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(3) The sulfonates were prepared by alkylation, with methyl trifluoromethanesulfonate, of the corresponding dimethylaminobenzenesulfonic esters. These in turn were prepared from the appropriate alcohols and *p*-dimethylaminobenzenesulfonyl chloride in pyridine.

(4) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967.

(5) The cmc's at 25° for Ia and Ic (measured by surface-tension techniques) are 0.9×10^{-2} and 1.2×10^{-2} *M,* respectively; Ib is too reactive for a cmc measurement at 25°, but its cmc is presumably in the same range.

(6) See, for example, R. E. Robertson, *Can. J. Chem.,* **31,** 589 (1953).

(7) Prepared using (+)-2-octanol ($[\alpha]^{25}\mathrm{D}$ 8.99° ($CHCl_3$)) obtained from Norse Laboratories, Inc.

(8) See, for example, (a) A. Ochoa-Solano, G. Romero, and C. Gitler, *Science,* **156,** 1243 (1967); (b) J. P. Guthrie, *J. Chem. Soc., Chem. Commun.,* 897 (1972); (c) J. R. Knowles and C. A. Parsons, *Nature* (*London*), **221,** 53 (1969); (d) C. A. Blyth and J. R. Knowles, *J. Amer. Chem. Soc.,* **93.** 3017 (1971); (e) C. Gitler and A. Ochoa-Solano, *ibid.,* **90.** 5004 (1968); (f) T. E. Wagner, C. Hsu, and C. S. Pratt, *ibid.,* **89,** 6366 (1967).

(9) There are a few physical studies in the literature concerning the binding of hydrophobic, negatively charged dye molecules to cationic micelles (see R. L. Reeves, R. S. Kaiser, and H. W. Mark, *J. Colloid Interface Sci.,* **45,** 396 (1973), and references cited there). These results indicate that mixed aggregates of varying size form over a wide concentration range, even below the cmc of pure surfactant. Molecules of I and SLS probably aggregate at low concentrations also; however, our results indicate that aggregates must be at or above a certain critical size (which corresponds to a "kinetic" cmc for the surfactant molecules) in order to induce the chemical effects observed here.

(10) 8.3×10^{-3} M; *cf.* ref 5.

(11) Moss and coworkers (ref 2f) have observed that cationic micelles *do* affect the rate of 2-octylamine deamination, but alter the stereochemistry only in the presence of "hydrophobic" counterions such as ClO_4^-. Formation of "less aqueous micelles" resulting from strong binding of the poorly hydrated counterions was invoked to explain this; a prediction was made that the ClO_4^- effect might be too weak to perturb the stereochemistry of solvolytic displacement reactions. We have found that the presence of ClO_4^- does not, in fact, alter the inability of cationic micelles to change the rate and stereochemistry of the reactions studied here. However, one can think of SLS molecules (applying the Moss terminology) as extremely hydrophobic "counterions" which bind much *more* strongly to *micelles* (and *exclude more water*) than does ClO_4^- Thus there is a certain analogy between Moss' observations and those observed here under conditions where $[\mathrm{SLS}] \simeq [\mathrm{I}]$. Our effect has no counterpart, however, in the micellar effect on rates of deamination reactions (which are accelerated by cationic micelles, even in the presence of ClO_4^-), or under conditions of high anion/substrate ratio ([substrate] < cmc), where the ClO_4^- amine deamination effect disappears but the SLS solvolytic displacement effect persists.)

(12) We cannot rigorously determine, using data presently in hand, whether or not the tight binding of SLS to micelles formed from I results in an actual covalent intermediate; *i.e.,* whether the retention component arises from a "double displacement" process involving a neutral dialkyl sulfate intermediate. However, we believe it unlikely that double displacement would result in the sort of saturation effect observed here; the reasons are basically those outlined by Moss and coworkers in ref 2f. In any case, experiments are under way aimed at resolving this question.

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Synthesis of a 1,5-Naphthoquinone

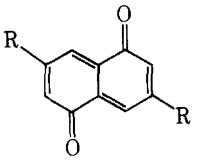
Sir:

We wish to report the synthesis of an unequivocal 1,5-naphthoquinone, the 3,7-di-*tert*-butyl-1,5-naphthoquinone (**1a**). Of the three possible extended naphthoquinones, **1–3**, only **2** was known.[1] The synthesis of **1** seemed of interest with respect to the structure of naphthazarin (1,4- *vs.* 1,5-quinoid)[2-4] and to recent calculations on quinones.[5,6]

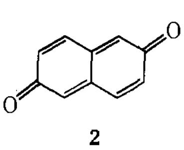
Table I. Calculated[15] Electron Affinities ($-E_A$) (eV) of Naphthoquinones

	Naphthoquinone					
	1,2-	1,4-	1,5-	1,7-	2,6-	2,3-
$-E_A$	2.98	3.09	3.62	3.61	3.75	3.66

Attempts to prepare **1** electrochemically[7] or under conditions suitable for the preparation of **2** failed,[8] indicating the higher reactivity of **1.** Oxidation experiments of 1,5-dihydroxynaphthalene with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dioxane or lead tetraacetate in acetic acid carried out in our laboratories yielded brown amorphous substances and no compound with the tentative properties (uv, reduction) of **1.**



1, R = H
1a, R = *t*-Bu



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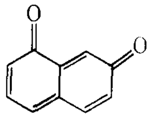


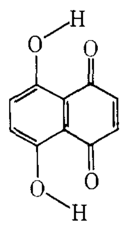
3

In order to decrease the high reactivity of **1** we introduced a shielding group into positions, 3 and 7, namely *tert*-butyl. As is known and has recently been shown by the synthesis of highly reactive ring systems, *e.g.,* pentalene[9] and cyclobutadiene,[10] *tert*-butyl groups exert a high stabilizing effect with only minor changes of the π-electron system.[11]

Dehydrogenation of 1,5-dihydroxy-3,7-di-*tert*-butylnaphthalene by DDQ under nitrogen in methylene chloride yielded in a nearly quantitative reaction after evaporation red crystals of **1a.** The structure follows from the easy reduction to the conjugate hydroquinone and from spectral data: nmr ($CDCl_3$) 1.27 (s, 18 C (CH_3)$_3$), 6.52, 7.67 (2d, 2 × 2, H 2, 6 and H 4, 8, $J \approx 2$ Hz); ir (CCl_4) 2970 (CH_3), 1620 (C=C), 1625 (C=O), 1594 cm^{-1} (C=C); uv$_{max}$ (CCl_4) 475, 462 nm sh; mass spectrum (70 eV) *m/e* (rel intensity) $[M^+ + 2]$ 272 (3), 257 (4), 201 (1). As in other cases[12] the mass spectrum of this quinone shows only a very small peak at the molecular mass (*m/e* 270). The existence of a molecular ion *m/e* (found) 270.1614, (calcd for $C_{18}H_{22}O_2$ 270.1619) could be shown by high resolution mass spectrometry,[13] tlc R_F ($CHCl_3$, silica gel) 0.2. **1a** is stable at room temperature under anhydrous conditions, however, with moisture 5-hydroxy-3,7-di-*tert*-butyl-1,4-naphthoquinone is slowly formed.

We have already shown for the anthraquinone series[14] that the calculated energy of the LUMO's (electron affinities)[15,16] seems to be a good measure for the stability[17] of quinones. As can be seen from Table I the easily obtainable naphthoquinones possess E_A values of nearly −3 eV whereas the values of **1–3** are found to be in the range from −3.6 to −3.75 eV. 1,5-Dihydroxy-3,7-di-*tert*-butylnaphthalene (mp 230–232° dec) was prepared by 1,5-dichlorosulfonation[19] of 2,6-di-*tert*-butylnaphthalene (10% yield) followed by fusion with KOH (65%).

1a possesses an unusually low C=O stretching frequency (1625 cm^{-1}, CCl_4) as compared with 1,4-naphthoquinone (1675 cm^{-1}, CCl_4)[20] and other para one-ring quinones (1690–1660 cm^{-1}). This observation can be explained by the extended conjugated π-electron system of **1a,** which correlates to the value of another two-ring quinone, 4,4′-diphenoquinone (1634 cm^{-1}, CCl_4),[20] and is a strong argument against the formulation of naphthazarin in the tautomeric form **5**.[2] With regard to the strong hydrogen bond in naphthazarin,[21] **5** should have a strong shift to lower wave numbers for the C=O vibration compared with **1a**,[22] whereas the observed value for naphthazarin is 1623 cm^{-1} (CCl_4).



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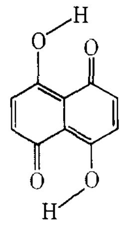

5

A similar conclusion can be drawn from the shift of the $\pi \rightarrow \pi^*$ transition[23] from 1,4-naphthoquinone (λ_{max} ($CHCl_3$) 335 nm (ϵ 3040)) to 5-hydroxy-1,4-naphthoquinone (λ_{max} ($CHCl_3$) 429 nm (ϵ 3800)) and to naphthazarin (λ_{max} ($CHCl_3$) 524 nm (ϵ 6050)). Assuming a shift of a comparable order (90-100 nm/OH) on introducing one hydroxy group in the peri position of **1** the absorption of **5** should occur at much longer wavelengths than observed for naphthazarin.[24]

Further evidence for the structure of naphthazarin as 5,8-dihydroxy-1,4-naphthoquinone follows from the calculated standard heats of formation[15] for **4** ($\Delta H_f° = -99$, 1 kcal/mol) and **5** ($\Delta H_f° = -85$, 1 kcal/mol). Neglecting entropy and solvation effects the value for the equilibrium constant K (25°) = [**5**]/[**4**] should be $K = 4.9 \times 10^{-11}$.[26]

Our results show that former X-ray studies which describe *one* modification of naphthazarin as 1.5-quinoid[3] permit no conclusions to be made as to the structure of naphthazarin in solution.

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(24) A similar bathochromic shift by hydroxy groups in peri position to the quinone carbonyls is observed in the anthraquinone series (9,10-anthraquinone: 321 nm, 1,4-dihydroxy-9,10-anthraquinone: 479 nm).[25] A 1,5-quinoid structure for 1,4-dihydroxy-9,10-anthraquinone can be excluded.[14]
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(26) The ring protons in the nmr spectrum of naphthazarin are all equivalent.[4,27] As one referee pointed out, this fact may be an indication for the existence of **5** as intermediate. This is not excluded by our findings, but also in this case the equilibrium concentration of **5** is governed by the value of *K*.
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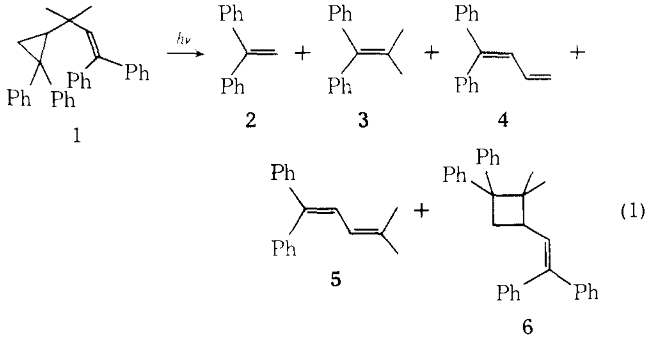
σ–π Interaction. A Cyclopropyl-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

Sir:

One of the most general and synthetically useful of photochemical reactions is the di-π-methane rearrangement.[3] It was therefore of interest to ascertain if the counterpart process in which one π bond is replaced by a three ring will occur.

Presently, (A) we report the photochemistry of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) to afford 1,1-diphenylethylene (**2**), 1,1-diphenylisobutylene (**3**), 1,1-diphenyl-1,3-butadiene (**4**), 1,1-diphenyl-4,4-dimethyl-1,3-butadiene (**5**), and 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane (**6**). (B) We also note evidence that diphenylethylene (**2**) and diphenyldimethylbutadiene (**5**) are primary photoproducts, while diphenylisobutylene (**3**) and diphenylbutadiene (**4**) are secondary. (C) We describe the photochemistry of vinylcyclobutane **6** and give evidence that it is the reaction intermediate leading to diphenylisobutylene (**3**) and diphenylbutadiene (**4**). Interesting regiospecificity is noted. (D) We provide evidence that both steps of the reaction are singlet processes. (E) We give results which exclude 3,3-dimethyl-1,1-diphenyl-1-butenylidene (**7**) as an intermediate. (F) We present a mechanism for formation of the primary products which is precisely parallel to that of the ordinary di-π-methane rearrangement.

Direct irradiation[4] of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) gave five products (**2**, **3**, **4**, **5**, and **6**) as depicted in eq 1.



(1)