triphenylmethyl cation intermediates.[9]
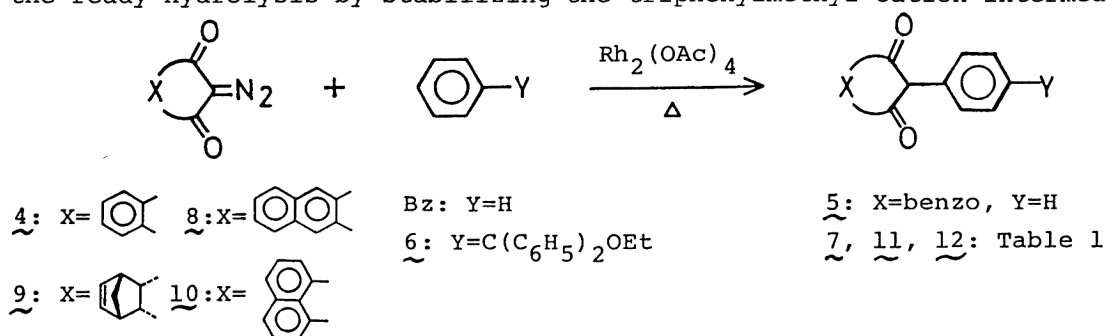

Table 1. Rh(II)-Catalyzed reactions of 2-diazo-1,3-diones with ethoxytriphenylmethane [a]

2-Diazo-1,3-dione	Temp/°C	Time/h	Product [b]	Yield/%
4	110	1.5	7 [c]	76
8	110	1.5	15	39
9	110	1.5	11 [d]	52
10	100	0.5	12 [d]	25

a) Performed at neat mixtures using 5-7 equiv. of ethoxytriphenylmethane. b) After chromatography on silica gel. c) Purplish tinged solid due to a slight contamination with 14. d) Colorless solid decomposing (dehydration) above ca. 150 °C.

These products are sensitive to acids: $\underset{\sim}{7}$ turns deep green on dissolution in CH_2Cl_2-CF_3COOH (4:1 v/v), from which the quinodimethane $\underset{\sim}{14}$[10] was obtained as dark purple crystals in 54% yield after removal of solvents and recrystallizations. The carbinols $\underset{\sim}{11}$ and $\underset{\sim}{12}$ also showed similar color change, but in these cases attempts to isolate the corresponding quinodimethanes $\underset{\sim}{16}$ and $\underset{\sim}{17}$ in similar way were unsuccessful because of their ready hydration reaction back to the carbinols in solutions. However, nearly pure $\underset{\sim}{16}$ and $\underset{\sim}{17}$ were obtained by thermal dehydration of $\underset{\sim}{11}$ and $\underset{\sim}{12}$ at about 150 °C in vacuo. The carbinol $\underset{\sim}{11}$ is a good precursor to the non-annulated quinodimethane $\underset{\sim}{13}$: refluxing a solution of $\underset{\sim}{11}$ and N-phenylmaleimide (1.0 equiv., for removal of liberated cyclopentadiene as a Diels-Alder adduct) in $\underline{o}$-dichlorobenzene for 2 h afforded $\underset{\sim}{13}$[10] in 40% yield.
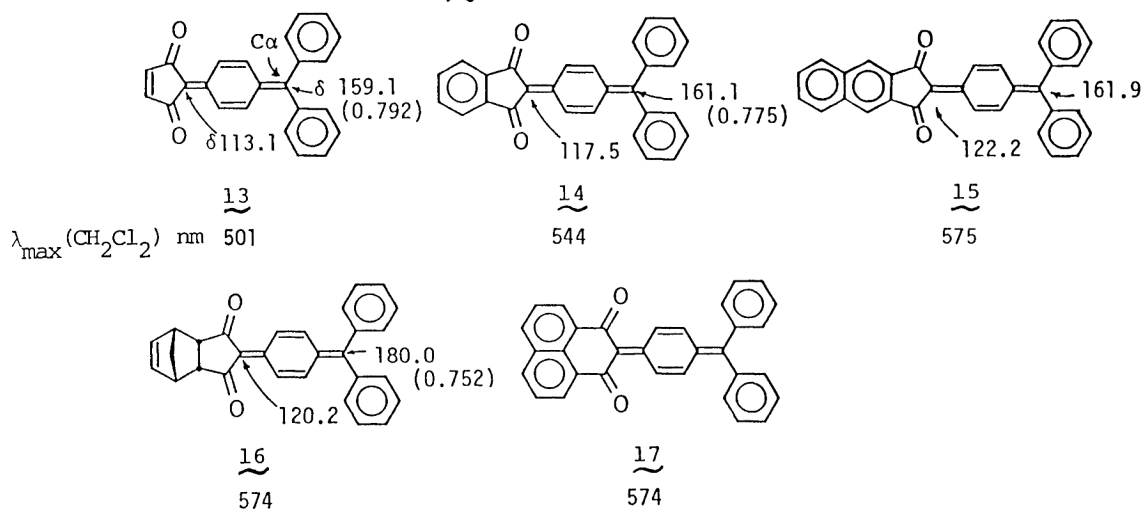

Fig. 1. Selected ^{13}C-NMR and UV-Vis spectral data, and calculated electron density of $\underset{\sim}{13\text{-}17}$.

The five quinodimethanes here synthesized can be classified into two groups in respect to their stability: $\underset{\sim}{13}$, $\underset{\sim}{14}$, and $\underset{\sim}{15}$ are fairly stable in the quinodimethane forms, while $\underset{\sim}{16}$ and $\underset{\sim}{17}$ are unstable and readily undergo hydration. This grouping seems to relate intimately to the degree of polarization of the molecules as seen in their ^{13}C-NMR chemical shifts (Fig. 1): C_αs of $\underset{\sim}{13\text{-}16}$ resonate down-field in the order of $\underset{\sim}{16} \gg \underset{\sim}{15} \rangle \underset{\sim}{14} \rangle \underset{\sim}{13}$, indicating considerably greater resonance contribution of the dipolar structure $\underset{\sim}{C}$ in $\underset{\sim}{16}$ relative to that in $\underset{\sim}{13\text{-}15}$. This trend is consistent with the calculated electron density on C_α by Hückel MO calculation (the values in parentheses in Fig. 1). Accordingly, the decreased polarization of $\underset{\sim}{13\text{-}15}$ compared with $\underset{\sim}{16}$ is ascribable to antiaromatic destabilization of a cyclopentadienone structure. The greater polarization of $\underset{\sim}{14}$ (or $\underset{\sim}{15}$) than $\underset{\sim}{13}$ is in line with the smaller antiaromatic destabilization of indenone than cyclopentadienone.

The UV-Vis spectra of $\underset{\sim}{13\text{-}17}$ show a broad and strong absorption in visible region and display appreciable solvatochromism (e.g. Fig. 2 for $\underset{\sim}{14}$). The visible absorption of $\underset{\sim}{14}$ (also $\underset{\sim}{13}$ and $\underset{\sim}{15}$) red-shifts in polar solvents in consonant with the decreased polarization of the molecule in the ground state. Some highly polar quinodimethanes have been reported to show reversed solvent effects.[4] In acidic solutions, $\underset{\sim}{14}$ is reversibly protonated at one of the carbonyl groups to form the triphenylmethyl cation $\underset{\sim}{18}$ which is responsible for the green coloration (Fig. 2).

    In summary, novel, physicochemically interesting quinodimethanes were prepared
in short steps through Rh(II)-catalyzed reactions of 2-diazo-1,3-diones with
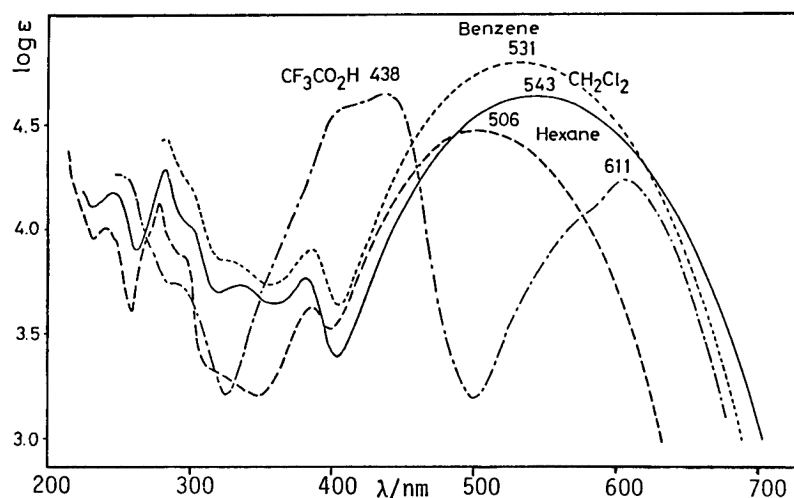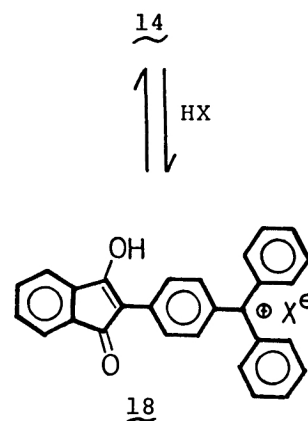ethoxytriphenylmethane.

Fig. 2. UV-Vis spectra of 14 in various solvents.

References

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   New York (1983), Vols. I and II.

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   Gillson, J. Am. Chem. Soc., 98, 3916 (1976).

3) K. Takahashi, N. Hirata, and K. Takase, Tetrahedron Lett., 1970, 1285.

4) A recent review for related compounds: K. Takahashi, Yuki Gosei Kagaku Kyokai
   Shi, 44, 806 (1986).

5) For alkylation of benzene with α-diazoketones via cycloheptatrienyl interme-
   diates, see M. A. McKervey, D. N. Russell, and M. F. Twohig, J. Chem. Soc.,
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6) The substituent effects on the reaction rate suggest an addition-isomerization
   mechanism (i.e. intermediacy of a norcaradiene) rather than an electrophilic
   substitution mechanism, though no intermediates were detected under the
   reaction conditions. The details will be reported elsewhere.

7) Reasonable spectral and/or analytical data were obtained for the new compounds
   other than 13, 14, and 15 whose spectral data are given in Figs. 1 and 2, and
   Ref. 10.

8) Rapid elution from a short silica gel column gave the unhydrolyzed product as
   a major component.

9) ^{1}H-NMR spectrum of 7 in $CDCl_3$ shows a singlet signal of the aliphatic methine
   proton at δ 4.17, whereas 11 and 12 do not show such a singlet.

10) 13: mp 151 °C; ^{1}H-NMR ($CDCl_3$), δ 6.97 (2H, s), 7.15-7.55 (12H, m), 8.40 (2H, d,
    J=10 Hz); ^{13}C-NMR ($CDCl_3$), δ 113.06, 125.14, 128.20, 130.18, 132.56, 132.67,
    137.79, 140.34, 144.81, 145.54, 149.08, 196.22. 14: mp 235 °C; ^{1}H-NMR ($CDCl_3$),
    δ 7.1-7.6 (12H, m), 7.6-8.0 (4H, m), 8.75 (2H, d, J=10 Hz). 15: mp 213 °C;
    ^{1}H-NMR ($CDCl_3$), δ 7.2-8.2 (16H, m), 8.34 (2H, m), 8.93 (2H, d, J=10 Hz).