Selective Oxidations with Activated Carbon: Applications to Substrates containing Acidic Allylic Methine and Methylene Groups

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Butenoates substituted at the γ-position with an acidifying group, *e.g.*, COR, CO_2R, SO_2R, and $PO(OR)_2$, undergo a regioselective oxidation (in which a methine group is converted into a carbinol function and a methylene group into a keto moiety) in the presence of activated carbon.

Recently, we described[1] a remarkable oxidative rearrangement induced by 5% palladium–charcoal. Thus in ethyl acetate at ambient temperature, the reagent (4 mass equiv.) effected the conversion of the cephem dioxides (**1a**) and (**1b**) into the hydroxy-derivatives (**2a**) and (**2b**) (*ca.* 60% yield in each case) within a few hours. We now report that the palladium is unnecessary for the success of such reactions! Under appropriate conditions, activated carbon will effect not only the (**1b**) → (**2b**) transformation but also the oxidation of substrates incorporating acidic allylic methine and methylene groups.

When activated carbon (Darco G-60) (4 mass equiv.) was stirred vigorously with a solution of the cephem dioxide (**1b**) (1 mmol) in ethyl acetate for 24 h and the product purified by silica-gel chromatography, the hydroxy-derivative (**2b**) was isolated in 78% yield as an analytically pure foam. Crystallisation of the material from dichloromethane–diethyl ether provided compound (**2b**) as its diethyl ether solvate, m.p. 90—91 °C (lit.,[1] 70—81 °C). The amount of activated charcoal required to effect the afore-cited transformation could be reduced (to 2 mass equiv.) when triethylamine (2 mol. equiv.) was present. The reaction then took *ca.* 6 h [the yield of the purified hydroxy-derivative (**2b**) was unaffected].

That the sulphonyl group was not an essential structural feature for the oxidation was shown by the response of Hagemann's ester (**3a**). The last-cited compound (1 mmol) reacted with activated charcoal (4 mass equiv.) in ethyl acetate over 3 days to give the hydroxy-derivative (**3b**) (50% yield after SiO_2 chromatography). The structure of compound (**3b**), which was isolated as a chromatographically homogeneous syrup, followed from its high-resolution mass spectrum (which featured a peak at *m/z* 198.0901 corresponding to $C_{10}H_{14}O_4$), its i.r. spectrum (which showed an OH absorption at 3 450 cm^{-1}), and its ^1H n.m.r. spectrum [which incorporated signals at δ 3.90 (disappearing on addition of D_2O) for the OH group and at δ 6.00 for the olefinic hydrogen atom ($CDCl_3$)].

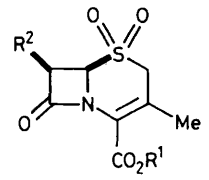
The regiochemical outcome of the foregoing reaction reveals that the oxidation need not be accompanied by a migration of the double bond.

Dimethyl glutaconate (**4**)[2] (8 mmol) also reacted with activated carbon (10 mass equiv.) in ethyl acetate. After 4 days, the ketone (**5**) (53% yield after recrystallisation), m.p. 61—62 °C, was isolated as a bright-yellow solid. In addition to being characterised analytically, compound (**5**) displayed a u.v. absorption (EtOH) at 225 nm (ε 4 600) for the ene-dione chromophore. Its ^1H n.m.r. spectrum ($CDCl_3$) possessed two one-proton doublets (*J* 16 Hz) at δ 6.93 and 7.62 for the olefinic hydrogen atoms.

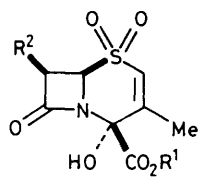
The phosphonate (**6**) (1 mmol) reacted with activated carbon (10 mass equiv.) in ethyl acetate containing triethylamine (1 mmol) over a 24 h period to give the ketone (**7**) (45% yield after SiO_2 chromatography). The structure of the ketone (**7**), which was isolated as a yellow oil, was established by spectroscopic methods. In particular, the mass spectrum (chemical ionisation) featured a prominant peak at *m/z* 265.0841, attributed to a protonated molecular ion. The ^1H n.m.r. spectrum (220 MHz, $CDCl_3$) showed a triplet (*J* 18 and 18 Hz) at δ 7.08 and a double doublet (*J* 20 and 18 Hz) at δ 7.55 for the PCH : CH moiety.

Overall, a 4-electron transfer is involved in the conversion of the substrates (**4**) and (**6**) into the products (**5**) and (**7**). Presumably, the alcohols (**8**) and (**9**) are intermediates in these reactions. The regioselectivity observed in the (**6**) → (**7**) transformation is noteworthy.

The afore-cited results are of interest in a number of respects. To our knowledge, they demonstrate the first application of activated charcoal as an oxidant in organic

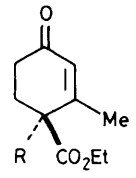


(**1**)



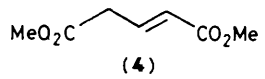
(**2**)

a; R^1 = $PhCH_2$, R^2 = H
b; R^1 = Ph_2CH, R^2 = $PhOCH_2CONH$

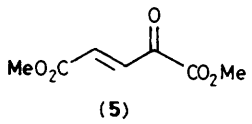


(**3**)

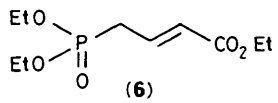
a; R = H
b; R = HO



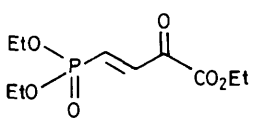
(**4**)



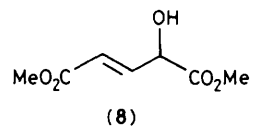
(**5**)



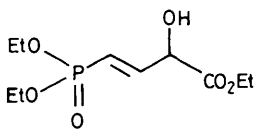
(**6**)



(**7**)



(**8**)



(**9**)

synthesis.† Clearly, the reagent can serve as a selective and mild oxidising agent, providing access to sensitive compounds which might be difficult to prepare by conventional methods. The ketonic products (**5**) and (**7**) are potentially of value as dienophiles in Diels–Alder reactions. Finally, some interesting mechanistic issues are posed by the present findings.

† Oxygen and activated charcoal have been employed to convert L-ascorbic acid into its dehydro-derivative (see: M. Ohmori, H. Higashioka, and M. Takagi, *Agric. Biol. Chem.*, 1983, **47**, 607 and references therein).

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