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Organic Photochemical Rearrangements of Triplets and Zwitterions; Mechanistic and Exploratory Organic Photochemistry[‡]

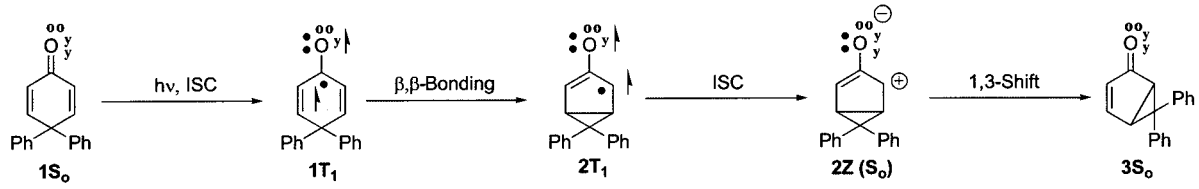
Howard E. Zimmerman*[a] and Vijay Suryanarayan[a]

Keywords: Zwitterions / Diradicals / Photochemistry / Rearrangements / Computation

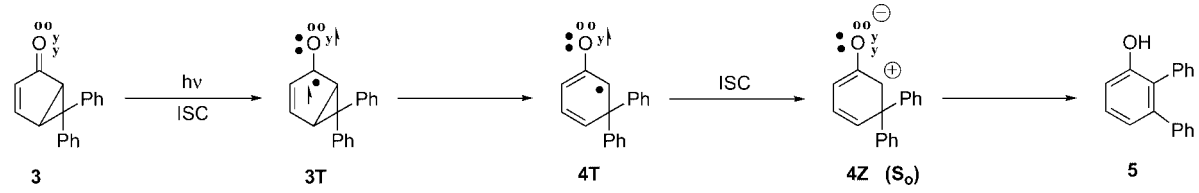
There has been some controversy about the mechanisms of reactions of enones and dienones. The question has been whether a zwitterion or diradical is involved as the intermediate. In the case of ground state species it has not been recognized that zwitterions may have diradical character. In triplet reactions there is the question of whether the rearrangements take place at the initial T1 stage or subsequently as S0 ground state zwitterions or diradicals. We now have some new rearrangements bearing on these questions. In some cases it is the triplet which rearranges, while in others it is the S0 zwitterion. The zwitterion vs. diradical nature of the S0 species has been assessed by both experimental as well as theoretical means. Similarly, both experiment and computational theory have been used to determine at what stage the triplet rearrangements occur and to determine the characteristics of the rearranging species.

Introduction

It was as early as 1961 that photochemical rearrangements beginning as triplets on excitation were postulated to rearrange via zwitterions.[1] This first example was the Type A rearrangement of 2,5-cyclohexadienones [note Equation (1); the circle-dot-y notation designates electrons in the sp, π, and p_y orbitals, respectively[1b]]. Still another example was the Type B bicyclic photochemical reaction of bicyclo[3.1.0]hex-3-en-2-ones,[2] as illustrated in Equation (2). In both cases the initial triplet T1 undergoes skeletal rearrangement prior to the penultimate intersystem crossing to ground state S0.



(1)



(2)

In the Type A example the triplet undergoes β,β-bonding and only then undergoes intersystem crossing to the ground state zwitterion **2Z**. In the case of the Type B bicyclic re-

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[a] Department of Chemistry, University of Wisconsin – Madison, Madison, Wisconsin 53706, USA
E-mail: zimmerman@chem.wisc.edu

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arrangement [Equation (2)], the triplet undergoes scission of the internal three-membered ring bond, followed by intersystem crossing to afford zwitterion **4Z**. This species then undergoes a pinacolic rearrangement and aromatization.[2] The experimental evidence supporting these early suggestions is considered subsequently along with our discussion of the present research and further relevant literature.

Interestingly, there is a common feature in these triplet rearrangements, namely one initial bond-altering step of the excited state which then leads the excited state onward and only subsequently to ground state. However, the involvement of zwitterions is not without controversy. Thus, it has been suggested that the species formed are diradicals and not zwitterions.[3]

The theme of the present research was development of related rearrangements in new systems and exploration of their mechanisms using both experimental and computational approaches.

Results

Synthesis of Reactants and Potential Photoproducts

The first reactants of interest were the diaryl tricyclic systems **9**, **10a**, and **10b**. These were prepared by reaction of diaryldiazomethanes with indenone. The reaction is shown in Scheme 1. In the case of (*p*-cyanophenyl)(phenyl)diazomethane it provided both the *exo* and *endo* stereoisomers with little selectivity. Details are given in the Experimental Section.

Also of interest was the bromotetralone **17**. This was synthesized using the sequence in Scheme 2. This involved Michael addition of benzyl Grignard reagent to the Knoevenagel reactant **11**, followed by basic hydrolysis in two steps, then cyclization with polyphosphoric acid, and NBS bromination.

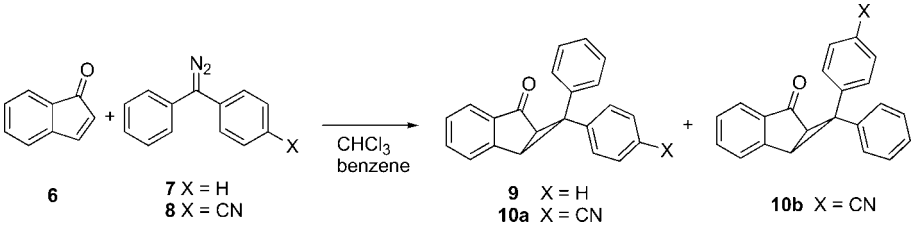
Finally, our preliminary photochemical efforts led to a 2,3-diaryl-substituted naphthol which proved to be mechanistically interesting. Thus, this was synthesized as outlined in Scheme 3.

Initial Efforts – the Photochemistry of the Benzobicyclic Ketones

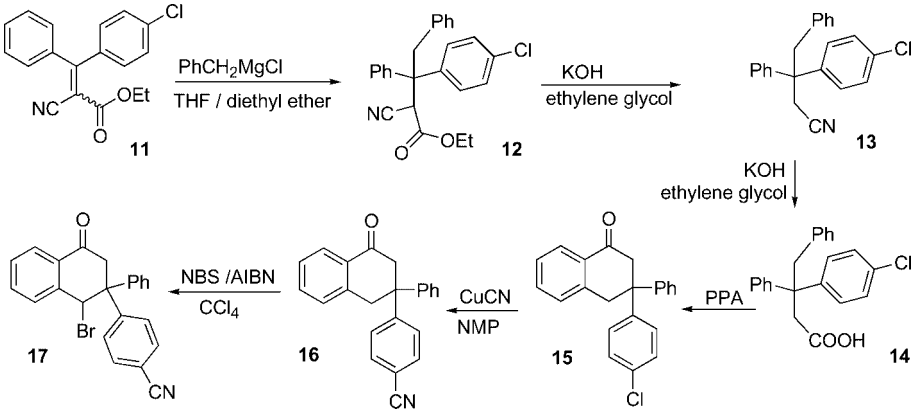
The photochemistry of the unsubstituted benzobicyclohexenone **9** was studied initially with the idea that scission of the internal bond would lead to a zwitterion or diradical of present interest. As noted in Equation (3), photolysis of bicyclic compound **9** in benzene led to the known[4] 2,3-diphenylnaphthol (**26**), the known[5] 3,4-diphenylnaphthol (**27**) and photoproduct **25** whose structure was determined spectroscopically (^{1}H NMR, ^{13}C NMR, HRMS and IR; note the Experimental Section). In initial runs with short irradiation times, the ratio of **26**/**25** was close to 40:60 in slight favor of **25**; and the sum of these remained in a 75:25 ratio to **27**.

Interestingly, the ratio of these photoproducts was dependent on the photolysis time with naphthalenone **25** disappearing on extended photolysis with an increase of formation of 2,3-diphenylnaphthol (**26**) relative to 3,4-diphenylnaphthol (**27**).

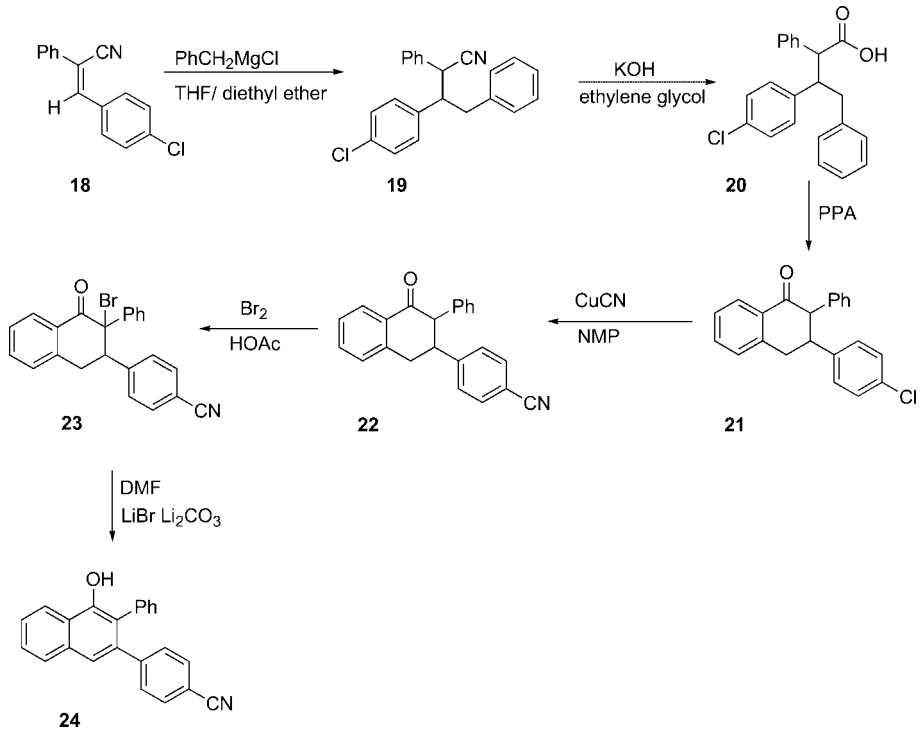
When the photolysis was repeated in methanol, the products obtained were 3,4-diphenylnaphthol (**27**) (44%) along with **25** (2.4%) and methyl ester **28** (42%) as depicted in



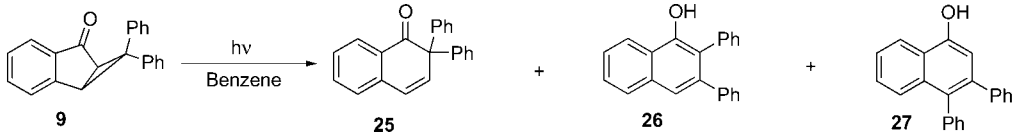
Scheme 1. Synthesis of the benzobicyclic reactants.



Scheme 2. Synthesis of a bromotetralone of interest.



Scheme 3. Synthesis of a 2,3-disubstituted naphthol.



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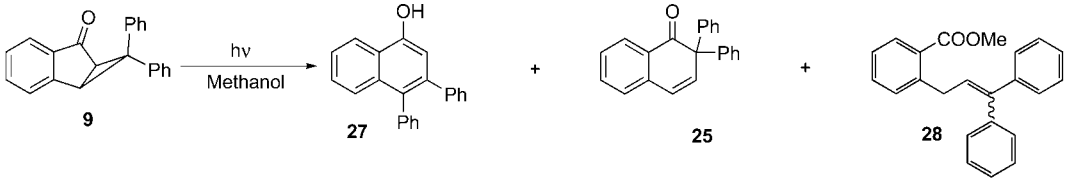


(4)

Equation (4). The dependence on extent of irradiation and on solvent is considered in the Discussion Section (vide infra).

The Multiplicity of the Benzobicyclic Reactions

With these reactions in mind, the question remained whether the multiplicity of the reactions could be assumed to be the same as in the simpler, bicyclic reactions studied earlier [e.g. Equation (2)] where triplets were involved. In the present case, the reactant has a benzoyl chromophore and thus a triplet energy near that of acetophenone (E_T = 74 kcal/mol). Thus, we used cyclohexadiene quenching runs as outlined in Figure 1. That cyclohexadiene (E_T = 53 kcal/mol) nicely quenched the reaction of benzobicyclic ketone **9** in a linear fashion established the triplet multiplicity. The

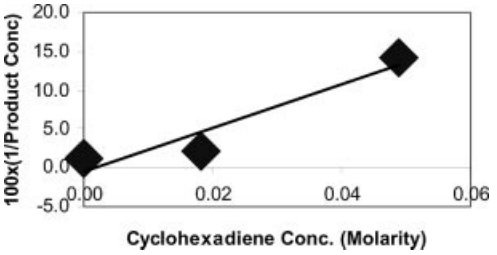


Figure 1. Inverse of conversion vs. quencher concentration.

slope gives $A(k_q/k_r)$ where k_r is the triplet reaction rate, k_q is the quenching rate, and A represents light absorbed in millieinsteins per reaction time.

Evidence on Zwitterion vs. Diradical Migrations

Having observed these rearrangements of the unsubstituted benzobicyclohexenone, we proceeded to investigate the behavior of the counterparts **10a** and **10b** in which one aryl group was *para*-substituted with a cyano moiety. In methanol both of the known[6] 3/4-(*p*-cyanophenyl)-4/3-phenylnaphthols were formed with the 3-(*p*-cyanophenyl)-4-phenyl isomer **29a** predominating.

The product ratio of **29a/29b** (65:35) was independent of the reactant stereochemistry. Additionally, the methoxycarbonyl ring-opened product **30** was observed as a 50% product; see Equation (5).

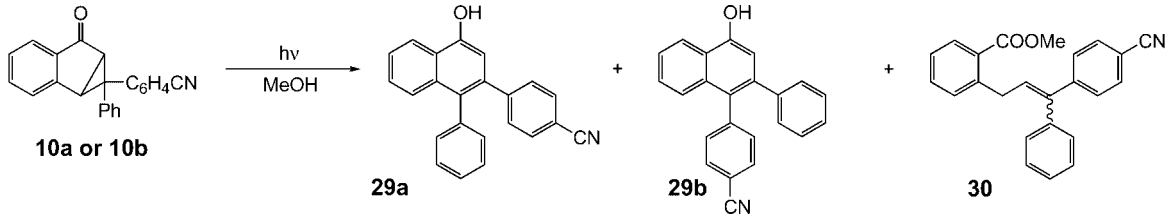
In dramatic contrast, a different reaction course was observed in benzene [note Equation (6)]. Here naphthalenone **31** and (independently synthesized, vide supra) 3-(*p*-cyanophenyl)-2-phenylnaphthol (**24**) were encountered. On extended photolysis, the naphthol became the only product. That the naphthalenone **31** was a reaction intermediate leading to **24** was suggested by its independent photolysis which afforded **24**.

Still another approach was pursued. The reactions in methanol of the diastereomeric bicyclic compounds **10a** and **10b** to afford naphthols **29a** and **29b** (vida supra) clearly proceeded via an intermediate with the central three-membered ring bond severed. One possibility was a six-membered ring oxyallyl species [see Equation (7)]. Hence, it was of interest to ascertain whether this species could be generated independently without light and whether the regioselectivity would be the same or different as found in the photochemistry. The "Favorskii-like" generation of the zwitterionic oxyallyl species employed the reaction of bromo ketone **17** with base. The ratio of the regioisomeric pair, **29a** and **29b**, proved to be the same as in the photolysis of bicyclic compounds **10a** and **10b**.

Computational Aspects and Methodology – the Type A Species

In parallel with the experimental photochemical behavior, we proceeded to investigate the chemistry computationally, using the dimethyl analog of zwitterions **2Z**, **4Z**, and **35Z**. Our computations utilized a 6-31g* basis set along with density functional B3LYP, CASSCF and HF-MP2 methodology. In the case of CASSCF the active space required was determined as (8,8) for the monocyclics and (10,10) for the benzo derivatives, using the Nemukhin–Weinhold approach in which bonds and lone-pairs involved in excitation were computed, then selected and, finally, used as a basis. Since CASSCF does not include correlation energies, for interests' sake these were obtained by extractions from density functional computations. The purpose was to determine if the differences were of the correct order of magnitude.

Rather than using synthetic simulations of solvent, a direct approach was employed. Thus, in the oxygen plane, two methanol molecules were inserted with the hydrogen atoms oriented as to aim at the p_y orbital lobes. In the case of four



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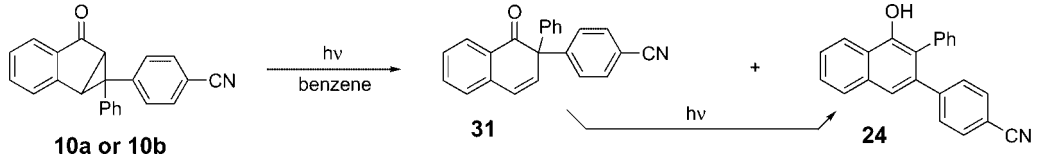

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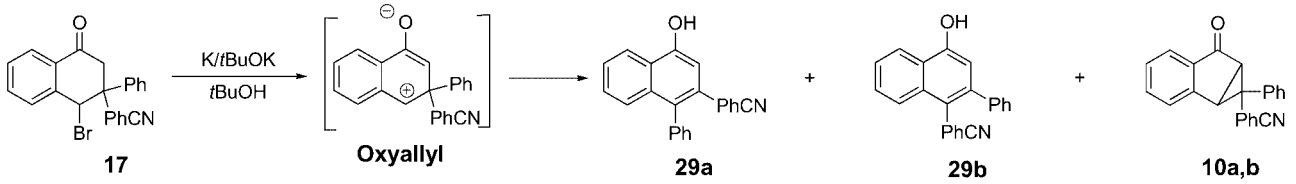


(7)

Table 1. B3LYP results for Type A zwitterion **2Z**.

Species	Relative energy (Hartrees)[a]	Relative energy (minus MeOH)[a]	Relative energy (kcal/mol)	Correlation energy (Hartrees)
Zwitterion, no methanol molecules	0	0	0.00000	2.8404
Zwitterion, two methanol molecules	–231.4704	0.0416[b]	26.1040	4.393
Zwitterion, four methanol molecules	–462.9318	0.0742[c]	46.5605	5.948
Methanol	–115.7144	–	–	–

[a] –385.9737 Hartrees as the zero. [b] 231.4288 per 2 MeOH molecules. [c] 462.8576 per 4 MeOH molecules.

Table 2. CASSCF results for Type A zwitterion **2Z**.

Species	Relative energy (Hartrees)[a]	Natural occupation analysis HOMO	LUMO
Zwitterion, no methanols molecules	0	1.59887	0.34516
Zwitterion, two methanol molecules	230.0339	1.71439	0.27879
Zwitterion, four methanol molecules	460.1333	1.83586	0.15107

[a] –383.59978 Hartrees as the zero.

Table 3. CASSCF results: monocyclic Type B and benzobicyclic Type B species.

Species	Relative energy (Hartrees)	Natural occupation analysis HOMO	LUMO
Type-B zwitterion **4Z**	–383.60871	1.64538	0.34958
Benzo zwitterion **35Z**	–536.32070	1.44264	0.55675
Benzo zwitterion **35Z**, 4 methanol molecules	–996.40054	1.78910	0.19627

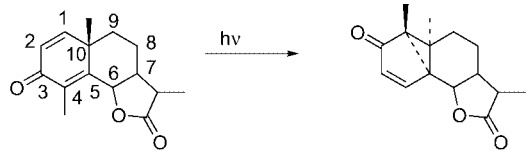
methanol molecules, these solvent molecules were added and placed above and below the molecular plane. With two and with four solvent molecules, geometry optimization was performed. The in-plane methanol molecules did not move appreciably, while those above and below the molecular plane moved slightly more.

All of the computational results are summarized in Tables 1, 2, and 3.

Discussion

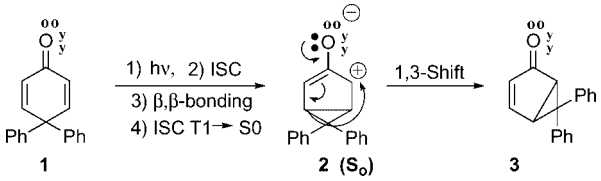
Background

Our interest in photochemistry involving zwitterionic rearrangements goes back decades.[1] An early example of the Type A rearrangement was the Santonin-to-Lumisantonin rearrangement as shown in Equation (8).



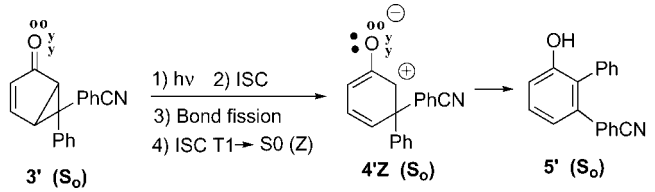
(8)

The structure of Santonin had been established by Woodward and Yates.[7] That of Lumisantonin derived from the work of Barton et al.[8] It was at that point that we first suggested the intervention of zwitterions in a mechanism leading to Lumisantonin. Actually, this was a time when photochemical reactions had not yet been described in terms of electronic excited state structures. Thus, the mechanism in Equation (9) [see also Equation (1)] is one we presented in our early series which correlated the known photochemical reactions with their electronically excited structures. Equation (9) provides the example of the Type A cyclohexadienone rearrangement.



(9)

Similarly, our mechanism for the photochemistry of bicyclo[3.1.0]hex-2-en-3-ones involved enolate zwitterions as noted in Equation (10) [note also Equation (2)].



(10)

However, there has been some controversy about whether these species really are zwitterions or diradicals. A reasonable definition of zwitterions relies on whether one has a largely closed shell species. If the principal configurations mainly have one electron promoted to an antibonding MO

while one remains in the bonding set, we would term the species a diradical. Conversely, with the virtual orbitals largely vacant and the bonding orbitals close to doubly occupied, the species would be termed a zwitterion.

In the ground state (i.e. S0), depending on the extent of single electron promotion, one might consider terming the species a zwitterion or a diradical. But these correspond to the same S0 ground state. In valence bond terminology one is merely dealing with resonance structures of one species. In the case of triplets one clearly has a diradical.

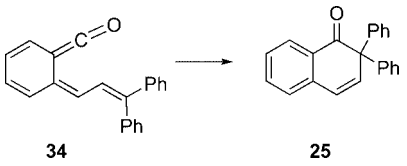
For the Type A rearrangement, there has been some question whether the species shown are actually intermediates or are merely points on the reaction hypersurface.[3c] In a very pretty computational study Robb et al.[3c] has verified that our original pathway shown in Equation (1) is correct. Somewhat earlier, using an AM1 computation, Kletskii et al.[9] also confirmed the nature of species involved. Discussion of our own computations on our systems is delayed to a section below.

But, perhaps, the most convincing evidence tends to derive from experimental observations. Thus, our early studies revealed that the Type A rearrangements have very high quantum yields, often approaching unity.[10] This signifies that there are no efficient conical intersections or points of triplet intersystem crossing occurring prior to the transition state being reached. Otherwise, the quantum yields would be low as a consequence of the reacting species being returned to reactant ground state. A second piece of evidence was the generation of the zwitterion **Z (S0)** by a ground state "Favorskii-like" approach generating the zwitterion directly without the use of light.[11]

Still another example involving zwitterions is seen in the preferential phenyl migration in the photolysis of 6,6-diarylbicyclo[3.1.0]hex-3-en-2-ones [refer to Equation (10)].[12] In this reaction the internal three-membered ring bond is severed to afford a divalent species. If this species were a diradical, the cyanophenyl group would migrate in preference, but does not.[12] Additionally, the effect of acid on the photorearrangements of these species was highly suggestive of a zwitterion.[2a]

Photochemistry of the Benzobicylic Ketones – the Diphenyl System

Perhaps based on intuition or based on thoughts of possible mechanisms, the two reaction intermediates **25** and **34** were considered as involved in much of the photochemistry of the benzobicyclic ketones with ketene **34** being a precursor to diphenylnaphthalenone **25** [Equation (11)].

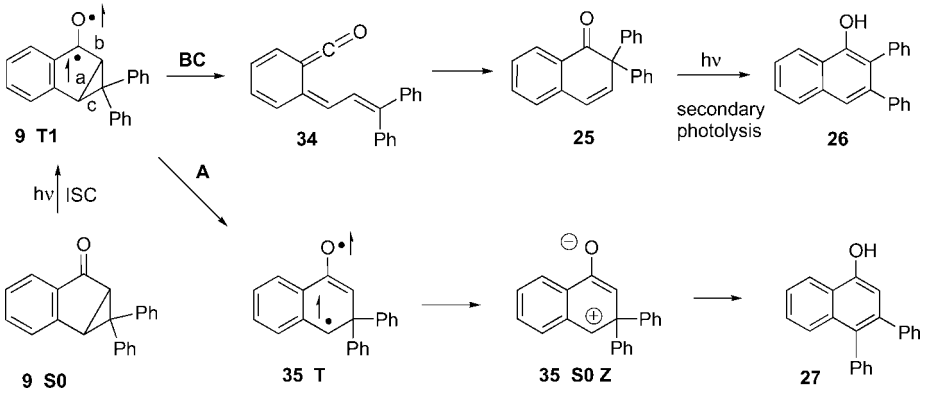


34 **25** (11)

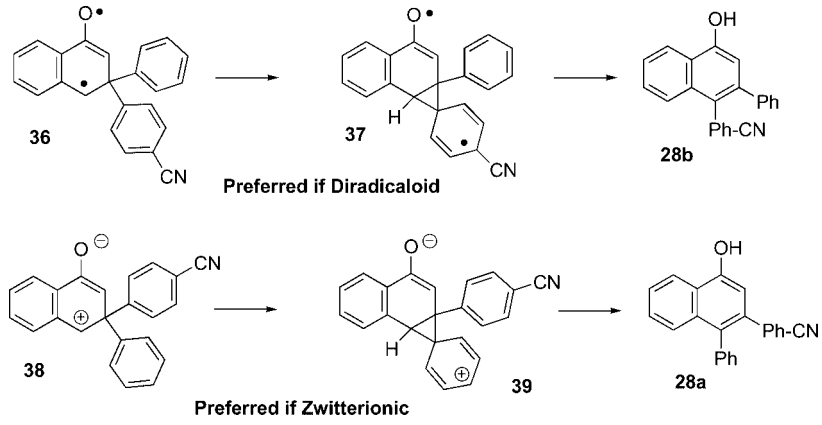
In fact, the photolysis of benzobicyclic ketone **9** as shown in Scheme 4 afforded (inter alia) the two photoproducts **25** and **26**. A complete mechanism for the photolysis of benzobicyclic ketone **9** is given in Scheme 4.

As noted above, 2,2-diphenylnaphthalenone (**25**), 2,3-diphenylnaphthol (**26**), and 3,4-diphenylnaphthol (**27**) were isolable photoproducts, while the diphenyl ketene **34** was not detectible. However, evidence for the intermediacy of this ketene is present (vide infra). It is seen that the 3,4-diphenylnaphthol arises by scission of internal bond a, while 2,2-diphenylnaphthalenone (**25**) and 2,3-diphenylnaphthol (**26**) arise from fission of bonds b and c. Additionally, 2,3-diphenylnaphthol proved to be a secondary photoproduct, being formed from 2,2-diphenylnaphthalenone. Its formation from zwitterion **35 S0** is mechanistically ruled out by the loss of aromaticity if a phenyl group were to bond to C-2. It did prove possible to trap the intermediate ketene **34** by photolysis in methanol [note Equation (4)]. This intermediate proceeded to undergo pericyclic six-membered ring closure as indicated in Equation (11). Thus, in the photochemistry there were two distinct routes – **A** and **BC** – encountered (note Scheme 4). The partition proved to depend on the solvent employed.

Interestingly, path **A** occurs to a greater extent in methanol, while Path **BC** is favored by use of benzene. To the



Scheme 4. Postulated mechanisms in the photolysis of benzobicyclic ketone **9**.



Scheme 5. Phenyl migration preference signifies zwitterionic character; dependence of migrations on zwitterionic vs. diradical character.

extent that the carbonyl moiety has its p_y orbital hydrogen-bonded as in methanol, the n-π* species utilizes its π-system, with the one added electron, to break the internal three-membered ring bond. Conversely, in absence of hydrogen bonding as in benzene, the p_y orbital interacts with bond b (note Scheme 4), while the π-system interacts with bond c. This is reminiscent of our earlier comment[1] that n-π* excited states exhibit dual sources of reactivity – that arising from the singly occupied p_y orbital and that resulting from the reactivity of the extra π-electron.

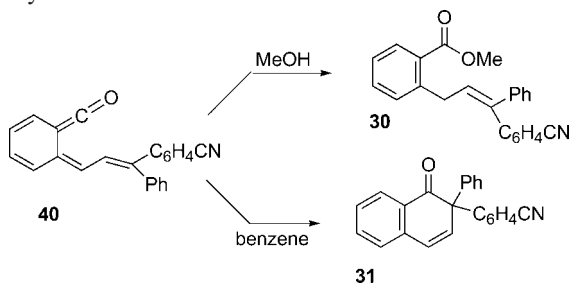
Photochemistry of the Benzobicylic Ketones – the Cyanophenyl System

With the diphenyl-substituted benzobicyclic system giving general mechanistic outlines, *p*-cyano substitution provided further insight. The reaction of the diastereomeric 6-(*p*-cyanophenyl)-6-phenylbenzobicyclo[3.1.0]hexanones **10a** and **10b** led to the 3,4-diarylnaphthols **29a** and **29b** in competition with formation of ketene **40** [see Equation (5) and Scheme 6]. Interestingly the phenyl migration product 3-(*p*-cyanophenyl)-4-phenylnaphthol (**29a**) was the major isomer being formed in a ratio of 65:35 relative to the cyanophenyl migration isomer. This is understood if the center to which the species undergoing aryl migration is electron-deficient rather than odd-electron in character; see Scheme 5. A related and important point is that the same ratio of **29a/29b** resulted independent of the reactant diastereomer, **10a** or **10b**, utilized, thus indicating a common intermediate such as **38**.

Hence, the direct generation of the ground state (i.e. S0) zwitterion **38**, utilizing the first step of a Favorskii reaction as described in Equation (7), is particularly meaningful. The same products – 3-(*p*-cyanophenyl)-4-phenylnaphthol (**29a**) and 4-(*p*-cyanophenyl)-3-phenylnaphthol (**29b**) – as in the photochemistry were formed and in the same 80:20 ratio (within experimental error).

The ratio was independent of the bromo ketone stereochemistry. This ground state approach provides further evidence for the intermediate zwitterion species **38**.

In addition to the naphthol photoproducts 2-(*p*-cyanophenyl)-2-phenylnaphthalenone (**31**) was isolated from photolysis of the parent cyano-benzobicyclohexenone **10** in benzene. In the photolysis in methanol the open-chain ester **30** was also isolated. This clearly results from the trapping of ketene **40** (Scheme 6); see Equation (5). The significance of formation of naphthalenone **31** is that this then accounts for formation of 3-(*p*-cyanophenyl)-2-phenylnaphthol (**24**), since the latter is just a di-π-methane-like product resulting from migration of one of the aryl groups at C-2 to the styryl moiety at C-3.



Scheme 6. Reaction of the intermediate ketene **40**.

Computational Aspects of the Diradical – Zwitterion Problem

In view of the controversy[3] about the mechanism of the reactions involving diradical-zwitterion intermediates computations were undertaken. The case of the Type B bicyclic rearrangement is typical. Most of the computational results have been of the "gas-phase" variety, sometimes with a generalized dielectric being imposed, but with an explicit molecule of water being introduced in one case.

Probably the most reliable assessment of the electronic nature of the molecular wavefunction is natural orbital analysis.[13] This affords the electron occupation of the bonding and antibonding natural orbital molecular orbitals. We recognize that these natural molecular orbitals represent the inclusion of the various configurations in terms of scf MOs. A species which could be termed a true diradical will have occupations of the bonding and antibonding MOs as 1:1 as in S1. A true closed shell zwitterion will have a HOMO occupation of 2:0 as in S0.

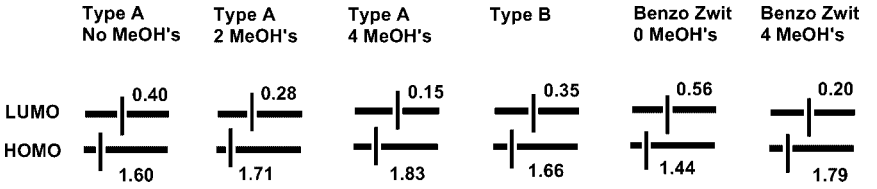


Figure 2. Natural orbital occupancies.

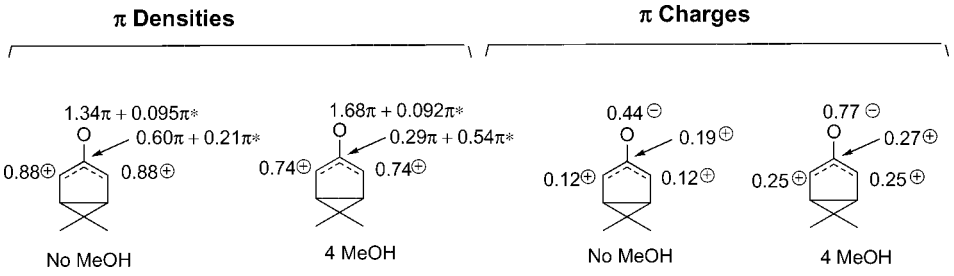


Figure 3. Electron densities and charges in the π-system.

If we now refer to Tables 1, 2, and 3, as summarized in Figure 2, we note that the antibonding natural MOs are weakly populated, while the electron density in the highest energy bonding MOs have electron densities approaching two. Further, as a test, in the case of the Type A species, methanol molecules have been explicitly put in proximity of the carbonyl oxygen atom. The first two were put in the molecular plane, and the next two above and below the molecular plane. It is seen (note Figure 2) that as methanol solvation is increased, the occupancy of the virtual orbitals diminishes, and the bonding MOs approach an occupancy of two as in a closed shell.

A further result of interest is the effect of solvent, here methanol, on the diradical character of the species. Here we select the Type A species to illustrate the point. Thus, using the Weinhold NBO analysis to give bond orbital densities, we find (Figure 3) carbon atoms 2 and 6 to be electron-deficient with less than unit density while the oxygen p-π orbital is electron-rich. The effect of methanol molecules clustering around the oxygen atom enhances the polarization dramatically. The carbonyl carbon atom is minimally electron-deficient; considerable density has been fed to the antibonding π* bond. Overall we see with four methanol molecules a total of 1.4 electrons being transferred to the oxygen p-π orbital. The charges are also listed in Figure 3. Interestingly, the Type A rearrangement occurs nicely in polar solvents while in benzene it becomes a minor process. We also need to note that there clearly is some diradical character in the oxyallyl moiety, but this is minimal and overridden by the zwitterionic nature of the species. Additionally, we conclude that "gas-phase" computations exaggerate this diradical character of the zwitterions. One can best term these species as "zwitterionic with some diradicaloid" character.

Conclusions

The evidence is that the photochemical processes in the Type A, the bicyclic Type B, and the benzo Type B – proceed by mechanisms in which the penultimate step is rearrangement of a zwitterion. This evidence is both experimental and computational. The experimental evidence rests on (1) a preference of phenyl groups to migrate compared with *p*-cyanophenyl counterparts, and (2) generation of the same ground state species from a Favorskii-like generation. Additionally, in this study a number of new transformations have been discovered.

Experimental Section

General Procedures: Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel (60–80 mesh) mixed with 1% of Sylvania 2282 (green) phosphor and slurry-packed into quartz columns to allow monitoring with a hand-held UV lamp. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75.4 MHz, respectively, with TMS as an internal standard. Photolysis experiments were carried out in an enclosed box with a 400 W medium-pressure mercury lamp in a quartz immersion well with a 0.2 M copper sulfate filter solution and under nitrogen.

Synthesis of Inden-1-one (6): A useful and simpler method was employed for the synthesis of inden-1-one.[14] To a stirred solution of 2.09 g (10 mmol) of 3-bromoindan-1-one[15] in 20 mL of diethyl ether, 3.03 g (30 mmol) of triethylamine was added dropwise at room temperature over 10 min. The hydrobromide salt separated out during addition. The reaction mixture was stirred for further 1 h and quenched with cold water. The organic layer was separated, washed well with water, brine and dried with anhydrous sodium sulfate. Removal of ether under vacuum afforded 1.0 g (77.0%) of **6** as pale yellow oil which was pure enough (purity >99%) to be used directly for further reactions. ^{1}H NMR ($CDCl_3$): δ = 5.89 (d, J = 6.0 Hz, 1 H), 7.06 (d, J = 6.9 Hz, 1 H), 7.23 (t, J = 6.9 Hz, 1 H), 7.34 (t, J = 6.9 Hz, 1 H), 7.43 (d, J = 6.9 Hz), 7.57 (d, J = 6.0 Hz, 1 H) ppm.

Synthesis of (*p*-Cyanophenyl)(phenyl)diazomethane (8):[16] A mixture of 3.5 g (69 mmol) of hydrazine hydrate, 50 mL of absolute ethanol and 10 g of anhydrous sodium sulfate was heated to reflux. A solution of 718 mg (3.47 mmol) of *p*-cyanobenzophenone in 50 mL of ethanol and 20 mL of benzene was added over 8 h, at which point

the reaction mixture had a light yellow color. The mixture was refluxed overnight. The solution was filtered under gravity to remove the sodium sulfate and the solvent removed under vacuum. The residual solid, on crystallization from absolute ethanol, afforded *p*-cyanobenzophenone hydrazone as light yellow needles, 230 mg (30.2%); m.p. 165 °C. ^{1}H NMR ($CDCl_3$): δ = 5.41 (s, 2 H), 7.24–7.84 (m, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 113.28, 118.48, 126.52, 128.60, 128.79, 130.21, 133.44, 137.69, 138.26, 146.99 ppm. HRMS: calcd. for $C_{14}H_{11}N_3$ 221.0953 (monoisotopic); found 221.0954. To a solution of 230 mg (1.04 mmol) of *p*-cyanobenzophenone hydrazone in 20 mL of dry diethyl ether was added 1.0 g of anhydrous sodium sulfate, 906 mg (4.23 mmol) of yellow mercuric oxide and 0.50 mL of saturated ethanolic potassium hydroxide. The reaction mixture was stirred in the dark overnight (care was taken to avoid light by covering the flask with aluminium foil). Filtration under gravity with care to exclude light left a deep orange solution which was concentrated in vacuo to afford 170 mg (74.8%) of **8**. This was crystallized from diethyl ether/hexane (80:20) as violet needles; m.p. 109 °C. ^{1}H NMR ($CDCl_3$): δ = 7.24–7.61 (m, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 107.68, 119.41, 123.76, 126.97, 127.08, 127.30, 129.81, 132.53, 133.01, 136.06 ppm. HRMS: calcd. for $C_{14}H_9N_3$ 219.0796; found 219.0791.

Synthesis of 1,1-Diphenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (9): To a solution of 1.32 g (10.19 mmol) of indenone in 20 mL of benzene and 20 mL of chloroform was added a solution of 2.23 g (11.5 mmol) of diphenyldiazomethane in 20 mL of benzene through a hypodermic needle over 4 h. A gentle reflux was maintained during the addition. After the addition was complete, the reaction mixture was further refluxed for 3 h and stirred at room temperature overnight. The reaction mixture was diluted with water. The organic phase was dried and concentrated in vacuo to afford a semisolid which on column chromatography (hexane/ethyl acetate, 9:1) and crystallization from benzene/hexane (1:1) afforded 1.1 g (36.5%) of pure **9**, m.p. 130 °C. ^{1}H NMR ($CDCl_3$): δ = 3.20 (d, J = 5.1 Hz, 1 H), 3.68 (d, J = 5.1 Hz, 1 H), 7.01–7.54 (m, 14 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 36.04, 41.70, 59.80, 123.94, 126.34, 126.34, 126.99, 127.20, 127.33, 128.34, 128.820, 131.63, 133.89, 136.69, 136.95, 144.51, 150.94, 200.78 ppm. HRMS: calcd. for $C_{22}H_{16}O$ 296.1202; found 296.1189.

Synthesis of 1-(*p*-Cyanophenyl)-1-phenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (Diastereomers 10a and 10b): To a solution of 1.32 g (10.19 mmol) of indenone in 20 mL of benzene and 20 mL of chloroform was added a solution of 2.52 g (11.5 mmol) of **8** in 20 mL of benzene through a hypodermic needle over 4 h. A gentle reflux was maintained during the addition. After the addition was complete, the reaction mixture was further refluxed for 3 h and stirred at room temperature overnight. The reaction mixture was diluted with water. The organic phase was dried and concentrated in vacuo to afford a semisolid. Column chromatography (hexane/ethyl acetate, 9:1) afforded a mixture of the diastereomers which were separated after repeated crystallizations from hexane/ethyl acetate (8:2). **10a**: Yield: 700 mg (21.4%); m.p. 170 °C. ^{1}H NMR ($CDCl_3$): δ = 3.22 (d, J = 5.1 Hz, 1 H), 3.71 (d, J = 5.1 Hz, 1 H), 7.06–7.54 (m, 13 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 35.66, 41.29, 59.41, 111.16, 118.72, 124.43, 126.44, 127.03, 127.90, 128.02, 129.23, 132.25, 132.28, 134.51, 136.20, 143.03, 150.50, 200.32 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 321.1154; found 321.1142. **10b**: Yield: 640 mg (19.57%); m.p. 179 °C. ^{1}H NMR ($CDCl_3$): δ = 3.17 (d, J = 5.4 Hz, 1 H), 3.67 (d, J = 5.4 Hz, 1 H), 7.06–7.60 (m, 13 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 36.32, 41.67, 58.24, 111.15, 118.91 124.23, 126.48, 127.52, 127.70, 127.82, 128.78, 131.80, 132.72, 134.28, 136.49, 149.34, 150.31, 199.93 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 321.1154; found 321.1147.

Irradiation of 1,1-Diphenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (9) in Benzene: A solution of 250 mg (0.84 mmol) of **9** in 250 mL of benzene was purged with nitrogen for 1 h. The irradiation was then carried out with a 0.2 M $CuSO_4$ filter solution for 10 min. TLC indicated the absence of the starting material. The solvent was removed under vacuum and the residue subjected to column chromatography (hexane, hexane/ethyl acetate, 19:1, 9:1) to afford the following products:

Fraction 1. 2,3-Diphenyl-1-naphthol (26): Crystallized from hexane, Yield: 70 mg (28.2%), m.p. 129 °C (ref.[4] m.p. 128–130 °C).^{1}H NMR ($CDCl_3$): δ = 5.70 (s, 1 H), 7.13–8.35 (m, 15 H) ppm.

Fraction 2. 2,2-Diphenyl-2*H*-naphthalen-1-one (25): Crystallized from hexane/pentane, 1:1, Yield: 115 mg (46.3%), m.p. 124 °C. ^{1}H NMR ($CDCl_3$): δ = 6.52 (d, J = 9.6 Hz, 1 H), 6.76 (d, J = 9.6 Hz, 1 H), 7.25–7.58 (m, 13 H), 8.06 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 63.18, 123.81, 127.50, 127.57, 127.94, 128.07, 128.23, 128.63, 128.66, 128.88, 129.09, 129.34, 129.53, 134.90, 137.90, 139.06, 142.71, 200.21 ppm. HRMS: calcd. for $C_{22}H_{16}O$ 296.1201; found 296.1194. The IR spectrum contained a carbonyl stretching peak at 1684 cm^{-1}.

Fraction 3. 3,4-Diphenyl-1-naphthol (27): Yield: 60 mg (24.1%), m.p. 142 °C (ref.[5] m.p. 142–143 °C). ^{1}H NMR ($CDCl_3$): δ = 5.40 (s, 1 H), 6.92 (s, 1 H), 7.09–7.64 (m, 13 H), 8.27 (d, J = 9.0 Hz, 1 H) ppm.

Irradiation of 1-(*p*-Cyanophenyl)-1-phenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (10) in Benzene: A solution of 250 mg (0.77 mmol) of the diastereomer isomer **10a** in 250 mL of benzene was purged with nitrogen for 1 h. The irradiation was then carried out with a 0.2 M $CuSO_4$ filter solution for 10 min. The ^{1}H NMR spectrum showed a 60% conversion to products. The solvent was removed under vacuum and the residue subjected to column chromatography (hexane, hexane/ethyl acetate, 19:1) to afford the following products:

Fraction 1. 3-(*p*-Cyanophenyl)-2-phenyl-1-naphthol (24): Recrystallized from hexane/diethyl ether, 9:1, Yield 90 mg (36.4%), m.p. 177 °C. ^{1}H NMR ($CDCl_3$): δ = 5.74 (s, 1 H), 7.18–7.57 (m, 12 H), 7.85 (m, 1 H), 8.33 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 110.54, 119.24, 120.57, 121.45, 122.94, 124.06, 126.49, 127.63, 127.99, 128.61, 129.86, 130.70, 131.44, 131.81, 133.85, 134.91, 137.99, 146.57, 149.07 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 321.1154; found 321.1144.

Fraction 2. 2-(*p*-Cyanophenyl)-2-phenyl-2*H*-naphthalen-1-one (31): Yield 85 mg (34.4%), m.p. 141 °C. ^{1}H NMR ($CDCl_3$): δ = 6.45 (d, J = 9.8 Hz, 1 H), 6.82 (d, J = 9.8 Hz, 1 H), 7.08–7.64 (m, 12 H), 8.06 (d, J = 6.9 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 63.33, 111.51, 119.10, 125.01, 127.93, 128.13, 128.15, 128.29, 129.93, 129.16, 130.15, 130.71, 131.66, 131.71, 135.46, 137.50, 141.49, 148.53, 199.15 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 344.1051 [M + Na]$^+$; found 344.1047 [M + Na]$^+$.

Under similar experimental conditions, the irradiation of the diastereomer **10b** afforded **24** and **31** with a yield of 35.1% and 36.8%, respectively.

Irradiation of 1,1-Diphenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (9) in Methanol: A solution of 250 mg (0.84 mmol) of the tricyclic compound **9** in 250 mL of methanol was purged with nitrogen for 1 h. The irradiation was then carried out with a 0.2 M $CuSO_4$ filter solution for 10 min. The ^{1}H NMR indicated 10% of unreacted starting material. The solvent was removed under vacuum and the residue subjected to column chromatography (hexane, hexane/ethyl acetate, 19:1) to afford the following products:

Fraction 1. Methyl 2-(3,3-Diphenylallyl)benzoate (28): Yield 115 mg (41.8%), pale yellow oil, ^{1}H NMR ($CDCl_3$): δ = 3.83 (s and d merged, 5 H), 6.26 (t, J = 7.8 Hz 1 H), 7.19–7.44 (m, 13 H), 7.89 (d, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.48, 52.20, 126.30, 125.96, 127.21, 127.58, 128.05, 128.29, 128.50, 130.18, 130.81, 130.85, 132.29, 140.09, 142.62, 142.65, 142.74, 168.37 ppm. HRMS: calcd. for $C_{23}H_{20}O_2$ 351.1361 $[M + Na]^+$; found 351.1375 $[M + Na]^+$.

Fraction 2. 2,2-Diphenyl-2*H*-naphthalen-1-one (25): Yield 6 mg (2.4%).

Fraction 3. 3,4-Diphenyl-1-naphthol (27): Yield 109 mg (43.9%).

Irradiation of 1,1-Diphenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (9) in Methanol with 1,3-Cyclohexadiene as Quencher: Three different experiments were performed under identical photolysis conditions. The conversion to products in all cases was determined by ^{1}H NMR ($CDCl_3$).

(a) A solution of 11.8 mg (0.04 mmol) of **9** in 80 mL of methanol and 120 mg of 1,3 cyclohexadiene (1.5 mmol, 0.018 M solution) was purged with nitrogen for 1 h. Irradiation was carried out in a 0.2 M $CuSO_4$ filter solution for 10 min, and the resulting solution was concentrated under vacuum. ^{1}H NMR of the residue showed 50% of starting ketone **9**.

(b) A solution of 11.8 mg (0.04 mmol) of **9** in 80 mL of methanol and 316 mg of 1,3 cyclohexadiene (50 mmol, 0.049 M solution) was purged with nitrogen for 1 h. After irradiation for 10 min, the resulting solution was concentrated under vacuum. ^{1}H NMR of the residual semisolid revealed the presence of 93% unconverted starting material **9**.

(c) A solution of 11.8 mg (0.04 mmol) of **9** in 80 mL of methanol was purged with nitrogen for 1 h. After irradiation for 10 min, the resulting solution was concentrated under vacuum. ^{1}H NMR confirmed the presence of 12% of unconverted ketone **9**.

Irradiation of 1-(*p*-Cyanophenyl)-1-phenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (10) in Methanol: A solution of 250 mg (0.77 mmol) of the diastereomer **10a** in 250 mL of methanol was purged with nitrogen for 1 h. The irradiation was then carried out with a 0.2 M $CuSO_4$ filter solution for 10 min. The ^{1}H NMR showed a complete conversion of starting ketone to products. The solvent was removed under vacuum and the residue subjected to column chromatography (hexane, hexane/ethyl acetate, 19:1, 9:1, and 6:1) to afford the following products:

Fraction 1. Methyl 2-[3-(*p*-Cyanophenyl)-3-phenylallyl]benzoate (30): Yield 137 mg (50.5%), colorless oil. ^{1}H NMR ($CDCl_3$): δ = 3.81 (d, J = 7.5 Hz, 2 H), 3.85 (s, 3 H), 6.33 (t, J = 7.5 Hz, 1 H), 7.14–7.44 (m, 11 H), 7.67 (d, J = 6.0 Hz, 1 H), 7.91 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.36, 52.10, 110.37, 119.65, 126.23, 127.64, 128.24, 128.46, 128.68, 129.06, 129.28, 130.48, 130.91, 131.13, 132.05, 132.49, 133.53, 138.86, 143.00, 167.46 ppm. HRMS: calcd. for $C_{24}H_{19}NO_2$ 353.1416; found 353.1428.

Fraction 2. 3-(*p*-Cyanophenyl)-4-phenyl-1-naphthol (29a): Yield 81 mg (32.0%), m.p. >250 °C. ^{1}H NMR ($CDCl_3$): δ = 5.51 (s, 1 H), 6.87 (s, 1 H), 7.11–7.65 (m, 12 H), 8.27 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 109.51, 109.59, 119.05, 122.30, 124.72, 124.99, 126.49, 126.73, 127.95, 129.24, 130.76, 131.25, 131.86, 133.68, 136.76, 138.62, 147.49, 153.00 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 320.1076 [M – H]; found 320.1063 [M – H].

Fraction 3. 4-(*p*-Cyanophenyl)-3-phenyl-1-naphthol (29b): Yield 44 mg (17.6%), m.p. 208 °C. ^{1}H NMR ($CDCl_3$): δ = 5.654 (s, 1 H), 6.93 (s, 1 H), 7.05–7.57 (m, 12 H), 8.30 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 110.76, 111.15, 119.29, 122.17, 123.94, 125.71, 126.16, 127.11, 127.67, 128.23, 130.17, 131.94, 133.04, 139.25, 141.38, 144.37, 151.65 ppm. HRMS: calcd. for $C_{23}H_{15}NO$ 321.1154; found 321.1141.

Under similar conditions, the irradiation of the diastereomer **10b** in methanol gave identical results with an experimental error of ±2%.

Synthesis of Ethyl 3-Benzyl-3-(*p*-chlorophenyl)-2-cyano-3-phenylpropionate (12): A solution of 26.0 g (85 mmol) of ethyl α-cyano-β-phenyl-β-(*p*-chlorophenyl)acrylate (**11**)[17] in 30 mL of dry THF was added over 45 min at room temperature to a Grignard solution prepared from 10.37 g (90 mmol) of benzyl chloride and 2.2 g (90 mmol) of magnesium turnings in 25 mL of dry diethyl ether. When the spontaneous reflux had subsided the reaction mixture was stirred and heated to reflux for another 3 h. The mixture was then poured onto cracked ice, acidified with 20% hydrochloric acid, extracted with ethyl acetate, dried and concentrated under vacuo. The crude product thus obtained was washed with diethyl ether to remove unreacted **11**. Crystallization from ethanol afforded 14.0 g (40.8%) of **12** as a mixture of inseparable diastereomers, m.p. 125 °C. ^{1}H NMR ($CDCl_3$): δ = 0.80–0.953 (m, 3 H), 3.07–3.14 (m, 1 H), 3.80–3.99 (m, 3 H), 4.30 (s, 1 H), 6.56–6.64 (m, 2 H), 6.72–6.79 (m, 2 H), 7.04–7.46 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.66, 25.84, 44.41, 54.50, 62.87, 116.74, 127.98, 128.01, 128.06, 128.18, 128.33, 128.38, 129.01, 129.21, 130.61, 130.76, 131.30, 131.35, 133.47, 134.01, 135.51, 135.54, 141.11, 164.96, 165.06 ppm. HRMS: calcd. for $C_{25}H_{22}ClNO_2$ 403.1339; found 403.1330.

Synthesis of 3-Benzyl-3-(*p*-chlorophenyl)-3-phenylpropionitrile (13): A solution of 10 g (24.81 mmol) of **12**, 1.38 g (24.81 mmol) of potassium hydroxide and 40 mL of ethylene glycol was heated under reflux under nitrogen for 3 h. It was then cooled, diluted with water and acidified with 20% hydrochloric acid to afford a colorless solid. Filtration and crystallization from ethanol afforded 8.0 g (97.4%) of nitrile as colorless plates, m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 2.93 (s, 1 H), 3.58 (s, 1 H), 6.64 (m, 2 H), 7.04–7.35 (m, 14 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.34, 44.63, 49.39, 118.05, 127.18, 127.48, 127.87, 128.19, 128.62, 128.66, 129.40, 130.56, 133.22, 135.66, 143.77, 144.46 ppm. HRMS: calcd. for $C_{22}H_{18}ClN$ 331.1128; found 331.1122.

Synthesis of 3-Benzyl-3-(*p*-chlorophenyl)-3-phenylpropionic Acid (14): A solution of 8.0 g (24.13 mmol) of **13** was refluxed with 4.05 g (72.39 mmol) of KOH in 30 mL of ethylene glycol under nitrogen for 6 h. The cooled reaction mixture was poured onto crushed ice and acidified with 20% hydrochloric acid to pH = 2–3. Crude **14** was collected by filtration and crystallized from hexane as colorless plates, 7.8 g (92.6%), m.p. 175 °C. ^{1}H NMR ($CDCl_3$): δ = 2.99 (s, 2 H), 3.65 (s, 2 H), 6.61 (d, J = 8.1 Hz, 2 H), 7.00–7.28 (m, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 41.12, 43.68, 49.31, 126.63, 126.77, 127.81, 128.20, 128.22, 129.72, 131.11, 132.41, 137.14, 145.71, 146.47, 176.93 ppm. HRMS: calcd. for $C_{22}H_{19}ClO_2$ 349.0996 $[M - H]^-$; found 349.1005 $[M - H]^-$.

Synthesis of 3-(*p*-Chlorophenyl)-3-phenyl-1,2,3,4-tetrahydronaphthalene-1-one (15): A mixture of 5.0 g (14.25 mmol) of **14** and 20.0 g of polyphosphoric acid, preheated at 110 °C for 30 min, was stirred with heating at the same temperature for 6 h. After cooling, it was poured onto cracked ice and extracted with ethyl acetate (3 times). The combined extracts were dried and concentrated under vacuum to afford the crude product. Column chromatography (ethyl acetate/hexane, 10:90) furnished 2.6 g (54.8%) of pure **15** as pale yellow semisolid. IR ($CDCl_3$): $\tilde{\nu}$ = 2969, 1694 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.41 (s, 2 H), 3.74 (s, 2 H) ppm. 7.11–7.507 (m, 12 H), 7.92 (d, 1 H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ = 42.42, 48.60, 51.16, 126.83, 126.96, 127.10, 127.22, 128.702, 128.83, 129.07,

132.50, 132.56, 134.40, 141.89, 144.53, 145.819, 196.75 ppm. HRMS: calcd. for $C_{22}H_{17}ClO$ 332.0968; found 332.0957.

Synthesis of 3-(*p*-Cyanophenyl)-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (16): A solution of 2.0 g (6.0 mmol) of **15** and 2.16 g (24.0 mmol) of cuprous cyanide in 10 mL of *N*-methylpyrrolidone was refluxed with stirring under nitrogen for 24 h. The reaction mixture was cooled to room temperature, diluted with 10 mL of 10% ammonium hydroxide solution and extracted with 30 mL of ethyl acetate (3 times). The combined organic layers were washed with water, dried and concentrated under vacuum. The crude product on column chromatography (ethyl acetate/hexane, 1:6) afforded **16** as a pale yellow solid which was crystallized from hexane/diethyl ether (1:1), yield 580 mg (30.0%), m.p. 223–225 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 3.44 (s, 2 H), 3.78 (s, 2 H), 7.15–7.72 (m, 12 H), 7.93 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 42.10, 49.23, 50.82, 110.71, 118.70, 126.93, 127.19, 127.45, 128.11, 129.04, 132.45, 132.53, 134.61, 141.37, 144.37, 144.92, 151.45, 196.18 ppm. HRMS: calcd. for $C_{23}H_{17}NO$ 323.1310; found 323.1318.

Synthesis of 4-Bromo-3-(*p*-cyanophenyl)-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (17): A solution of 484 mg (1.5 mmol) of **16**, 264 mg (1.5 mmol) of NBS, 5.0 mg (0.03 mmol) of AIBN in 10 mL of carbon tetrachloride was refluxed for 5 h. After cooling the reaction mixture to room temperature, the solution was filtered. The filtrate on concentration under vacuum afforded crude **17** which was crystallized from hexane/diethyl ether (9:1), yield 450 mg (74.5%), m.p. 91 °C. ^{1}H NMR ($CDCl_3$): δ = 3.76 (m, 1 H), 3.95 (m, 1 H), 6.29 (m, 1 H), 7.06–7.97 (m, 13 H) ppm. MS: calcd. for $C_{23}H_{16}BrNO$ – Br 322.3; found 322.1; *m*/*z* = 277.1, 244.1, 219.0, 194.0, 167.0, 149.0, 118.0, 83.9, 68.0.

Reaction of 4-Bromo-3-(*p*-cyanophenyl)-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (17) with Potassium *tert*-Butoxide. Generation of the Zwitterion in the Dark: A solution of 402 mg (1.0 mmol) of bromo compound **17** in 7.0 mL of *tert*-butyl alcohol and 112 mg (1.0 mmol) of potassium *tert*-butoxide was stirred in dark for 12 h. The reaction mixture was then poured onto crushed ice and acidified with 10% HCl to pH = 2–3. The solid which separated was extracted with ethyl acetate, and the organic phase was dried with anhydrous sodium sulfate. Column chromatography using hexane and hexane/ethyl acetate (19:1, 9:1 and 6:1) afforded the following products:

Fraction 1. 1-(*p*-Cyanophenyl)-1-phenyl-1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (Diastereomers 10a and 10b): Yield 178 mg (55.4%). Ratio of **10a/10b** = 60:40 (by ^{1}H NMR).

Fraction 2. 3-(*p*-Cyanophenyl)-4-phenyl-1-naphthol (29a): Yield 114 mg (35.5%).

Fraction 3. 4-(*p*-Cyanophenyl)-3-phenyl-1-naphthol (29b): Yield 29 mg (9.0%).

Synthesis of 3-Benzyl-2-(*p*-chlorophenyl)-2-phenylpropanenitrile (19): To a freshly prepared solution of benzylmagnesium chloride (12 mmol) in diethyl ether was added 2.39 g (10 mmol) of **18**[18] in 10 mL of anhydrous THF over 15 min and the mixture refluxed in an oil bath for 4 h. The mixture was then cooled, poured onto crushed ice and the acidified with cold 10% HCl to pH = 2–3. Column chromatography (ethyl acetate/hexane, 1:19) and crystallization from hexane afforded 2.4 g (72.5%) of the pure product, m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 3.11–3.26 (m, 3 H), 4.03–4.05 (d, J = 5.1 Hz, 1 H), 6.92–6.96 (m, 4 H), 7.19–7.33 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 39.84, 42.66, 52.50, 119.18, 127.13, 128.11, 128.32, 128.65, 128.97, 129.05, 129.13, 130.10, 133.68, 134.21, 137.19, 138.62 ppm. HRMS: calcd. for $C_{22}H_{18}ClN$ 331.1128; found 331.1127.

Synthesis of 3-Benzyl-2-(*p*-chlorophenyl)-2-phenylpropanoic Acid (20): A solution of 1.65 g (5.0 mmol) of **19** and 2.75 g (2.0 mmol) of KOH was refluxed in 10 mL of ethylene glycol for 5 h. The reaction mixture was then poured onto ice/water and then acidified with 10% HCl to pH = 2–3. The crude product was filtered and dried under vacuum. Recrystallization from hexane/diethyl ether (1:1) afforded 1.47 g (84.0%) of the pure carboxylic acid, m.p. 141 °C. ^{1}H NMR ($CDCl_3$): δ = 2.48–2.52 and 3.147 (m, 1 H), 2.72–2.83 (m, 1 H), 3.52–3.60 (m, 1 H), 3.84–3.91 (t, 1 H), 6.66–6.72 (m, 2 H), 6.89–7.53 (m, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 39.95, 41.90, 50.53, 57.46, 58.01, 126.18, 126.35, 127.71, 128.19, 128.24, 128.27, 128.41, 128.58, 128.61, 128.88, 128.96, 129.13, 129.31, 129.37, 129.87, 130.06, 132.08, 132.65, 136.31, 136.73, 139.01, 139.06, 139.22, 139.96, 178.08, 179.45 ppm. HRMS: calcd. for $C_{22}H_{19}ClO_2$ 349.0995 $[M - H]^-$; found 349.0982 $[M - H]^-$.

Synthesis of 3-(*p*-Chlorophenyl)-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (21): A mixture of 1.25 g (3.5 mmol) of **20** and 7.0 g of polyphosphoric acid was heated for 6 h. The reaction mixture was poured onto ice/water and extracted with ethyl acetate. The organic layer was dried and concentrated under vacuum to afford the crude product which was purified by column chromatography (hexane/ethyl acetate, 9:1) as colorless shining needles, yield 860 mg (74.1%), m.p. 174 °C. ^{1}H NMR ($CDCl_3$): δ = 3.17–3.24 (dd, J = 4, 16 Hz, 1 H), 3.35–3.450 (m, 1 H), 3.65–3.75 (dt, J = 4, 12 Hz, 1 H), 3.93–3.97 (d, J = 12 Hz, 1 H), 6.95–7.58 (m, 12 H), 8.09–8.10 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 47.94, 61.18, 68.37, 127.04, 127.43, 128.17, 128.54, 128.79, 128.80, 129.03, 129.05, 129.46, 132.69, 134.14, 138.40, 141.08, 142.59, 197.88 ppm. HRMS: calcd. for $C_{22}H_{17}ClO$ 355.0866 $[M^+ + Na]$; found 355.0866 $[M^+ + Na]$.

Synthesis of 3-(*p*-Cyanophenyl)-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (22): A mixture of 800 mg (2.4 mmol) of **21** and 883 mg (9.9 mmol) of cuprous cyanide in 10 mL of *N*-methylpyrrolidone was refluxed under nitrogen for 24 h. After cooling to room temperature, the reaction mixture was diluted with 15 mL of 10% ammonium hydroxide solution and extracted with ethyl acetate. The organic phase was washed well with water, dried and concentrated under vacuum. The residual semisolid was chromatographed (hexane/ethyl acetate, 9:1) to afford 201 mg (25.9%) of pure **22**, m.p. 192 °C. ^{1}H NMR ($CDCl_3$): δ = 3.15–3.25 (dd, J = 4, 16 Hz, 1 H), 3.38–3.42 (m, 1 H), 3.77–3.78 (dt, J = 4, 12 Hz, 1 H), 3.96 (d, J = 12 Hz, 1 H), 6.93–7.59 (m, 12 H), 8.10 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 37.41, 48.68, 60.84, 110.99, 118.95, 127.28, 127.64, 18.26, 128.57, 128.68, 128.79, 129.36, 132.53, 134.29, 137.96, 142.036, 147.85, 197.27 ppm. HRMS: calcd. for $C_{23}H_{17}NO$ 323.1310; found 323.1308.

Synthesis of 2-Bromo-3-(*p*-cyanophenyl)-2-phenyl-1,2,3,4-tetrahhydronaphthalen-1-one (23): To a solution of 484 mg (1.5 mmol) of 22 in 10 mL of acetic acid was added dropwise a solution of 120 mg (1.5 mmol) of bromine in 5.0 mL of acetic acid over a period of 10 min. The reaction mixture was stirred at ambient temperature for 2 h and then poured onto crushed ice. The yellow product was filtered and crystallized from hexane as a pale yellow solid, yield 480 mg (79.8%), m.p. 107–109 °C. ^{1}H NMR ($CDCl_3$): δ = 3.07–3.08 (m, 1 H), 3.53–3.57 (dd, 1 H), 3.58–3.79 (m, 1 H), 6.81–6.84 (d, 2 H), 7.07–7.60 (m, 10 H), 8.27–8.28 (d, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.94, 53.12, 57.22, 110.53, 124.96, 126.69, 126.90, 127.25, 127.69, 128.00, 128.78, 128.82, 129.37, 130.32, 130.48, 133.32, 136.44, 199.13 ppm. MS: calcd. for $C_{23}H_{16}BrNO$ – HBr 321.3; found 321.2; *m*/*z* = 291.0 232.1, 187.1 172.2, 149.1, 118.1, 85.1, 71.1.

Synthesis of 3-(*p*-Cyanophenyl)-2-phenylnaphthol (24): A solution of 400 mg (1.2 mmol) of **23**, 93 mg (1.2 mmol) of lithium carbonate,

and 24 mg (0.3 mmol) of lithium bromide in 5.0 mL of dimethylformamide was heated at 100 °C for 4 h. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was poured onto crushed ice and acidified with 20% hydrochloric acid. The crude product was filtered, washed with water and crystallized twice from hexane/diethyl ether (9:1) as pale yellow crystals, yield 298 mg (77.4%), m.p. 177 °C.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds, methodology and input files.

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