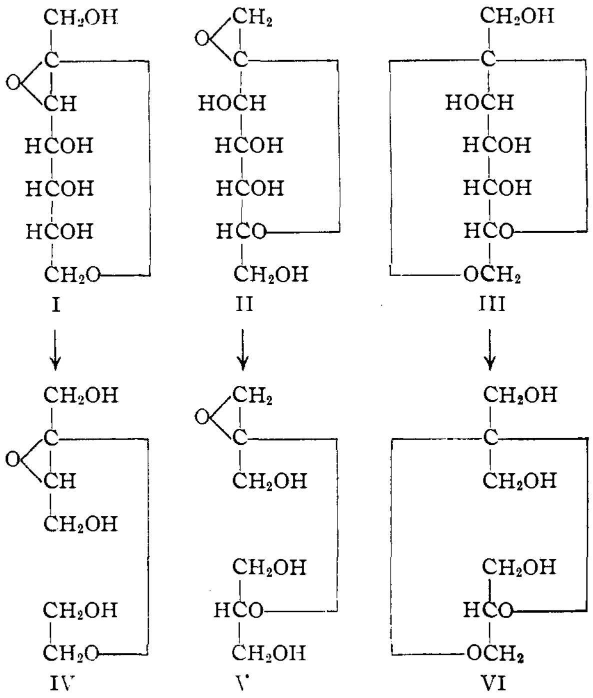

upon treatment with *p*-nitrobenzoyl chloride furnished a 30% yield (based on the weight of the reduced dialdehyde) of glycerol tri-(*p*-nitrobenzoate) of m.p. 193–195°. The fate of the remainder of the molecule has not been determined, but it does not seem possible that it could have been converted to glycerol under the experimental conditions.

Isolation of the *p*-nitrobenzoate of glycerol rather than that of ethylene glycol (m.p. 141°), which would be expected if sedoheptulosan had formula I, can be explained only on the basis of formula II or III. Of these we prefer formula III because of the failure of tetratosylsedoheptulosan to react with sodium iodide at 100° even though it must contain a primary tosyloxy group. This sluggish behavior has been reported as a characteristic of the primary tosyloxy group adjacent to the carbonyl group in 1-tosyl-2,3,4,5-diisopropylidene-D-fructose,[7] 1,4-ditosyl-2,3-isopropylidene-D-xylulose,[7] and 1-tosyl-2,3:4,6-diisopropylidene-L-sorbose.[8] On the other hand, a normal replacement of the primary tosyloxy group by an iodine atom should be expected from the tetratosyl derivative of II.

From these experiments, and certain other data that are in themselves inconclusive, it now appears that sedoheptulosan should be represented by formula III, and that it has the same ring structure that occurs in the known 1,6-anhydrides of glucose, mannose, altrose, galactose, and idose. A repetition of the methylation studies is now under way in an attempt to resolve the contradiction with the earlier work.

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[7] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **120**, 607 (1937).

[8] T. S. Gardner and J. Lee, *J. Org. Chem.*, **12**, 733 (1947).

Aromatic Cyclodehydrogenation. X. Studies on Ring Oxygen Compounds. Dinaphtho[1,2,1',2']-furan[1]

BY MILTON ORCHIN AND LESLIE REGGEL

In connection with another problem,[2] it became of interest to synthesize 1-(*o*-tolyl)-1-(2'-naphthyl)-1,2-dihydronaphthalene (IV). A possible route to IV appeared to be the reaction of *o*-tolylmagnesium bromide with 1-keto-2-(1'-tetralylidene)-1,2,3,4-tetrahydronaphthalene (I); 1,2-addition to the carbonyl group would give the carbinol, II, whereas 1,4-addition to the conjugated system would give the desired intermediate ketone, III. It was thought that if 1,4-addition took place, III might be separated *via* the semicarbazone and then be reduced and dehydrogenated to yield IV. The anticipated results were not obtained, however. About 61% of the starting ketone, I, was recovered when the Grignard reaction mixture was decomposed and the solvents removed. The balance of the product was treated with semicarbazide, and the ketonic material was recovered by hydrolysis and reduced by the Huang-Minlon modification of the Wolff–Kishner method; the crude reduced material was dehydrogenated, but no pure product could be isolated. The material that did not form a semicarbazone, presumed to be the carbinol, II, formed by 1,2-addition, or its dehydration product, was catalytically dehydrogenated. A small amount of 1-(*o*-tolyl)-2-(1'-naphthyl)-naphthalene (V) was isolated, but the main product was a colorless substance, $C_{20}H_{12}O$, melting point 155.0–156.5°, which formed a red 2,4,7-trinitrofluorenone complex, an orange *s*-trinitrobenzene complex, and an orange dipicrate, m.p. 164.5–165.2°. Interestingly enough, the ultraviolet absorption spectrum of this compound proved to be identical with that of a compound we had previously shown to be present in a mixture obtained by direct cyclodehydrogenation of the ketone, I.

In the earlier work it was shown that treatment of the ketone, I, with a palladium-on-charcoal catalyst resulted[3] in the formation of a mixture from which it was possible to isolate dibenzo[c,kl]-xanthene (VIII); ultraviolet absorption spectra showed the presence of another substance, which could not be obtained pure, to which the structure of dinaphtho[1,2,1',2']furan (VII) was assigned. The spectrum of VII, as previously obtained from mixtures of VII and VIII, was identical with the spectrum of the compound of melting point 155.0–156.5° obtained in the present work; no trace of VIII could be detected. The isolation of the dinaphthofuran, VII, in the present investigation, strengthens the case for the assigned structure but it cannot as yet be considered as completely substantiated.

In attempting to account for the formation of the furan, VII, it was thought that the Grignard reagent might have reduced I to VI, and that VI, present in the fraction that did not form a semicarbazone, might have produced VII on dehydro-

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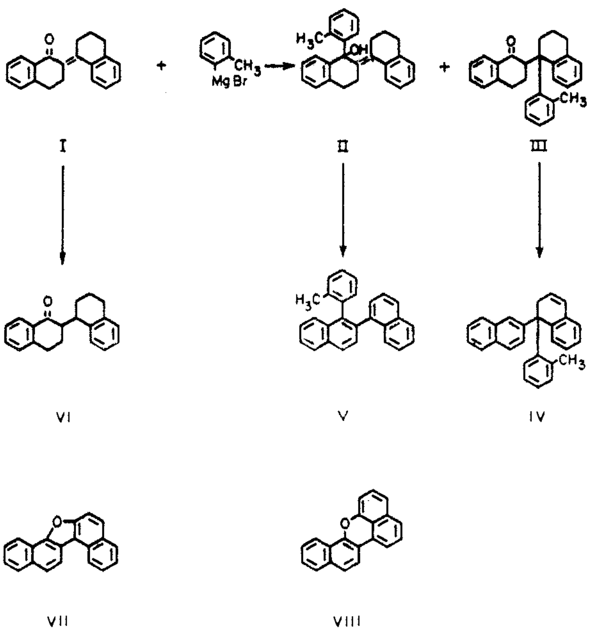
[1] Not subject to copyright.

[2] M. Orchin, L. Reggel and R. A. Friedel, THIS JOURNAL, **73**, 1449 (1951).

[3] M. Orchin, L. Reggel and R. A. Friedel, *ibid.*, **71**, 2743 (1949).

genation. This appeared to be likely, as we have shown that the saturated ketone, VI (which is readily obtained from the unsaturated ketone, I) does not form a semicarbazone. Accordingly, a sample of VI was dehydrogenated; dibenzo[c,kl]xanthene (VIII) and not the furan, VII, was readily isolated from the product. It is thus apparent that the cyclodehydrogenation of VI follows a similar course to that of I, and that VI is not the precursor of dinaphtho[1,2,1',2']furan (VII). It is, perhaps, conceivable that the material that gave VII on dehydrogenation contained either II or III, and that these substances underwent cyclodehydrogenation to VII with elimination of the tolyl group. No further work is contemplated to establish a mechanism for the formation of VII.[4]



Experimental[7]

Reaction of 1-Keto-2-(1'-tetralylidene)-1,2,3,4-tetrahydronaphthalene (I) with *o*-Tolylmagnesium Bromide.—To the Grignard reagent prepared from 17.10 g. of *o*-bromotoluene, 2.67 g. of magnesium and 70 ml. of ether there was added a solution of 10.96 g. of I in 75 ml. of benzene. The mixture was refluxed with stirring for 16 hours and was then decomposed with ammonium chloride solution. The organic layer was washed with saturated sodium chloride, dried over sodium sulfate, and the solvents removed at the water pump. The solid that formed was filtered and washed with cold 60–68° petroleum ether, giving 6.69 g. (61%) of I, m.p. 119–129°; recrystallization from alcohol gave 5.51 g. of I, m.p. 127.5–132.0°, mixed m.p. 128.5–134.0°. The filtrate was distilled (vacuum pump, bath at 290°), giving 3.68 g. of a gum that could not be crystallized. It was dissolved in 25 ml. of ethanol, 5 g. of semicarbazide hydrochloride and 5 ml. of pyridine were added, the mixture was refluxed for 5 hours, and allowed to cool. The precipitate (semicarbazone of III?) was filtered; benzene was added to the filtrate, the benzene solution was washed with dilute sulfuric acid, water, and sodium chloride, dried over calcium chloride, and evaporated to dryness, giving 2.76 g. of dark material (originally thought to be II or a dehydration product of II). To this was added 0.20 g. of 30% palladium-on-charcoal,[8] and the mixture was heated at 305–315° for 40 minutes and then at 345–355° for 40 minutes. There was evolved 183 ml. of gas (S.T.P.); considerable water also was given off. The product was chromatographed on alumina. There was obtained 0.612 g. of oil (least strongly adsorbed), which, after two recrystallizations, gave a small amount of 1-(*o*-tolyl)-2-(1'-naphthyl)-naphthalene[2] (V), m.p. 169–172.0°, mixed m.p. with an authentic sample 170.8–173.0°; 0.172 g. of pink solid (most strongly adsorbed), which was shown by ultraviolet absorption spectra to consist largely of VII; and an intermediate fraction, 0.734 g. of white solid, which was strongly blue-fluorescent on the chromatogram column. Three recrystallizations from 90–100° petroleum ether gave 0.216 g. of VII, white plates, m.p. 155.0–156.5° (constant). *Anal.* Calcd. for $C_{20}H_{12}O$: C, 89.5; H, 4.5. Found: C, 90.3; H, 4.4. The complex with 2,4,7-trinitrofluorenone[9] was recrystallized from benzene, giving dull-red crystals; on slow heating, these sintered at 224.0–224.5°, began to melt in the range 225.5–227.5°, resolidified, and then melted sharply at 230.0–231.0°. *Anal.* Calcd. for $C_{33}H_{17}N_3O_8$: C, 67.9; H, 2.9; N, 7.2. Found: C, 69.0, 68.8; H, 3.0, 3.3; N, 8.2, 8.1. A solution of 1 mole of VII and 2 moles of *s*-trinitrobenzene in ethanol gave a 1:1 complex, orange needles, m.p. 178.2–179.2° (not recrystallized). *Anal.* Calcd. for $C_{26}H_{15}N_3O_7$: C, 64.9; H, 3.1. Found: C, 64.8; H, 3.4. The dipicrate, prepared from 1 mole of VII and 2 moles of picric acid in absolute ethanol, was not recrystallized; it formed silky orange needles, m.p. 164.5–165.2° after softening at 164.0°. *Anal.* Calcd. for $C_{32}H_{18}N_6O_{15}$: N, 11.6. Found: N, 11.5.

The semicarbazone fraction (see above) was hydrolyzed with hydrochloric acid, and the resulting material (0.434 g. dark oil) was reduced by the Huang-Minlon modification of the Wolff–Kishner reaction.[10] The product was dehydrogenated with palladium-on-charcoal[7] at 300–350°, and the resulting material was chromatographed on alumina. The ultraviolet spectra showed that most of the product was 1,2'-dinaphthyl; small amounts of dinaphtho[1,2,1',2']-uran and of benz[j]fluoranthene[11] also were present.

Dibenzo[c,kl]xanthene (VIII) from 1-Keto-2-(1,2,3,4-tetrahydro-1'-naphthyl)-1,2,3,4-tetrahydronaphthalene (VI).—One and four-tenths grams of VI and 0.10 g. of palladium-on-charcoal[8] were heated for 30 minutes at 300–310° and then for 30 minutes at 340–350°; 315 ml. (S.T.P) of gas was evolved (69% of the theoretical for the conversion of VI to VII or VIII). The product was chromatographed on alumina. There were obtained 0.041 g. of naphthalene, identified by mixed melting point; 0.396 g. of a colorless oil; 0.035 g. of a yellow solid, not further investigated; 0.468 g. of a yellow solid (blue-green fluorescence on column); and 0.290 g. of an orange oil (most strongly adsorbed). The second fraction gave an unstable, red trinitrofluorenone complex (from benzene), which decomposed on attempted recrystallization. This fraction may have been 1,2'-dinaphthyl[3]; it was not further investigated, as both VII and VIII form very stable trinitrofluorenone complexes.[3] The fourth fraction was recrystallized from alcohol, giving 0.28 g. of VIII, m.p. 161.0–162.5°, mixed m.p. 162.0–164.8°. The fifth fraction was shown to be 2-(1'-naphthyl)-1-naphthol[3] by means of the ultraviolet spectrum.

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[4] Dinaphtho[2,3,1',2']furan has been reported to have m.p. 158–159°[5], 160–161°[6a]; dipicrate, red, m.p. 170–171°.[6a] Dinaphtho[2,1,1',2']furan has been reported to have m.p. 158.5°[6b]; picrate, dark red, m.p. 163–163.5°[6b]; dipicrate, brick red, m.p. 168.5°.[6b] As far as we are aware, there has been no rigorous proof of structure for either of these compounds, and it is possible that one of them is identical with our dinaphtho[1,2,1',2']furan.

[5] G. R. Clemo and R. Spence, *J. Chem. Soc.*, 2811 (1928).

[6] (a) V. Merz and W. Weith, *Ber.*, **14**, 187 (1881); (b) O. Eckstein, *ibid.*, **38**, 3660 (1905).

[7] All melting points corrected. Microanalyses by G. L. Stragand, University of Pittsburgh. We wish to thank R. A. Friedel and Marion Springer for the spectra measurements.

[8] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

[9] M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946); M. Orchin, L. Reggel and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947); E. O. Woolfolk and M. Orchin, "Organic Syntheses," Vol. 28, p. 91, John Wiley and Sons, Inc., New York, N. Y., 1948.

[10] Huang-Minlon, THIS JOURNAL, **71**, 3301 (1949).

[11] M. Orchin and L. Reggel, *ibid.*, **69**, 505 (1947); M. Orchin and L. Reggel, *ibid.*, **73**, 436 (1951).