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CHROMIUM^{VI} COMPLEX CATALYZED BENZYLIC OXIDATIONS IN THE PRESENCE OF TERT.BUTYL HYDROPEROXIDE

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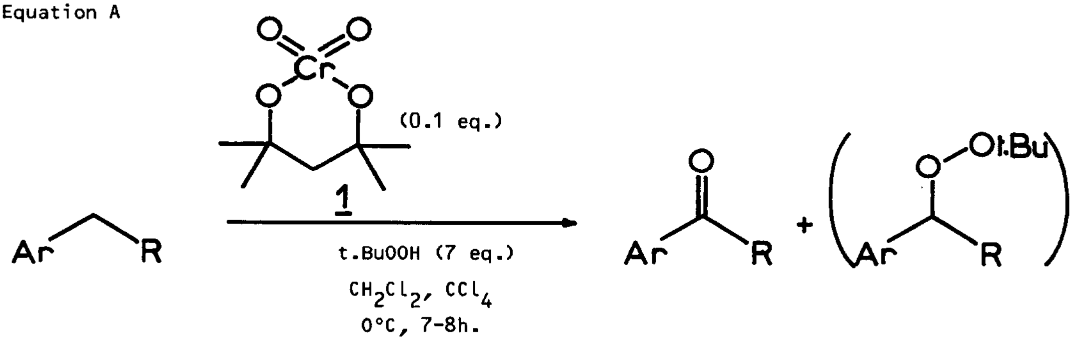
Summary : In using t.BuOOH and a small quantity of 2,4-dimethylpentane-2,4-diol cyclic chromate, benzylic methylene groups are oxidised into carbonyl functions ; t.butylperoxy compounds are postulated as intermediates.

Benzylic and allylic oxidations by Cr^{VI} complexes require generally a large excess of the chromium reagents (1). Since these reagents are relatively expensive and environmentally hazardous, it would be advantageous to develop oxidizing methods which require only catalytic amounts of Cr^{VI} (2,3). Following our research on metal catalyzed oxidations (1c,4), we became interested in the use of readily available Cr^{VI} complex 1 recently described by Corey's group and which bears a ditertiary 1,3-diol ligand allowing the oxidation of alcohols in a homogeneous neutral medium (3).

In this paper, we report that the oxidation of the benzylic carbon-hydrogen bond is easily performed by excess of t.BuOOH and a small amount of the cyclic chromate ester 1 (equation A).

Equation A



The experiments (cf. table) were carried out at 0°C under an argon atmosphere in dry methylene chloride using 5-6M anhydrous solutions of t.BuOOH in CH_2Cl_2 (5) and 0.2M solutions of 1 in CCl_4 (3). With 7 eq. of t.BuOOH and 0.1 eq. of 1, tetralin 2 led in 7.5 h to α-tetralone 3 with

54% yield (run 1) (6). This result has to be compared with other preparative methods using Cr^{VI} reagents : 3 was obtained from 2 using 5 eq. of CrO_3 in AcOH-acetone (yield : 55%) (7), or 15 eq. of the Ratcliffe-Collins reagent (yield : 26%) (8), or 8 eq. of the Jones reagent (yield : 68%) (9), or 16 eq. of 2.2'-bipyridinium chlorochromate (yield : 63%) (9). Catalytic oxidation of 2 into 3 by heating for one day in the presence of t. BuOOH and 0.3 eq. of the highly toxic $Cr^{o}(CO)_6$ complex (yield : 88%) was also reported (10).

Table 1 : Oxidations by 1 (0.1 eq.)/t.BuOOH (7 eq.) at 0°C in 7-8 h.

Run	Starting compounds	Product ketones (a)	Conversion %	Selectivity (b) %
1	tetralin : 2	α-tetralone : 3	84	65 (c)
2	diphenylmethane	benzophenone	46	87 (d)
3	bibenzyl	deoxybenzoin	28	29
4	fluorene	fluorenone	53	57 (e)
5	indan	1-indanone	86	70
6	6-methoxy-1,2,3,4-tetrahydronaphtalene	6-methoxy-1-tetralone + 7-methoxy-1-tetralone	85	37 20
7	9-t.butylperoxyfluorene 4	fluorenone	81	82

(a) Ketones were identified by comparison of physical data with those for authentic materials

(b) The selectivity corresponds to the isolated yield calculated on recovered starting material

(c) Similar results were obtained when the oxidation was carried out in the presence of 3-Å molecular sieves

(d) 1-t.butylperoxy-1,1-diphenyl-methane was also obtained (selectivity = 8%)

(e) 9-t.butylperoxyfluorene 4 was also obtained (selectivity = 39%).

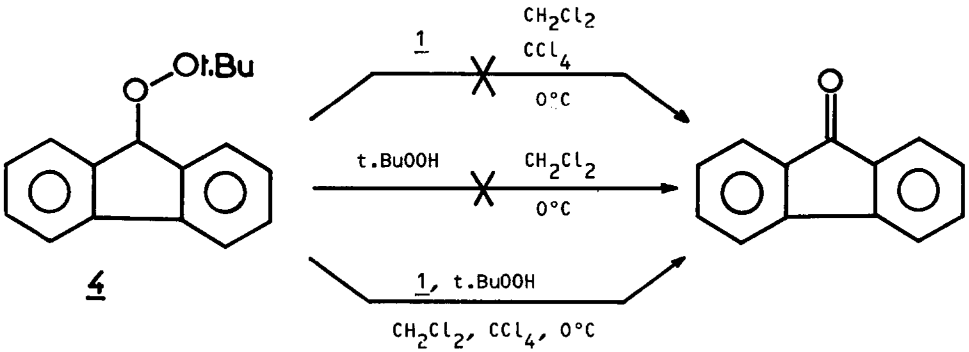
The other oxidations carried out with 1/t.BuOOH (runs 2-6) show the general catalytic character of this new benzylic oxidation procedure. The low yield of deoxybenzoin (run 3) obtained from 1,2-diphenyl-ethane was expected since oxidation of 1,2-diaryl alkanes by Cr^{VI} reagents leads generally to the breaking of the carbon-carbon σ-bonds (1a, 1b, 11). Obtention of a mixture of

6- and 7-methoxy-1-tetralone from 6-methoxy-1,2,3,4-tetrahydronaphthalene (run 6) contrasts with the stereoselectivity observed in other chromic oxidations (10, 12, 13).

Beside aromatic ketones, some t.butylperoxy compounds were obtained particulary from fluorene (run 4) where 9-t.butylperoxyfluorene 4 was isolated with 21% yield (14) ; neither this peroxy derivative nor the corresponding ketone were observed if 1 was omitted from the reaction mixture.

The mechanism of this oxidation remains unclear. Regeneration by t.BuOOH of the cyclic chromate ester 1 from a reduced intermediate seems to be inefficient (3, 15) ; chromium peroxo species formed *in situ* are susceptible to participate in the oxidation process (16). Interestingly, we have established, from experiments performed at 0°C from 9-t.butylperoxyfluorene 4 (equation B) that the t. butylperoxy compounds isolated in a few cases are potential intermediates in the pathway leading to the ketones : in fact, 4 was unchanged in a solution of 1 (0.1 eq.) or t.BuOOH (7 eq.) but furnished fluorenone in the presence of both 1 and t.BuOOH (run 7). Thus, it appears that an *in situ* formation of a new complex is required to obtain evolution of 4 into fluorenone.

Equation B



Further work with other chromium reagents is in progress to extend the practicality of this method.

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13. In the work described in ref. (10), (12a)-(12c), only 6-methoxy-1-tetralone was isolated while in that of ref. (12d), a small amount (1%) of 7-methoxy-1-tetralone was also observed.
14. 4 was identified by I.R., N.M.R. (singlet at 5.92 ppm) mass spectrum and reduction by Li AlH_4 into 9-hydroxyfluorene.
15. Contrary to oxidations of alcohols into ketones by 1/peracid which reach satisfactory turnover numbers (3), oxidation of cholestanol and 4,4-dimethyl-cholestanol by 1/t.BuOOH was observed with a turnover number smaller than 2.
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