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Palladium-Catalyzed Cyclopropanation of Unsaturated Endoperoxides. A New Peroxide-Preserving Reaction

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This paper is dedicated to Professor Armin de Meijere on the occasion of his 70th birthday.

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Abstract: Unsaturated bicyclic endoperoxides are efficiently cyclopropanated with excess diazomethane in the presence of catalytic palladium(II) acetate [$Pd(OAc)_2$] in a stereoselective manner. This method represents a new peroxide-preserving transformation. Whereas the unsaturated endoperoxides in the [2.2.1] series are attacked by the carbene from the *exo* face, the analogs with larger bridges are preferentially attacked from the face *syn* to the peroxo bridge. Only in the case of the benzannelated [2.2.2] system does the attack occur exclusively from the face proximal to the benzene ring. Certain strained cyclopropanated endoperoxides are reduced by diazomethane to give *cis*-diols. 2-Methylfuran endoperoxide gives rise to *cis*-1-formyl-2-acetylcyclopropane in excellent yield.

Keywords: cyclopropanation; diazomethane; palladium; singlet oxygen; stereoselectivity

The selective diazene reduction of unsaturated endoperoxides still constitutes the single most important breakthrough in the synthesis and characterization of stable saturated endoperoxides.[1] Many peroxides previously postulated as intermediates in the singlet oxygenation of cyclic dienes have thus been rendered stable enough for further exploration of chemical, physical and spectroscopic properties.[2] The notorious instability of unsaturated endoperoxides is doubtless a consequence of the weak peroxide bond (~36 kcal mol^{-1}) that is compounded by the additional strain brought on by the double bond in the bicyclic framework. In particular, endoperoxides in the 2,3-dioxabicyclo[2.2.1]heptane series (7-carbo- and heterocyclic analogs; Figure 1) such as the naturally occurring and physiologically active prostaglandin endoperoxides are, as expected, among the least stable bicyclic endoperoxides. To date, except for the selective diazene reduction method, there does not appear to be any other method whereby the etheno bridge in the 2,3-dioxabicyclic system combines with a reagent or reagents under conditions mild and selective enough to preserve the thermally as well as reagent-labile peroxide linkage.[3] Herein, we report *the second peroxide-preserving reaction* that is applicable to most endoperoxides with a few exceptions.

The requisite unsaturated endoperoxides used in this study were readily obtained by photooxygenation of the respective cyclic 1,3-dienes at low temperatures.[4] In the cases where the unsaturated endoperoxide was unstable at 0 °C or room temperature (**5** and **9**), they were generated *in situ*. In all the other cases the endoperoxides were stable at room temperature and were isolated before cyclopropanation. The cyclopropanations were carried out by slow addition of an ether solution of diazomethane (generated from Diazald®) at 0 °C in diethyl ether in the presence of catalytic amounts of $Pd(OAc)_2$ at −78 °C to a stirred solution of endoperoxide in CH_2Cl_2 either at −78 °C in the case of **5** and **9**, or at 0 °C in all the other cases,

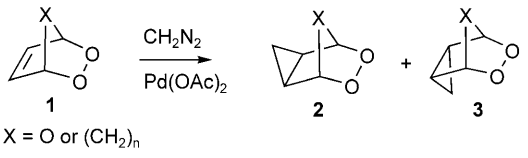


Figure 1. $Pd(OAc)_2$-catalyzed cyclopropanation of unsaturated endoperoxides.

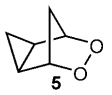
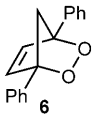
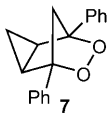
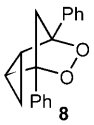
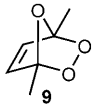
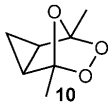
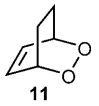
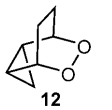
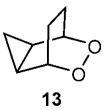
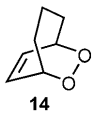
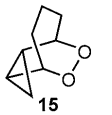
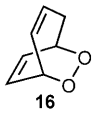
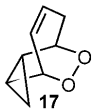
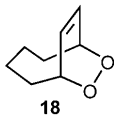
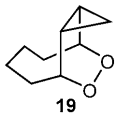
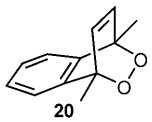
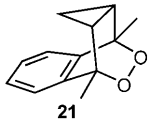
followed by allowing the mixtures to warm up to room temperature.[5] In most cases, the cyclopropanated endoperoxide was obtained in good to excellent yield. The crude product mixtures were practically free of any by-products as well as starting materials. For spectroscopic and analytical purposes, the cyclopropanation products were purified at low temperature (−30 °C) by column chromatography (or preparative TLC) on SiO_2.[6] Although all cyclopropanated products exhibited greater thermal stability than the unsaturated counterparts, their purity was determined by means of their NMR spectra as well as by iodometric titration (>98% in each case) since they are notoriously unstable and potentially explosive when neat and did not survive shipment. The starting materials, products, product ratios and isolated yields are depicted in Table 1.

In cases where stereoisomers were formed, the *endo-exo* ratios were determined by NMR, in particular by inspecting the absorptions of the cyclopropane protons. Compound **13** was independently synthesized from the known norcaradiene-singlet oxygen adduct by diazene reduction.[7] Once the structures of **12** and **13** were established, the assignments of the other *endo* and *exo* isomers were straightforward. Also the spectra of the known carbocyclic analogs were used to confirm the stereochemical assignments.[8]

The stereoisomeric ratios in the cyclopropanation of the unsaturated peroxides suggest that there is stereochemical bias in the carbene additions. In the carbo- and heterobicyclic [2.2.1] systems, the facial selectivity is clearly that favoring the *exo* attack. It is a well known fact that norbornene and its derivatives are attacked by a variety of cycloaddends on the *exo* face of the bicyclic system. This *exo* preference, owing to its uncertain origin, has been called factor X by Huisgen.[9] Houk et al. later offered a consistent rationalization of this effect invoking greater eclipsing of the newly formed bonds during the attack at the *endo* face with the C–C and C–H bonds on the bridgehead carbon, whereas the *exo* attack can occur with nearly ideal staggering with respect to the aforementioned bonds.[10] In the case of 1,4-diphenyl system **6**, however, the *ortho* hydrogens in the phenyl rings are interfering with the approach of the carbene at the *exo* face to the extent that the overwhelming *exo* preference is somewhat diminished to allow for the *endo* attack in 10% relative yield. In the case of the 2,5-dimethylfuran endoperoxide **9**, only the *exo* product was formed as well. The substitution at both bridgehead positions of the endoperoxide, as is the case with other analogs such as **6**, **7** and **8**, imparts the molecule increased stability; thus compound **10** was stable enough at room temperature as well as on silica gel at low temperature to allow purification and characterization. On the other hand, the monomethyl-substituted analog **22** was not stable and decomposed upon warming the reaction mixture to room temperature to give *cis*-1-formyl-2-acetylcyclopropane **24**[11] in 65% overall yield from 2-methylfuran. This reaction constitutes an excellent method for the synthesis of *cis*-1,2-diacylcyclopropanes from a furan precursor in a one-pot procedure in two steps.

The formation of the diacylcyclopropane suggests that diazomethane might have served as a reducing agent for the endoperoxide, since furan endoperoxides (ozonides) are converted to 1,4-dicarbonyl compounds upon reduction with an oxygen atom acceptor such as PPh_3 or $(CH_3)_2S$ (DMS).[12] The mechanism depicted in Figure 2 is consistent with our results. The

Table 1. Cyclopropanation of unsaturated endoperoxides.

Entry	Diene-$^1O_2$-Adduct[a]	Product(s)[b] (ratios)	Yield [%][c]
1	 **4**	 **5**	58
2	 **6**	 **7** 90  **8** 10	82
3	 **9**	 **10**	73
4	 **11**	 **12** 60  **13** 40	78
5	 **14**	 **15**	69
6	 **16**	 **17**	57
7	 **18**	 **19**	85
8	 **20**	 **21**	92

[a] Prepared from the respective cyclic 1,3-dienes by photooxygenation.
[b] NMR spectra of all products are available in the Supporting Information.
[c] Isolated yields after low-temperature column chromatography.

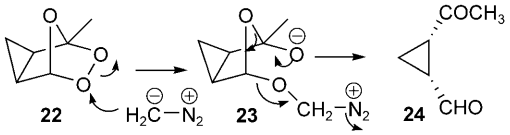


Figure 2. Deoxygenation of cycloprotonated ozonide **22** with diazomethane.

postulate that diazomethane acted as a reducing agent in the case of **22** was strenghtened by the fact that the cyclopropanation of the $^1O_2$-adducts of 6,6-diphenylfulvene[13] and spiro[3.4]hepta-4,6-diene,[14] **25** and **28** did not yield the expected endoperoxides; instead, the *cis*-diols **27** and **30** were isolated in high yields in each case by reduction with diazomethane (Figure 3).

The mechanism that satisfactorily rationalizes the formation of **27** and **30** from **26** and **29**, respectively, is analogous to the one depicted in Figure 2. After diazomethane attack at the peroxide oxygen and subsequent protonation and loss of nitrogen, the resulting hemiacetal expels formaldehyde to give the diols **27** and **30**. The mechanism for this transformation is shown in Figure 4.

It is noteworthy that ascaridole (**31**) failed to react with diazomethane in the presence of $Pd(OAc)_2$, even when a very large excess of CH_2N_2 was used, presumably due to the presence of the bridgehead isopropyl group that presents steric hindrance in the approach of the palladium-carbene complex to the etheno bridge. Also the stereoselective cyclopropanation of the 1,4-dimethylnaphthalene-$^1O_2$ adduct deserves some comment: in this case, the cyclopropanation occurs exclusively *anti* to the peroxo bridge, by contrast to the non-benzannelated counterpart. Obviously, the interaction of the Pd catalyst with the benzene ring is a factor that favors the approach of the palladium carbene complex from the face proximal to the benzene ring. In order to test this hypothesis we reacted the carbocyclic analog **32** with $Pd(OAc)_2$-CH_2N_2 and found that the benzobicyclo[2.2.2]system in **32** (Figure 5) was cyclopropanated exclusively from the

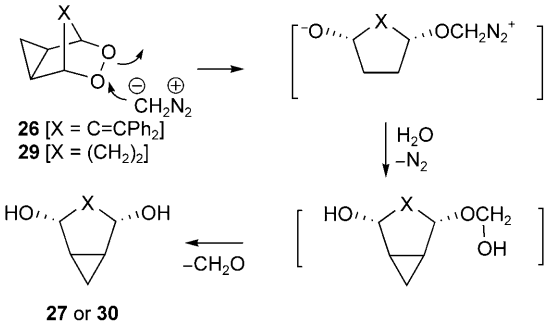


Figure 4. Mechanism of diazomethane reduction of **26** and **29** to diols **27** and **30**.

face proximal to the benzene ring (*endo*) to give **33** as the sole product.[15] These results corroborate the findings of Anciaux, Hubert et al. that Pd-catalyzed cyclopropanations are exceedingly sensitive to the steric effects of the substrate.[16]

The product ratios presented in Table 1 also suggest that the approach of Pd-carbene complex from the face proximal to the peroxo bridge in the case of dioxabicyclo[n.2.2]systems ($n=2$, 3, 4) is favored. This preference is more pronounced when the n-bridge is larger than 2. Whereas **11** gives rise to only a slight excess of **12** over **13**, compounds **14**, **16** and **18** give almost exclusively (by NMR) the *syn* products **15**, **17**, **19**, respectively. This stereochemical preference may be due to greater steric hindrance presented by the larger bridges in **14**, **16** and **18**. Transition state calculations of $Pd(OAc)_2$-catalyzed cyclopropanations with diazomethane are hampered by the fact that the mechanistic details of these reactions have not been elucidated; experimental evidence and theoretical studies suggest that the cyclopropanations with metallocarbenes are exothermic.[17–20] A recent DFT study by Straub[21] on the Pd-catalyzed cyclopropanation of alkenes renders Pd(II) a precatalyst; the actual catalytic resting state is $Pd(\eta^2\text{-}C_2H_4)_n$ ($n=2$ or 3) which undergoes reversible ligand exchange reactions. Also in accord with Anciaux et al.'s study,[16] the Pd-coordinated carbene reacts with the olefin that is coordinat-

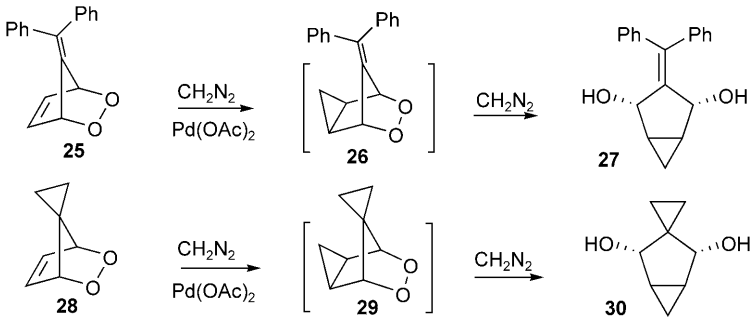


Figure 3. Reduction of endoperoxides **26** and **29** by diazomethane.

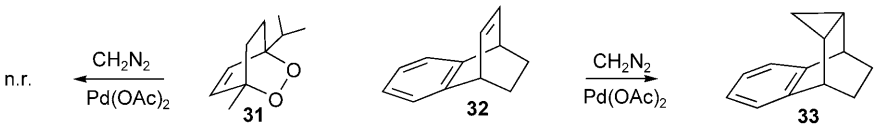
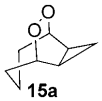
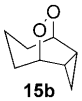
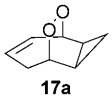
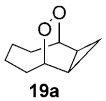
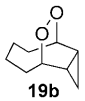


Figure 5. Reactivities of ascaridole (**31**) and benzobicyclo[2.2.2]octadiene (**32**) toward diazomethane-$Pd(OAc)_2$.

ed to the same metal *via* a palladacyclobutane before it undergoes reductive elimination to the cyclopropane. Whatever the exact mechanism, it is obvious that the facial selectivity of carbene transfer to the double bond in a bicyclic system is controlled to a great extent by steric factors. Despite the exothermicity of these reactions, and the likelihood of early transition states, a comparison of the enthalpy differences of the stereoisomeric products should reflect to a significant extent the stereochemical issues encountered in the transition states of these cyclopropanations. Based on these considerations we carried out *ab initio* calculations on the products in the [n.2.2] series. Electronic energy optimizations were carried out at the MP2/6-31G* level with ZPVE corrections calculated at HF/6-31G*, and scaled by 0.9153 as recommended by Scott and Radom.[22] Thermal corrections were not made. Stationary points were found for all compounds. The results, given as ΔH_{isom}, are listed in Table 2, and are in good qualitative agreement with the observed experimental stereoisomer ratios.

The *syn* isomer **12** is more stable than **13** by only 1.3 kcal mol^{-1}, reflecting the slightly greater steric hindrance presented by the peroxo bridge than the ethano bridge. This fact manifests itself in the slightly higher proportion of **12** *vs.* **13** (60:40). Of the two conformers of **14**, **14a** is more stable than **14b** by 2.1 kcal mol^{-1}, thus the *syn* approach of the metallocarbene is favored. After the formation of the cyclopropanated products (in both cases, the most stable conformer was considered), the *syn* endoperoxide **15a** is substantially more stable (by 5.9 kcal mol^{-1}) than the *anti* isomer **15b**. Finally, in the 2,3-dioxa-[4.2.2] series, the *syn* isomer **19a** is considerably more stable than the *anti* isomer **19b**. In both cases the methylene groups in the propano and butano bridges, respectively, appear to present considerably more steric hindrance than the peroxo bridge. Also **17a** turned out to be more stable than **17b** by 2.3 kcal mol^{-1} and was isolated as the sole product. This result is also in line with a report by de Meijere et al. that the cyclopropanation of bicyclo[3.2.2]nona-2,6,8-triene, the carbocyclic analog of **16**, by the Furukawa method (Et_2Zn/CH_2I_2) likewise gave exclusively the *exo*-product stemming from carbene addition from the face distal to the propeno bridge.[23]

Table 2. Calculated enthalpies of cyclopropanation of dioxabicyclo[n.2.2]alkenes.

Entry	Stereoisomers		ΔH_{isom} [kcal mol^{-1}][a]
1	 **12**	 **13**	1.3 (**12**→**13**)
2	 **14a**	 **14b**	2.1 (**14a**→**14b**)
3	 **15a**	 **15b**	5.9 (**15a**→**15b**)
4	 **17a**	 **17b**	2.3 (**17a**→**17b**)
5	 **19a**	 **19b**	13.7 (**19a**→**19b**)

[a] Optimized at the MP2/6-31G* level with frequencies computed at the HF/6-31G* level using the Spartan06 software package. ZPVEs were scaled by 0.9153 as recommended by Scott and Radom.[22]

The stereochemical assignments of the cyclopropanation products deserve some comment. The *endo* and *exo* 5,6-dioxabicyclo[3.2.1]nonanes **12** and **13** are representative of the other *endo* and *exo* isomers. In all cases where the cyclopropane ring is *syn* to the peroxo bridge, the secondary proton *syn* to the peroxo bridge absorbs downfield (1.2 ppm) whereas it absorbs upfield (0.5 ppm) when it is *syn* to the ethano bridge, in analogy to the carbocyclic system.[8] Moreover, the tertiary cyclopropane protons *syn* to the ethano bridge in **12** absorb at 1.17 ppm, the same protons *syn* to the peroxo bridge absorb at 1.65 ppm in **13** (Figure 6). The *endo* stereochemistry in the case of **21** was readily established by the fact that the secondary cyclopropane proton *syn* to the benzene ring absorbs upfield, at −0.9 ppm due to the diamagnetic anisotropy of the aromatic ring. In the carbocyclic analog **33**, the same proton absorbs at −1.0 ppm.

Finally, it is noteworthy that $Rh_2(OAc)_4$ did not prove to be an effective catalyst for the cyclopropanation of unsaturated bicyclic endoperoxides with diazomethane: neither **4** nor **11** underwent cyclopropanation under the same conditions using $Rh_2(OAc)_4$ as catalyst; in fact, no traces of **5**, or **12**/**13**, respectively, were detected in the NMR spectra of the reaction mixtures. In the case of **4**, only *cis*-4,5-epoxy-2-pentenal and *cis*-1,2,3,4-diepoxycyclopentane were ob-

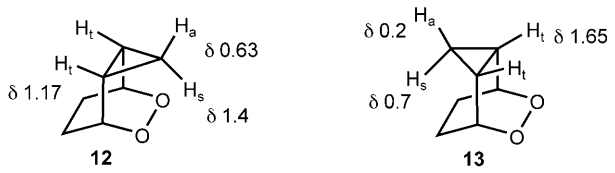


Figure 6. Chemical shifts of the cyclopropane protons in **12** and **13**.

tained, as described by Ohloff et al.[24] whereas only unchanged starting material was recovered from **11**. These results are in line with the findings of Dzhemilev et al., who investigated the efficiency of a variety of transition metal catalysts in cyclopropanations of alkenes with diazomethane, and found that, for instance, norbornene did not react with CH_2N_2/$Rh_2(OAc)_4$, whereas Pd-based catalysts [$Pd(OAc)_2$ or $Pd(acac)_2$] were quite effective.[25] Moreover, two attempts to cyclopropanate endoperoxide **11** with ethyl diazocarboxylate (EDA) in the presence of catalytic amounts of $Rh_2(OAc)_4$ failed, leading to an intractable mixture in which no peroxidic material was found.

In summary, we have uncovered a new peroxide-preserving reaction that allows the stereoselective synthesis of cyclopropanated endoperoxides that have not previously been accessible by other methods. Moreover, the highly strained endoperoxides such as **25** and **28** are efficiently reduced under the conditions to give *cis*-diols. In addition, the one-pot conversion of 2-methylfuran to *cis*-1-formyl-2-acetylcyclopropane represents an excellent method for the synthesis of compounds of this type.

Experimental Section

Typical Procedure For Singlet Oxygenations-Cyclopropanations

A solution of cyclic diene (5 mmol) in 15 mL of CH_2Cl_2 was photooxygenated at 0 °C (cyclopentadiene, spiro[3.4]hepta-4,6-diene, 1,4-diphenylcyclopentadiene, 2-methylfuran, and 2,5-dimethylfuran were photooxygenated at −78 °C) in the presence of 3 mg of tetraphenylporphyrin (TPP) under a positive pressure of dry oxygen while irradiating the stirred solutions with a 400 W high-pressure sodium lamp. The progress of the reaction was monitored by TLC. After completion of the singlet oxygen addition, $Pd(OAc)_2$ (5 mol% of diene) was added, followed by dropwise addition of an ether solution of a 20-fold excess of diazomethane (prepared earlier from Diazald®)[14] at the temperature at which the photolyses (0 °C in the case of **11**, **14**, **16**, **18**, **20** **31**, **32**, or −78 °C in the case of **4**, **6**, **9**, **25**, **28**) were conducted. After complete addition, the mixture was stirred for 30 min before the cold-bath was removed and the mixture allowed to warm up to room temperature. After stirring the mixture for another 2 h, the solution was filtered through Celite, the solvent removed at reduced pressure and the residue purified by low-temperature column chromatography at −30 °C on SiO_2 (petroleum ether/CH_2Cl_2, 1:1). In the case of **27** and **30**, CH_2Cl_2/MeOH (10:1) was used for chromatography. The products were identified by means of spectral data (see Supporting Information).

Supporting Information

Spectral data for all cyclopropanation products are available as Supporting Information.

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