NOTES

Oxidaton of Tetralin with tert-Butyl Chromate

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Previous works on the oxidation of cyclohexene[1a,b] and of terpenoids[2a-e] with *tert*-butyl chromate have revealed that an active methylene group adjacent to a double bond was preferentially oxidized to an α, β-unsaturated ketonic group. Also, some aromatic compounds[3] have been oxidized with the same oxidant; e. g., dihydrosafrole was mainly oxidized to piperonylic acid. The present work deals with the oxidation of tetralin with this oxidant.

Experimental

Tetralin, distilled repeatedly, was used as the sample; b. p. 90°C/18 mmHg, n_D^{25} 1.5388, d_4^{25} 0.9669. Gas chromatography using a column of P. E. G. −6000 on celite at 150°C and helium (60 cc./min.) as a carrier gas showed that the sample tetralin was contaminated by 2.9% of naphthalene.

Experiment I.—A *tert*-butyl chromate solution was prepared from 197 g. of chromic anhydride, 394.5 g. of *tert*-butyl alcohol, 1100 g. of benzene, 50 g. of glacial acetic acid and 100 g. of acetic anhydride in the same manner as in the previous report[2c] except that the oxidant solution was concentrated to 66% in volume before use. This oxidant solution was added drop by drop, to a solution of 50 g. of tetralin in 75 g. of benzene, and the oxidation was carried out under the conditions shown in Table I. Then, the whole reaction mixture was treated as usual (cf. Ref. 1b or 2c). In this manner, 44.5 g. of a neutral product and 1.8 g. of an acidic one were obtained. The latter (1.8 g.) was chromatographed on silica gel using ethyl alcohol-chloroform mixture, The first fraction gave 0.5 g. of *o*-carboxyhydrocinnamic acid (m. p. 166~167°C[4]; Found: C, 61.62; H, 5.54%) and the other fraction gave *o*-phthalic acid (m. p. and mixed m. p., 191~191.5°C).

A gas chromatogram of the neutral product showed three peaks, which corresponded to those of tetralin (retention time at 160°C: 5 min.), naphthalene (10 min.) and α-tetralone (32 min.) respectively. The chromatogram indicated the presence of 3.1% of naphthalene in the neutral product, corresponding to 2.8% for the tetralin used.

A portion (10 g.) of the neutral product was chromatographed on silica gel using mixture of ethyl acetate and *n*-hexane. The first fraction gave 5.5 g. of tetralin unchanged (b. p., n_D^{25}, d_4^{25}; the IR spectrum accorded with that of tetralin), while the second one gave 3.5 g. of α-tetralone (b. p. 124~125°C/10 mmHg, n_D^{25} 1.5655, d_4^{25} 1.0914, λ_{max}^{EtOH} 247 mμ[5]: ε 11790), which in turn gave 2, 4-dinitrophenylhydrazone (m. p. 255°C (decomp.)) (Found: N, 17.01%), semicarbazone (m. p. 219~221°C) (Found: N, 20.80%), and oxime (m. p. 102~103°C) (Found: N, 8.46%). As for the determination of the α-tetralone in the neutral product, Fujita's procedure[6] was used. The reliability of this procedure was confirmed by using a known mixture containing pure α-tetralone in tetralin.

Experiment II.—A *tert*-butyl chromate solution was prepared in the same manner as above, except that the benzene solution was concentrated to 55% in volume. To this oxidant, 50 g. of tetralin in 50 g. of benzene was added drop by drop. After the oxidation had been carried out under the conditions shown in Table I, the reaction mixture was treated as in Experiment I.

Results

The results are summarized in Table I. It was found that a methylene group adjacent to a benzene nucleus of tetralin was preferentially oxidized to a ketonic group, with *tert*-butyl chromate giving α-tetralone. However, no formation of 1,4-naphthoquinone was observed, unlike the *tert*-butyl chromate oxidation of cyclohexene, which afforded *p*-benzoquinone, and also unlike the chromic acid oxidation of α-tetralone[7], in acetic acid which gave 1, 4-naphthoquinone. A slight degradative oxidation

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TABLE I. CONDITIONS AND RESULTS IN THE OXIDATION OF TETRALIN

Reaction condition				Reaction product (wt % to the sample)			
Experiment	Sample/ Chromic acid	Temp. °C	Time day	α-Tetralone	o-Carboxyhydrocinnamic acid	o-Phthalic acid	Tetralin unchanged
I	1 : 5.2	18~25	16	35	1	0.6	48
II	1 : 5.2	18 then, 46~48	1 15	45	2	12	17

of α-tetralone occurred to give *o*-carboxyhydrocinnamic acid and *o*-phthalic acid. Undoubtedly, *o*-carboxyhydrocinnamic acid is the degradative product of α-tetralone through 1, 2-diketone, i. e., 3, 4-dihydro-1, 2-naphthoquinone, while *o*-phthalic acid is produced by the further oxidation of *o*-carboxyhydrocinnamic acid.

Summary

The oxidation of tetralin with *tert*-butyl chromate gave a relatively good yield of α-tetralone as the major product. Thus, it was seen that this oxidant oxidizes a methylene group of an alicyclic ring, adjacent to a benzene nucleus, to a ketonic group, forming α-ketone.

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