Another rearrangement of 1-indolepropionic acid was made at 245° for 2 hr. in a stainless steel rocker autoclave. Again, a 41% yield of 3-indolepropionic acid was obtained.

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Photodehydrogenation of Resin Acids

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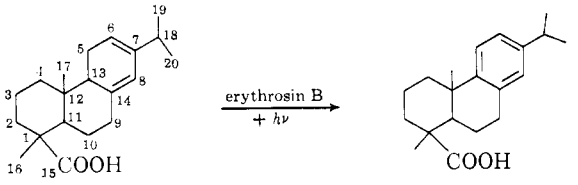
The photosensitized oxidation of the seven major resin acids in pine gum has been studied in these laboratories.[2-4] It was noted that in the *absence* of oxygen, irradiation of levopimaric,[2] palustric,[3] and neoabietic[4] acids, in solution with a sensitizing dye, resulted in bleaching of the dye. It was the purpose of the present work to investigate the nature and effect of the "bleaching reaction" upon the pine gum resin acids. Ergosterol under these conditions has been shown to undergo a dehydrogenation–dimerization[5] while pentaphenylcyclohexa-1,3-diene was converted to pentaphenylbenzene.[6] The photosensitized oxidation of ergosterol and lumisterol is accompanied by dehydrogenation to heteroannular trienes.[7]

Visible light irradiation of deaerated ethanol solutions of levopimaric acid (I) and erythrosin B in varying ratios indicated that about one mole of dye was required for reaction with two moles of resin acid. Under these conditions, the product of the photochemical reaction was found to be dehydroabietic acid (II; 20% isolable yield), indicating that dehydrogenation to an aromatic system had occurred.



I II

Irradiation of palustric acid ($\Delta^{7,13}$) in the presence of a molar amount of erythrosin B also gave dehydroabietic acid (21% isolable yield) as the irradiation product.

When applied to neoabietic acid ($\Delta^{7(18),8(14)}$), the reaction under investigation gave a mixture of four volatile compounds as determined by gas chromatography of the methyl ester of the crude product, plus considerable nonvolatile material, presumably polymer. None of the volatile esters could be crystallized; however, two of the compounds exhibited ultraviolet spectra characteristic of conjugated trienes.[8]

Dehydroabietic (II), pimaric, isopimaric, and abietic ($\Delta^{7,9(14)}$) acids did not react under similar conditions. The first three have been found to be unreactive toward photosensitized oxidation as well.[4] Abietic acid has been observed to react slowly on photosensitized oxidation to give chiefly nonperoxidic products.[4,9]

An attempt was made to replace the greater part of the sensitizer with an easily reducible compound, which in itself was not a sensitizer, in order to establish a hydrogen exchange situation promoted by only a catalytic amount of light-activated sensitizer. This effort was successful with the demonstration that the irradiation of levopimaric acid in the presence of a catalytic amount of erythrosin B and a molar amount of nitromethane gave dehydroabietic acid in 17% isolable yield.

Suitable blanks were run for all the reactions herein reported which established that no reaction occurred in the dark, in the absence of sensitizing dye, in the absence of resin acid, or in the absence of nitromethane (other than a very rapid bleaching of the small amount of dye present in the latter case).

Schenck[10] has proposed that the irradiation of sensitizers results in their elevation to diradicals. He has suggested hydrogen abstraction from the substrate by the diradical to give a monoradical, as the possible course of any competing dehydrogenation reaction which might occur during photosensitized oxidation. Diradicals of the type pictured by Schuller,[3,4] *et al.*, would be especially suited geometrically for hydrogen abstraction from two adjacent carbon atoms upon a single collision, yielding a new double bond.

Experimental[11]

Varying Ratios of Levopimaric Acid to Erythrosin B.—Four 95% ethanol solutions, each 0.02 *M* in levopimaric acid, and containing 1/2, 1/4, 1/6, and 1/8 molar ratios of erythrosin B/resin acid, respectively, were charged to 100-ml. reactors,[2] purged with prepurified nitrogen, stoppered, and irradiated simultaneously, with a 15-w. fluorescent lamp. All the runs but the 1/2 ratio bleached within 22 hr. while this ratio was unbleached after 111 hr. of irradiation.

A run of the 1/2 ratio was made and irradiation continued until no additional change in $[\alpha]_D$ occurred. More erythrosin B was added (1.5/2 molar ratio) and irradiation continued for 21 hr. with no further change in $[\alpha]_D$ observed.

Dehydroabietc Acid (II) from Levopimaric Acid (I).—A solution of 11.9 g. of erythrosin B in 2700 ml. of 95% ethanol was filtered and 8.17 g. of levopimaric acid dissolved in the filtrate (0.005 *M* in dye and 0.01 *M* in resin acid). The solution was charged to the 40-w. reactor,[2] purged with prepurified nitrogen, the reactor sealed (stoppered), and irradiation initiated. Two external air blasts were directed on the reactor to hold the temperature around 30°. After 20 hr. of irradiation, the specific rotation became constant at $[\alpha]^{27}D$ −30°. Irradiation was continued for 10 hr. more to ensure completeness of reaction. The solvent was removed under reduced pressure and the dry residue extracted with ether. The ether was filtered, washed with water, and the ether removed. The residue (8.0 g.) exhibited no absorption maximum in the 272-mμ region. It was converted to a cyclo-

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article is not copyrighted.

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(10) G. O. Schenck, *Naturwissenschaften*, **40**, 205 (1953).

(11) All melting points are uncorrected and all specific rotations and ultraviolet spectra are in 95% ethanol.

hexylamine salt in acetone solution; yield 3.59 g. (33%). The mother liquor was concentrated and gave a black viscous oil. The free acid was liberated from the salt using an aqueous phosphoric acid–ether mixture. The crude acid was placed on a silicic acid (100-mesh) column, 1.25-in. diameter, containing 68 g. of adsorbent, and eluted with 1200 ml. of benzene. The effluent was collected in 75-ml. aliquots and the solvent blown off with nitrogen. The residue from fractions 3–9 were combined and crystallized from 95% ethanol to give 0.98 g. of dehydroabietic acid; $[\alpha]^{25}D$ +62.7° (*c* 1.1); λ_{max}^{alc} 276 mμ (α 2.19), 268 mμ (α 2.12); m.p. 169–171°; infrared spectrum essentially identical to that of an authentic sample. Two further crops of 0.48 g., $[\alpha]^{26}D$ +60° (*c* 1.0), and 0.14 g. were obtained for a total of 1.60 g. or 20% conversion from levopimaric acid. The remainder of the material from the column could not be crystallized.

Dehydroabietic Acid (II) from Palustric Acid.—A solution of 21.6 g. of erythrosin B and 7.42 g. of palustric acid in 2450 ml. of 95% ethanol (0.01 *M* in dye and 0.01 *M* in resin acid) was irradiated for 40 hr. and worked up as described in the preceding example; yield of crude residue, 6.5 g. A small portion was esterified with diazomethane; $[\alpha]^{25}D$ +38° (*c* 0.56), no absorption maximum exhibited in the 266-mμ region. The ester was gas chromatographed and a single, large peak was obtained, at the same emergence time as a sample of authentic methyl dehydroabietate. The remainder of the residue was converted to 5.28 g. (61%) of cyclohexylamine salt. The mother liquor on concentration gave a black-red oil. The acid was regenerated from the salt and the crude product cleaned up on a silicic acid column as before, employing benzene as the eluent. The purified product was crystallized from 95% ethanol to give 1.29 g. of dehydroabietic acid; m.p. 171–173°; $[\alpha]^{26}D$ +62.8° (*c* 1.1); λ_{max}^{alc} 276 mμ (α 2.23) 268 mμ (α 2.18); infrared spectrum essentially identical to that of an authentic sample. A second crop weighing 0.26 g. was obtained of $[\alpha]^{26}D$ +64.2° (*c* 1.0) for a total yield of 21% from the starting palustric acid. The remainder of the material from the column could not be crystallized.

Neoabietic Acid, Erythrosin B, and Light.—A solution of 23.8 g. of erythrosin B and 8.17 g. of neoabietic acid in 2700 ml. of 95% ethanol (0.01 *M* in dye and 0.01 *M* in resin acid) was irradiated for 42.5 hr. and worked up as in the preceding examples. The crude residue gave only a small yield of a gummy cyclohexylamine salt. A portion of the residue, $[\alpha]^{28}D$ −22 (*c* 1.2), was esterified with diazomethane and gas chromatographed at 250° on a GE SE-52 silicone column. Four peaks were obtained: peak 1, no absorption from 220–320 mμ; peak 2, λ_{max}^{alc} 243 mμ; peak 3, (major peak) λ_{max}^{alc} 264,274 (major max.) 284 mμ; peak 4, λ_{max}^{alc} 264,274 (major max.) 285 mμ. (Methyl abietate emerges between peaks 1 and 2.) A considerable proportion of the sample injected was not volatile under these conditions. None of the products from the 4 peaks could be crystallized.

Dehydroabietic Acid (II) from Levopimaric Acid (I), Erythrosin B, Light, and Nitromethane.—A solution of 7.55 g. of levopimaric acid, 0.125 g. of erythrosin B, and 13.4 ml. of nitromethane in 2485 ml. of 95% ethanol (0.01 *M* in resin acid, 0.10 *M* in nitromethane, and 0.00006 *M* in dye) was irradiated for 54.5 hr. (final $[\alpha]D$ +25°) and worked up as in the preceding examples except that the ether extraction was omitted. A quantitative yield of acidic residue was obtained; it exhibited no absorption in the 272-mμ region. The residue was converted to the cyclohexylamine salt in a yield of 7.7 g. (77%); concentration of the mother liquor gave a red oil. The salt was recrystallized from ethanol; yield 4.20 g. The acid was regenerated from the combined crops of salt as before and the crude acid purified as in the preceding examples, by elution through a silicic acid column with benzene followed by crystallization from 95% ethanol. The yield of dehydroabietic acid was 1.02 g. of m.p. 168–170°; $[\alpha]^{25}D$ +64° (*c* 0.98); λ_{max}^{alc} 276 mμ (α 2.13), 268 mμ (2.06); infrared spectrum essentially identical to that of an authentic sample. A second crop of 0.28 g. of $[\alpha]^{28}D$ +61.3° (*c* 1.1) was obtained for a total yield of 1.30 g. or 17% from levopimaric acid. The remainder of the material from the column could not be crystallized.

Sensitizers.—The following compounds were found to function as sensitizers[3,4] for dehydrogenation after the manner of erythrosin B: 9,10-phenanthrenequinone, benzil, chloranil (in benzene solution), eosin YS, and 9,10-anthraquinone.

Attempted Reaction of Abietic, Pimaric, Isopimaric, and Dehydroabietic Acids with Erythrosin B and Light.—A solution of 0.05 g. of erythrosin B in 33 ml. of 95% ethanol was filtered and 0.100 g. of the resin acid dissolved in the filtrate (0.01 *M* in resin acid and 0.0017 *M* in dye). The solution was charged to a 100-ml. reactor,[2] purged with prepurified nitrogen, stoppered, and irradiated with a 15-w. fluorescent lamp for 12 hr. In all four cases, essentially no change in color of the solution nor of specific rotation occurred as a result of the irradiation.

Blank Experiments.—A measurement of specific rotation before and after an extended test period (6 to 44 hr.) was used to determine if reaction had occurred. For all of the reactions described above, suitable blanks were run which determined that no reaction occurred in the dark, in the absence of sensitizing dye, in the absence of resin acids, or in the absence of nitromethane (other than a rapid bleaching of the small amount of dye present in the latter case).

Dehydrogenation of a Tetrahydrofuran. The Preparation of 3,4-Diphenylfuran

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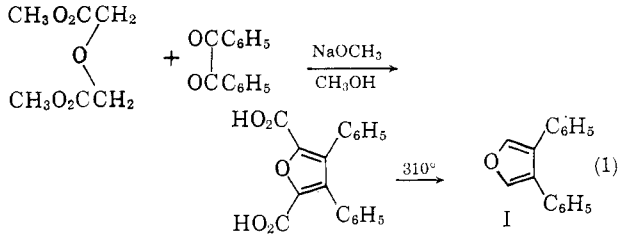
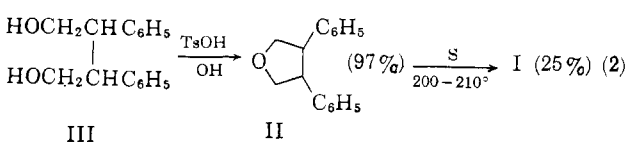
Although the preparation of furans by dehydrogenation of 2,5-dihydrofurans has been reported in a few instances in the literature,[2,3] the tetrahydrofurans seem to have been peculiarly reluctant to undergo dehydrogenation. This note describes the first example, of which we are aware, of successful dehydrogenation of a tetrahydrofuran.

The preparation of 3,4-diphenylfuran (I) in unspecified yield according to sequence (1) was described some time ago by Backer and Stevens.[4] It seemed to us that dehydrogenation of 3,4-diphenyltetrahydrofuran (II) might provide an alternative convenient route to the furan I.



The required tetrahydrofuran was readily obtained in 97% yield by a remarkably clean acid-catalyzed cyclization of 2,3-diphenylbutane-1,4-diol (III) with continuous removal of water. The dehydrogenation of tetrahydrofuran II could not be effected with selenium at a variety of temperatures with and without solvent, nor with sulfur in boiling dimethylformamide. The latter method had been very successful in the dehydrogenation of aryldihydrofurans.[2] Pyrolysis of II with elemental sulfur at 200–210°, however, resulted in the formation of furan I, isolated in 25% yield. Hydrogen sulfide evolution was negligible below 200° in this reaction. These reactions are pictured in sequence 2.



III II

(1) Fellow of the Alfred P. Sloan Foundation.

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