

NOTES

Symmetrical Biaryls from Diazotized Amines.
Reducing Agents. IIBY EDWARD R. ATKINSON, D. HOLM-HANSEN,
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We have continued our systematic examination¹ of those reducing agents which might convert diazotized amines to symmetrical biaryls. As in the previous work diazotized anthranilic acid has been used and the work has been confined to aqueous solutions. None of the agents here described are as effective as those previously studied but our results are of interest because the use of "standard" conditions and a single diazotized amine makes possible a comparison of the relative effectiveness of these agents.

Experimental

Copper Powder in Aqueous Suspension.—It has been reported that the use of this agent leads to the formation of the RH product,² the RX product,³ and the biaryl,⁴ the latter being obtained in 60% yield when diazotized *o*-nitroaniline was used.

Our general experimental procedure has already been described.¹ Ten grams of anthranilic acid was diazotized in the usual way and in a typical run the diazo solution was added during thirty minutes to a suspension of 10 g. of activated⁵ copper powder suspended in 70 cc. of water; temperature was 5–10°. At the conclusion of the addition the mixture gave a negative diazo test with β -naphthol. An excess of solid sodium bicarbonate was added to dissolve the acidic products and a mixture of copper powder (6 g.) and hydrated cuprous oxide was filtered from the solution. The filtrate was acidified to precipitate a cream colored solid which was separated into diphenic acid, m. p. 215–220° (32% yield), and *o*-chlorobenzoic acid, m. p. 133–140° (54% yield), by the use of boiling ligroin (b. p. 90–120°) in which the diphenic acid is only slightly soluble.

Copper Powder in Dilute Ammonium Hydroxide Solution.—Vorländer and Meyer⁶ had obtained a 20% yield of diphenic acid along with an unidentified substance of high melting point by use of this reagent. In our work the procedure used was the same as that described in the preceding paragraph; the copper powder however was suspended in a mixture of 30 cc. of water and 30 cc. of concentrated ammonium hydroxide. It was found by experiment that the metal could be used as received without the customary washing to remove oil. At the conclusion of the reaction the ammoniacal solution was filtered free of excess

copper (5–6 g.); the amount of metal consumed is of no significance for a separate experiment showed it to be attacked by the ammoniacal solution in the absence of the diazo solution. The filtrate was carefully acidified with hydrochloric acid at about 60° to precipitate the crude product, which was then leached with 50 cc. of boiling water. It was then recrystallized from glacial acetic acid, the less soluble portion consisting of diphenylamine-2,2'-dicarboxylic acid (10% yield), the more soluble portion being diphenic acid (67–71% yield).

Formic Acid.—This reagent, in conjunction with small amounts of copper powder, has brought about biaryl formation⁷ but the procedures have been confined to essentially anhydrous conditions. Tobias⁸ observed deamination in the naphthylamine sulfonic acid series under aqueous conditions.

We observed that when solutions of benzenediazonium formate were mixed with 23 *N* formic acid in a variety of proportions no reaction occurred unless the mixture was warmed; salicylic acid was formed in at least 70% yield and no other product was detected. When copper powder was added to the cold mixture nitrogen was slowly evolved and after working up the products in the usual way there were isolated benzoic acid (40%), impure diphenic acid (10%), and a small amount of tar. The crude product also gave a positive ferric chloride test.

Ethyl Alcohol.—The use of this material (either with or without the use of copper) in deamination is well known but Gattermann and Erhardt⁹ obtained by its use a 22% yield of biphenyl from diazotized aniline and a number of other investigators have obtained small amounts of the biaryl when studying its action on a variety of diazotized amines.

Ten grams of anthranilic acid was diazotized in the usual way using hydrochloric acid. The resulting solution (volume = 100 cc.) was then mixed with an equal volume of 95% ethyl alcohol and warmed. In some experiments the diazo solution was allowed to flow into boiling alcohol. In all experiments the only organic product isolated was salicylic acid (50–75% yield). Acetaldehyde was formed in small amounts. The procedure used in isolating the acid was such that any ethyl salicylate originally formed would be hydrolyzed.

When the diazo solution was mixed with an equal volume of ethyl alcohol and the mixture stirred at 0° with 2 g. of copper powder, large amounts of acetaldehyde were formed and the diazo compound was entirely destroyed at the end of thirty minutes; the copper was completely dissolved. From the crude product there was obtained by sublimation benzoic acid (50% yield) contaminated with a small amount of *o*-chlorobenzoic acid. From the residue there was isolated 0.2 g. of impure azobenzene-2,2'-dicarboxylic acid, m. p. 231–238° dec., which was further

(1) Atkinson, *et al.*, *THIS JOURNAL*, **63**, 730 (1941).(2) Ayling, Gorvin and Hinkel, *J. Chem. Soc.*, 613 (1941).(3) Ullmann, *Ber.*, **20**, 1879 (1896).(4) Niementowski, *ibid.*, **34**, 3327 (1901).(5) Kleiderer and Adams, *THIS JOURNAL*, **55**, 4225 (1933).(6) Vorländer and Meyer, *Ann.*, **320**, 142 (1902).(7) (a) Gerugross and Dunkel, *Ber.*, **57**, 739 (1924); (b) Brydowna, *Chem. Abstr.*, **22**, 2372 (1928).(8) Tobias, *Ber.*, **23**, 1631 (1890).(9) Gattermann and Erhardt, *ibid.*, **23**, 1226 (1890).

identified by its conversion to the hyarazo compound, m. p. 188–193° dec.

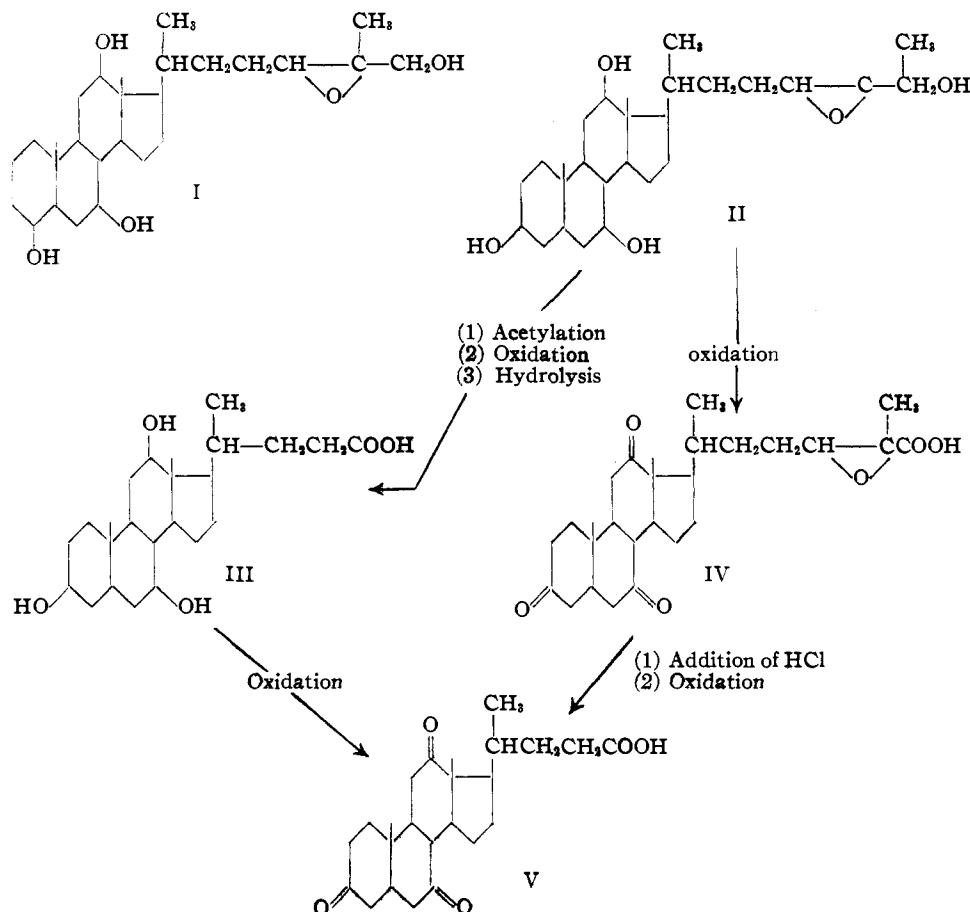
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Scymnol

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In 1898, Hammarsten¹ showed that the bile of the northern shark, *Scymnus borealis*, lacks the common bile acids, containing in their place the sulfuric acid ester of a polyhydric alcohol, scymnol, $C_{27}H_{46}O_5$. Since then scymnol has been found in the bile of other sharks, and also rays, and it is now regarded² as a typical component of the bile of all elasmobranch fish. Windaus³ and Tschesche⁴ have demonstrated the relation of scymnol

tion of a hydroxyl group on ring A remained uncertain. Tschesche contended that it did not occupy the C_8 -position, because degradation of scymnol gave a triketo acid, which was isomeric, but not identical with, 3,7,12-triketocholelic acid. Mild reduction of Tschesche's acid yielded the known 7,12-diketocholic acid. Because of the apparent ease with which the new triketo acid underwent enolization, Tschesche considered position C_4 the most likely point of attachment of the hydroxyl group. More recently, Asikari⁵ revised Tschesche's formula by attaching the unplaced hydroxyl group to the C_8 -position, (II). His evidence favoring this revision was based on the observation that scymnol may readily be degraded to cholic acid (III) by way of the oxidation of its tetra-acetate.



to bile acids, and the latter has assigned to it the provisional formula I. In this formula the posi-

It was one of the objects of the present investigation to prove definitely the location of the hydroxyl group and to explain the contradictory results obtained by Tschesche and Asikari. The scymnol used in the present study was isolated

- (1) Hammarsten, *Z. physiol. Chem.*, **24**, 322 (1898).
- (2) Cook, *Nature*, **147**, 388 (1941).
- (3) Windaus, Bergmann and König, *Z. physiol. Chem.*, **189**, 148 (1930).
- (4) Tschesche, *ibid.*, **203**, 263 (1931).

- (5) Asikari, *J. Biochem. (Japan)*, **29**, 319 (1939).