

o-Xylylenes and Isoindenes as Reaction Intermediates

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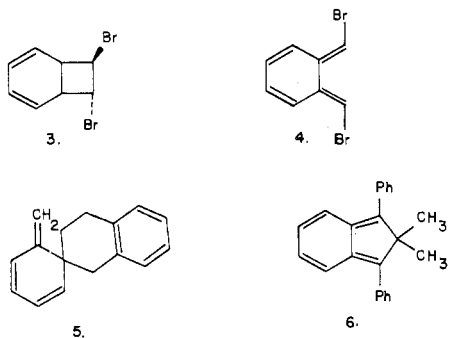
Received April 1, 1980

After being largely ignored for many years, the simple structures *o*-xylylene (1) and isoindene (2) (also called



o-quinodimethanes) and their derivatives are now under active investigation from theoretical, physical, physical organic, and synthetic organic viewpoints.

The earliest report in which an *o*-xylylene structure was implicated was the reaction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylylene with iodide ion to give 1,2-dibromobenzocyclobutene.^{1,2} This assignment was confirmed by Cava and Napier,³ who showed that 3, and not the

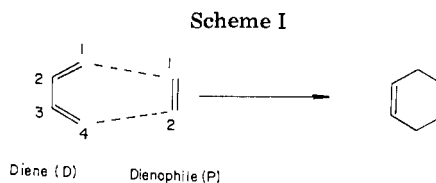


o-xylylene structure 4, was the correct structure for Finkelstein's product. However, Cava and co-workers later showed that 4 was an intermediate in the reaction by trapping it with a number of dienophiles.⁴ Also, Jensen and co-workers⁵ proposed that the reaction of 1,2-diphenylbenzocyclobutene with dienophiles involved the corresponding 1,4-diphenyl-*o*-xylylene.

In 1961, two significant reports appeared. One described the generation of the parent *o*-xylylene by a Hofmann elimination at high temperature,⁶ as evidenced by isolation of the "spirodimer" 5. The second demonstrated the generation of *o*-xylylenes and isoindenes by elimination of bromine from *o,o'*-dibromoxylylene derivatives.⁷ The former were identified by trapping with dienophiles, and one derivative, 6, was isolated.

My interest in *o*-xylylenes lies in their photochemical formation. Early reports which stimulated this interest were, first, the formation of phenyl-substituted *o*-xylylenes on photodecarbonylation of 2-indanones⁸ described by Quinkert, and, second, a proposal by Griffin et al.⁹ of the intermediacy of an isoindene in a photo-

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chemical phenyl migration. Photochemical formation of reactive intermediates has advantages in that they can often be generated under conditions (e.g., temperature) and in concentrations (e.g., by flash photolysis) not possible by ground-state reactions. Thus, spectra and decay kinetics can be studied.

Theoretical Aspects

o-Xylylene and isoindene have been described as "biradicaloid hydrocarbons". The term biradicaloid means "Those molecular geometries at which a simple MO picture shows two approximately non-bonding molecular orbitals containing a total of two electrons in the ground state. . .".¹⁰ Thus, *o*-xylylene has a HOMO-LUMO gap of 0.58β , while for butadiene it is 1.24β .¹¹ Like biradicals, which have a pair of degenerate, nonbonding orbitals (e.g., tetramethylene), biradicaloids are reactive species. The first calculations¹² on *o*-xylylene and its derivatives revealed the small HOMO-LUMO separation, and it was concluded that the systems had not been isolated because of their reactivity. Modern work has shown that the reactivity of *o*-xylylenes does not preclude their isolation. Even the parent can be prepared by matrix isolation^{10,13} where its dimerization⁶ is prevented, and suitably substituted *o*-xylylenes and isoindenes have been prepared at ambient temperatures.^{7,14-17}

(1) H. Finkelstein, Dissertation, Strassburg, 1910, cited in ref 2 and discussed in ref 3.

(2) W. Oppolzer, *Synthesis*, 11, 793 (1978).

(3) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, 79, 1701 (1957).

(4) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, 81, 6458 (1959).

(5) F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, 80, 6149 (1958).

(6) L. A. Errede, *J. Am. Chem. Soc.*, 83, 949 (1961).

(7) K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961).

(8) G. Quinkert, *Pure Appl. Chem.*, 9, 607 (1964).

(9) G. W. Griffin, A. F. Marcantonio, H. H. Kristinsson, R. C. Pettersson, and C. S. Irving, *Tetrahedron. Lett.*, 2951 (1965).

(10) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, 96, 3280 (1974).

(11) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π -electron Calculation", W. H. Freeman, San Francisco, CA, 1965.

(12) (a) A. J. Namiot, M. E. Dyatkina, and I. K. Syrkin, *C. R. Acad. Sci. URSS*, 48, 285 (1945); (b) M. E. Dyatkina and I. K. Syrkin, *Acta Physicochem. URSS*, 21, 23 (1946).

(13) E. Migirdicyan and J. Baudet, *J. Am. Chem. Soc.*, 97, 7400 (1975).

(14) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, 98, 8510 (1976).

(15) R. J. Palensky and H. A. Morrison, *J. Am. Chem. Soc.*, 99, 3507 (1977).

(16) W. R. Dolbier, Jr., K. Matsue, H. J. Dewey, D. V. Horak, and J. Michl, *J. Am. Chem. Soc.*, 101, 2136 (1979).

(17) D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 171 (1975), and reference cited.

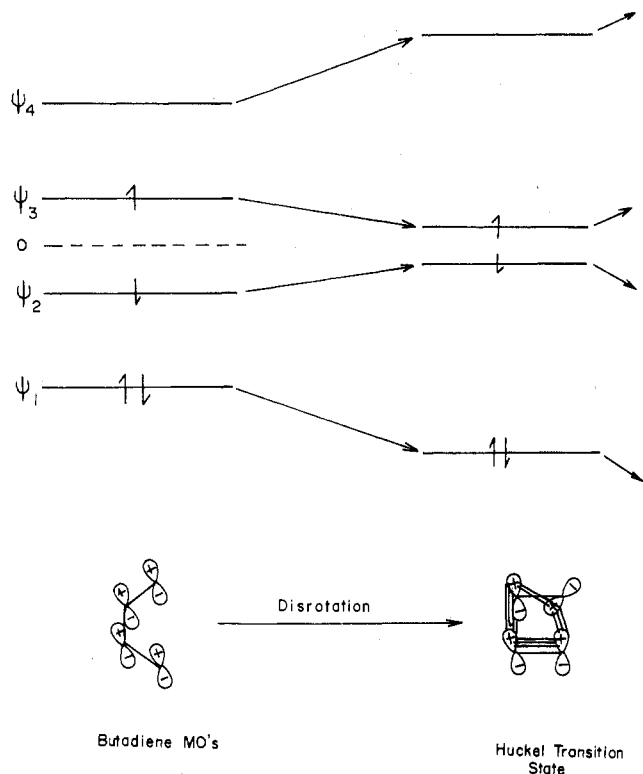


Figure 1. Orbital correlation diagram for the π system of butadiene in the disrotatory closure to cyclobutene (from ref 20).

The electronic structure of biradicaloids is important for two reasons. Firstly, the small HOMO-LUMO gap (which usually means these levels are close to the nonbonding level) results in high reactivity in cycloadditions and electrocyclic reactions, according to perturbation theory¹⁸ (see Scheme I). For example, in the Diels-Alder reaction between a diene and a dienophile, the π stabilization energy at the transition state (δE^π) is given by

$$\delta E^\pi = \frac{(C_{1D}^{\text{occ}}C_{1P}^{\text{unocc}} + C_{4D}^{\text{occ}}C_{2P}^{\text{unocc}})^2}{E_D^{\text{occ}} - E_P^{\text{unocc}}} - \frac{(C_{1D}^{\text{unocc}}C_{1P}^{\text{occ}} + C_{4D}^{\text{unocc}}C_{2P}^{\text{occ}})^2}{E_D^{\text{unocc}} - E_P^{\text{occ}}} 2\beta^2$$

The C 's are the coefficients of the AO's at the appropriate atoms of the diene (D) and dienophile (P). The highest occupied and lowest unoccupied orbitals are involved in the approximation, and β is the resonance integral between the interacting AO's. For dienes which are biradicaloids, the $E^{\text{occ}} - E^{\text{unocc}}$ terms are small, making δE^π large, resulting in low activation energy. Pericyclic reactions can be treated similarly.

The second reason for studying biradicaloids is that any molecule can become biradicaloid at suitable geometries,¹⁹ and, according to current theory, these geometries are important in photochemistry.¹⁹⁻²² Con-

sider the photochemical ring closure of butadiene to cyclobutene. Figure 1 shows how the π -MO's of butadiene change with disrotation. At some point the orbitals originating as ψ_2 and ψ_3 become degenerate, and the system is biradicaloid according to the above definition.

In the Hückel approximation, the ground state ($\psi_1^2\psi_2^2$), the first excited state ($\psi_1^2\psi_2\psi_3$), and the doubly excited state ($\psi_1^2\psi_3^2$) are degenerate at the biradicaloid geometry, but this degeneracy disappears when electron-electron interactions are introduced.²³ This doubly excited state is proposed to be important in returning molecules to the ground state and has been termed "funnel" or "pericyclic minimum".^{19,22,24} Thus, studying molecules whose ground state is biradicaloid (e.g., *o*-xylylene) could lead to increased understanding of photochemical reactions.

Recent theoretical work on *o*-xylylene (and on the meta and para isomers) has dealt with the spectroscopy and excited states of these species.^{10,13,16,25-27} Briefly, the conclusions are as follows. The ground state of *o*-xylylene is a singlet,^{10,25} and calculations agree with experimental data.¹⁰ The ground state of *p*-xylylene is also a singlet while that of the meta isomer is a triplet.^{10,25} The ground state of *o*-xylylene should be planar.¹⁰ A particularly interesting result is the occurrence of a low-lying, doubly excited singlet state in this biradicaloid hydrocarbon.^{10,16,27}

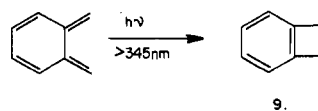
Curiously, the ground-state energies of these species relative to their aromatic isomers (e.g., isoindene vs. indene) have apparently not been measured, but calculations have been made. I will return to this matter again when discussing our own results.

o-Xylylenes and Isoindenes via "Extrusion Reactions"²⁸

Loss of a small molecule from cyclic systems is probably the most general way of generating *o*-xylylenes (e.g., loss of N_2 from 7 or CO from 8). Photolysis of



7 was used by Flynn and Michl¹⁰ to prepare the *o*-xylylene under matrix conditions. The absorption spectrum of 1 (EPA glass, 77 K) had λ_{max} 373 nm, and the fluorescence was also observed with λ_{max} 456 nm. When the glass was warmed, the spiro dimer 5 was formed. Irradiation of 1 ($\lambda > 345$ nm) at 77 K resulted in formation of benzocyclobutene (9). Although there is one



(18) (a) M. J. S. Dewar "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969, Chapter 6. (b) For an early application to the reactivity of cyclopentadiene, see E. W. Garbisch and R. F. Sprecher, *J. Am. Chem. Soc.*, **88**, 3434 (1966). (c) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley-Interscience, 1976.

(19) J. Michl, *Photochem. Photobiol.* **25**, 141 (1977).

(20) (a) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564, 1566 (1966); (b) *Acc. Chem. Res.*, **4**, 272 (1971).

(21) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969).

(22) J. Michl, *Mol. Photochem.*, **4**, 243, 257 (1972).

(23) For discussion, see (a) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, 1975, pp 179-184. (b) A. Devaquet, *Pure Appl. Chem.*, **41**, 455 (1975).

(24) J. Michl, *Pure Appl. Chem.*, **41**, 507 (1975).

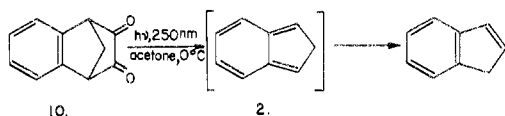
(25) J. Baudet, *J. Chim. Phys. Physicochim. Biol.*, **68**, 191 (1971).

(26) N. C. Baird, *J. Am. Chem. Soc.*, **94**, 4941 (1972).

(27) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977).

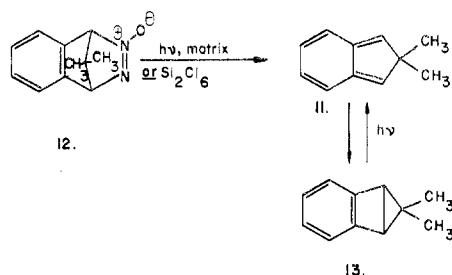
(28) The term "chelotropic reactions" is probably better reserved for reactions known to be concerted, which these photochemical reactions probably are not.

report²⁹ of the parent isoindene as an intermediate, it has not yet been characterized. Warrenner and co-workers²⁹ obtained indene on irradiation of diketone 10.



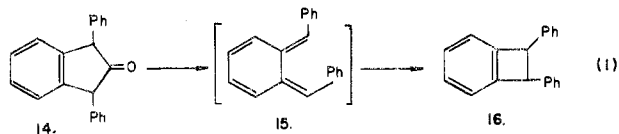
Diels–Alder adducts of isoindene were obtained in the presence of *N*-methylmaleimide, and formation of indene from 2 was explained by a 1,5-hydrogen shift. Decarbonylation of an α -diketone was also employed to generate 2-spirocyclopropylisoindene.^{29b}

Recently Dolbier, Michl, and co-workers¹⁶ obtained 2,2-dimethylisoindene (11) from the azoxy precursor 12.



Dimethylisoindene gave yellow solutions which were stable in the absence of air. A Diels–Alder adduct with dimethyl maleate was obtained, and in the NMR spectrum vinylic proton resonances showed at δ 6.08 and 6.55, indicative of a nonaromatic system. Photolysis of 11 gave the benzobicyclo[2.1.0]pentene 13, which reverts thermally or photochemically to the isoindene. Species 13 had been proposed as a chemical intermediate (in a different reaction) by Berson and Pomerantz³⁰ in 1964. 2,2-Dimethylisoindene has also been reported by Palensky and Morrison, who obtained stable, yellow solutions on photolysis of 1,1-dimethylindene.¹⁵

Photodecarbonylation of 2-indanones has proved to be a very general way of generating *o*-xylylenes. Quinkert and co-workers^{8,31} have employed this reaction to prepare a number of aryl-substituted *o*-xylylenes and their cyclization products, the benzocyclobutenes (e.g., eq 1). These authors^{31b} showed that stereomutation



of the isomers of 14 and loss of CO occurred from the same singlet excited state, which is consistent with a stepwise, nonchelotropic CO elimination. It is also interesting that the aryl-substituted *o*-xylylenes, e.g., 15, are in thermal equilibrium with the cyclized isomers, the benzocyclobutenes, e.g., 16.⁸ This contrasts with the parent *o*-xylene 1 in which cyclization to benzocyclobutene requires irradiation.¹⁰ In one study,

(29) (a) R. N. Warrenner, R. A. Russell, and T. S. Lee *Tetrahedron Lett.*, 49 (1977); (b) R. N. Warrenner, P. A. Harrison, R. A. Russell, and M. N. Paddon-Row, *ibid.*, 2031 (1977).

(30) J. A. Berson and M. Pomerantz, *J. Am. Chem. Soc.*, 86, 3896 (1964).

(31) (a) G. Quinkert, J. Palmowski, H. P. Lorenz, W. W. Wiersdorff, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, 10, 198 (1971); (b) G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *Justus Liebigs Ann. Chem.*, 693, 44 (1966).

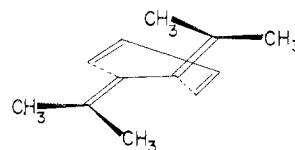
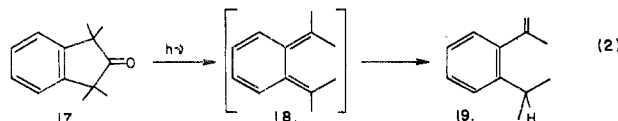


Figure 2. Nonplanar configuration of 7,7,8,8-tetramethyl-*o*-xylylene.

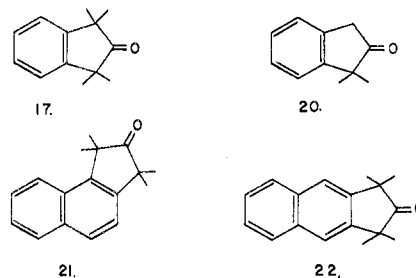
Quinkert and co-workers were able to observe *o*-xylylenes by flash photolysis.³²

My interest in photodecarbonylation was initiated by the report of Starr and Eastman³³ of the decarbonylation of 1,1,3,3-tetramethylindan-2-one (17). The product was 1-isopropenyl-2-isopropylbenzene (19), and a



biradical intermediate was proposed. It seemed to us that the tetramethyl-*o*-xylylene 18 might be observable by flash photolysis.

Initial experiments with 17 showed that a long-lived transient, absorbing in the range 330–400 nm, was indeed present. Therefore the series of methylated 2-indanones 17, 20–22 were prepared to study their



photodecarbonylation as a route to *o*-xylene intermediates. Both 17 and 20 gave long-lived transients on flash photolysis in hexane. The transients have λ_{max} 350 and 360 nm respectively. These transients are assigned as the *o*-xylylenes 23 and 24, respectively. Note that the absorptions of 23 and 24 are at shorter wavelength than that of *o*-xylene itself (λ_{max} 373 nm¹⁰). This must mean that the former are nonplanar (unlike *o*-xylene), and must be twisted about the "essential" single bonds.^{34a} This conclusion is supported by inspection of space-filling models, which show that these methyl derivatives, particularly 23, cannot be planar. The shape of 23 is shown in Figure 2.



The decay of transients 23 and 24 is sluggish, with first-order rate constants for decay of 0.0020 and 0.038 s⁻¹, respectively.³⁵ The decay of 23-*d*₁₂ (deuterated in

(32) K. H. Grellmann, J. Palmowski, and G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, 10, 196 (1971).

(33) C. R. Starr and R. H. Eastman, *J. Org. Chem.*, 31, 1393 (1966).

(34) For details of the flash photolysis experiments, see (a) K. K. de Fonseka, J. J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, 101, 3277 (1979); (b) K. K. de Fonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *ibid.*, 99, 8257 (1977).

(35) These correspond to lifetimes (rate constant⁻¹) of the order of minutes.

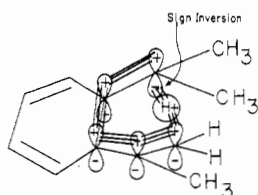
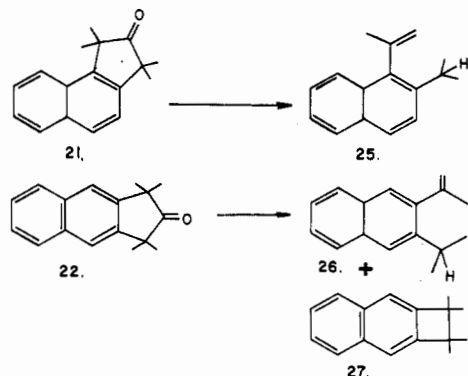


Figure 3. Orbital symmetry diagram for transition state of antarafacial 1,5-hydrogen shift. Note there are ten electrons and one sign inversion, and the process is ground state forbidden and excited state allowed.²⁰

the methyl groups) showed a primary kinetic isotope effect of 3.9, showing that hydrogen migration is involved in the rate-determining step.³⁶ The decay rate was dependent on the light intensity of the monitoring beam, showing that the transients are photolabile and subject to secondary photolysis.³⁷

The above data are all consistent with an antarafacial 1,5-hydrogen shift as the decay process. The geometry of the *o*-xylenes **23** and **24** (Figure 2) is suitable for the antarafacial process, which is ground state forbidden,^{20,38} thus accounting for the slow decay rates. That the process is observed at all is undoubtedly due to the driving force for aromatization.³⁹ The photochemical process is symmetry allowed,^{20,38,40} which explains the photolabile nature of these transients. An orbital diagram showing the transition state for migration is given in Figure 3.

Compounds **21** and **22** show quite different photochemical behavior. First, the products of irradiation



are different, **21** giving the styrene derivative **25** while **22** gives styrene **26** and tetramethylbenzocyclobutene **27**. Benzindanone **22** is the only compound we have studied in which cyclization product is formed on photolysis.

Transients with different properties are observed from **21** and **22**. Ketone **21** gives a long-lived transient (survives indefinitely in the dark) with short wavelength absorption (the λ_{\max} is obscured by the ketone absorption). The transient decays rapidly on secondary photolysis, giving **25**; it is assigned the *o*-xylene structure **28**.

(36) 1,1-Dimethyl-2-indanone (**20**) gives only 1-isopropenyl-2-methylbenzene as the primary photoproduct.

(37) Values of rate constants given are for low, limiting monitoring beam intensities.

(38) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, 1970.

(39) It has been predicted that the ground-state, antarafacial 1,5-hydrogen shift should be observable in suitable systems: R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).

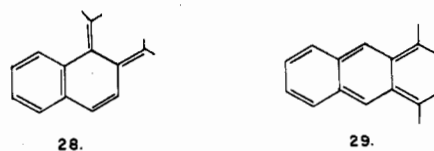
(40) The photochemical process is known: E. F. Kiefer and C. H. Tanna, *J. Am. Chem. Soc.*, **91**, 4478 (1969).

In the case of the linear ketone **22** a short-lived transient is observed (estimated lifetime 5 μ s).⁴¹ This transient has long-wavelength absorption (range 500–550 nm),⁴² which compares favorably with the spectrum of the 2,3-naphthoquinodimethanes **30**⁴³ and **31**.⁴⁴



Thus, the transient is assigned the structure **29**, which can undergo either a 1,5-hydrogen shift or cyclization to afford **26** or **27**, respectively.^{34a}

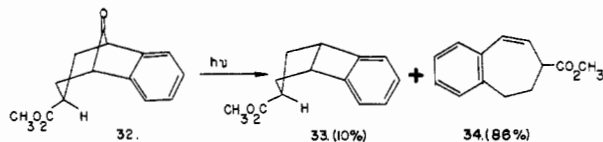
The above results on **23**, **28**, and **29** are consistent with a simple MO picture. In particular, the HOMO-LUMO gaps for planar geometries are 0.59 β , 0.72 β , and 0.34 β , respectively;^{34a} twisting about the single bonds increases this gap, particularly for **28**. This, of course,



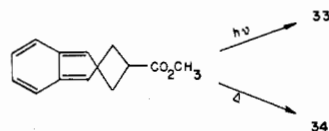
accounts for the shifts in the long-wavelength absorption bands of **28** and **29** relative to the parent **23**. It also accounts for the different reactivities, since most biradicaloid **29** has the shortest decay time while least biradicaloid **28** is long lived.

A further point of interest is the formation of cyclization product **27** from **29**. Miller, Michl, and co-workers⁴⁴ reported that the constrained **31** did not cyclize thermally. The difference may be due to the nonplanar geometry of tetramethyl derivative **29**, in which allowed conrotatory ring closure is geometrically favorable.

In work related to ours, Weiss⁴⁵ has described the photolysis of the bicyclic 2-indanone derivative **32**. The



major products were the benzocyclobutene derivative **33** and benzocycloheptadiene **34**. It was proposed that, since the fraction of **33** increased with simultaneous irradiation at 313 and 366 nm, the reaction involved *o*-xylene **35**, which could give **34** thermally or **33** on



secondary photolysis. The isoindene intermediate was trapped with maleic anhydride. Formation of **34** involved a 1,5-hydrogen shift which, according to space-filling models, must be suprafacial. Flash photolysis experiments in which the lifetime of the isoindene **35**

(41) Accurate decay rate could not be measured since the lifetime was at the detection limit of our equipment.

(42) Absorption detected photographically, which did not reveal position of λ_{\max} .

(43) *o*-Quinodimethane **30** has λ_{\max} 541 nm: M. Gisen and J. Wirz, *Helv. Chim. Acta*, **59**, 2273 (1976).

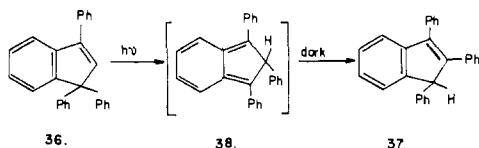
(44) Species **31** has reported λ_{\max} 555 nm: P. P. Steiner, R. D. Miller, H. J. Dewey and J. Michl, *J. Am. Chem. Soc.*, **101**, 1820 (1979).

(45) D. S. Weiss, *J. Am. Chem. Soc.*, **97**, 2550 (1975).

is compared with tetramethyl-*o*-xylylenes would be interesting.

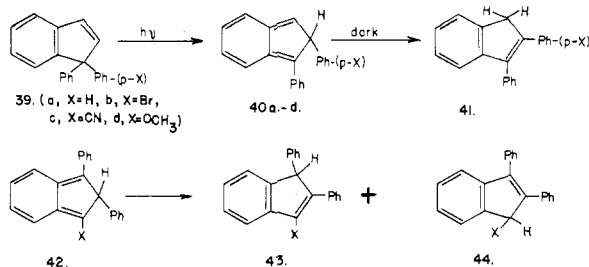
Isoindenes via Aryl Migration

Some time ago Griffin and co-workers⁹ reported the photomigration of phenyl in 1,1,3-triphenylindene (36) and proposed that formation of 1,2,3-triphenylindene (37) involved intermediacy of 1,2,3-triphenylisoindene.



Subsequently I pointed out that the mechanism (photochemical phenyl migration followed by a dark 1,5-hydrogen migration) was consistent with orbital symmetry considerations.⁴⁶ More recently, we have shown^{34b} that this mechanism is correct, and that photochemical aryl migration appears to be a general way of generating aryl isoindenes.

Flash photolysis^{34b} of a series of 1,1-diarylundenes (39a-d and 36) showed transients with lifetimes in the



millisecond range, absorbing from 400 to 500 nm. The absorption is in reasonable agreement with that of *o*-xylylenes.^{31,32} In the case of triphenylisoindene, the intermediate was further characterized by chemical trapping and by (proton) NMR at -70°C where the lifetime is several hours.^{34b}

The decay process for these isoindene transients was shown to be the 1,5-hydrogen shift, which in this case is suprafacial and thermally allowed. Kinetic isotope effects (k_H/k_D) for 40a and 38 were 6.15 and 3.7, showing that the hydrogen migrates in the rate-determining step. Also, the activation parameters were $E_a = 13.1$ kcal/mol and $\Delta S^\ddagger = -8.9$ eu for 40a and $E_a = 14.4$ kcal/mol and $\Delta S^\ddagger = 19.7$ eu for 38. The negative entropies of activation also support a concerted mechanism for the 1,5-hydrogen shift.^{34b}

The activation energy data reported above for the decay of the isoindenes are interesting in that they can be used with literature data to estimate, for the first time, the difference in energy between an isoindene and an indene. Miller and Boyer⁴⁷ report an activation energy of 33.2 kcal mol⁻¹ for the thermal conversion of 1-phenylindene to the isoindene. One can obtain the ground-state energy of the isoindene with respect to that of the indene from the difference in the activation energies of the forward and reverse reactions. The compound chosen to model the reverse reaction should have a phenyl group at the 1-position since Miller and Boyer⁴⁷ found that the substitution of a phenyl group for a hydrogen atom at the start position of a H mi-

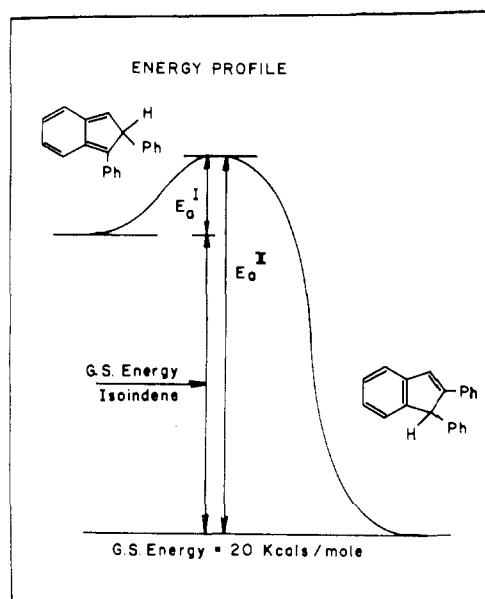


Figure 4. Energy vs. reaction coordinate profile for the 1,2-diphenylisoindene to 1,2-diphenylindene conversion.

gration in the thermal reaction increases the rate by about 130. We have chosen 1,2-diphenylindene as the model compound and have assumed that the activation energy, E_a^{II} of Figure 4, for the thermal conversion of the diphenylindene is the same as that measured by Miller and Boyer⁴⁷ for 1-phenylindene. This leads to a value of about 20 kcal mol⁻¹ for the difference in the energies of 1,2-diphenylindene and 1,2-diphenylisoindene.

As the value reported above for the energy difference between the diphenylisoindene and the diphenylindene is the only value available that is based on experimental data, it was worthwhile to estimate that energy difference using other techniques. Accordingly, the techniques proposed by Benson⁴⁸ to estimate the differences in the enthalpies of species in the gas phase, using group additivity methods, might be relevant to the case of the isoindene-indene conversion in solution. Initially the standard enthalpy change at 298 K was estimated for the conversion of the unsubstituted indene to the isoindene from the values for the standard enthalpies of formation, 42.0 and 68.6 kcal mol⁻¹, respectively. In this case all the group additivity values were available, and the estimate led to a value of $\Delta H = 26.6$ kcal mol⁻¹. Not all the group additivity values were available to estimate directly the standard enthalpies of formation of 1,2-diphenylindene and 1,2-diphenylisoindene, but one could estimate a value of 25 kcal mol⁻¹ for the difference in enthalpies of 1,2-diphenylindene and 1,2-diphenylisoindene. The estimate from the group additivity method for calculating enthalpies of formation in the gas phase is thus in reasonable agreement with the value, 20 kcal mol⁻¹, calculated from the experimental data in solution.⁴⁹ Thus, a measure of the "driving force" for reactions in which the *o*-xylylene system is

(48) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1975.

(49) Qualitative rules for estimating Dewar resonance energies and π -electron calculations give values of 21 and 18.9 kcal/mol, respectively, for the stability for 2 vs. indene. See N. C. Baird, *J. Chem. Educ.*, **48**, 509 (1971); M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1979); C. de Llano, Ph.D. Thesis, University of Texas, Austin, 1968. We thank Dr. N. C. Baird, University of Western Ontario, for these data and references.

(46) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

(47) L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, **93**, 650 (1971).

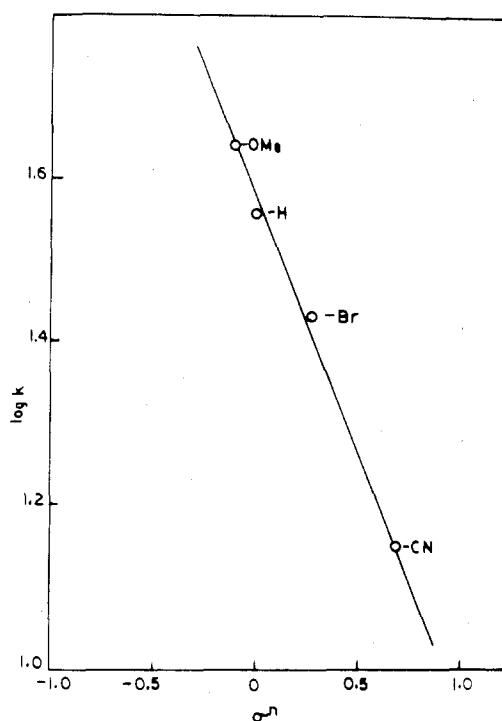


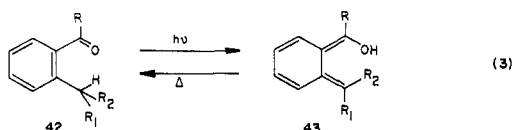
Figure 5. Correlation of rates of rearomatization of isoindenes 39a-d with σ .

aromatized, such as 1,5-hydrogen shifts or Diels-Alder additions, is now available.

Decay kinetics of the series of isoindenes⁵⁰ (40a-d) has provided insight to the polarity of the transition state for suprafacial 1,5-hydrogen migration.^{34b} Thus, a plot of $\log k$ for decay of transients 40a-d vs. the Hammett constant σ gives a linear relationship with slope $\rho = -0.6$, shown in Figure 5. This means that the migration start for 1,5-hydrogen shift in 40 is slightly electron deficient. This is contrary to what one would have expected on the basis of a cyclopentadienide plus migrating proton model, in which charge is transferred from hydrogen to the ring.⁵¹ It is consistent, however, with the results of thermolysis of 40a-d,⁵⁰ where electron-withdrawing substituents favor migration. It is also consistent with the results of Wilson and Petit,⁵² who showed that in hydrogen migration in a series of isoindenes, 42, hydrogen migrated away from X when X was electron withdrawing (e.g., when X = CN or CO₂CH₃), as shown by the change in the ratio of products as X was varied.

o-Xylylenes by Photochemical 1,5-Hydrogen Shift

o-Alkyl aromatic ketones undergo internal hydrogen abstraction on photolysis (photoenolization)⁵³ to give hydroxy-*o*-xylylenes (e.g., 42 \rightarrow 43). Evidence for



(50) The photochemical aryl migration always involves predominantly the substituted phenyl group: J. J. McCullough and M. R. McClory, *J. Am. Chem. Soc.*, **96**, 1962 (1974).

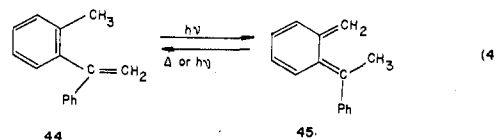
(51) J. R. de Dobbelaere, J. M. F. van Dijk, J. W. de Haan, and H. U. Buck, *J. Am. Chem. Soc.*, **99**, 392 (1977).

(52) W. A. Petit and J. W. Wilson, *J. Am. Chem. Soc.*, **99**, 6372 (1977).

(53) P. G. Sammes, *Tetrahedron*, **32**, 405 (1976), has reviewed this area.

photoenol 43 comes from trapping in Diels-Alder reactions,⁵⁴ incorporation of deuterium in the *o*-alkyl groups in D₂O,⁵⁴ and flash photolysis studies.^{55,56} A detailed discussion will not be attempted here, but the $n-\pi^*$ triplet of ketone 42 is believed to undergo the hydrogen abstraction. Conversion of 42 \rightarrow 43 and the reverse are formally 1,5-hydrogen shifts, although flash photolysis results suggest that the reaction is complicated.^{55,56}

The all-carbon analogue of reaction 3 is less well-studied but is currently attracting attention as a synthetic reaction. The reaction is the formation of *o*-xylylenes on irradiation of *o*-alkylstyrenes, e.g., reaction 4.^{34a,57-59} *o*-Xylylenes such as 45 have been trapped



with, e.g., cyclohexene^{58,59} which demonstrates the synthetic potential.

No physical work has been done on this reaction, but we can make the following comments. The forward reaction (44 \rightarrow 45) presumably occurs because the 1,5-hydrogen shift can be antarafacial and photochemically allowed in the open-chain system. Isoindenes could not be generated in a similar fashion.⁴⁶ The *o*-xylylenes could return to *o*-alkylstyrenes by supra- or antarafacial migrations, the latter causing the transient to be photochemically labile (cf. ref 34b), and, indeed, Dr. Hornback has told us that the yields in his reactions vary with wavelength of irradiation.⁶⁰ More work on this method of generating *o*-xylylenes is to be expected.

Synthetic Applications of *o*-Xylylenes

These species have been utilized as intermediates in a number of elegant synthesis^{2,61} of important compounds. In most cases, the precursor of the *o*-xylylene has been a benzocyclobutene, which on thermolysis affords the *o*-xylylene. There are now many examples in the literature, and we will mention only two; many others are covered in Oppolzer's reviews.^{2,61}

Kametani and co-workers⁶² have used this scheme in a total synthesis of estrone.^{62,63} Benzocyclobutene 46 gave 47 on thermolysis, via the *o*-xylylene 48.

Interestingly, Kametani⁶⁴ and Barbour⁶⁵ have noted 1,5-hydrogen shifts in *o*-quinodimethane generated on thermolysis of 1-cyano-1-alkylbenzocyclobutenes. Ka-

(54) (a) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.* **83**, 2213 (1961);

(b) D. R. Arnold and C. P. Hajiantoniou, *Can. J. Chem.*, **56**, 1970 (1978).

(55) G. Porter and M. F. Tchir, *J. Chem. Soc. A*, 3772 (1971).

(56) (a) D. M. Findlay and M. F. Tchir, *J. Chem. Soc., Faraday Trans. I*, **72**, 1096 (1976); (b) R. Haag, J. Wirz, and P. J. Wagner, *Helv. Chim. Acta*, **60**, 2595 (1977).

(57) A. C. Pratt, *J. Chem. Soc., Chem. Commun.*, 183 (1974).

(58) J. M. Hornback, *Tetrahedron Lett.*, 3389, (1976).

(59) (a) J. M. Hornback and R. D. Barrows to be published; (b) J. M. Hornback, L. G. Mawhorter, S. E. Caulson, and R. A. Bedont, *J. Org. Chem.*, **44**, 3698 (1979).

(60) J. M. Hornback, personal communication.

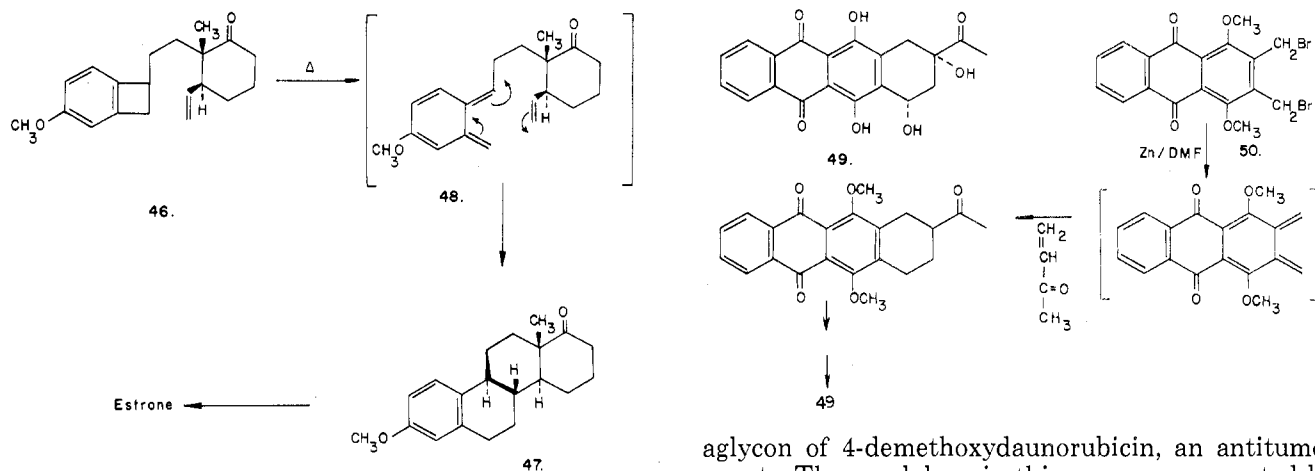
(61) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977).

(62) T. Kametani, H. Nemoto, H. Ishikawa, K. Shiroshima, H. Matsumoto, K. Fukumoto, F. Satoh, and H. Inoue, *J. Am. Chem. Soc.*, **99**, 3461 (1977).

(63) An alternate route employing an *o*-xylylene is described by R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **101**, 215 (1979).

(64) T. Kametani, M. Tsubuki, Y. Shiratori, Y. Hato, H. Nemoto, M. Ihara, K. Fukumoto, F. Sato, and H. Inoue, *J. Org. Chem.*, **42**, 2672 (1977).

(65) A. D. Barbour, Ph.D. Thesis, University of California, Santa Cruz, 1975; *Diss. Abstr. Int. B*, **37**, 220 (1976).



metani⁶⁴ found that a bulky alkyl substituent can control the mode of conrotatory ring opening so that Z-type cyano-*o*-xylenes, but not E-type, are formed. Also, the E-type species formed with small alkyl groups can undergo 1,5-hydrogen shift which competes with Diels-Alder trapping of the *o*-xylylene. Barbour⁶⁵ found that 1,5-hydrogen shift competes with dimerization of the *o*-xylylene in the absence of dienophiles. Thus, the 1,5-shift should be borne in mind when Diels-Alder trapping of alkyl-*o*-xylenes is to be used synthetically.

Kerdesky and Cava⁶⁶ have described an *o*-xylylene route to 4-demethoxydaunorubicin (49), which is the

(66) F. A. J. Kerdesky and M. P. Cava. *J. Am. Chem. Soc.*, **100**, 3635 (1978).

aglycon of 4-demethoxydaunorubicin, an antitumor agent. The *o*-xylylene in this case was generated by elimination of bromine from the α,α' -dibromoxylene 50, using zinc.⁷

Concluding Remarks

o-Xylenes and isoindenes have, in the last 20 years, become well recognized as reaction intermediates. They are currently being studied by physical methods and are being used in systematic synthesis. Interest in these species seems certain to continue.

The collaboration of Dr. K. de Fonseca, Dr. A. J. Yarwood, and the late Dr. C. Manning is gratefully acknowledged. I also thank Dr. J. M. Hornback for sending unpublished information. The work at McMaster was supported by the Natural Science and Engineering Research Council of Canada.

Structural Criteria for the Mode of Bonding of Organoactinides and -lanthanides and Related Compounds

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Received December 17, 1979

The prediction and then the synthesis of uranocene by Streitwieser and Muller-Westerhoff was a spectacular success for orbital symmetry theory. It began with Streitwieser's observation that the highest occupied molecular orbitals of the octagonal dianion obtained by adding two electrons to cyclooctatetraene (COT) have appropriate symmetry to engage in bonding with the uranium 5f orbitals. They then visualized the possible existence and stability of the sandwich compound U(COT)₂, somewhat analogous to ferrocene and other 3d metallocenes.¹ It culminated with Muller-Westerhoff's observation that UCl₄ reacts with C₈H₈²⁻ ion, in tetrahydrofuran solution, to form uranocene, U(COT)₂, in good yield.¹

Soon thereafter, we determined the crystal structure of uranocene and established that it indeed has a symmetrical π complex or sandwich structure, as predicted.² In the course of that work we came to realize that very little was known about the structure and bonding in organoactinides and organolanthanides. We have endeavored to change that situation in the intervening years. A dominant question concerning organometallic compounds of the f metals is the degree to which "covalency" is important in the bonding.

The organometallic chemistry of the actinides and lanthanides with carbocyclic ligands began with the synthesis of the cyclopentadienide compounds in the early 1950s. Three recent Accounts³ have described

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