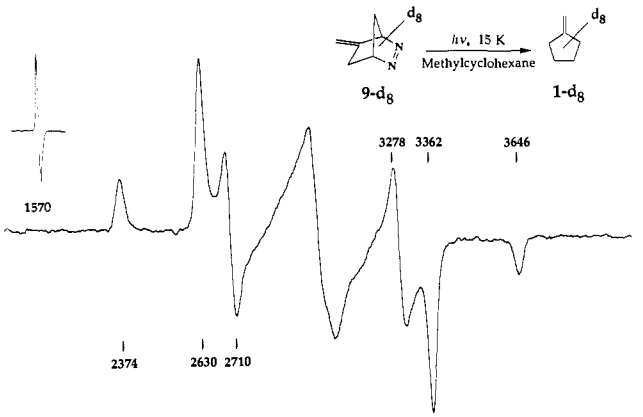
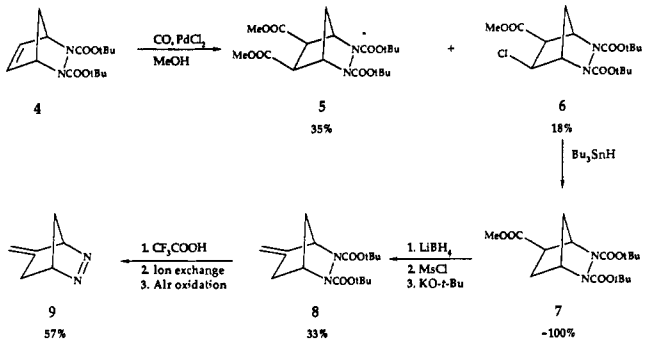



**Figure 1.** ESR spectrum of **1-$d_8$** showing the line positions and the splitting expected of the $x$ and $y$ lines. The inset shows the $\Delta m = 2$ transition at 1570 G.

**Scheme I**




the desired semilocalized diradical **1** as the major product.[9] The ESR spectrum of the perdeuterated diradical **1-$d_8$** from photolysis of **9-$d_8$** in methylcyclohexane glass was also examined. The zero-field parameter $E$ is not fully resolved in the **1-$h_8$** spectrum but is readily extracted from the spectrum of the perdeuterated derivative **1-$d_8$** (Figure 1). Thus, for **1**, $D = 0.0591 \pm 0.0006$ cm$^{-1}$ and $E = 0.002\,54 \pm 0.000\,03$ cm$^{-1}$. The $D$ value for **1** is approximately halfway between that of **2** (0.0265 cm$^{-1}$)[5a,b] and **3** (0.084 cm$^{-1}$)[4] and somewhat smaller than those for semilocalized four-membered ring diradicals.[2] The small value of $E$ is typical of four- and five-membered ring diradicals[2,4] (e.g., **2**, $E = 0.005\,50$; **3**, $E = 0.0020$).

Determination of the Curie law behavior of **1** yields a straight line; therefore, **1** is a ground-state triplet.[10] The triplet **1** decomposes irreversibly at 40 K limiting the range of the Curie-Weiss plot.

The transformation from **1** to **2** is a triplet-triplet conversion. Therefore, the conversion of the semilocalized triplet diradical **1** to the more highly delocalized trimethylenemethane triplet **2** can be followed entirely using ESR (Figure 2). It was established in this way that in the isopentane matrix the rearrangement of **1** to **2** is a *photochemical reaction*.[11] The first photoproduct from the irradiation at 340 nm of **9** is the semilocalized diradical **1**. Continued irradiation of the diradical **1** at 340 nm results in a decrease in **1** and an increase in the more stable triplet **2**. The chromophore in this transformation is probably the allyl radical which absorbs over the range 210-400 nm.[12] By irradiating the sample at 400 nm, triplet **1** was converted smoothly to **2** with isosbestic behavior (Figure 2). The azo compound **9** shows no sensitivity to light at 400 nm, so its photolysis does not intrude at that wavelength. This rules out the direct conversion of **9** to **2** which can, in principle, occur at 340 nm.

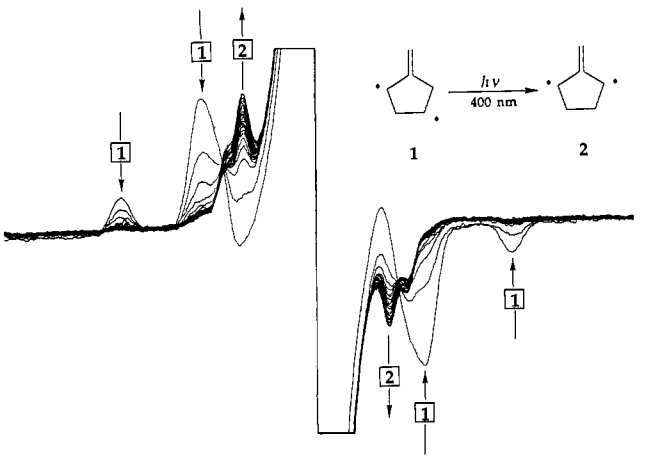



**Figure 2.** Photochemical isomerization of triplet **1** to triplet **2** by irradiation of 400 nm and 15 K. The matrix is methylcyclohexane.

**Acknowledgment.** This work was generously supported by the National Science Foundation under Grant CHE 8603280. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(9) Cf.: Adam et al. (Adam, W.; Gunther, E.; Hössel, P.; Platsch, H.; Wilson, R. M. *Tetrahedron Lett.* **1987**, *28*, 4407) who reported photolysis of the 7,7-dimethyl-5-methylene-2,3-diazabicyclohept-2-ene in the presence of oxygen. They detected very little peroxide which would be indicative of trapping of diradical intermediates. Thus, the low-temperature ESR method may have the advantage, over oxygen trapping, of forestalling untoward decomposition pathways of the diradicals which would obscure their formation.

(10) It is also possible that singlet and triplet are degenerate.

(11) The very interesting rearrangement of 2,3-diazabicyclo[2.2.1]hept-2-ene-7-spirocyclopropane apparently also proceeds by a 1,2-hydrogen migration to yield a trimethylenemethane.[2b] The 1,2-shift is ascribed to a tunneling reaction from a vibrationally excited precursor. We cannot rule out the tunneling reaction, but, as in our experiments, deuterium substitution had little effect on the outcome of the reaction.[2b] Accordingly, a photoreaction might be important in this instance as well.

(12) Maier, G.; Reisenauer, H. P.; Rohde, B.; Dehnicke, K. *Chem. Ber.* **1983**, *116*, 732. Burrell, E. J., Jr.; Bhattacharyya, P. K. *J. Phys. Chem.* **1967**, *71*, 775. See, also: Ha, T.-K.; Baumann, H.; Oth, J. F. M. *J. Chem. Phys.* **1986**, *85*, 1438.

## Selective Hydrocracking of Monosaccharide Carbon-Carbon Single Bonds under Mild Conditions. Ruthenium Hydride Catalyzed Formation of Glycols

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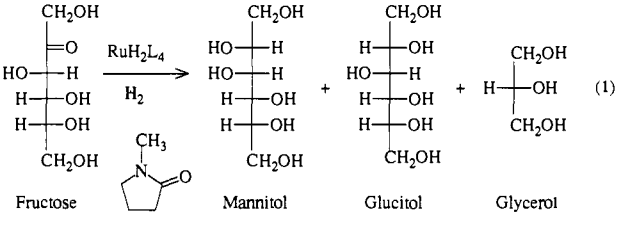
Carbohydrates exhibit unusually rich chemical functionality but limited stability. Homogeneous transition-metal catalysts should offer the unique combination of high selectivity and reactivity needed to effectively manipulate these important substrates. We show here how this relatively unexplored catalyst-substrate combination can be exploited to (a) accomplish the facile hydrocracking of specific C-C single bonds and (b) provide a foundation for new approaches to biomass conversion.

Fructose is readily hydrogenated (100 °C, 20 atm $H_2$, $N$-methyl-2-pyrrolidinone solvent) in the presence of 0.02 equiv of $H_2Ru(PPh_3)_4$ (eq 1, Table I expt 1).[1] The expected products,




(1)

Table I. Hydrocracking of Sugars by $H_2Ru(PPh_3)_4$

| | expt no. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | Experimental Conditions[a] | | | | | | | |
| [sugar], mM | 64 | 63 | 64[b] | 64 | 63 | 72 | 64[c] | 64[d] |
| [Ru], mM | 1.36 | 0.47 | 2.04 | 1.90 | 1.92[e] | 1.98 | 1.93 | 2.07 |
| [$OH^-$], mM[f] | 0.00 | 0.95 | 0.95 | 0.19 | 0.94 | 4.66[g] | 1.88 | 0.19 |
| time, h | 24.0 | 22.8 | 24.0 | 2.0 | 1.7 | 1.5 | 2.0 | 7.0 |
| % conv[h] | 83 | 78 | 48 | 70 | 76 | 92 | 85 | 66 |
| % mass bal[i] | 98 | 79 | 73 | 84 | 77 | 72 | 76 | 86 |
| | Products, mol/mol Ru[j] | | | | | | | |
| ethylene glycol | 1.0 | 16.8 | 2.1 | 1.9 | 4.3 | 8.4 | 6.0 | 0.9 |
| propylene glycol | 0.2 | 1.0 | – | 0.1 | 0.1 | 0.4 | 0.2 | 0.1 |
| $C_3$ sugars[k] | – | 2.9 | 1.1 | 0.8 | 3.8 | 1.9 | 0.8 | – |
| glycerol | 14.2 | 84.3 | 5.9 | 16.9 | 16.8 | 25.9 | 7.0 | 8.2 |
| $C_4$ sugars[k] | – | 2.2 | 0.4 | 0.4 | 1.2 | 1.0 | 0.7 | 0.4 |
| threitol | 0.4 | 6.9 | 0.4 | 0.5 | 0.8 | 1.9 | 0.9 | 0.9 |
| erythritol | 0.5 | 5.9 | 0.4 | 0.8 | 0.9 | 2.0 | 3.3 | 7.1 |
| $C_5$ sugars[k] | – | 1.1 | 0.7 | 0.5 | 0.4 | 0.2 | 0.3 | – |
| $C_5$ alditols | – | 4.2 | 0.4 | 0.9 | 0.9 | 1.1 | 1.6 | 0.4 |
| $C_6$ ketoses[l] | 8.0 | 27.2 | 15.8 | 10.0 | 7.6 | 2.8 | 1.8 | 0.1 |
| $C_6$ aldoses[m] | – | 1.5 | 0.5 | 0.1 | 0.4 | 0.3 | 3.2 | – |
| mannitol | 16.8 | 4.7 | 0.4 | 3.8 | 1.3 | 0.7 | 1.1 | 0.2 |
| other hexitols[n] | 13.2 | 6.9 | 0.3 | 2.3 | 1.1 | 1.1 | 5.5 | 0.1 |
| misc | 0.1[o] | 0.7[o] | – | 0.2[o] | – | – | 2.3[o] | 17.5[p] |

[a] Unless otherwise noted, sugar = fructose, solvent = *N*-methyl-2-pyrrolidinone, $T$ = 100 °C, $P(H_2)$ = 20 atm, see Supplementary Material for details. [b] $T$ = 50 °C, $P(H_2)$ = 1 atm. [c] Sugar = glucose. [d] Sugar = *manno*-2-heptulose. [e] Very similar results with $H_2Ru(CO)(PPh_3)_3$ as catalyst. [f] Added in the form of 1 M aqueous KOH. [g] Very similar results with anhydrous KO-*t*-Bu as the base. [h] Percent of initial sugar converted to products other than starting sugar or its isomers. [i] Weight percent of initial sugar accounted for by identified products at end of reaction (see footnote 5). [j] These "turnover" numbers do not take into account stoichiometric considerations; capillary GC analysis after oximation with $MeONH_2$ or $BnONH_2$ and silylation with *N*-trimethylsilylimidazole (see footnote 1). [k] Almost exclusively 2-ketoses. [l] Fructose, sorbose, psicose, tagatose, and dendroketose. [m] Mostly glucose and mannose. [n] Mostly glucitol. [o] Glucono- and mannono-lactones. [p] $C_7$ sugars = 10.6, $C_7$ alditols = 6.9.

mannitol and glucitol (64%), account for 77% of the products.[2] The only other major product, glycerol (15%), corresponds to the unprecedented homogeneous hydrocracking of the fructose C(3)–C(4) single bond (18% of the products based on $C_6H_{12}O_6 + 2H_2 \rightarrow 2C_3H_8O_3$). Heterogeneously catalyzed sugar hydrocracking reactions are known,[3] but these require relatively severe conditions (typically 200 °C, 100 atm $H_2$) and give complex mixtures containing significant amounts of partially deoxygenated products such as propylene glycol.

The selectivity for hydrocracking over simple hydrogenation can be dramatically improved (1:4 → 5:1) by the addition of 0.015 equiv of a potassium hydroxide cocatalyst.[4] This also permits the achievement of over 50 turnovers (expt 2) or reaction conditions as mild as 50 °C and 1 atm pressure (expt 3). The conversion of fructose to glycerol is only doubled (15% → 30%), however, due to a marked increase in sugar degradation reactions (2% → 20%)[5] and a moderate decrease in selectivity amongst the hydrocracked products ($C_3/(C_2 + C_4)$ = 6.8 → 2.7). These effects are further delineated in expts 4–6 which show how the product

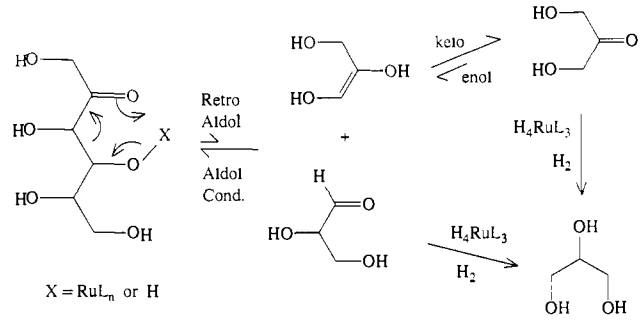



**Figure 1.** Proposed mechanism for hydrocracking of fructose.

distributions behave as a function of hydroxide ion concentration.[6] Graphical analysis of the data shows that the first increment of base (0.003 equiv, expt 4) is most important, with all reaction characteristics approaching asymptotic values at about 0.05–0.1 equiv of KOH. This unoptimized system already offers glycol yields comparable to patented high-temperature/pressure heterogeneous catalysts.[3]

The nature of the active catalyst is undoubtedly complex. Under hydrogen, the loaded $H_2Ru(PPh_3)_4$ catalyst precursor forms $H_2(H_2)Ru(PPh_3)_3$,[7,8] a known ketone hydrogenation catalyst.[9,10] The presence of KOH is not expected to alter this significantly,[9] although the base may facilitate coordination of a sugar alkoxy anion to the ruthenium.[11] As the reaction proceeds, infrared

(1) Experimental Details and a sample GC analysis [(a) *Analysis of Carbohydrates by GLC and MS*; Biermann, C. J., McGinnis, G. D., Eds.; CRC Press: Boca Raton, FL, 1988. (b) Andrews, M. A. *Carbohydr. Res.*, in press] are available as Supplementary Material.

(2) Fructose has been previously hydrogenated to mannitol and glucitol with $HRuCl(PPh_3)_3$ (Kruse, W. M.; Wright, L. W. *Carbohydr. Res.* **1978**, *64*, 293–296).

(3) (a) van Ling, G.; Ruijterman, C.; Vlugter, J. C. *Carbohydr. Res.* **1967**, *4*, 380–386. (b) Hanford, W. E. U.S. Patent 2 209 055, July 1940. (c) Conradin, F.; Bertossa, G.; Giesen, J. U.S. Patent 3 030 429, Apr 1962. (d) Kasehagen, L. U.S. Patent 3 396 199, Aug 1968. (e) Sirkar, A. K. U.S. Patent 4 380 678, Apr 1983. (f) Arena, B. J. U.S. Patent 4 401 823, Aug 1983. (g) Tanikella, M. S. S. R. U.S. Patent 4 404 411, Sep 1983. (h) Dubeck, M.; Knapp, G. G. U.S. Patent 4 476 331, Oct 1984. (i) Arena, B. J. U.S. Patent 4 496 780, Jan 1985.

(4) Tertiary amines are not effective cocatalysts. Water in the solvent (up to 0.1%) has no significant effect.

(5) This mass loss, which occurs very early in the reaction, is undoubtedly due to alkaline degradation reactions that yield polyhydroxylic carboxylic acids, both monomeric and polymeric (de Bruijn, J. M.; Kieboom, A. P. G.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 176–183). These would not be detected by the GC derivatization schemes[1] employed in the present analyses.

(6) No other reaction variable (temperature, hydrogen pressure, catalyst concentration/ratio) has been found to have as significant an effect.

(7) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1970**, *92*, 3011–3016.

(8) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.

(9) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969–2974.

(10) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536–7542.

(11) Cf. Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1154–1156.

spectra show the formation of $H_2Ru(CO)(PPh_3)_3$ and $H_2Ru(CO)_2(PPh_3)_2$, presumably due to decarbonylation of aldose sugars present (vide infra).[12] This does not immediately lead to loss of catalytic activity, however, since $H_2Ru(CO)(PPh_3)_3$ also hydrocracks fructose (expt 5, footnote *e*).

Clues to the hydrocracking mechanism are provided by the cleavage products and intermediate sugars observed. The primary C–C cleavage site (especially at low base concentrations) is always $\beta$ to the sugar carbonyl group; the major product of fructose cleavage being glycerol, of glucose cleavage ethylene glycol and erythritol (expt 7), and of *manno*-2-heptulose cleavage glycerol and erythritol (expt 8). This cleavage site selectivity, together with the strong base catalysis observed, suggests that a retro-aldol reaction (possibly metal-enhanced) may be involved (Figure 1).[13,14]

Sugars are known to undergo a complex set of reactions in aqueous alkaline solution including isomerization (e.g. fructose → glucose), retro-aldolization, and degradation.[15] The same reactions take place in the nonaqueous solvent used here. Thus fructose heated to 100 °C in the presence of catalytic amounts of potassium hydroxide or potassium *tert*-butoxide yields a complex mixture of $C_2$–$C_6$ sugars consistent with that expected for fructose isomerization and multiple, reversible aldol reactions.[16] A very similar mixture of sugars is observed in the early stages of the Ru/KOH-catalyzed hydrogenation of fructose.

The final product distributions in these hydrocracking reactions appear to be controlled by a competition between sugar hydrogenation and retro-aldol cleavage. The carbonyl groups in short chain $C_2$–$C_4$ sugars are more readily hydrogenated than those in $C_5$–$C_6$ sugars since the former are less involved in hemiacetal and hemiketal formation.[17] Increasing the base concentration accelerates the cleavage to small retro-aldol derived sugars, thereby raising the ultimate percentage of hydrocracked products.[18] Higher base concentrations also cause the sugar isomerization and reversible aldol scrambling reactions to compete more effectively with hydrogenation, resulting in the decline in selectivity amongst the hydrocracked products.

The chemistry observed here therefore appears to be a combination of a sugar retro-aldol reaction and a metal-catalyzed carbonyl group hydrogenation. The net result of these otherwise ordinary reactions is the strikingly facile hydrocracking of specific C–C single bonds, a reaction with virtually no precedent in homogeneous transition-metal catalysis,[19] even for functionalized substrates[14] such as sugars. These findings furthermore provide one of the first fundamental bases for the rational development of nonbiological approaches to biomass conversion.

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**Supplementary Material Available:** Experimental details and a sample GC analysis (5 pages). Ordering information is given on any current masthead page.

(12) Andrews, M. A.; Klaeren, S. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1266–1267.

(13) The preferential stereochemistries observed in the primary $C_4$ and $C_5$ alditols produced are also consistent with predictions made by a retro-aldol mechanistic scheme.

(14) An apparent retro-aldol reaction has also been observed in the transfer hydrogenation of benzoylacetone by ethylene glycol at 200 °C catalyzed by $RuCl_2(PPh_3)_3$: Sasson, Y; Blum, J.; Dunkelblum, E. *Tetrahedron. Lett.* **1973**, 3199–3202.

(15) de Bruijn, J. M.; Kieboom, A. P. G.; van Bekkum, H. *Sugar Tech. Rev.* **1986**, *13*, 21–52.

(16) El Khadem, H. S.; Ennifar, S.; Isbell, H. S. *Carbohydr. Res.* **1987**, *169*, 13–21.

(17) Angyal, S. J. *Adv. Carrbohydr. Chem. Biochem.* **1984**, *42*, 15–68.

(18) The selectivity for hydrocracking decreases as the reaction proceeds, however, since the hydroxide concentration drops rapidly due to its consumption in the formation of carboxylate salts.[5]

(19) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

# ESR Evidence for the Stereospecific Formation of the Chair Cyclohexane-1,4-diyl Radical Cation from Both Bicyclo[2.2.0]hexane and 1,5-Hexadiene

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Cyclohexane-1,4-diyl has assumed considerable interest as a prototype structure associated with the hypothetical biradical pathway in the Cope rearrangement and in the cleavage of bicyclo[2.2.0]hexanes,[1] largely because of the stereochemical requirement for *chairlike* structures at the product-determining stage of these isomerizations.[2,3] These elusive biradicals have resisted further characterization, however, and thermal generation of an identical parent diyl from both 1,5-hexadiene (**1**) and bicyclo[2.2.0]hexane (**2**) has been questioned on the basis of the discordant free energies of formation obtained for the transition states derived from these two reactants.[1f] Similar questions of conformation and of a common identity from different precursors naturally arise for the radical cation (**3**),[4-8] and here we report spectroscopic evidence that the chair form of **3** is produced stereospecifically by the oxidation of both **1** and **2**.

As shown in Figure 1, virtually identical ESR spectra were obtained by the radiolytic oxidation of **1** and **2** in a haloethane matrix, the binomial seven-line pattern ($A$(6 H) = 12.0 (1) G; $g$ = 2.0026 (4)) from **1** having previously been assigned to **3**.[6] That the spectral correspondence represents a true identity of signal carriers and not just a verisimilitude[9] was established by the exact parallelism observed in the growth of the spectrum from the cyclohexene radical cation (**4**) when the two samples were annealed or photobleached.[6] Furthermore, while the seven-line pattern was also generated from solid solutions of **1** and **2** in $CF_2ClCFCl_2$, only the spectrum of **4** was revealed from the corresponding $CFCl_3$ solutions. All these results accord with the conclusion that **3** is a common intermediate along the oxidation pathways from **1** and **2** to **4**.

(1) (a) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; Chapter 6, Sections IVA and IVB, pp 163–176. (b) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142. (c) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay 5, pp 311–390 and especially Section IV, pp 353–372. (d) Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* **1987**, *109*, 5893. Dewar, M. J. S.; Jie, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1451. (e) Osamura, Y.; Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 3362. (f) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

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(8) For 1,4-diphenyl-**3**: (a) Adam, W.; Grabowski, S.; Miranda, M. A.; Rübenacker, M. *J. Chem. Soc., Chem. Commun.* **1988**, 142. (b) Miyashi, T.; Konno, A.; Takahashi, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3676.

(9) Cf.: Qin, X.-Z.; Pentecost, T. C.; Wang, J. T.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1987**, 450.

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