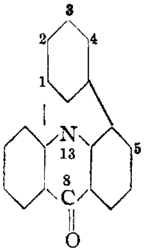
butyllithium in 250 cc. of ether was stirred and refluxed for forty-eight hours, and then carbonated by pouring on crushed, solid carbon dioxide. After working up the reaction products by conventional procedures there was isolated 1.5 g. (6.3%) of 9-(*o*-carboxyphenyl)-carbazole, melting at 182–184°.

Anal. Calcd. for $C_{19}H_{13}O_2N$: N, 4.88; neut. equiv., 287. Found: N, 4.73; neut. equiv., 288.

A mixed melting point determination with an authentic specimen prepared earlier from carbazole, *o*-iodobenzoic acid, potassium carbonate and copper bronze[5] showed no depression.

Decarboxylation, by heating the acid between 350–360°, gave a 90% yield of 9-phenylcarbazole. 9-(*o*-Carbomethoxyphenyl)-carbazole,[5] prepared from the acid and diazomethane, melted at 139–140° after crystallization from methanol.

8-Indolo[3,2,1-de]acridin-8-one.—A mixture of 7.5 g. (0.026 mole) of 9-(*o*-carboxyphenyl)-carbazole and 8.5 g. of phosphorus pentachloride was allowed to react in 50 cc. of xylene, at room temperature, for forty-five minutes. The solution was then cooled to 0°; 6 cc. of stannic chloride[6] was added; and after fifteen minutes, the brick-red complex was hydrolyzed by iced concd. hydrochloric acid. The ketone[6] obtained in this manner in 70% yield, melted at 180–181° after crystallization from xylene.



Anal. Calcd. for $C_{19}H_{11}ON$: N, 5.2. Found: N, 5.23.

.The oxime of 8-indolo[3,2,1-de]acridin-8-one, prepared from the ketone and hydroxylamine, melted at 175–176° after crystallization from dilute ethanol.

Anal. Calcd. for $C_{19}H_{12}ON_2$: N, 9.85. Found: N, 9.76.

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(5) Eckert, Seidel and Endler, *J. prakt. Chem.*, **104**, 85 (1922).

(6) Fieser and Fieser, THIS JOURNAL, **57**, 782 (1935).

DEPARTMENT OF CHEMISTRY
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On the Reaction of Hydrogenation and Dehydrogenation through Disproportionation of Hydrogen in Abietic Acid

BY TORSTEN HASSELSTROM, E. A. BRENNAN AND SAM HOPKINS, JR.

When Steele's abietic acid is heated at an elevated temperature in the presence of a catalyst belonging to the platinum or nickel series, a mixture is obtained consisting of dehydro-, dihydro- and tetrahydroabietic acids.[1] The same acid mixture is encountered in the acid fraction of ordinary rosin oil[2] and in small quantities in the resin acid fraction of vacuum distilled sulfate pulp talloel.[3]

From these acid mixtures the dehydroabietic acid may be isolated as the trihydrate of sulfodehydroabietic acid and dihydroabietic acid as the lactone of hydroxytetrahydroabietic acid.[4] The sulfodehydroabietic acid, recently designated by Campbell and Morgana[5] as the 6-sulfo acid yields dehydroabietic acid on hydrolysis with sulfuric acid.[6]

This work was undertaken to investigate further the reactions of dehydrogenation through disproportionation of hydrogen in abietic acid. It was observed that when Steele's abietic acid is heated for a short period of time at about 160–170°, together with 1–2% of iodine, this conversion takes place, inasmuch as such treated abietic acid on sulfonation yielded about 40% of trihydrate of 6-sulfodehydroabietic acid and 20% of lactone of hydroxytetrahydroabietic acid. Furthermore, it was made evident that ordinary gum or wood rosin may be subjected to the same treatment and that the resulting rosin on sulfonation yields the pure trihydrate of 6-sulfodehydroabietic acid and the lactone of hydroxyabietic acid in amounts directly proportional to the amount of iodine used.

Experimental

The Preparation of the Dehydro- and Dihydroabietic Acids from Steele's Abietic Acid.—The starting material used for this purpose was prepared according to Steele[7] and Palkin and Harries.[8] The sodium tetrahydroabietate had the following characteristics: m. p. 197–205° (cor.), $(\alpha)_D$ -92.6 (1% ethanol); the regenerated Steele's abietic acid melted at 164–168° (cor.), $(\alpha)_D$ -89 (1% ethanol.—Thirty-five grams of Steele's abietic acid was heated to 160° and while kept at that temperature for about five minutes 0.525 g. of iodine was added in five portions. The heating was then continued for two hours and the temperature kept at 160–170°.[9] After cooling 25 g. of the treated acid was pulverized and added in portions during constant stirring to 125 cc. of concentrated sulfuric acid sp. gr. 1.84. The sulfonation was carried out at a temperature below 20°. After about one and one-half hours the sulfonation mixture was poured into one liter of ice and water and the precipitate then removed by filtration and washed until washings clouded the acid filtrate. The soluble material

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(1) (a) Fleck and Palkin, THIS JOURNAL, **60**, 921 (1938); (b) Littmann, *ibid.*, **60**, 1419 (1938).

(2) Brennan, Cairncross, Hasselstrom and Hull, U. S. Patent 2,272,628 (1937).

(3) Hasselstrom, McPherson and Hopkins, *American Paper Trade Journal*, **68**, 41 (1940).

(4) (a) Hasselstrom, U. S. Patent 2,121,032 (1938). (b) U. S. Patent 2,121,033 (1938). (c) Hasselstrom and McPherson, THIS JOURNAL, **60**, 2340 (1938).

(5) Campbell and Morgana, *ibid.*, **63**, July (1941).

(6) Fieser and Campbell, *ibid.*, **60**, 2631 (1938).

(7) Steele, *ibid.*, **44**, 1333 (1922).

(8) Palkin and Harries, *ibid.*, **56**, 1935 (1934).

(9) With equal results the mixture may be heated for 15–20 minutes at 185–195°.

was extracted with 750 cc. of boiling water and the insoluble material removed by filtration. The aqueous solution was evaporated to dryness whereby 15 g. (40%) of crude trihydrate of sulfodehydroabietic acid was obtained m. p. 221° (cor.) decompn.

For further identification the sulfonate was converted into the dimethyl ester: m. p. 177–177.5° (cor.), which did not lower the melting point in the mixed melting point test with authentic material.[4c]

Anal. Calcd. for $C_{22}H_{32}O_6S$: C, 64.69; H, 7.86. Found: C, 65.05; H, 7.78.[10]

The insoluble material obtained from the water extraction of the sulfonation product was dissolved in ether and the ether extracted with two portions of 100 cc. of a 3% sodium hydroxide solution and then with water. After drying the ether solution with anhydrous sodium sulfate and evaporating the ether, 5 g. of a solidifying residue was obtained which yielded 1.5 g. (20%) of lactone of hydroxytetrahydroabietic acid which, when recrystallized from acetone, melted at 131.5–132° (cor.). This material did not produce any lowering of melting point with a sample of the authentic compound.[11]

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.78; H, 10.48.

The sodium hydroxide solution containing the acidic material from the preparation of the lactone was made acid with hydrochloric acid and yielded 10 g. of a hard resin which was not investigated further.

The Preparation of Dehydro- and Dihydroabietic Acid from Rosin.[12]—Ordinary N-wood rosin was subjected to the same treatment as above, but using varying amounts of iodine as a catalyst. This treated rosin, when subjected to sulfonation, yielded the trihydrate of sulfodehydroabietic acid and lactone of tetrahydroabietic acid isolated in the following amounts:

Catalyst, %	Apparent softening point, °C.	(α)D (1% ethanol solution)	Acid number	Sulfonic acid, %	Lactone, %
(1) 0.0	76.0	− 7.4°	162.3	4.0	4.2
(2) .1	75.5	−19.5°	162.9	3.5	3.4
(3) .2	76.5	−10.0°	163.4	9.5	2.0
(4) .5	74.5	− 8.1°	162.7	11.0	3.0
(5) 1.0	73.0	− 3.5°	160.8	16.0	4.0
(6) 1.5	70.5	+16.5°	158.1	41.0	4.6
(7) 2.0	69.0	+25.8°	155.2	48.0	4.7

The trihydrate of the sulfonate of dehydroabietic acid was recrystallized from water and was obtained pure after two crystallizations from this solvent, melting at 223–224° (cor.) decompn.[13]

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[10] All analyses by Mr. S. Gottlieb, Columbia University, New York City, New York.

[11] Hasselstrom, Brennan and McPherson, THIS JOURNAL, **60**, 1267 (1938).

[12] Subject matter for U. S. Patent Application.

[13] Crude talloel from sulfate pulp black liquor may be subjected to the same treatment whereby the isolated resin acids show the following characteristics: m. p. 173–175° (cor.); [α] +54.1° (1 g. in 100 cc. of ethanol), giving high yields of the trihydrate of sulfonate of dehydroabietic acid on sulfonation. Subject matter for U. S. Patent Application.

Depression of the Melting Point of α-Toxicarol and Related Compounds in Soft-glass Capillary Tubes*

BY HOWARD A. JONES AND JOHN W. WOOD

Values obtained by different investigators for the melting point of α-toxicarol have shown considerable variance. Cahn, Phipers and Boam[1] state that the presence of varying amounts of β-toxicarol in most samples of α-toxicarol largely accounts for this. These workers report 232–233° for the melting point of pure α-toxicarol, but others have not been able to prepare samples with this value.

The writers have now found that the type of glass from which the capillary tubes are made has a marked effect on the melting point of this substance. Lower values were observed in soft-glass tubes. In Table I are shown the melting points of various samples of α-toxicarol and β-toxicarol, rotenone, deguelin, and anthracene (used as a check) in different types of glass and in silica tubes. Preliminary results in cleaned and uncleaned tubes were not significantly different, contrary to the experience of Schoorl[2] and of George[3] with certain alkali-sensitive substances. Nevertheless all tubing was allowed to remain overnight in sulfuric acid dichromate solution, rinsed thoroughly with distilled water, let stand at least three days in distilled water with several changes of water a day, and then dried, drawn to capillary size and used within two or three days. In one case soft glass capillaries were cleaned in this same way after drawing and the melting point of α-toxicarol in these was not significantly different from that in tubes drawn from cleaned soft glass. To obtain a rough indication of the relative alkalinity of the glasses and the silica used the *p*H of a suspension of 5 g. of the powdered (60 mesh) material in 5 cc. water (*p*H 5.9) was determined with a Beckman *p*H meter (glass electrode) fifteen to twenty minutes after the addition of the water. Melting points were determined in a modified Markley melting-point apparatus[4] by means of a carefully standardized thermometer. In addition, some determinations were made by the microscope hot stage method with the sample resting on soft-glass slides.

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[1] Cahn, Phipers and Boam, *J. Chem. Soc.*, 513 (1938).

[2] Schoorl, *Z. physik. Chem.*, **A160**, 158 (1932).

[3] George, *Helv. Chim. Acta*, **15**, 924 (1932).

[4] Schechter and Haller, *Ind. Eng. Chem., Anal. Ed.*, **10**, 392 (1938).