Table I. Second-Order Rate Constants for the Diels–Alder Reaction between 9,10-Dimethylanthracene and Acrylonitrile at 28.0 °C in Lithium Perchlorate–Diethyl Ether Solution

$k_2 \times 10^6$, M^{-1} s^{-1}	$[LiClO_4]$, M	$k_2 \times 10^6$, M^{-1} s^{-1}	$[LiClO_4]$, M
1.28	0	8.11	2.99
4.34	1.20	9.85	3.88
5.37	1.82	11.4	4.55

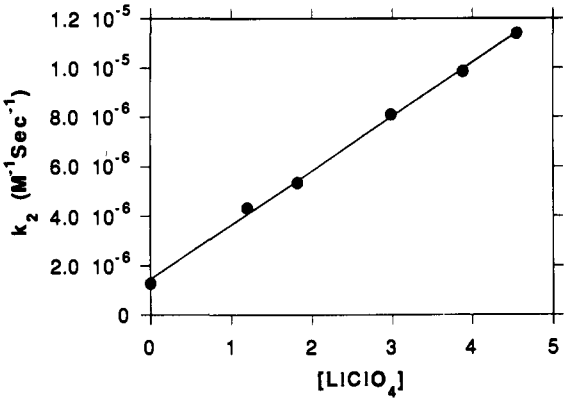

Figure 1. Second-order rate constants for the Diels–Alder reaction between acrylonitrile and 9,10-dimethylanthracene at 28.0 °C in ether versus lithium perchlorate concentration.

The linear correlation ($r = 0.999$; slope $= 2.25 \times 10^{-6}$) argues that there is a first-order dependence on $[LiClO_4]$. Lewis acid catalysis of the Diels–Alder reaction is often used in organic synthesis, although relatively few detailed kinetic studies have been reported.[8] The function of the Lewis acid is well understood in terms of FMO theory, and several ab initio studies have quantified this effect.[9] Enhanced endo/exo selectivity is also observed under Lewis acid catalysis.[10] Typically, strong Lewis acids such as aluminum chloride, boron trifluoride, or tin(IV) chloride have been used, although softer species such as copper(I)[11] have also been employed, especially for sensitive substrates such as furan. In the present case we propose that lithium ion is acting as the Lewis acid[12] by complexing with the cyano group nitrogen of acrylonitrile. Gas-phase lithium ion affinities have been measured for a series of compounds, and the values for ethers, carbonyl compounds, and nitriles are all similar.[13] Ab initio calculations reproduce the experimental results.[14]

As additional examples, we have examined the reactions of fumaronitrile with DMA and isoprene with dimethyl acetylenedicarboxylate.[15] Since both fumaronitrile and dimethyl acetylenedicarboxylate have two activating groups, there are two possible sites for lithium ion complexation. For each reaction, a plot of the second-order rate constants versus $[LiClO_4]^2$ was reasonably linear. The rates for these two reactions in 4 M LPDE are accelerated by factors of 50 and 150, respectively, relative to the purely thermal reactions.

Other sources of relatively uncomplexed lithium ions behaved similarly while a perchlorate salt lacking Lewis acidity had virtually no effect on the rates. For instance, a 1.9 M solution of lithium hexafluorophosphate in ether yields a rate constant of 1.2×10^{-5} M^{-1} s^{-1} for the Diels–Alder reaction between DMA and AN. In contrast, solutions of 1.6 M tetra-*n*-butylammonium perchlorate in tetrahydrofuran (Bu_4NClO_4 is insoluble in ether) showed no significant rate differences while comparable lithium perchlorate–tetrahydrofuran solutions showed accelerations, although much less than those observed with LPDE.[16]

In conclusion, we have presented evidence for the three systems studied here that the rate accelerations observed in LPDE are consistent with lithium ion catalysis of the Diels–Alder reaction. In addition, the accelerating effect of LPDE is not universal, suggesting that if a Diels–Alder reaction cannot be catalyzed by a Lewis acid, then LPDE may be of no value. Fortunately most reactions do not fall into this category.

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Supplementary Material Available: Listing of rate data for the reactions of fumaronitrile with DMA and isoprene with dimethyl acetylenedicarboxylate and plots of the data (2 pages). Ordering information is given on any current masthead page.

(8) (a) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 872 and references therein. (b) Kiselev, V. D.; Shakirov, I. M.; Konovalov, A. I. *Zh. Org. Khim.* **1986**, *22*, 1034. (c) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070 and references therein.

(9) (a) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127 and references therein. (b) Guner, O. F.; Ottenbrite, R. M.; Shillady, D. D.; Alston, P. V. *J. Org. Chem.* **1987**, *52*, 391.

(10) A report on the enhanced endo selectivity of a Diels–Alder reaction produced by concentrated lithium perchlorate–diethyl ether solutions had appeared prior to that of ref 1, although no mention was made of increased reaction rates. See ref 2b.

(11) (a) Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675. (b) Moore, J. A.; Partain, E. M., III. *J. Org. Chem.* **1983**, *48*, 1105. (c) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 1700.

(12) For a recent discussion on the Lewis acidity of lithium ion, see: Pushin, A. N.; Tkachenko, S. E.; Martynov, I. V. *Dokl. Akad. Nauk SSSR* **1988**, *299*, 154.

(13) (a) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920. (b) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986, p 319 f.

(15) The data is available as supplementary material.

(16) For instance, for the reaction of DMA and AN in tetrahydrofuran (THF), the second-order rate constants in pure THF, 1.6 M $(n\text{-}Bu)_4ClO_4$–THF, and 1.6 M $LiClO_4$–THF were 1.4×10^{-6}, 1.4×10^{-6}, and 2.2×10^{-6} M^{-1} s^{-1}, respectively.

Two-Carbon Intercalation. 4-Cyclooctenones by Tandem Application of Double Tebbe and Claisen Reactions

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The intriguing structural characteristics and remarkable biological activities of natural products possessing fused eight-membered rings have made them attractive targets for synthesis.[1] However, the possibility of incorporating this uncommon carbocyclic feature into other well-known classes of pharmacologically important molecules, e.g., steroids, in an effort to potentiate biological response does not appear to have been pursued. Presumably, this is a direct consequence of the absence of a concise, reliable, and efficient scheme for effecting the enlargement of smaller functionalized rings.

(1) Notable examples include the following. (a) Cycloaraneosene: Kato, N.; Tanaka, S.; Takeshita, H. *Chem. Lett.* **1986**, 1989. (b) Ceroplastol II and albolic acid: Kato, N.; Takeshita, N.; Kataoka, H.; Ohbuchi, S.; Tanaka, S. *J. Chem. Soc., Perkin Trans. 1* **1989**, 165. (c) Ophiobolin C: Rowley, M.; Tsukamoto, M.; Kishi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2735. (d) Ceroplastol I: Boeckman, R. K., Jr.; Arvanitis, A.; Voss, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 2737. (e) Precapnelladiene: Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 7352. (f) Poitediol: Gadwood, R. C.; Lett, R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 3869. (g) Neolemnanyl acetate: Majetich, G.; Lowery, D.; Khetani, V. *Tetrahedron Lett.* **1990**, *31*, 51.

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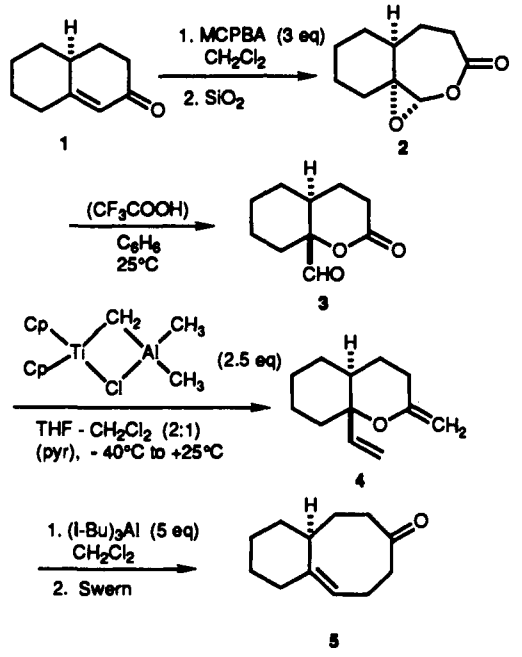
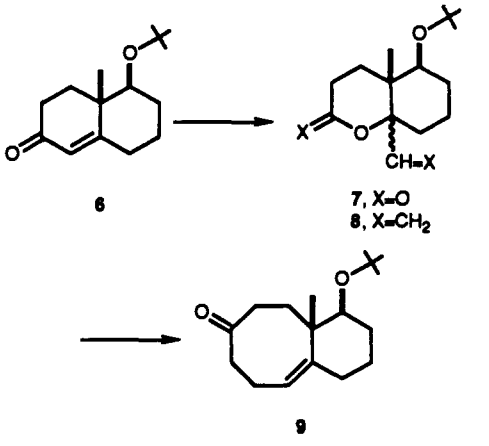
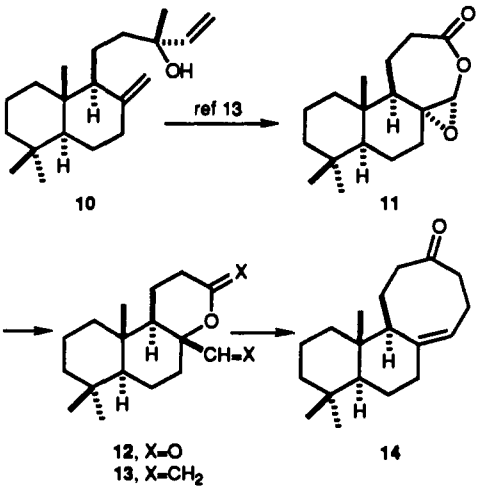
Scheme I



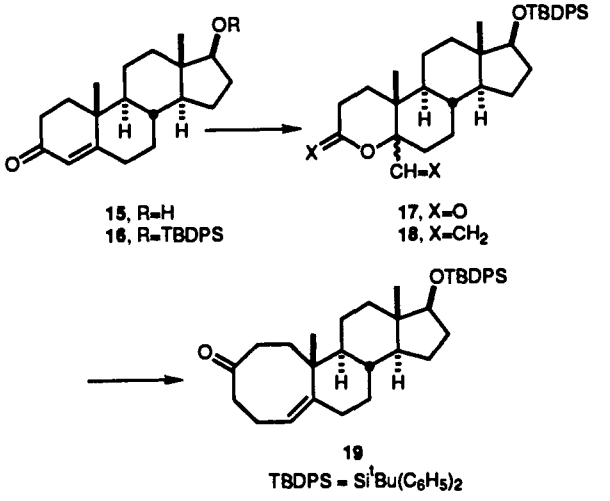
Scheme II



Scheme III



Scheme IV



We[1c,2] and others[3] have previously documented examples of Claisen ring expansion reactions that afford medium-ring unsaturated ketones. Adaptation of this [3.3] sigmatropic process as the concluding step in a short sequence that effectively intercalates a $-CH_2CH_2-$ unit between C-1 and C-2 of a 2-cyclohexenone has now been successfully realized. The synthetic opportunities offered by the new reaction sequence can be gleaned from the response of octalone **1** as detailed in Scheme I.

Oxidation of **1** with 3 equiv of MCPBA according to DeBoer and Ellwanger[4] produced **2**, isomerization of which in the presence of trifluoroacetic acid[5] generated the trans-fused aldehydo lactone **3** (88%). Subsequent exposure of **3** to 2.5 equiv of freshly prepared[6] Tebbe reagent[7] resulted in efficient methylenation of both carbonyl groups. A 69% isolated yield of acid-sensitive **4** could be routinely realized provided all glassware was base-washed prior to use.[8] This unparalled application of a double Tebbe olefination set the stage for Tribal promoted Claisen rearrangement[2c,9] of **4** (25 °C, 15 min). The resultant stereoisomerically pure alcohol (86%) was directly oxidized to **5** under Swern conditions (86%).[10]

An initial opportunity to assess the inertness of ether functionality during the sequence was provided by optically pure enone **6**[11] (Scheme II). As expected, its conversion to **7**[12] proceeded as efficiently as in the earlier example. Condensation with 2.5 equiv of the Tebbe reagent was likewise rapid and ususually clean provided that a trace quantity of pyridine was present (83% of **8**). The subsequent Tribal promoted isomerization of **8** showed

(2) (a) Kang, H.-J.; Paquette, L. A. *J. Am. Chem. Soc.* **1990**, *112*, 3252. (b) Paquette, L. A.; Sweeney, T. J. *J. Org. Chem.* **1990**, *55*, 1703; *Tetrahedron* **1990**, *46*, 4487. (c) Paquette, L. A.; Friedrich, D.; Rogers, R. D. *J. Org. Chem.*, in press. (d) Ezquerra, J.; He, W.; Paquette, L. A. *Tetrahedron Lett.* **1990**, *31*, 6979.

(3) (a) Rhoads, S. J.; Brandenburg, C. F. *J. Am. Chem. Soc.* **1971**, *93*, 5805. (b) Rhoads, S. J.; Watson, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 5813. (c) Demole, E.; Enggist, P.; Borer, C. *Helv. Chim. Acta* **1971**, *54*, 1845. (d) Petrzilka, M. *Helv. Chim. Acta* **1978**, *61*, 2286, 3075. (e) Pitteloud, R.; Petrzilka, M. *Helv. Chim. Acta* **1979**, *62*, 1319.

(4) DeBoer, A.; Ellwanger, R. E. *J. Org. Chem.* **1974**, *39*, 77. In this instance, the accompanying trans isomer is destroyed during the chromatography on silica gel.

(5) Pinhey, J. T.; Schaffner, K. *Tetrahedron Lett.* **1965**, 601; *Aust. J. Chem.* **1968**, *21*, 1873.

(6) Aged reagent was found to induce internalization of the *exo*-methylene double bond with greater facility. An increase in the relative proportion of organometallic to 8 equiv was yet more troublesome in this regard.

(7) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

(8) This consideration extends to the NMR tubes utilized for the spectral analyis of these vinyl ethers.

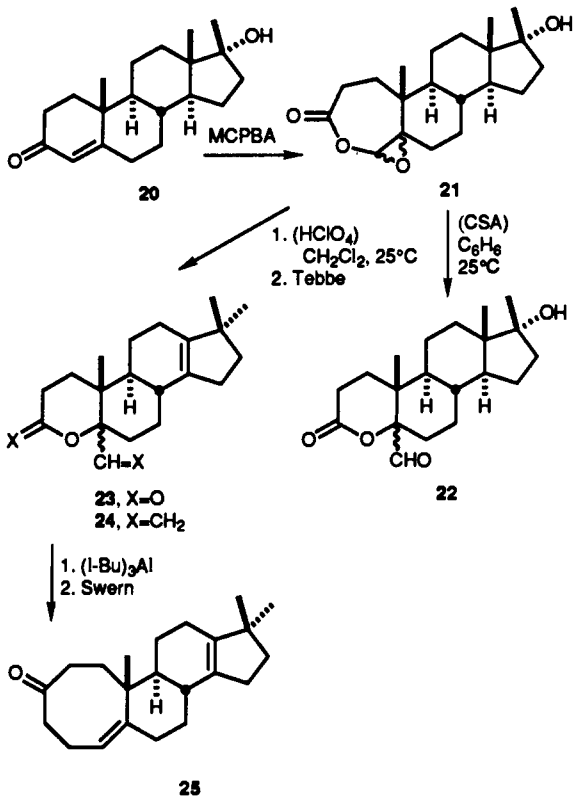
(9) Mori, I.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron* **1984**, *40*, 4013.

(10) The direct conversion of **4** to **5** can be accomplished thermally as well (KOH-coated soft glass, toluene solvent, sealed tubes, 190 °C). Details will be provided in the full paper.

(11) Prepared by regioselective reduction ($NaBH_4$, MeOH) and *tert*-butylation ($CH_2{=}C(CH_3)_2$, H_2SO_4) of optically pure Wieland–Miescher, ketone: Buchschacher, P.; Fürst, A. *Org. Synth.* **1985**, *63*, 37. Gutzwiller, J.; Buchschacher, P.; Fürst, A. *Synthesis* **1977**, 167.

(12) The structure assigned to each new compound was in accord with its IR, 300-MHz ^1H NMR, ^{13}C NMR, and high-resolution mass spectra. C and H combustion analyses, when obtained, were within 0.4%.

Scheme V



only one unusual characteristic, viz., its rate was approximately 20 times slower than that of **4**. As will be shown, this kinetic retardation is not due to the presence of added oxygen functionality, but to the proximal angular methyl group, presumably because of the added steric encumbrance it brings to the Claisen transition state.

Manool (**10**) has also served as a starting point for implementation of the intercalation process (Scheme III). Conversion of **10** to epoxy lactone **11**[13] set the stage for isomerization to **12** (2 M NaOH, MeOH: dilute HCl; 100%) and 2-fold methylenation (64% of **13**). In an informative experiment, exposure of **13** to 10 equiv of Tribal in CH_2Cl_2 resulted in completion of the desired ring expansion within 15 min at room temperature. As in **4**, the sigmatropic process is facilitated by the absence of an alkyl group at the proximal angular site.

Most indicative of the synthetic versatility of this methodology are the results achieved with testosterone (**15**) and its 17β-methyl homologue **20**. Following silylation of **15** (95%), oxidation with MCPBA[14] was effected as before (85%) and the stereoisomeric mixture was isomerized to **17** (94%) with a catalytic amount of *d*-camphor-10-sulfonic acid in benzene at 25 °C (Scheme IV). The ensuing Tebbe reaction, performed under the standard conditions, furnished **18** efficiently (92%) as a prelude to the ring expansion. In the presence of a solution of excess Tribal (5 equiv) in CH_2Cl_2, the Claisen rearrangement of **18** required 6 h to go to completion (compare **13**). Swern oxidation of the resulting cyclooctenol (64% isolated) afforded **19** (82%).

The hydroxyl group in **20**, unlike **15**, was left unprotected (Scheme V). Peracid oxidation furnished **21** (70%), an intermediate that could be isomerized to **22** without dehydration of the tertiary carbinol, or to **23** via carbocation formation, Wagner-Meerwein shift, and ultimate dehydration (88%). The availability of **23** in this manner made possible the acquisition of **25** in good overall yield (**23** → **24**, 93%; (*i*-Bu)$_3$Al, 63%; Swern, 78%). That the Claisen rearrangement of **24** required 6 h at 25 °C for completion is further substantiation of the rate-retarding steric role played by the angular methyl substituent.

The methodology herein described provides the groundwork and incentive for considerable further experimentation. It is our intention to report on further studies in this area and some interesting synthetic applications at a future time.[15]

(13) Grant, P. K.; Liau, T. L.; Temple, W. A. *Aust. J. Chem.* **1979**, *32*, 1353. We are indebted to Professor Grant for amplification of the experimental details and a generous sample of crude manool extract.

(14) For earlier applications of this oxidation to steroids and diterpenes, see: (a) References 5 and 13. (b) Gorodetsky, M.; Danieli, N.; Mazur, Y. *J. Org. Chem.* **1967**, *32*, 760. (c) Chang, C. W. J.; Pelletier, S. W. *Tetrahedron Lett.* **1966**, 5483. (d) Pelletier, S. W.: Chang, C. W. J.; Iyer, K. N. *J. Org. Chem.* **1969**, *34*, 3477. (e) Abad, A.; Agulló, C.; Arnó, M.; Cuñat, A. C.; Zaragozá, R. J. *J. Org. Chem.* **1989**, *54*, 5123.

(15) The financial support of this work by the National Institutes of Health (Grant GM-30827) is gratefully acknowledged.

Novel Magnetic Properties of a Doped Organic Polymer. A Possible Prototype for a Polaronic Ferromagnet

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There are many approaches to the preparation of organic materials with novel magnetic behaviors.[1] Of these, perhaps the least explored has been the "polaronic ferromagnet", christened by Fukutome in a recent theoretical work.[2] We describe here an initial experimental approach to such a structure and evidence for significant *ferromagnetic couplings* in the material.

The general approach to magnetic organic materials that we have been pursuing is schematized in the drawing.[3] In the polaronic ferromagnet, the spin-containing moiety is a polaron: the partially delocalized radical cation (anion) that one obtains on oxidative (reductive) doping of a conjugated polymer. Using a Wittig polymerization route described previously,[3b] we have prepared the octadecyloxy substituted poly(*m*-phenylene-octatetraene) derivative PMPOT-18.[4] The key design features are (1) *m*-phenylene as the ferromagnetic coupling unit;[5] (2) a tetraene as the easily oxidized "polaron" precursor; and (3) *O*-alkyl groups to enhance polymer solubility. Concerning the last point, PMPOT-18 is soluble in a variety of organic solvents and forms

(1) For a recent overview, see: *Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials*, 197th National Meeting of the American Chemical Society, Dallas TX; American CHemical Society: Washington, DC, 1989. Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1-562.

(2) Fukutome, H.; Takahashi, A.; Ozahi, M. *Chem. Phys. Lett.* **1987**, *133*, 34-38.

(3) (a) Dougherty, D. A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 25-32. (b) Dougherty, D. A.; Kaisaki, D. A. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 71-79. Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618-7619.

(4) PMPOT-18: MW by GPC (toluene, 40 °C; polystyrene standard): M_N = 6130; M_W = 15 800 (monomer weight 449); ^{1}H NMR ($CDCl_3$) δ 0.85 (m, 3 H), 1.28 (br s, 30 H), 1.43 (br s, 2 H), 1.78 (br s, 2 H), 3.9 (br s, 2 H), 6.4-6.8 (br, 11 H); IR (thin film, cm^{-1}): 680 (m), 972 (m), 998 (s), 1465 (s), 1568 (s), 2852 (s), 2922 (s), 3018 (m); UV ($CHCl_3$) λ_{max} = 400 nm, additional peak at 422 nm, sh at 382 nm. Films for doping were ca. 90 μm thick. Elemental anal. Calcd for $C_{32}H_{50}O$: C, 85.27; H, 11.18; O, 3.55. Found: C, 84.24; H, 10.72; O, 4.22; Br, 0.18; P, 0.27.

(5) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1990**, *112*, 4074-4075. Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147-2156. Berson, J. A. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, pp 455-536. Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 195-258.

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