before[16] that monoazo dye molecules seem to be under rather little control by serum albumin, even when they are bound to it. It is as if the protein cannot really grip them strongly; but with larger substrates, long chain aliphatics and disazobenzene dyes, the interaction is strong enough to affect a number of events beyond the simple binding step.

Experimental Section

The full names of the dyes (abbreviated in Table I) and their source are as follows: *N,N*-dimethyl-*p*-phenylazoaniline (DMAA), *p*-(*p*-dimethylaminophenylazo)benzoic acid (PMR), *o*-(*p*-dimethylaminophenylazo)benzoic acid (OMR), *p*-(*p*-dimethylaminophenylazo)benzenesulfonate (MO), *p*-(*p*-dibutylaminophenylazo)benzenesulfonate (BO), 4-phenylazoaniline (AAB), *N,N*-dimethyl-4,4′-azodianiline (ADAB), and 4-phenylazo-1-naphthylamine (**PAN**) were all purchased from Eastman Co. as the sodium salts, and recrystallized from ethanol–water. The dyes ethyl orange and propyl orange {*p*-(*p*-diethylaminophenylazo)benzenesulfonate and *p*-(*p*-dipropylaminophenylazo)benzenesulfonate} were synthesized by coupling sulfanilic acid with the appropriate *N,N*-dialkylaniline, and chromatographing on silica gel to isolate the pure dyes.

The source and general techniques for handling the proteins were much the same as before,[16] in which we started by deionizing the bovine serum albumin (recrystallized fraction V). The photochromism investigations also used previous methods,[6] except that a Cary 14 was used, and the data were computer fitted. The lower (4°) temperatures were achieved by water jacketing all surfaces with which the absorption cells were in contact both during irradiation and spectrophotometry, plus impinging cold nitrogen across the cell faces in both stages. Temperatures were measured by immersing an Anschutz thermometer directly into the cell contents at the end of each run. The 4° pH measurements were calibrated by standard 0.05 *M* inorganic phosphate buffer (pH 6.98) and 0.05 *M* carbonate buffer (pH 10.22).

(16) R. Lovrien and T. Linn, *Biochemistry*, **6**, 2281 (1967).

Communications to the Editor

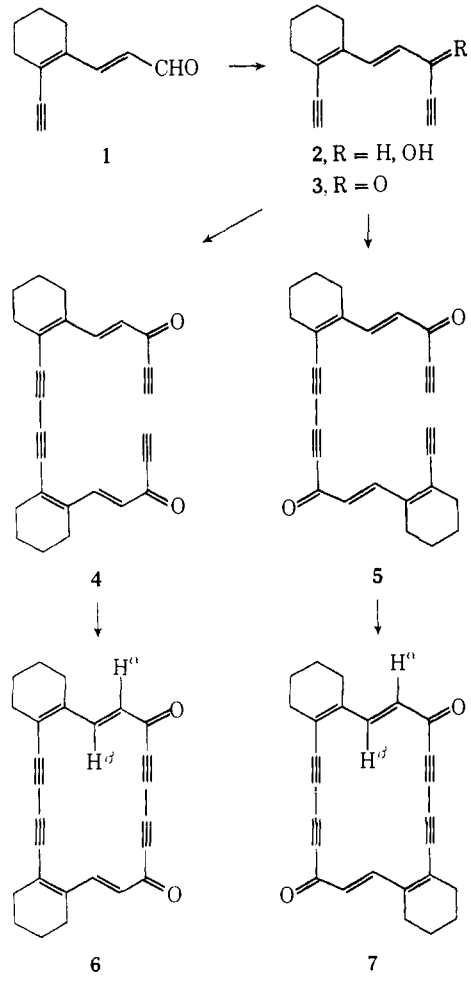
Synthesis of Alkylated Cyclooctadecatetraenetetrayne-1,6-diones and 1,10-diones (Tetradehydro[18]annulenediones)[1]

Sir:

We have recently described[2] a synthesis of the tetraalkylated tetradehydro[18]annulene-1,6-dione (**6**), but no determination was made as to whether it possessed quinonoid character. We have now synthesized the related tetraalkylated tetradehydro[18]annulene-1,10-dione (**7**), as well as the dialkylated tetradehydro[18]-annulene-1,6-dione (**11**) and -1,10-dione (**12**). The electrochemistry of these diketones has been investigated by Breslow, *et al.*,[3] as described in the following communication, and evidence for the quinonoid nature of **6**, **11**, and **12** has been obtained.

The aldehyde **1** has been prepared[4] in 45% yield by homologation of 2-ethynyl-1-cyclohexenecarboxaldehyde, and the yield has now been increased to 60–65% by careful attention to reaction conditions.[5] Treatment of **1** with 1.4 mol equiv of ethynylmagnesium bromide[6] in tetrahydrofuran for 16 hr at room temperature gave 85–90% of **2** (mp 62–63°),[7] which was oxidized to **3** (mp 59–60°)[7] in 80–85% yield with manganese dioxide[8] in ether for 30 min at room temperature.

Oxidative coupling of **3** with oxygen, cuprous chloride, ammonium chloride, and concentrated hydrochloric acid in aqueous ethanol and benzene ("Glaser conditions")[9] for 2 hr at 60–65°, followed by chromatography on silica gel (Woelm, activity III), led mainly to the diketones **4** (30% yield) and **5** (30% yield, yellow



(1) Unsaturated Macrocyclic Compounds. 102. For part 101, see P. J. Beeby and F. Sondheimer, *Angew. Chem.*, **85**, 406 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 411 (1973).

(2) K. Yamamoto and F. Sondheimer, *Angew. Chem.*, **85**, 41 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 68 (1973).

(3) R. Breslow, D. Murayama, R. Drury, and F. Sondheimer, *J. Amer. Chem. Soc.*, **96**, 249 (1974).

(4) R. H. McGirk and F. Sondheimer, *Angew. Chem.*, **84**, 897 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 834 (1972).

(5) R. H. McGirk, private communication.

(6) E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syn.*, **39**, 56 (1959).

(7) Uv, ir, and ^{1}H nmr spectra compatible with the assigned structures were obtained for all new compounds.

(8) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(9) See G. Eglinton and W. McCrae, *Advan. Org. Chem.*, **4**, 225 (1963).

Table I. ^{1}H Nmr parameters (τ Values) of **6**, **7**, **11**, and **12** at 60 MHz (Internal Standard, TMS)

Compd	H^α	H^β	H^γ	Allylic CH_2	Nonallylic CH_2	CH_3
6 ($CDCl_3$)	3.82 (d)[a]	0.94 (d)[a]		7.7 (m)	8.3 (m)	
6 (CF_3COOD)	3.63 (d)[a]	0.07 (d)[a]		7.7 (m)	8.2 (m)	
7 ($CDCl_3$)[b]	3.84 (d)[a]	1.06 (d)[a]		7.7 (m)	8.3 (m)	
7 (CF_3COOD)	3.57 (d)[a]	0.13 (d)[a]		7.6 (m)	8.2 (m)	
11 ($CDCl_3$)	3.87 (d)[a]	1.17 (d of d)[c]	3.47 (d)[d]			7.97 (s)
11 (CF_3COOD)	3.70 (d)[a]	0.30 (d of d)[c]	3.43 (d)[d]			7.99 (s)
12 (CF_3COOD)[e]	3.67 (d)[a]	0.37 (d of d)[c]	3.30 (d)[d]			7.93 (s)

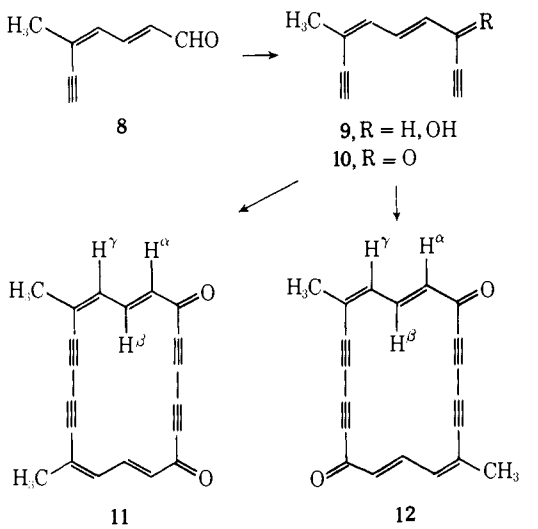
[a] J = 16 Hz. [b] The spectrum of **7** in $CDCl_3$ was determined on a Bruker HFX-90 instrument (90 MHz, fast Fourier transform, 2000 scans), due to its low solubility in this solvent. [c] J = 16, 12 Hz. [d] J = 12 Hz. [e] The spectrum of **12** in $CDCl_3$ was not determined, due to its low solubility in this solvent.

crystals,[7,10] eluted before **4**). Substance **4** was identical with that obtained by an unambiguous route,[2] and could be further coupled under "Glaser conditions" (2 hr at 65°) to give the previously described[2] bright red 1,6-dione **6**[11] in 50% yield. On the other hand, the isomeric diketone **5** could not be coupled under "Glaser conditions" and decomposed under "Eglinton conditions" (cupric acetate in pyridine).[9] However, coupling of **5** with oxygen, cuprous chloride, and *N,N,N′,N′*-tetramethylenediamine in acetone ("Hay conditions")[12] for 2 hr at 30°, followed by repeated filtration through silicic acid, gave 30% of the 1,10-dione **7** as sparingly soluble bright yellow needles:[10] *m/e* 364; λ_{max} ($CHCl_3$) 272 sh (ϵ 21,400), 287 (28,800), 304 (30,800), 329 sh (24,700), 346 (27,900), 367 nm (27,600), with absorption at >500 nm; ν_{max} (KBr) 2210 (m), 2140 (w) (C≡C), 1620 (s) (C=O) cm^{-1}.

The starting material for the synthesis of the diketones **11** and **12** was *cis*-3-methyl-2-penten-4-ynal,[13] which was homologated to the liquid aldehyde **8**[7,14] in 70% yield by the method used for the synthesis of **1**. Substance **8** was then converted to the ketone **10** (mp 76–77.5°)[7] *via* the alcohol **9** in 55% overall yield, as described for the transformation of **1** to **3**. Finally, coupling of **10** under "Glaser conditions" for 2 hr at 60° directly led to the diketones **11** and **12**.

The relatively soluble diketone **11** was removed from the reaction residue by trituration with chloroform. Chromatography on silica gel yielded 13% of **11** as orange needles:[10] *m/e* 284; λ_{max} ($CHCl_3$) 279 sh (ϵ 27,100), 298 sh (27,600), 316 (53,500), 328 (48,400), 448 nm (3800), with absorption at >550 nm; ν_{max} (Nujol) 2220 (w), 2160 (m) (C≡C), 1625 (s) (C=O) cm^{-1}. The very insoluble diketone **12** remaining in the reaction residue was taken up in a large volume of chloroform. Purification by repeated filtration through silicic acid gave 5% of **12** as yellow needles:[10] *m/e* 284; λ_{max} ($CHCl_3$) 269 sh (ϵ 22,800), 284 (34,700), 300 (44,900), 333 sh (36,900), 343 (38,000), 361 nm (32,900), with absorption at >500 nm; ν_{max} (Nujol) 2220 (m), 2160 (w) (C≡C), 1625 (s) (C=O) cm^{-1}.

The tetradehydro[18]annulenediones **6**, **7**, **11**, and **12** dissolved in CF_3COOH to form highly colored solutions: longest wavelength λ_{max} **6**, 510 nm; **7**, 454 sh nm; **11**, 488 nm; **12**, 450 sh nm. The ^{1}H nmr spectra of **6**, **7**, **11**, and **12** in $CDCl_3$ and CF_3COOD are given in Table I. They confirm the structures of these diketones and give no indication of any appreciable ring current. The relative structural assignments of **11** and **12** follow unequivocally from the correspondence of the electronic spectrum of **11** with that of **6**[11] and of **12** with that of **7**. The assignments of **11** and **12** are confirmed by their colors and relative solubilities, and the correspondence of the ir spectra in several respects with those of **6** and **7**, respectively.



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(10) The substance decomposed on attempted melting point determination.

(11) For comparison with **7**, **11**, and **12**, the electronic spectrum of **6** was determined in chloroform: λ_{max} 277 (ϵ 16,800), 296 (22,900), 315 (31,200), 336 (30,200), 464 nm (3000), with absorption >550 nm.

(12) See A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962).

(13) E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 937 (1946); I. M. Heilbron, E. R. H. Jones, and M. Julia, *ibid.*, 1430 (1949).

(14) The synthesis of **8** was carried out by Dr. J. Ojima, and we thank him for providing a sample.

Electrochemistry of Some Tetradehydro[18]annulenediones

Sir:

Recently several tetradehydro[18]annulenediones have been prepared.[1,2] These can be considered to be quinones related to the corresponding tetradehydro[18]annulene[3] in the same way that benzoquinone is related to benzene. Since the reduction potentials

(1) K. Yamamoto and F. Sondheimer, *Angew. Chem.*, **85**, 41 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 68 (1973).

(2) N. Darby, K. Yamamoto, and F. Sondheimer, *J. Amer. Chem. Soc.*, **96**, 248 (1974).

(3) T. Nomoto, K. Fukui, and M. Nakagawa, *Tetrahedron Lett.*, 3253 (1972).