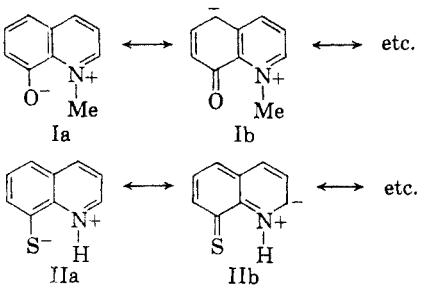
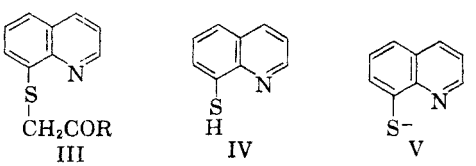
tion of ethanol to a reddish blue color; on the other hand, dilution of the concentrated solution with pyridine caused the color to be very greatly diminished.



The preparation of two *S*-alkyl type derivatives of 8-mercaptoquinoline is now reported. The reaction of phenacyl chloride with 8-mercaptoquinoline in pyridine solution gave 8-quinolyl phenacyl sulfide (III, R = C_6H_5); 8-quinolyl acetonyl sulfide (III, R = CH_3) was similarly prepared from chloroacetone and the thiol. Both of these compounds were colorless, either in the solid state or as their solution in organic solvents.

S-benzoyl 8-quinolyl sulfide, as reported previously,[3] was colorless. This compound gave a colorless solution in ethanol unchanged by the addition of water; however, this aqueous ethanolic solution gradually developed a red color, the more rapidly on warming. Thus it seems likely that the long wave-length absorption reported[1] for the benzoyl derivative in 50% ethanol should be attributed to the partial hydrolysis of this thiol ester, in which case the objection to the C=C—C=S chromophore for this substance is invalid.

Alkaline solutions of 8-mercaptoquinoline were colorless or nearly so, and the acidic solution was yellow confirming earlier observations.[3]



The above observations together with the change in the red color of the dihydrate to the pale violet color of the liquid 8-mercaptoquinoline[1] find a ready explanation in structure II. The existence in ionizing solvents of 8-mercaptoquinoline in the purple zwitterionic form is not unexpected in view of the greater acidity of thiol compounds as compared with hydroxyl compounds, this zwitterionic form being presumably modified in hydroxylic solvents and in the solid red dihydrate by hydrogen bonding. In nonpolar solvents the zwitterionic form would be relatively less stable (compare the *N*-heteroaromatic hydroxy compounds[4]) and the colorless nature of such solutions[1] finds explanation in the predominance of the tautomeric form (IV), the pale violet color of the pure liquid thus indicates an autoprotolytic equilibrium between IV and II. The effect of dilution of the pyridine solution can be attributed to a solvolytic equilibrium involving pyridinium ions and the anion (V), the latter entity accounting also for the lack of color of the aqueous alkaline solution of the thiol.

(3) A. Edinger, *Ber.*, **41**, 937 (1908).
(4) S. F. Mason, *J. Chem. Soc.*, 5016 (1957).

EXPERIMENTAL

S-Benzoyl 8-mercaptoquinoline was prepared by Edinger's method[3] and had m.p. 110° (lit.[3] 110°); preparation of this compound under nitrogen was found advantageous.

8-Quinolyl acetonyl sulfide. Chloroacetone was added to a solution of 8-mercaptoquinoline in pyridine and the solution was set aside overnight under nitrogen. The next day the mixture was stirred into water and the mixture was set aside for several days to crystallize. The solid was collected and purified by low temperature recrystallization from ethanol. The product was 8-quinolyl acetonyl sulfide, m.p. 54–54.5°.

Anal. Calcd. for $C_{12}H_{11}NOS$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.28; H, 4.97; N, 6.11.

8-Quinolyl phenacyl sulfide. Phenacyl chloride in pyridine was added to an equimolecular amount of 8-mercaptoquinoline in pyridine and the mixture was kept for 24 hr. under nitrogen and then poured into water to yield a solid. This solid was recrystallized from ethanol to give 8-quinolyl phenacyl sulfide m.p. 133°.

Anal. Calcd. for $C_{17}H_{13}NOS$: C, 73.12; H, 4.69; N, 5.02. Found: C, 73.01; H, 4.70; N, 4.76.

Acknowledgment. The author is indebted to Dr. W. Zimmermann and his staff for the microanalyses.

NOTE ADDED IN PROOF: Substantially similar conclusions concerning the color of 8-mercaptoquinoline have been reached by A. Albert and G. B. Barlin [*J. Chem. Soc.*, 2384 (1959)] in a paper which appeared after the submission of this note.

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Hydrogenolytic Cleavage of Menthofuran[1]

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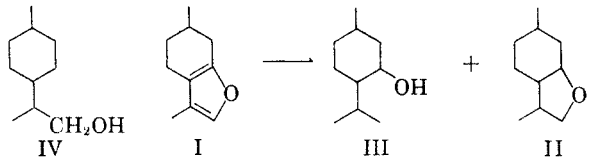
Recently, Wienhaus[2] carried out the catalytic hydrogenation of menthofuran (I) over platinum black in acetic acid, reporting tetrahydromenthofuran (II) as the sole product. It is known, however, that in the presence of Adams' catalyst furan compounds are not only hydrogenated to tetrahydrofurans, but often subjected to hydrogen-

(1) Abstracted partly from the Master thesis submitted by W. Tagaki, March 1, 1956, and presented at the monthly meeting of Kansai Branch of the Agricultural Chemical Society of Japan, Kyoto, January 26, 1957.
(2) H. Wienhaus and H. Dewein, *Ber.*, **91**, 256 (1958).

olysis also.[3] Thus, it appears that the hydrogenolysis of I may result either in the formation of menthol (III) or *p*-menthane-9-ol (IV).



IV I III II

IIIa. (+)-*neo*menthol
IIIb. (+)-*neoiso*menthol

Independently of Wienhaus,[2] we have carried out the catalytic hydrogenation of I using Adams' catalyst and acetic acid and have found that cleavage occurs to the extent of about 20% to give a mixture of menthols. The remaining 80% of the product was II formed by ring hydrogenation. The cleaved product was converted quantitatively to the 3,5-dinitrobenzoate. By chromatography of this ester on an alumina column it was found that the cleavage product was entirely composed of (+)-*neo*menthol (IIIa) and (+)-*neoiso*menthol (IIIb) without any *p*-menthane-9-ol, (IV). The direction of hydrogenolytic cleavage of I observed here agrees with that reported by Shuikin and Belsky[4] who used a different catalyst.

Variation of the hydrogenation temperature between 20° and 60° did not affect the extent of ring cleavage, but did change the ratio of IIIb to IIIa, as shown in Table I, from 2:1 at 20° to 1.2:1 at 60°. This result is of interest from both the stereochemical and preparative point of view, since *neoiso*menthol is considered to be the most unstable isomer[5] and is more difficult to prepare than any of the other isomeric menthols.

The formation of IIIa and IIIb in the hydrogenation substantiates the common observation regarding *cis*- addition of hydrogen to ethylenic bonds in the presence of catalysts, since in both IIIa and IIIb the hydroxyl and *iso*propyl groups are *cis* to each other. The corresponding *trans*-isomers, (−)-menthol and (+)-*iso*menthol were not obtained in the catalytic hydrogenation. On the other hand, the stereochemistry of the major product II is not certain. An attempt to correlate the steric configuration of II with that of isomeric menthol by cleaving the ether bond with acetyl chloride failed, resulting in IV. As discussed by Smith and Fuzek,[3] II is probably not an intermediate in the transformation of I into III, since II no longer reacted with hydrogen under the same experimental conditions. We are now making an effort to establish the stereochemistry of II and the result will be reported.

EXPERIMENTAL[6]

Menthofuran (I) synthesized by the method reported by Pallaud and Berna[7] showed the following constants; $[\alpha]_D^{21}$ + 93° (*c*, 9.63 in methanol), b.p. 91.5–92.5° (18 mm.).

Catalytic hydrogenation. Only the procedure at 20° is described. The reductions at 40° and 60° were carried out by the same procedure using the same amount of sample and reagent. The amount of hydrogen uptake and the content of menthol (measured by acetylation) in the product were not much affected by temperature.

TABLE I[a]

COMPOSITION (%) OF THE CRUDE MENTHYL 3,5-DINITROBENZOATE

T,[b] °C.	F-I: M.P. 150–155°	F-II: M.P. 85–145°	F-III: M.P. 95–99°	R[c]	F-III/F-I[d]
20	26	4	52	9	2.0
40	29	8	49	9	1.7
60	38	5	45	4	1.2
	32	3	64	—	2.0

[a] The bottom line represents the analysis of an authentic mixture (2:1) of (+)-*neoiso*menthyl- (m.p. 99–100°) and (+)-*neo*menthyl 3,5-dinitrobenzoate (m.p. 154–155°). [b] Hydrogenation temperature. [c] Resinous substance. [d] The accuracy was ±0.1 in duplicate analysis.

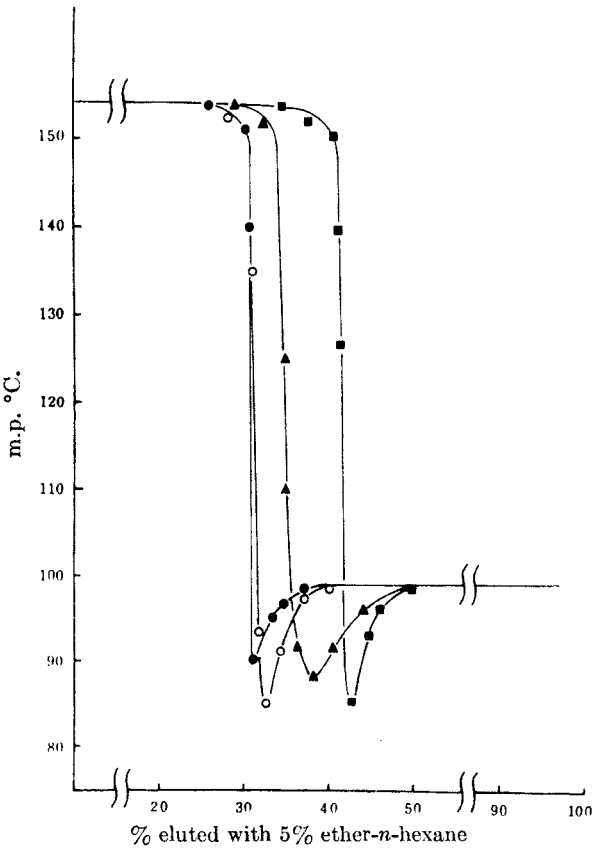


Fig. 1. Alumina chromatography of Menthyl 3,5-dinitrobenzoate (See Table I): ●, authentic mixture; ○, 20°; ▲, 40°; ■, 60°

(3) H. A. Smith and J. F. Fuzek, *J. Am. Chem. Soc.*, **71**, 415 (1949), and the references there cited.

(4) N. I. Shuikin and I. F. Belsky, *Proc. Acad. Sci. U.S.S.R. (English Translation)*, **116**, 905 (1957).

(5) E. L. Eliel, *Experimentia*, **9**, 91 (1953).

(6) All melting and boiling points are uncorrected.

(7) R. Pallaud and J. Berna, *Ind. Parfum.*, **8**, 154 (1953); *Chem. Abstr.*, **47**, 10179 (1953).

The hydrogenation temperature was controlled by the circulation of water through the jacket surrounding the hydrogenation flask. In the flask were placed freshly distilled menthofuran (I), 3.210 g., (0.0214 mol.), platinum oxide (60 mg.), and acetic acid (30 ml.). At the beginning of the shaking, the hydrogenation mixture should be colorless.[8] After 4 hr., the absorption of hydrogen ceased at 1120 ml. (0.466 mol.; measured at 20°). From the hydrogenation mixture a colorless oil (3.000 g.) was obtained, b.p. 88–100° (18 mm.) which contained 20.1% menthol mixture.

The hydrogenation product was treated with 3,5-dinitrobenzoyl chloride in pyridine and then steam-distilled. The undistilled residue solidified to give the crude 3,5-dinitrobenzoate (0.829 g.). From the distillate, tetrahydromenthofuran (II) was obtained, b.p. 91–92° (20 mm.). α_D^{17} −20.8° (homogeneous), d_4^{25} 0.9286, n_D^{25} 1.4610, MR (calcd.) 45.62, (obsd.) 45.58.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.90; H, 11.81.

The crude 3,5-dinitrobenzoate (100 mg.) was purified by passing an *n*-hexane solution of the 3,5-dinitrobenzoate through a layer of alumina (1 g.). The removal of *n*-hexane from the effluent gave colorless needles (86 mg.), while a resinous substance (9 mg.) adsorbed on the alumina was eluted with ether.

The purified 3,5-dinitrobenzoate (20.0 mg.) was chromatographed on an alumina column (alumina 15 g.; height 15 cm.) using *n*-hexane mixed with 5% ether as developing solvent. The effluent was collected in small fractions and the solvent was removed from each fraction. After the melting points had been determined, as shown in Fig. 1, the fractions were combined into three parts: Fraction I 6.0 mg. (m.p. 150–154°), Fraction II 1.0 mg. (m.p. 85–145°), and Fraction III 12.1 mg. (m.p. 95–99°). From the results obtained by the above preliminary purification and by chromatography, the composition of crude ester was calculated as shown in Table I.

When recrystallized from methanol, Fraction I and Fraction III melted at 154–155° and 99–100° respectively, and were shown to be (+)-*neo*menthyl- and (+)-*neoiso*menthyl 3,5-dinitrobenzoate, by mixed melting point determinations with authentic samples. Fraction II was a mixture of these two isomers.

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(8) R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.*, **72**, 399 (1950).

Differentiation of Glyceraldehyde from Other Trioses by Means of 2,4-Dinitrophenylhydrazine[1]

SAMUEL C. SMITH, P. M. ALTHOUSE, AND J. W. SHIGLEY

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In an effort to identify some oxidation products of glycerides by 2,4-dinitrophenylhydrazone derivatives it was discovered that the literature is rather vague concerning the 2,4-dinitrophenylhydrazone of glyceraldehyde.

Neuberg,[2] using a saturated solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid at 0°, prepared glyceraldehyde 2,4-dinitrophenylhydrazone which melted at 166–167°. Neuberg and Collatz[3] reported the 2,4-dinitrophenylosazone of glyceraldehyde to melt at 265° (dec.). Later, Neuberg and Strauss[4] reported that the bishydrazone (osazone) of methyl glyoxal can be obtained quantitatively from dihydroxyacetone and glyceraldehyde with 2,4-dinitrophenylhydrazine in hydrochloric acid. This 2,4-dinitrophenylosazone melted at 298°.[5]

In the present investigation two methods were used to study the dinitrophenylhydrazones and osazones of glyceraldehyde, dihydroxyacetone, and pyruvaldehyde (methyl glyoxal). The results appear in Table I.

Infrared spectra of the products melting at 164–166° were all similar with peaks at: 3.05, 6.15–6.20, 6.28, 7.45, 8.18, 8.70–8.90, 9.15–9.35, 10.28, 10.75–10.90, 11.73–11.95, and 12.00 μ. Infrared spectra of the products melting at 297–299° were all similar with peaks at: 3.08, 6.19, 6.27, 6.32, 6.65, 7.40–7.50, 7.60, 7.95, 8.23–8.28, 8.73, 9.20, 9.47, 10.68, 10.92, 11.90–12.00, and 13.43–13.70 μ.

The results show that glyceraldehyde 2,4-dinitrophenylhydrazone can be prepared in hydrochloric acid at 5°, but the 2,4-dinitrophenylosazone of pyruvaldehyde forms at other temperatures. In the case of dihydroxyacetone and pyruvaldehyde, however, the 2,4-dinitrophenylosazone of pyruvaldehyde forms at all the temperatures tried. This osazone which melts from 250–298° can be recrystallized from dioxane or pyridine to melt at 297–299°.

These data show that by the use of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid at 5° glyceraldehyde can be differentiated from the other trioses.

EXPERIMENTAL

Preparation of dinitrophenylhydrazones and osazones. Two methods were used to study the dinitrophenylhydrazones and osazones of glyceraldehyde (Nutritional Biochemicals #6559), dihydroxyacetone (Nutritional Biochemicals #4386), and pyruvaldehyde (methyl glyoxal), (K&K #2995L 30% soln.). The first was that of Brady and Elsmie[6] in which a saturated solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid was added to an aqueous solution of the triose. The second method was that of Allen[7] as modified

(1) This Communication has been authorized for publication on October 15, 1958, as Paper No. 2302 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

(2) I. S. Neuberg, *Biochem. Z.*, **255**, 1 (1932).

(3) C. Neuberg and H. Collatz, *Biochem. Z.*, **223**, 494 (1930).

(4) C. Neuberg and E. Strauss, *Arch. Biochem.*, **11**, 457 (1946).

(5) E. Simon and C. Neuberg, *Biochem. Z.*, **232**, 479 (1931).

(6) O. L. Brady and G. V. Elsmie, *Analyst*, **51**, 77 (1926).

(7) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).