

An Experimental and Theoretical Study of the Type C Enone Rearrangement: Mechanistic and Exploratory Organic Photochemistry¹

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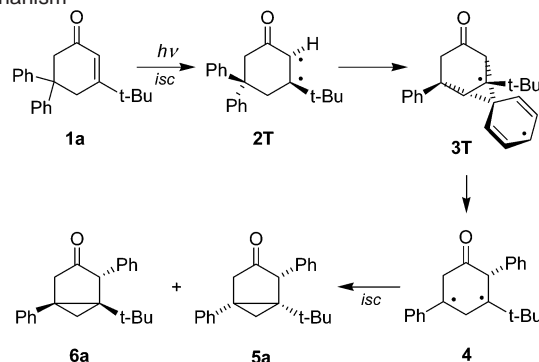
Abstract: We recently described a new photochemical rearrangement which we termed a Type C process. The reaction involves a δ to α aryl migration in 5-disubstituted cyclohexenones also having bulky C-3 substituents. In contrast to most cyclohexenone rearrangements, the reaction occurs via a twisted $\pi-\pi^*$ excited triplet rather than the usual $n-\pi^*$ state. The electronic nature of the rearrangement was assessed using migration selectivity with *p*-anisyl and *p*-cyanophenyl groups. A synthesis of the reactants was elaborated, and the product structures were established by X-ray and NMR analysis. The reaction mechanism was established further with DFT and CASSCF computations. In the latter, localized NBO basis orbitals permitted proper selection of the active space. The nature of the diradical intermediates as well as the transition states was established computationally. Sensitization experiments with regioselectivities the same as those in direct irradiation confirmed the triplet multiplicity of the process.

Introduction

Our previous study² uncovered the Type C rearrangement and suggested a mechanism. According to this mechanism, the reaction occurs on a triplet hypersurface with the $\pi-\pi^*$ excited triplet species **2T** being a key intermediate for this reaction. The subsequent phenyl migration through the half-migrated species **3T** occurs on the triplet hypersurface, and only after the migration is complete, or near completion, does intersystem crossing lead the system to the S_0 ground-state surface concomitant with ring-closure to diastereomeric products **5a** and **6a** (note Scheme 1).

To check this mechanism experimentally, it was decided to study relative migratory aptitudes of aryl groups. 4-Methoxyphenyl and 4-cyanophenyl substituents have been used previously to establish mechanisms of other photochemical transformations: for example, the Type A dienone,³ Type B enone,⁴ and Type B bicyclic rearrangements.⁵ Thus, it was natural to use this approach presently in the case of the Type C Enone Rearrangement. The two enones **1b** and **1c** were synthesized

Scheme 1. Type C Enone Rearrangement and Its Proposed Mechanism



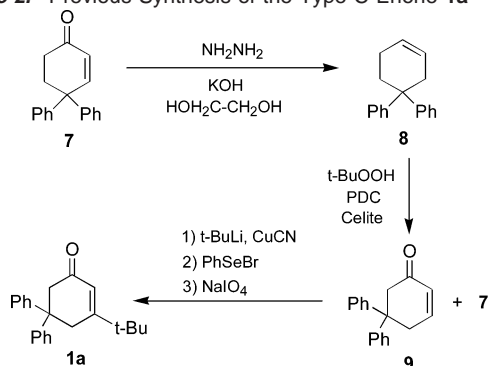
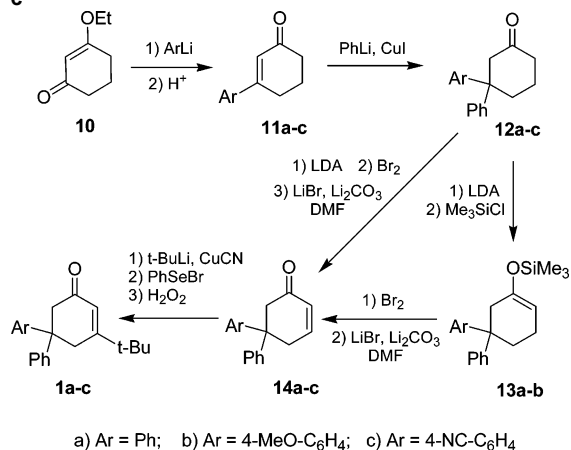
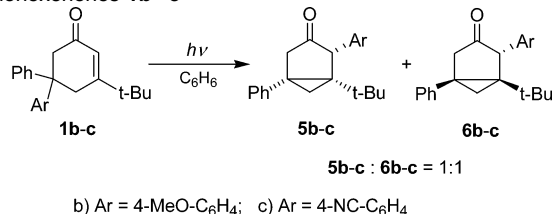
with the idea that the relative preference for δ to α migration of *p*-substituted phenyl vs phenyl groups in these compounds would provide information regarding the electronic factors controlling this reaction.

Synthesis

The previously designed² synthesis of the parent Type C enone **1a** (Scheme 2) has some evident drawbacks. First, it is not very efficient and convenient since in the key step, allylic oxidation of cyclohexene **8**, the desired cyclohexenone **9** is only a minor product with the major product being enone **7**, the ratio of **7** to **9** being 4:1. This approach also poses difficulties in introducing para groups such as cyano.

Hence the new synthetic approach in Scheme 3 was developed. This synthesis began with the addition of the aryllithium or phenylmagnesium bromide to 3-ethoxycyclohexenone **10**. A key step of this synthesis is the conjugate addition of lithium

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- (2) Zimmerman, H. E.; Nesterov, E. E. *J. Am. Chem. Soc.* **2002**, *124*, 2818–2830.
- (3) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486–4487. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527–4540. (c) Zimmerman, H. E.; J. O. Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 3354–3356.
- (4) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042. (b) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047. (c) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749–3760. (d) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879–886. (e) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887–896.
- (5) (a) Zimmerman, H. E.; Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 3354–3356. (b) Zimmerman, H. E.; Nasielski, J.; Keese, R.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895–4903.

Scheme 2. Previous Synthesis of the Type C Enone **1a****Scheme 3.** Improved Synthesis of 3-*tert*-Butyl-5,5-diaryl Enones **1a–c****Scheme 4.** Photochemistry of Para-Substituted 5-Aryl-5-phenyl Cyclohexenones **1b–c**

diphenylcuprate to enones **11a–c** to form 3,3-diarylcyclohexanones **12a–c**. Curiously, the reverse sequence with para-substituted cuprates reacting with enone **11a** afforded product only in poor or vanishing yields.

The enones **14a–c** were obtained by bromination–dehydrobromination directly under kinetically controlled conditions and also via the silyl enol ether **13**. Finally, the desired β -*tert*-butyl group was introduced by conjugate addition of lithium di-*tert*-butyl cuprate to enones **14a–c**. This was followed by selenylation of the copper enolate followed by oxidative selenoxide elimination.⁶

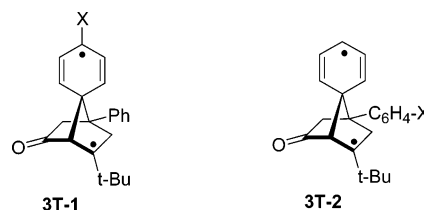
Results

Irradiation of *p*-methoxyphenyl **1b** and *p*-cyanophenyl **1c** enones in benzene solution proceeded smoothly to give only products derived from Type C enone rearrangements, thus providing further support for the rearrangement generality. See Scheme 4. For anisyl enone **1b** the reaction occurred selectively with exclusive migration of the anisyl group and with formation

Table 1. Calculated and Experimental ¹H NMR Chemical Shifts for Diastereomeric Photoproducts **5a** and **6a**^{a,b}

5a			6a		
atom	δ calcd, ppm	δ expt, ppm	atom	δ calcd, ppm	δ expt, ppm
H2a	2.48	2.73	H2a	2.64	2.73
H2b	3.34	3.39	H2b	2.99	3.15
H4 ^c	3.48	3.62	H4 ^c	4.31	4.34
H6a	1.78	1.87	H6a	2.13	1.92
H6b	0.35	0.41	H6b	1.11	1.11

^a GIAO RHF/6-31G(df,pd)//B3LYP/6-31G(d,p). ^b Calculated energies (B3LYP/6-31G(d,p)) for **5a** –928.0220560 a.u., for **6a** –928.0258215 a.u. ^c Note a remarkably high downfield shift for *endo* proton H4 in **6a** compared with *exo* proton in **5a**.

**Figure 1.** Alternative half-migrated species.

of the two diastereomeric bicyclic ketones **5b** and **6b** in an approximate ratio of 1:1. No products corresponding to phenyl group migration were found for this reaction up to 75% conversion. The products and their ratio were not changed when the irradiation was performed in the presence of 10-fold excess of acetophenone triplet sensitizer. Note Scheme 4.

Interestingly, the corresponding photolysis of cyanophenyl enone **1c** again led only to cyanophenyl migration products and, again, afforded two diastereomers **5c** and **6c** in an approximately 1:1 ratio (see Scheme 4). Similar to the case of the anisyl counterpart, acetophenone sensitization led to the same products in the same ratio as that in direct irradiation.

It turned out to be very easy to experimentally monitor the Type C photochemical rearrangement by ¹H NMR and even assign the product distribution as the reaction proceeds. This is possible because a singlet peak corresponding to an *endo* proton H4 in **6a–c** is deshielded and shifted almost 1 ppm downfield as compared with *exo*-H4 in **5a–c** (note Table 1). Remarkably, this deshielding effect is perfectly predicted by GIAO ab initio computation of NMR shifts for the photoproducts **5a** and **6a** (Table 1).

Computational Results: Density Functional and Nemo-khlin–Weinhold CASSCF/NBO Methods. In view of the new reaction encountered with its complex mechanism, computational treatments proved both necessary and inviting. For example, the preferential migration of the substituted aryl groups in the Type C reaction of enones **1b** and **1c** needed to be understood. It is clear, qualitatively, that the half-migrated triplet species **3T-1** should be lower in energy than its counterpart **3T-2** due to the greater resonance stabilization (note Figure 1). However, their relative stabilities must differ enough to account

(6) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.

(7) For example, in a photorearrangement of 4-(4-cyanophenyl)-4-phenylcyclohex-2-enone the ratio of cyanophenyl to phenyl migration is 15:1, see ref 4.

Table 2. Comparison of Energies of Reacting Intermediates **3T** for Two Competing Pathways^{a,b}

enone	migration intermediate	CASSCF/NBO computations ^c					
		DFT (UB3LYP) computations		(10,10) active space		(14,14) active space	
		absolute energy, a.u.	relative energy, kcal/mol	absolute energy, a.u.	relative energy, kcal/mol	absolute energy, a.u.	relative energy, kcal/mol
1b	3T-1	-1042.439049	0	-1035.809534 ^d	0	—	—
	3T-2	-1042.438111	0.6	-1035.808699 ^d	0.5	—	—
1c	3T-1	-1020.165753	0	-1013.696226	0	-1013.739082	0
	3T-2	-1020.161048	3.0	-1013.692251	2.5	-1013.736363	1.7

^a 6-31G* (6-31+G* for N and O) basis set was used throughout the computations. ^b Geometries were optimized at UB3LYP level of theory. ^c Single-point energy computations. ^d Computation with (10,9) active space.

for such an absolute migratory preference.⁷ This is just one of many questions we needed to consider computationally.

To assess the problem of the relative energies of **3T-1** and **3T-2**, we ran unrestricted density functional (i.e., DFT) methods with a B3 hybrid exchange-correlation functional and a LYP correlation functional (UB3LYP). This led to the results given in Table 2 (columns 3 and 4). The energy differences predicted a lower energy for migration of the para-substituted aryl group in agreement with experiment.

Considering the complex nature of biradical triplets **3T-1** and **3T-2** with possibly more than one configuration needed for an adequate description of them, it was of real interest to compare CASSCF results with those of the density functional. Normally, multiconfigurational computations on such complex systems as involved in the present study require an approach with a very large active space. The basic requirement for a proper computation is that one should include all of those configurations involving MOs from which and to which electron excitation is appreciable. However, current restrictions permit inclusion of only a limited number of orbitals into the active space (up to 14 in Gaussian 98).

Since molecules such as **3T-1** have a much larger number of potentially important molecular orbitals, one needs a way to select the orbitals which have the heaviest impact. An intuitive selection of MOs to comprise the active set is not safe. However, the dilemma is largely avoided using the Nemukhin–Weinhold “Complete Orthonormal Set of Natural Bond Orbitals (NBOs) Localized Basis Orbital” approach. This method uses those group orbitals which are most involved in delocalization.⁹ Thus, these orbitals, being placed into the CASSCF active space, contribute most to the correlation energy.

For example, for a conjugated enone moiety one needs to consider only five localized molecular orbitals with a total of six electrons. The MOs consist of four butadiene-like π orbitals (two bonding and two antibonding) and one nonbonding n_y orbital on oxygen. Thus, if a CASSCF computation starts with these localized MOs being placed into an active space, it will require only a (6,5) active space to reliably describe the enone moiety. Inclusion of a still larger active space adds σ framework involvement. These localized orbitals nicely correspond to the chemist’s Lewis structure picture (two-center “bonds” and one-center “lone pairs”). Using NBOs⁸ allows starting the CASSCF computation with those orbitals in the active space which are of utmost importance and thus ensures getting reliable computational results with a minimal active space. It should be noted

that, although the computation starts with localized MOs as an initial guess, the subsequent MCSCF treatment leads to an expansion of the MOs throughout **3T-1** and **3T-2**. The results of these computations are given in Table 2. For the cyanophenyl enone **1c** a (10,10) active space was first utilized. One can see now that this method predicts the cyanophenyl migration to be a more favorable process compared with phenyl migration (preference 2.5 kcal/mol) and is quite close to the prediction of the UB3LYP result of 3.0 kcal/mol. To check the validity of the active space selection, we performed a rather lengthy computation with an expanded (14,14) active space. The 14 bond orbitals used as a basis consisted of the π and π^* orbitals of the overlapping cyano π bond, the three bonds (six orbitals) of the nonmigrating benzene ring, the two π bonds (four orbitals) of the migrating ring, and then the two lone pair orbitals. This led to a 1.7 kcal/mol preference, suggesting that the (10,10) computation was a reasonable approximation. In the case of the methoxyphenyl enone **1b** the CASSCF/NBO computation with (10,9) active space gave a 0.5 kcal/mol preference for the methoxyphenyl migration. Again, this result came very close to the DFT prediction (0.6 kcal/mol).

In addition, for the cyanophenyl enone **1c**, DFT computations were utilized to establish the nature of the reactant excited states and parts of the excited and ground-state hypersurfaces in general. These results are given in Table 3. They will be considered in the context of the reaction mechanism in the Discussion section below.

Discussion of Computations

There are two aspects to the computation which should be discussed. One is the practicality of the methodology employed, and the second is discussion of the results themselves. In the Results section, we have noted the utility of employing localized group orbitals as a starting point in obtaining a CASSCF active space which is within practical limits and yet includes the important components of the configurational wavefunctions.

As an example, Figure 2 shows molecular orbitals (NBOs) which were used for CASSCF/NBO(10,10) treatment of the *p*-cyanophenyl migration intermediate **3T-1**. It should be additionally noted that, although the computation starts from localized MOs, a subsequent SCF treatment leads to “expansion” of these orbitals throughout the entire molecule, which ensures that all the local factors (e.g., other substituents present) not included originally into the consideration are now taken into account. One example of this “expansion” is shown in Figure 3. During the CASSCF treatment an initial localized NBO corresponding to the radical *p*-hybridized lone pair on carbon C3 (referred to as “lone pair 2” in Figure 2) is transformed to

(8) NBO 5.0. Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001.

(9) Nemukhin, A. V.; Weinhold, F. *J. Chem. Phys.* **1992**, *97*, 1095–1108.

Table 3. Energies of the Intermediate Species Included in the Photochemistry of Enone **1c**

species ^a	triplet hypersurface		singlet hypersurface ^b	
	abs energy, a.u.	relative energy, kcal/mol	abs energy, a.u.	relative energy, kcal/mol
Cyanophenyl Migration				
A, π - π^* twisted triplet 2T'	-1020.15387825	26.2	-1020.1955741	0
B, TS 2T \rightarrow 3T-1	-1020.13144910	40.2	-1020.1533007	26.5
C, half-migrated species 3T-1	-1020.1531002	26.7	-1020.1339865	38.6
Phenyl Migration				
D, π - π^* twisted triplet 2T''	-1020.1539451	26.2	-1020.1956917	0
E, TS 2T \rightarrow 3T-2	-1020.1297017	41.4	-1020.1462874	31.0
F, half-migrated species 3T-2	-1020.1483233	29.7	-1020.1267297	43.3

^a Geometry of the triplet species was optimized with UB3LYP/6-31G* level. ^b B3LYP/6-31G* single-point computations on the corresponding triplet geometries. Note: These computations used a less intricate basis than those in Table 2.

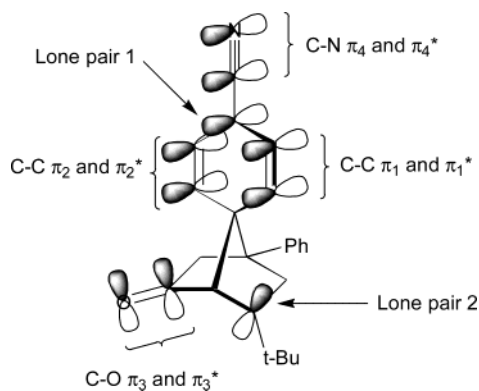


Figure 2. Natural bond orbitals (NBOs) used for CASSCF/NBO (10,10) computation of cyanophenyl migration intermediate **3T-1**. (14,14) computation additionally includes nonmigrating phenyl orbitals.

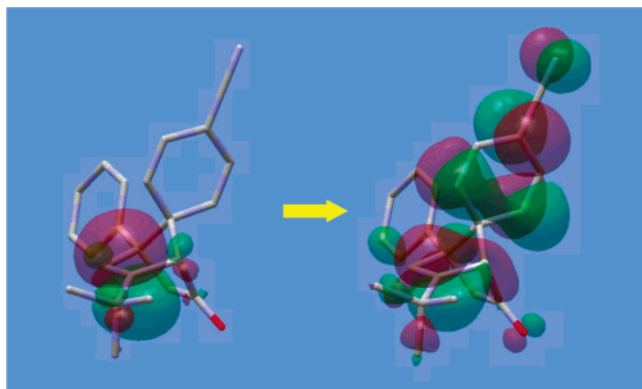


Figure 3. Expansion and delocalization of localized NBOs during CASSCF treatment: an orbital corresponding to lone pair on carbon C3 before (left) and after (right) CASSCF/NBO computation.

a fully delocalized MO, which still, to some extent, keeps its original character.

To be able to compare energies of two different species obtained with CASSCF computations, one needs to use the same active space size as well as to employ same basis orbitals in the active space. This ensures accessibility of similar configurations in both computations and inclusion of comparable correlation effects. For this reason when computing the phenyl migration intermediate **3T-2** (which lacks a cyano group on the migrating aryl) corresponding π and π^* molecular orbitals of the cyano group from the second nonmigrating aryl were included in the active space, thus keeping the same (10,10) active space size which was used for the intermediate **3T-1** (see Figure 2).¹⁰ Similarly, we used a (10,9) active space size during the methoxyphenyl enone **1b** computations both for methoxy-

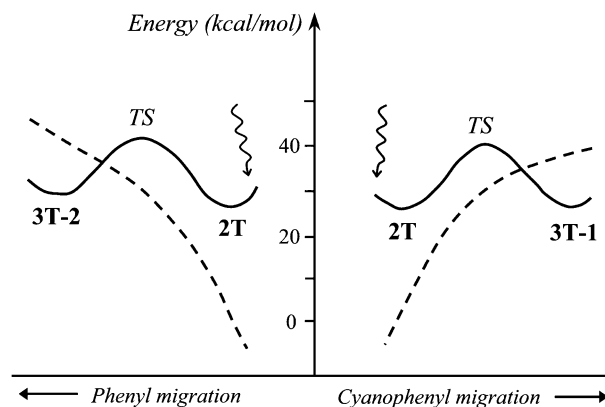


Figure 4. Schematic representation of two alternative reaction pathways for the Type C rearrangement of cyanophenyl enone **1c**. Solid lines correspond to triplet hypersurface, and dashed lines correspond to S_0 .

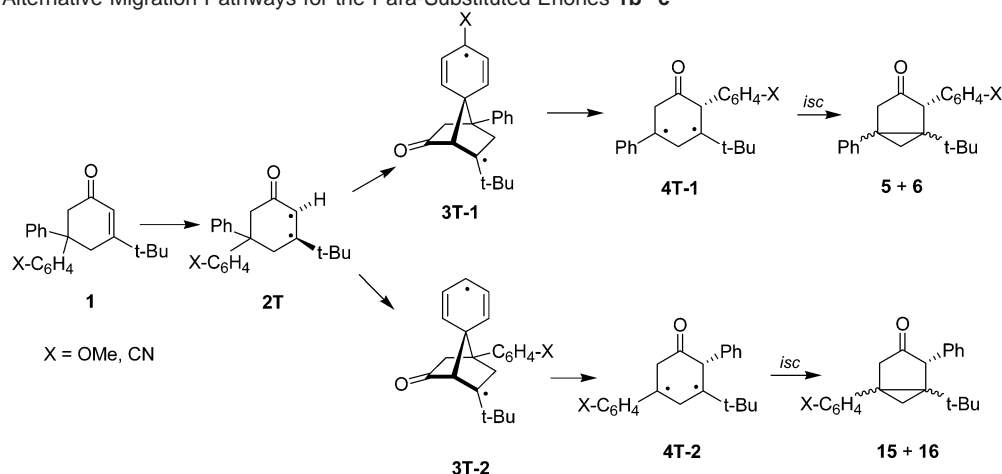
phenyl- and phenyl-migrated intermediates. Inclusion of the methoxy lone pair from the methoxy group oxygen of the nonmigrating aryl superficially seems superfluous but ensures contribution to the correlation energies in both cases. That both CASSCF/NBO and DFT computations gave almost the same energy preference for the para-substituted phenyl migration (see Table 1) provides support for the treatment.

The second important consideration is whether one can use energies of half-migrated diradical intermediates **3T** alone to predict computationally the relative efficiencies of aryl migrations. These intermediates represent local minima on triplet hypersurfaces, while the relative rates and thus the migratory aptitudes are determined by the heights of corresponding activation barriers (i.e. transition state energies). However, for many well-understood photochemical reactions of enones (e.g. the Type B enone rearrangement) computational studies revealed certain parallelisms between the energies of the half-migrated intermediates and the corresponding transition states.^{11a} Thus, the much easier to compute half-migrated biradicals were used instead of actual transition states for theoretical modeling of the various photochemical processes.^{11b-d}

To validate our use of the half-migrated intermediates **3T**, we ran DFT computations, for both T_1 and S_0 , of part of the reaction pathway for phenyl vs cyanophenyl migrations for

(10) The computations with extended (14,14) active space additionally included the π system of the nonmigrating aromatic ring in the active space (see Experimental Section for more details).

(11) (a) Zimmerman, H. E.; Kutateladze, A. G. *J. Org. Chem.* **1995**, *60*, 6008–6009. (b) Zimmerman, H. E.; Sebek, P. *J. Am. Chem. Soc.* **1997**, *119*, 3677–3690. (c) Zimmerman, H. E.; Sebek, P.; Zhu, Z. *J. Am. Chem. Soc.* **1998**, *120*, 8549–8550. (d) Zimmerman, H. E.; Alabugin, I. V.; Smolenskaya, V. N. *Tetrahedron* **2000**, *56*, 8621–8631.

Scheme 5. Two Alternative Migration Pathways for the Para-Substituted Enones **1b–c**

enone **1c**. The results are given in Table 3 and graphically presented in Figure 4. We note that consideration of transition-energy barriers gives a 1.2 kcal/mol preference for the cyanophenyl migration in parallel, but with somewhat smaller results than those obtained with half-migrated biradicals **3T-1** and **3T-2**.

Interestingly, these computations also support our suggestion that the key step—aryl migration—occurs on triplet hypersurface. From Figure 4 we see that the initial $\pi-\pi^*$ triplet can intersystem-cross into a ground-state surface only after it has moved past the transition-state barrier. A possible intersystem-crossing to S_0 might occur at the point after the transition state where the triplet and ground-state surfaces cross (see Figure 4). However, were it to occur, this would revert the molecule downhill back to the starting ground-state enone. Thus, for the rearrangement to occur, it must proceed through the triplet intermediate **3T**. A subsequent intersystem crossing leading to final products probably further occurs somewhere near the ring-opened intermediate **4T**.

Discussion: Mechanistic Aspects

The first point to be made is that in our previous report of the Type C rearrangement, the triplet excited state was noted to undergo the reaction. That the regioselectivity is the same for sensitized and direct irradiations, strongly suggests that the triplet is the reactive species in the direct irradiations as well.

Second, our previous² and present computations showed that the reaction originates from a twisted $\pi-\pi^*$ triplet **2T** (see Scheme 5). The twisting of the π C=C bond minimizes energy with the computed 35° dihedral angle for the triplet. Although for some of the known enone photochemical processes^{12,13} participation of the twisted $\pi-\pi^*$ triplet has also been suggested on experimental¹⁴ and theoretical¹⁵ grounds, this is quite different from the more common $n-\pi^*$ triplet reactions of conjugated enones where the $n-\pi^*$ triplet is the lower-energy

species. In the present study the source of the difference seems to arise from steric enhancement of enone twisting about the α,β -bond of the β -*tert*-butyl substituted enones. For these compounds, in contrast to the ordinary $n-\pi^*$ triplets, the $\pi-\pi^*$ triplet **2T** has the excitation primarily localized on the C=C double bond with strong diradical character of this bond and high electron density on the α -carbon. That this electronic feature is indeed a consequence in twisting of the π C=C bond is supported by the CASSCF/NBO computations of the triplet.² Moreover, the Type C rearrangement requires a bulky group (as *tert*-butyl) attached to the β -carbon, which facilitates this π -bond twisting and makes the $\pi-\pi^*$ triplet more energetically favorable compared with the $n-\pi^*$ triplet.¹⁶

A priori, while there is no doubt that the reaction starts as a triplet process, the rearrangement key step—aryl migration—might occur either completely on the triplet hypersurface, or at some point with intersystem crossing to the ground-state S_0 surface. Both possibilities are known in conjugated enone photochemistry. For example, in a case of a typical Type B enone rearrangement the aryl migration occurs in triplet state,⁴ while for the Type A dienone rearrangement, an aryl migration occurs in a ground-state singlet zwitterion.³ Our test of relative migratory aptitudes was designed to address this problem. In the Type B enone rearrangement, it is known^{4d,e} that the rate-limiting step is formation of a triplet-bridged species which is the counterpart to the one involved presently.

The experimentally found exclusive preference for the para-substituted aryl groups to migrate independently of the electronic character of the substituent supports the conclusion that this migration occurs in triplet state, and not on a singlet, zwitterionic hypersurface. Two different migration possibilities are depicted in Scheme 5. With the reaction occurring via the intermediacy of the triplet half-migrated intermediate **3T-1**, both cyano and methoxy substituents in the migrating group qualitatively are expected to stabilize the developing odd-electron center in the aromatic ring, thus lowering the energy of the intermediate **3T-1**. This explains why it is the para-substituted groups which exclusively migrate in a course of Type C enone rearrangement.

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- (16) This is a necessary requirement for the Type C rearrangement to occur in solution. However, in solid-state photochemistry this reaction may occur even without a bulky substituent, when crystalline environment facilitates it. One known example is the photoreaction of 4,5,5-triphenylcyclohex-2-enone (see ref 2).

Conclusions

The Type C enone rearrangement which includes long-range δ to α aryl migration occurs as a triplet reaction. Preference for para-substituted aryl groups to migrate independently of the nature of the substituent supports the mechanism including a key step—transannular aryl migration—to occur in triplet state followed by intersystem crossing to a singlet ground state. The CASSCF/NBO computational approach was shown to be a useful and reliable way for treatment of medium-sized open-shell biradical species where a multiconfigurational method is desirable.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel (Aldrich, 60 Å, 200–400 mesh, or Silica gel 60 Geduran 35–75 μ m) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns to allow monitoring with a hand-held UV lamp. All solvents were additionally purified and dried by standard techniques. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, and are reported in ppm downfield from tetramethylsilane.

3-Ethoxycyclohex-2-enone 10 was prepared according to a published procedure¹⁷ from 60.0 g (0.54 mol) of 1,3-cyclohexandione. This gave 75.0 g (100%) of the product as a colorless oil, bp 110–110 °C/4.5 mmHg (lit.¹⁷ bp 88 °C/2.5 mmHg).

3-Phenylcyclohex-2-enone 11a. A solution of phenylmagnesium bromide was prepared from 55.0 g (0.35 mol) of bromobenzene in 200.0 mL of ether and 8.6 g (0.36 mol) of Mg in 100.0 mL of ether. To the solution of this Grignard reagent a solution of 40.5 g (0.29 mol) of 3-ethoxycyclohex-2-enone (**10**) in 200.0 mL of ether was added dropwise at room temperature. The resulting mixture was stirred at reflux conditions for 3 h and then allowed to cool to room temperature. It was carefully quenched with 150.0 mL of 10% HCl, followed by addition of 200.0 mL of concentrated HCl. The resulting mixture was stirred at room temperature for 2.5 h. Then 400.0 mL of ether and 800.0 mL of water were added, the organic fraction was separated and washed successively with water, a saturated solution of NaHCO_3 , water, and brine, and dried over Na_2SO_4 . Concentration in vacuo gave crude solid product which was recrystallized from ether–hexane mixture to yield 37.5 g (75%) of **11a** as a yellow crystalline material, mp 59–61 °C (lit.¹⁸ mp 64–65 °C).

3,3-Diphenylcyclohexanone 12a. A solution of PhLi (222.7 mL of 0.73 M solution in ether–hexane, 162.6 mmol) was added dropwise to a stirred at 0 °C suspension of 15.53 g (81.3 mmol) of CuI in 200.0 mL of ether. The resulting mixture was stirred for 20 min, and a solution of 10.0 g (58.1 mmol) of 3-phenylcyclohex-2-enone (**11a**) in 100.0 mL of ether was added dropwise, followed by stirring for 2.5 h at 0 °C. The reaction mixture was poured into a separation funnel filled with a mixture of ice – concentrated aqueous NH_4Cl and ammonia solutions, and shaken vigorously for 10 min. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic fractions were washed with water and concentrated NaCl solution, and dried over Na_2SO_4 . After concentrating in vacuo, the oily residue was crystallized from ether–hexane to give 5.3 g of crude crystalline product. A mother liquor left after the crystallization was concentrated and subjected to chromatography on silica gel (column 16.0 cm \times 4.0 cm, eluent ethyl acetate–hexane 1:5). Fraction with R_f 0.40 gave additional 2.6 g of the product. Combined material was recrystallized from ether–hexane mixture to yield 7.4 g (51%) of **12a**

as colorless crystals, mp 110–113 °C (lit.¹⁹ mp 114–115 °C). ^1H NMR (CDCl_3) δ 7.33–7.14 (m, 10H), 2.96 (s, 2H), 2.58 (t, J = 5.8 Hz, 2H), 2.36 (t, J = 6.8 Hz, 2H), 1.75–1.62 (m, 2H).

1-(Trimethylsilyloxy)-5,5-diphenylcyclohex-1-ene 13a. A solution of *n*-BuLi (51.1 mL of 1.2 M solution in hexanes, 61.3 mmol) was added at –70 °C to a stirred solution of 7.74 g (76.6 mmol) of diisopropylamine in 40.0 mL of THF, followed by a stirring for 10 min at this temperature. To the resulting solution of LDA a solution of 33.4 g (38.8 mL, 0.306 mol) of trimethylchlorosilane in 40.0 mL of THF was added followed by the dropwise addition of a solution of 7.66 g (30.6 mmol) of 3,3-diphenylcyclohexanone (**12a**) in 60.0 mL of THF. The resulting mixture was stirred at –70 °C for 5 min, quenched with 45.0 mL of triethylamine followed by the addition of saturated aqueous solution of NaHCO_3 . The further workup included extracting with pentane, washing with water and 0.1 M aqueous solution of citric acid, and drying over Na_2SO_4 . Concentration in vacuo afforded crude solid product, which was recrystallized from pentane to give 7.42 g (75%) of **13a** as colorless crystals, mp 102–104 °C. ^1H NMR (CDCl_3) δ 7.29–7.11 (m, 10H), 4.81 (narrow m, 1H), 2.58 (s, 2H), 2.26 (t, J = 6.3 Hz, 2H), 1.81–1.71 (m, 2H), 0.22 (s, 9H).

5,5-Diphenylcyclohex-2-enone 14a. A mixture of 3.43 g (9.7 mmol) of 1-(trimethylsilyloxy)-5,5-diphenylcyclohex-1-ene (**13a**) and 2.81 g (20.4 mmol) of K_2CO_3 in 250.0 mL of ether was stirred and cooled to –75 °C, and a solution of 1.68 g (10.2 mmol) of bromine in 56.0 mL of CCl_4 was added via a dropping funnel as rapidly as possible (temperature of the reaction mixture should remain below –65 °C). When the addition was complete, the cold reaction mixture was poured into saturated aqueous solutions of NaHCO_3 and NaCl. The organic layer was washed with water and dried over Na_2SO_4 . This reaction was repeated with another 3.43 g portion of the silyl ether **13a**. The combined product solutions from these two runs were concentrated and dried in vacuo, which afforded 7.95 g of the bromide as a yellow oil. This bromide was dissolved in 90.0 mL of anhydrous DMF, and to this solution were added freshly vacuum-dried LiBr (6.34 g, 72.9 mmol) and Li_2CO_3 (3.60 g, 48.6 mmol). The resulting mixture was stirred at 135 °C for 5 h. Then it was allowed to cool to room temperature, poured into 600 mL of water, and extracted with two 250-mL portions of ether–pentane (1:1); the combined organic fraction was washed with water and dried over Na_2SO_4 . Concentration in vacuo gave solid product, which was recrystallized from CH_2Cl_2 –hexane mixture to afford 4.2 g (75% based on **13a**) of **14a** as colorless crystals, mp 104–106 °C (lit.² mp 104–105 °C).

3-tert-Butyl-5,5-diphenylcyclohex-2-enone 1a. The reaction of 3.50 g (14.1 mmol) of 5,5-diphenylcyclohex-2-enone (**14a**) was performed according to a previously published procedure², and gave 1.96 g (46%) of **1a** as colorless crystals, mp 102–104 °C (lit.² mp 102–104 °C).

3-(4-Methoxyphenyl)cyclohex-2-enone 11b. A solution of 16.0 g (85.7 mmol) of 4-bromoanisole in 100.0 mL of ether was added dropwise to a stirred at 0 °C solution of *n*-BuLi (84.0 mL of 1.02 M solution in hexanes, 85.7 mmol), and the resulting mixture was stirred for 2 h at this temperature. Then the temperature was decreased to –70 °C, and a solution of 10.0 g (71.4 mmol) of 3-ethoxycyclohex-2-enone (**10**) in 60.0 mL of ether was added dropwise. After the addition was complete, the reaction mixture was stirred for additional 2 h at –70 °C, and the cold mixture was quenched with 70.0 mL of 10% HCl. The reaction mixture was allowed to warm to room temperature followed by addition of 70.0 mL of concentrated HCl. After stirring for 1.5 h at room temperature, water (100 mL) and ether (200 mL) were added, and the organic fraction was separated and washed successively with water, saturated aqueous NaHCO_3 , water, and brine and was dried over Na_2SO_4 . Concentration in vacuo afforded a yellow

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solid, which was recrystallized from ether–hexane mixture to yield 9.5 g (66%) of **11b** as colorless crystals, mp 81–83 °C (lit.²⁰ mp 83–84 °C).

3-(4-Methoxyphenyl)-3-phenylcyclohexanone 12b. To a stirred at 0 °C suspension of 11.92 g (62.4 mmol) of CuI in 150.0 mL of ether a solution of PhLi (145.1 mL of 0.86 M solution in ether–hexanes, 124.8 mmol) was added via a dropping funnel, and the resulting mixture was stirred for 20 min at this temperature. A solution of 9.0 g (44.6 mmol) of 3-(4-methoxyphenyl)cyclohex-2-enone (**11b**) in 150.0 mL of ether was added dropwise, followed by stirring for 3 h at 0 °C. The reaction mixture was quenched with aqueous ammonia and concentrated NH₄Cl solutions, and the resulting mixture was vigorously stirred for 1.5 h at room temperature. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic fraction was washed with water and brine and dried over Na₂SO₄. After concentrating in vacuo, the oily residue was separated by chromatography on silica gel (column 48.0 cm × 4.0 cm, eluent ethyl acetate–hexane 1:3) to give the following fractions:

(a) 4.0 g of diphenyl as a yellow solid, *R_f* 0.83;

(b) 1.2 g of unidentified product as a yellowish solid, *R_f* 0.74;

(c) 7.4 g (59%, or 76% based on consumed starting material) of **12b** as a yellowish oil, *R_f* 0.43. ¹H NMR (CDCl₃) δ 7.31–7.16 (m, 5H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 2.93 (dd, *J*₁ = 18.0, *J*₂ = 15.6 Hz, 2H), 2.58–2.50 (m, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.74–1.63 (m, 2H); HRMS *m/e* 280.1467 (calcd for C₁₉H₂₀O₂ 280.1463);

(d) 1.9 g of the starting enone **11b** as a yellowish solid, *R_f* 0.16.

1-(Trimethylsilyloxy)-5-(4-methoxyphenyl)-5-phenylcyclohex-1-ene 13b. The reaction was performed according to a procedure similar to the one for compound **13a**. Reaction of 5.99 g (59.3 mmol) of diisopropylamine in 30.0 mL of THF, 39.5 mL of 1.20 M solution of *n*-BuLi in hexanes (47.4 mmol), 25.83 g (237.0 mmol) of chlorotrimethylsilane in 50.0 mL of THF, and 6.64 g (23.7 mmol) of 3-(4-methoxyphenyl)-3-phenylcyclohexanone (**12b**) in 50.0 mL of THF gave a yellow oil, which was dissolved in pentane (80.0 mL), and insoluble crystalline material was removed by filtration. The filtrate was concentrated in vacuo to afford 7.67 g (92%) of **13b** as a yellowish oil. ¹H NMR (CDCl₃) δ 7.30–7.10 (m, 5H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 4.83–4.77 (m, 1H), 3.77 (s, 3H), 2.56 (s, 2H), 2.22 (t, *J* = 6.0 Hz, 2H), 1.80–1.71 (m, 2H), 0.22 (s, 9H).

5-(4-Methoxyphenyl)-5-phenylcyclohex-2-enone 14b. The compound was synthesized by a procedure similar to the one for compound **14a**. Two separate runs with each run including 3.43 g (9.7 mmol) of 1-(trimethylsilyloxy)-5-(4-methoxyphenyl)-5-phenylcyclohex-1-ene (**13b**) and 2.81 g (20.4 mmol) of K₂CO₃ in 250.0 mL of ether, and 1.63 g (10.2 mmol) of bromine in 55.0 mL of CCl₄ afforded 7.05 g of the bromide as an orange oil. This bromide was brought into reaction with 5.12 g (58.8 mmol) of LiBr and 2.90 g (39.2 mmol) of Li₂CO₃ in 90.0 mL of DMF, and the crude product was purified by chromatography on silica gel (column 43.0 cm × 4.0 cm, eluent ethyl acetate–hexane 1:3). A fraction with *R_f* 0.31 was collected and yielded, after concentration in vacuo, 3.1 g (57%) of **14b** as an orange oil. ¹H NMR (CDCl₃) δ 7.31–7.13 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.99 (dt, *J*₁ = 10.0, *J*₂ = 4.1 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.04 (dt, *J*₁ = 10.0, *J*₂ = 1.8 Hz, 1H), 3.76 (s, 3H), 3.19 (s, 2H), 3.16 (dd, *J*₁ = 4.1, *J*₂ = 1.8 Hz, 2H); HRMS *m/e* 278.1304 (calcd for C₁₉H₁₈O₂ 278.1307).

3-tert-Butyl-5-(4-methoxyphenyl)-5-phenylcyclohex-2-enone 1b. A solution of *t*-BuLi (16.9 mL of 1.7 M solution in pentane, 28.8 mmol) was added to a stirred suspension of 1.29 g (14.4 mmol) of CuCN in 50.0 mL of ether at 0 °C, and the resulting mixture was stirred at this temperature for 20 min, followed by the dropwise addition of a solution of 2.00 g (7.2 mmol) of 5-(4-methoxyphenyl)-5-phenylcyclohex-2-enone **14b** in 50.0 mL of ether. After the addition was complete, the

reaction mixture was stirred at 0 °C for 3 h. A solution of PhSeBr was prepared by dropwise addition of 2.53 g (0.81 mL, 15.8 mmol) of Br₂ to a solution of 5.10 g (16.4 mmol) of diphenyldiselenide in 50.0 mL of ether at intensive agitation.⁶ The resulting solution of PhSeBr was rapidly added to the reaction mixture. After the stirring for an additional 5 min at 0 °C, the reaction mixture was poured into a mixture of 200.0 mL of 5% HCl and 200.0 mL of ether–pentane (1:1). The organic fraction was washed with saturated NaHCO₃ solution and water and dried over Na₂SO₄. After concentrating in vacuo, the oily residue was dissolved in 80.0 mL of CH₂Cl₂. Pyridine (5.17 g, 65.5 mmol) was added, and a solution of H₂O₂ (prepared from 9.37 mL of 30% H₂O₂ and 8.0 mL of water, 91.7 mmol) was carefully added at intensive stirring with ice–water cooling (the temperature of the reaction mixture should be kept below 30 °C). After the addition was complete, the resulting mixture was intensively stirred at room temperature for 30 min, and it was then poured into a mixture of 150.0 mL of 7% NaHCO₃ and 150.0 mL of CH₂Cl₂. The aqueous layer was extracted with CH₂-Cl₂, the combined organic fraction was washed successively with 10% HCl, water, and brine and dried over Na₂SO₄. Concentration in vacuo gave a dark-orange oil, which was separated by chromatography on silica gel (column 42.0 cm × 4.0 cm, eluent ethyl acetate–hexane 1:3). A fraction with *R_f* 0.36 was collected, which afforded 1.08 g of crude **1b** as an orange oil. It was crystallized and further recrystallized from hexane to give 0.83 g (35%) of colorless crystals, mp 122–123 °C. ¹H NMR (CDCl₃) δ 7.30–7.13 (m, 5H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.94 (br s, 1H), 3.76 (s, 3H), 3.16 (s, 2H), 3.06 (s, 2H), 1.05 (s, 9H); UV (benzene), nm: 334 (ε = 48), 286 (ε = 1000); HRMS *m/e* 334.1927 (calcd for C₂₃H₂₆O₂ 334.1933).

Preparative Solution Photolysis of 3-tert-Butyl-5-(4-methoxyphenyl)-5-phenylcyclohex-2-enone 1b (Direct Irradiation). A solution of 200 mg (0.6 mmol) of enone **1b** in 80.0 mL of benzene was irradiated in a Pyrex tube placed next to a water-cooled 400-W medium-pressure mercury lamp equipped with a 2-mm Pyrex filter for 8 h. Nitrogen was passed through the solution for 1 h before and during the photolysis. After concentrating in vacuo, the oily residue was separated by column chromatography on silica gel (column 50.0 cm × 2.5 cm, eluent ethyl acetate–hexane 1:5) to give the following fractions:

(a) 30 mg (15%) of unidentified product as a yellow oil, *R_f* 0.58;

(b) 61 mg (31%) of 1-*tert*-butyl-*exo*-2-(4-methoxyphenyl)-5-phenylbicyclo[3.1.0]hexan-3-one (**5b**) as a colorless solid, *R_f* 0.52. It was recrystallized from ether–hexane mixture to give colorless prisms, mp 171–174 °C. The structure of the product **5b** was confirmed by a single-crystal X-ray analysis. ¹H NMR (CDCl₃) δ 7.59–7.53 (m, 2H), 7.43–7.23 (m, 7H), 6.94 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 3H), 3.57 (s, 1H), 3.36 (ddd, *J*₁ = 18.3, *J*₂ = 3.3, *J*₃ = 1.1 Hz, 1H), 2.70 (d, *J* = 18.3 Hz, 1H), 1.85 (dd, *J*₁ = 5.9, *J*₂ = 3.3 Hz, 1H), 0.62 (s, 9H), 0.38 (d, *J* = 5.9 Hz, 1H); HRMS *m/e* 334.1926 (calcd for C₂₃H₂₆O₂ 334.1933);

(c) 54 mg (27%) of 1-*tert*-butyl-*endo*-2-(4-methoxyphenyl)-5-phenylbicyclo[3.1.0]hexan-3-one (**6b**) as a colorless solid, *R_f* 0.45. It was recrystallized from ether–hexane mixture to give colorless crystals, mp 136–137 °C. ¹H NMR (CDCl₃) δ 7.49–7.43 (m, 2H), 7.39–7.23 (m, 3H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.29 (s, 1H), 3.81 (s, 3H), 3.14 (dt, *J*₁ = 19.1, *J*₂ = 2.3 Hz, 1H), 2.72 (d, *J* = 19.1 Hz, 1H), 1.87 (dt, *J*₁ = 6.3, *J*₂ = 2.3 Hz, 1H), 1.05 (d, 6.3 Hz, 1H), 0.67 (s, 9H); HRMS *m/e* 334.1935 (calcd for C₂₃H₂₆O₂ 334.1933);

(d) 35 mg (18%) of the starting material as a yellowish oil, crystallizing upon standing, *R_f* 0.36.

Preparative Solution Photolysis of 3-tert-Butyl-5-(4-methoxyphenyl)-5-phenylcyclohex-2-enone 1b (Sensitized Irradiation). A solution of 100 mg (0.3 mmol) of enone **1b** and 0.36 g (3.0 mmol) of acetophenone in 40.0 mL of benzene was irradiated in a Pyrex tube placed next to a water-cooled 400-W medium-pressure mercury lamp equipped with 2-mm Pyrex filter for 4 h. Nitrogen was passed through the solution for 1 h before and during the photolysis. After concentrating in vacuo, acetophenone was removed by vacuum distillation (1 mmHg)

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at 80 °C, leaving 100 mg of oily residue. ¹H NMR analysis of the residue showed 70% conversion of the starting material with the ratio of products **5b** to **6b** to be 1:1.2. No formation of any other products was observed.

3-(4-Cyanophenyl)cyclohex-2-enone 11c. A solution of *n*-BuLi (47.6 mL of 1.2 M solution in hexanes, 57.1 mmol) was added slowly to a stirred at -70 °C solution of 10.0 g (54.9 mmol) of 4-bromobenzonitrile in 300.0 mL of THF (temperature of the reaction mixture should remain below -65 °C during the addition). After the addition was complete, the resulting mixture was stirred for 1 h at -70 °C, followed by dropwise addition of a solution of 6.99 g (49.9 mmol) of 3-ethoxycyclohex-2-enone (**10**) in 60.0 mL of THF. The resulting mixture was further stirred for 2 h at this temperature and then carefully quenched with 40.0 mL of 10% HCl. The reaction mixture was allowed to warm gradually to room temperature, concentrated HCl (15.0 mL) was added, and the resulting mixture was additionally stirred for 1.5 h. Then it was poured into 300.0 mL of water and extracted with two 300.0 mL portions of ether. The organic fraction was washed successively with water, saturated NaHCO₃, water, and brine and dried over Na₂SO₄. Concentration in vacuo afforded a mixture of products as a dark oil. One of the byproducts, 3-butylcyclohex-2-enone, was removed by distillation in vacuo (0.5 mmHg) at 110 °C, and the oily residue was crystallized from methanol to give 3.2 g of crude **11c** as yellow crystals. A mother liquor left after the crystallization was separated by chromatography on silica gel (column 47.0 cm × 4.0 cm, eluent ethyl acetate-hexane 1:2), and the following fractions were collected:

(a) 1.1 g (9%) of 3-(4-pentanoyl-phenyl)cyclohex-2-enone **17** as a yellowish solid, *R_f* 0.42. It was recrystallized from ether-hexane mixture to give colorless crystals, mp 74–76 °C. ¹H NMR (CDCl₃) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 6.46 (t, *J* = 1.5 Hz, 1H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.79 (td, *J₁* = 6.5, *J₂* = 1.5 Hz, 2H), 2.51 (t, *J* = 6.5 Hz, 2H), 2.25–2.13 (m, 2H), 1.79–1.66 (m, 2H), 1.48–1.35 (m, 2H), 0.96 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃) δ 199.76, 199.52, 158.31, 142.96, 137.75, 128.40 (2C), 126.66, 126.21 (2C), 38.40, 37.18, 27.99, 26.33, 22.69, 22.39, 13.89; HRMS (ESI) *m/e* 257.1548 ([M + H]⁺) (calcd for C₁₇H₂₁O₂ 257.1541);

(b) 2.1 g of **11c** as yellowish solid, *R_f* 0.28.

The combined product material was recrystallized from methyl *tert*-butyl ether to give 4.5 g (46%) of **11c** as colorless crystals, mp 90–91 °C (lit.²¹ mp 79–81 °C).

3-(4-Cyanophenyl)-3-phenylcyclohexanone 12c. To a stirred at 0 °C suspension of 2.66 g (13.9 mmol) of CuI in 80.0 mL of ether was added dropwise a solution of PhLi (30.6 mL of 0.91 M solution in ether, 27.9 mmol), and the resulting mixture was stirred for 1 h at 0 °C. Then the reaction mixture was allowed to warm to room temperature, and a solution of 1.83 g (9.3 mmol) of 3-(4-cyanophenyl)cyclohex-2-enone (**11c**) in a mixture of 7.0 mL of THF and 7.0 mL of ether was slowly added, followed by the stirring at room temperature for additional 3 h. Concentrated solutions of NH₄Cl (50 mL) and ammonia (50 mL) were added, and the reaction mixture was transferred into a separation funnel and shaken vigorously until all inorganic material dissolved in the aqueous layer and the organic layer became clear and transparent. The organic fraction was washed with water and brine and dried over Na₂SO₄. After concentrating in vacuo, the oily residue was separated by chromatography on silica gel (column 43.0 cm × 4.0 cm, eluent ethyl acetate-hexane 1:2), and a fraction with *R_f* 0.44 was collected which afforded 1.4 g (55%) of **12c** as a very viscous, yellow oil. ¹H NMR (CDCl₃) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.35–7.13 (m, 7H), 2.99 (d, *J* = 15.0 Hz, 1H), 2.90 (d, *J* = 15.0 Hz, 1H), 2.65–2.53 (m, 2H), 2.38 (t, *J* = 6.9 Hz, 2H), 1.75–1.63 (m, 2H); HRMS (ESI) *m/e* 298.1204 ([M + Na]⁺) (calcd for C₁₉H₁₇NONa 298.1208).

5-(4-Cyanophenyl)-5-phenylcyclohex-2-enone 14c. A solution of *n*-BuLi (5.3 mL of 1.12 M solution in hexanes, 5.9 mmol) was added

to a stirred at -70 °C solution of 0.74 g (7.4 mmol) of diisopropylamine in 30.0 mL of THF, and the resulting solution was stirred for an additional 20 min at this temperature. A solution of 1.30 g (4.7 mmol) of 3-(4-cyanophenyl)-3-phenylcyclohexanone (**12c**) in 20.0 mL of THF was added to the resulting LDA solution, followed by stirring for 1 h at -70 °C. Then a solution of 1.18 g (7.4 mmol) of Br₂ in 44.0 mL of CCl₄ was slowly added at this temperature, and the resulting mixture was further stirred for 2 h. After quenching with 20.0 mL of water, the reaction mixture was warmed to room temperature, extracted with ether, washed successively with saturated aqueous NaHCO₃, water, and brine, and dried over Na₂SO₄. It was concentrated and dried in vacuo to afford 2.0 g of the crude bromoketone as an orange oil. This bromoketone was dissolved in 30.0 mL of anhydrous DMF, and freshly vacuum-dried LiBr (1.47 g, 17.0 mmol) and Li₂CO₃ (0.84 g, 11.3 mmol) were added to this solution. The resulting mixture was stirred at 135 °C for 5 h. Then it was allowed to cool to room temperature, poured into 150 mL of water, extracted with two 100-mL portions of ether-pentane (2:1), and the combined organic fractions were washed with water and dried over Na₂SO₄. After concentration in vacuo, the oily residue was purified by chromatography on silica gel (column 54.0 cm × 2.5 cm, eluent ethyl acetate-hexane 1:2). A fraction with *R_f* 0.34 afforded 0.75 g (58%) of **14c** as a colorless solid, which was further recrystallized from a mixture of hexanes-ether-dichloromethane to give colorless crystals, mp 156–157 °C. ¹H NMR (CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.34–7.19 (m, 5H), 7.16–7.11 (m, 2H), 7.01 (dt, *J₁* = 10.2, *J₂* = 4.2 Hz, 1H), 6.07 (dt, *J₁* = 10.2, *J₂* = 1.8 Hz, 1H), 3.24–3.16 (m, 4H); HRMS *m/e* 273.1157 (calcd for C₁₉H₁₅NO 273.1154).

3-*tert*-Butyl-5-(4-cyanophenyl)-5-phenylcyclohex-2-enone 1c. The compound **1c** was synthesized by a procedure similar to the one for compound **1b**. Reaction of 0.60 g (2.2 mmol) of 5-(4-cyanophenyl)-5-phenylcyclohex-2-enone (**14c**) in 20.0 mL of THF, 5.16 mL of 1.7 M solution of *t*-BuLi in pentane (9.5 mmol), 0.39 g (4.3 mmol) of CuCN in 10.0 mL of ether, and a solution of PhSeBr prepared from 1.56 g (5.0 mmol) of diphenyl diselenide in 5.0 mL of ether and 0.78 g (4.9 mmol) of Br₂ gave the intermediate selenoketone. This was dissolved in 30.0 mL of methylene chloride and oxidized with 3.21 g of 30% H₂O₂ (28.3 mmol) in the presence of 1.59 g (20.1 mmol) of pyridine. The material after the reaction was purified by chromatography (column 50.0 cm × 2.5 cm, eluent ethyl acetate-hexane 1:3), and a fraction with *R_f* 0.42 afforded 0.28 g (39%) of **1c** as a yellowish solid. An additional recrystallization from ether-hexane mixture gave **1c** as a colorless crystals, mp 161–165 °C. ¹H NMR (CDCl₃) δ 7.56 (d, *J* = 9.0 Hz, 2H), 7.31–7.17 (m, 5H), 7.15–7.10 (m, 2H), 5.97 (s, 1H), 3.19 (s, 2H), 3.07 (s, 2H), 1.05 (s, 9H); UV (benzene), nm: 334 (ε = 52), 282 (ε = 550); HRMS (ESI) *m/e* 352.1683 ([M + Na]⁺) (calcd for C₂₃H₂₃NONa 352.1677).

Preparative Solution Photolysis of 3-*tert*-Butyl-5-(4-cyanophenyl)-5-phenylcyclohex-2-enone 1c (Direct Irradiation). A solution of 100 mg (0.3 mmol) of enone **1c** in 30.0 mL of benzene was irradiated in a Pyrex tube placed next to a water-cooled medium-pressure mercury lamp equipped with 2-mm Pyrex filter for 3.5 h. Nitrogen was passed through the solution for 1 h before and during the photolysis. After concentrating in vacuo, the oily residue was separated by column chromatography on silica gel (column 39.0 cm × 1.5 cm, eluent ethyl acetate-hexane 1:3) to give the following fractions:

(a) 13 mg (13%) of unidentified product as a yellowish oil, *R_f* 0.75;

(b) 18 mg (18%) of 1-*tert*-butyl-*exo*-2-(4-cyanophenyl)-5-phenylbicyclo[3.1.0]hexan-3-one (**5c**) as a colorless oil, *R_f* 0.64. ¹H NMR (CDCl₃) δ 7.59–7.10 (m, 9H), 3.66 (s, 1H), 3.36 (dm, *J* = 17.9 Hz, 1H), 2.74 (d, *J* = 17.9 Hz, 1H), 1.91 (dd, *J₁* = 6.4, *J₂* = 2.1 Hz, 1H), 0.61 (s, 9H), 0.43 (d, *J* = 6.4 Hz, 1H); HRMS *m/e* 329.1776 (calcd for C₂₃H₂₃NO 329.1780);

(c) 22 mg (22%) of 1-*tert*-butyl-*endo*-2-(4-cyanophenyl)-5-phenylbicyclo[3.1.0]hexan-3-one (**6c**) as a colorless solid, *R_f* 0.50. It was recrystallized from ether-hexane mixture to give colorless prisms, mp 165–168 °C. The structure of the product **6c** was confirmed by a single-

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crystal X-ray analysis. ^1H NMR (CDCl_3) δ 7.61–7.11 (m, 9H), 4.41 (s, 1H), 3.24 (dt, $J_1 = 17.5$, $J_2 = 2.2$ Hz, 1H), 2.77 (d, $J = 17.5$ Hz, 1H), 1.99 (dt, $J_1 = 6.6$, $J_2 = 2.2$ Hz, 1H), 1.15 (d, $J = 6.6$ Hz, 1H), 0.68 (s, 9H); HRMS m/e 329.1787 (calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$ 329.1780);

(d) 38 mg (38%) of the starting material **1c** as a colorless solid, R_f 0.36.

Preparative Solution Photolysis of 3-tert-Butyl-5-(4-cyanophenyl)-5-phenylcyclohex-2-enone 1c (Sensitized Irradiation). A solution of 50 mg (0.15 mmol) of enone **1c** and 0.18 g (1.5 mmol) of acetophenone in 15.0 mL of benzene was irradiated in a Pyrex tube placed next to a water-cooled medium-pressure mercury lamp equipped with 2-mm Pyrex filter for 1.5 h. Nitrogen was passed through the solution for 1 h before and during the photolysis. After concentrating in vacuo, acetophenone was removed by vacuum distillation (1 mmHg) at 80 °C, leaving 50 mg of oily residue. ^1H NMR analysis of the residue showed conversion of the starting material 60% with the ratio of products **5c** to **6c** to be 1:1.4. No formation of any other products was observed.

Computational Procedures. Ab initio and DFT computations were performed on Intel Pentium III-based multiprocessor cluster with Linux OS using the Gaussian 98²² computational package. Geometry optimization of intermediates **2T** and **3T** was performed with UB3LYP method. Geometry of the transition states between **2T** and **3T** was obtained by QST3 computations followed by IRC analysis. The CASSCF/NBO computations were done by the following way. A preliminary CASSCF(4,4) single-point computation was accompanied by NBO analysis,⁸ with the resulting localized NBOs been written into

a checkpoint (*.chk) file using a command “AONBO=c” in the NBO command line. Then the NBO output was analyzed, and the orbitals of interest were chosen. The final CASSCF run was performed starting from the checkpoint file with these NBOs having been placed into the active space (using a command “guess=(check,alter)” in the command line). The size of the active space was varied, depending on the particular species to analyze. Thus, the computations of cyanophenyl enone **1c** half-migrated species **3T-1** and **3T-2** utilized active space (10,10). It included the following orbitals: two (π and π^*) orbitals of C=O group, five (two π , two π^* and a p-type lone pair) orbitals on a migrating aryl group, p-type lone pair on carbon C3, and two conjugated with aromatic π system π and π^* orbitals of a cyano group (for the intermediate **3T-2** with *phenyl* group migrated, these two orbitals were included from the cyano group of a *nonmigrating* aryl to keep consistency of the active space). Similar to that, computations of the methoxyphenyl enone **1b** case involved (10,9) active space. Here one p-type lone pair orbital of methoxy group was used instead of two orbitals of cyano group in the enone **1c** case. The computations of the cyanophenyl enone intermediates **3T-1** and **3T-2** with extended (14,14) active space involved all the same orbitals as mentioned above for the (10,10) active space computation except for the two (π and π^*) orbitals of C=O group which were not included (total eight orbitals). In addition to them, six π orbitals (three π and three π^*) of the nonmigrating aromatics were added, thus bringing the active space to (14,14). An example of the CASSCF/NBO input and output files is given in Supporting Information.

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Supporting Information Available: Examples of Gaussian 98 input and output files for CASSCF/NBO treatment; X-ray coordinates of compounds **5b** and **6c** (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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