sponded to 82% of dehydroiodination, and fluoride ion was absent. The ethereal filtrate was distilled through a short column. When almost all the ether was removed, the residue was distilled under reduced pressure. The main fraction appeared to consist of 1,5-dihydroperfluorooctene-4 (by examination of infrared spectrum).

Treatment of 4,4-dihydro-3-iodoperfluoroheptane with dibutylamine. To ice-cooled 4,4-dihydro-3-iodoperfluoroheptane (13.231 g., 0.02876 mole) was added dibutylamine (3.716 g., 0.02876 mole) over a period of *ca.* 10 min. After standing for 10 days at room temperature, distillation *in vacuo* over citric acid afforded 8.61 g. of material. The yield was 99% as determined from the weight of the distillate and 95% as determined by analysis for iodide ion in the residue. Some fluoride ion was also present. The crude 4-hydroperfluoroheptene-3 was distilled from phosphorus pentoxide using a 16-cm. column packed with glass helices, b.p. 69–70°; n_D^5 1.2800 (estimated). The infrared spectrum supported the postulated structure.

Anal. Calcd. for C_7HF_{13}: C, 25.32; F, 74.38. Found: C, 25.18; F, 74.29.

Treatment of 4-hydroperfluoroheptene-3 with butylamine. To 4-hydroperfluoroheptene-3 (4.822 g., 0.0145 mole) in ether (10 ml.) at 0° butylamine (1.071 g., 0.0146 mole) was added slowly with stirring over a period of 15 min. Almost immediately a white precipitate was formed. Stirring at 0° was continued for an additional 8 hr.

The next day the material was filtered under nitrogen pressure. The precipitate, butylamine monohydrofluoride, was dissolved in water and analyzed for fluoride ion. The amount (0.0061 mole) corresponded to 87% yield.

Anal. Calcd. for $C_4H_{12}FN$: C, 51.57; H, 12.98; F, 20.40; N, 15.04. Found: C, 51.90; H, 12.95; F, 20.20; N, 15.24.

The filtrate was distilled at room temperature at reduced pressure and collected in a Dry Ice–cooled receiver. The material, 1.5 g. (53% yield), collected at 1 mm. consisted of the mixture of isomers IX and X. This was then redistilled, b.p. 49–51° (10 mm.) n_D^{25} 1.3342.

Anal. Calcd. for $C_{11}H_{11}F_{12}N$: C, 34.29; H, 2.88; F, 59.18; N, 3.63. Found: C, 34.26; H, 2.85; F, 58.89; N, 3.59.

The yellow residue left in the distillation flask was subsequently distilled under reduced pressure (using a short column) to yield a material, b.p. 47–49° (0.15 mm.), n_D^{25} 1.4060, identified as XII.

Anal. Calcd. for $C_{15}H_{20}F_{10}N_2$: C, 43.06; H, 4.82; F, 45.41; N, 6.70. Found: C, 43.81; H, 4.70; F, 45.92; N, 6.83.

Treatment of the tautomeric mixture IX *and* X *with butylamine.* To the tautomeric mixture IX and X (1.60 g., 0.00415 mole) in ether (5 ml.), butylamine (0.585 g., 0.00800 mole) was added at 0° with stirring over a period of 10 min. Almost immediately a white precipitate was formed. Stirring at 0° was continued for an additional 6 hr. Subsequently the mixture was stirred at room temperature for an additional 24 hr. The material was filtered under nitrogen pressure and the precipitate was analyzed for fluoride ion. The amount (0.003 mole) corresponded to 40% yield, assuming two moles of fluoride ion for each mole of amine added. The filtrate was distilled at reduced pressure to yield 1.10 g. of XII.

Reaction of 1,5-dihydroperfluorooctene-4 (VIa) *with dibutylamine.* To ice-cooled 1,5-dihydroperfluorooctene-4 (0.547 g., 0.00149 mole) was added dibutylamine (0.190 g., 0.00147 mole). The resulting mixture was shaken and allowed to stand for 76 days in a desiccator. The resulting precipitate, dibutylamine monohydrofluoride, was filtered under nitrogen pressure and washed with hexane; yield 0.060 g., corresponding to 55% of compound XIVa, based on the original amount of amine.

Reaction of 4-hydroperfluoroheptene-3 with diethylamine. To 4-hydroperfluoroheptene-3 (4.934 g., 0.0149 mole) was added diethylamine (1.458 g., 0.0199 mole); the resulting solution was sealed in a glass tube and heated at 55° for 90 hr. The resulting solution was orange, and a brown precipitate was deposited on the sides of the tube. The tube was cooled, opened, and the orange liquid (4.31 g.) was decanted from the precipitate. This material was distilled at room temperature under reduced pressure. The fraction (3.5 g.) collected at 35 mm. consisted of diethylamine and 4-hydroperfluoroheptene-3. The fraction (0.4 g.) collected at 1 mm. appeared to be the desired material; however, its infrared spectrum pointed to a conjugated system inasmuch as bands at 6.08 and 6.35 μ were observed.

Anal. Calcd. for $C_{11}H_{11}F_{12}N$: C, 34.29; H, 2.88; F, 59.18; N, 3.63. Found: C, 34.27; H, 2.77; F, 55.13; N, 4.33.

Heat treatment of 4-hydroperfluoroheptene-3. 4-Hydroperfluoroheptene-3 (4.8 g.) purified by distillation over phosphorus pentoxide was heated in a sealed tube at 190–195° for 67 hr. Gas-phase chromatography and infrared spectroscopy of the product showed it to be pure starting material.

WYANDOTTE, MICH.

[CONTRIBUTION FROM THE MEDICINAL DIVISION, MALLINCKRODT CHEMICAL WORKS]

Reactions of Carbonium Ions with Dithiooxamides

RICHARD N. HURD, GEORGE DE LA MATER, AND JOHN P. MCDERMOTT

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Xanthydrol reacts in glacial acetic acid with thioacetamide to form 9-thioacetamidoxanthene (I) and with dithiooxamide to form *N,N'*-bis(9-xanthenyl)dithiooxamide (II). Triphenylmethanol similarly forms *N,N'*-ditrityldithiooxamide (III). However, the reaction of benzhydrol and dithiooxamide in glacial acetic acid leads to dibenzhydryl dithioloxalate (IV). Possible mechanisms for these reactions are discussed.

In the course of preparation of a number of *N,N'*-disubstituted dithiooxamides, we have studied several possible synthetic routes to these compounds.[1] One of these involves the reactions of carbonium ions with thioamides under the conditions recommended some years ago for the use of xanthydrol as a reagent for the characterization of unsubstituted amides.[2]

Table I summarizes the results we obtained by

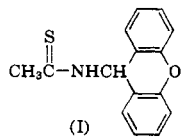
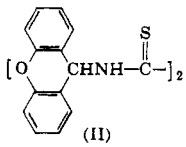
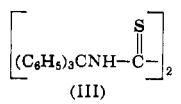
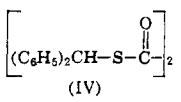
(1) R. N. Hurd, G. De La Mater, G. C. McElheny R. J. Turner, and V. H. Wallingford, *J. Org. Chem.*, 26, 3980 (1961).

(2) R. F. Phillips and B. M. Pitt, *J. Am. Chem. Soc.*, 65, 1355 (1943).

reactions of stoichiometric amounts of alcohols and thioamides in warm glacial acetic acid. The formation of 9-thioacetamidoxanthene (I) and N,N′-bis(9-xanthenyl)dithiooxamide (II) is quite analogous to the formation of *N*-(9-xanthenyl)amides.[3] Triphenylmethanol and dithiooxamide react only if a little concentrated sulfuric acid is added to the reaction mixture. None of the expected product, N,N′-dibenzhydryldithiooxamide, was isolated from the reaction of benzhydrol with dithiooxamide.

TABLE I

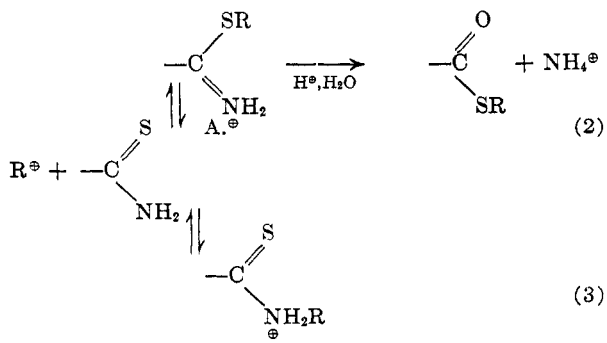
REACTIONS OF THIOAMIDES AND ALCOHOLS IN GLACIAL ACETIC ACID

Alcohol	Thioamide	Product	Yield, %
Xanthydrol	Thioacetamide	 (I)	55
Xanthydrol	Dithiooxamide	 (II)	57
Triphenylmethanol	Dithiooxamide	 (III)	76
Benzhydrol	Dithiooxamide	 (IV)	45

Thus, under the same acidic conditions by which xanthydrol and triphenylmethanol react with thioamides to give the corresponding *N*-alkyl thioamides, benzhydrol reacts with dithiooxamide to give dibenzhydryl dithioloxalate (IV). Two mechanisms can be proposed to explain these facts.

Mechanism 1.

$$ROH + H^+ \rightleftharpoons R^+ + H_2O \quad (1)$$



(2)

(3)

Of the three alcohols used in this study, xanthydrol is the most basic and benzhydrol the least basic.[4] We propose that alkylation of dithiooxamide by xanthydrol in the absence of sulfuric acid involves the carbonium ion, although in too small concentration to be observed with the naked eye. Benzhydrol and triphenylmethanol are sufficiently less basic that sulfuric acid is necessary to produce the corresponding carbonium ions at a concentration great enough to yield an observable reaction rate.[5]

Equation 2 indicates that the carbonium ion may alkylate the thioamido sulfur atom to give intermediate A. In the case of xanthydryl and triphenylmethyl cations, *S*-alkylation is presumed to be reversible because of the relatively high stability of the carbonium ion. Such reversibility in the case of the benzhydryl cation is not so favored and the *S*-benzhydryl intermediate undergoes the well known acidic hydrolysis of a thiolimidic ester (isothioamide) to the corresponding thiolic ester (IV).[6] Formation of products I–III (inc.) proceeds by electrophilic attack of the xanthydryl and triphenylmethyl cations upon the thioamide nitrogen. In Equation 3 this step is shown as reversible, since addition of a small amount of concentrated sulfuric acid to the glacial acetic acid solutions of I–III instantly generates the bright yellow color characteristic of the carbonium ion. The eventual isolation of products I–III instead of the corresponding *S*-alkylated products is not necessarily evidence of greater ease of alkylation of the N atom by the carbonium ions as opposed to alkylation of the S atom. It may be only a consequence of the reversibility of both the *S*- and the *N*-alkylation reactions, coupled with the greater thermodynamic stability of the N-alkylated products.

This mechanism presumes that xanthydrol and triphenylmethanol react by electrophilic attack of their carbonium ions as described above (Equations 1 and 3), but that IV is formed by an S_N2 nucleophilic attack of dithiooxamide upon protonated benzhydrol. This reaction would also be promoted by sulfuric acid.

The evidence at hand is not sufficient to specify

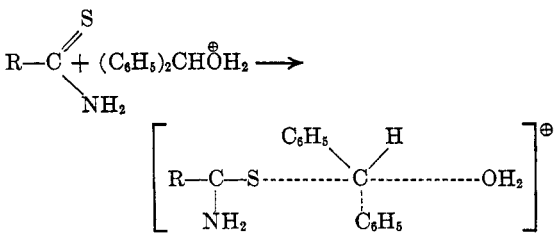
(3) Oxamide, in contrast to dithiooxamide, failed to give a satisfactory 9-xanthenyl derivative because of its insolubility in glacial acetic acid.[2]

(4) The relative basicities of these three alcohols have been shown by spectroscopic determination under similar conditions of the equilibrium constant (K_{R^+}) for each alcohol in the reaction $R^\oplus + H_2O \rightleftharpoons ROH + H^\oplus$. The measurements were made at 25–27° upon reaction systems formed by addition of aliquots of acetic acid solutions of the alcohols to varying concentrations of sulfuric acid. For xanthydrol, $pK_{R^+} = -0.84$ [N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957)]; for triphenylmethanol, $pK_{R^+} = -6.63$ [N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955)]; for benzhydrol, $pK_{R^+} = -13.3$ (*ibid.*). In the last case it was noted that the benzhydryl cation becomes increasingly unstable at sulfuric acid concentrations below 75–85%. For the behavior of benzhydryl cations generated by sulfuric acid, see C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **72**, 4748 (1950).

(5) V. Gold and W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

(6) R. N. Hurd and G. De La Mater, *Chem. Revs.*, **61**, 45 (1961).

Mechanism 2.



(4)

further the mechanism involved in these reactions. It is noted that, whichever mechanism proves to be correct, thioamides show promise as tools for distinguishing between relatively stable and unstable carbonium ions. Formation of II and III must occur in two steps. In the case of II, an attempt was made to isolate the intermediate, *N*-(9-xanthenyl)dithiooxamide, by use of equimolar amounts of the reactants under such conditions that dithiooxamide was always the reactant in excess in the acidic solution. Since II was the only product isolated, it appears that formation of II from N-(9-xanthenyl)dithiooxamide occurred more rapidly than formation of this intermediate.

Benzhydrol does not react with dithiooxamide in either warm, dry benzene or xylene in the presence of zinc chloride; only the starting materials are recovered.[7]

Isolation of I and II in substantial yields upsets a recent statement by Bredereck and co-workers[8] that N-(9-xanthenyl)thioamides cannot be obtained by the reactions of thioamides with xanthydrol in glacial acetic acid. Bredereck attributed his lack of success to decomposition of xanthydrol in warm glacial acetic acid. It is our experience that the maximum reaction time (40 minutes) proposed by Phillips and Pitt[2] must be observed when xanthydrol is used; longer reaction times result in greatly decreased yields of I or II due to disproportionation of xanthydrol.[2,9] With triphenylmethanol, no time restriction is necessary in the preparation of III.

The structures given to I, II, and III (Table I) are consistent with their infrared spectra, which exhibit —N—C=S absorptions characteristic of *N,N'*-disubstituted dithiooxamides.[1] There is no infrared spectral evidence of thioenolic (—N=C—SH) tautomers of I, II, or III. Assignment of thioamido rather than isothioamido structures to I, II, and III is substantiated by their relatively high melting points and by the fact that they do not undergo acidic hydrolyses under the conditions of their formation.

Identification of IV, a new thiolic ester, is made through its analyses and the characterization of its hydrolyses products (see Experimental section) as well as by its infrared spectrum. This spectrum contains absorptions characteristic of the benzhydryl group and strong carbonyl absorption at 1675 cm.$^{-1}$, a frequency reported to be characteristic of all thiolic esters.[10] The ultraviolet spectrum of IV, however, does not have a maximum absorption peak at or near 230 mμ, a wave length that has been suggested[11] on the basis of very limited evidence as being characteristic for thiolic esters.

EXPERIMENTAL[12]

N,N'-Bis-(9-xanthenyl)dithiooxamide (II). A mixture[13] of dithiooxamide (8.44 g., 0.08 mole) and xanthydrol (32.00 g., 0.016 mole) in glacial acetic acid (448 ml.) was warmed for 40 minutes on the steam bath, cooled to room temperature, and filtered to separate II. Small additional crops of II were obtained from the filtrate. A total yield of 22.07 g. (57% of theory) was easily isolated. II, after several recrystallizations from dioxane, was obtained as a pale yellow solid, m.p. 236.8–237° (dec.) (corr.).

Anal. Calcd. for $C_{28}H_{20}N_2O_2S_2$: N, 5.83; S, 13.34. Found: N, 5.74; S, 13.36.

II is insoluble in hot water, ethanol, isopropyl alcohol, acetone, petroleum ether, and Cellosolve; slightly soluble in warm chloroform, carbon tetrachloride, ethylene dichloride, dioxane, toluene, and xylene; and appreciably soluble in pyridine.

The infrared spectrum of II has sharp bands of equal intensity at 11.07 μ and 11.58 μ, one of which, at least, is due to the —N—C=S groups.[1] Concurrent expected —N—C=S absorption in the range 6.51–6.70 μ is obscured by massive absorption of the aromatic rings.

9-Thioacetamidoxanthene (I). I, m.p. 167.9–168.4° (corr.), was obtained in 55% yield and purified as a white solid by techniques analogous to those used for II.[13]

Anal. Calcd. for $C_{15}H_{13}NOS$: N, 5.48; S, 12.55. Found: N, 5.45; S, 11.81.

N,N'-Ditrityldithiooxamide (III). The crude precipitate, obtained by filtration at 30° of a mixture[13] of triphenylmethanol (420 g., 1.61 moles), dithiooxamide (96.0 g., 0.8 mole), concentrated sulfuric acid (89 ml.), and glacial acetic acid (2500 ml.) that had been warmed at 70° for 45 minutes, was recrystallized from a hot solution of ethylene dichloride (750 ml.) and carbon tetrachloride (250 ml.) to give 342 g. (78% of theory) of pink III, m.p. 262.8–263.9° (corr.).

Anal. Calcd. for $C_{40}H_{32}N_2S_2$: N, 4.63; S, 10.59. Found: N, 4.57; S, 10.30.

Characteristic —N—C=S absorption[1] in the infrared spectrum of III occurs at 11.31 μ. Like II, characteristic —NC=S absorption in the range 6.51–6.70 μ is obscured.

Dibenzhydryl dithioloxalate (IV). Yellow IV (8.4 g., 45%) precipitated on cooling a mixture of benzhydrol (14.72 g., 0.08 mole), dithiooxamide (4.80 g., 0.04 mole), concentrated sulfuric acid (8.7 ml.)[14] and glacial acetic acid (224 ml.) that had been warmed to 55° for 90 minutes. Recrystal-

(7) These reaction conditions are those used successfully by Bredereck *et al.*[8] to prepare *N*-(9-xanthenyl)thioamides.

(8) H. Bredereck, R. Gompper, and D. Bitzer, *Chem. Ber.*, **92**, 1139 (1959).

(9) R. Meyer and E. Saul, *Ber.*, **26**, 1276 (1893).

(10) This frequency is insensitive to the structural factors which cause carbonyl frequency shifts in normal esters. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., London, second ed., 1955, p. 188.

(11) B. Sjöberg, *Z. physik. Chem.*, **52B**, 209 (1942).

(12) Analyses were performed by the Department of Chemical Control, Mallinckrodt Chemical Works, St. Louis 7, Mo. The authors wish to thank Miss E. M. Bettinger for assistance in interpretation of the infrared spectra.

(13) Complete solution of the initial amounts of reactants is not necessary.

(14) When a smaller amount (1.1 ml.) of concentrated sulfuric acid is used, the yield of IV drops to 3.5 g.

lization from methyl isobutyl ketone gave pure IV, m.p. 191.2–193.4° (corr.).

Anal. Calcd. for $C_{28}H_{22}O_2S_2$: C, 73.97; H, 4.87; S, 14.10. Found: C, 74.11; H, 4.74; S, 14.12; N, none.

IV is insoluble in water and ethanol, slightly soluble in acetone and methyl isobutyl ketone, and soluble in toluene.

IV was characterized by its saponification products, oxalic acid, and benzhydryl mercaptan obtained by refluxing 1.5 g. in ethanol (20 ml.) and 10% potassium hydroxide solution (10 ml.) for several hours. After acidification (to *p*H 2) of the mixture with 5% hydrochloric acid, oxalic acid was obtained by first separating the benzhydryl mercaptan as a benzene extract, then concentrating *in vacuo* the aqueous solution to about 5 ml., whereupon precipitation occurred. Oxalic acid was separated from salt in this precipitate by ether extraction. It was identified by m.p. (184°)[15] comparison of its infrared spectrum with that of authentic oxalic acid, and determination of its neutralization equivalent: Calcd., 63.03; found, 63.96.

The presence of benzhydryl mercaptan in the saponification mixture was shown by its oxidation to dibenzhydryl disulfide, m.p. 150–152° (corr.).[16] In this case saponification was accomplished under nitrogen, and the reaction mixture then was made only weakly acidic (*p*H 5–6). The mercaptan was oxidized *in situ* to the disulfide by addition of a standard 1N iodine solution in the manner described by Biilman.[16]

IV was also characterized by fusion with benzylamine[17] to give *N,N'*-dibenzyloxamide, m.p. 218.5–221.1° (corr.).[18]

St. Louis 7, Mo.

(15) Lit.: 189.5°; E. Bamberger and M. Althausse, *Ber.*, 21, 1901 (1888).

(16) Lit.: 152°; E. Biilmann, *Ann.*, **364**, 328 (1907).

(17) The reaction conditions used were those developed by O. C. Dermer and J. King, *J. Org. Chem.*, **8**, 171 (1943), for the preparation of *N*-benzylamide derivatives of unsubstituted amides.

(18) Lit.: 222–223°; *cf.* J. Strakosch, *Ber.*, **5**, 694 (1872).

[Contribution from the Organic Process Development Department, Texas Division, Dow Chemical Co.]

Halogenation of Aldehydes. Chlorination of Propanal

CLARENCE R. DICK

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The chlorination of propanal in aqueous hydrochloric acid can be controlled in such a manner as to produce either 2-chloropropanal or 2,2-dichloropropanal in yields exceeding 85%. Previously unreported 2,2-dichloropropanal, 2,2-dichloropropanol, and 2,4,6-tris(1,1-dichloroethyl)-*s*-trioxane were prepared and characterized.

While vapor phase chlorination of aliphatic ketones[1] produces good yields of 2-chloro ketones, application of the same technique to aldehydes results in the production of the corresponding acyl halides.[2] Although the haloform reaction of methyl ketones is well known, the chlorination of aldehydes in an alkaline medium results in both aldol condensation and/or oxidation. With the exception of ethanal, the chlorination of aldehydes in aqueous acid had not been evaluated until Guinot and Tabeteau[3] reported that 2-chlorobutanal and 2-chlorohexanal could be prepared in good yields in the presence of hydrochloric acid at approximately 15°. By raising the temperature to 30° after monochlorination of acetaldehyde was complete, 2,2-dichloroethanal was also prepared in 85% yield. Krattiger[4] refined the method and produced 2-chlorobutanal in 70% yields. However, the application of these procedures to propanal gives 2-chloropropanal (I) in only 35% yield and 2,2-dichloropropanal (II) in less than 10% yield.

In the previously described methods,[3,4] the initial acid concentration was either 2.5*N* or 6–8*N*, and it was allowed to increase freely during the course of the reaction. The work herein described was carried out under controlled acid concentrations and demonstrates that not only the acid concentration but the acid type determines the reaction products. The results of a series of reactions designed to determine the effects of controlled acid concentration at 10–15° are shown in Table I.

TABLE I

Effects of Acid Concentration on Product Ratio

Run No.	Initial Acid Concentration, *N*	Range of Concentration[a] during Reaction, *N*	Yield of 2-Chloropropanal, %	Yield of Propionic Acid, %
1	0	0–0.5	0	98
2	3 (HCl)	2.9–3.1	8	90
3	4.5 (HCl)	4.5–4.7	90	<5
4	6 (HCl)	6.1–6.3	92	<5
5	10 (HCl)	10–11	30	0[b]
6	6 (H_2SO_4)	6–6.1[c]	74	24
7	6 (H_2SO_4)	6–6.1[d]	0	95

[a] Total acid concentration (phenolphthalein end point). [b] The principal product was a high-boiling neutral material produced by the aldol reaction. [c] 100% conversion of propanal. [d] 20% conversion; one mole aldehyde converted by one mole chlorine.

At low acid concentrations (Runs 1 and 2) oxidation predominated and at high concentrations (Run 5) the product consisted of chlorinated aldol-type

(1) R. Justoni, *Chim. e ind. (Milan)*, **24**, 89–94, 195–201 (1942).

(2) R. W. Tess, and G. W. Hearne, U. S. Patent 2,490,386 (1949).

(3) H. Guinot and J. Tabeteau, *Compt. rend.*, **231**, 234 (1950).

(4) A. Krattiger, *Bull. soc. chim. France*, 222 (1953).