A similar reaction at room temperature gave 1 g. (11%) of *trans-β*-bromostyrene, 2.5 g. (15%) of β-bromostyrene dibromide, 0.5 g. (7%) of parent acid, and 2.4 g. of undistillable residue. The β-bromostyrene contained some chlorine.

Silver cis-cinnamate (6 g., 0.03 mole) was similarly treated with bromine in boiling carbon tetrachloride to produce 0.4 g. (10%) of *trans-β-bromostyrene*, b.p. 55–57° (0.6 mm.), m.p. 4–5°, 2.2 g. (25%) of *β-bromostyrene dibromide*, 2.1 g. of tarry, resinous residue, and 0.4 g. (12%) of parent acid, identified by melting point (63–64°) and mixture melting point.

Silver cis-stilbene-α-carboxylate (17 g., 0.05 mole) in 250 ml. of dry boiling carbon tetrachloride was treated with bromine and worked up as before. From the carbonate wash water, 1.7 g. of starting acid, m.p. 169–171°, was obtained. Evaporation of the carbon tetrachloride left 7.2 g. of viscous oil, free of bromine by qualitative analysis. Addition of this oil to methanol gave a white solid of indeterminate melting point with infrared spectrum similar to the original oil, both showing strong carbonyl peaks at 5.75 and 5.88 μ.

Anal. Calcd. for $(C_{16}H_{12}O_5)_5$: C, 67.61; H, 4.22; Mol. wt., 1420. Found: C, 67.68; H, 4.58; Mol. wt. 1405 (Rast.).

The polymeric oil dissolved in boiling aqueous potassium hydroxide. No neutral fraction could be isolated. Acidification precipitated 0.8 g. of the parent acid, m.p. 169–171°.

Similar reactions carried out in cold carbon tetrachloride and in benzene at room temperature and at the boiling point gave the same material in about the same yield.

Silver trans-stilbene-α-carboxylate (8.3 g., 0.025 mole) was treated in the same way producing 7 g. of viscous oil and 0.6 g. of original acid, m.p. 134–136°. The oil gave a white precipitate in methanol or ethanol with the same properties as from the *cis*-acid. Sodium fusion indicated no halogen and the infrared spectra of the two materials were identical.

Silver p-methoxyphenylacetate (9 g., 0.033 mole) was treated with bromine in boiling carbon tetrachloride and worked up as above. From the carbonate wash, 1.2 g. (23%) of original acid was recovered. Distillation of the carbon tetrachloride residue gave no material corresponding to the benzyl bromide or alcohol and left 2.5 g. of neutral, tarry, bromine containing resin.

The *m*-methoxy isomer was similarly brominated. After filtering off the silver bromide, crystals appeared in the carbon tetrachloride so it was evaporated, leaving a crystalline solid entirely soluble in sodium bicarbonate. Acidification gave 10 g. (82%) of *2-bromo-5-methoxyphenylacetic acid*, m.p. 112–115°. Recrystallization from acetone and from water sharpened the melting point to 114–115° (lit. 115°) neutral equivalent, 241, 244 (calcd. 245).

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4′-Nitro-2-stilbenol

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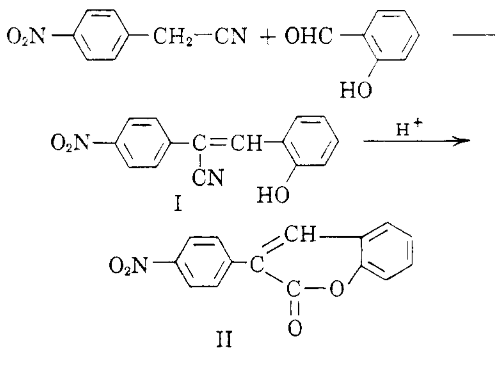
Received May 31, 1957

The only previously reported synthesis of 4′-nitro-2-stilbenol[1] is that of Merckx.[2] He attempted to prepare it by condensing *p*-nitrophenylacetonitrile and salicylaldehyde, followed by acid hydrolysis of the resulting *o*-hydroxy-2-phenylcinnamonitrile (I). These reactions have been repeated in our laboratories and the product of acid hydrolysis of I shown to be 3-*p*-nitrophenyl coumarin (II), rather than the desired 4′-nitro-2-stilbenol.

Our product, a yellow crystalline material melting at 260° (Merckx reported 257°), was insoluble in alkali and was recovered unchanged after treatment with acetic anhydride, a lack of reactivity inconsistent with that expected if the compound were the stilbenol and contained an ortho phenolic group. Analysis indicated the empirical formula $C_{15}H_9NO_4$, as contrasted with $C_{14}H_{11}NO_3$, the formula of the desired stilbenol.



The ready tendency of *o*-hydroxy-α-phenylcinnamonitriles and of *o*-hydroxy-α-phenylcinnamic acids to form coumarins is well known.[3–6] An authentic sample of II was prepared from *p*-nitrophenylacetic acid and salicylaldehyde,[5] and gave no melting point depression on admixture with our product. Merckx's "4′-nitro-2-stilbenol," therefore, is 3-*p*-nitrophenylcoumarin. The observation by Merckx that "saponification" of the nitrile occurs only in those cyanostilbenes prepared from salicylaldehydes (*i.e.*, having an ortho hydroxyl available to form a six-membered ring) is thus explained as coumarin formation. Similarly, the anomalously-melting 2′,4′-dinitro-2-stilbenol[7,8] reported by Merckx must be assumed to be 3-(2′,4′-dinitrophenyl)-coumarin.

We have prepared 4′-nitro-2-stilbenol by demethylation of the known 4-nitro-2′-methoxystilbene.[9] The stilbenol thus prepared is an alkali-soluble, dark yellow microcrystalline solid. Acetylation with acetyl chloride gave the acetyl ester.[5]

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(1) Cullinane (ref. 5), in his preparation of II, obtained an oily by-product which he acetylated to obtain 4-nitro-2′-acetoxystilbene.

(2) R. Merckx, *Bull. soc. chim. Belges*, **58**, 460 (1949).

(3) W. Borsche and F. Streitberger, *Ber.*, **37**, 3163 (1904).

(4) T. Kiewiet and H. Stephens, *J. Chem. Soc.*, 639 (1931).

(5) N. M. Cullinane, *J. Chem. Soc.*, **123**, 2053 (1923).

(6) N. P. Buu-Hoï and D. Lavit, *J. Org. Chem.*, **21**, 21 (1956).

(7) P. Ruggli and O. Schmid, *Helv. Chim. Acta*, **18**, 253 (1935).

(8) J. M. Gulland and R. Robinson, *J. Chem. Soc.*, **127**, 1493 (1925).

(9) P. Pfeiffer, *Ber.*, **48**, 1795 (1915).

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 $C_{15}H_9NO_4$: 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 H_2SO_4 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°. Pfeiffer[9] 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 $C_{14}H_{11}NO_3$: 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 H_2SO_4 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 $C_{16}H_{13}NO_4$: C, 68.0; H, 4.6; N, 4.9. Found: C, 68.0; H, 4.7; N, 4.9.

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[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

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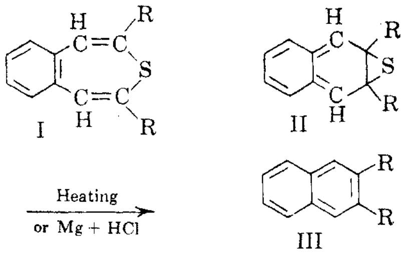
Received June 3, 1957

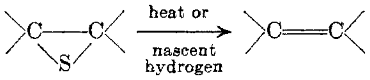
Scott[1] obtained by condensation of diethyl 2,2'-thiodiacetate with *o*-phthalaldehyde in absolute methanol containing sodium methoxide, an orange acid (referred to in this note as Scott's acid) which he designated 3-benzothiepin-2,4-dicarboxylic acid, Ia. This substance and its derivatives have lately 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.



a, R = COOH; b, R = $COOCH_3$

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 sulfides[4] could better be explained; we wish however not to exclude valency tautomerism. (I ⇄ II).



The formulation of Scott's acid as 2,3-dihydronaphthalene-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 recalls[5] 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 reminiscent[6] of the formation of such salts from ethylene sulfides.

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

[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).