organic bases was confirmed by preparing and identifying the hydrochlorides of the bases and by conducting mixed melting points of the salts with authentic samples prepared by treating *p*-toluenesulfonic acid with the appropriate base in ether.

Summary

The 5-, 6-, 7- and 8-(*p*-toluenesulfonoxy)-quinolines yielded primarily the corresponding 1,2,3,4-tetrahydro derivatives on catalytic hydrogenation with a palladium catalyst, whereas the 2- and 3-isomeric esters gave the 1,2,3,4-tetrahydroquinoline salt of *p*-toluenesulfonic acid. The 4-ester is very unstable.

The *p*-toluenesulfonoxypyridines were reduced to pyridinium and piperidinium *p*-toluenesulfonates, the 3-isomer being hydrogenated completely and rapidly, the 4-isomer more slowly, and the 2-isomer most slowly.

The 2-(*p*-toluenesulfonoxy)-quinoline was more rapidly reduced than the corresponding benzenesulfonoxy derivative.

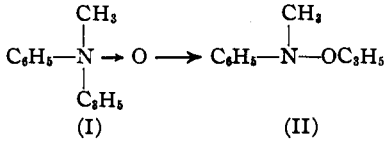
RENSSELAER, N. Y. RECEIVED SEPTEMBER 12, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rearrangement of Allyl Groups in Dyad Systems. Amine Oxides

BY ROGER F. KLEINSCHMIDT AND ARTHUR C. COPE

Meisenheimer has shown that allylmethylaniline oxide (I) rearranges readily on heating with aqueous sodium hydroxide to give O-allyl-N-methyl-N-phenylhydroxylamine (II).[1] The



(I) (II)

structure of the isomerization product was established by reduction with zinc dust and acetic acid to methylaniline and allyl alcohol, by hydrogenation to O-propyl-N-methyl-N-phenylhydroxylamine, and by hydrolysis with hydrochloric acid. The hydrolysis products which were isolated were methylaniline, *p*-chloro-methylaniline, and acrolein. Their formation was attributed to cleavage of II in two ways; into allyl alcohol and $C_6H_5N(CH_3)$-Cl (which by rearrangement could give chloromethylaniline), and into methylaniline and acrolein. Allylethylaniline oxide and benzylmethylaniline oxide[2] later were shown to rearrange in the same way, although the structures of the isomerization products were not proved in these cases.

Beyond calling attention to the similar mobility of allyl groups in allyl thiocyanate and in the allyl ethers of phenols and enols,[3] Meisenheimer made no commitment concerning the mechanism of the rearrangement. Considering the analogy of tautomerism in triad and dyad systems, it seemed to us very probable that the isomerization could be explained as a rapid, thermal rearrangement of an allyl group in a dyad system, resembling the Claisen rearrangement. If this interpretation is correct, the only function of the sodium hydroxide present in the reaction mixture is to convert the amine oxide from a salt into the free base. Another possible mechanism is an anionotropic shift, in which the $C_6H_5N(CH_3) \rightarrow O$ fragment separates as an anion and recombines through oxygen rather than nitrogen. We have re-investigated the rearrangement, in order to confirm the structures of the compounds concerned and obtain evidence for the mechanism of the reaction.

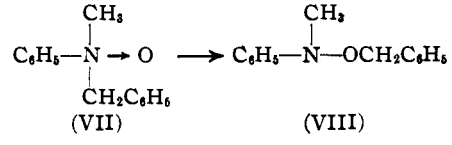
Oxidation of allylmethylaniline with perbenzoic acid gave the amine oxide, I, which rearranged rapidly in alkaline solution to the isomer, II. Preliminary attempts to synthesize II by an independent method which would confirm its structure were unsuccessful, but it was possible to synthesize the 2,4-dinitro derivative of II by the sequence of reactions

$$\underset{\text{(III)}}{NH(COOC_2H_5)OC_3H_5} \xrightarrow{KOH} \underset{\text{(IV)}}{H_2NOC_3H_5} \xrightarrow{2,4\text{-}(NO_2)_2C_6H_3Cl} 2,4\text{-}(NO_2)_2C_6H_3NHOC_3H_5 \xrightarrow{CH_2N_2}$$

$$\underset{\text{(V)}}{} \qquad \underset{\text{(VI)}}{2,4\text{-}(NO_2)_2C_6H_3N(CH_3)OC_3H_5}$$

Nitration of II with fuming nitric acid in glacial acetic acid gave the same dinitro derivative, confirming its structure.

Benzylmethylaniline oxide (VII) also was prepared and rearranged by heating in alkaline solution. The isomerization product proved to be O-benzyl-N-methyl-N-phenylhydroxylamine, VIII. Its structure was established by hydrolysis with dilute hydrochloric acid, which yielded benzaldehyde, methylaniline, and *p*-chloro-methylaniline. Cleavage of VIII by hydrogenation to benzyl alcohol and methylaniline verified this structure.



(VII) (VIII)

The fact that the benzyl group does not undergo inversion during the rearrangement furnishes no

(1) Meisenheimer, *Ber.*, **52**, 1667 (1919).

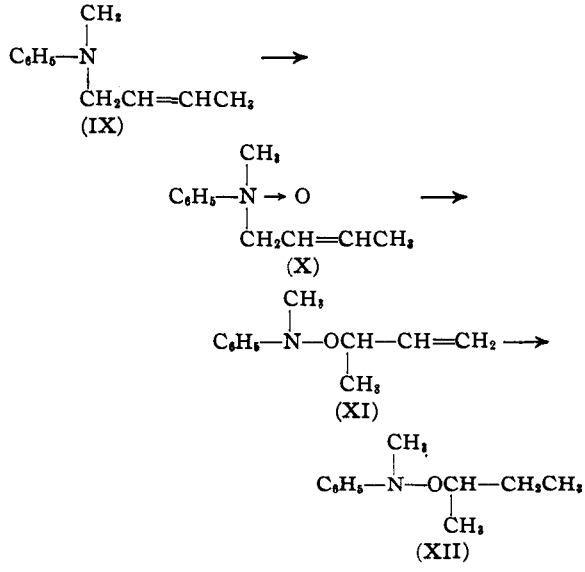
(2) Meisenheimer, Greeske and Willmersdorf, *ibid.*, **55**, 513 (1922).

(3) As in the Claisen rearrangement and related reactions: see Tarbell *Chem. Rev.*, **27**, 495 (1940).

direct evidence concerning the mechanism of the rearrangement of the allyl compound, I. The benzyl ethers of phenols rearrange without inversion in the presence of acidic catalysts to *o*- and *p*-benzyl substituted phenols, while the allyl ethers ordinarily rearrange with inversion to *o*-allyl substituted phenols.[3] The fact that VII rearranges below 100° in the absence of acidic catalysts illustrates the great lability of this dyad system compared to related triad systems, such as the benzyl ethers of phenols and enols.

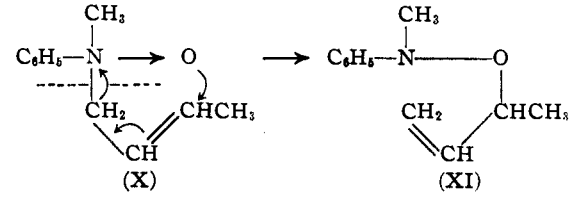
The isolation of VIII in good yield from the rearrangement of VII in the presence of sodium hydroxide indicates that the benzyl group becomes attached to the oxygen as it is detached from the nitrogen. If the mechanism were purely anionotropic, anion interchange should result in the formation of benzyl alcohol and compounds derived from methyl phenylhydroxylamine as by-products.

In order to obtain amine oxides which would demonstrate whether or not inversion occurred during the rearrangement, cinnamylmethylaniline and crotylmethylaniline (IX) were prepared and converted to the oxides. It was not possible to isolate a pure product from the rearrangement of cinnamylmethylaniline oxide. Crotylmethylaniline oxide (X) isomerized rapidly on heating in alkaline solution and formed O-methylvinylcarbinyl-N-methyl-N-phenylhydroxylamine (XI).



Establishment of the structures of IX and XI proves that inversion of the crotyl group occurs in the rearrangement. The structure of IX could not be proved by reduction, because cleavage of the crotyl group took place and methylaniline was the product when IX was hydrogenated in the presence of palladinized charcoal.[4] Its structure was proved by nitrosation, alkaline hydrolysis of the nitroso compound, and hydrogenation of the unsaturated aliphatic amine which was formed. The product was *n*-butylmethylamine, confirming structure IX. XI was reduced catalytically to O-*s*-butyl-N-methyl-N-phenylhydroxylamine (XII). The structure of XII was proved by hydrolysis with hydrochloric acid, which gave *s*-butyl alcohol, methylaniline and *p*-chloro-methylaniline.

On the basis of this proved case of inversion, an intramolecular, cyclic mechanism is proposed for the rearrangement.



This mechanism is analogous to the commonly accepted mechanism for the Claisen rearrangement,[3] except for differences which distinguish dyad from triad systems. The transitory chelate is a five-membered ring, and a change in valence occurs in the isomerization, as it does in dyad prototropy.

Other related dyad systems are being investigated.

Experimental[5]

O-Allyl-N-methyl-N-phenylhydroxylamine (II).—**Allylmethylaniline**[6] (14.7 g.) was converted to the oxide by stirring with a 40% molar excess of perbenzoic acid in 400 ml. of chloroform at 0° for fifteen minutes. The oxide was extracted with six 50-ml. portions of cold 5% hydrochloric acid. The extracts were made alkaline by adding 19 g. of sodium hydroxide, and the solution was steam distilled. II, which separated as an oil from the distillate, was extracted with ether and washed with 5% hydrochloric acid (to remove any allylmethylaniline present) and water. Distillation yielded 12.8 g. (78%) of II, b. p. 94–95° (11 mm.); $n^{25}D$ 1.5204; d^{25}_4 0.9785; M_D calcd.[7] 49.54, found 50.68 (exaltation 1.14).

Nitration of II.—A solution of II (2.0 g.) in 15 ml. of glacial acetic acid was cooled to 10° and fuming nitric acid (4 g., sp. gr. 1.51) was added with stirring while the temperature was kept below 10°. The mixture was poured into 300 ml. of water and ice. The product, which contained considerable tar, was treated with Norite and crystallized from alcohol. Recrystallization to constant melting point from carbon tetrachloride and pentane gave 1.28 g. of VI, m. p. 76–78° (not depressed on mixture with the known sample described below).

O-Allyl Hydroxyurethan (III).—Hydroxyurethan was prepared by the method of Jones[8] and alkylated with allyl bromide under conditions used for similar alkylations by Jones[8] and Hecker.[9] Hydroxyurethan (98.5 g.) was converted into the potassium salt with a solution of potassium hydroxide (53 g.) in absolute alcohol. Allyl bromide (121 g.) was added with cooling at room temperature, after which the mixture was refluxed for two hours. III was

(4) This is analogous to the cleavage of N-benzyl linkages by hydrogenation. See Baltzly and Buck, THIS JOURNAL, **65**, 1984 (1943).

(5) Melting and boiling points are uncorrected.

(6) Wedekind, *Ber.*, **32**, 519 (1899).

(7) In the calculated molecular refractions, the Eisenlohr values are used (Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911)), and 2.48 for *N* in hydroxylamines (Brühl, *Ber.*, **26**, 2508 (1893)). The aromatic hydroxylamine and urethan derivatives in which the nitrogen is attached directly to the benzene ring show an exaltation of 1.09–1.50 units. These values are comparable to the exaltations shown by aromatic amines (v. Auwers, *Z. physik. Chem.*, **148**, 125 (1930)).

(8) Jones, *Am. Chem. J.*, **20**, 40 (1898).

(9) Hecker, *ibid.*, **50**, 444 (1913).

separated from O,N-diallyl hydroxyurethan, formed as a by-product, by extraction with 10% sodium hydroxide, following the procedure used by Jones and Hecker. The acidic fraction yielded 50.8 g. (37%) of III, b. p. 108° (12.5 mm.); $n^{25}D$ 1.4425; d^{25}_4 1.0526; M_D calcd. 36.32, found 36.57.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.64; H, 7.63. Found: C, 49.95; H, 7.73.

The neutral fraction yielded 19.7 g. (11%) of O,N-diallyl hydroxyurethan, b. p. 93° (11 mm.); $n^{25}D$ 1.4438; d^{25}_4 0.9853; M_D calcd. 49.71, found 49.91.

Anal. Calcd. for $C_8H_{13}NO_3$: C, 58.36; H, 8.16. Found: C, 58.23; H, 8.24.

O-Allyl Hydroxylamine (IV).—III (34.3 g.) and 30 g. of potassium hydroxide in 70 ml. of water were refluxed for one hour. The product was extracted with methylene chloride, dried over sodium sulfate, and distilled through an adiabatic, total reflux, variable take-off type column with a 30 × 1.1 cm. section packed with glass helices. The yield of IV was 9.9 g. (58%), b. p. 98–99°; $n^{25}D$ 1.4300; d^{25}_4 0.9074; M_D calcd. 20.81, found 20.81.

Anal. Calcd. for C_3H_7NO: C, 49.29; H, 9.65. Found: C, 49.61; H, 9.76.

The hydrochloride of IV was obtained in 66% yield by steam distilling the hydrolysis product into dilute hydrochloric acid and evaporating to dryness *in vacuo*. After recrystallization from absolute alcohol and dry ether it had m. p. 171–171.5°.[10]

Anal. Calcd. for C_3H_8NOCl: C, 32.89; H, 7.36. Found: C, 32.61; H, 7.34.

IV reacted with α-naphthyl isocyanate to give α-$C_{10}H_7NHCONHOC_3H_5$, which was recrystallized from chloroform and pentane; m. p. 124–125.5°.

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82. Found: C, 69.35; H, 5.79.

O-Allyl-N-2,4-dinitrophenylhydroxylamine (V).—IV (3.1 g.), 2,4-dinitrochlorobenzene (8.6 g.) and anhydrous potassium acetate (5.0 g.) were refluxed in absolute alcohol solution for three hours. On cooling, 7.3 g. of crude V separated, m. p. 82–84°. Recrystallization from carbon tetrachloride and pentane gave orange needles of V, m. p. 87–88°

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.19; H, 3.79. Found: C, 45.24; H, 3.88.

O-Allyl-N-methyl-N-2,4-dinitrophenylhydroxylamine (VI).—To a solution of 2.0 g. of V in cold acetone was added an approximately equivalent quantity of diazomethane in cold ether. After standing in an ice-bath for several hours, the solvent was removed *in vacuo*. The residue was treated with Norite and crystallized from alcohol. After recrystallization from carbon tetrachloride and pentane, VI was obtained as fine yellow needles, 0.85 g., m. p. 76.5–77.5°.

Anal. Calcd. for $C_{10}H_{11}N_3O_5$: C, 47.43; H, 4.38. Found: C, 47.76; H, 4.54.

O-Allyl-N-phenylhydroxyurethan.—N-Phenylhydroxyurethan was prepared conveniently by the method of Bamberger and Tschirner[11] in small quantities, but larger amounts decomposed partially during distillation and a modified method was used. In a 500-ml. three-necked flask fitted with a mercury sealed stirrer and a dropping funnel were placed 300 ml. of dry ether, 84.5 g. of freshly prepared, dry N-phenylhydroxylamine,[12] 71.5 g. of sodium bicarbonate and 25 g. of anhydrous sodium sulfate. The mixture was cooled in an ice-bath and 84 g. of ethyl chlorocarbonate was added slowly with stirring. Stirring was continued for one hour, after which the reaction mixture was allowed to stand in a refrigerator for twenty-four hours. The mixture was filtered and the ether was removed by evacuation. The residue crystallized on seeding. It was filtered and pressed dry on a sintered glass funnel, yielding 88.5 g. (63%) of light tan N-phenylhydroxyurethan, m. p. 45.5–47°.

A mixture of N-phenylhydroxyurethan (30 g.), anhydrous potassium carbonate (25.2 g.), allyl bromide (22 g.) and acetone (30 g.) was refluxed gently for four hours. The mixture was diluted with water and extracted with ether. The extracts were washed successively with 5% sodium hydroxide, 5% hydrochloric acid and water. After drying over sodium sulfate the O-allyl-N-phenyl hydroxyurethan was distilled. It was a pale yellow liquid; yield 31.6 g. (86%), b. p. 112° (1.3 mm.); $n^{25}D$ 1.5128; d^{25}_4 1.0797; M_D calcd. 60.43, found 61.57 (exaltation 1.14).

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.25; H, 6.94.

Several attempts to hydrolyze the above urethan to O-allyl-N-phenylhydroxylamine in the presence of acids or bases were unsuccessful. Bamberger[13] has reported similar results with O-methyl-N-phenyl hydroxyurethan.

O-Allyl-N-methyl Hydroxyurethan.—A solution of 25.7 g. of III in an equivalent amount of 10% sodium hydroxide was cooled in an ice-bath while 22.3 g. of redistilled methyl sulfate was added slowly with stirring. The mixture was heated at 80–90° for fifteen minutes, after which 2–3 g. of sodium hydroxide was added to decompose any excess methyl sulfate. The solution was extracted with ether and the extracts were dried over sodium sulfate. Distillation yielded 23.4 g. (83%) of O-allyl-N-methyl hydroxyurethan, b. p. 88–89.5° (19–21 mm.); $n^{25}D$ 1.4303; d^{25}_4 0.9965; M_D calcd. 40.94, found 41.29.

Anal. Calcd. for $C_7H_{13}NO$: C, 52.81; H, 8.23. Found: C, 53.07; H, 8.24.

N-Allyl-N-methyl-2,4-dinitroaniline.—Allylmethylamine[14] (13.7 g.) was added slowly to a refluxing solution of 38.5 g. of 2,4-dinitrochlorobenzene and 20 g. of anhydrous potassium acetate in absolute alcohol. After refluxing for six and one-half hours, the mixture was cooled. The yellow crystals which separated were recrystallized from dilute alcohol, yielding 39 g. of crude product, m. p. 55–56°. Recrystallization from carbon tetrachloride and pentane gave pale yellow needles, m. p. 61–62°.

Anal. Calcd. for $C_{10}H_{11}N_3O_4$: C, 50.63; H, 4.76. Found: C, 50.70; H, 4.89.

This amine was recovered unchanged after treatment with perbenzoic acid in attempts to convert it to the oxide, which would be an isomer of VI.

Benzylmethylaniline Oxide Picrate.—The following method is more convenient than previous preparations.[2,15] To 450 ml. of a dry solution of perbenzoic acid in methylene chloride[16] containing 0.12 mole of active oxygen, 23.7 g. (0.12 mole) of benzylmethylaniline[6] was added slowly with stirring and cooling in ice. After six hours at 0–5°, a solution of 27.5 g. of picric acid in 30 ml. of acetone was added and the mixture was kept in the refrigerator overnight. The picrate crystallized on addition of pentane; yield 49.2 g. (92%), m. p. 125–127° (dec.).

This picrate was also prepared by oxidizing benzylmethylaniline picrate (2 g.) in methylene chloride solution with an equivalent quantity of perbenzoic acid at 0°; yield after crystallization from alcohol 1.65 g., m. p. 130–131° (dec.).

O-Benzyl-N-methyl-N-phenylhydroxylamine (VIII).—Benzylmethylaniline oxide picrate (58.7 g.) was converted into the corresponding hydrochloride by a procedure described by Meisenheimer.[17] The crude hydrochloride was dissolved in 300 ml. of 10% sodium hydroxide and heated at 80–90° for six hours. The oil which separated was ex-

(10) Brady and Peakin, *J. Chem. Soc.*, 226 (1930), report m. p. 172°.

(11) Bamberger and Tschirner, *Ber.*, **52**, 1120 (1919).

(12) "Organic Syntheses," Coll. Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 445.

(13) Bamberger and Landau, *Ber.*, **52**, 1109 (1919).

(14) Zeile and Meyer, *Z. physiol. Chem.*, **256**, 131 (1938).

(15) Meisenheimer, Glawe, Greeske, Schorning and Vieweg, *Ann.*, **449**, 202 (1926).

(16) Prepared as in "Organic Syntheses," Coll. Vol. I, second ed., John Wiley & Sons, Inc., New York, N. Y., 1941, p. 431, except that the perbenzoic acid was extracted with methylene chloride instead of chloroform.

(17) Meisenheimer, *Ann.*, **355**, 120, 140 (1911).

tracted with benzene. The extracts were washed successively with dilute solutions of sodium bisulfite, hydrochloric acid and sodium bicarbonate. The product was distilled through an 8-inch Vigreux column; yield of VIII, 24.8 g. (87%), b. p. 89–90° (0.01 mm.); $n^{25}D$ 1.5693; d^{25}_4 1.0531; M_D calcd. 64.88, found 66.38 (exaltation 1.50).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.78; H, 7.49.

Structure of VIII.—VIII (5.0 g.) was hydrolyzed by refluxing with 100 ml. of 10% hydrochloric acid for two hours. Extraction of the acid solution with ether and distillation gave 1.0 g. of benzaldehyde, b. p. 73–74° (19 mm.), which was identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. with a known sample 235.5–237°. The acid solution was made alkaline and extracted with ether. Distillation yielded 1.4 g. of methylaniline, b. p. 91° (19 mm.) (identified as the picrate, m. p. and mixed m. p. 143–144°), and 0.9 g. of *p*-chloro-methylaniline, identified as the picrate, m. p. 153–154°, and the acetyl derivative, m. p. 90–92°.

VIII (5.0 g.) was also cleaved by hydrogenation in alcohol solution in the presence of palladinized charcoal to 1.7 g. of benzyl alcohol (m. p. and mixed m. p. of the α-naphthyl urethan with a known sample 129–131°) and 2.7 g. of methylaniline, identified as the picrate.

Cinnamylmethylaniline.—A mixture of 40.9 g. of cinnamyl chloride, 28.7 g. of methylaniline, 18.0 g. of powdered anhydrous sodium carbonate and 100 ml. of benzene was refluxed and stirred for seven and one-half hours. Refluxing was continued one hour longer after adding 100 ml. of 5% sodium hydroxide, in order to destroy any excess cinnamyl chloride. The benzene layer was separated, dried over sodium sulfate and distilled through a Vigreux column. The yield of cinnamylmethylaniline was 48 g. (80%), b. p. 153° (0.33 mm.); $n^{25}D$ 1.6231.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67. Found: C, 86.18; H, 7.78.

Cinnamylmethylaniline picrate was recrystallized from dilute alcohol; m. p. 127–128° (dec.).

Anal. Calcd. for $C_{22}H_{20}N_4O_7$: C, 58.40; H, 4.46. Found: C, 58.25; H, 4.66.

Cinnamylmethylaniline Oxide Picrate.—A solution of 18.0 g. of cinnamylmethylaniline in 35 ml. of methylene chloride was added at 0° to 300 ml. of methylene chloride containing an equivalent quantity of perbenzoic acid. After about three hours a solution of 18.4 g. of picric acid in 25 ml. of acetone was added. The solution was concentrated to half its original volume by evacuation at 0°, and pentane was added. After seeding and standing the picrate crystallized; yield 24.3 g. (64%), m. p. 107–110° (dec.). Recrystallization from methylene chloride and pentane gave yellow needles, m. p. 109–110.5° (dec.).

Anal. Calcd. for $C_{22}H_{20}N_4O_8$: C, 56.41; H, 4.30. Found: C, 56.66; H, 4.49.

The above picrate was converted to the hydrochloride (not purified), which was heated with aqueous sodium hydroxide according to the procedure described for the preparation of VIII. Attempted distillation at low pressures of the oil which separated resulted in decomposition.

Crotylmethylaniline.—Pure crotyl chloride[18] (72.4 g.) was added to 80.4 g. of methylaniline. An exothermic reaction occurred after slight warming. The mixture was refluxed for two hours on a steam-bath and allowed to stand overnight. After adding 10% sodium hydroxide, the product was extracted with ether and dried over sodium sulfate. Distillation through a Widmer column gave 101.3 g. (84%) of crotylmethylaniline, b. p. 119° (14 mm.); $n^{25}D$ 1.5503; d^{25}_4 0.9461; M_D calcd. 54.40, found 54.35.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.71; H, 9.52.

Crotylmethylaniline picrate was recrystallized from methyl alcohol; m. p. 80–82°.

Anal. Calcd. for $C_{17}H_{18}N_4O_7$: C, 52.30; H, 4.65. Found: C, 52.07; H, 4.96.

Structure of IX.—Hydrogenation of IX in alcohol, dilute hydrochloric acid or glacial acetic acid in the presence of palladinized charcoal proceeded very rapidly, but led to methylaniline in each case.

IX was characterized by nitrosating a 10-g. sample, hydrolyzing the nitroso compound (not isolated) in alkaline solution, and steam distilling the resulting secondary aliphatic amine into dilute hydrochloric acid. The acid solution was hydrogenated in the presence of palladinized charcoal. After removing the solvent *in vacuo*, the white solid product was recrystallized from acetone and ether, yielding 0.49 g. of *n*-butylmethylamine hydrochloride, m. p. 172–174°.[19] A 10-g. sample of *n*-butylmethylaniline treated in the same way, but not hydrogenated, yielded 0.51 g. of the same hydrochloride, which was proved to be identical by mixed m. p. The close correspondence in yields indicates that IX contains little if any of the isomer, (methylvinylcarbinyl)-methylaniline.

Crotylmethylaniline Oxide Picrate.—A methylene chloride solution of the oxide, prepared as described below, was extracted with fifteen 20–25 ml. portions of water. The aqueous extracts were extracted with ether to remove traces of methylene chloride, and treated with alcoholic picric acid. On cooling the picrate separated slowly. After repeated recrystallization from methyl alcohol it had m. p. 93.5–94°.

Anal. Calcd. for $C_{17}H_{18}N_4O_8$: C, 50.25; H, 4.47. Found: C, 50.27; H, 4.56.

O-Methylvinylcarbinyl-N-methyl-N-phenylhydroxylamine (XI).—IX (20 g.) was oxidized with an equivalent quantity of perbenzoic acid in cold methylene chloride solution. The oxide was extracted with 200 ml. of 5% hydrochloric acid, and the extracts were made alkaline with 150 ml. of 10% sodium hydroxide. The alkaline solution was refluxed for one-half hour. The oil which separated was extracted with ether, washed successively with dilute hydrochloric acid, dilute sodium hydroxide and water, and dried over sodium sulfate. Distillation yielded 11.9 g. (54%) of XI, b. p. 98–99° (16 mm.); $n^{25}D$ 1.5117; d^{25}_4 0.9607; M_D calcd. 54.16, found 55.33 (exaltation 1.17).

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 74.76; H, 8.71.

Structure of XI.—XI (18 g.) was hydrogenated in ether solution in the presence of 1 g. of palladinized charcoal during three hours. The solution was filtered, washed with dilute hydrochloric acid and dilute sodium hydroxide, and dried over sodium sulfate. Distillation gave 13.2 g. (73%) of O-*s*-butyl-N-methyl-N-phenylhydroxylamine (XII), b. p. 99–99.5° (11.5 mm.); $n^{25}D$ 1.4991; d^{25}_4 0.9447; M_D calcd. 54.63, found 55.72 (exaltation 1.09).

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.56; H, 9.66.

XII (5 g.) was hydrolyzed by refluxing with 100 ml of 10% hydrochloric acid for one hour. This solution was distilled slowly through a Vigreux column until 4 ml. of distillate had collected. Saturation of the distillate with potassium carbonate gave 1.6 g. of *s*-butyl alcohol, identified as the 3,5-dinitrobenzoate, m. p. and mixed m. p. with a known sample 73–75°. Methylaniline (1.9 g.) and *p*-chloromethylaniline (1.1 g.) were isolated from the acid solution and identified as the picrates.

Summary

Occurrence of the following rearrangements, originally reported by Meisenheimer, has been confirmed: allylmethylaniline oxide (I) → O-allyl-N-methyl-N-phenylhydroxylamine (II); benzylmethylaniline oxide (VII) → O-benzyl-N-methyl-N-phenylhydroxylamine (VIII).

Crotylmethylaniline oxide (X) has been found

(18) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2163 (1942).

(19) Franchimont and van Erp, *Rec. trav. chim.*, **14**, 324 (1895) report m. p. 170–171°.

to rearrange with inversion of the crotyl group into O-methylvinylcarbinyl-N-methyl-N-phenylhydroxylamine (XI).

On the basis of this case of rearrangement with inversion, an intramolecular, cyclic mechanism for the reaction is proposed. The rearrangement is related to the Claisen and similar rearrangements in the same way that dyad and triad prototropic systems are related.

NEW YORK, N. Y. RECEIVED AUGUST 14, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL CO., INC.]

2-Phenylthiolane[1] Derivatives

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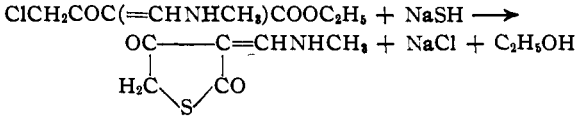
The establishment of the structure for one of the forms of biotin by du Vigneaud and co-workers[2] has increased greatly the interest in compounds of the thiolane series, particularly those substituted in the 2-, 3- and 4-positions. The present paper deals with the synthesis and some reactions of 2-phenylthiolane derivatives which also have substituents in other positions of the heterocyclic nucleus. Several substituted thiolenes (dihydrothiophenes) were also prepared during the course of the investigation.

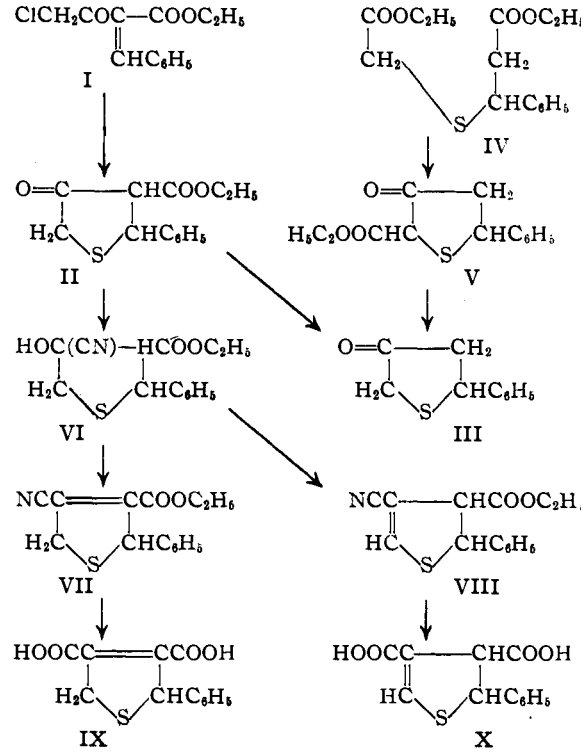
The reaction of sodium hydrosulfide with ethyl α-methylaminomethylene-γ-chloroacetoacetate has been shown[3] to give methylaminomethylenethiotetronic acid. It seemed possible that ring closure in this type of compound might



under the proper conditions be induced to occur through addition of the thiol group across the *alpha* double bond. In accord with this idea it has now been found that when ethyl α-benzylidene-γ-chloroacetoacetate (I) is added to one equivalent of sodium hydrosulfide in absolute alcohol, sodium chloride separates immediately and 3-carbethoxy-2-phenyl-4-thiolanone (II) is formed as the principal product. If the reaction mixture is kept cold during the addition of the chloro ester a considerable amount of another compound is produced.

Although this was not studied extensively, it appears to be the thiolactone, 3-benzylidene-2,4-thiolanedione. The ethyl α-benzylidene-γ-chloroacetoacetate was prepared from benzaldehyde and ethyl γ-chloroacetoacetate either in the presence of hydrogen chloride[4] or piperidine acetate,[5] the latter catalyst giving the best results.

The keto ester, II, undergoes reactions similar to those reported for ethyl 1-cyclopentanone-2-carboxylate.[6] It gives a reddish-brown color with ferric chloride solution and forms a characteristic green copper salt, a 2,4-dinitrophenylhydrazone, m. p. 144–144.5°, an anil, and an anilanilide, m. p. 161–162°.



When carbethoxymethyl β-carbethoxy-α-phenylethyl sulfide (IV), obtained by the reaction of ethyl thioglycolate with ethyl cinnamate in the presence of piperidine, was cyclized by means of sodium ethoxide in ether at room temperature[7] an isomeric ester, 5-carbethoxy-2-phenyl-4-thiolanone (V) was obtained. Some ethyl cinnamate was also formed during the reaction. This second keto ester, V, gives a bluish color with ferric chloride and no copper salt could be obtained. In addition V gives a 2,4-dinitrophenylhydrazone, m. p. 158–159°, and an

(1) This is the name given in "Ring Index" by Patterson and Capell. The terms "thiophane" and tetrahydrothiophene have also been used for this ring system.

(2) du Vigneaud, *Science*, **96**, 455 (1942).

(3) Bernary and Ebert, *Ber.*, **56**, 1897 (1923).

(4) Claisen, *Ann.*, **218**, 170 (1883).

(5) Cope and Hofmann, THIS JOURNAL, **63**, 3456 (1941).

(6) Dieckmann, *Ann.*, **317**, 51 (1901); Linstead and Wang, *J. Chem. Soc.*, 807 (1937).

(7) Bennett and Scorah, *J. Chem. Soc.*, 194 (1927), cyclized bis-(β-carbethoxyethyl) sulfide to the keto ester by a similar procedure.