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

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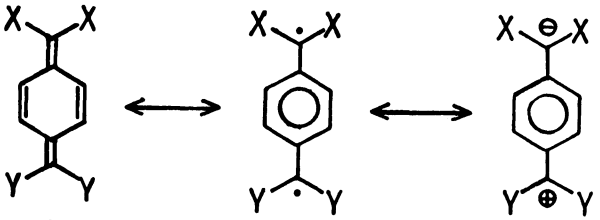
Title compounds, whose polarization is decreased by antiaromaticity of cyclopentadienone, have been synthesized through a novel Rh(II)-catalyzed arylation of cyclic 2-diazo-1,3-diones.

p-Quinodimethanes (3,6-dimethylene-1,4-cyclohexadienes) are intriguing molecules from both synthetic and physicochemical points of view. Simple p-quinodimethanes, especially the parent compound 1, are highly reactive species and have been used for the synthesis of [2.2]-paracyclophanes.$^{1)}$ 7,7,8,8-Tetracyano-p-quinodimethanes (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 A-C), polarization of the molecules is amplified by favorable resonance contribution of the dipolar structure C. The amplification is so effective that such a molecule as 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 C constitutes one of the terminals, it will counteract polarization and in consequence contribute to stabilization of the molecule. We here describe the facile synthesis of such kind of molecules, the title compounds, involving a novel Rh(II)-catalyzed arylation of cyclic 2-diazo-1,3-diones.

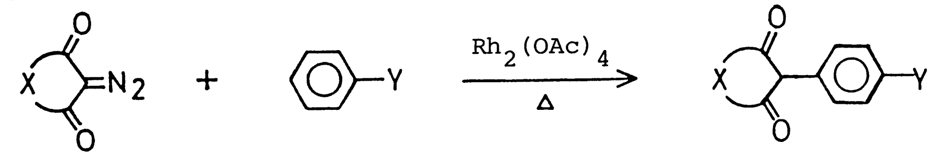


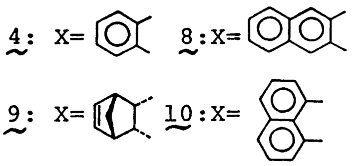
A B C

1: X=Y=H
2: X=Y=CN
3: X=CN, CY_2=cycloheptatrienylidene

As a key reaction for the construction of carbon skeleton of the title compounds, 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 (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)





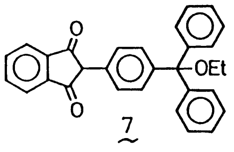
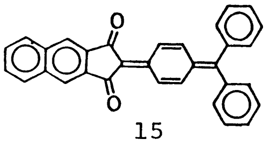
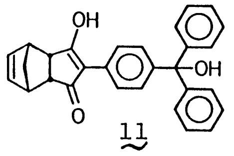
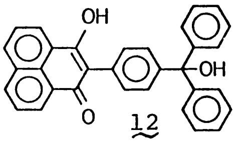
Bz: Y=H

6: Y=$C(C_6H_5)_2OEt$

5: X=benzo, Y=H

7, 11, 12: Table 1

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	 c) 7	76
8	110	1.5	 15	39
9	110	1.5	 d) 11	52
10	100	0.5	 d) 12	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: 7 turns deep green on dissolution in CH_2Cl_2-CF_3COOH (4:1 v/v), from which the quinodimethane 14[10)] was obtained as dark purple crystals in 54% yield after removal of solvents and recrystallizations. The carbinols 11 and 12 also showed similar color change, but in these cases attempts to isolate the corresponding quinodimethanes 16 and 17 in similar way were unsuccessful because of their ready hydration reaction back to the carbinols in solutions. However, nearly pure 16 and 17 were obtained by thermal dehydration of 11 and 12 at about 150 °C in vacuo. The carbinol 11 is a good precursor to the non-annulated quinodimethane 13: refluxing a solution of 11 and N-phenylmaleimide (1.0 equiv., for removal of liberated cyclopentadiene as a Diels-Alder adduct) in o-dichlorobenzene for 2 h afforded 13[10)] in 40% yield.

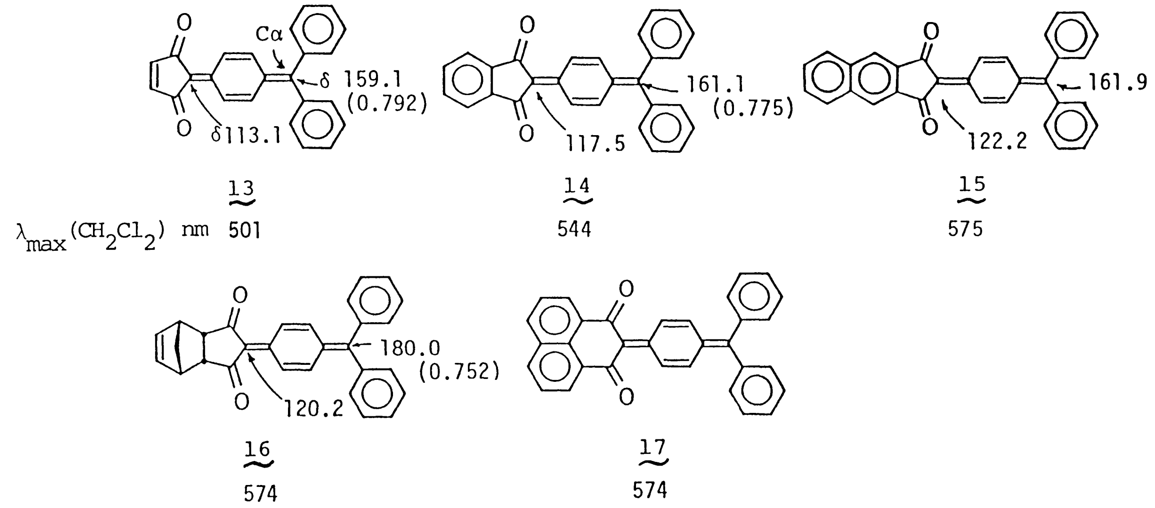


Fig. 1. Selected ^{13}C-NMR and UV-Vis spectral data, and calculated electron density of 13-17.

The five quinodimethanes here synthesized can be classified into two groups in respect to their stability: 13, 14, and 15 are fairly stable in the quinodimethane forms, while 16 and 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 13-16 resonate down-field in the order of 16 $\gg$ 15 $>$ 14 $>$ 13, indicating considerably greater resonance contribution of the dipolar structure C in 16 relative to that in 13-15. 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 13-15 compared with 16 is ascribable to antiaromatic destabilization of a cyclopentadienone structure. The greater polarization of 14 (or 15) than 13 is in line with the smaller antiaromatic destabilization of indenone than cyclopentadienone.

The UV-Vis spectra of 13-17 show a broad and strong absorption in visible region and display appreciable solvatochromism (e.g. Fig. 2 for 14). The visible absorption of 14 (also 13 and 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, 14 is reversibly protonated at one of the carbonyl groups to form the triphenylmethyl cation 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.

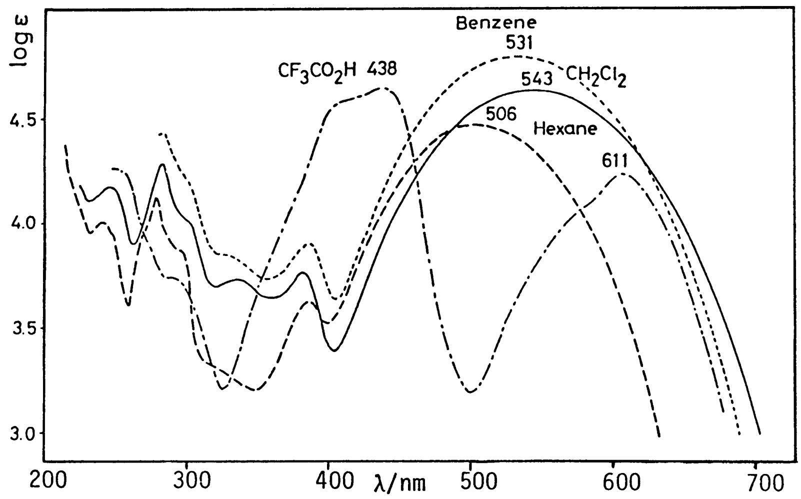


Fig. 2. UV-Vis spectra of 14 in various solvents.

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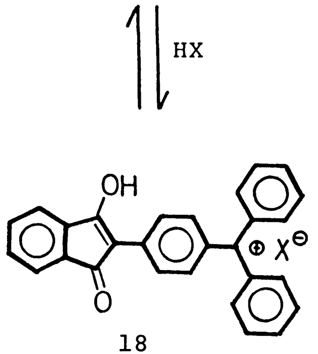

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6) The substituent effects on the reaction rate suggest an addition-isomerization mechanism (i.e. intermediacy of a norcaradiene) rather than an electrophilic substitution mechanism, though no intermediates were detected under the reaction conditions. 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).

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