The melting points of the chelates studied were found not to change appreciably after storage of the compounds at room temperature for a period of 1 year.

Mixed melting points were determined for the following pairs of compounds after grinding approximately equal quantities together in a small mortar. Values obtained: Copper chelates: methyl-ethyl, 97–100°; heptyl-octyl, 56–61°; decyl-dodecyl, 46–50°; dodecyl-tetradecyl, 45–49°. Nickel chelates: heptyl-octyl, 95–96°; decyl-dodecyl, 72–75°; dodecyl-tetradecyl, 71–74°.

Molecular Weights. The molecular weights of the chelates were determined cryoscopically in 1,4-dioxane using weighed quantities of the solute and solvent and using a thermometer which could be estimated to ±0.01C°. The concentration of the solutions was about 0.1*M*. The apparatus used was capable of an accuracy of about ±5% in the M.W. The dioxane used was refluxed over sodium and distilled through an efficient fractionating column. A value of 4.63 was used for K_f.

Analyses. The organic portions of the compounds were destroyed by repeatedly evaporating with mixtures of hydrochloric, nitric, and sulfuric acids. Copper was determined in the residues gravimetrically with 8-hydroxyquinoline, and nickel gravimetrically with dimethylglyoxime. Nitrogen was determined by the Kjeldahl method using separate samples.

Acknowledgments. The writer is indebted to Miss Dorothy L. Anderson and Mr. Robert Berberich for invaluable technical assistance and to Miss M. I. Mistrik and Mr. J. F. Reed for certain of the analyses.

PITTSBURGH 35, PA.

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Preparation of *N,N′*-Bis(α-haloacyl)hydrazines[1]

ALFRED KREUTZBERGER

Received September 18, 1956

The preparation of several *N,N′*-bis(α-haloacyl)hydrazines from hydrazine hydrate and α-haloacid halides or α,α′-dihaloacid anhydrides respectively is described.

The well known benzidine rearrangement of hydrazo compounds proceeding under the influence of acids sometimes fails, *e.g.*, with hydrazothiazoles-(2,2′).[2] However, in this case, it was found possible to bring about the benzidine rearrangement by means of phthalic anhydride.[3] In order to test the scope of the applicability of the phthalic anhydride reaction on isomeric hydrazothiazoles, an effort was made to synthesize hydrazothiazole-(4,4′) and -(5,5′). Interaction of 2,4-dimethyl-5-bromothiazole[4] with hydrazine hydrate in a sealed tube gave only decomposition products. Thiazolinones, such as 2-phenylthiazolinone-(4),[5] do not react with hydrazine hydrate. The *N,N′*-bis(α-haloacyl)hydrazines (II) and thioamides either did not react or formed the ammonium halides as decomposition products. Although synthesis of the hydrazothiazoles-(4,4′) or -(5,5′) was not achieved, preparation of some α-haloacylhydrazines is described here since examples of this class of substances do not appear to have been recorded previously in the literature.

Although the reaction of acid chlorides (III) with hydrazine hydrate is a standard procedure for preparing *N,N′*-diacyl-hydrazines (IV),[6] no literature references are to be found dealing with the application of this reaction utilizing the simpler acid chlorides, *e.g.* III, R = CH_3, $C_6H_5CH_2$, C_2H_5, or C_3H_7. Consequently, *N,N′*-diphenacetylhydrazine (IV, R = $C_6H_5CH_2$) was prepared from phenacetyl chloride (III, R = $C_6H_5CH_2$) and hydrazine hydrate. These components reacted vigorously to give a 28% yield of IV (R = $C_6H_5CH_2$), a compound hitherto accessible only through protracted procedures.[7]

In a similar manner the preparation of II was accomplished by the reaction of α-haloacid halides (I) with hydrazine hydrate.[8] The investigation of the end products of this reaction indicated the formation of considerable amounts of the corresponding α-haloacids with lesser amounts of II. Better yields of II were obtained by using inert solvents such as

---

[1] This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, Baltimore, Md.

[2] D. Markees, M. Kellerhals, and H. Erlenmeyer, *Helv. Chim. Acta*, **30**, 304 (1947); H. Beyer, H. Schulte, and G. Henseke, *Chem. Ber.*, **82**, 143 (1949).

[3] H. Beyer and A. Kreutzberger, *Chem. Ber.*, **84**, 518 (1951).

[4] G. M. Dyson and R. F. Hunter, *J. Indian Chem. Soc.*, **8**, 147 (1931).

[5] P. Chabrier and S. Renard, *Compt. rend.*, **226**, 582 (1948).

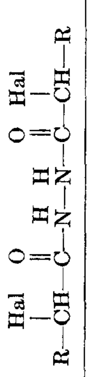
[6] H. Wieland, *Die Hydrazine*, Verlag Ferdinand Enke, Stuttgart (1913).

[7] A. Pinner and Göbel, *Ber.*, **30**, 1889 (1897); T. Curtius and E. Boetzelen, *J. prakt. Chem.*, [2] **64**, 318 (1901); G. Klein and W. Fuchs, *Biochem. Z.*, **213**, 49 (1929).

[8] Hydrazine hydrate has been found to effect reductive dehalogenation of some halogenocompounds [see *e.g.* B. W. Howk and S. M. McElvain, *J. Am. Chem. Soc.*, **55**, 3372 (1933)]. Consequently, anhydrous hydrazine was not used by the author since it is known to be an even stronger reducing agent than hydrazine hydrate [see *e.g.*, S. Dutt and K. Sen, *J. Chem. Soc.*, 3420 (1923); 2971 (1925)].

TABLE I

N,N'-BIS(α-HALOACYL)HYDRAZINES



$$R-\overset{Hal}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{Hal}{\overset{|}{C}H}-R$$

(II)

Starting Material	Most Suitable Diluent	End Product	Yield, %	Recrystallized from	M.P., °C. (Corr.)	Analyses C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	Hal Calcd.	Hal Found
I, R = H Hal = Cl	Chloroform	II, R = H Hal = Cl (IIa)	21.7	Ethyl acetate	172–173	25.97	26.17	3.27	3.50	15.15	14.91	Cl 38.33	Cl 37.98
I, R = CH_3[11] Hal = Br	Ethyl acetate	II, R = CH_3 Hal = Br (IIb)	19.2	Ethyl acetate	221–222	23.86	23.99	3.34	3.36	9.28	9.03	Br 52.93	Br 53.25
I, R = C_2H_5[11] Hal = Br	Ethyl acetate	II, R = C_2H_5 Hal = Br (IIc)	27.7	Methanol-water 3:1	240					8.49	8.68	Br 48.44	Br 48.38
I, R = C_6H_5[12] Hal = Cl	Ethyl acetate	II, R = C_6H_5 Hal = Cl (IId)	48.5	Acetone-water 3:2	227–228					8.31	8.39	Cl 21.03	Cl 21.24

ether, chloroform, benzene, dioxane, or ethyl acetate. In particular, use of ethyl acetate turned out to be very advantageous, since at room temperature it will dissolve large amounts of α-haloacids but practically no II. Separation of II is therefore easily accomplished. Because of the much greater reactivity of the α-haloacid halides compared to ethyl acetate used as solvent, the latter will not react with hydrazine hydrate under the conditions employed. Furthermore, to avoid the possible formation of long-chained molecules by the concurrent reaction of the α-halogen in I, it was expedient in this reaction to have I always present in excess, a condition that was also used in the interaction of higher molecular diamines with haloacid halides.[9] The stoichiometric ratio of 1 mole of hydrazine hydrate to 2 moles of I turned out to be the most favorable one. The compounds (II) prepared in this way are compiled in Table I.[10] They are soluble in all common organic solvents upon boiling except ether, petroleum ether, and carbon disulfide. In hot water, IIa is easily soluble, IIb slightly soluble, and IIc and IId are insoluble.

The yield of II could be improved considerably in those cases where the anhydrides of the α-haloacids corresponding to I were known. The results obtained from the reaction of α,α'-dihaloacid anhydrides (V) with hydrazine hydrate are given in Table II.

TABLE II

N,N'-BIS(α-HALOACYL)HYDRAZINES FROM α,α'-DIHALOACID ANHYDRIDES

Starting Material	End Product	Yield in %
V, R = H Hal = Cl	IIa	49.6
V, R = CH_3[13] Hal = Br	IIb	44.6
V, R = C_2H_5[13] Hal = Br	IIc	55.6

EXPERIMENTAL

N,N'-Diphenacetylhydrazine (IV) (R = $C_6H_5CH_2$). To 30 g. of phenylacetyl chloride stirred and cooled with ice were added slowly 5 g. of hydrazine hydrate. A vigorous reaction occurred, and a white material precipitated. The latter, after standing overnight, was vacuum-filtered, dissolved in

---

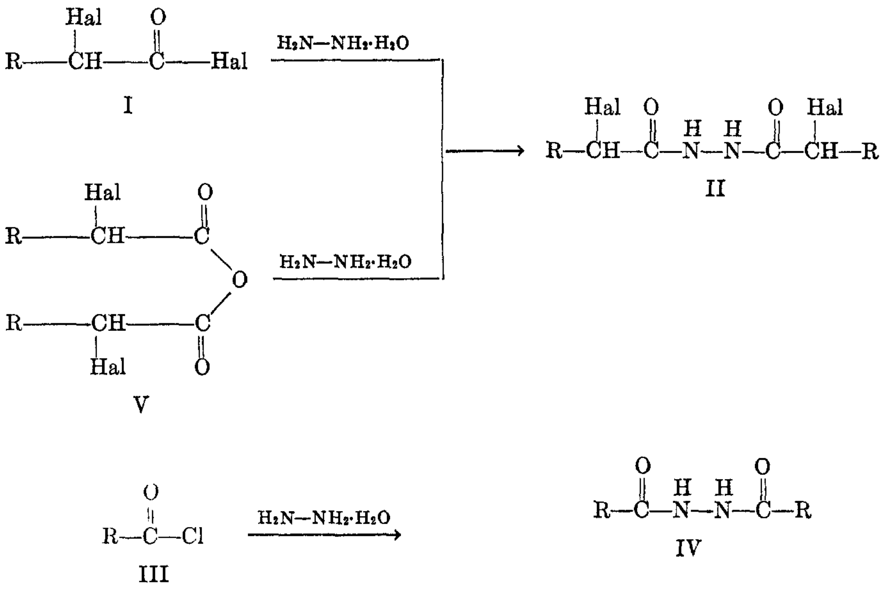
[9] T. v. Braun, F. Dengel, and A. Jacob, *Ber.*, **70**, 994 (1937).

[10] While this work was in progress, a patent [P. Schlack, German Patent No. 819,405 (to Kunstseidefabrik Bobingen, Germany) October 31, 1951; *Chem. Abstr.*, **47**, 2202 (1953)] was published describing IIa as obtained by a different route, namely, from α-chloroacetic anhydride and carbazic acid. By contrast the synthesis described in this paper does not necessitate conversion of hydrazine hydrate into carbazic acid. The identity of IIa obtained by the patented procedure given with the product obtained by the process described in this paper was confirmed by mixed melting point.

[11] T. Volhard, *Ann.*, **242**, 161 (1887).

[12] C. Bischoff and P. Walden, *Ann.*, **279**, 122 (1894).

[13] C. Bischoff and P. Walden, *Ber.*, **27**, 2949 (1894).



25 ml. of hot pyridine, and, while still hot, water was added until crystallization started. Thus, 7.3 g. (28.2%) of well-shaped leaflets were obtained, melting at 243°. No depression in melting point occurred when mixed with an authentic sample.[7]

As an example for the formation of II from I: *N,N'-Bis(α-chlorophenylacetyl)hydrazine (IId).* An amount of 8.3 g. of hydrazine hydrate was added dropwise to a well stirred and ice cooled solution of 63 g. of phenylchloroacetyl chloride (I, R = C_6H_5, Hal = Cl) in 200 ml. of ethyl acetate, thereby precipitating a white material. The reaction contents were heated for 1.5 hours on the steam bath, filtered hot, and the filter cake extracted several times with 300 ml. portions of ethyl acetate. The ethyl acetate extracts, upon cooling, furnished 27.2 g. (48.5%) of a microcrystalline white substance (IId), which, upon recrystallization from acetone-water (3:2), was obtained as white needles, melting at 227–228°.

As an example for the preparation of II from V: *N,N'-Bis(α-bromobutyryl)hydrazine (IIc).* To an ice cooled solution of 63.2 g. of α-bromobutyric anhydride (V, R = C_2H_5, Hal = Br) in 300 ml. of absolute ether 5 g. of hydrazine hydrate was added dropwise with stirring, thereby forming a white precipitate. When the hydrazine hydrate had been added, the reaction mixture was heated for 2 hr. on the steam bath to gentle boiling and then filtered hot. The filter cake was repeatedly digested with 500 ml. of ethyl acetate. From the ethyl acetate extracts, upon cooling, a total yield of 18.4 g. (55.6%) of white needles was obtained. After recrystallization from a methanol-water mixture (3:1), the needles melted at 240°.

Acknowledgment. The author is very much indebted to the Olin Mathieson Chemical Corporation for their generous support of this work.

COLUMBUS, OHIO.