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; $[\alpha]^{25}\text{D}$ +62.7° (*c* 1.1); $\lambda_{\max}^{\text{alc}}$ 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., $[\alpha]^{26}\text{D}$ +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; $[\alpha]^{25}\text{D}$ +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°; $[\alpha]^{26}\text{D}$ +62.8° (*c* 1.1); $\lambda_{\max}^{\text{alc}}$ 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 $[\alpha]^{26}\text{D}$ +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, $[\alpha]^{28}\text{D}$ −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, $\lambda_{\max}^{\text{alc}}$ 243 mμ; peak 3, (major peak) $\lambda_{\max}^{\text{alc}}$ 264,274 (major max.) 284 mμ; peak 4, $\lambda_{\max}^{\text{alc}}$ 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 $[\alpha]\text{D}$ +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°; $[\alpha]^{25}\text{D}$ +64° (*c* 0.98); $\lambda_{\max}^{\text{alc}}$ 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 $[\alpha]^{28}\text{D}$ +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

Donald G. Farnum[1] and Merrill Burr

Department of Chemistry, Cornell University, Ithaca, New York

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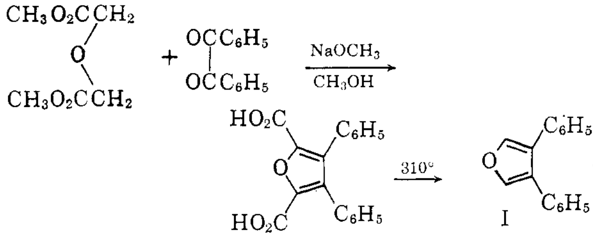
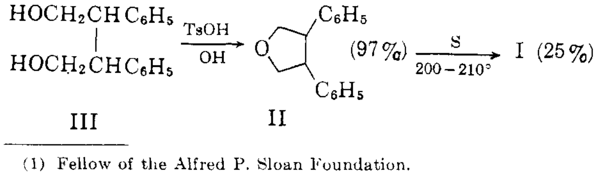
Although the preparation of furans by dehydrogenation of 2,5-dihydrofurans has been reported in a few instances in the literature,[2,3] the tetrahydrofurans seem to have been peculiarly reluctant to undergo dehydrogenation. This note describes the first example, of which we are aware, of successful dehydrogenation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



(1)

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.



(2)

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[1] Fellow of the Alfred P. Sloan Foundation.

[2] H. Wynberg, *J. Am. Chem. Soc.*, **80**, 364 (1958)

[3] J. F. Bel'skii, N. I. Shuĭkin, and R. A. Karakhanov, *Dokl. Akad. Nauk, SSSR.*, **132**, 585 (1960); *Chem. Abstr.*, **54**, 24623 (1960).

[4] H. J. Backer and W. Stevens, *Rec. trav. chim.*, **59**, 423 (1940).

In view of Wynberg's observation that an aryl substituent seemed essential for the dehydrogenation of dihydrofurans,[2] it is probable that the aryl substituents permit dehydrogenation of II. We do not intend to pursue this investigation further.

Experimental

2,3-Diphenylbutane-1,4-diol (III).—A mixture of *meso*-2,3-diphenylsuccinic acid[5] (m.p. 227–229°, 27 g., 0.10 mole) and lithium aluminum hydride (7.6 g., 0.20 mole) in dry ether (300 ml.) was boiled under reflux for 12 hr. Excess lithium aluminum hydride was destroyed by dropwise addition of wet ethanol to the stirred cooled slurry. The mixture was then shaken with cold aqueous 5% phosphoric acid and the layers separated. The aqueous layer was washed several times with methylene chloride and the combined organic extracts were dried over magnesium sulfate and evaporated to dryness. Recrystallization of the solid residue from benzene afforded colorless crystals, m.p. 142–143.5° (20 g., 83%).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.21; H, 7.42.

The infrared spectrum in Nujol mull included absorption at 3.0, 6.24, and 9.6 μ.

3,4-Diphenyltetrahydrofuran (IV).—The diol III (8.0 g., 0.033 mole) was dissolved in hot benzene (100 ml.) and *p*-toluenesulfonic acid monohydrate (3.0 g., 0.016 mole) was added. The solution was boiled under reflux and the evolved water was collected in a Dean–Stark trap. After 4 hr., 0.75 ml. (0.042 mole, 86%) of water had collected. An additional 2 hr. of boiling did not afford any more water. The mixture was cooled, washed once with water, once with dilute aqueus sodium bicarbonate, dried over magnesium sulfate, filtered, and evaporated to dryness on a rotary evaporator. The white, crystalline residue was recrystallized once from aqueous ethanol to give colorless needles m.p. 86–86.5° (7.2 g., 97%).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.39; H, 7.19.

The infrared spectrum in dichloromethane solution had no absorption at 2.5–3.2 μ, but included a strong band at 9.5 μ.

3,4-Diphenylfuran (II).—A mixture of the tetrahydrofuran IV (1.0 g., 4.5 mmoles) and sulfur (1.0 g., 31 mmoles) was melted and heated under a slow steam of nitrogen. No gas evolution was detected until the temperature reached 200°. Gas bubbles appeared and the odor of hydrogen sulfide then became evident. Heating was continued at 200–210° for 5 hr. The mixture was cooled and the crystalline mass was extracted several times with boiling ether. The ether extracts were concentrated on the steam bath, cooled, filtered, and the filtrate was evaporated to dryness. The residue was twice recrystallized from 95% ethanol to give pale yellow needles (0.25 g., 25%), m.p. 108–111° (dec. 109–110.5°[1]).

The infrared spectrum exhibited absorption at 6.24, 6.50, 9.50, and 11.40 μ in dichloromethane solution.

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(5) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 1709 (1922).

Formation of Tetrahydrofuran Derivatives from 1,4-Diols in Dimethyl Sulfoxide[1]

BERNARD T. GILLIS AND PAUL E. BECK

Department of Chemistry, Duquesne University, Pittsburgh 19, Pennsylvania

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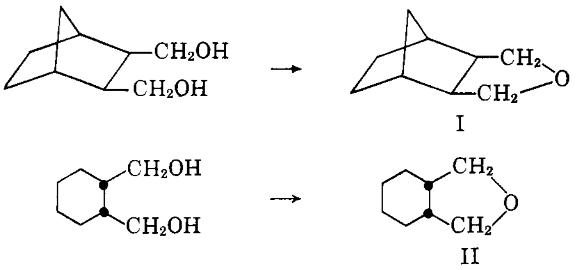
Three methods are prominent for the preparation of tetrahydrofuran derivatives from primary, secondary, and tertiary 1,4-diols. These are strong acid,[2] sulfonyl chloride–organic base,[3] and dehydration over alumina.[4] These methods, however, generally suffer from low yields and a mixture of products.

Recently, Traynelis, *et al.*,[5] have reported that secondary and tertiary alcohols are dehydrated to olefins when heated in dimethyl sulfoxide.

In an attempt to prepare 2,3-dimethylene[2.2.1]bicycloheptane, *endo-cis*-bicyclo[2.2.1]heptane-2,3-dimethanol was heated for thirteen hours at 156–166° in dimethyl sulfoxide. Instead of the desired diene, the cyclic ether, 2-oxatetrahydro-*endo*-dicyclopentadiene (I), was formed in 98% yield.



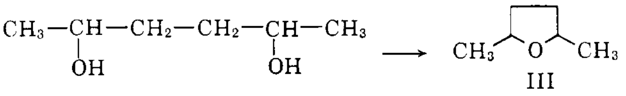
I

II

In view of this result, a study was undertaken to determine the scope of this facile dehydration using primary, secondary and tertiary 1,4-diols. A one to twelve ratio of diol to dimethyl sulfoxide was used.[6]

When *cis*-hexahydrophthalyl alcohol was heated in dimethyl sulfoxide at 159–161° for fourteen hours a 66% yield of *cis*-hexahydrophthalan (II) was obtained.

Similarly, the secondary diol, 2,5-hexanediol, when heated at 180° for eighteen hours in dimethyl sulfoxide furnished 2,5-dimethyltetrahydrofuran (III) in 68% yield.



III

Utilization of the tertiary diols, 2,5-dimethyl-2,5-hexanediol and 3,6-dimethyl-3,6-octanediol, resulted in 52% and 70% yields of products which contained the tetrahydrofuran derivatives, 2,2,5,5-tetramethyltetrahydrofuran (IV) and 2,5-diethyl-2,5-dimethyltetrahydrofuran (V), respectively.

The former diol leading to IV was heated at 167° for seventeen hours in dimethyl sulfoxide. Investigation of liquid product by gas chromatography showed it to be a mixture with the composition of 75.5%, 9.1%, and 15.5%, respectively. The infrared spectrum of this product was devoid of —OH bands but contained a very small carbon–carbon double bond stretching band at 6.05 μ. That the 15.5% component was

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(1) This research was carried out under grant G17836 from the National Science Foundation, whose support is gratefully acknowledged.

(2)(a) S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Org. Chem.*, **19**, 1449 (1954); (b) G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953); (c) Y. S. Zal'kind and V. Markaryan, *J. Russ. Phys. Chem. Soc.*, **48**, 538 (1916); (d) T. A. Favorskaya and N. P. Ryzkova, *Zh. Obshch. Khim.*, **26**, 423 (1956); (e) T. A. Favorskaya and O. V. Sergievskaya, *ibid.*, **25**, 150 (1955); (f) E. Pace, *Atti. Accad. Lincei*, **7**, 757 (1928); (g) I. L. Kotlyarevskii, M. S. Shvartsberg, and Z. P. Trotsenko, *Zh. Obshch. Khim.*, **30**, 440 (1960).

(3)(a) K. Alder and W. Roth, *Ber.*, **88**, 407 (1955); (b) D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 1593 (1950).

(4)(a) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *ibid.*, **82**, 1218 (1960); (b) R. C. Olberg, H. Pines, and V. N. Ipatieff, *ibid.*, **66**, 1096 (1944); (c) see ref. 2b.

(5) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

(6) Dr. Vincent Traynelis of the University of Notre Dame has found that primary 1,4-, 1,5-, and 1,6-diols are dehydrated to the cyclic ethers in dimethyl sulfoxide (private communication).