of *o*-bromoethylbenzene in 200 ml. of dry ether was then added slowly. Reaction started at once. The temperature was moderated by cooling so that a mild reflux was maintained. After the addition was complete (1 hr.) the mixture was refluxed for 2 hr. Freshly distilled diethylsulfate (126 g., or 0.820 mole) in 200 ml. of dry ether was then added with cooling at such a rate that a mild reflux was maintained. After further refluxing for 2 hr. the mixture was poured into 200 ml. of ice cold 10% sulfuric acid. The ether layer was washed with 200 ml. of 10% sulfuric acid, five times with 500-ml. portions of water, and dried over anhydrous sodium sulfate. Removal of ether and fractional distillation yielded 32.5 g. (57.8%) of an oil boiling at 70–73° (17 mm.); n_D^{20} 1.5033 (lit.[6] 1.5034).

General procedure for the synthesis of 8-nitroquinolines and 1,10-phenanthrolines.

A. Use of sulfuric acid. A stirred mixture of one molar proportion of the appropriate aromatic amine, 1 mole of arsenic acid hemihydrate, 4 moles of sulfuric acid in 96.8% solution (10 moles in the preparation of 3-ethylphenanthroline) and a volume of water equal to one third of the volume of sulfuric acid used was heated to 100° and treated with 3.5 moles of glycerol or 2 moles of 1-chloropentanone-3 at such a rate that the temperature did not exceed 140°. Heating was continued at this temperature for 2 hr. (25 min. in the preparation of 5,6-diethylphenanthroline). The mixture was then poured into water, made alkaline, and the precipitate removed by filtration. Both filtrate and precipitate were extracted with hot benzene. After removal of the solvent the 8-nitroquinolines prepared by this method were crystallized from the solvents indicated in Table I. The phenanthrolines were all crystallized from benzene–petroleum ether except 5,6-diethyl-1,10-phenanthroline for which petroleum ether alone was used.

B. Use of phosphoric acid. A stirred mixture of one molar proportion of aromatic amine, 2 moles of arsenic acid hemihydrate and 85% phosphoric acid (100 ml. per 0.1 mole of amine) was heated to 100° and 1-chloropentanone-3 (1.3 moles) or α-ethylacrolein (2 moles) added dropwise at such a rate that the temperature did not exceed 105°. This temperature was maintained for an additional 0.5 hr. The reaction mixture was then poured on ice and neutralized with concentrated ammonium hydroxide. The resulting precipitate and filtrate were extracted with hot benzene, and the combined extracts evaporated to dryness. The 8-nitroquinolines prepared by this method were crystallized from the solvents indicated in Table I. 3,8-Diethylphenanthroline was crystallized from benzene–petroleum ether.

8-Aminoquinolines. These were all prepared by the catalytic reduction (Adams' catalyst) of the corresponding 8-nitroquinolines except 4,6-diethyl-8-aminoquinoline for which stannous chloride in ethanol was used as the reducing agent. 4,6-Diethyl- and 5,6-diethyl-8-aminoquinolines were oils which were used directly for the preparation of the phenanthrolines, without further purification.

Acknowledgment. The authors are grateful to the Monsanto Chemical Co. for a generous gift of *o*-ethylaniline.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Steric Requirements in the Cyclization of Naphthalene Derivatives

CARL DJERASSI AND GEORGE R. PETTIT[1]

Received October 15, 1956

While polyphosphoric acid cyclization followed by dehydrogenation of γ-(2-naphthyl)butyraldehyde (Ia) yields exclusively phenanthrene, the corresponding substituted ketones Ib, Ic and Id lead predominantly to linear cyclization products of the anthracene series. These results are ascribed to steric interference of the 4 and 5 substituents in the phenanthrene series and are not operative in the next lower homolog as demonstrated by the cyclization of 5-(2′-naphthyl)pentan-3-one (VIc) to 1-ethyl-3H-benz[e]indene (VII).

It has been reported recently[2] that the polyphosphoric acid cyclization of 6-(2′-naphthyl)-3-hexanone (Ic) followed by dehydrogenation yielded the linear product 1-ethylanthracene (IIc) rather than 4-ethylphenanthrene (IIIc). This unexpected result was ascribed to the well known steric interference between the substituents in the 4 and 5 positions of the phenanthrene system.[3] In order to confirm this supposition and to eliminate the possibility that the cyclization agent played a role, it was decided to examine the scope of this steric effect by altering the size of the ketonic side chain.

Cyclization of 2-β-(2′-naphthyl)-ethylcyclohexanone (Id)[4] followed by dehydrogenation furnished the linear product, benz[*a*]anthracene (IV) and no benzo[*c*]phenanthrene (V) could be detected by ultraviolet examination of the mother liquors. On the other hand, similar treatment of 5-(2-naphthyl)pentan-2-one (Ib), prepared from γ-(2-naphthyl)butyryl chloride and dimethyl cadmium, yielded a mixture of 1-methylanthracene (IIb) and 4-methylphenanthrene (IIIb). The former could be isolated directly in crystalline form while the presence of 4-methylphenanthrene was demonstrated by oxidation of the crude reaction mixture and isolation of 6-methyldiphenic acid.

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[1] Monsanto Predoctorate Research Fellow 1954–1956. Present address, Norwich Pharmacal Company, Norwich, N. Y.

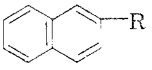
[2] H. Bendas and C. Djerassi, *J. Am. Chem. Soc.*, **78**, 2474 (1956).

[3] *Cf.* M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940) and later papers.

[4] This ketone was prepared by the Stork reaction [G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954)] using cyclohexanone pyrrolidine enamine or by alkylation of 2-ethoxycarbonylcyclohexanone.

Finally, γ-(2-naphthyl)butyraldehyde (Ia)[5] was subjected to the same reaction sequence whereupon only phenanthrene (IIIa), uncontaminated by anthracene (IIa), was formed. It is clear, therefore, that even with polyphosphoric acid, cyclization into the C-1 position of 2-substituted naphthalenes is the preferred course but that the reaction is quite sensitive to steric interference and becomes noticeable already when a methyl group (*cf.* Ib) is attached to the carbonyl group.

The above observed steric effects operate only in the formation of 6-membered rings (phenanthrene *vs.* anthracene ring closure). This is demonstrated by the behavior of 5-(2′-naphthyl)pentan-3-one (VIc) which yielded only 1-ethyl-3H-benz[*e*]indene (VII)[6] in marked contrast to the observed linear cyclization[2] of the next higher homolog (Ic → IIc).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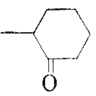
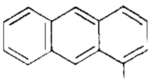
b R=$(CH_2)_3COCH_3$
c R=$(CH_2)_3COC_2H_5$

d R=$(CH_2)_2$—
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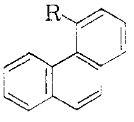
b R=CH_3
c R=C_2H_5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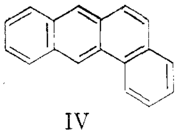
b R=CH_3
c R=C_2H_5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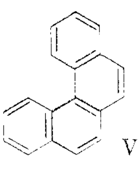
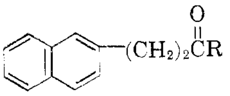
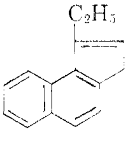
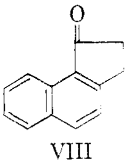

V


VIa R=OH
b R=Cl
c R=C_2H_5


VII


VIII

EXPERIMENTAL[7]

2-β-(2′-Naphthyl)ethylcyclohexanone (Id). (*a*) *From cyclohexanone pyrrolidine enamine.*[4] A solution of 4.15 g. of cyclohexanone and 3.3 g. of pyrrolidine in 100 cc. of benzene was heated to reflux under a water separator and the calculated amount of water was produced within 2 hr. The benzene was removed *in vacuo* and the crude enamine was heated under reflux for 50 hr. with 10 g. of β-(2-naphthyl)ethyl bromide. The methanol was then distilled and the residue was heated on the steam bath for 30 min. with excess water. After cooling, the product was isolated by means of benzene and distilled. The fraction (1.35 g.) boiling at 150–175° and 0.5 mm. was chromatographed on 40 g. of acid-washed alumina and the ketone was eluted with 1:1 hexane-benzene. Crystallization from ethanol furnished 0.63 g. (5.9%) of colorless needles, m.p. 61.5–63°, $\lambda_{max}^{CHCl_3}$ 5.83μ.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.52; H, 8.17.

When the reaction was carried out with a 50% excess of bromide in ethylene glycol solution at 120–125° for 14 hr., the principal product (30% yield) proved to be *β,β′-(2-naphthyl)hydroxyethyl ether* which crystallized from hexane as colorless hemispheres, m.p. 38–39.5°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.00; H, 7.56.

The *3,5-dinitrobenzoate* crystallized as pale yellow needles from hexane-acetone, m.p. 106.5–107.5°.

Anal. Calcd. for $C_{21}H_{18}N_2O_7$: C, 61.46; H, 4.42. Found: C, 61.32; H, 4.48.

(*b*) *From 2-ethoxycarbonylcyclohexanone.* The potassium derivative of 2-ethoxycarbonylcyclohexanone (6.6 g.) was prepared from 1.5 g. of potassium sand in 10 cc. of toluene and after the addition of 9.6 g. of β-(2-naphthyl)ethyl bromide in 20 cc. of toluene, the mixture was heated under reflux for 40 hr. The crude alkylation product was boiled for 4.5 hr. with 150 cc. of glacial acetic acid and 40 cc. of concd. hydrochloric acid. Isolation with ether, distillation *in vacuo*, and recrystallization from ethanol afforded 0.38 g. of 2-β-(2′-naphthyl)ethylcyclohexanone (Id), m.p. 59.5°. No attempt was made to improve the yield in this reaction.

Conversion of 2-β-(2′-naphthyl)ethylcyclohexanone (Id) *to benz[a]anthracene* (IV). A mixture of 0.40 g. of the ketone Id and 10 g. of polyphosphoric acid was heated with frequent stirring for 3 hr. on the steam bath and for an additional 4 hr. at 165°. After addition of water, the product was extracted with ether, washed with alkali and water, evaporated and chromatographed on 15 g. of alumina (activity I). Elution with hexane provided 0.3 g. of an oil which contained no carbonyl impurity by infrared spectral examination.

The cyclization product was dehydrogenated for 1 hr. at 300° in a carbon dioxide atmosphere with 0.15 g. of 30% palladium-charcoal catalyst and the solid residue, after separation of the catalyst and removal of solvent, was recrystallized from ethanol to give 0.18 g. of benz[*a*]anthracene (IV), m.p. 155–157°, trinitrofluorenone complex,[8] m.p. 220–221°. Identity was established by mixture melting point determination and infrared comparison with an authentic sample of the hydrocarbon.[9] The ultraviolet absorption spectrum[10] of the crude and of the pure dehydrogenation product confirmed the absence of benzo[*c*]phenanthrene (V) (m.p. 68°).

5-(2′-Naphthyl)-pentan-2-one (Ib). A Grignard solution prepared in an atmosphere of nitrogen from 2.43 g. of magnesium, 14.2 g. of methyl iodide and 50 cc. of ether was treated at 0° with 9.8 g. of dry cadmium chloride. After heating under reflux for 20 min., the ether was replaced by dry benzene and a solution of 17.4 g. of γ-(2-naphthyl)butyryl

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[5] Lithium aluminum hydride reduction [*cf.* F. Weygand, *et al.*, *Angew. Chem.*, **65**, 525 (1953)] of γ-(2-naphthyl)butyric acid *N*-methyl anilide or desulfurization of ethyl γ-(2-naphthyl)thiobutyrate with acetone-deactivated Raney nickel proved unsatisfactory and the aldehyde Ia was finally prepared by careful oxidation of γ-(2-naphthyl)butyl alcohol.

[6] An authentic specimen was synthesized from 2,3-dihydrobenz[e]inden-1-one (VIII) and ethylmagnesium bromide.

[7] Melting points and boiling points are uncorrected. We are indebted to Mrs. Dolores Phillips for all ultraviolet and infrared spectral measurements and to Dr. A. Bernhardt, Mülheim, Germany, for the microanalyses.

[8] M. Orchin and E. W. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

[9] We are grateful to Dr. M. S. Newman (Ohio State University) for an authentic specimen.

[10] For a comparison of the relevant ultraviolet absorption spectra see R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, Inc., New York, 1951.

chloride[11] in 35 cc. of benzene was added. After stirring for 1 hr. at room temperature and for 3 hr. under reflux, the mixture was decomposed with ice and sulfuric acid and the product was extracted with ether. Chromatography on 500 g. of alumina, elution with 1:1 hexane-benzene and recrystallization from hexane afforded 8.6 g. (51%) of the desired ketone, m.p. 42–43.5°, $\lambda_{max}^{CHCl_3}$ 5.81μ.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.21; H, 7.85.

Cyclodehydration of 5-(2'-naphthyl)pentan-2-one (Ib). Polyphosphoric acid (30 g.) cyclization of 3.0 g. of 5-(2'-naphthyl)pentan-2-one (Ib) was carried out in the above described manner to yield after chromatography 1.84 g. of colorless, nonketonic oil. A 1.66 g. sample of it was dehydrogenated with 0.6 g. of 30% palladium-charcoal and the dehydrogenation product (1.26 g.), dissolved in 6 cc. of glacial acetic acid, was treated dropwise on the steam bath with a solution of 3.15 g. of chromium trioxide in 8 cc. of 33% acetic acid. After heating for an additional hour on the steam bath, the mixture of quinones (0.98 g.) was isolated with ether and oxidized directly by heating under reflux for 2 hr. with 4 cc. of 30% hydrogen peroxide and 15 cc. of acetic acid. After standing overnight, the orange colored crystals (0.38 g., m.p. 166–167.5°) of 1-methyl-9,10-anthraquinone[12] were collected. Identity was established by mixture melting point determination with an authentic specimen[13] prepared from 1-methylanthracene (IIb).[13]

The filtrate from the oxidation was concentrated to a small volume, made basic with sodium bicarbonate solution and extracted with chloroform (discarded). Acidification of the aqueous solution, extraction with chloroform and recrystallization of the chloroform residue from aqueous methanol afforded 0.24 g. of *6-methyldiphenic acid,* m.p. 226–227°, undepressed upon admixture with an authentic sample of this acid[14] prepared by oxidation of 4-methyl-9,10-phenanthraquinone.

γ-(2-Naphthyl)butyraldehyde (Ia). A solution of 4.0 g. of γ-(2-naphthyl)butyric acid was reduced with 0.87 g. of lithium aluminum hydride in a mixture of ether and tetrahydrofuran (25 min. reaction period). After processing in the usual manner there was isolated (after recrystallization from hexane) 3.4 g. (92%) of *γ-(2-naphthyl)butyl alcohol,* m.p. 37–38°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.81; H, 8.01.

An ice cold solution of 0.7 g. of the above alcohol in 10 cc. of acetone (distilled from permanganate) was treated with 0.85 cc. of an 8*N* chromium trioxide solution[15] and the reaction mixture was diluted immediately with a large volume of water. The crude neutral product was chromatographed on 15 g. of acid washed alumina and the combined 4:1 hexane-benzene eluates were distilled at a bath temperature of 210–215° and 0.005 mm.; yield, 0.34 g., $\lambda_{max}^{CHCl_3}$ 5.79μ.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.62; H, 7.38.

The *semicarbazone* was recrystallized from benzene-hexane and exhibited m.p. 119–120°.

Anal. Calcd. for $C_{15}H_{18}N_3O$: C, 70.28; H, 7.07. Found: C, 70.79; H, 7.00.

In connection with two alternate approaches[4] to the aldehyde Ia, it was necessary to prepare *γ-(2-naphthyl)butyric acid N-methyl anilide,* m.p. 101–102.5° (from ethanol).

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.56; H, 6.61; N, 4.96; as well as *ethyl γ-(2-naphthyl)thiobutyrate,* b.p. 168–172° at 1 mm.

Anal. Calcd. for $C_{16}H_{18}OS$: C, 74.39; H, 7.02; S, 12.43. Found: C, 74.48; H, 7.09; S, 12.32.

Conversion of γ-(2-Naphthyl)butyraldehyde (I) *to Phenanthrene* (IIIa). The cyclization of the aldehyde and dehydrogenation was performed in the above described manner and only phenanthrene (m.p. 92–94°) could be isolated. Ultraviolet inspection[10] of the crude product indicated the absence of anthracene (IIa), which, in any event, would have been isolated with ease because of its high m.p. (216°).

5-(2'-Naphthyl)pentan-3-one (VIc). β-(2-Naphthyl)propionyl chloride (VIb)[16] was treated with diethylcadmium in exactly the same fashion as described above in the dimethyl cadmium reaction of the corresponding butyryl chloride and furnished 71% of the desired ketone VIc, m.p. 41.5–42.5° (from hexane), $\lambda_{max}^{CHCl_3}$ 5.82μ.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C. 84.91; H, 7.55.

1-Ethyl-3H-benz[e]indene (VII). (a) *From 2,3-dihydrobenz[e]inden-1-one* (VIII). A solution of 2.5 g. of 2,3-dihydrobenz[*e*]inden-1-one (VIII)[17] in 35 cc. of benzene was added with stirring to a cooled solution of ethylmagnesium bromide prepared from 1.32 g. of magnesium, 6.5 g. of ethyl bromide, and 50 cc. of ether. After heating under reflux for 2.5 hr., the reaction mixture was decomposed by the addition of ammonium chloride solution and the neutral product was crystallized from hexane to afford 2.54 g. (86%) of the ethyl carbinol, m.p. 80–84° with sintering at 70°. This substance was very unstable and was transformed during recrystallization from ethanol into 1-ethyl-3H-benz[*e*]indene (VII), m.p. 42–43°. Dehydration of the carbinol could also be accomplished in 86% yield with phosphorus oxychloride in pyridine.[18]

The hydrocarbon was rapidly oxidized in the air to a colored oil by standing overnight and it was best characterized as the stable, deep red 2,4,7-trinitrofluorenone complex which crystallized as platelets from benzene-ethanol, m.p. 140–141.5°. By converting the entire product into this complex, a 64% over-all yield could be realized in the Grignard reaction. The hydrocarbon could be regenerated by passing a benzene solution over an alumina column.

Anal. Calcd. for $C_{28}H_{19}N_3O_7$: C, 66.01; H, 3.76; N, 8.25. Found: C, 65.51; H, 3.65; N, 8.13.

(b) *From 5-(2'-naphthyl)pentan-3-one* (VIc). Cyclization of 1.0 g. of the ketone VIc with 10 g. of polyphosphoric acid for 1.5 hr. on the steam bath yielded a greenish oil which was dissolved in hexane and passed over a column of 30 g. of alumina. The hexane-eluted, colorless hydrocarbon (0.66 g.) furnished 1.0 g. of the above described trinitrofluorenone complex of 1-ethyl-3H-benz(*e*)indene (VII), m.p. 130–135°, raised to 139–141° after recrystallization from benzene-

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(11) The acid chloride was prepared with thionyl chloride at room temperature since appreciable amounts of 4-keto-1,2,3,4-tetrahydrophenanthrene were formed when the reaction mixture was heated.

(12) L. F. Fieser and H. Heymann, *J. Am. Chem. Soc.,* **64,** 376 (1942); O. Fischer and A. Sapper, *J. prakt. Chem.,* [2], **83,** 201 (1911).

(13) This was obtained in a second cyclization-dehydrogenation in which the crude product was not oxidized but rather purified *via* its 2,4,7-trinitrofluorenone complex (m.p. 218–219°) and decomposed on alumina to 1-methylanthracene [m.p. 84–85°; for literature references see W. L. Mosby, *J. Org. Chem.,* **18,** 964 (1953)]. Identity of this hydrocarbon was established by mixture melting point determination and by infrared and ultraviolet spectral comparison with a specimen for which we are indebted to Dr. D. L. Turner [*J. Am. Chem. Soc.,* **72,** 4318 (1950)].

(14) D. Aziz and J. C. Breckenridge, *Can. J. Research,* **28B,** 26 (1950).

(15) *Cf.* K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.,* 39 (1946); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.,* **21,** 1547 (1956) and references cited therein.

(16) F. Mayer and A. Sieglitz, *Ber.,* **55,** 1835 (1922).

(17) Prepared by hydrogen fluoride cyclization of β-(2-naphthyl)propionic acid (VIa) according to M. F. Ansell and D. H. Hey, *J. Chem. Soc.,* 2874 (1950).

(18) For precautions see H. Dannenberg and A. Rahman, *Ber.,* **88,** 1405 (1955).

ethanol. Decomposition of a sample of the complex by passage over alumina afforded the crystalline hydrocarbon (m.p. 40°) and identity was established by mixture melting point and infrared comparison with samples of the hydrocarbon and its trinitrofluorenone complex synthesized according to procedure (a).

Detroit, Mich.

[Contribution from the Monsanto Chemical Company, Plastics Division]

4-Imidazolidinethiones

JOHN D. CHRISTIAN[1]

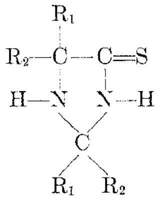
Received September 20, 1956

The isolation of 2,2,5,5-tetramethyl-4-imidazolidinethione from the reaction of acetone cyanohydrin with carbon disulfide and ammonium hydroxide has been verified. High yields of this and other substituted 4-imidazolidinethiones were obtained by the reaction of ketones with ammonium sulfide and either HCN or alkali cyanide.

The literature pertaining to 4-imidazolidinethiones has never been placed in order and the relevant findings of several investigators have been left uncorrelated. Gatewood and Johnson[2] investigating the action of hydrogen sulfide on α-aminoacetonitrile and α-aminopropionitrile found that dithiopiperazines were produced. α-Aminoisobutyronitrile, however, yielded a well defined crystalline material, melting at 153–155°, with the empirical formula $C_7H_{14}N_2S$. Upon acid hydrolysis this product gave α-aminoisobutyric acid. From these results they assigned structure I to the product. This is the earliest report of a 4-imidazolidinethione in the literature.

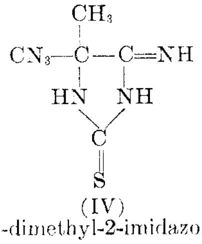
Abe[3] reported that methyl ethyl ketone by successive treatment with hydrogen cyanide, ammonia, and hydrogen sulfide produced "4-thio-2,5-dimethyl-2,5-diethyldesoxyhydantoin," II, melting at 67°. Similar treatment of alkyl aryl ketones was reported to produce α-aminothioamides while aryl ketones yielded dibenzohydryl disulfides.

Bucherer and Brandt[4] reacted cyclohexanone cyanohydrin and freshly prepared ammonium sulfide to obtain a compound, m.p. 225°, to which they assigned structure III. They assigned structure I to a similar product, melting at 155–156° which they obtained from acetone cyanohydrin and ammonium sulfide. Methyl ethyl ketone cyanohydrin and ammonium sulfide yielded a product $C_6H_{18}N_2S$ (II), m.p. 58–63°.[5] Later, Bucherer and Lieb[6] reported that they had obtained by reacting cyclohexanone cyanohydrin with carbon disulfide and 25% ammonium hydroxide in ethanol an unidentified product melting at 225°.[6] In the absence of ethanol, these reactants produced a compound, m.p. 261–265°.[7] Cyclohexanone cyanohydrin, carbon disulfide and gaseous ammonia gave products melting at 223°[8] and 195°.[9] Acetone cyanohydrin, carbon disulfide, and ammonium hydroxide were found to yield a compound $C_7H_{14}N_2S$, m.p. 154–155°;[10] gaseous ammonia gave this compound and another, m.p. 297°.[11]



Compound	R_1	R_2	Nomenclature
I	CH_3	CH_3	2,2,5,5-tetramethyl-4-imidazolidinethione
II	CH_3	C_2H_5	2,5-diethyl-2,5-dimethyl-4-imidazolidinethione
III	$—(CH_2)_5—$		7,14-diazadispiro-(5.1.5.2)pentadecane-15-thione

Carrington[12] prepared a series of "5,5-disubstituted-2,4-dithiohydantoins" which were found to react with ammonia to give the corresponding "4-imino-2-thiohydantoin." It was his opinion that "4-imino-5,5-dimethyl-2-thiohydantoin" (IV), m.p. 300–302° dec., was the unidentified material melt-



(IV)

4-imino-5,5-dimethyl-2-imidazolidinethione

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[1] Present address: Grace Chemical Co., Box 4906, Memphis 7, Tenn.

[2] Gatewood and Johnson, *J. Am. Chem. Soc.*, **50**, 1424 (1928).

[3] Abe, *Science Repts. Tokyo Bunrika Daigaka*, Sect. A, 2, 1 (1934); through *Chem. Abstr.*, **28**, 4383.

[4] Bucherer and Brandt, *J. prakt. Chem.*, **140**, 129 (1934).

[5] The difference in melting points from that reported by Abe may be due to a separation of stereoisomeric pairs.

[6] Bucherer and Lieb, *J. prakt. Chem.*, **141**, 5 (1934).

[7] Probably V.

[8] Probably III.

[9] Probably VI.

[10] Probably I.

[11] Probably IV.

[12] Carrington, *J. Chem. Soc.*, 681, 684 (1947).