ing, a bright lemon-yellow precipitate formed which was filtered, washed with alcohol and dried to give 6.4 g. (quantitative) of the poly-*p*-xylylidene (II), m.p. > 400°. The alcohol filtrate gave 13.4 g. (77%) of triphenylphosphine oxide, m.p. 158–159°.

Compound II was extracted with benzene to remove lower molecular weight material. Infrared and oxygen analyses indicated that II had an average value of $n = 9$, with aldehyde end groups.

*Anal.* Calcd. for $(C_8H_6)_n$: C, 94.1; H, 5.9. Calcd. for $C_{80}H_{60}O_2$: C, 91.2; H, 5.7; O, 3.0. Found: C, 91.0; H, 5.8; O, 3.2.[10]

Reaction of II with bromine in carbon tetrachloride gave a colorless solid, primarily the saturated, brominated analog of II, $C_{80}H_{60}Br_{18}O_2$.

*Anal.* Calcd. for $(C_8H_6Br_2)_n$: C, 36.6; H, 2.4; Br, 61.0. Calcd. for $C_{80}H_{60}Br_{18}O_2$: C, 38.5; H, 2.4; Br, 57.8. Found: C, 34.3; H, 2.2; Br, 55.9.

**2-Methoxy-5-methylal-α-chlorotoluene (III).**—Anisaldehyde was chloromethylated according to the procedure of Quelet and Allard.[6] The yield of III was 65%.

**(2-Methoxy-5-methylalbenzyl)-triphenylphosphonium Chloride (IV).**—A mixture of 74.7 g. (0.40 mole) of 2-methoxy-5-methylal-α-chlorotoluene (III) and 131 g. (0.50 mole) of triphenylphosphine in 600 ml. of xylene was heated under reflux for 20 hours. The off-white crystalline product was isolated by filtration, washed with xylene and dried *in vacuo* at 60°; yield 173.7 g. (97%), m.p. 207–209°. An analytical sample was recrystallized from dimethylformamide to give colorless needles, m.p. 208–210°.

*Anal.* Calcd. for $C_{27}H_{24}Cl_2O_2P$: C, 72.6; H, 5.4; Cl, 7.9. Found: C, 72.2; H, 5.7; Cl (total), 7.6.

**Polymerization of IV.**—To a solution of 10.0 g. (0.021 mole) of IV in 100 ml. of ethanol was added a solution of 0.16 g. (0.023 g. atom) of lithium dissolved in ethanol (100 ml.). The colorless poly-*m*-xylylidene (V) which precipitated from solution was isolated by filtration, washing with methanol and dried *in vacuo* at 60°. The yield of V was 2.4 g. (81%), with the polymer melt temperature of about 180° and inherent viscosity of 0.31.[7] The infrared spectrum showed the presence of unsaturation and carboxyaldehyde, presumably as end groups. No band attributable to the phosphonium salt group[8] was observed.

*Anal.* Calcd. for $(C_9H_9O)_n$: C, 81.2; H, 6.81; O, 12.02. Found: C, 80.9, 80.7; H, 6.34, 6.44; O, 12.15, 12.07.

The preparation of V also was carried out by the action of anhydrous sodium methylate on IV in dimethyl sulfoxide solution. The polymer obtained had an inherent viscosity of 0.21.[7]

**(4-Hydroxyphenyl)-triphenylphosphonium Bromide (VI).**—A mixture of 84 g. (0.33 mole) of triphenylphosphine and 56 g. (0.32 mole) of *p*-bromophenol was melted and stirred together under nitrogen. The mixture was heated for 4 hours at 200°, cooled to room temperature then mixed with 50 ml. of anisole and 50 ml. of cyclohexane. The top layer was separated and rejected, and the bottom layer was diluted with an additional 25 ml. of anisole and set aside in the refrigerator for 48 hours. In this manner 77 g. (44% based on a solvate with one mole of anisole) of a coarse, crystalline product was obtained essentially free of gummy by-products. The product was purified by recrystallization from anisole. Analysis of a freshly crystallized sample showed 14.6% ionic bromide *vs.* the calculated 18.4%. A direct oxygen analysis gave 5.82 and 5.88%. This and the bromide analysis corresponded to a solvate containing one mole of anisole. Prolonged heating *in vacuo* removed the solvent. The infrared spectrum showed no carbonyl and two types of benzene rings, both mono- and disubstituted. No band attributable to the phenolic hydroxyl could be detected.

*Anal.* Calcd. for $C_{24}H_{20}OPBr$: C, 66.2; H, 4.60. Found: C, 66.5, 66.2; H, 4.69, 4.81.

---

[10] The method of J. Unterzaucher, *Analyst*, **77**, 584 (1952), was employed for direct oxygen determination.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

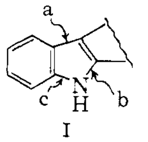
# Dehydration of α-Phenylcyclohexanone Oxime

BY ERNEST WENKERT AND BUFORD F. BARNETT

RECEIVED NOVEMBER 9, 1959

The pyrolysis of α-phenylcyclohexanone oxime in a closed system and the characterization of the resulting products are described. The oxidation of tetrahydrocarbazole to carbazole by cyclohexanone oxime and the significance of this novel dehydrogenation in relation to the oxime pyrolysis is discussed. Both the thermal and acid-catalyzed conversions of 2-hydroxylaminobiphenyl to azo, azoxy and amino systems are portrayed. A variant of the Neber reaction on an ester of 2-phenylcyclohexanone oxime is described.

The most common methods of synthesis of indolic compounds (I) involve the formation of bonds a or b of the heterocyclic ring (*cf.* I) at the end of a reaction sequence, *e.g.*, the Fischer or Reissert syntheses. However, an occasion may arise which would demand the creation of bond c (*cf.* I) as the final step of a series of conversions of aromatic precursors. Such procedure is illustrated by three recently reported, different syntheses of carbazole derivatives. The pyrolysis of *o*-nitrobiphenyl with ferrous oxalate[1] as well as the pyrolysis or ultraviolet irradiation of *o*-axidobiphenyl[2] have been shown to yield carbazole, while the pyrolysis of α-phenylcycloalkanone oximes has led to 2,3-cycloalkindoles.[3] The last of these processes appears to be of potentially widest utility. For this reason a study of the pyrolysis of α-phenylcyclohexanone oxime was undertaken. While, as will be seen, this pyrolysis in a closed system was of greatly inferior synthetic value to that already explored in an open system,[3b] it led to valuable tangential information



I

Heating of a benzene solution of α-phenylcyclohexanone oxime (IIa) in a sealed tube at 270° for twenty-four hours yielded a complex mixture of products from which the following substances could be isolated and characterized: carbazole (III), tetrahydrocarbazole (IV), α-phenylcyclohexanone (IIb), *trans*-2-phenylcyclohexanol (Va), *o*-hydroxybiphenyl (VIa), *trans*-2-phenylcyclohexylamine (Vb), *o*-aminobiphenyl (VIb), ε-phenyl-ε-caprolac-

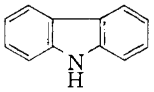
---

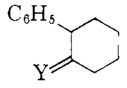
[1] H. C. Waterman, *J. Org. Chem.*, **14**, 289 (1949).

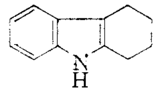
[2] P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

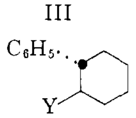
[3] (a) D. Ginsburg and R. Pappo, *ibid.*, **75**, 1094 (1953); (b) D. Ginsburg and A. Loffler, *Nature*, **172**, 820 (1953).

tam (VII), ε-phenylcaproamide (VIIIa), ε-phenylcapronitrile (VIIIb), the olefinic amide and nitrile, IXa and b, respectively, and ammonia. Both the acidic and basic products were isolated in separate runs and characterized as their 3,5-dinitrobenzoates. The liquid alcohol Va also was converted into such a derivative. Except for the nitriles VIIIb and IXb, all neutral products could be separated by alumina chromatography. Both nitriles coeluted with the ketone IIb. As a consequence this mixture was hydrolyzed with sulfuric acid to carboxylic acids, converted to the amides VIIIa and IXa and then separated by chromatography.

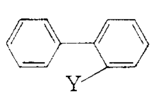

III

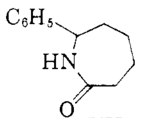

IIa, Y = NOH
b, Y = O
c, Y = NH


IV


V

a, Y = OH
b, Y = NH$_2$
c, Y = NOH
d, Y = N = )$_2$


VI

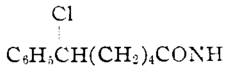

VII

$C_6H_5(CH_2)_5R$
VIII

$C_6H_5CH{=}CH(CH_2)_3R$
IX

a, R = CONH$_2$
b, R = CN

With the exception of the lactam VII and amide IXa, all pyrolysis products are of known constitution and were identified by comparison with authentic samples. The lactam proved to be identical with the Beckmann rearrangement product of α-phenylcyclohexanone oxime (IIa), readily obtained by treatment of the latter with tosyl chloride in pyridine. Its structure was shown to be VII (and hence its precursor IIa has its hydroxyl function oriented *anti* to the neighboring phenyl group) by its conversion to the olefinic amide IXa. Acid hydrolysis of the lactam, followed by treatment with nitrous acid, thionyl chloride and ammonia, led to ε-phenyl-ε-chlorocaproamide (X). Further treatment with ammonia or collidine transformed X into the amide IXa. The latter's structure was established by the conversion of δ-benzoylvaleric acid into the chloroamide X, by sodium borohydride reduction and thionyl chloride and ammonia treatments.

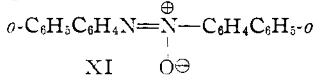


$$C_6H_5\overset{Cl}{CH}(CH_2)_4CONH_2$$

X

While the pyrolysate contained yet other compounds, only the above twelve organic products lent themselves to ready identification. However, they were sufficient to recognize the co-occurrence of three different chemical processes during the pyrolysis of the starting oxime: (a) cyclization to heterocyclic compounds, (b) oxidation–reduction reactions, and (c) rearrangement–cleavage reactions. Since even a major product, carbazole (III), represented an anomalous state of oxidation, an investigation of its genesis appeared likely to shed some light on process b.[4] As the oxime IIa might have undergone oxidation prior to cyclization, or *vice versa*, both the cyclization behavior of *o*-hydroxylaminobiphenyl (VIc) and the oxidizability of tetrahydrocarbazole (IV) were investigated.

Reduction of *o*-nitrobiphenyl by zinc and ammonium chloride afforded *o*-hydroxylaminobiphenyl (VIc). Refluxing of a toluene solution of the latter yielded *o*-aminobiphenyl (VIb), characterized as an acetamide, and *o*-azoxybiphenyl (XI), while pyrolysis of its benzene solution at 250° in a sealed tube gave the same products as well as *o*-azobiphenyl (VId). These results are closely analogous to those reported for the pyrolysis of phenylhydroxylamine.[5] The lack of production of carbazole suggested that in its formation from the oxime IIa cyclization must take place at an early stage in the reaction sequence.



$$o\text{-}C_6H_5C_6H_4N{=}\underset{O^{\ominus}}{\overset{\oplus}{N}}{-}C_6H_4C_6H_5\text{-}o$$

XI

Two compounds, hydroxylamine and starting oxime IIa, were considered likely candidates as oxidizing agents in the possible conversion of tetrahydrocarbazole IV to carbazole III. Hydroxylamine, a substance of intermediate state of oxidation among inorganic nitrogen compounds, has revealed recently unusual reducing capacity.[6] However, it did not prove to be an effective oxidizing agent, since it could be shown that pyrolysis of a benzene solution of hydroxylamine and tetrahydrocarbazole led to no carbazole. On the other hand, pyrolysis of a benzene solution of cyclohexanone oxime and tetrahydrocarbazole gave high yields of carbazole. The last reaction indicates that *oximes may be useful reagents for the dehydrogenation of hydroheteroaromatic compounds.*

It now was clear that α-phenylcyclohexanone oxime (IIa) could act as the oxidizing agent of its own cyclization product. In this capacity it would have been reduced to a hydroxylamine, which, in turn, could have served as the precursor of α-phenylcyclohexanone (IIb), its amine IIc and ammonia[7]

$$\underset{\text{Vc}}{-\overset{|}{C}HNOH} \xrightarrow{\Delta} \underset{\text{IIc}}{>C{=}NH} + H_2O \rightleftarrows \underset{\text{IIb}}{>C{=}O} + NH_3$$

Since compounds IIb and c can serve as oxidizing agents also, their disproportionation into Va and

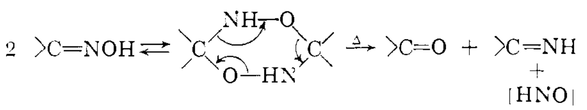
---

[4] It was of interest that even the dry distillation of oximes (of 2-phenyl-2-cyclohexenone and 2-phenyl-2-cycloheptenone) has led to products of abnormal oxidation states (carbazole and 2,3-cycloheptindole, respectively).[3]

[5] E. Müller and E. Lindemann, *Angew. Chem.*, **46**, 681 (1933).

[6] E. Wenkert, B. S. Bernstein and J. H. Udelhofen, THIS JOURNAL, **80**, 4899 (1958).

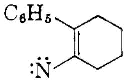
[7] It is of interest that the pyrolysis of benzophenone oxime also leads to ketone and imine products [A. Lachman, THIS JOURNAL, **46**, 1477 (1924); "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 234]. The mechanism of the thermal transformation of this ketoxime cannot be the same as that of oxime IIa and can be represented best as



However, the possibility of IIa undergoing a similar disproportionation along side with that discussed above is not excluded.

VIa, and Vb and VIb, respectively, can account for the presence of all pyrolysis products in abnormal states of oxidation. Furthermore, since the early stages of these disproportionations, *i.e.*, those prior to the formation of aromatic substances (VI), most likely are equilibrium processes, it was not surprising to find the reduction products V in their most stable, hence *trans*, stereochemical configuration.

While the present data do not permit a detailed analysis of the mechanism of the thermal conversion of $\alpha$-phenylcyclohexanone oxime (IIa) into tetrahydrocarbazole (IV), the enamine diradical XII or its cation or free radical counterparts are the most likely intermediates. However, the possible intermediacy of XII, a species postulated to be the intermediate in the Neber rearrangement,[8] suggested that the synthesis of indolic systems from oximes might be realized by way of the Neber process. A good omen in this regard was the report of the conversion of *o*-azidobiphenyl into carbazole by pyrolysis or irradiation,[2] a reaction which involves the intervention of a diradical analogous to XII.[9]



XII

Since tosylation of 2-phenylcyclohexanone oxime (IIa) already had yielded a Beckmann product (VII), a 3,5-dinitrobenzoate was prepared for the Neber reaction. Treatment of a benzene solution of the ester with triethylamine yielded mainly trivial products, the oxime IIa, 3,5-dinitrobenzoic acid and a small amount of ethyl 3,5-dinitrobenzoate, probably due to the presence of water and ethanol in distilled commercial triethylamine. However, a minor reaction product was tetrahydrocarbazole. While exploration of this novel synthesis of a heterocycle has not yet been pursued further, the present result indicates strongly that under suitable circumstances the Neber reaction may be used for the construction of aromatic heterocyclic substances.

The availability of an ample supply of *o*-hydroxylaminobiphenyl (VIc) permitted an inspection of the behavior of this compound toward acid. This was of interest because of the possibility of an acid-catalyzed dehydration leading to yet a new method of synthesis of carbazoles.[10]

However, heating of *o*-hydroxylaminobiphenyl (VIc) in a 20% sulfuric acid solution at 100° led to good yields of *o*-azoxybiphenyl (XI) and *o*-aminobiphenyl (VIb), isolated and characterized as its benzamide. Similar results were obtained from a run involving a dilute aqueous *p*-toluenesulfonic acid solution under a nitrogen atmosphere. A pyrolysis of the latter solution of VIc in a nitrogen-swept sealed tube at 250° yielded the same two products and *o*-azobiphenyl (VId) in addition.

## Experimental

**Pyrolysis of $\alpha$-Phenylcyclohexanone Oxime.**—A solution of 10.00 g. of $\alpha$-phenylcyclohexanone oxime (IIa), m.p. 173–174° (lit.[11] m.p. 174–175°), in 30 ml. of benzene was poured into a Carius tube, cooled in a Dry Ice–acetone-bath and the tube sealed and allowed to warm to room temperature. Thereupon the tube was placed into an electrically heated furnace and left for 24 hr. at 270°. After opening of the tube, during which process a strong odor of ammonia was emitted, the contents were transferred to a separatory funnel, the Carius tube rinsed several times with benzene and the combined brown organic solutions extracted with water, 10% sodium hydroxide and 10% hydrochloric acid solutions. Extraction of the water washings with various organic solvents and further work-up failed to yield any appreciable quantity of organic products. Isolation of products from the acidic, basic and neutral extracts was carried out in the following manner.

**Acidic Products.**—Acidification of the sodium hydroxide solution with hydrochloric acid, extraction of the mixture with ether and evaporation of the latter yielded 450 mg. of a tar-like material. It was dissolved in 10 ml. of pyridine, 2 ml. of benzoyl chloride was added, and the mixture allowed to stand for 12 hr. It then was poured into ice-water, the supernatant solution decanted and the remaining oily black residue dissolved in benzene. Chromatography of the resulting organic solution on 50 g. of alumina gave only one major product, on elution with 1:1 petroleum ether–benzene. Crystallization from petroleum ether afforded 700 mg. of colorless crystalline *o*-hydroxybiphenyl benzoate, m.p. 73–76°, m.m.p. 73–75° with an authentic sample (m.p. 74–76°); infrared spectrum identical with that of an authentic specimen.

**Basic Products.**—Basification of the hydrochloric acid solution with sodium hydroxide, extraction of the mixture with ether and evaporation of the latter yielded 800 mg. of an oily residue. Benzoylation as above and chromatography on 30 g. of alumina gave two major products. Elution with 3:1 benzene–ether afforded 620 mg. of crystalline *trans*-2-phenylcyclohexylamine benzoate, m.p. 179–182°, m.m.p. 180–182° with an authentic sample (m.p. 181–182°); infrared spectrum identical with that of an authentic specimen. Elution with 1:1 benzene–ether yielded 600 mg. of a solid, which on crystallization from cyclohexane proved to be *o*-benzamidobiphenyl, m.p. 83–86°, m.m.p. 82–84° with an authentic sample (m.p. 85–86°); infrared spectrum identical with that of an authentic specimen.

**Neutral Products.**—The combined neutral benzene solutions from five pyrolysis runs, which had been extracted with six 100-ml. portions of water, sodium hydroxide and hydrochloric acid solutions, were washed with saturated sodium chloride solution, filtered through dry sodium sulfate and concentrated under reduced pressure to *ca.* a 150-ml. volume. The concentrate was placed on a 10 × 50 cm. chromatography column, packed with 5 kg. of alumina. The mixture was eluted with 5-l. portions of solvents of increasing polarity. Elution with petroleum ether gave 7.50 g. of fraction A; 9:1 petroleum ether–benzene, 9.46 g. of B; 3:1 petroleum ether–benzene 5.45 g. C; 1:1 petroleum ether–benzene, 3.72 g. D; benzene, 2.30 g. E; 3:1 benzene–ether, 4.51 g. F; 1:1 benzene–ether, 3.80 g. G; ether, 3.30 g. H; 3:1 ether–methanol, 4.00 g. I. Since these fractions still consisted of mixtures, they were rechromatographed individually on alumina columns, containing a 30:1 ratio of alumina to sample, and 100-ml. fractions were collected by an automatic fraction collector. Progress of the separation was followed by spot infrared spectral analysis. Of the various compounds finally isolated the following were identified readily by their characteristic absorptions: $\alpha$-phenylcyclohexanone (IIb) by its peaks at 5.8, 6.65, 6.85 and 8.85 $\mu$; tetrahydrocarbazole (IV) by peaks at 2.85, 3.4, 7.6, 7.73 $\mu$, by a strong peak at 6.85 $\mu$ and shoulder at 6.95 $\mu$; carbazole (III) by peaks at 2.8, 7.55, 8.12 $\mu$, a doublet at 6.90 and 6.96 $\mu$, and the lack of a 3.4 $\mu$ peak; the nitriles VIIIb and IXb by their absorption at 4.5 $\mu$.

---

[8] D. J. Cram and M. J. Hatch, THIS JOURNAL, **75**, 33, 38 (1953).

[9] Curiously, no cyclization has been reported to take place during the irradiation of $\beta$-phenylethyl azide[2] or the Neber reactions on phenylacetone oxime tosylates.[8] This inactivity may be due in part to a strict steric requirement—a rigidly held, close proximity of the two intramolecularly interacting functional groups. The first case does not fulfill this requirement at all, while the second case may not either, should the more stable configuration of its enamine diradical require a *trans* orientation of the aryl group and the nitrogen atom.

[10] However, *cf.*, E. Bamberger, *Ber.*, **27**, 1347 (1894), and subsequent papers.

[11] J. von Braun, H. Gruber and G. Kirchboun, *Ber.*, **55**, 3670 (1926).

Chromatography of fraction A yielded 200 fractions which could be combined on the basis of their spectral properties into eight fractions, A-1 through A-8. Crystallization of A-4 afforded α-phenylcyclohexanone, leaving A-4a as mother liquor.

Dissolution of fraction B in benzene precipitated carbazole (B-1). Chromatography of a mixture of the residual solution and A-1, A-4a, A-5, A-6 and A-8 yielded 70 fractions whose combination resulted in B-2 to B-9 fractions. More α-phenylcyclohexanone was obtained by the crystallization of fractions B-2, 3 and 4.

Chromatography of a mixture of fraction C and the mother liquors B-3a, 4a, 5, 6, 8 and 9 gave 140 fractions whose combination resulted in ten fractions, C-1 through C-10. Crystallization of C-1 and 2 led to more ketone IIb, C-4 to tetrahydrocarbazole and C-5 to carbazole.

Dissolution of fraction D in benzene–cyclohexane precipitated more carbazole (D-1). Gradient elution chromatography of a mixture of the mother liquor and C-1a, 4a, 5a and 10 gave 257 fractions, combined into D-2 to D-9. Crystallization of D-2 afforded more ketone IIb and D-3 more carbazole.

Fraction E proved to be mostly carbazole. Neither fraction F nor G gave recognizable products. Hence they were combined with H and the mixture chromatographed. The resulting 390 fractions were combined into fractions H-1 to H-11. Crystallization of H-1 yielded more ketone IIb, H-3 the lactam VII and H-5 the amide VIIIa. Fraction H-11 appeared to be an alcohol. Its conversion to a 3,5-dinitrobenzoate in the usual manner led to the derivative of Va.

Chromatography of fraction I and H-2, 3a, 4, 5a, 6, 7 and 10 gave 380 fractions whose combination resulted in the isolation of fractions I-1 to I-14. Crystallization of I-3 yielded more amide VIIIa, while I-6 and 7 gave the olefinic amide IXa.

Since a spectral analysis of fractions A-2, B-2a and C-1a revealed the presence of nitriles as well as ketone IIb, they were combined and the mixture rechromatographed. However, two such separation attempts, with the use of alumina of different activities, failed. As a consequence, all chromatographic fractions were recombined, their solvents completely removed, and the resulting oil refluxed with 50 ml. of 20% sulfuric acid for 2 hr. The cooled mixture was extracted with ether, and the extract evaporated to dryness. The oily residue was refluxed with 30 ml. of thionyl chloride for 1 hr. Thereupon it was poured into excess ice-cold ammonium hydroxide. The precipitated material was filtered, dissolved in a small amount of benzene and chromatographed on 250 g. of alumina. Elution with 1:1 benzene–ether gave first the saturated amide VIIIa and then the unsaturated one IXa.

The yields of all recognizable products, isolated in the above manner, follow. Crystallization from petroleum ether gave 12.49 g. of α-phenylcyclohexanone (IIb), m.p. 56–58°; crystallization from benzene–cyclohexane yielded 7.39 g. of carbazole (III), m.p. 238–240°; crystallization from petroleum ether afforded 1.25 .g of tetrahydrocarbazole (IV), m.p. 116–118°; crystallization from cyclohexane gave 1.20 g. of ε-phenylcaproamide (VIIIa), m.p. 94–96°; crystallization from aqueous ethanol afforded 4.1 g. of *trans*-2-phenylcyclohexanol 3,5-dinitrobenzoate, m.p. 120–121°, corresponding to a minimum yield of 2.1 g. of the alcohol Va itself. The authenticity of these compounds was substantiated by direct comparison with samples of known constitution. Crystallization from aqueous ethanol led to 1.2 g. of ε-phenyl-ε-caprolactam (VII), m.p. 136–138°; crystallization from cyclohexane yielded 2.4 g. of the unsaturated amide IXa. Both compounds were identical with substances whose characterization is described below. Finally, the minimum yields of nitriles, based on the recovery of their hydrolysis products, amounted to 1.3 g. of ε-phenylcapronitrile (VIIIb) and 2.7 g. of the unsaturated nitrile IXb.

**ε-Phenyl-ε-chlorocaproamide (X).**—Sodium borohydride, 2 g., was added in small portions with vigorous stirring to a 5% sodium carbonate solution of 4 g. of δ-benzoylvaleric acid. The mixture then was stirred for 2 hr. It was acidified by dropwise addition of 10% hydrochloric acid, saturated with sodium chloride and extracted with ether. The extract was washed with saturated brine solution, filtered through anhydrous sodium sulfate and evaporated under reduced pressure. The residue was refluxed with 20 ml. of thionyl chloride for 30 min. and the cooled solution poured into 75 ml. of ice-cold ammonium hydroxide. The precipitate, forming on standing, was crystallized from aqueous ethanol yielding colorless crystals of ε-phenyl-ε-chlorocaproamide, m.p. 90–92°.

*Anal.* Calcd. for $C_{12}H_{16}ONCl$: C, 64.02; H, 7.08; N, 6.05. Found: C, 64.35; H, 7.31; N, 5.86.

**Amide IXa.**—A collidine solution (10 ml.) of the above chloroamide was refluxed for 1 hr., poured into water, acidified with 10% hydrochloric acid and extracted with ether. Vacuum removal of the solvent led to an oily residue, whose ethanol solution could be decolorized with Norite. Crystallization from aqueous ethanol gave 1.6 g. of the amide IXa, m.p. 106–107°; spectra: ultraviolet (95% ethanol), $\lambda_{max}$ 252 mμ (log ε 4.40), $\lambda_{min}$ 223 mμ (log ε 3.68); infrared ($CHCl_3$), NH 2.83(m), 2.92(m) C=O, 5.96(s), C=C 6.27(m)μ.

*Anal.* Calcd. for $C_{12}H_{15}ON$: C, 75.98; H, 7.99; N, 7.40. Found: C, 75.58; H, 7.90; N, 7.57.

**ε-Phenyl-ε-caprolactam (VII).**—*p*-Toluenesulfonyl chloride, 16.5 g., was added to a solution of 9.5 g. of α-phenylcyclohexanone oxime in 25 ml. of anhydrous pyridine, cooled to 0–5° in a salt–ice-bath. After thorough mixing by shaking the solution was left in the bath, but allowed to warm up slowly to room temperature over a period of 12 hr. The mixture then was poured into 400 ml. of water, made acidic with 10% hydrochloric acid and allowed to stand for 2 hr. The resulting precipitate, 12.3 g., consisted of long needles, m.p. 122–129°, which on crystallization from aqueous ethanol gave ε-phenyl-ε-caprolactam, m.p. 139–141°; infrared spectrum ($CCl_4$): NH 2.94(m)μ, C=O 6.04(s)μ, C=C 6.21(m) μ.

*Anal.* Calcd. for $C_{12}H_{15}ON$: C, 75.98; H, 7.99; N, 7.40. Found: C, 75.74; H, 8.19; N, 7.45.

A mixture of 5 g. of the lactam and 50 ml. of 20% hydrochloric acid was refluxed for 2 hr. After the solution was cooled in an ice-bath to 0–5°, a solution of 5 g. of sodium nitrite in 20 ml. of water was added slowly with vigorous swirling. Thereupon the solution was allowed to warm to room temperature, saturated with sodium chloride and extracted with ether. The extract was washed with saturated brine solution, filtered through anhydrous sodium sulfate and evaporated. The residue was refluxed with 20 ml. of thionyl chloride for 2 hr., poured into 100 ml. of concentrated ammonium hydroxide and left standing. The supernatant liquid was decanted from the newly formed brown oil and the latter washed with water and 5% hydrochloric acid solution. The oil was extracted with three 30-ml. portions of boiling petroleum ether. The combined extracts were decolorized with Norite and concentrated, yielding colorless crystals of the amide IXa, m.p. 104–106°, m.m.p. 104–107°; infrared spectrum identical with that of the above sample.

**Pyrolysis of Tetrahydrocarbazole (IV).** **(a) With Hydroxylamine.**—A solution of 1.00 g. of tetrahydrocarbazole and 4.0 g. of hydroxylamine in 20 ml. of benzene was heated in a Carius tube at 270° for 24 hr. The cooled mixture then was washed with water, 10% sodium hydroxide and 10% hydrochloric acid solutions. It was filtered through anhydrous sodium sulfate, concentrated and chromatographed on 50 g. of alumina. Elution with 300 ml. of petroleum ether gave 650 mg. of tetrahydrocarbazole, m.p. 112–116°. Further elution with 300 ml. of 9:1 petroleum ether-benzene yielded 150 mg. more of starting material, m.p. 111–114°. While its m.p. was slightly low, its infrared spectrum was the same as that of tetrahydrocarbazole.

**(b) With Cyclohexanone Oxime.**—A solution of 4.00 g. of tetrahydrocarbazole and 10 g. of cyclohexanone oxime in 20 ml. of benzene was heated in a sealed Carius tube at 270° for 24 hr. When the tube was cooled and opened, a strong odor of ammonia was emitted. The reaction mixture was washed with 50-ml. portions of water, 10% sodium hydroxide, 10% hydrochloric acid and saturated brine solutions. It then was filtered through anhydrous sodium sulfate, concentrated to a 40-ml. volume and chromatographed on 200 g. of alumina. Elution with petroleum ether gave 900 mg. of tetrahydrocarbazole, m.p. 116–119°, while elution with 9:1 petroleum ether–benzene yielded 2.40 g. of carbazole, m.p. 236–242°.

***o*-Hydroxylaminobiphenyl (VIc).**—A solution of 5.0 g. of ammonium chloride in 50 ml. of water was added to a solution of 5.0 g. of *o*-nitrobiphenyl in 75 ml. of 95% ethanol. After thorough mixing, 5 g. of zinc amalgam was added and the mixture refluxed and stirred vigorously for 45 min. Thereupon 50 ml. of water was added, the solution filtered and the residue washed with 100 ml. of ether. The aqueous filtrate was extracted with three 50-ml. portions of ether. All ether solutions were combined, washed with saturated brine solution, filtered through anhydrous sodium sulfate and evaporated under vacuum. The orange semi-solid residue was dissolved in hot petroleum ether. Cooling led to 3.4 g. of yellow granular crystals, m.p. 63–69°, which on crystallization from petroleum ether changed to 2.8 g. of colorless crystals of *o*-hydroxylaminobiphenyl, m.p. 69–71°.

*Anal.* Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.79; H, 6.11; N, 7.54.

**Rearrangements of *o*-Hydroxylaminobiphenyl (VIc). (a) Pyrolytic Reactions.**—A solution of 4.00 g. of *o*-hydroxylaminobiphenyl in 100 ml. of toluene was refluxed under a nitrogen atmosphere for 12 hr. It then was extracted with 10% hydrochloric acid solution. The acid extract was neutralized with sodium hydroxide and extracted with ether. The solvent of the organic extract then was evaporated, the residue dissolved in pyridine and treated with 15 ml. of acetic anhydride and the solution allowed to stand for 12 hr. The solution was poured into water. The resulting precipitate was washed with saturated sodium carbonate solution and water, dissolved in ethanol and decolorized with Norite and crystallized from aqueous ethanol. It yielded 800 mg. of *o*-acetamidobiphenyl, m.p. 118–120° (lit.[12] m.p. 119°), identical with an authenic sample.

The initial toluene solution was washed with saturated brine solution, filtered through dry sodium sulfate and chromatographed on alumina. Elution with petroleum ether yielded 120 mg. of *o*-azobiphenyl (VId), m.p. 136–139° (lit.[13] m.p. 144.5°), identical with an authentic sample. Further elution with benzene–ether gave 850 mg. of *o*-azoxybiphenyl (XI), m.p. 160–163° (lit.[13] m.p. 158°) after crystallization from aqueous acetone, identical with an authentic sample.

*Anal.* Calcd. for $C_{24}H_{19}ON_2$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.56; H, 5.47; N, 8.07.

A similar pyrolysis was carried out with a solution of 1.00 g. of *o*-hydroxylaminobiphenyl in 20 ml. of anhydrous benzene. The solution was placed into a nitrogen-swept Carius tube, sealed and heated at 270° for 24 hr. The identical work-up as above led to 150 mg. of *o*-acetamidobiphenyl, 50 mg. of *o*-azobiphenyl and 600 mg. of *o*-azoxybiphenyl.

**(b) Acid-catalyzed Reactions.**—A solution of 1.00 g. of *o*-hydroxylaminobiphenyl in 20 ml. of 20% sulfuric acid was heated on a steam-bath for 2 hr. After dilution of the cooled dark mixture with water it was extracted with ether and chloroform. Evaporation of the organic extracts to dryness and chromatography of the residue on alumina yielded 610 mg. of *o*-azoxybiphenyl (XI), m.p. 158–161°. Basification of the aqueous acid solution with 5% sodium hydroxide solution, extraction with ether and chloroform and evaporation of the organic extracts gave a residue, which was dissolved in pyridine, treated with 2 ml. of benzoyl chloride and heated on the steam-bath for 10 min. The cooled pyridine solution then was poured into water, and the resulting precipitate filtered and crystallized from benzene. This afforded 300 mg. of *o*-benzamidobiphenyl, m.p. 84–86°, identical with the specimen above. Adjustment of the basic aqueous solution of the initial reaction mixture to *p*H 7 and exhaustive extraction with ether and chloroform led to no more products.

A solution of 1.00 g. of *o*-hydroxylaminobiphenyl and of 1.00 g. of *p*-toluenesulfonic acid in 20 ml. of water was placed into a nitrogen-swept Carius tube, sealed and heated at 270° for 24 hr. The identical work-up as above yielded 75 mg. of *o*-azobiphenyl (VId), 550 mg. of *o*-azoxybiphenyl (XI) and 170 mg. of *o*-benzamidobiphenyl.

A solution of 4.00 g. of *o*-hydroxylaminobiphenyl and 4.00 g. of *p*-toluenesulfonic acid in 50 ml. of water was refluxed for 4 hr. under a nitrogen atmosphere. To the cooled reaction mixture there were added 50 ml. of 10% sulfuric acid solution, and the mixture was worked up as before, except that the basic products were acetylated rather than benzoylated. This run afforded 685 mg. of *o*-acetamidobiphenyl and 1.10 g. of *o*-azoxybiphenyl (XI). Ether–acetone elution of the chromatogram and crystallization from aqueous acetone gave 600 mg. of unrecognized black glistening crystals.

**α-Phenylcyclohexanone Oxime 3,5-Dinitrobenzoate.**—3,5-Dinitrobenzoyl chloride, 7.00 g., was added to a solution of 5.00 g. of α-phenylcyclohexanone oxime (IIa) in 20 ml. of anhydrous pyridine. After the initial heat of the reaction had subsided, the mixture was heated gently on the steam bath for 2 min. It then was cooled and poured with vigorous stirring into 200 ml. of cold water. The separating oil was allowed to settle and solidify. After decantation of the supernatant liquid the residue was washed with 10% hydrochloric acid and with water, dissolved in ethanol, decolorized with Norite and crystallized. Recrystallization from ethanol yielded 10.5 g. of white needles of the desired ester, m.p. 116–117°.

*Anal.* Calcd. for $C_{19}H_{17}O_6N_3$: C, 59.54; H, 4.43; N, 10.96. Found: C, 59.51; H, 4.92; N, 10.83.

A solution of 3.70 g. of the ester and 4 ml. of commercial triethylamine in 75 ml. of anhydrous benzene was refluxed for 48 hr. The wine-red reaction mixture was evaporated under vacuum, redissolved in benzene and extracted with water, 5% sodium hydroxide and 10% hydrochloric acid solutions. Acidification of the basic extract with 10% hydrochloric acid, extraction with ether, evaporation of the organic extract and crystallization of the residue from aqueous ethanol yielded 1.15 g. of 3,5-dinitrobenzoic acid, m.p. 204–207°, identical with an authentic sample. Chromatography of a concentrate of the initial benzene solution of alumina gave 25 mg. of tetrahydrocarbazole (IV), m.p. 116–120°, on elution with petroleum ether, 125 mg. of ethyl 3,5-dinitrobenzoate, m.p. 95–97° (lit.[12] m.p. 96°) (identical with an authentic sample), on elution with cyclohexane and crystallization from aqueous ethanol, and 1.15 g. of α-phenylcyclohexanone oxime, m.p. 168–171°, on elution with ether and crystallization from petroleum ether.

---

(12) F. Bell, *J. Chem. Soc.*, 2773 (1928).

(13) G. Friebel and B. Rassow, *J. prakt. Chem.*, **63**, 453 (1901).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

# A New Synthesis of the Hydrophenanthrene Nucleus

BY ERNEST WENKERT, R. D. YOUSSEFYEH AND RONALD G. LEWIS

RECEIVED APRIL 11, 1960

Reactions of the dry sodium salts of β-naphthol and its various α-alkyl derivatives with different alkyl halides and the three-step conversion of a resulting naphthalenone to a hydrophenanthrone are described.

A common feature of the recent large number of total syntheses of steroids, diterpenes and triterpenes is the extensive use of the Robinson cyclohexenone synthesis. Its application in the field of diterpene synthesis has meant invariably the construction of a hydrophenanthrene nucleus,[1] derivatives of I, by a route similar, although not identical in detail, to that employed by Cornforth and Rob-

---

(1) *Cf.* (a) G. Stork and J. W. Schulenberg, THIS JOURNAL, **78**, 250 (1956); (b) P. N. Rao and K. Raman, *Tetrahedron*, **4**, 294 (1958); (c) R. B. Turner, E. G. Herzog, R. B. Morin and A. Riebel, *Tetrahedron Letters*, 7 (1959).