to Dr. Peter Lim for infrared interpretations, Dr. Lloyd K. Moss and group for paper chromatography and Mr. O. P. Crews, Jr., and group for the large-scale preparation of intermediates.

Addendum.—The 5,8-dideaza-5,6,7,8-tetrahydrofolic acid (XI) at 80 mγ/ml. gave 50% inhibition of growth of *S. faecalis* on a Flynn folic acid medium containing 1mγ/ml. of folic acid. Compound XVIIa was inactive at 1γ/ml. We wish to thank Dr. Dorris Hutchison of Sloan-Kettering Institute for these data.

MENLO PARK, CALIF.

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Synthesis of Carboxylic Acid Hydrazides and *s*-Triazoles of the Anthraquinone Series

BY ERWIN KLINGSBERG

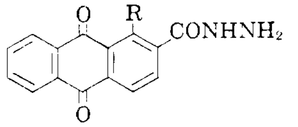
RECEIVED MAY 5, 1958

2-Anthraquinonecarboxylic acid hydrazide, its 1-chloro and 1-amino derivatives, and certain related diaroylhydrazines were prepared. Some of these compounds were converted to *s*-triazoles.

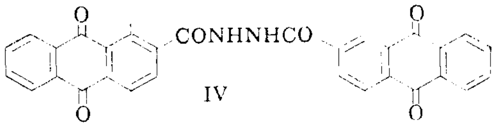
The present paper describes the preparation of certain 2-anthraquinonecarboxylic acid hydrazide derivatives, and the conversion of some of them to anthraquinonyl *s*-triazoles. Both classes of compounds are of interest by virtue of their relationship to anthraquinonyl oxadiazoles, which have recently acquired importance as vat dyestuffs.[1]

2-Anthraquinonecarboxylic Acid Hydrazides.—At the outset of this investigation, the preparation of the parent compound, 2-anthraquinonecarboxylic acid hydrazide itself, was undertaken. The reaction of 2-anthraquinonecarbonyl chloride with a large excess of hydrazine gave an apparently intractable product with a high indefinite melting point and a low nitrogen content. Ester hydrazinolysis under normal conditions was also discouraging; although 1-amino and 1,4-diamino-2-anthraquinonecarboxylic esters are reported to react normally with hydrazine,[2] ethyl 2-anthraquinonecarboxylate did not react, but was recovered unchanged after refluxing with hydrazine in methyl Cellosolve solution.

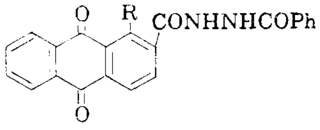
It was, found however, that in the absence of organic solvent the ester is reduced rapidly by aqueous hydrazine hydrate to the deep red hydroquinone. This is converted to the hydrazide, which is oxidized readily to a good yield of the desired product (I).[2a]



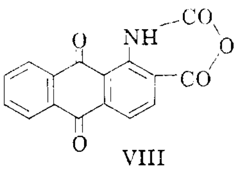
I, R = H
II, R = Cl
III, R = NH_2



IV



V, R = H
VI, R = Cl
VII, R = NH_2



VIII

It is not apparent why the carbethoxy group is more readily subject to nucleophilic attack when the anthraquinone system is in reduced, and probably anionic, form.

After the hydrazide I had been prepared and characterized, re-examination of the reaction between 2-anthraquinonecarbonyl chloride and hydrazine showed that the product was a mixture of a 55% yield of I with a 45% yield of bis-aroylhydrazine (IV). These are readily separable by crystallization from *o*-dichlorobenzene. It is noteworthy that so much diacylation occurs, despite the limited solubility of the acid chloride and the presence of a large excess of hydrazine. Under similar conditions, 1-chloro-2-anthraquinonecarbonyl chloride gives a good yield of the hydrazide II without a significant degree of diacylation.

2-Anthraquinonecarbonyl chloride and its 1-chloro derivative react with benzhydrazide to give the bis-aroylhydrazines V and VI.

For the preparation of the 1-amino hydrazide III, 3,4-phthaloylisatoic anhydride (VIII) was used. This compound was prepared readily by the phosgenation of 1-amino-2-anthraquinonecarboxylic acid, as described in the patent literature,[3] although it melts much higher than reported. It reacts with hydrazine to give III,[4] and with benzhydrazide to give VII.

2-Anthraquinonyl *s*-Triazoles.—Stollé[5] has described the conversion of dibenzoylhydrazine to the dichloroaldazine or "hydrazide dichloride," which reacts with aniline to give triphenyltriazole.

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[1] U. S. Patents 2,464,831, March 22, 1949; 2,749,352, June 5, 1956; 2,759,948, August 21, 1956.

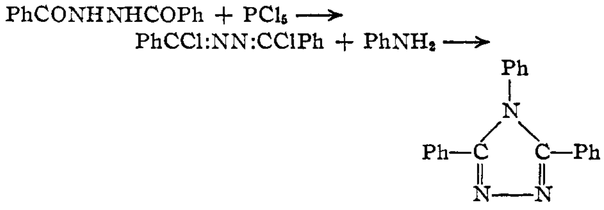
[2] P. V. Laakso, R. Robinson and H. P. Vandrewala, *Tetrahedron*, **1**, 103 (1957).

[2a] NOTE ADDED IN PROOF.—The author has now learned that the preparation of this compound from methyl 2-anthraquinonecarboxylate and hydrazine hydrate was reported by J. Shavel, Jr., F. Leonard, F. H. McMillian and J. A. King (*J. Am. Pharm. Assoc.*, **42**, 402 (1953)). There is no indication whether reduction to the hydroquinone was observed during hydrazinolysis.

[3] British Patent 719,193, November 24, 1954.

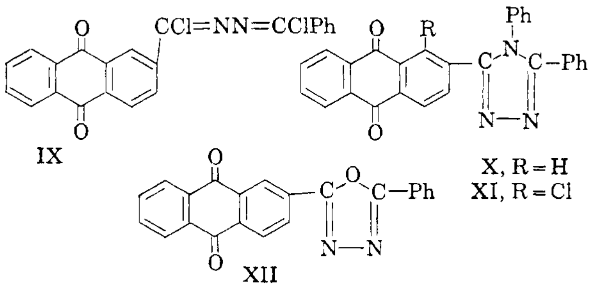
[4] U. S. Patent 2,717,898, September 13, 1955; British Patent 731,008, June 1, 1955; *cf.* ref. 2.

[5] R. Stollé, *J. prakt. Chem.*, **73**, 288 (1906); **75**, 416 (1907).



$PhCONHNHCOPh + PCl_5 \longrightarrow PhCCl{:}NN{:}CClPh + PhNH_2 \longrightarrow$

The extension of this reaction to V would give the dichloride IX and from it the triazole X.



IX

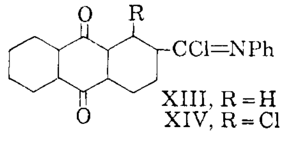
X, R = H

XI, R = Cl

XII

Phosphorus pentachloride was found to react with V at 145° to give a product of m.p. about 213–216° and a chlorine content of about 85% of the theoretical value for IX. A purer product could not be obtained, either by crystallization or by changing the reaction conditions. The difficulty with the reaction is probably the strong tendency for the formation of oxadiazole; apparently Stollé always obtained some diphenyloxadiazole in the reaction of dibenzoylhydrazine with phosphorus pentachloride. Although the oxadiazole XII was not isolated from the reaction product of V with phosphorus pentachloride, it was obtained in good yield from V and thionyl chloride.

When the impure dichloroaldazine IX was allowed to react with aniline, the triazole X was isolated from the reaction mixture as a pale yellow solid of m.p. 275–276°, recoverable unchanged from its brownish-red vat. The structure is confirmed by two additional syntheses by chloroimide–carbohydrazide condensation.[6] Thus N-phenylbenzimidyl chloride reacts with 2-anthraquinonecarboxylic acid hydrazide to give X and, conversely, N-phenyl-2-anthraquinonecarboximidyl chloride (XIII; obtained from 2-anthraquinonecarboxanilide and thionyl chloride) reacts with benzhydrazide to give X. The chloro derivative XI was obtained by the reaction of benzhydrazide with 1-chloro-N-phenyl-2-anthraquinonecarboximidyl chloride (XIV), prepared from 1-chloro-2-anthraquinonecarboxanilide and phosphorus pentachloride.

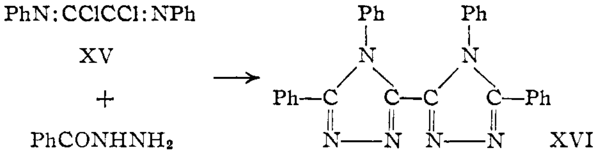


XIII, R = H

XIV, R = Cl

During the later stages of this investigation, an interesting synthesis of anthraquinonyl triazoles appeared in the German patent literature.[7] The reaction employed was a variant of the chloroimide–hydrazide condensation,[8] in which the chloroimide reacts, not with a hydrazide, but with a hydrazide anil.

Diphenyloxalimidyl chloride (XV) and benzhydrazide gave a poor yield of the bitriazolyl (XVI)



$PhN{:}CClCCl{:}NPh$ XV + $PhCONHNH_2$ → XVI

in ultraviolet absorption it closely resembles 3,4,5-triphenyl-1,2,4-triazole, indicating the absence of significant conjugation across the bitriazolyl bond.

Experimental[9]

2-Anthraquinonecarboxylic Acid Hydrazide (I).—A mixture of 6.0 g. (0.021 mole) of ethyl 2-anthraquinone carboxylate, 125 ml. (2.1 moles) of 85% hydrazine hydrate and 125 ml. of water was refluxed vigorously with occasional shaking for 45 minutes. The addition of two or three drops of octyl alcohol helped to combat foaming. The deep red solution then was cooled, diluted, and oxidized by bubbling an air stream through it. (If desired, dilute hydrogen peroxide may be used as an oxidizing agent; it helps in discharging the last traces of red color from the suspension.) The yellow-brown product then was filtered, washed, and dried; yield 5.6 g. (98%). Crystallization from 450 ml. of *o*-dichlorobenzene gave 4.6 g. of product with m.p. 240–242° dec., somewhat dependent upon the rate of heating. A small sample was crystallized from xylene for analysis.

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: C, 67.7; H, 3.8; N, 10.5. Found: C, 68.1; H, 3.8; N, 10.5.

Ethyl 2-anthraquinonecarboxylate was recovered unchanged (m.p. and mixed m.p.) after being refluxed for 4.5 hours in solution with hydrazine hydrate in methyl Cellosolve.

Reaction of 2-Anthraquinonecarbonyl Chloride and Hydrazine.—2-Anthraquinonecarbonyl chloride (10.8 g., 0.040 mole) was added over a 5-minute period to a stirred refluxing solution of 15 ml. (0.30 mole) of 100% hydrazine hydrate in 300 ml. of methanol. After being stirred and refluxed for one hour, the product was filtered and dried; yield 11.3 g. Crystallization from *o*-dichlorobenzene (10 ml. per g.) gave a 52% recovery of 2-anthraquinonecarboxylic acid hydrazide (I), similar in properties to that prepared above. The yield was thus 55% of the theoretical.

The portion insoluble in *o*-dichlorobenzene was 40% of the total, corresponding to a 45% yield of 1,2-bis-(2-anthraquinonecarbonyl)-hydrazine (IV). It was a yellow solid, dec. 340–344°. Crystallization from dimethylformamide (300 ml. per g.) gave a 60% recovery of yellow needles, m.p. 354–355° dec.

Anal. Calcd. for $C_{30}H_{16}N_2O_6$: C, 72.0; H, 3.2; N, 5.6. Found: C, 71.8; H, 3.1; N, 5.8.

Under the same reaction conditions, 1-chloro-2-anthraquinonecarbonyl chloride gave an 80% yield of **1-chloro-2-anthraquinonecarboxylic acid hydrazide (II)**, a yellow solid with an indefinite m.p. of about 295°. It could be crystallized in small quantities from *o*-dichlorobenzene.

Anal. Calcd. for $C_{15}H_9ClN_2O_2$: C, 60.0; H, 3.0; Cl, 11.8; N, 9.2. Found: C, 60.2; H, 3.0; Cl, 11.7; N, 9.1.

1-(2-Anthraquinonylcarbonyl)-2-benzoylhydrazine (V).—Ten grams (0.037 mole) of 2-anthraquinonecarbonyl chloride was dissolved in 200 ml. of refluxing xylene in a 500-ml. 3-neck flask. Efficient stirring was desirable. A solution of 7.0 g. (0.051 mole) of benzhydrazide in 50 ml. of boiling xylene then was added, with immediate formation of a heavy yellow precipitate. After being stirred and refluxed for 45 minutes, this was cooled, filtered, washed with benzene, and dried, giving 14.5 g. of crude product of m.p. 268–272° (theoretical yield 13.7 g.). It was purified by

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[6] A. Étienne, in Grignard, "Traité de Chimie Organique," Tome XXI, Paris, 1953, p. 896.

[7] W. Eckert and W. Dauner, Auslegeschrift 1,001,992; February 7, 1957.

[8] M. Busch and C. Schneider, *J. prakt. Chem.*, **89**, 310 (1914).

[9] Melting points are corrected.

crystallization from boiling carbitol (40 ml. per g.), giving about 85% recovery of yellow product of m.p. 298–300°. Crystallization from *o*-dichlorobenzene (about 175 ml. per g.) raised the m.p. to 303°.

Anal. Calcd. for $C_{22}H_{14}N_2O_4$: C, 71.4; H, 3.8; N, 7.6. Found: C, 71.1; H, 3.8; N, 7.7.

Under similar conditions, 1-chloro-2-anthraquinonecarbonyl chloride gave a quantitative yield of **1-(1-chloro-2-anthraquinonylcarbonyl)-2-benzoylhydrazine (VI)**, m.p. 286–287°. Crystallization from methyl Cellosolve (60 ml. per g.) raised the m.p. to 299–300°, with a 75% recovery. Further crystallization from *o*-dichlorobenzene raised the m.p. to 306–307°.

Anal. Calcd. for $C_{22}H_{13}ClN_2O_4$: C, 65.3; H, 3.2; Cl, 8.8; N, 6.9. Found: C, 65.5; H, 3.3; Cl, 8.6; N, 7.0.

3,4-Phthaloylisatoic Anhydride (1,2-Dihydro-4*H*-anthr-[1,2-d]-*m*-oxazine-2,4,7,12-tetrone) (VIII).—1-Amino-2-anthraquinonecarboxylic acid was purified by recrystallization from glacial acetic acid (100 ml. per g.). Its m.p. was 298–299° dec., somewhat dependent upon the rate of heating. A mixture of 10.0 g. (0.037 mole) of the acid and 100 ml. of nitrobenzene was stirred in an oil-bath at 140–150° and treated with a steady stream of phosgene for three hours. The mixture then was cooled and freed of excess phosgene in a stream of air. The yellow-orange product was filtered and washed with benzene; yield 9.2 g. (84% of theoretical). It melted at 318–319° dec., and may be crystallized from chlorobenzene without change in m.p. It is reported[8] to decompose at 245°.

Anal. Calcd. for $C_{16}H_7NO_5$: C, 65.5; H, 2.4; N, 4.8. Found: C, 65.2; H, 2.5; N, 5.1.

1-Amino-2-anthraquinonecarboxylic Acid Hydrazide[4](III).—A mixture of 8.0 g. (0.027 mole) of 3,4-phthaloylisatoic anhydride, 24 ml. of hydrazine hydrate (both 85% and 100% strength have been used; 0.41–0.48 mole), 65 ml. of methanol and 95 ml. of nitrobenzene was stirred for 0.5 hour at 75°, and then filtered. The bright brick-red product was washed with methanol and dried; yield 6.9 g. (90%). It could be crystallized from methyl Cellosolve (55–65 ml. per g.) with a recovery of 80–85%. A sample was further purified for analysis by crystallization from *o*-dichlorobenzene. It had an unreproducible m.p. above 250°.

Anal. Calcd. for $C_{15}H_{11}O_3N_3$: C, 64.1; H, 3.9; N, 15.0. Found: C, 64.5; H, 4.0; N, 14.9.

1-(1-Amino-2-anthraquinonecarbonyl)-2-benzoylhydrazine (VII).—To 125 ml. of stirred refluxing chlorobenzene was added 1.5 g. (5.2 millimoles) of 3,4-phthaloylisatoic anhydride, followed by 0.9 g. (6.6 millimoles) of benzhydrazide. The solution, which became clear after a few minutes, was refluxed 1.5 hours and then cooled and filtered, yielding 1.4 g. of red-orange solid of m.p. 296–298°. Dilution of the filtrate with petroleum ether gave an additional 0.5 g. of product, which was crystallized from 65 ml. of *o*-dichlorobenzene to give 0.3 g. of m.p. 292–294°. The combined yield of 1.7 g. represents 85% of theoretical. The melting point of the analytical sample, crystallized from *o*-dichlorobenzene, was 295–296°.

Anal. Calcd. for $C_{22}H_{15}N_4O_3$: C, 68.5; H, 3.9; N, 10.9; O, 16.6. Found: C, 68.2; H, 4.0; N, 11.2; O, 16.9.

2-(2-Anthraquinonyl)-5-phenyl-1,3,4-oxadiazole (XII).—A mixture of 0.50 g. (1.35 millimoles) of 1-(2-anthraquinonecarbonyl)-2-benzoylhydrazine (V), 5.0 ml. of thionyl chloride and 2–3 drops of pyridine, after being kept overnight at room temperature without any change in appearance, was refluxed for 0.5 hour on a steam-bath. The mixture rapidly became clear and then deposited a yellow solid. Dilution with a little benzene and filtration gave 0.45 g. (94% yield) of product of m.p. 287–288°. Crystallization from *o*-dichlorobenzene or methyl Cellosolve raised the m.p. to 288–289°.

Anal. Calcd. for $C_{22}H_{12}N_2O_3$: C, 75.0; H, 3.4; N, 8.0. Found: C, 75.3; H, 3.4; N, 8.2.

Impure 1-(α-Chlorobenzylidene)-2-[(2-anthraquinonyl)-chloromethylene]-hydrazine (IX).—A mixture of 0.3 g. (0.8 millimole) of V and 0.8 g. (4 millimoles) of phosphorus pentachloride was ground up and heated in an oil-bath at 145°. The mixture sintered rapidly and bubbled. It was stirred as well as possible for 10 minutes and then cooled, triturated with a little benzene, and filtered, giving 0.3 g. of bright yellow solid of m.p. 212–213°. Crystallization from toluene raised the m.p. to 213–216°. A chlorine determination showed that the product was very impure.

Anal. Calcd. for $C_{22}H_{12}Cl_2N_2O_2$: Cl, 17.4. Found: Cl, 14.7.

Repeated crystallization from toluene or carbon tetrachloride had little effect on m.p. or chlorine content. Results were no better when the reaction was attempted in the presence of phosphorus oxychloride or toluene.

3-(2-Anthraquinonyl)-4,5-diphenyl-*s*-triazole (X). a. **From IX.**—A mixture of 0.4 g. of impure IX, 0.11 ml. of aniline and 2.0 ml. of dimethylaniline was stirred for 0.5 hour at 170–175°, and then digested in dilute hydrochloric acid and filtered, giving 0.4 g. of pale buff solid of m.p. 254–265°. Crystallization from dilute acetic acid and then xylene raised the m.p. to 275°.

Anal. Calcd. for $C_{28}H_{17}N_3O_2$: C, 78.7; H, 4.0; N, 9.9. Found: C, 78.8; H, 4.2; N, 10.1.

This substance gave a brown-red vat, from which it was recovered unchanged on aeration. It gave no m.p. depression on admixture with the products obtained by the chloroimide–carbohydrazide condensations described below.

b. **From 2-Anthraquinonecarboxanilide.**—A mixture of 2.00 g. (6.1 millimoles) of 2-anthraquinonecarboxanilide and 25 ml. of thionyl chloride was refluxed for two hours, the thionyl chloride then being removed by evaporation. Final traces were removed by adding 15 ml. of *o*-dichlorobenzene and distilling off a few ml. until the b.p. reached 180°. Benzhydrazide (1.00 g., 7.3 millimoles) was added to the mixture, which was stirred and refluxed in the oil-bath for one hour. The product was chilled, diluted with a little benzene, filtered, and washed; yield 1.57 g. (60%) of yellow product of m.p. 260–264° (small additional amounts were obtainable from the filtrate). Crystallization from 95 ml. of xylene gave 1.15 g. (44% of theoretical) of product of m.p. 274–275°. Further crystallization from xylene or dilute acetic acid raised the m.p. to 275–276°.

Anal. Calcd. for $C_{28}H_{17}N_3O_2$: C, 78.7; H, 4.0; N, 9.9. Found: C, 78.8; H, 4.2; N, 9.8.

c. **From 2-Anthraquinonecarboxylic Acid Hydrazide.**—N-Phenylbenzimidyl chloride[10] was prepared from 0.3 g. (1.5 millimoles) of benzanilide by refluxing for one hour in 1.0 ml. of thionyl chloride, excess thionyl chloride then being removed by heating. After the addition of 3.0 ml. of *o*-dichlorobenzene and 0.3 g. (1.1 millimoles) of 2-anthraquinonecarboxylic acid hydrazide, the mixture was stirred in the oil-bath at 180° for 1.5 hours and cooled. The product was collected and dried. It was a buff-colored solid of m.p. 245–260°, yield 0.3 g. (approximately 60%). It was purified as described above, to give a product of the same m.p., mixed m.p. and analysis.

1-Chloro-2-anthraquinonecarboxanilide.—To a refluxing solution of 25 ml. (25 g., 0.27 mole) of aniline in 400 ml. of ethanol was added 12.4 g. (0.041 mole) of 1-chloro-2-anthraquinonecarbonyl chloride. The mixture was refluxed with occasional shaking for 20 minutes, cooled, and filtered. The pale yellow product was washed with alcohol and dried; yield 13.6 g. (92%), m.p. 255–259°. Crystallization from 135 ml. of *o*-dichlorobenzene gave 11.9 g. (80% of theoretical) of product of m.p. 264–265°.

Anal. Calcd. for $C_{21}H_{12}ClNO_3$: C, 69.7; H, 3.3; Cl, 9.8; N, 3.9. Found: C, 69.5; H, 3.4; Cl, 9.7; N, 4.0.

1-Chloro-N-phenyl-2-anthraquinonecarboximidyl Chloride (XIV).—A mixture of 6.00 g. (0.0166 mole) of 1-chloro-2-anthraquinonecarboxanilide, 4.2 g. (0.020 mole) of phosphorus pentachloride and 45 ml. of toluene was refluxed for three hours, diluted with 45 ml. of hexane, and chilled. Filtration and washing with petroleum ether gave 5.95 g. of product, which was crystallized from 450 ml. of methylcyclohexane to give 5.00 g. (79%) of yellow product, m.p. 180–182°.

Anal. Calcd. for $C_{21}H_{11}Cl_2NO_2$: C, 66.3; H, 2.9; Cl, 18.7; N, 3.7. Found: C, 66.2; H, 3.1; Cl, 18.6; N, 4.1.

3-(1-Chloro-2-anthraquinonyl)-4,5-diphenyl-*s*-triazole (XI).—A solution of 0.32 g. (0.84 millimole) of 1-chloro-N-phenyl-2-anthraquinonecarboximidyl chloride in 15 ml. of *o*-dichlorobenzene was warmed to about 140° and stirred while 0.12 g. (0.88 millimole) of benzhydrazide was added over a 10-minute period. The mixture was then refluxed for 10 minutes, cooled, diluted with hexane, and filtered,

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[10] J. V. Braun and W. Pinkernelle, *Ber.*, **67**, 1218 (1934).

yielding 0.28 g. (72%) of buff-colored solid of m.p. 261–264°. Crystallization from dilute acetic acid or Pentasol raised the m.p. to 275°.

Anal. Calcd. for $C_{28}H_{16}O_2N_3Cl$: C, 72.9; H, 3.5; N, 9.1; Cl, 7.7. Found: C, 72.5; H, 3.7; N, 9.2; Cl, 8.1.

4,4',5,5'-Tetraphenyl-3,3'-bi-*s*-triazole (XVI).—A mixture of 5.9 g. (0.021 mole) of diphenyloxalimidyl chloride[11] and 6.4 g. (0.047 mole) of benzhydrazide in 50 ml. of *o*-dichlorobenzene was stirred for one hour in an oil-bath at 120°. The reaction mixture was cooled overnight, and filtered to remove some yellow salt-like material which was discarded. Dilution of the filtrate with hexane gave 2.6 g. of pale yellow solid with a very indefinite m.p., approximately 270–290°. Crystallization from 60 ml. of chlorobenzene gave 1.15 g. (12%) of product with m.p. 300–306°. Crystallization from Pentasol alternating with chlorobenzene raised the m.p. to 308–309.5°.

Anal. Calcd. for $C_{28}H_{20}N_6$: C, 76.4; H, 4.5; N, 19.1. Found: C, 76.3; H, 4.6; N, 19.1.

This compound showed an absorption maximum in the ultraviolet at 253 mμ (ε 26500) (10 mg. per liter in dimethylformamide buffered with 0.4% ammonium acetate). Under the same conditions, 3,4,5-triphenyl-*s*-triazole showed maximum absorption at 255 mμ (ε 18,800).

Acknowledgment.—The author is indebted to F. C. Dexter for the spectral data and to O. E. Sundberg and his associates for the microanalyses.

BOUND BROOK, N. J.

[11] R. Bauer, *Ber.*, **40**, 2650 (1907).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE HOOKER ELECTROCHEMICAL CO.]

Fluorine-containing Secondary Diamines[1,2]

BY BURTON S. MARKS[3a] AND GEORGE C. SCHWEIKER[3b]

RECEIVED DECEMBER 9, 1957

N,N'-Substituted derivatives of 2,2,3,3,4,4-hexafluoropentane-1,5-diamine have been safely prepared by the lithium aluminum hydride reduction of the corresponding N,N'-substituted perfluoroglutaramides. The base strengths of these fluorine-containing secondary diamines have been determined in order to assess the loss of basicity due to the inductive effect of the CF_2 groups.

As part of a study in the preparation of fluorinated polyamides for investigations of special condensation elastomers, it was required to prepare compounds having the general structure $(CF_2)_n(CH_2NHR)_2$, wherein R = alkyl or fluoroalkyl group. It is believed that compounds of this general type have not been prepared before. Primary fluorinated diamines (where R = H) have been previously prepared[4] by reduction of perfluorodinitriles in acetic anhydride over platinum oxide, and then hydrolysis of the acetylated diamines. The attempted preparation of 2,2,3,3-tetrafluorobutane-1,4-diamine by lithium aluminum hydride reduction of perfluorosuccinamide resulted in an explosion.[5] An investigation into the cause of the detonation indicated that an unstable complex formed which could detonate at room temperature. It further was shown that perfluoroadipamide as well as certain fluorinated monocarboxamides formed complexes which also could be detonated; but these compounds decomposed less violently and at elevated temperatures. Similar difficulties with unstable complexes were experienced by Karo[6] in the preparation of 2,2,2-trifluoroethylamine and N-ethyl-2,2,3,3,4,4,4-heptafluorobutylamine.

In the present study, a number of synthetic routes for the preparation of fluorine-containing secondary diamines have been investigated. It has been shown that fluoroalkyl tosylates could be made to react with alkali halides to give the corresponding fluoroalkyl halides.[7] This evidence suggested that an analogous reaction of the tosyl esters with an amine might plausibly produce the substituted secondary amine desired. The reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-di-*p*-toluenesulfonate with methylamine at 165° did not give the desired product, but instead gave a mixture of unidentified products and tars, from which N-methyl-*p*-toluenesulfonamide was isolated in small quantities. Recent work,[8] in which aniline and 2,2,3,3,4,4,4-heptafluorobutyl tosylate have been allowed to react at 230° to yield N-2,2,3,3,4,4,4-heptafluorobutylaniline, has shown the feasibility of this type of reaction for aniline. However, under similar conditions, attempts to treat the tosyl ester with ammonia or diethylamine gave tarry decomposed mixtures from which the desired products could not be isolated.[8] The 2,2,3,3,4,4-hexafluoropentane-1,5-di-*p*-toluenesulfonate was prepared by the reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-diol with *p*-toluenesulfonyl chloride in yields of 45–65%. Small amounts of the corresponding mono-*p*-toluenesulfonate also were obtained. Catalytic reduction of fluorinated amides has not been used widely. A reduction of trifluoroacetamide over copper chromite to yield the corresponding amine has been reported by Henne[9]; however, yields or experimental conditions were not given. Henne also reported a similar reduction of trifluoroacetamide over platinum to yield 2,2,2-trifluoroethanol instead of 2,2,2-trifluoroethylamine.

In an attempt to prepare N,N'-dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine, N,N'-dimethylperfluoroglutaramide was treated at 175°

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[3] (a) Continental Can Co., Metals Division, Research and Development, Chicago, Ill. (b) Velsicol Chemical Corp., Research and Development Department, Chicago, Ill.

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