the *trans*-75°-decalol was attempted by the method of Baker and Schuetz[9] who reported that when 2-naphthol was hydrogenated at room temperature and high pressure over platinum oxide in acetic acid, the crude product obtained was essentially the pure *trans*-75°-decalol. When this work was repeated, it was found that such was not the case but the *cis*-105° isomer was the main product. Thus starting with 550 g. of 2-naphthol, the hydrogenation product was first separated into neutral and acidic components and the acidic *ar*-tetralol amounted to at least 14%. The neutral fraction was crystallized from hexane to remove the large majority of the *cis*-105°-decalol and this isomer was obtained in 36% yield. The mother liquor residues were distilled in vacuum and yielded 28% mixed decalins, 20% of mixed decalols which consisted mostly of the *cis*-18° isomer and a small amount (0.1%) of the *trans*-53° alcohol. Although no pure *trans*-75° material was isolated it cannot be stated that none is present, but if so, it is a very minor reaction product. When this hydrogenation was run on a smaller scale, the amount of hydrogenolysis was less and the crude product was a solid. It would thus appear that the conclusion of Baker and Schuetz[9] that their crude reaction product was pure *trans*-75°-decalol is erroneous and was due to the fact that their mixture was not purified.

Experimental

Hydrogenation of 2-Naphthol.—A total of 550 g. of 2-naphthol was hydrogenated at high pressure and room temperature using platinum oxide catalyst. For example, in one of the runs, 150 g. of 2-naphthol, 160 ml. of ether, 160 ml. of glacial acetic acid and 3.0 g. of platinum oxide were placed in a glass lined hydrogenation bomb and shaken at room temperature under an initial pressure of 3200 p.s.i. After 15 hours, 6.5 mole equivalents had been absorbed and the shaking was stopped. The runs were combined at this stage.

After removal of the catalyst by filtration, the catalyst was washed with ether and the washings combined with the filtrate. The ether–acetic acid solution was then made alkaline by the cautious addition of concentrated sodium hydroxide solution. Ether was added from time to time to replace that lost by evaporation during the neutralization. The ether layer was separated from the aqueous alkaline layer containing the *ar*-tetralol, washed with water and saturated sodium chloride solution. After drying, the ether was evaporated and the residue dissolved in the minimum quantity of hexane. Several crops of crystals, all melting from 100–104°, were collected and then combined and recrystallized from hexane, yield 210 g. of *cis*-105°-decalol, m.p. 104.0–104.5°.

All hexane mother liquors were evaporated and the residues combined and distilled through a 35-plate tantalum wire-packed column[10] at a reflux ratio of 10 to 1. The following fractions were collected: (1) decalin, 148 g., b.p. 81–84° (20 mm.); (2) *trans*-53°-decalol (impure), 1.5 g., b.p. 125–131° (20 mm.); (3) mixed decalols, 120 g., b.p. 131–138 (20 mm.); (4) *ar*-2-tetralol (impure), 20 g., b.p. 155–158° (20 mm.).

From fraction 2, m.p. 44–46°, 0.4 g. of pure *trans*-53°-decalol, m.p. 53.4–54.7°, was obtained by repeated recrystallization from pentane. Portions of fraction 3, liquid at room temperature, were converted to half phthalates[1] and yielded mainly the solid half phthalate of *cis*-18°-decalol, m.p. 145–148° (lit.[1] 153°). Fraction 4, m.p. 36–38°, was recrystallized from hexane and after one crystallization melts at 51–52°. Further crystallizations yielded material melting 61–62°; this result is in agreement with the known dimorphic character of *ar*-2-tetralol whose two forms melt 53–54° and 62°.[11] Apparently the tetralol was not completely extracted from ether by the alkali in the first step in the separation.

Preparation of Acetates.—The decalyl acetates were prepared by the method of Leroux.[12] The properties reported by Hückel[8] are in agreement with those found in the present research except we were unable to obtain the acetate of *cis*-105°-decalol as a solid; Hückel reports m.p. 32°. The boiling points of the esters of the decalols are as follows with the literature value given in parentheses: I, 136° (19 mm.) (122° (9 mm.)); II, 135° (15 mm.) (not reported[13]); III, 132° (20 mm.) (110° (9 mm.)) and IV, 133° (18 mm.) (118° (9 mm.)).

Infrared Spectra.—The spectra of the decalyl acetates and steroidal acetates were determined with a Model 21 Perkin–Elmer infrared spectrophotometer equipped with a NaCl prism. The carbon disulfide solutions were studied in a KBr cell of 0.1 mm. thickness with no comparison cell in the reference beam. The frequency measurements are estimated to have an uncertainty of less than ±2 cm.$^{-1}$ and the slit width used in the high resolution studies was 5 cm.$^{-1}$. The exact maxima for the acetates are as follows: I, 1244 cm.$^{-1}$; II, 1248, 1238 cm.$^{-1}$; III, 1248, 1240 cm.$^{-1}$; IV, 1247, 1235, 1213 cm.$^{-1}$. The value for cholestanyl acetate is 1243 cm.$^{-1}$ and for epicholestanyl acetate are 1257, 1247, 1237 cm.$^{-1}$. The spectra of the decalols were determined n carbon disulfide solution at a concentration of 10 g. per liter and at a cell thickness of 0.9 mm. on a Baird infrared spectrophotometer equipped with a NaCl prism. The exact maxima for the decalols are as follows: I, 1057, 1029 cm.$^{-1}$; II, 1050, 1012 cm.$^{-1}$; III, 1062, 1022 cm.$^{-1}$; IV, 1007 cm.$^{-1}$.

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Effect of Xanthylation on the Recovery of DNP-Amins Acids from Acid Protein Hydrolysates[1]

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Thompson[2] observed the destruction of DNP-amino acids after acid hydrolysis in the presence of tryptophan or the protein lysozyme which contains 10.6% tryptophan.[3] The acid stability of dixanthyltryptophan[4] prompted us to determine recoveries of N^5-DNP-L-lysine and of di-DNP-L-lysine from DNP-lysozyme and xanthyl-DNP-lysozyme. As shown in Table I recovery of N^5-DNP-L-lysine was 56% of theoretical from DNP-lysozyme and 91% from xanthyl-DNP-lysozyme after the substituted protein was refluxed for twenty-four hours in 6 *N* HCl. Similarly, recovery of di-DNP-L-lysine was 78% of the theoretical from DNP-lysozyme and 97% from xanthyl-DNP-lysozyme. The recovery of approximately one mole

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of di-DNP-L-lysine and 5 moles of N^{ϵ}-DNP-L-lysine per mole of lysozyme confirms the previous analyses of Green and Schroeder[5] and of Lewis, *et al.*[3]

TABLE I

RECOVERY OF N^{ϵ}-DNP-L-LYSINE AND DI-DNP-L-LYSINE FROM DNP-LYSOZYME AND XANTHYL-DNP-LYSOZYME

Sample	Quantity analyzed,[a] μM	N^{ϵ}-DNP-L-lysine recov.[b] μM	%	Di-DNP-L-lysine recov.[b] μM	%
DNP-Lysozyme	1.20	3.37	56.0	0.94	78.0
Xanthyl-DNP-lysozyme	1.34	6.10	91.0	1.31	97.5

[a] Calculated from determination of primary amide groups.[6,7] [b] Calculated from absorbancy at 3460 Å. in glacial acetic acid.

The increased recovery of the DNP-lysines after xanthylation is probably due to the formation of dixanthyltryptophan in the intact protein. This is also indicated by the formation of the characteristic purple color of dixanthyltryptophan in these solutions. Data which indicate that dixanthyltryptophan itself is non-destructive of DNP-alanine under protein hydrolysis conditions is included in Table II. A 56% recovery of DNP-DL-alanine was obtained in the presence of tryptophan. This was increased to a recovery of 82% in the presence of dixanthyltryptophan and 85% in the presence of xanthyllysozyme and in the control. These results suggest that xanthylation of other proteins after reaction with DNFB will result in higher recoveries of DNP-amino acids in acid hydrolysates of proteins.

TABLE II

EFFECT OF ADDED COMPOUNDS ON THE RECOVERY OF DNP-DL-ALANINE FROM ACID SOLUTIONS

Compound[a]	Mg.	Recovery, %
Control	..	85
Tryptophan	10	56
Dixanthyltryptophan	30	82
Xanthyllysozyme	100	85

[a] These quantities provide approximately 10 moles of tryptophan per mole of DNP-DL-alanine.

Experimental

DNP-Lysozyme was prepared by the method described by Sanger[7] for DNP-insulin. Lysozyme (100 mg.) was treated with DNFB (400 mg.) in bicarbonate buffer and 85 mg. of DNP-lysozyme was isolated.

Xanthyl-DNP-lysozyme was prepared by dissolving DNP-lysozyme (100 mg.) and xanthydrol (112 mg.) in 10 ml. of 90% acetic acid. At the end of one hour at room temperature the product was precipitated with ether and washed three times with ether at the centrifuge. The xanthyl-DNP-lysozyme (65 mg.) was dried over calcium chloride and paraffin.

Isolation and determination of N^{ϵ}-DNP-L-lysine and di-DNP-L-lysine from DNP-lysozyme and xanthyl-DNP-lysozyme were carried out according to Porter.[8] Synthesis of the two DNP-lysines which were used as standards was also accomplished by the method of Porter. Absorbancy measurements of the DNP-lysines were made with a Beckman DU spectrophotometer at 3460Å.

Protein concentrations were determined by primary amide group analyses. The protein solutions were autoclaved for one hour in 2 *N* H_2SO_4 at 20 lb. pressure, after which the ammonia was determined as described by Porter.[8]

DNP-DL-alanine was synthesized by the method of Porter.[8] For the stability study DNP-DL-alanine (1.0 mg.) was refluxed twenty-four hours in 12 *N* HCl in the presence of tryptophan (10 mg.), dixanthyltryptophan (30 mg.) and xanthyllysozyme (100 mg.). The DNP-DL-alanine in the solution was chromatographed over silica gel according to Porter[8] and determined photometrically at 4000 Å.

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Amebacidal Agents. II. 5-Acyl- and 5-Alkyl-7-dialkylaminomethyl-8-quinolinols

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Interesting amebacidal activity has been reported in a group of Mannich base derivatives of halogenated quinolinols.[1] A similar series of alkylated quinolinols was synthesized following the initial observation of activity. The intermediate 5-acyl-8-quinolinols were prepared by means of the Friedel–Crafts reaction using 8-quinolinol.[2] Reduction of these ketones to the 5-alkyl-8-quinolinols was accomplished by catalytic hydrogenation with 5% palladium-on-charcoal.[2] This reaction was extended with great difficulty to the preparation of several long-chain acylated quinolinols. Reduction of the long-chain acylated quinolines was confirmed by the disappearance of the characteristic infrared absorption band at 5.96 μ.[3]

When the Mannich reaction with 8-hydroxy-5-quinolyl methyl ketone,[2] was attempted, using two molar equivalents of amine and paraformaldehyde only one basic side chain was introduced. Infrared data strongly suggest that the piperidyl methyl group entered the aromatic nucleus at position 7 rather than the α-position of the acetyl substituent.[4] Compound VI, Table I, and 5-chloro-7-(1′-piperidylmethyl)-8-quinolinol dihydrochloride[5] possess similar infrared absorption patterns with bands at 11.6, 12.10, 12.42, 12.75 μ, and 11.66, 12.24, 12.54, 12.75 μ, respectively. Both spectra differ greatly in this region from the spectra of several 5-substituted 8-quinolinols.

The amebacidal activity[6] of these compounds was observed to decrease with increasing molecular weight.

Experimental

8-Hydroxy-5-quinolyl Octyl Ketone (X).—Anhydrous aluminum chloride (120 g.) was added in small portions with cooling to a mixture of 70.5 g. (0.40 mole) of pelargonyl chloride and 45.0 g. (0.31 mole) of 8-quinolinol in 200 g. of nitrobenzene. The mixture was heated at 75° for 16 hours.

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