removed, suspended in methyl alcohol in which it is nearly insoluble, the resulting mixture centrifuged and the semi-solid separated out and subjected to a high vacuum in order to remove traces of the solvent.

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.25; H, 11.18. Found: C, 83.47; H, 11.07.

This carbinol is highly unsaturated and is very susceptible to air oxidation. It cannot be distilled without decomposition. When distilled with phenyl isocyanate, a nearly colorless hydrocarbon comes over which becomes immediately deep red upon condensation, and on redistillation comes over at about 101° (0.5 mm.). This highly colored hydrocarbon, which is also formed together with water by the distillation of the carbinol with potassium hydrogen sulfate, shows properties that resemble those of carotene and vitamin A. With a solution of antimony trichloride in chloroform, this hydrocarbon yields instantly a purple color which changes immediately into blue and finally on longer standing into light brown. On standing at room temperature in presence of air, it undergoes a change from a clear red to a dirty brown color. It decolorizes bromine water instantly, thereby changing into a light brown colored liquid. Unfortunately, the quantities obtained were too small to carry out further studies on the structure of this hydrocarbon. However, from its preparation and qualitative reactions, one may tentatively assign to it structure (IV), although cyclization might have occurred to produce a different structure. No definite answer with regard to the structure of this hydrocarbon can therefore be given at present.

Summary

1. The following compounds have been synthesized and some of their reactions studied: methylethylallylcarbinol, 4-methyl-1,3-hexadiene, 4-bromo-4-methyl-1-hexene, 1,4-dibromo-4-methyl-2-hexene, 1,2,4-tribromo-4-methylhexane and 1-bromo-4-methyl-2,4-hexadiene.

2. A carbinol, 3,7-dimethyl-1-(1′,1′,3′-trimethyl-3′-cyclohexenyl-2′)-nona-1,5,7-trien-3-ol, related to vitamin A has been synthesized by the condensation of 1-bromo-4-methyl-2,4-hexadiene with α-ionone in presence of magnesium. This carbinol yields on dehydration a highly colored hydrocarbon which has properties that resemble those of carotene and vitamin A.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

The Structure of Troeger's Base

BY M. A. SPIELMAN[1]

Troeger's base $C_{17}H_{18}N_2$ is a substance formed by the condensation of formaldehyde with *p*-toluidine in acid solution.[2] Troeger assigned to his compound formula I and adduced as evidence two principal reactions. The first of these was with acetic anhydride to form a rather intractable diacetyl derivative which he believed to be dimolecular with respect to the base. The second reaction was with oxides of nitrogen and resulted in the evolution of carbon dioxide and the formation of a dinitrosamine of anomalous composition. Löb,[3] Goecke[4] and Lepetit, Maffei and Maimeri[5] have isolated Troeger's base, and the first two authors have proposed structures not in keeping with the empirical formula which now seems well established. Eisner and Wagner[6] have recently encountered the base in connection with their study of the condensation of aromatic amines with formaldehyde; they have confirmed earlier work in a general way and have suggested II as a tentative formula. Although this rationalizes the formation of a dinitroso and diacetyl derivative, it is obviously open to serious objections on stereochemical grounds.

Experiments described in this paper have led to an entirely different interpretation of the reactions of Troeger's base, and formula III is here offered as best representing the chemical properties of this interesting substance. The formula is drawn so that the tetrahydroquinazoline structure is apparent, but when a molecule is constructed from atomic models it is found to be symmetrical and composed of four six-membered rings condensed without strain.

The absence of any reaction with phenyl isocyanate or with phenyl mustard oil rendered improbable the presence of imino hydrogen atoms, and resistance to reduction with metals and acids or sodium and alcohol eliminated the grouping —N=C<. Acetylation proceeded readily, and a diacetyl derivative (V) was iso-

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(1) National Research Council Fellow.

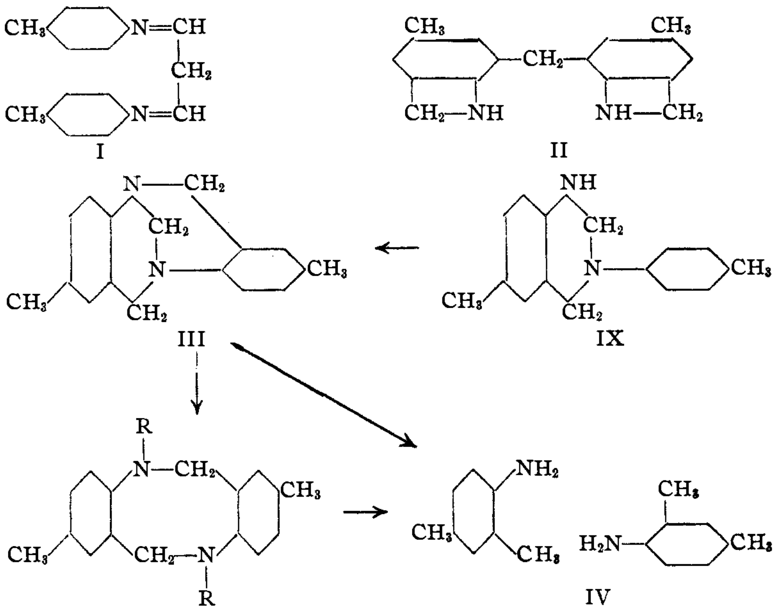
(2) Troeger, *J. prakt. Chem.*, [2] **36**, 227 (1887).

(3) Löb, *Z. Elektrochem.*, **4**, 428 (1898).

(4) Goecke, *ibid.*, **9**, 470 (1903).

(5) Lepetit and Maimeri, *Atti accad. Lincei*, [5] **26**, 558 (1917); Lepetit, Maffei and Maimeri, *Gazz. chim. ital.*, **57**, 862 (1927).

(6) Eisner and Wagner, THIS JOURNAL, **56**, 1938 (1934).



V R = $COCH_3$
VI R = COC_6H_5
VII R = NO
VIII R = H

lated, *but the reaction involved the loss of one carbon atom.* The loss was in the form of formaldehyde which was characterized as the methone derivative.[7] Benzoylation to form VI also entailed a similar loss, a reaction not without parallel in analogous heterocyclic systems.[8] The dinitrosamine described by Troeger is undoubtedly VII, and the carbon dioxide which he observed as a by-product came from the oxidation of the formaldehyde first liberated. Attempts to prepare the base VIII by hydrolysis of V or cautious reduction of VII led to resinous solids of no value in this study. The ring system is that of Schroeter and Eisleb's dianthranilide.[9]

Degradation with hydriodic acid at 200° gave as a single isolable product 4-amino-1,3-xylene (IV). When the base was first boiled with hydriodic acid and then reduced with tin and hydrochloric acid, the same substance was formed, and in amounts greater than could have been obtained had there been but one xylidine nucleus in each molecule. Similarly, the dinitrosamine (VII) gave, on reduction with tin and hydrochloric acid, more than one equivalent of 4-amino-1,3-xylene.

As a final check on the proposed structure, Troeger's base was synthesized by condensing the tetrahydroquinazoline (IX)[10] with formaldehyde in acid solution.

Experimental Part

Troeger's Base (III).—Goecke's "chemical method" of synthesis was found to be satisfactory. The product was twice crystallized as the hydrochloride from dilute hydrochloric acid and twice as the free base from dilute alcohol. The snow-white, felted crystals melted at 135–136° and showed a pronounced tendency to become electrified when rubbed.

Anal. Calcd. for $C_{17}H_{18}N_2$: C, 81.60; H, 7.20; N, 11.20. Found: C, 81.54; H, 7.30; N, 11.00.

The hydrochloride could not be prepared as an individual substance, but varied in composition with the method of drying. Air-dried, it melted at 213°, and analyses fitted best for the monohydrate of a monohydrochloride.

Anal. Calcd. for $C_{17}H_{18}N_2 \cdot HCl \cdot H_2O$: C, 66.95; H, 6.95; H_2O, 5.90; neut. equiv., 304. Found: C, 67.67; H, 7.00; H_2O, 5.47; neut. equiv., 308.

The picrate recrystallized from alcohol melted at 188–189° in agreement with the value reported by Troeger but above that of Eisner and Wagner.

Anal. Calcd. for $C_{23}H_{21}N_5O_7$: C, 57.62; H, 4.39. Found: C, 57.29; H, 4.46.

The diacetyl derivative (V) was formed in nearly quantitative yield by boiling 2 g. of base with 30 cc. of acetic anhydride. The odor of formaldehyde was noticeable. The acetyl derivative was isolated by decomposing the excess of reagent with water and then pouring the reaction mixture into 100 cc. of water. It is very insoluble in alcohol but crystallized well by dilution of an acetic acid solution with water; microcrystalline rods, m. p. 286–288°.

Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.49; H, 6.89; mol. wt., 322. Found: C, 74.45; H, 6.79; mol. wt. (Rast), 324.

To demonstrate the formation of formaldehyde during acetylation, a 1-g. sample was boiled with 10 cc. of acetic anhydride in a flask arranged so that the effluent vapors passed into 50 cc. of water. After the reaction, 50 cc. of 1% methone solution was added to the water trap and a crop of silky needles soon separated; m. p. and mixed m. p. 184–186°. The acetylation mixture was diluted to precipitate most of the diacetyl derivative. Addition of 50 cc. of methone solution caused the separation of a mixture of formaldehyde methone and diacetyl derivative which was easily separated into its components by virtue of the insolubility of the latter in alcohol. The combined crops of formaldehyde methone weighed 0.14 g. A blank experiment gave negative results.

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[7] Klein and Linser, *Mikrochem.*, Pregl Festschr., 204 (1929).

[8] Meyer and Jacobson, Vol. II (3), p. 1237; compare also pp. 445, 482 and 488–492.

[9] Schroeter and Eisleb, *Ann.*, **367**, 101 (1909).

[10] Von Walther and Bamberg, *J. prakt. Chem.*, [2] **73**, 209 (1906); Ref. 6, p. 1942.

The diacetyl derivative could not be hydrolyzed with alcoholic potash, but with sirupy phosphoric acid gave a red, amorphous, basic material which did not melt completely at 300°.

The dibenzoyl derivative (VI) was prepared by the addition of benzoyl chloride to a pyridine solution of the base; platelets from toluene–alcohol, m. p. 290–291°.

Anal. Calcd. for $C_{30}H_{26}N_2O_2$: C, 80.68; H, 5.87. Found: C, 80.90; H, 6.14.

The dinitroso derivative (VII) was formed by adding sodium nitrite to a solution of the hydrochloride in dilute hydrochloric acid. It is practically insoluble in alcohol but crystallizes as needles from glacial acetic acid and as plates from toluene; m. p. 246–247° (254–255° corr.).

Anal. Calcd. for $C_{16}H_{16}N_4O_2$: C, 64.84; H, 5.44. Found: C, 64.83, 64.94; H, 5.57, 5.28.

General Chemical Properties.—Troeger's base is unaffected by sodium and boiling alcohol, and practically so by tin and hydrochloric acid. It is not oxidized by mercuric oxide in ether or by ammoniacal silver nitrate, and forms no silver salt. It gives no evidence of coupling with diazotized *p*-toluidine in acid or alkaline solution. It may be recovered unchanged after standing overnight with phenyl isocyanate or phenyl mustard oil in dry benzene solution.

Reduction.—One gram of base was sealed in a bomb tube with 15 cc. of hydriodic acid (*d.* 1.57) and 1 g. of red phosphorus and heated to 200° for ten hours. The clear solution was made alkaline and steam distilled. The oily droplets floating on the surface of the distillate were benzoylated by shaking the alkaline suspension with benzoyl chloride. The solid was filtered off and crystallized once from dilute alcohol. The needles of 4-benzoylamino-1,3-xylene weighed 0.45 g.; m. p. and mixed m. p. 188°. No other product was isolated.

To achieve a more complete degradation, a 1-g. sample was boiled for ten hours with 15 cc. of hydriodic acid and a little red phosphorus. Tin and concd. hydrochloric acid were then added and the mixture was boiled until about 40 g. of tin had been consumed. After dilution with 300 cc. of water the tin was removed with hydrogen sulfide. The filtered solution was concentrated to small volume, made alkaline, steam distilled, and the distillate was benzoylated as before. The product was crystallized from dilute alcohol. The first crop weighed 0.82 g. and melted at 188–189°. The mother liquors were worked over and another 0.10-g. crop melting at 185° was obtained. In view of the manipulations involved, the amount isolated seems safely above what might be expected if there were only one xylidine nucleus in each molecule of the original base. A control experiment with the same steps showed that recovery of recrystallized material is 70–80%.

One gram of the dinitroso derivative (VII) was reduced directly with tin and hydrochloric acid to which alcohol was added in the early stages to increase solubility. It was worked up as in the foregoing experiment. The first crop of 4-benzoylamino-1,3-xylene weighed 0.72 g. and melted at 187–188°. Dilution of the mother liquor gave 0.05 g. melting at 185°. One xylidine molecule per mole of base would have yielded a maximum of 0.77 g. of benzoyl derivative had all manipulations and reactions been quantitative.

Synthesis.—To a solution of 10 cc. of alcohol, 5 cc. of concd. hydrochloric acid and 2 cc. of formaldehyde (*ca.* 40%) was added in small portions with shaking 1 g. of 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (IX). After standing overnight the mixture was diluted with water and made alkaline with ammonia. An oil separated and soon solidified. It was filtered off, washed thoroughly and crystallized once as the hydrochloride from dilute hydrochloric acid; yield 0.72 g., m. p. 210–211°. The free base melted at 135–136° and the m. p. was not depressed by mixture with Troeger's base. The picrate was prepared and found to be identical with the authentic specimen.

Summary

On the basis of experiments involving acylation, nitrosation and drastic reduction, Troeger's base has been shown to be 1,2′-methylene-3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline. A synthesis has been accomplished.

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