portant stereodefined acyclic molecules as well as an improved route to biologically active β-hydroxy δ-valerolactones heretofore difficult to access by more traditional means.

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Supplementary Material Available: General synthetic procedure and complete spectral data for all compounds synthesized as well as X-ray crystal structure data (25 pages). Ordering information is given on any current masthead page.

Atom Transfer Cycloaddition. A Facile Preparation of Functionalized (Methylene)cyclopentanes

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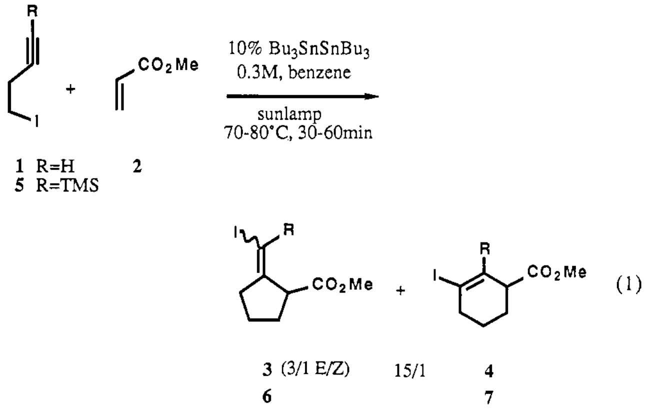
The ability to sequence radical reactions to accomplish multiple transformations in a single step is an asset of free radical reactions in organic synthesis.[2,3] In designing such sequences, it is advantageous to permit long lifetimes for intermediate radicals so that desired reactions can occur. On the other hand, the chain-transfer step should be as rapid as possible to prevent diversion of the final radical along undesired pathways. While a variety of useful radical sequences have recently been developed, the methods available to conduct these free radical reactions are actually quite few. The most commonly employed method uses a tin hydride reagent to mediate the radical sequence.[4,5] In the tin hydride method, radical substituents have little effect on the rate of hydrogen atom abstraction, and, to a first approximation, most radicals have similar lifetimes with respect to H-atom abstraction.[6] This can be a serious problem, particularly in the design of sequences containing a relatively slow intermediate step. While free-radical reactions based on halogen atom transfer have long been known,[7,8] the unique capability of such "atom transfer based"[9,10] methods to control the course of sequential free radical reactions has not been recognized. We now report the sequencing of a free radical addition and cyclization reaction which is uniquely controlled by iodine atom transfer. This simple method for the preparation of (iodomethylene)cyclopentanes is termed "atom transfer cycloaddition".[9]

Sunlamp irradiation for 30 min of a solution of butynyl iodide (**1**) (0.3 M) and methyl acrylate (0.3 M) in benzene (~80 °C) containing 10 mol % hexabutylditin produced a mixture of (iodomethylene)cyclopentane **3** and cyclohexenyl iodide **4**.[11] The



ratio of **3**/**4** was 15:1, and (iodomethylene)cyclopentane **3** was a 3:1 mixture of stereoisomers with the *E*-isomer predominating.[12]

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(1) Sloan Foundation Fellow, 1985-87; Dreyfus Teacher-Scholar, 1985-89; Eli Lilly Grantee, 1985-87; Merck Faculty Development Awardee, 1986-87; Recipient of a National Institutes of Health Career Development Award, 1987-92.

(2) Examples of sequential radical reactions include the following (a) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811. (b) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. (c) Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553. (d) Breslow, R.; Olin, S. S.; Groves, J. T. *Tetrahedron Lett.* **1968**, 1837. (e) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1726. (f) Chatzopoulos, M.; Montheard, J.-P. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1975**, *280*, 29. (g) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (h) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *Ibid.* **1983**, *105*, 3741. (i) Stork, G.; Sher, P. M. *Ibid.* **1983**, *105*, 6765. (j) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337. (k) Moriya, O.; Kakihana, M.; Urata, Y.; Sugizaki, T.; Kageyama, T.; Ueno, Y.; Endo, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1401. (l) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (m) Beckwith, A. L. J.; Roberts, D. H.; Schiesser, C. H.; Wallner, A. *Tetrahedron Lett.* **1985**, *26*, 3349. (n) Winkler, J. D.; Sridar, V. *J. Am. Chem. Soc.* **1986**, *108*, 1708. (o) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2216. (p) Stork, G.; Sher, P. M.; Chen, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6384. (q) Curran, D. P.; Kuo, S.-C. *J. Am. Chem. Soc.* **1986**, *108*, 1106. (r) Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943.

(3) For an excellent recent review, see: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. See, also: Hart, D. J. *Science (Washington, D. C.)* **1984**, *223*, 883.

(4) Related methods using germanium and mercuric hydrides are common. Germanium hydride: (a) Pike, P.; Hershberger, S.; Hershberger, J. *Tetrahedron Lett.* **1985**, *26*, 6289. (b) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am.* Chem. *Soc.* **1983**, *105*, 3578. Mercuric hydride: (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *224*, 553. (d) Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

(5) Other important methods to control radical reactions involve the use of allyl (and vinyl) tin reagents and thiohydroxamic acid esters (Barton method). Allyl stannanes: (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Keck, G. E.; Yates, J. B. *J. Organomet. Chem.* **1983**, *248*, C21. (c) Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037. (d) Baldwin, J. E.; Kelly, D. R. *J. Chem. Soc., Chem. Commun.* **1985**, 683. Allyl sulfides: (e) Keck, G. E.; Byer, J. H. *J. Org. Chem.* **1985**, *50*, 5442. Allyl sulfones: (f) Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897. Leading references to the Barton method: (g) Barton, D. H. R.; Motherwell, W. B. *Heterocycles* **1984**, *21*, 1. (h) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

(6) For recent reviews, see: (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, **1980**; pp 162-283. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (c) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2, Chapter 3 . (d) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299. (e) The series edited by Kochi is still an outstanding source of relevant mechanistic data. Kochi, J. K. *Free Radicals*; Wiley: New York, 1973. (f) Giese, B. *Angew. Chem., Int. Engl.* **1983**, *22*, 753.

(7) For a review of halogen atom abstraction, see: Danen, W. C. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1974; Vol. 5, pp 1-100. Poutsma, M., in ref 6e, Vol. II, p 23. See, also: (a) Hiatt, R.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 25. (b) Castelhano, A. L.; Griller, D. *Ibid.* **1982**, *104*, 3655.

(8) The driving force in most work is the formation of a stabilized radical. For some examples, see: (a) Giese, B.; Leining, M. *Chem. Ber.* **1986**, *119*, 444. (b) Fields, D. L., Jr.; Schecter, H. *J. Org. Chem.* **1986**, *51*, 3369. (c) Kuwae, Y.; Kamachi, M.; Hayashi, K.; Viehe, H. G. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2325. (d) Sam, T. W.; Sutherland, J. K.; *J. Chem. Soc., Chem. Commun.* **1971**, 970. (e) Traynham, J. G.; Hsieh, H. H. *J. Org. Chem.* **1973**, *38*, 868. (f) Brown, E. D.; Sam, T. W.; Sutherland, J. K.; Torre, A. *J. Chem. Soc., Perkin Trans 1* **1975**, 2326. (g) Kharasch, M. S.; Skell, P. S.; Fisher, P. *J. Am. Chem. Soc.* **1948**, *70*, 1055. (h) Nakano, T.; Kayama, M.; Matsumoto, H.; Nagai, Y. *Chem. Lett.* **1981**, 415. (i) Kraus, G. A.; Landgrebe, K. *Tetrahedron Lett.* **1984**, *25*, 3939. Kraus, G. A., Landgrebe, K. *Tetrahedron* **1985**, *41*, 4039. Degueil-Castaing, M.; DeJeso, B.; Kraus, G. A.; Landgrebe, K.; Maillard, B. *Tetrahedron Lett.* **1986**, *27*, 5927. (j) Pezechk, M.; Brunetiere, A. P.; Lallemand, J. Y. *Tetrahedron Lett.* **1986**, *27*, 3715.

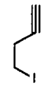
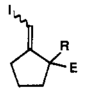
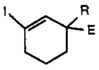
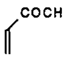
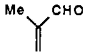
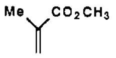
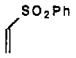
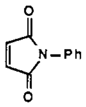
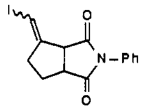
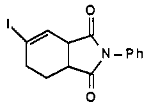
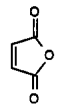
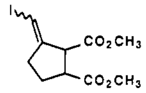
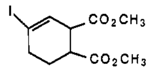
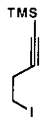
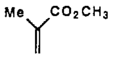
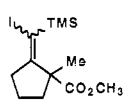
(9) We use the term "atom transfer" to emphasize the method of control of the radical reaction. Of central importance is the nature of the chain-transfer step. In the tin hydride method, the chain is transferred by hydrogen abstraction from the reagent. In the atom transfer method, the chain is transferred by halogen atom abstraction from the starting halide. Atom transfer methods based on hydrogen atom abstraction from the starting material are also known. For examples and references, see: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. Gottschalk, P.; Neckers, D. C. *J. Org. Chem.* **1985**, *50*, 3498.

(10) (a) Curran, D. P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1986**, *108*, 2489. (b) Curran, D. P.; Kim, D. *Tetrahedron Lett.* **1986**, *27*, 5821.

(11) General experimental procedure: A solution of alkene (0.62 mmol), alkynyl iodide (1.55 mmol), and hexabutylditin (0.06 mmol) in dry, degassed benzene (1.8 mL) was irradiated for 40 min with a 275-W sunlamp. The temperature was maintained at 80 ± 5 °C by controlling the distance of the lamp from the reaction vessel. If starting alkene remained, additional ditin (0.06 mmol) was added, and irradiation was continued for 40 min. The reaction was concentrated under reduced pressure, and the residue was purified by medium pressure liquid chromatography.

0002-7863/87/1509-6558$01.50/0

Table I. Atom Transfer Cycloaddition Reactions of Butynyl Iodides with Electron Deficient Alkenes[a]

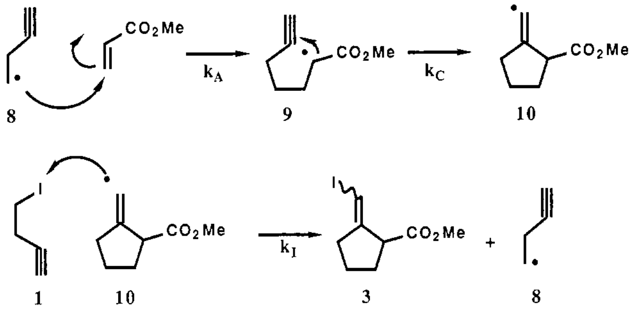
			products				
entry	iodide	alkene	5-exo	6-endo	5-exo/6-endo	E/Z	yield[b] %
							
a	1		R = H, E = CN		7/1	2/1	41
b	1		R = H, E = $COCH_3$		10/1	1.2/1[c]	46
c	1		R = Me, E = CHO		8/1	7.3/1	27
d	1		R = Me, E = CO_2CH_3		23/1	10/1	56
e	1		R = H, E = SO_2Ph		9/1	5/1	68
f	1				11/1	3.3/1	41
g	1				9/1	2.4/1	48[d] (65)[e]
h				not detected		(8/1)[f]	45

[a] Reaction conditions, see footnote 11. [b] Yields refer to isolated yield of purified products after flash chromatography or MPLC. [c] The E/Z assignment should be regarded as tentative. [d] The products were isolated after methanolysis of the anhydride (MeOH, reflux) and diazomethane treatment. [e] ^1H NMR yield against an internal standard. [f] The stereochemistry of these products has not yet been assigned.

The isolated yield of **3** after chromatographic purification was 45%. The yield was improved to 65% in a similar experiment using 2.5 equiv of butynyl iodide **1**. The union of **1** and **2** in this formal "[3 + 2] cycloaddition" reaction represents an unusually direct method for the formation of functionalized (methylene)cyclopentanes.[13]

A proposed propagation sequence for this reaction is outlined in Scheme I. The best option available to the initial radical **8** is well precedented[6f] intermolecular addition to the electron deficient acrylate **2** to produce stabilized radical **9**. In turn, **9** prefers cyclization and partitions via the 5-exo mode (to generate vinyl radical **10**) and the 6-endo mode (not shown). While intermolecular addition of **10** to the acrylate must be a reasonably facile alternative, a much more rapid reaction supersedes this undesired pathway. In a chain-transfer step, near-diffusion controlled iodine atom abstraction from **1** produces (E/Z)-**3** and the initial radical **8**.[10] The unique capabilities of the iodine atom transfer reaction to control this sequence are apparent. In the absence of an overt hydrogen atom donor (such as Sn–H), maximum lifetimes are permitted for intermediate radicals **8** and **9**, which undergo relatively slow reactions. However, the final radical **10** is rapidly consumed in the chain-transfer step, the driving force of which is the production of a more stable alkyl radical from a less stable vinyl radical. [10] Undesired side reactions of the final radical, such as addition to the acrylate, are avoided.[14]

Scheme I



A variety of examples of this process have been conducted, and the results are summarized in eq 1 and Table I. The effects of olefin substitution are readily anticipated based on known substituent effects in radical addition reactions.[6f] Addition of **1** to monosubstituted electron deficient alkenes (Table I, entries a, b, e) generally proceeds with reasonable selectivity for exo-cyclization and low to modest selectivity for formation of the E-vinyl iodide. The use of 1,1-disubstituted olefins (entries c, d) provides an increase in both exo- and E-selectivity. β-Alkyl substitution is well known to retard the addition step, but substitution with a β-activating group is useful (entries f and g). Substitution of the terminal alkyne provides an increase in exo-selectivity. For example, addition of trimethylsilyl-substituted alkyne **5** to methyl acrylate (eq 1) produces the 5-exo product **6** in 55% isolated yield as an unassigned 1.1:1 mixture of stereoisomers. The 6-endo product **7** could not be detected. Methyl methacrylate provides a similar result (Table I, entry h).

From the standpoint of synthetic utility, the intermediate vinyl iodides can be directly reduced by in situ treatment with tin hydride. For example, addition of 1 molar equivalent of tri-n-butyltin hydride to the crude reaction mixture resulting from eq

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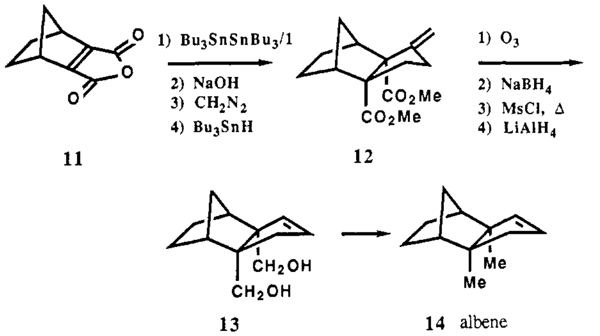
(12) The intermediate ester-substituted radical has been independently generated from the corresponding α-iodo ester and shown to give similar ratios of products. Curran, D. P.; Chang, C. T. *Tetrahedron Lett.* **1987**, *28*, 2477.

(13) Recent reviews of "cyclopentaannulation": (a) Paquette, L. A. *Top. Curr. Chem.* **1983**, *119*, 1; **1979**, *79*, 41. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (c) Ramaiah, M. *Synthesis* **1984**, 529.

(14) Two related tin hydride mediated reactions have been reported: Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980. Cekovic, Z.; Saicic, R. *Tetrahedron Lett.* **1986**, *27*, 5893. Both rely on the introduction of a radical stabilizing group (phenyl) to prevent addition of the final radical to the acrylate.

1, followed by standard initiation with AIBN, produced the corresponding (methylene)cyclopentane **3** (I = H) in 52% overall yield from methyl acrylate. As expected, attempts to convert **1** and **2** directly to **3** (I = H) by tin hydride treatment were not successful.

An illustration of the new method is provided by a total synthesis of the simple natural product albene (eq 2).[15] Atom transfer addition of **1** to **11** was followed by conversion of the anhydride to the dimethyl ester and reductive deiodination. By this sequence, diester **12** was isolated in 55% overall yield from **11**. Routine transformations provided **13** (32% overall), which has previously been deoxygenated[15b] to provide albene **14**. The yields of these intermediate steps have not been extensively optimized.



(2)

In summary, this atom transfer cycloaddition reaction provides an unusually direct method for the formation of substituted (methylene)cyclopentanes. Although modest yields (typically 40–60%) are the rule, the straightforward simplicity of this one-step route may make it attractive for synthetic applications. The unique advantages of control of the free-radical sequence by iodine atom transfer are apparent, and the design of other atom transfer based sequences will be reported in the near future.

Acknowledgment. We thank the National Institutes of Health (GM-33372) for funding of this work.

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(15) (a) Baldwin, J. E.; Barden, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6656. Baldwin, J. E.; Barden, T. C. *J. Org. Chem.* **1981**, *46*, 2442. (b) Trost, B. M.; Renaut, P. *J. Am. Chem. Soc.* **1982**, *104*, 6668.

Electronic Transitions of Polyacenequinone Radical Anions in the 1–2 μm Region

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Received June 19, 1987

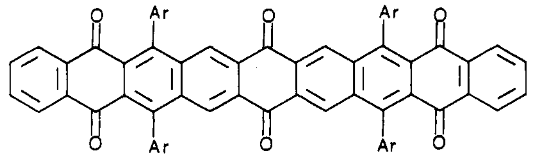
Studies from this laboratory have led to the syntheses of linear, polyquinoidal polyacenes like compound **1**.[1,2] It was proposed that, "...quinoidal derivatives would have interesting possibilities for substantially varying the electronic structure of a large molecular framework, and by appropriately choosing quinone-, semiquinone-, and hydroquinone-type moieties the reactivity and the optical, magnetic, and electrical properties could be controlled."[1] In this communication, we report initial results on the optical properties of such compounds, with emphasis on radical anions (semiquinones) of compounds like **1**, which have intense absorptions in the near infrared (NIR) region between 1 and 2 μm. To our knowledge good precedent for this observation is lacking. We suggest that these bands result from $\pi^*-\pi^*$ excitations, that the bands are characteristic of di- or polyquinones, not monoquinones, that they should be shifted to the IR region in suitable cases, and that such bands may be found in other anion-radicals of appropriate structure. It is further noted that these observations could lead to applications in optics or electrooptics.

Table I. Physical Properties of Semiquinones

semiquinone	$-E°$ [a] (mV, SCE)	λ_{max} (nm) (log ε)[b]
$1^{•-}$	665, 981, 1265	1730 (4.43), 485 (4.11) 435 (4.17)
$2^{•-}$	420, 920	1335 (4.50), 1130 (4.08) 430 (3.78), 400 (3.78)
$3^{•-}$	256, 737	1560 (4.21), 1286 (3.80) 440 (3.68), 410 (3.62)
$4^{•-}$	-142, 586	900 (4.66), 805 (3.63) 485 (3.60), 450 (3.58)
$5^{•-}$	608, 1412	480 (3.89), 410 (3.97) 390 (3.71)
$6^{•-}$	960, 1565	595 (4.03), 390 (3.85)
$7^{•-}$	1048, 1655	650 (3.95), 440 (3.45)

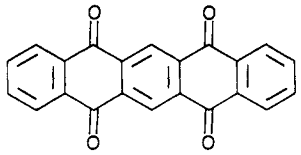
[a] DMF, Bu_4NBF_4 at glassy carbon. Center of anodic and cathodic peak potentials, the first number is for $Q/Q^{•-}$. [b] In DMF, Bu_4NBF_4.

Compound **1** was reduced electrochemically in DMF solution, 0.1 M in tetrabutylammonium tetrafluoroborate, by using a carbon felt electrode in a simple 2-compartment cell. Cyclic voltammograms were obtained by using a small glassy carbon analytical electrode prior to bulk electrolysis. The voltammogram for **1** displays three separate one-electron reversible couples (see Table I) followed by a fourth quasi-reversible couple. The potential for bulk electrolysis was set several millivolts cathodic of the first couple. After passage of 1.2 Faradays/mol, the electrolysis current had dropped to near the background level, and the absorbance spectrum of the resultant solution was measured with the exclusion of oxygen. Under such conditions, the optical spectrum did not change with time. Either exposure to oxygen or electrochemical reoxidation of the solution regenerated **1**, which could be reisolated by extraction and flash chromatography.



1

Ar = $(CH_3)_3C—C_6H_4$



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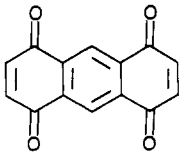
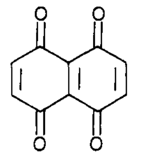


3



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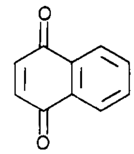

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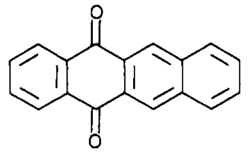

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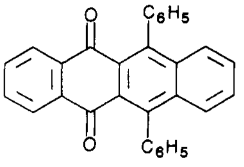

7

The absorption spectrum of **1** is quite ordinary. It shows the longest wavelength band at 440 nm, which is similar to the spectrum of the monoquinone model **7**.[3] The absorption spectrum

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(1) Thomas, A. D.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4160.
(2) Christopfel, W. C.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4169.
(3) UV-vis spectra in CH_2Cl_2 **7**: 245 (43 000), 296 (26 500), 394 (5500); **1**: 275 (46 000), 318 (116 000), 440 (26 000).

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