anthraquinone is more electrophilic than benzophenone,[18] electron transfer to $^3n,\pi^*$ anthraquinones should be more facile than to $^3n,\pi^*$ benzophenones. Thus, a primary process involving electron transfer from alkylamines to photoexcited **1** or **2** appears reasonable. Since amines bearing no α hydrogen, *e.g.*, *tert*-butylamine, participate in electron-transfer interactions with $^3n,\pi^*$ benzophenones,[17] we would expect ammonia to interact similarly with $^3n,\pi^*$ anthraquinones.

Geminate radical pairs formed by electron transfer (A in Scheme I) could react by several routes.[19] Reversal of electron transfer would result in quenching (eq 2). Adduct formation and elimination of a leaving group would give a substitution product (eq 4 and 5). Separation of geminate radicals by diffusion (eq 3) and subsequent reactions would result in carbonyl reduction and amine oxidation products.[20]

For the reactions of **1** and **2** with ammonia, the major route is adduct formation and elimination leading to the substitution product. Since little absorption due to the anion radical was observed, only a small fraction of geminate radicals undergoes separation. With diethylamine the major route involves separation of geminate radicals with no detectable substitution. A rationale for the different behaviors of ammonia and alkylamines lies in the possibility of α-proton loss from alkylamines (eq 6). Following electron transfer, **3**

$$\mathrm{RCH_2{-}\overset{+}{N}HR'} \longrightarrow \mathrm{H^+ + R\dot{C}HNHR'} \qquad (6)$$

could accept an α proton from the alkylaminium radical. The conjugate acid of **3** and the neutral carbon radical (eq 6) would be expected to associate only weakly allowing the radicals to diffuse apart. Stronger association leading to adduct formation would be expected for geminate radicals **3** and $H_3N\cdot^+$.

Photosubstitution giving 1- or 2-aminoanthraquinone occurs, but in very low yield, when 1- or 2-chloroanthraquinone is irradiated in *tert*-butyl alcohol containing ammonia. In both cases the major reaction forms adducts containing ammonia and *tert*-butyl alcohol derived fragments.

Research is in progress to elucidate further the mechanistic details and generality of these photosubstitution processes.

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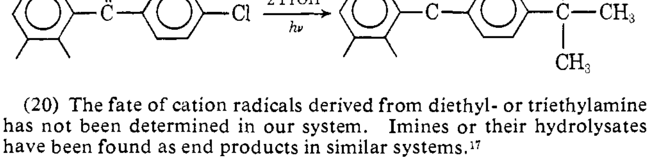
(18) Half-wave reduction potentials of anthraquinone and benzophenone in DMF are −0.33 and −1.22 V: P. H. Given, M. E. Peover, and J. Schoen, *J. Chem. Soc.*, 2674 (1958).

(19) A well-defined instance in which the mechanism of Scheme I appears to operate with a hydrogen atom donor was recently reported by F. A. Lamb and B. M. Vittimberga at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 28, 1972, Abstract No. ORGN-019.



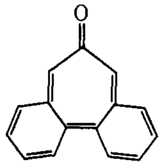
(20) The fate of cation radicals derived from diethyl- or triethylamine has not been determined in our system. Imines or their hydrolysates have been found as end products in similar systems.[17]

(21) National Science Foundation–Undergraduate Research Participant, summer 1970.

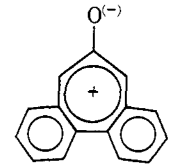
Dibenzo[*c*,*e*]tropone. A New, Potent Six π-Electron Component for Cycloadditions

Sir:

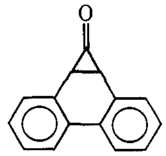
The *o*,*o*′-diphenoquinone moiety of dibenzo[*c*,*e*]tropone (CE) might be expected to make this molecule an exceptionally potent six electron component in cycloadditions, particularly those of the [6 + 4] variety. CE is also potentially capable of existing in a cyclopropanone valence tautomeric form (CE′). The relationship between CE and CE′ is thus essentially that of a Favorskii zwitterion and its corresponding cyclopropanone, a comparison which seems the more relevant in view of the expected high polarity of CE (see CE±). Finally there exists the interesting possibility that the high reactivity of the trienic termini of CE may be partially satisfied by a 1,3 covalent (homoaromatic) interaction. The normal dibenzotropones (*b*,*d* and *b*,*f*) are already well known and the abnormal dibenzotropone BE has recently been trapped by maleic anhydride and its stable conjugate acid prepared.[1] The present communication concerns the generation of CE and its trapping by dienes, the preparation of its relatively stable conjugate acid, and the interception of CE′ by means of a Favorskii-type reaction with methoxide–methanol.



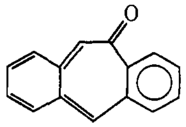
CE



CE±



CE′



BE

The symmetrical dibromide (DBK) of ketone K is readily available,[2] but did not prove a suitable precursor for CE (or CE′). Direct bromination of K is not feasible because of facile dibromination and the chromatographic instability of both the mono- and dibromides. Monobromination of the enol acetate of K (EA) does, however, afford pure monobromide (MBK). Conversion of K to EA required 40 hr of refluxing with isopropenyl acetate–toluenesulfonic acid. Bromination (Br_2) of EA at −78° in methylene chloride–chloroform gave MBK, mp 105–108° dec.[3]

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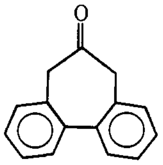
(1) N. L. Bauld and Y. S. Rim, *J. Amer. Chem. Soc.*, **89**, 179 (1967).

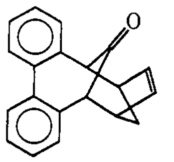
(2) T. L. Gilchrist and C. W. Rees, *J. Chem. Soc. C*, 1973 (1969).

(3) All substances reported as isolated gave satisfactory elemental analyses, nmr, and mass spectral data.

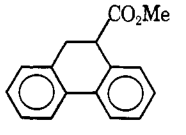
Treatment of MBK with a variety of bases (pyridine, triethylamine, 2,6-di-*tert*-butylpyridine, proton sponge, lithium tetramethylpiperidide) at low and high temperatures failed to give spectral evidence of CE or CE′. Trapping experiments with dienes were more successful, however. Elimination of MBK with triethylamine in methylene chloride containing excess cyclopentadiene yields a 1:1 adduct (A): mp 138°, nmr ($CDCl_3$) τ 2.01–2.11 (m, 2 H), 2.61–2.88 (m, 6 H), 3.77 (s, 2 H), 6.17 (d, J = 3 Hz, 2 H), 6.99 (brs, 2 H), 8.00 (d, J = 12 Hz, 1 H), 8.42–8.68 (m, 1 H); mass spectrum *m/e* 272.1207 (M). The adduct was shown to have exo stereochemistry at a 99.5% confidence level by *R* factor analysis of nmr shifts induced by Eu(fod)$_3$-d_{30}.[4–6] Exo stereochemistry is also found in the tropone–cyclopentadiene [6 + 4] adduct[7,8] and is in accord with theory.[9] As expected CE is much more reactive in {6 + 4} cycloadditions than is tropone; the addition of cyclopentadiene to CE is complete within minutes at most, at ambient temperatures, whereas the same diene requires 3 days to accomplish addition to tropone.[8] A {6 + 4} furan adduct was prepared in the same manner as for A. However, benzene ({6 + 4}) and heptafulvalene ({6 + 14}) failed to yield adducts, the former even though it was present as a solvent excess. The scope of the cycloadditive reactivity of CE is evidently circumscribed by its facile oligomerization. Nevertheless, it appears to be the most reactive trienic component presently available. As expected, it is not intercepted by dienophiles, such as *N*-phenylmaleimide, in {6 + 2} cycloadditions.



K



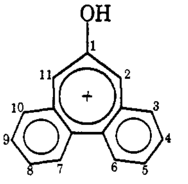
A



F

Addition of MBK to methanolic sodium methoxide gives product F, characterized (*inter alia*) by dehydrogenation (DDQ, refluxing toluene) and comparison of the latter product with authentic methyl 9-phenanthroate. Though alternative mechanisms are conceivable, this result suggests a Favorskii reaction of the valence tautomer CE′. It is interesting that DBK upon reaction with triethylamine gives a Favorskii-type product (9-phenanthroyl bromide).[2] We find that it does so even in the presence of excess cyclopentadiene. Thus, intermolecular cycloadditions of α-bromodibenzo[*c*,*e*]tropone could not be elicited.

Extraction of a CCl_4 solution of MBK with FSO_3H resulted in an intensely red solution displaying multiplets centered at τ 0.7 and 1.5. The low field multiplet is comprised of three lines which appear to be a singlet ($H_{2,11}$) surrounded by the A portion of an AXYZ spin system in which the A resonance ($H_{6,7}$) is coupled to only one ($H_{5,8}$) of X,Y,Z. HMO calculations indicate that the 2,11 positions of CA should be by far the most electron deficient. The 6,7 protons are of the planar biphenyl type (such as the 4,5 positions of phenanthrene) and are expected to be anisotropically shifted to low field. The ratio of the areas of the τ 1.5 and 0.7 absorptions is nearer to 2.0 than to the theoretical 1.5. Nevertheless, the evidence suggests that the predominant species in these solutions is, in fact, CA, though some impurity evidently contributes absorptions underlying the λ 1.5 peak.



CA

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[4] The *R* factor analysis was executed by Professor Davis, whom we warmly thank. The details will be presented elsewhere by Professors Davis and Willcott, though it may be noteworthy that the raw data had appeared more consistent with an endo addition. This further accentuates the importance of their method[5,6] for analyzing nmr shift data.

[5] M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972).

[6] R. E. Davis and M. R. Willcott, III, *ibid.*, **94**, 1744 (1972).

[7] S. Ito, Y. Fujise, T. Okuda, and U. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 1351 (1966).

[8] R. C. Cookson, B. V. Drake, J. Judec, and A. Morrison, *Chem. Commun.*, **15**, (1966).

[9] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

Book Reviews

Challenging Problems in Organic Reaction Mechanisms. By D. Ranganathan and S. Ranganathan (Indian Institute of Technology). Academic Press, New York, N. Y. 1972. xi + 160. $7.50.

This second book of problems by the authors partially reviews the literature from 1966 through 1971. There are 417 examples taken from over 460 references. The selection, not intended to be comprehensive, reflects the authors' interests and has been limited to no more than ten journals published in England, Germany, and the United States. Over 40% of the references came from *Tetrahedron Letters.* Three journals (*Chemical Communications, Journal of Organic Chemistry,* and *Journal of the American Chemical Society*) tied for second place with each providing about 12% of the references. Multiple selections from the work of any one individual were generally avoided; however, seven selections describe results one of the authors had previously published.

Material is easily located by either the Author Index, or the Compound Type Index, or the Reaction Type Index. A Problem Classification Index places each problem into one of three levels ranging from easy to very difficult. Just under 100 examples have Woodward–Hoffmann classifications.

An organic chemist will enjoy working the problems and will