For the (−)-isomer, $[\alpha]^{25}_D$ −1.53° in chloroform; m. p. 34–36°.

15-Methyloctadecanoic Acids (VI).—Ester V (12 g.) was reduced exactly as described by Huang-Minlon.[22] The diluted and acidified reaction mixture was extracted with ether, and the wet ether solution was passed through a tower containing 150 g. of Amberlite IRA-400 ion exchange resin (*cf.* ref. 21 for details of this procedure). After neutral materials had been washed from the column, the acid was eluted with hydrochloric acid in ether-ethanol solution. The eluate was washed with water until hydrochloric acid had been removed, then ether was evaporated and the residual acid was crystallized from acetone at −25°. The yield of crude acid was 9.0 g. (85.7%), m. p. 39.3–40.5° for the *dl-isomer*. This material was further crystallized from acetone until the m. p. became constant at 40.9–42.4°. A sample placed in a bath at 41.5° melted at once, and a sample which had stood for several days melted at 41.5–43.0°. This behavior indicating polymorphism is the same as that observed in the previous preparation of this compound.[23] Neutral equivalent, 298.0 (calcd. 298.5).

The pure **(+)-isomer** melted at 35.2–36.2°, $[\alpha]^{25}_D$ +1.12° in chloroform, neutral equivalent 298.0. The **(−)-isomer** melted at 35.2–36.1°, $[\alpha]^{25}_D$ −1.01° in chloroform, neutral equivalent, 298.9. A once-crystallized mixture of equal amounts of the (+)- and (−)-isomers melted at 41.2–42.4°.

The **tribromoanilides** were prepared as previously described,[24] except that the acid chlorides were prepared with thionyl chloride. For the *dl*-**isomer**, m. p. 103.6–104.4° (literature,[23] m. p. 102.6–103.8°). For the **(+)-isomer**, m. p. 104.4–105.5°, $[\alpha]^{25}_D$ +0.49° in chloroform. For the **(−)-isomer**, m. p. 104.4–105.3°, $[\alpha]^{25}_D$ −0.67° in chloroform.

Summary

The *dl*-, (+)- and (−)-forms of 15-methyloctadecanoic acid have been prepared by use of the keto ester synthesis. 3-Methylhexanoic acid was resolved to furnish the optically active starting materials.

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[22] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[23] Cason, Adams, Bennett and Register, *ibid.*, **66**, 1764 (1946).

[24] Cason, *ibid.*, **64**, 1106 (1942).

BERKELEY, CALIFORNIA RECEIVED MAY 6, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

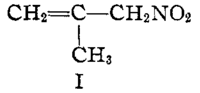
Hydroximyl Chlorides from Nitrostyrenes

BY CHARLES D. HURD, MAY E. NILSON[1] AND D. M. WIKHOLM[1]

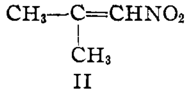
The reaction of nitrostyrene, benzene and aluminum chloride forms the subject matter of this investigation. No comparable reactions were known while the work was in progress, but in 1949 Lambert, Rose and Weedon[2] reported the reactions of benzene and aluminum chloride toward both of the nitroisobutylenes. 3-Nitro-2-methyl-1-propene (I) gave rise to 1-nitro-2-methyl-2-phenylpropane, essentially by addition of benzene across the double bond. 1-Nitro-2-methyl-1-propene (II) yielded phenyldimethylacetohydroximyl chloride, $C_6H_5C(CH_3)_2-CCl=NOH$, by a process involving not only addition but also rearrangement. Some chlorodimethylacetohydroximyl chloride was found also.

To behave analogously, ω-nitrostyrene, $C_6H_5-CH=CHNO_2$, should change to diphenylacetohydroximyl chloride, $(C_6H_5)_2CH-CCl=NOH$, in view of its structural similarity to 1-nitro-2-methyl-1-propene, $(CH_3)_2C=CHNO_2$. This reaction was indeed established. Also, *p*-chloro-ω-nitrostyrene, chlorobenzene and aluminum chloride were found to produce bis-*p*-chlorophenylacetohydroximyl chloride, $(ClC_6H_4)_2CH-CCl=NOH$. The yields realized were 70–85%.

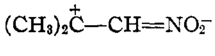
In considering the mechanisms of these reactions from I and II, one may assume that aluminum chloride, either as $AlCl_3$ or as $HAlCl_4$, withdraws electrons from the tertiary carbon of I, yielding $CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2NO_2$, which attacks benzene to form 1-nitro-2-methyl-2-phenylpropane. Since the same compound was not isolated from II, it must mean that the nitroalkane, as such, is not involved in the transformation of II into the hydroximyl chloride. To account for the latter, it is assumed that IIa, the resonance modification of II, becomes important in the presence of aluminum chloride and that its initial attack on benzene gives rise to III; but the double bond of III also is subject to reaction with aluminum chloride, thereby bringing its resonance form (IIIa) into play. The electron deficient carbon of IIIa promotes an intramolecular oxidation and reduction leading to IV (or a complex of it with aluminum chloride). Conversion of IV into the hydroximyl chloride by reaction with aluminum chloride is the final step


$CH_2=\underset{CH_3}{C}-CH_2NO_2$

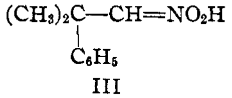
I


$CH_3-\underset{CH_3}{C}=CHNO_2$

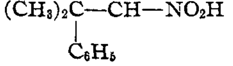
II


$(CH_3)_2\overset{+}{C}-CH=NO_2^-$

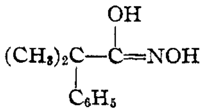
IIa


$(CH_3)_2\underset{C_6H_5}{C}-CH=NO_2H$

III


$(CH_3)_2\underset{C_6H_5}{C}-\overset{+}{C}H-\overset{-}{N}O_2H$

IIIa


$(CH_3)_2\underset{C_6H_5}{C}-\overset{OH}{C}=NOH$

IV

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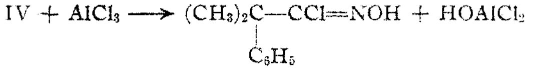
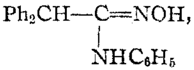
[1] Holders of Commercial Solvents Corporation Fellowships, 1942–1944 (D. W.), 1947–1948 (M. N.).

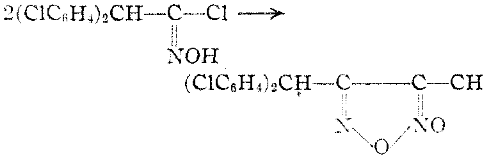
[2] Lambert, Rose and Weedon, *J. Chem. Soc.*, 42 (1949).



$$\mathrm{IV} + \mathrm{AlCl_3} \longrightarrow (\mathrm{CH_3})_2\underset{\displaystyle \mathrm{C_6H_5}}{\underset{|}{\mathrm{C}}}\text{—}\mathrm{CCl{=}NOH} + \mathrm{HOAlCl_2}$$

The above mechanism, involving an *aci*-nitroalkane (II) in the sequence of steps, is in keeping with existing knowledge that acidic reagents convert *aci*-nitroalkanes into hydroxamic acids. One such example[3] is the formation of benzoylacetohydroxamic acid, $CH_3C(OH){=}NOCOC_6H_5$, by reaction of sodium *aci*-nitroethane and benzoyl chloride.

The structure of diphenylacetohydroximyl chloride was established by oxidation to benzophenone, reaction with aniline to form N-hydroxy-N'-phenyldiphenylacetamidine,  $\mathrm{Ph_2CH}\text{—}\underset{\displaystyle \mathrm{NHC_6H_5}}{\underset{|}{\mathrm{C}}}\mathrm{{=}NOH}$, mild hydrolysis (with sodium acetate in 50% acetic acid) into diphenylacetohydroxamic acid, $Ph_2CHCONHOH$, and vigorous hydrolysis (6 *N* sulfuric acid) into diphenylacetic acid. The structure of the chloro analog was proven analogously. Also, bis-*p*-chlorophenylacetohydroximyl chloride was converted into 3,4-bis-(*p*,*p'*-dichlorobenzhydryl)-furoxan in the presence of sodium hydroxide or sodium carbonate solutions. Benzohydroximyl chloride is known[4] to change into 3,4-diphenylfuroxan in this way.



Experimental

Diphenylacetohydroximyl Chloride.—A cooled solution of 50 g. of ω-nitrostyrene (b. p. 57–58°) in 150 cc. of benzene was added dropwise, with stirring, to a suspension of 50 g. of anhydrous aluminum chloride in 100 cc. of benzene cooled to 10–15° in an ice-bath. The addition was completed in an hour and a half. After an additional half-hour of stirring, the dark solution was allowed to come to room temperature and stand overnight. On decomposition of the complex with ice and hydrochloric acid, a white solid formed and was separated by filtration. An additional 2 g. of this solid was obtained from the benzene layer, after washing with sodium carbonate solution and water, by concentration of the solution to half its volume under diminished pressure. The total yield of crude product was 59 g. or 71.5%. After two recrystallizations from benzene, the product was obtained as white needles melting at 165–166°.

Anal. Calcd. for $C_{14}H_{12}ClNO$: C, 68.41; H, 4.91; Cl, 14.43; N, 5.70. Found: C, 68.53; H, 4.84; Cl, 14.47; N, 5.59.

Bis-(*p*-chlorophenyl)-acetohydroximyl Chloride.—The reagents taken were 41 g. of *p*-chloro-ω-nitrostyrene of m. p. 112–113° in 250 cc. of chlorobenzene, and a suspension of 85 g. of aluminum chloride in 800 cc. of chlorobenzene. The procedure followed that given above. On decomposition of the complex with ice and hydrochloric acid after standing overnight, no precipitate formed, but 60.5 g. (85% yield) of crude product was obtained by concentration of the washed chlorobenzene layer under diminished pressure. A considerable amount of a tarry substance was also formed. After three recrystallizations from benzene, the bis-(*p*-chlorophenyl)-acetohydroximyl chloride melted at 142.5–143°.

Anal. Calcd. for $C_{14}H_{10}Cl_3NO$: C, 53.45; H, 3.20; Cl, 33.82; N, 4.45. Found: C, 53.43; H, 3.19; Cl, 33.44; N, 4.63.

Oxidations.—Diphenylacetohydroximyl chloride was oxidized by refluxing it with nitric acid (15 cc. of concd. nitric acid in 35 cc. of water) for one hour. The original solid changed to an oil which yielded a 2,4-dinitrophenylhydrazone of m. p. 222–224° and a phenylhydrazone of m. p. 134–135°, demonstrating that the oil was benzophenone.

Two grams of bis-(*p*-chlorophenyl)-acetohydroximyl chloride was refluxed for one hour with a mixture of 10 cc. of concd. nitric acid and 30 cc. of water. The resulting orange oil, when recrystallized from alcohol, yielded a white solid melting at 144–145.5°. The oxime obtained by the reaction with hydroxylamine melted at 135–135.5° after several recrystallizations from alcohol. The values given in literature[5] for the melting points of *p*,*p'*-dichlorobenzophenone and its oxime are 144–145° and 135°, respectively.

Reaction with Aniline. Diphenylacetohydroximyl Chloride.—Five-tenths gram of diphenylacetohydroximyl chloride was mixed with 0.6 g. of aniline. The paste thus formed grew warm and solidified on standing a few moments. It was triturated with ether. After a few hours the ether was distilled off and the residue was dissolved in dilute hydrochloric acid. Addition of sodium carbonate gave a white precipitate, m. p. 173–174° after recrystallization from alcohol; yield 0.4 g. or 63%. The compound contained no chlorine, and an alcoholic solution gave a violet color with one drop of ferric chloride, turning dark olive-green with a few more drops and turning red on heating. These colors were given by Müller[6] as characteristic of N-hydroxy-N'-phenylacetamidine and other amidoximes.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.45; H, 6.00. Found: C, 79.37; H, 6.08.

Bis-(*p*-chlorophenyl)-acetohydroximyl Chloride.—The procedure used was the same as that given above. After two recrystallizations from alcohol, bis-(*p*-chlorophenyl)-acetanilidoxime melted at 178–179° and gave the color reactions with ferric chloride characteristic of amidoximes.

Anal. Calcd. for $C_{20}H_{16}Cl_2N_2O$: C, 64.71; H, 4.34. Found: C, 64.85; H, 4.45.

Hydrolysis to the Hydroxamic Acid.—A mixture of 1 g. of diphenylacetohydroximyl chloride, 5 g. of sodium acetate and 40 cc. of 50% acetic acid was heated at 100° for two hours, then diluted with several volumes of water. The white precipitate (0.6 g., 65% of theoretical) gave an intense red color with ferric chloride solution as hydroxamic acids do. To purify the compound, it was dissolved in sodium hydroxide solution, reprecipitated by dilute hydrochloric acid, and shaken with sodium carbonate to dissolve any diphenylacetic acid which might have been formed. After recrystallization from ethyl acetate, the compound melted at 170–171°. Diphenylacetohydroxamic acid melts at 172°.[7] When mixed with an authentic sample of diphenylacetohydroxamic acid there was no depression in the melting point.

Hydrolysis to the Substituted Acetic Acid.—Half a gram of diphenylacetohydroximyl chloride was refluxed with 50 cc. of 6 *N* sulfuric acid for four hours. The resultant solid was recrystallized from hot water. A mixture with authentic diphenylacetic acid, also of m. p. 143–144°, was not depressed.

Anal. Calcd. for $C_{14}H_{12}O_2$: equiv. wt., 212.1. Found: equiv. wt., 211.5.

Refluxing 1.5 g. of bis-(*p*-chlorophenyl)-acetohydroximyl chloride for four hours with 6 *N* sulfuric acid gave no

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(3) Jones, *Am. Chem. J.*, **20**, 1 (1898).

(4) Werner and Buss, *Ber.*, **27**, 2193 (1894); Wieland, *ibid.*, **40**, 1675 (1907).

(5) Dittrich, *Ann.*, **264**, 175 (1891).

(6) Müller, *Ber.*, **22**, 2408 (1889).

(7) Jones and Hurd, THIS JOURNAL, **43**, 2432 (1921).

appreciable amount of alkali-soluble product but boiling it with 70% sulfuric acid gave a black tar from which 0.6 g. of a slightly yellow solid (m. p. 162.5–163°) was obtained after dissolving in sodium carbonate solution, filtering, acidifying, and recrystallizing two times from benzene-ligroin. The ethyl ester melted at 85–86°. The melting points given in literature[8] are 163–164° for bis-(*p*-chlorophenyl)-acetic acid and 88° for its ethyl ester.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2$: equiv. wt., 281.1. Found: equiv. wt., 284.3.

Reaction with Alkali.—It was observed that when bis-(*p*-chlorophenyl)-acetohydroximyl chloride was warmed with 10% sodium hydroxide solution, it became pasty and then resolidified. Recrystallization of the pale yellow solid from benzene–ligroin gave a white compound melting at 162.5–163°. The same compound was obtained when the hydroximyl chloride was warmed in a sodium carbonate solution. This compound is 3,4-bis-(*p*,*p*′-dichlorobenzohydryl)-furoxan.

Anal. Calcd. for $C_{28}H_{20}Cl_4N_2O_2$: C, 60.24; H, 3.61; N, 5.02; Cl, 25.40; mol. wt., 558. Found: C, 60.80; H, 3.32; N, 4.97; Cl, 25.58; mol. wt. (ebullioscopic in benzene), 574.

The furoxan is unaffected by nitric acid, either dilute or concentrated, or by alkaline permanganate. When 0.25 g. was dissolved in 100 cc. of glacial acetic acid and a solution of 7 g. of chromic oxide in 5 cc. of water and 25 cc. of glacial acetic acid was added, a white crystalline product melting at 144–146° was obtained after warming on the steam-bath for one hour and diluting the solution with water. The melting point of the oxime was 135–135.5°. This compound is identical to the *p*,*p*′-dichlorobenzophenone obtained by the nitric acid oxidation of bis-(*p*-chlorophenyl)-acetohydroximyl chloride.

Acknowledgments.—Microanalyses for carbon, hydrogen and nitrogen were performed by P. Craig, N. Mold, M. Hines and J. Anderson.

Summary

ω-Nitrostyrene and *p*-chloro-ω-nitrostyrene react with benzene or chlorobenzene in the presence of aluminum chloride to yield diarylhydroximyl chlorides. Several reactions of these compounds are presented.

EVANSTON, ILLINOIS RECEIVED APRIL 19, 1950

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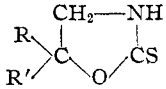
(8) Forrest, Stephenson and Waters, *J. Chem. Soc.*, 336 (1946).

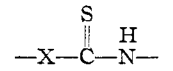
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Infrared Spectra and Tautomerism of 2-Thioöxazolidone and Congeners

BY MARTIN G. ETTLINGER[1]

In an investigation of the natural product *l*-5-vinyl-2-thioöxazolidone[2] (I, R = $CH=CH_2$, R′ = H), the presence of the thioncarbamate group was established by comparison of the

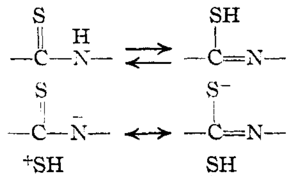
I 

II 

$-X-\overset{\overset{S}{\|}}{C}-\overset{H}{N}-$

X = O, S or N—

infrared absorption spectrum with spectra of known compounds containing the functional group II. These substances, being incompletely N-substituted thioamides, may exist in thione (III) or thiol (IV) forms, which are interconvertible through a common anion (V) and cation (VI). Each tautomer is a resonance hybrid;

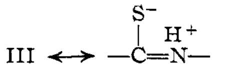


III $-\overset{\overset{S}{\|}}{C}-\overset{H}{N}- \rightleftarrows -\overset{\overset{SH}{|}}{C}=N-$ IV

V $-\overset{\overset{S}{\|}}{C}-\overset{-}{N}- \longleftrightarrow -\overset{\overset{S^-}{|}}{C}=N-$

VI $-\overset{\overset{^+SH}{\|}}{C}-\overset{H}{N}- \longleftrightarrow -\overset{\overset{SH}{|}}{C}=\overset{H_+}{N}-$

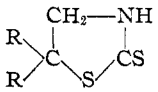
the dipolar structure VII contributes to III. The position of equilibrium between III and IV

 VII

III $\longleftrightarrow -\overset{\overset{S^-}{|}}{C}=\overset{H^+}{N}-$ VII

has often been discussed for compounds such as thiourea.[3] Chemical reactions, oxidation or alkylation, do not furnish evidence for decision. The weak, phenolic acidity of thioamides accords with either formula; since the less acidic tautomer must predominate, III cannot be excluded by the contention that a substance of such structure should be neutral.

Infrared spectra of numerous thioamides in oil suspension have recently been published by Randall, Fowler, Fuson and Dangl.[4] These workers correlated with the group II a "thioureide" absorption band at 6.3–6.9 μ. For one compound, 2-thiothiazolidone (VIII, R = H), the position of the acidic hydrogen could be inferred[5]

VIII 

from the spectrum. The solid absorbs at 3.2 and 6.6 μ, corresponding to hydrogen bonded imino and to dithiocarbamate groups, and not at 3.9 and 6–6.3 μ, required for the sulfhydryl group and carbon–nitrogen double bond of a thiol structure (IV). Hence, 2-thiothiazolidone is a true thione. The present paper supports and generalizes this conclusion.

In thioamides that contain no hydroxyl group

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(1) Member of the Society of Fellows, Harvard University.

(2) Astwood, Greer and Ettlinger, *J. Biol. Chem.*, **181**, 121 (1949).

(3) Taylor and Baker, eds., "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, pp. 151, 280–291.

(4) Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

(5) *Ibid.*, p. 66.