A Novel Synthesis of 4-Dioxy-2-enones from 1,3-Dienes using Pyridinium Dichromate–*tert*-Butyl Hydroperoxide

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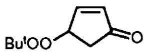
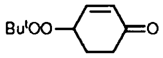
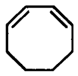
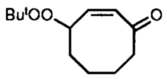
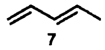
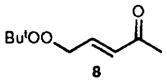
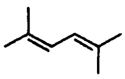
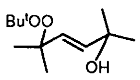
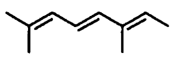
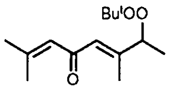
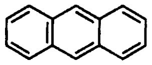
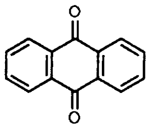
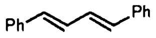
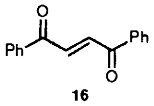
Treatment of 1,3-dienes with the pyridinium dichromate (PDC)–Bu^{t}OOH reagent system leads directly to the formation of 4-*tert*-butyldioxy-2-enones in good yield under mild reaction conditions.

The addition reaction of alkyl hydroperoxide and cyclopentadiene in the presence of Fe^{II} and Cu^{II} salts yields among other products, 4-alkoxycyclopent-2-ene.[1] Oxidative cleavage of endoperoxides of 1,3-dienes using acidic or basic reagents,[2a] Fe^{II}, Ti^{III}, Co^{II}, Rh^{I} and Pd^{0} salts or complexes[2b] gives rise to the corresponding 4-hydroxyenones as one of the products; however, the reactions generally lead to low yields and difficult separations.

The PDC–Bu^{t}OOH system has been shown to be very effective in a variety of oxidative transformations.[3] Interest-

Table 1 Reaction of 1,3-dienes with PDC–Bu^{t}OOH

Entry	Substrate	Product^a	Yield (%)^b
1	 **1**	 **2**	76
2	 **3**	 **4**	55
3	 **5**	 **6**	52
4	 **7**	 **8**	24^c
5	 **9**	 **10**	60
6	 **11**	 **12**	42^c
7	 **13**	 **14**	86
8	 **15**	 **16**	73

^{a} All the products gave satisfactory spectral and analytical data. ^{b} Yields refer to isolated products taking into account the recovery of starting matrials (6–20%). ^{c} Formation of some unidentified polymeric material lowers the yield in these cases.

ingly, when 1,3-dienes were treated with a PDC and Bu^{t}OOH mixture supported on silica gel (substrate : PDC : Bu^{t}OOH = 1 : 2 : 3) for 8–13 h,[†] the only products that could be isolated in a reasonable yield were the 4-*tert*-butyldioxy-2-enones.[‡] The results are shown in Table 1.

Both cyclic and acyclic dienes reacted with PDC–Bu^{t}OOH and this transformation is the first report of its type in the literature. Although substrates **13** and **15** initially gave the corresponding dioxyenones, only the diones could be isolated successfully. Surprisingly the diene moiety of the triene **11** did react enabling the isolation of compound **12**. In spite of the possibility of multiple reaction pathways open to the dienes **7** and **11** only **8** and **12** respectively, were obtained. Diene **9** with two tertiary centres at the diene termini gave **10** as expected.

A set of experiments was carried out with cyclopentadiene illustrating the use of Cr^{VI} reagent in this reaction. Replacing PDC with chromium trioxide and 4 equiv. of Bu^{t}OOH instead of 3 equiv., gave **2** in 74% yield. A catalytic amount of PDC (10 mol%) or chromium trioxide (10 mol%) and 6 equiv. of Bu^{t}OOH (at −5 °C, 24 h) in the reaction provided **2** in 65 and 70% yields respectively. Compounds **2**, **4**, **6** and **8** could be further converted to the corresponding 4-hydroxy-2-enones in quantitative yield following a closely related literature procedure for hydrogenolysis.[4]

The direct conversion of 1,3-dienes to the 4-dioxy-2-enones and their subsequent transformation to 4-hydroxy-2-enones could be useful in organic synthesis. *E.g.*, 4-hydroxycyclopent-2-enone which could be easily accessable from readily available and inexpensive cyclopentadiene, is a key intermediate in the synthesis of prostaglandins.[5] The mechanism of this reaction is being studied in our laboratory.

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[†] *General procedure*: Silica gel (1.505 g) and PDC (4 mmol, 1.505 g) were suspended in dichloromethane and cooled to 0 °C. This suspension was treated with Bu^{t}OOH (6 mmol, 0.8 ml, 70% solution in water) to give a crimson coloured mixture. After 10 min, a 1,3-diene (2 mmol) was added and the reaction was monitored by TLC. The reaction mixture was filtered using a sintered-glass funnel, through a pad of silica gel. The solvent was removed and the product was purified by column chromatography (silica gel, eluent 2% ethyl acetate in hexane).

[‡] 6–20% of the starting material was recovered. A small amount (5–10%) of a highly polar product formed in all these reactions has not been characterized.