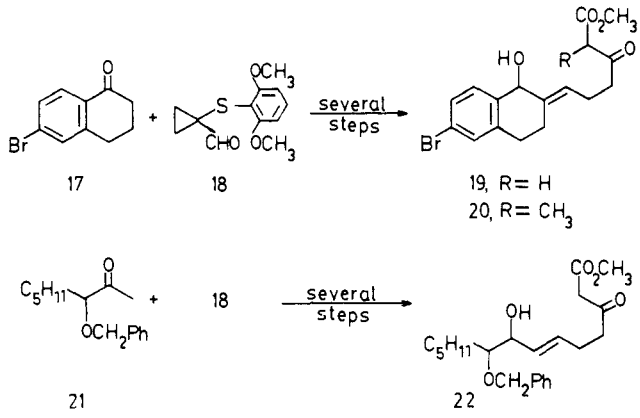
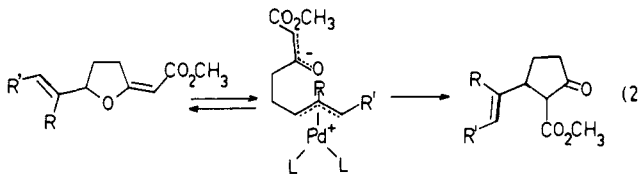



kylation of β-keto esters. The fact that **19, 20,** and **22** are readily available from the ketones **17** and **21** using a new conjunctive reagent **18**[11] makes this 1,3 shift a lynchpin in a new cyclopentanone synthesis. The formation of **10, 11,** and **12** illustrate applications of this new methodology in prostaglandin[9] and steroid synthesis.

The mechanism of this 1,3 shift can be thought to involve an oxidative addition of the allyl ether to palladium(0) as in eq 2 to form a zwitterion **23.**[12] This intermediate collapses by




C alkylation to form the observed product. The regiochemistry of the collapse is quite interesting in that a five-membered-ring product is observed, even in the case of R′ = H where seven-membered-ring formation could have proceeded by attack at the less hindered carbon of the allyl unit.[13] These results stand in stark contrast to cyclizations to form lactones in which the larger of the two possible ring sizes dominates even when an eight-membered ring results rather than a six.[14] Applications and additional mechanistic studies into this metal-catalyzed 1,3 shift are underway.[15] This new reaction illustrates an ability of a transition metal to change the normal rules of reactivity of an organic system.

**Acknowledgment.** We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for the generous support of our programs.

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(5) This compound has been fully characterized by spectral means and elemental analysis and/or elemental composition by high resolution mass spectroscopy.
(6) Selected spectral data are as follows. **8**: IR ($CHCl_3$) 1700, 1640 $cm^{-1}$; NMR (270 MHz) δ 0.87 (t, $J$ = 6 Hz, 3 H), 1.16–1.92 (m, 9 H), 2.27 (m, 1 H), 3.02 (m, 1 H), 3.29 (dddd, $J$ = 18.5, 9, 4.5, 1.5 Hz, 1 H), 3.67 (s, 3 H), 3.77 (m, 1 H), 4.35 (d, $J$ = 12 Hz, 1 H), 4.56 (two d, $J$ = 12 Hz, 1 H), 4.86 (m, 1 H), 5.35 (br s, 1 H), 5.67 (m, 2 H), 7.30 (br s, 5 H); mol wt calcd for $C_{22}H_{30}O_4$ 358.2144, found 358.2144. **5**: IR ($CCl_4$) 1700, 1635 $cm^{-1}$; NMR ($CCl_4$) δ 1.3–1.7 (m, 4 H), 1.62 (t, $J$ = 1 Hz, 3 H), 1.7–2.1 (m, 6 H), 2.5–3.3 (m, 2 H), 3.51 (s, 3 H), 4.5 (br t, $J$ = 7 Hz, 1 H), 5.55 (br m, 1 H), Anal. ($C_{14}H_{20}O_3$) C, H, mol wt. **6**: IR ($CCl_4$) 1695, 1635, 1590, 1555 $cm^{-1}$, NMR (270 MHz, $CCl_4$) δ 1.88–2.35 (m, 4 H), 2.81 (t, $J$ = 8 Hz, 2 H), 3.05 (m, 1 H), 3.33 (dddd, $J$ = 17.5, 8.7, 4.5, 1.5 Hz, 1 H), 3.68 (s, 3 H), 4.95 (t, $J$ = 7.2 Hz, 1 H), 5.39 (t, $J$ = 1.5 Hz, 1 H), 6.41 (br s, 1 H), 6.90 (d, $J$ = 8 Hz, 1 H), 7.26 (m, 2 H). Anal. ($C_{17}H_{17}BrO_3$) C, H. **7**: IR ($CCl_4$) 1700, 1638, 1595, 1485 $cm^{-1}$; NMR (270 MHz, $CDCl_3$) δ 1.88 (t, $J$ = 1.5 Hz, 3 H), 1.93 (m, 1 H), 2.25 (m, 3 H), 2.81 (t, $J$ = 8.2 Hz, 2 H), 3.01 (m, 1 H), 3.26 (dddq, $J$ = 18, 9, 5, 1.5 Hz, 1 H), 3.70 (s, 3 H), 4.93 (t, $J$ = 7.5 Hz, 1 H), 6.39 (s, 1 H), 6.90 (d, $J$ = 7.7 Hz, 1 H), 7.27 (m, 2 H). Anal. ($C_{18}H_{19}BrO_3$) C, H, mol wt. **12**: IR ($CHCl_3$) 1755, 1725, 1655 $cm^{-1}$; NMR (270 MHz, $CDCl_3$) δ 0.87 (t, $J$ = 6 Hz, 3 H), 1.16–1.79 (m, 8 H), 2.09 (m, 4 H), 3.02 and 3.00 (two d, $J$ = 11 Hz, 1 H), 3.24 (m, 1 H), 3.70 (m, 1 H), 3.75 and 3.74 (two s, 3 H), 4.28–4.56 (m, 2 H), 5.50 (dd, $J$ = 15, 7.5 Hz, 1 H), 5.63 (dd, $J$ = 15, 6.7 Hz, 1 H), 7.31 (m, 5 H); mol wt calcd for $C_{22}H_{30}O_4$ 358.2144, found 358.2154. (*E*)-**9**: IR ($CDCl_3$); 1760, 1740 $cm^{-1}$; NMR (270 MHz, $CDCl_3$) δ 1.04 (s, 3 H), 1.45–2.47 (m, 9 H), 2.47–2.88 (m, 2 H), 3.27 (m, 1 H), 3.73 (s, 3 H), 5.50 (br s, 1 H); $^{13}C$ NMR (15 MHz, $C_6D_6$) δ 13.7 (q), 22.7, 22.9, 23.1, 25.5, 29.1, 37.4, 51.7, 52.0, 59.3, 123.1, 135.4, 173.3, 213.3; mol wt calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1412. (*Z*)-**9**: IR ($CDCl_3$) 1760, 1740 $cm^{-1}$; NMR (270 MHz, $CDCl_3$) δ 1.38 (s, 3 H), 1.48–2.71 (m, 12 H), 3.61 (s, 3 H), 5.55 (m, 1 H); $^{13}C$ NMR ($C_6D_6$) δ 20.5 (q), 22.7, 23.4, 23.9, 25.7, 28.9, 37.6, 51.2, 56.3, 59.8, 123.5, 135.7, 171.0, 214.0; mol wt found 236.1415. (*E*)- + (*Z*)-**11**: IR ($CCl_4$) 1755, 1735, 1640, 1590, 1470 $cm^{-1}$; NMR (270 MHz, $C_6D_6$) 1.03 (s, 1 H, *E* isomer), 1.40 (s, 2 H, *Z* isomer), 1.5–2.40 (m, 9 H), 3.08 (s, 2 H), 3.34 (s, 1 H), 5.90 (br s, 0.33 H), 6.05 (br s, 067 H), 6.55 (d, $J$ = 7.5 Hz, 0.67 H), 6.57 (d, $J$ = 7.5 Hz, 0.33 H), 7.08 (d, $J$ = 7.5 Hz, 1 H), 7.15 (m, 1 H); $^{13}C$ NMR ($C_6D_6$) δ 14 (q), 20 (q), 24, 27, 27.7, 28, 37, 51, 52, 56, 60, 121, 123, 124, 128, 131, 133, 137, 140, 170, 204, 208, 213; mol wt calcd for $C_{18}H_{19}{}^{79}BrO_3$ 362.0518, found 362.0516. (*E*)- + (*Z*)-**10**: IR ($CDCl_3$) 1765, 1725, 1655, 1590, 1480 $cm^{-1}$; NMR (270 MHz, $CDCl_3$) δ 1.7–1.9 (m, 1 H), 2.3–2.6 (m, 5 H), 2.80 (t, $J$ = 8 Hz, 2 H), 3.26 (d, $J$ = 11.5 Hz, 1 H), 3.39 (td, $J$ = 11.5, 6.2 Hz, 1 H), 3.69 (s, 0.21 H), 3.76 (s, 2.79 H), 6.14 (br s, 0.07 H), 6.28 (br s, 0.93 H), 6.88 (d, $J$ = 7.5 Hz, 1 H), 7.25 (m, 2 H); $^{13}C$ NMR ($C_6D_6$) δ 25, 26, 28, 38, 48, 52, 59, 120, 122, 127.5, 130, 133, 137, 141, 169, 209. Anal. ($C_{17}H_{17}BrO_3$): C, H, Br, mol wt.
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(10) (a) For this run, addition of *O,N*-bis(trimethylsilyl)acetamide avoided concommitant decarbomethoxylation. (b) Most recent work in a related series showed 10 mol % ferric chloride in methylene chloride at 0 °C to be superior to the conditions reported herein.
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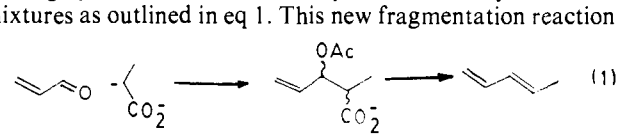
**Barry M. Trost,* Thomas A. Runge, Louis N. Jungheim**
*Samuel M. McElvain Laboratories of Organic Chemistry*
*Department of Chemistry, University of Wisconsin—Madison*
*Madison, Wisconsin 53706*
*Received October 12, 1979*

## A New Diene Synthesis via Organopalladium Chemistry

*Sir:*

Approaches to dienes via carbonyl olefination procedures usually lead to stereoisomeric mixtures. We report here that a new palladium catalyzed decarboxylative elimination of the adducts from enals and carboxylate enolates, a prototype for transition metal catalyzed fragmentation reactions, can lead to a highly stereocontrolled diene synthesis from erythro-threo mixtures as outlined in eq 1. This new fragmentation reaction




has also generated a cyclohexadiene synthesis in conjunction with Diels–Alder reactions. Application of this method to a synthesis of the insect sex pheromones bombykol[1] and codlemone[2] is also reported. We believe that this study represents the first case of activation of a substrate for loss of $CO_2$ by palladium catalysts.

Reported methods[3-5] that effect the elimination of β-hydroxycarboxylic acids to olefins do so with high stereospeci-

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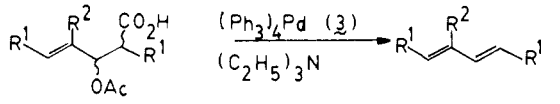
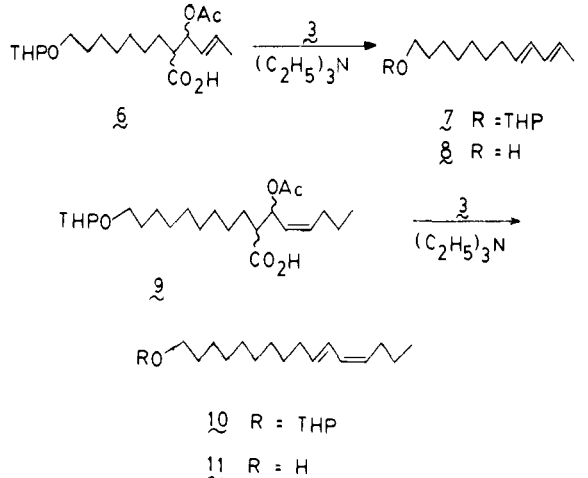
ficity[8]—a fact which necessitates stereodefined syntheses of the β-hydroxy compounds in order to translate into a stereodefined olefin synthesis.[3-8] Unfortunately, the most direct approach of adding the enolate of a carboxylic acid[9] to a carbonyl group produces a diastereomeric mixture, frequently in a 1:1 ratio. Here a stereoselective[8] diene synthesis where both stereoisomeric adducts can lead to the same diene is required. Addition of the dianion from propionic acid to (*E*)-2-phenylcrotonaldehyde and from phenylacetic acid to (*E*)-cinnamaldehyde followed by in situ acetylation with acetyl chloride led to precursors **1** and **2** as 1:1 and 3:1 diastereomeric mixtures in 84 and 92%, respectively. Subjection of **1** or **2** to 3–5 mol % of tetrakis(triphenylphosphine)palladium (**3**) and 1.1 equiv of triethylamine in refluxing THF or, preferably, in toluene at 85 °C produced the *E,E* dienes **4** and **5** in 61–84 and 76–89% yields. In subsequent studies, use of $Me_2SO$ as solvent further facilitates the reaction. For **4**, the *E,E* configuration is confirmed by the 15-Hz coupling constant for the newly introduced double bond, the quantitative formation of the Diels–Alder adduct with *N*-phenylmaleimide at room temperature to form an adduct identical with an authentic sample, and comparison with an authentic sample.[10] The high stereoselectivity of this diene synthesis was further verified by subjecting each diastereomer of **1** separately to the reaction conditions. For **5**, identification was confirmed by comparison with an authentic sample spectroscopically and by mixture melting point (151–153 °C).[11] Previously, diene **4** was only available as an isomeric mixture by the Wittig reaction in studies directed toward streptonigrin by Weinreb.[10]




**1** $R^1 = CH_3$, $R^2 = Ph$ **4**

**2** $R^1 = Ph$, $R^2 = H$ **5**

The stereochemistry of the double bond originally present in the precursor remains unaffected as illustrated in the synthesis of the insect sex pheromones codlemone (**8**)[12] and bombykol (**11**).[13,14] In the former case, reaction of **6** (diastereomeric ratio 1.3:1) with 3 mol % of catalyst at room temperature, 85 °C in $PhCH_3$, or reflux in THF led to **7** in 77–82% yield containing 22% *Z,E* isomer. Hydrolysis ($CH_3OH$, $H_2O$, TsOH, 60 °C) produced **8**. NMR and VPC confirmed the presence of two compounds (78:22, *E,E*/*Z,E*) with the 10,11 double bond being *E* in both.[15] Crystallization from pentane produced pure codlemone (**8**), mp 27.5–28.5 °C (lit.[12] mp 28 °C), whose spectral properties agree with those reported.




**6**

**7** R = THP

**8** R = H

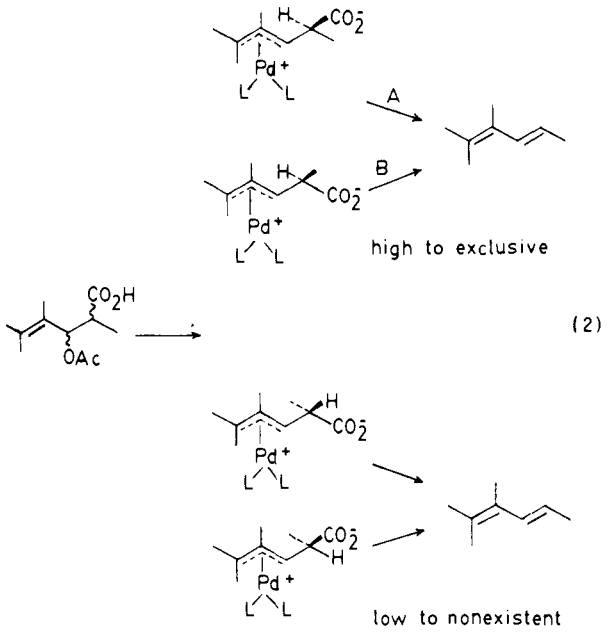
**9**

**10** R = THP

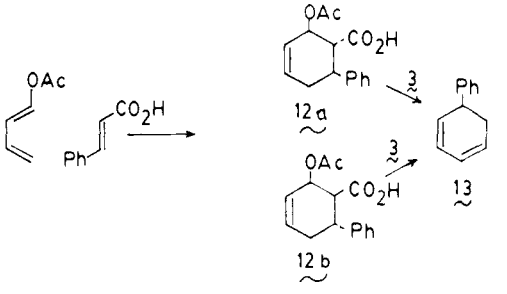
**11** R = H

Precursor **9** when subjected to the same conditions produced **10** contaminated by ~10% *Z,Z* isomer. Hydrolysis, as above, gave pure bombykol (**11**) after TLC separation whose properties agree with those reported.[13] NMR analysis at 270 MHz confirmed the *Z,E* stereochemistry as well: δ 5.29 (dt, $J$ = 10.8, 7.5 Hz), 5.64 (dt, $J$ = 15.0, 7.5 Hz), 5.94 (ddt, $J$ = 10.8, 10.8, 1.5 Hz), 6.30 (ddt, $J$ = 15.0, 10.8, 1.5 Hz).

The fact that the *Z,E* isomer forms in the latter case as well as the fact that the stereochemistry of the diene is independent of reaction time and shows no detectable variation with reaction temperature indicates the stereochemistry observed is kinetically controlled. In each case, a high to exclusive preference for introducing an *E* double bond is observed. A scheme to account for these observations is presented in eq 2. Such a scheme does not preclude interconversion among the isomers by any mechanism, but suggests that the relative rates of disengagement of $CO_2$ controls the stereochemistry of the diene.[16] To confirm that both anti (path a) and syn (path b) fragmentation pathways are possible, both isomers of **12** were subjected to **3** to give **13**[17,19d] in 75–85% yield. Such an interpretation assumes formation of the π-allyl complex and its subsequent fragmentation is faster than stereochemical isomerization of starting material.[16b]

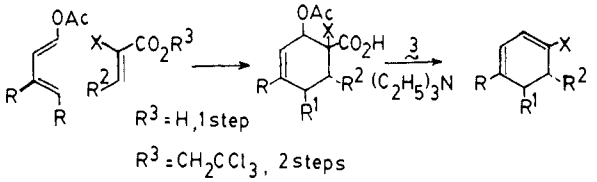



(2)

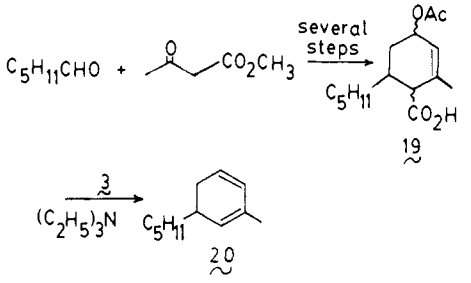



This last result also illustrates the use of this approach as a cyclohexadiene synthesis via Diels–Alder reactions. This approach was generalized as shown by the syntheses of dienes **14–18**.[17,18] Special note should be taken of the synthesis of **17** in which a dienolacetate is produced (thus heteroatom substitution on the diene is tolerated) and of **18** in which a 1,3 substitution pattern emerges from a cycloaddition sequence. An alternative cyclohexadiene synthesis with a similar substitution pattern is illustrated by the conversion of **19** into **20**[23] (71% yield). The precursor **19** stemmed from hexanal and methyl acetoacetate by condensation–decarboxylation,[20] reduction,[21] and acetylation.[21] Under these conditions aromatization has not been observed. Control of reaction time may

be necessary. For example, in the production of **15**, a reaction time of ~4 h sufficed; increasing the time to 18 h led to clean isomerization to methyl cyclohexa-1,4-diene-1-carboxylate[17,19e] which was isolated in 64% yield. Such an observation may be general.




| diene | R | $R^1$ | $R^2$ | X | % |
|---|---|---|---|---|---|
| **14** | H | H | H | H | 87 |
| **15**[19a] | H | H | $CO_2CH_3$ | H | 71 |
| **16**[19b] | H | $C_2H_5$ | H | H | 69 |
| **17**[19c] | H | H | H | OAc | 81 |
| **18**[17,23] | $CH_3$ | H | Ph | H | 77 |
| **19**[19b] | H | H | $C_2H_5$ | H | 69 |




Thus, this stereocontrolled diene synthesis represents a prototype fragmentation reaction catalyzed by palladium. It is interesting to note that loss of $CO_2$ to form diene is faster than loss of a proton to form a dienecarboxylic acid. Thus, this reaction complements the previous diene synthesis.[22] We attribute the high to exclusive stereocontrol observed to the complexation of the allyl cation by palladium in the intermediate which increases its lifetime and thus allows ejection of $CO_2$ in both a syn and anti fashion. Steric interactions presumably are responsible for formation of the *E* olefin. Thus, reactions in which the stereochemistry of the substrates determines the stereochemistry of the products is not always desirable. The present study illustrates one such case. The possibility that other fragmentation reactions may be initiated by palladium, or other transition metals, with benefits of the type reported here are under active investigation.

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(15) Subjection of the *E,E* and *Z,E* mixture to *N*-phenylmaleimide at room temperature allowed separation of the minor *Z,E* isomer pure: 270-MHz NMR $\delta$ 5.30 (dt, $J$ = 11.0, 7.5 Hz), 5.69 (dq, $J$ = 15.2, 7.1 Hz), 5.92 (dd, $J$ = 11.0, 11.0 Hz), 6.32 (dd, $J$ = 15.2, 11.0 Hz).
(16) (a) The possibility that the starting allyl acetates rapidly isomerized and fragmentation occurred stereospecifically from a single isomer cannot be rigorously excluded at this time but seems unlikely from our work in allylic alkylations. (b) See Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1979**, *100*, 3435; *J. Org. Chem.* **1976**, *41*, 3215. Also see ref 22a.
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(19) (a) Prepared by selective methanolysis of the Diels–Alder adduct of maleic anhydride and 1-acetoxy-1,3-butadiene. See ref 19f for literature on the diene. (b) Compounds **16** and **19** turn out to be identical although the substitutions on the precursors are quite differenc: Spangler, C. W.; Johndahl, T. P.; Spangler, B. *J. Org. Chem.* **1973**, *38*, 2478. (c) Structure supported by spectral data only. Diels–Adler reaction performed with trichloroethyl ester followed by reductive elimination with zinc. (d) Marvell, E. N.; Caple, G.; Delphey, C.; Platt, J.; Polston, N.; Tashiro, J. *Tetrahedron* **1973**, *29*, 3797. Reich, H. J.; Reich, I. L.; Wollowitz, S. *J. Am. Chem. Soc.* **1978**, *100*, 5981. (e) Mp 63–64 °C: Braun, A. M. *J. Org. Chem.* **1970**, *35*, 1208. (f) Bailey, W. J.; Barclay, R., Jr.; Baylouny, R. A. *Ibid.* **1962**, *27*, 1851.
(20) McCurry, P. M., Jr.; Singh, R. K. *Synth. Commun.* **1976**, 75.
(21) Reduction was performed on 3-methyl-4-carbomethoxy-5-*n*-pentylcyclohex-2-en-1-one with 9-BBN followed by hydrolysis with aqueous sodium hydroxide and acetylation with acetyl chloride.
(22) (a) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. (b) Tsiyi, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Ibid.* **1979**, 2075.
(23) $Me_2SO$ as solvent considerably enhances the rate and frequently the yield. The results reported for **18** and **20** were obtained in this solvent.

**Barry M. Trost,* Joseph M. Fortunak**
*McElvain Laboratories of Organic Chemistry*
*Department of Chemistry, University of Wisconsin—Madison*
*Madison, Wisconsin 53706*
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## Electron Affinity of $HO_2$ and $HO_x$ Radicals[1]

*Sir:*

The $HO_2\cdot$ radical is of great importance in flames, in oxidation at both low and high temperatures, in biological systems, and in the chemistry of the atmosphere (stratosphere and troposphere).[2a] The anion of the radical $HO_2^-$ appears very important in solution oxidations[2a] and in the aqueous chemistry of $O_3$. A related species $HO_3^-$ appears to be very important in the chemistry of $O_3$ reactions with saturated species at temperatures below 0 °C.[2b] A recent review[3] lists a value for the electron affinity of $HO_2\cdot$ [EA($HO_2\cdot$)] of 4.6 eV. This value comes from a necessarily crude estimate made over 40 years ago. It appears to be much too high to be plausible.

There is a considerable amount of fairly reliable data available on the aqueous thermochemistry of $H_2O_2$ and $HO_2^-$ [4,5] as well as on the related species $HO_2$ (aqueous) and

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