

EXPERIMENTAL^{10,11}

3-p-Nitrophenylcoumarin. (a)² To a warm solution of 32.4 g. of *p*-nitrophenylacetonitrile in 300 cc. of ethanol was added 21 cc. of salicylaldehyde, then 10 drops of piperidine. The mixture was refluxed 0.5 hr., cooled, and filtered. The yellow precipitate was then refluxed 45 min. (incomplete solution) in 400 cc. of acetic acid. The cooled mixture was poured onto ice, filtered, and the precipitate crystallized from 1 l. of dimethylformamide, to give 43.5 g. (81%) of fine needles, m.p. 260–262°, insoluble in alkali.

Anal. Calcd. for C₁₅H₉NO₄: C, 67.5; H, 3.4; N, 5.2. Found: C, 67.4; H, 3.4; N, 5.2.

An attempt to esterify this material by refluxing 5 g. of it in 50 cc. of acetic anhydride containing 8 drops of H₂SO₄ for 1 hr. gave only starting material on cooling.

(b)⁵ A mixture of 18 g. of *p*-nitrophenylacetic acid, 11 cc. of salicylaldehyde, and 5 cc. of piperidine was refluxed 1 hour, cooled, diluted with ethanol, and filtered. The yellow needles melted at 262°. On admixture with the product prepared by method (a), the melting point was unchanged.

4-Nitro-2'-methoxystilbene. A mixture of 15 cc. of *o*-methoxybenzaldehyde, 18 g. of *p*-nitrophenylacetic acid, and 10 cc. of piperidine was gently boiled 0.5 hr., and 50 cc. of ethanol added during cooling. The yellow crystals that separated (13.5 g., m.p. 110–111°) were recrystallized from 400 cc. of ethanol, to give 11 g. of yellow crystals, m.p. 115–117°. Pfeiffer⁹ reported m.p. of 122°.

4'-Nitro-2-stilbenol. A mixture of 6 g. of 4-nitro-2'-methoxystilbene and 40 g. of pyridine hydrochloride (Eastman, practical grade) was refluxed for 0.5 hr. and poured onto ice. The precipitate that separated was washed well with water and crystallized from ethanol, to give 4.5 g. (79%) of deep yellow crystals, m.p. 186–188°.

Anal. Calcd. for C₁₄H₁₁NO₃: C, 69.8; H, 4.6; N, 5.8. Found: C, 69.4; H, 4.7; N, 5.9.

4-Nitro-2'-acetoxystilbene. Four grams of 4'-nitro-2-stilbenol was refluxed in 25 cc. of acetyl chloride containing 5 drops of H₂SO₄ for 1 hr. The mixture was decomposed with ice and the product crystallized from ethanol to give 4 g. (85%) of yellow needles, m.p. 130–131°.

Anal. Calcd. for C₁₆H₁₃NO₄: C, 68.0; H, 4.6; N, 4.9. Found: C, 68.0; H, 4.7; N, 4.9.

RESEARCH DIVISION
POLAROID CORP.
CAMBRIDGE 39, MASS.

(10) All melting points are uncorrected.

(11) Microanalyses by Dr. Carol Fitz, Needham, Mass.

On the Constitution of the Condensation Product of *o*-Phthalaldehyde with Diethyl 2,2'-Thiodiacetate

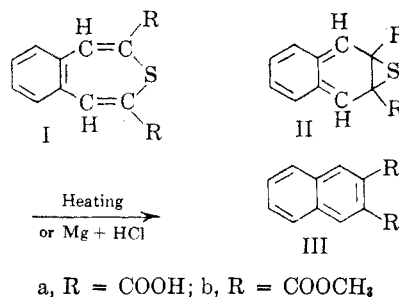
ALEXANDER SCHÖNBERG AND M. B. E. FAYEZ

Received June 3, 1957

Scott¹ obtained by condensation of diethyl 2,2'-thiodiacetate with *o*-phthalaldehyde in absolute methanol containing sodium methoxide, an orange acid (referred to in this note as Scott's acid) which he designated 3-benzothiepin-2,4-dicarboxylic acid, Ia. This substance and its derivatives have lately

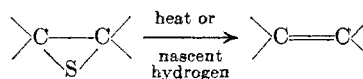
(1) G. P. Scott, *J. Am. Chem. Soc.*, **75**, 6332 (1953).

been reexamined by Dimroth^{2,3} who accepts structure I for Scott's acid and claims that the seven-membered ring systems "approaches" an aromatic system.³ This view necessitates completely or almost completely planar configuration for the seven-membered ring.



The extremely facile thermal elimination of sulfur in elementary form effected *inter alia* by boiling of Scott's acid in aqueous ethanol^{1,2b} (described as Ia → IIIa) would imply a highly strained molecule, which, however, is contradicted by Scott's statement that the seven-membered ring is only "somewhat" strained.

In this connection a significant observation was made by us, namely that Scott's acid reacts readily with nascent hydrogen in acid medium to give hydrogen sulfide and the acid IIIa. For such reasons and other considerations it seems desirable to suggest the adoption of formulation II in place of I whereby such reactions—especially the extremely facile thermal elimination of sulfur—characteristic for many tetrasubstituted ethylene sulfides⁴ could better be explained; we wish however not to exclude valency tautomerism. (I ⇌ II).



The formulation of Scott's acid as 2,3-dihydro-naphthalene-2,3-sulfido-2,3-dicarboxylic acid IIa is also in good agreement with its orange color (compare the *o*-quinonoid system). The dimethyl ester gives an addition product^{2b} with mercury (II) chloride (1:1), which recalls⁵ the formation of such addition products by ethylene sulfides; the addition of chlorine and bromine to Scott's ethyl ester leading to the formation of sulfonium salts is reminiscent⁶ of the formation of such salts from ethylene sulfides.

(2) (a) K. Dimroth and G. Lenke, *Angew. Chem.*, **68**, 519 (1956); (b) *Ber.*, **89**, 2608 (1956).

(3) K. Dimroth and H. Freyschlag, *Angew. Chem.*, **69**, 95 (1957).

(4) A. Schönberg in Houben-Weyl, *Methoden der Organischen Chemie*, 4th edition, Georg Thieme Verlag, Stuttgart, 1955, Vol. 9, pp. 166, 167.

(5) M. A. Youtz and P. P. Perkins, *J. Am. Chem. Soc.*, **51**, 3508 (1929).

(6) J. M. Stewart and H. P. Cordts, *J. Am. Chem. Soc.*, **74**, 5881 (1952).

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.

NATIONAL RESEARCH CENTRE OF EGYPT
DOKKI, CAIRO

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

D. K. BANERJEE AND S. K. BALASUBRAMANIAN

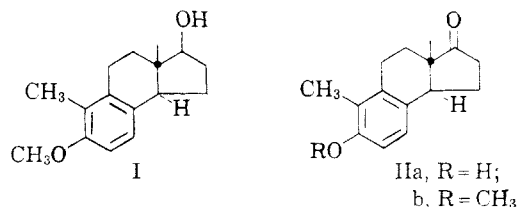
Received June 4, 1957

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 Robinson² 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 Panouse³ 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*-isomer¹ 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).

EXPERIMENTAL⁴

Oppenauer oxidation of I. The Oppenauer oxidation⁵ 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 C₁₇H₂₃N₃O₂: 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 $\lambda_{\text{max}}^{\text{alcohol}}$ 277 m μ , log ϵ 3.3.

Anal. Calcd. for C₁₆H₂₀O₂: 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 specimen¹).

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, reported² 230–231°). A sample was sublimed at 200° for analysis.

Anal. Calcd. for C₁₅H₁₈O₂: C, 78.26; H, 7.83. Found: C, 78.05; H, 8.25.

Acknowledgment. We wish to record our thanks to the late Professor C. Sannie for furnishing a sample of the phenolic ketone, m.p. 193°, to the Indian Institute of Science for the award of a scholarship to one of us (S.K.B.) and to Messrs. B. R. Seetharamiah and D. P. Bose for the microanalyses.

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).