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Roberto Ballardini, Graziano Varani
Centro di Studio sulla Fotochimica e Reattività degli
Stati Eccitati dei composti di coordinazione del C.N.R.
Università di Ferrara, Ferrara, Italy

Vincenzo Balzani*
Istituto Chimico "G. Ciamician" dell'Università and
Laboratorio di Fotochimica e Radiazioni d'Alta
Energia del C.N.R., Bologna, Italy

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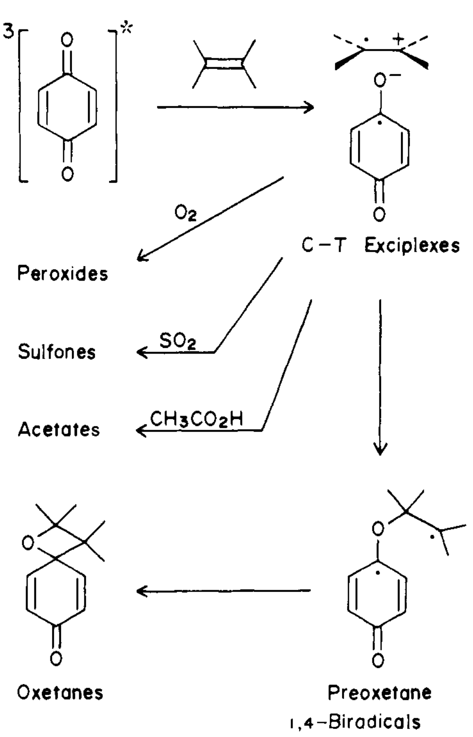
Photocyclizations Involving Quinone-Olefin Charge-Transfer Exciplexes

Sir:

The photocycloaddition of $^3n,\pi^*$ *p*-benzoquinone (*p*Bq) to various olefins to form oxetanes (Scheme I) has received a great deal of attention in recent years.[1] It has been well established that this reaction proceeds through an intermediate with biradical character that can be trapped by oxygen or sulfur dioxide.[2] This intermediate was at first thought to be the traditional preoxetane 1,4 biradical (Scheme I). However, the following results seem to indicate that this is not always the case: (1) experiments with simple unsymmetrical olefins demonstrate that the intermediate which is trapped by oxygen occurs on the reaction pathway *before* the branching into the two possible preoxetane 1,4 biradicals;[2f] (2) in the *p*Bq-cyclooctatetraene system this intermediate apparently is a very polar species as it can also be trapped by acetic acid;[2b] (3) furthermore, CNDO calculations for the triplet *p*Bq-ethylene system indicate that quite stable charge-transfer (C-T) exciplexes might be expected to exist,[2f] and that these could be the "intermediates" being trapped in the aforementioned experiments as summarized in Scheme I. To determine the extent to which triplet C-T exciplexes influence the photochemistry of *p*Bq with simple olefins, a series of olefins specifically designed to maximize the probability of intramolecular trapping of C-T exciplexes has been studied.

Scheme I



Argon ion laser irradiation[3] of *p*Bq in the presence of either 4-pentenoic acid[4] or *trans*-5-phenyl-4-pentenoic acid[4] afforded the δ-lactones **1a** and **1b**,[5] respectively (Scheme II). That these products were the δ-lactones **1a** and **1b** and not the γ-lactones was firmly established by the carbonyl stretching frequencies at 1735-1730 cm^{-1}. The stereochemistry of **1b** is most probably trans, although the coupling between the methinyl hydrogens (4.0 Hz) is smaller than expected. Distortion of the half-chair conformation of the δ-lactone ring in **1b**[6] by the two adjacent, bulky equatorial substituents might account for this decrease in the coupling constant. *cis*-5-Phenyl-4-pentonoic acid was studied also and found to undergo rapid isomerization to the trans acid followed by formation of **1b** as the only lactone product. The possibility that the lactones arise from the acid-catalyzed rearrangement of the corresponding oxetanes, which also occur in these reaction mixtures, has been excluded by control studies with the oxetanes. Therefore, this novel photolactonization seems to be most easily rationalized as the result of C-T exciplex trapping by a carboxylic acid functional group as outlined in Scheme II. The events depicted in Scheme II are intended to illustrate the electronic reorganization necessary to transform the exciplexes into the products, rather than the actual timing of these events. In fact collapse of the quinone-olefin C-T complexes probably proceeds without the localization of charge or spin density at either of the olefin-derived carbon atoms. Under these circumstances one would

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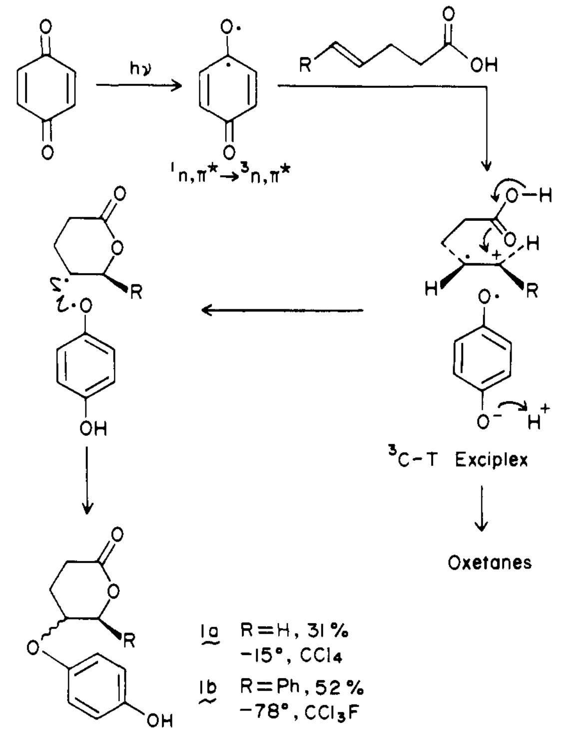
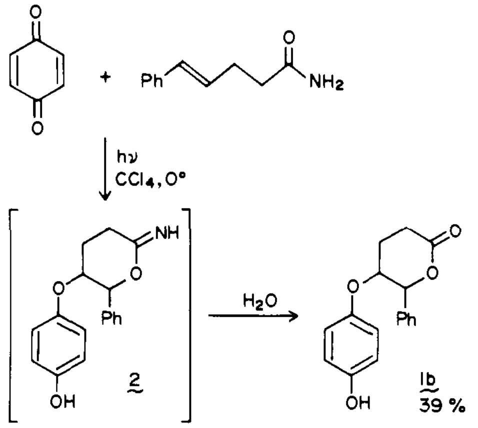
Scheme II



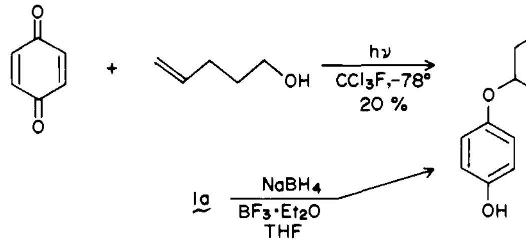
Scheme III



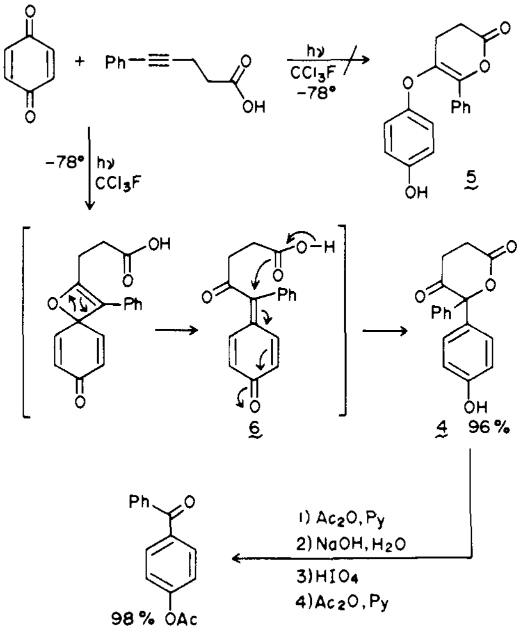
expect the regiospecificity to be governed by steric factors such as formation of the strain-free six-membered ring and maximum separation of the bulky aryl groups as in the case of **1b**. This type of collapse would require a tight radical-ion pair and indeed these reactions occur only in very nonpolar solvents such as CCl_4 and CCl_3F in which the radical-ion pair cannot dissociate. The regiospecificity found in this work is the same as that observed in the collapse of the thermally generated C-T complex between DDQ and 1,1-diphenylethylene.[7] In sharp contrast exactly the opposite regiospecificity has been observed for the exciplexes studied by Arnold and co-workers.[8] In these examples which did not involve quinone acceptors and which are conducted in polar solvents, the nucleophilic trapping step appears to involve the dissociated radical cation. Under these circumstances the regiospecificity will be governed by electronic factors such as stabilization of localized charge and/or spin densities.

To determine which polar functional groups might be most suitable for the trapping of these C-T exciplexes, *trans*-5-phenyl-4-pentenamide[4] and 4-pentenol[4] were examined. In the amide system (Scheme III) the lactone **1a** was obtained in higher yield (39%) than when prepared directly from the trans acid under the same conditions (20%). The lactone formed in this reaction seems to arise from the hydrolysis of the intermediate iminolactone **2**. In the alcohol system (Scheme IV) the expected ether **3** was formed. The structure of **3** was confirmed by synthesis from **1a** with $NaBH_4$-BF_3 in THF.

Scheme IV



Scheme V



Finally, all previous attempts to trap analogous *p*Bq-acetylene intermediates with oxygen had failed.[9] In an effort to intercept acetylenic intermediates with carboxylic acids, *p*Bq was irradiated in the presence of 5-phenyl-4-pentynoic acid to afford a single product in nearly quantitative yield (Scheme V). The degradation of this product as outlined in Scheme V proved that it was the ketolactone **4** rather than the enol lactone **5**. Since **5** is the expected product of C-T exciplex trapping, and since **4** would be expected to arise via the usual carbonyl-acetylene photoproduct **6**,[10] it must be concluded that electron transfer in carbonyl-acetylene exciplexes is insufficient to induce trapping by carboxylic acids. Indeed, this behavior is indicated by the Weller relationship[11] which predicts the *p*Bq-styrene C-T exciplex to be ~11 kcal/mol more stable than the *p*Bq-phenylacetylene C-T exciplex.

In conclusion, quinone-olefin C-T exciplexes not only seem to account for chemistry previously attributed to preoxetane 1,4 biradicals,[2b,f] but also to signal the existence of the new ionic photochemical reactions. Thus, photocyclizations such as those described here should be added to the growing list of carbonyl-olefin exciplex chemistry.[12]

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(3) A Coherent Radiation Model 53A argon ion laser was used in all of the photoreactions described here. The maximum combined power of all of the visible lines is ~6 W in the following lines: 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2). These lines were used to selectively excite the *p*Bq n,π^* transition: $\lambda_{\max}^{\text{hexane}}$ 458 nm (ϵ 21) and 479 (11). While the laser source is not always essential for the success of reactions of this type, the yields of products is often drastically reduced when these reactions are conducted with conventional ultraviolet light sources. For instance the yield of **4** dropped from nearly quantitative to 36% when the light source was the 3500-Å lamps of a Rayonet photochemical reactor.

(4) The success of these reactions is critically dependent upon the purity of the starting materials and solvents. Matheson Freon-11 and Fisher carbon tetrachloride (99 mol %) could be used without further purification.

(5) All photoproducts were characterized spectroscopically and by elemental analysis of their acetate derivatives. The photoproducts and/or their acetates had the following data. **1a:** mp 101.9–102.5 °C; IR (KBr) 3340, 1730 cm^{-1}; NMR (Unisol) (δ, ppm) 3.98–4.16 (m, 2 H), 4.60–5.10 (m, 1 H). Acetate of **1b:** mp 109–110 °C; IR (KBr) 1735 (lactone) 1758 cm^{-1} (acetate); NMR ($CDCl_3$) (δ, ppm) 4.59 (dd, $J = 4$, 10 Hz, 1 H), 5.57 (d, $J = 4$ Hz, 1 H). Acetate of **3**: mp 63.5–64.0 °C; IR (KBr) 1760 cm^{-1}; NMR ($CDCl_3$) (δ, ppm) 3.60 (complex, 5 H). Acetate of **4**: mp 82.2–82.7 °C; IR (KBr) 1755 (acetate), 1735 cm^{-1} (sh) (lactone and α-acetoxy ketone); NMR ($CDCl_3$) (δ, ppm) 2.22–3.01 (m, 4 H).

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R. Marshall Wilson,* Arlene K. Musser
Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

Received September 14, 1979

Synthesis of η^2-Coordinated Enamines by Amination of a Platinum(II) Coordinated Allene. A Chemical and X-ray Diffraction Study

Sir:

During our studies on the reaction of amines with Pt(II) coordinated allenes,[1] we observed a novel reaction of primary aromatic amines with 1,1-dimethylallene (DMA), leading to η^2-coordinated secondary enamines. To our knowledge this observation represents the first example of successful trapping of a fairly unstable enamine by a transition metal ion. Since the ligand produced can be easily displaced from the metal without decomposition, the method can be useful for synthetic purposes, even if at present it is hard to speculate about its applicability to other metal ions. We report here our preliminary results in this field, including the first structural characterization of a metal–enamine η^2 complex.

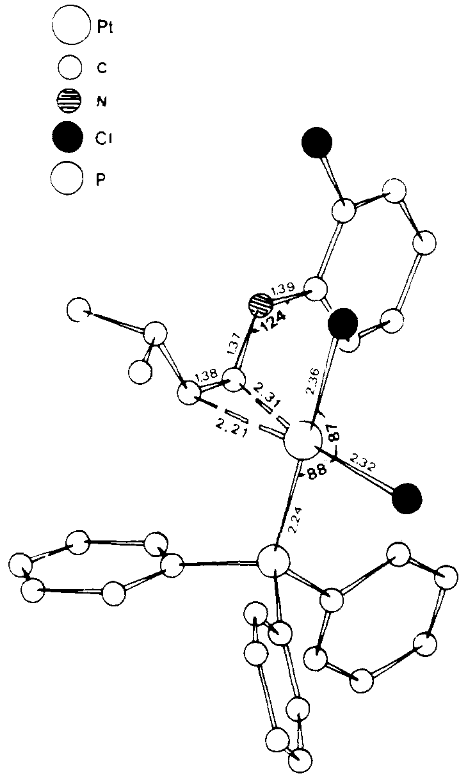
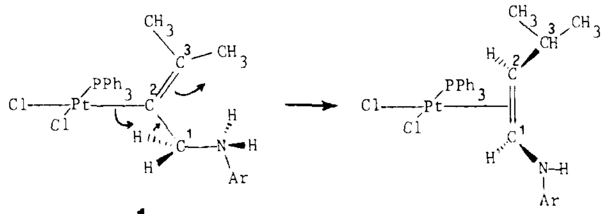


Figure 1. Molecular structure of *cis*-dichloro-η^2-[(*Z*)-2-chloro-*N*-(3-methylbut-1-enyl)benzenamine](triphenylphosphine)platinum(II).

The β-ammonioalkenyl complexes (**1**) obtained upon addition of primary aromatic amines to *cis*-$PtCl_2(DMA)(PPh_3)$[1] are nearly insoluble in the reaction solvent ($CHCl_3$ or CH_2Cl_2) and indefinitely stable after crystallization. However, they undergo a rather unexpected rearrangement if their precipitation is slowed down by the use of larger amounts of solvent, giving the corresponding enamine complexes (**2**). For instance, on addition of an equimolar amount of 2-chloroaniline to a solution of 1.0 mmol of $PtCl_2(DMA)(PPh_3)$ in 20 mL of $CHCl_3$ while the mixture is kept at room temperature for 8 h, a fairly soluble yellow compound (**2**, Ar = 2-ClC_6H_4), mp 151–153 °C, is obtained in ~80% yield. The molecular formula **2** was inferred by the elemental analysis and the IR[2] and ^{1}H, and ^{13}C NMR spectra of the compound[3] and the ^{1}H NMR spectrum of the displaced enamine ligand,[4] the ultimate evidence being furnished by the results of an X-ray diffraction analysis. The ^{1}H NMR spectrum (270 MHz), recorded at room temperature, shows very broad signals for the isopropyl, NH, and olefinic protons. At low temperature (−30 °C) the spectrum becomes fully resolved, displacing two equally intense sets of signals for each CH and NH proton and for each methyl group.[3] The observed spectra indicate the presence in solution of two slowly interconverting isomers in equal abundance, most likely rotamers about the Pt-‖ axis.[5]



1 **2**

Treatment of **2** with sodium cyanide in chloroform solution results in the displacement of the coordinated organic moiety $ArNHCH{=}CHCHMe_2$ without decomposition or enamine–imine isomerization,[6,7] as evidenced by the ^{1}H NMR spectrum of the resulting colorless solution.[4]

The structure of **2** (Ar = 2-ClC_6H_4) was elucidated by a three-dimensional X-ray structural analysis.[8] Figure 1 shows the molecular structure as viewed along the *c* axis; some internal geometrical parameters are also indicated. The complex displays the usual square-planar arrangement of the ligands

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