EXPERIMENTAL

A small quantity of Scott's acid (prepared as described in the modified procedure of Dimroth,[2b] orange needles, m.p. 233–234° dec.) was dissolved in hot aqueous ethanol containing a few drops of concentrated hydrochloric acid and small pieces of pure magnesium were added. The solution gradually became paler (temp. *ca.* 40°) and hydrogen sulfide gas was detected. The almost colorless solution was then concentrated, neutralized with sodium bicarbonate solution, filtered, and the filtrate acidified with hydrochloric acid. After standing at 0° for 2 days the almost colorless crystalline solid which deposited was collected, dried, and sublimed.[1] The sublimate, colorless crystals, was shown to be the anhydride of naphthalene-2,3-dicarboxylic acid by m.p. (243°; literature 245–246°) and mixed m.p. and the other properties described in the literature.

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DOKKI, CAIRO

trans-1-Keto-8-methyl-4,5-(3′-methyl-4′-hydroxybenzo)hydrindane

D. K. BANERJEE AND S. K. BALASUBRAMANIAN

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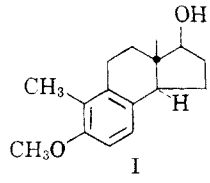
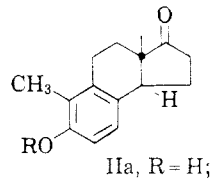
The preparation of the *trans* tricyclic ketone IIa by the oxidation of the *trans* alcohol I with sodium dichromate in acetic acid followed by demethylation with hydrobromic acid in acetic acid was previously reported by us.[1] Recently we had occasion to prepare more of the methoxy-ketone (IIb) by Oppenauer oxidation of the alcohol (I). The product, after purification through its semicarbazone, melted at a higher temperature than that previously reported.[1] Purification of the dichromate–acetic acid oxidation product through its semicarbazone, or by chromatography, or by repeated crystallization also yielded the higher melting product together with some of the unchanged alcohol (I). Demethylation of the purified methoxy ketone (IIb) with hydriodic acid in acetic acid furnished the phenolic ketone (IIa) in better yield; the melting point of the latter was higher than that previously reported,[1] but was identical with that reported by Martin and Robinson[2] for the *trans*-isomer. The present work, therefore, confirms the configurations assigned by the British workers to isomers of the phenolic ketone (IIa). Recently Sannie and Panouse[3] have also reported the preparation of two isomers of the same phenolic ketone by a different method. The isomer, m.p. 193°, kindly furnished by them, did not depress the melting point of the *cis*-isomer[1] obtained by us. The *trans*-configuration assigned to this isomer by these workers does not therefore appear to be correct.

(1) D. K. Banerjee, S. Chatterjee, C. N. Pillai, and M. V. Bhatt, *J. Am. Chem. Soc.*, **78**, 3769 (1956).
(2) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 491 (1943).
(3) C. Sannie and J. J. Panouse, *Bull. soc. chim. France*, 1435 (1956).



I



IIa, R = H;
b, R = CH_3

EXPERIMENTAL[4]

Oppenauer oxidation of I. The Oppenauer oxidation[5] of 0.5 g. of I was carried out as usual with 2 g. of aluminum isopropoxide and 5 g. of cyclohexanone in 30 ml. of benzene. The cyclohexanone was removed by distillation under reduced pressure and the crude residue was distilled at 130°/1 mm. to give the methoxy ketone (IIb) as colorless prisms, which after being washed with small amounts of petroleum ether melted at 110–113°.

The *semicarbazone* was obtained as a very sparingly soluble white powder, m.p. 277–278° (dec.).

Anal. Calcd. for $C_{17}H_{23}N_3O_2$: N, 13.95. Found: N, 14.34.

The ketone (IIb) on regeneration from the semicarbazone by refluxing for 4 hr. with 10% alcoholic sulfuric acid melted at 115–116°. Ultraviolet spectrum $\lambda_{max}^{alcohol}$ 277 mμ, log ε 3.3.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.61; H, 8.41.

Reduction of 6 mg. of the aforementioned methoxy ketone (IIb) with 2 mg. of sodium borohydride in methanol yielded the methoxy alcohol (I), m.p. 129–130° (undepressed by admixture with an authentic specimen[1]).

Purification of the sodium dichromate–acetic acid oxidation product of I. The crude oxidation product, m.p. 90–98°, prepared as reported earlier,[1] was crystallized from methanol. The first fraction consisted of huge colorless prisms, m.p. 112–115°, which after repeated recrystallization melted at 115–116°. The mother liquors deposited fine clusters of needles, m.p. 116–120°, which after several crystallizations yielded the unchanged methoxy alcohol (I).

In another experiment 270 mg. of the crude oxidation product was dissolved in petroleum ether (40–60°) containing a trace of benzene and chromatographed on a column of 6 g. of acid-washed alumina. Elution with the same solvent gave 170 mg. of the methoxy ketone (IIb) as a lightly colored solid, m.p. 100–105°, which after one crystallization from methanol yielded 72 mg. of a product, m.p. 110–112°, and this was rechromatographed. Elution with petroleum ether (40–60°) gave the pure methoxy ketone, m.p. 115–116°. Elution with benzene gave 68 mg. of the methoxy alcohol (I), m.p. 126–128°.

Ketone IIa. Demethylation of the methoxy ketone (IIb) was carried out by heating for 4 hr. with hydriodic acid in acetic acid. The phenolic ketone (IIa) was obtained in approximately 50% yield from the alkali soluble portion. On recrystallization from benzene the pure phenolic ketone melted at 229–231° (evacuated capillary tube, reported[2] 230–231°). A sample was sublimed at 200° for analysis.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.05; H, 8.25.

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DEPARTMENT OF ORGANIC CHEMISTRY
INDIAN INSTITUTE OF SCIENCE
BANGALORE 3, INDIA

(4) All melting points are uncorrected.
(5) C. Djerassi, *Org. Reactions*, **6**, 235 (1951).