Reactions of Fatty Acid Chlorides[1] II. Synthesis of Monohydrazides or Dihydrazides by Acylation of Hydrazine Hydrate With Saturated Fatty Acid Chlorides[2]

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Abstract

The acylation of hydrazine hydrate with a series of saturated fatty acid chlorides containing from eight to 18 carbon atoms was studied under a variety of conditions in order to obtain the desirable fatty acid monohydrazides. Optimum yields were obtained (ranging from 31.5% to 75% as the series ascended from C-8 to C-18) for the even-numbered monohydrazide members through the use of a large excess of hydrazine hydrate in several organic solvents. Diethyl ether was found to be suitable if the acid chloride is dissolved in it and added slowly to a cold mixture of hydrazine hydrate in ether.

The Schotten-Baumann technique was found suitable for the preparation of the symmetrically substituted fatty acid dihydrazides in better than 82% yields when one mole of hydrazine hydrate was acylated with two of acid chlorides.

Physical and chemical properties of both series of fatty nitrogen derivatives are briefly treated. Stearic monohydrazide was condensed with acetonylacetone to give a substituted pyrrole. An unsymmetrical dihydrazide was prepared by the acylation of myristic monohydrazide with lauroyl chloride.

Stearic dimethylhydrazide was prepared by the acylation of dimethylhydrazine with stearoyl chloride. Two quaternizations of this product were carried out.

Introduction

As a synthetic route to monoacylated hydrazines ($RCONHNH_2$) or to *sym*-diacylated hydrazines (RCONHNHCOR) the acylation of hydrazine hydrate with aliphatic acid chlorides has attracted relatively little attention. Monohydrazides were obtained almost exclusively from the reaction of hydrazine or its hydrate with esters (3,4,5,9).

Apparently dibromofumaryl chloride is one of very few aliphatic acid chlorides that converts to a monohydrazide in good yield. In ethereal solution the *bis*-monohydrazide, $H_2NNHCOCBr{=}CBrCONHNH_2$, was obtained (12). A number of attempts to employ acid chlorides as starting materials for the synthesis of monohydrazides (7,13,17) were not successful because a simultaneous formation of considerable quantities of *sym*-dihydrazides occurs, according to the equation:

$$2RCOCl \quad + \quad 3NH_2NH_3OH \quad \longrightarrow$$
$$RCONHNHCOR \quad + \quad 2N_2H_5Cl \quad + \quad 3H_2O$$

Some data indicate the relative proportions of mono- and *sym*-diacylated products produced in acylations with a cyclopentenyl-substituted fatty acid chloride, chaulmoogryl chloride (11), but no attempt to prepare the higher members of the fatty acid series of both mono- and dihydrazides by acylation with acid chloride was apparently made.

Two aliphatic acid chlorides that were converted into *sym*-dihydrazides by reaction with hydrazine hydrate are tiglyl, $CH_3CH = C(CH_3)COCl$ (6), and trimethylacetyl (pivalyl) chlorides (17). The Schotten-Baumann dibenzoylation of hydrazine sulfate has been reported in "Organic Syntheses" (7). Dihydrazides were undesirable products when either acid chlorides or esters were used as acylating agents in attempts to prepare monohydrazides. Occasionally the *sym*-dihydrazides were referred to as *sec*-hydrazides; (the distinction may be noted between sec-amides, $(RCO)_2NH$, in which both acyl groups are attached to the same nitrogen atom). These compounds have considerably less value than monohydrazides as reactive chemical intermediates. Only a few of the fatty dihydrazides were characterized by melting points.

This communication deals with the acylation of hydrazine hydrate with a series of saturated fatty acid chlorides containing from eight to 18 carbon atoms under diverse conditions. They lead respectively to either the fatty monohydrazides in acceptable but not excellent yields or to the fatty *sym*-dihydrazides. The complete series of even-numbered fatty acid derivatives containing from eight to 18 carbon atoms in the acyl residue was prepared and characterized. Apparently four of the *sym*-dihydrazides were not previously reported.

Experimental Procedures

The required fatty acid chlorides were fractionally distilled grades containing less than 0.1% free fatty acid, prepared from good quality fatty acids and phosphorus trichloride in the manner previously described (15). Octanoyl chloride was prepared from Eastman's octanoic acid, mp 15–16C, and 30% excess phosphorus trichloride. It was distilled once before it was fractionally distilled through an all-glass Raschig-ring packed column: bp 75.5–77C/10 mm, $d_4^{25} = 0.9446$, $n_D^{25} = 1.4321$, M_D (calcd.) = 44.02, M_D (obsvd.) = 44.67, $+\Delta M = 0.65$ (14). A sample was converted to methyl esters and corresponded to 99.1% C-8 homolog by gas-chromatographic analysis.

Fatty Acid Monohydrazides

Fatty acid monohydrazides of octanoic, decanoic, lauric, myristic, palmitic, and stearic acids were prepared in yields ranging from 31.5% to 75% by the acylation of hydrazine hydrate in various organic solvents. The acylation of 85% aqueous hydrazine hydrate in diethyl ether with lauryl chloride for the preparation of lauric monohydrazide is typical.

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TABLE I

Effect of Reaction Variables on Yield of Lauric Monohydrazide

Run No.	Temperature, C	Lauroyl chloride mmoles	Ether ml	Molar ratio[a] N_2H_4/LC	Solvent for N_2H_4	ml	Percentage of yield (recrystallized) Mono-	Di-	Misc.
1	35	21.0	50	20:1	C_2H_5OH	500	24.5	31.4	15[b]
2	0–5	41.9	50	20:1	C_2H_5OH	100	53.5	32.5	4[b]
3	0–5	41.9	10	30:1	C_2H_5OH	100	28.4	50.6	2[b]
4	0–5	41.9	50	30:1	C_2H_5OH	100	51.7	31.2	2[b]
5	0–5	41.9	100	20:1	C_2H_5OH	50	59.0	22.8	
6	0–5[c]	41.9	200	20:1	C_2H_5OH and $(C_2H_5)_2O$	50 50	65.2	10.6	1[b]
7	0–5[c]	41.9	200	20:1	$(C_2H_5)_2O$	100	67.7	9.7	3[d], Trace[e]

[a] Hydrated form of hydrazine was used as an 85% aqueous solution.
[b] Ethyl laurate.
[c] Nonhomogeneous reaction medium during formation.
[d] Lauric monohydrazide hydrochloride.
[e] Lauric acid.

TABLE II

Effect of Reaction Variables on Yield of Octanoic Monohydrazide

Run No.	Temperature, C	Octanoyl chloride mmoles	Ether ml	Molar ratio[a] N_2H_4/OC	Solvent for N_2H_4,	ml	Percentage of yield (recrystallized) Mono-	Di-	Misc.
1	0–5	58.1	25	20:1	C_5H_5N	90		65.7	11[b]
2	0–5	58.1	100	20:1	C_2H_5OH	50	7.1	45.5	20[c]
3	0–5[d]	58.1	100	20:1	$(C_2H_5)_2O$	100	31.5	39.9	3[a], 2[f]

[a] Hydrated form of hydrazine was used as an 85% aqueous solution.
[b] Mixture of octanoic acid and anhydride.
[c] Ethyl octanoate.
[d] Nonhomogeneous reaction medium during formation.
[e] Octanoic monohydrazide hydrochloride.
[f] Octanoic acid.

Lauric Monohydrazide. Lauryl chloride, n_D^{25} = 1.4427 (10 ml, 9.17 g, 41.9 mmoles), in 200 ml of diethyl ether was added slowly to a stirred nonhomogeneous mixture of 42.0 g (838 mmoles) hydrazine hydrate (49.4 g of 85% aqueous solution, Matheson) in 100 ml of diethyl ether at 0–5C. After complete addition, the mixture was stirred for 1 hr, then filtered. The filtrate was evaporated on the steam bath to remove the ether and poured into water to precipitate a white solid. The solid, after filtration and water-washing, gave, recrystallization from the minimum quantity of 95% ethanol, 0.7 g lauric monohydrazide, mp 103–104C. The original precipitate was washed with water, dried, and weighed 8.6 g dry. Recrystallization from 600 ml of 1:5 benzene/95% ethanol mixture gave as a first crop 0.8 g of lauric *sym*-dihydrazide, mp 150.5–151.5C and, from the filtrate on successive concentrations, a total of 5.3 g of monohydrazide, mp 103.5–105C. Yield: 6.0 g lauric monohydrazide (28.0 mmoles, 67.7%); 0.8 g lauric *sym*-dihydrazide (2.02 mmoles, 9.7%).

In Table I are presented data to indicate the effect of variations in molar ratios of reactants, solvents, and temperature upon the yields of lauric monohydrazide. Table II illustrates the results obtained when variations of this technique were applied to the preparation of octanoic monohydrazide. Table III gives the optimum yields for the syntheses of the homologous monohydrazides, employing the method exemplified by Run 7, Table I, with diethyl ether as the only solvent.

TABLE III

Fatty Acid Monohydrazides from Saturated Fatty Acid Chlorides

Monohydrazide	Optimum yield, %	Melting point, C Reported	Reference	Found
Octanoic	31.5	88.8– 89.6	9	87 – 88
Decanoic	49.1	98.5– 99.1	9	97 – 98
Lauric	67.7	104.7–105.5	9	
		104.5	7a	105 –105.8
Myristic	63.0	109.4–110	9	108.8–109.9
Palmitic	69.5	112.2–112.4	9	
		111	7a	110 –111
Stearic	75.0	115.6–116.2	9	
		112 –114		
		114	12a	114.8–115.5

Stearic Dimethylhydrazide (92% "technical") (1,1-dimethyl, 2-stearyl hydrazine). Stearoyl chloride was prepared in the usual manner from a commercial grade 90% stearic acid (HumKo Hystrene 9018) with 30% excess phosphorus trichloride. Excess PCl_3 and dissolved HCl were removed by holding the acid chloride at 80C under vacuum for 1 hr. The crude product analyzed 93% acid chloride and contained 92% C–18 and 8% C–16 components. The nondistilled crude stearoyl chloride (268 g, 0.831 mole) was added dropwise over 3 hr with stirring to a solution of 165 g (2.75 moles) of 1,1-dimethylhydrazine (Food Machinery and Chemical Corporation) in 1.5 liters of anhydrous diethyl ether at 35–40C. The suspension was stirred for 2 hr after addition was complete, the precipitate washed with water on the filter and dried to give 244.2 g crude product, mp 75–76C, A.N. = 2.06. The product was recrystallized from ethanol to yield 221 g (0.685 mole, 82.4%) of 92% stearic dimethylhydrazide, mp 78–79C. Analysis: Calcd. for 92% $C_{20}H_{42}N_2O$, 8% $C_{18}H_{38}N_2O$; N, 8.67. Found: N, 8.68%.

Fatty Acid sym-Dihydrazides

Lauric sym-Dihydrazide. Lauroyl chloride, n_D^{25} = 1.4427 (10 ml, 9.17 g, 41.9 mmoles), was added dropwise with stirring to a solution of 1.86 g (46.4 mmoles, 10% molar excess) of sodium hydroxide and 1.06 g (21.0 mmoles) of hydrazine hydrate (1.25 g of 85% aqueous solution, Matheson) in 100 ml of water at C–5C. After addition was complete, stirring was continued for 30 min, then the white precipitate was filtered, washed on the filter with two 100-ml portions of warm water, and dried under vacuum. Recrystallization from the minimum quantity of 1:1 95% ethanol/benzene mixture gave 6.8 g (17.2 mmoles, 81.9%) lauric *sym*-dihydrazide, mp 149–150C [reported (3) 149C].

Table IV indicates the effects of variations in molar ratios and temperature upon the yields of lauric *sym*-

TABLE IV

Effect of Reaction Variables on Yield of Lauric *Sym*-Dihydrazide by Schotten-Baumann Acylation

Run No.	Temperature, C	Lauroyl chloride mmoles	Sodium hydroxide mmoles	Water ml	Molar ratio[a] N_2H_4/LC	Yields, percentage (recrystallized) Di-	Mono-	Misc.
1	35	21.0	23.2	50	1:1	55.3	11.0	8.0
2	0–5	41.9	46.4	100	5:1	49.0	44.1	trace
3	0–5	41.9	46.4	100	2:1	63.1	24.2	
4	0–5	41.9	46.4	100	1:1	71.7	16.5	1.0
5	0–5	41.9	46.4	100	1:2	81.9	trace	

[a] Hydrated form of hydrazine was used as an 85% aqueous solution.
[b] Sodium laurate.

dihydrazide in Schotten-Baumann acylations. Table V gives the optimum yields for the homologous sym-dihydrazides by this procedure (according to Run 5, Table IV) with melting points for the products.

Unsymmetrical Dihydrazides

N-Myristoyl, N′-Lauroylhydrazine. Lauroyl chloride, $n_D^{25} = 1.4427$ (10 ml, 9.17 g, 41.9 mmoles), in 50 ml of dry benzene was added slowly with stirring to 9.63 g (39.8 mmoles) of myristic monohydrazide, mp 108–109.9C, dissolved in 100 ml of anhydrous pyridine at 40C. After the addition was complete, stirring was continued for 1 hr, then the entire mixture was poured into 2 liters of water and the resulting mixture was heated on the steam bath to eliminate the benzene. The precipitate was filtered, washed copiously with warm water on the filter, dried, and recrystallized from 1:1 95% ethanol/benzene mixture to give 14.2 g (33.4 mmoles, 84%) N-myristoyl, N′-lauroylhydrazine, mp 141–141.2C. Analysis: Calcd. for $C_{26}H_{52}N_2O_2$, C, 73.53; H, 12.34; N, 6.60. Found: C, 73.39; H, 12.68; N, 6.56.

Hydrazide Derivatives

N-Stearamido-2,5-Dimethylpyrrole. A mixture of 14.9 g (50.0 mmoles) of stearic monohydrazide and 5.7 g (50.0 mmoles) acetonylacetone (Eastman) was refluxed in 50 ml of anhydrous ethanol for 6 hr. Upon cooling, the precipitate was filtered and washed with ice-cold ethanol; upon recrystallization from ethanol it gave 16.7 g (44.5 mmoles, 89%) of N-stearamido-2,5-dimethylpyrrole, mp 72.2–74.2C. Analysis: Calcd. for $C_{24}H_{44}N_2O$; C, 76.53; H, 11.78; N, 7.44. Found: C, 76.57; H, 11.58; N, 7.38.

Quaternizations of 92% Stearic Dimethylhydrazide. Stearic dimethylhydrazide (200 g, 0.619 mole) was heated at 80C for 24 hr with 550 g (4.35 moles) of benzyl chloride. The crude product was washed with diethyl ether to remove the excess benzyl chloride and dried under vacuum. The technical product, dimethylbenzylstearoylhydrazinium chloride, had a melting point of 115–120C. Analysis: Calcd. for 92% $C_{27}H_{49}ClN_2O$, 8% $C_{25}H_{45}ClN_2O$; N, 6.21; Cl, 7.88. Found: N, 6.24; Cl, 7.97.

Stearic dimethylhydrazide (184 g, 0.570 mole) in 1 liter of isopropanol was reacted with methyl chloride in an autoclave at 90C and 100 psig until the required quantity of methyl chloride gas had been absorbed. The crude alcohol-free quaternary salt, trimethylstearoylhydrazinium chloride, (170 g, 0.455 mole, 79.8%) had a mp 165–170C (dec.). Analysis: Calcd. for 92% $C_{21}H_{45}ClN_2O$, 8% $C_{19}H_{41}ClN_2O$; N, 7.48%; Cl, 9.49%. Found: N, 7.30; Cl, 9.45%.

Discussion

Syntheses of Mono- and Dihydrazides

The acylation of hydrazine hydrate with fatty acid chlorides represents a good laboratory synthesis for monohydrazides because of the ease of separation of the mixture of mono- and diacylated products formed under the optimum conditions. The large solubility differences between these products exhibited in solvents like ethanol or benzene make this separation possible. The necessity for the use of large excesses of hydrazine hydrate however implies that the synthesis is expensive. When the acid chloride dissolved in ether is added slowly to 20 moles of hydrazine hydrate in ether with no other base to neutralize the evolved hydrogen chloride, the initially formed monohydrazide cannot yield significant quantities of monohydrazide hydrochloride in the ether/water reaction medium in competition with excess hydrazine hydrate [base strengths N_2H_5OH, $RCONHNH_2$; for example, K_b, 24C for $N_2H_5OH = 3 \times 10^{-6}$, $C_6H_5NHNH_2 = 1.6 \times 10^{-9}$, $H_2NCONHNH_2 = 2.7 \times 10^{-11}$, $CH_3CONHNH_2 = 1.7 \times 10^{-11}$ (10)].

Monohydrazides in the C–8 to C–18 range are sufficiently insoluble in ether to be precipitated out before any extensive degree of reacylation can occur. A maximum of ether for acid chloride solvent and a minimum for hydrazine hydrate appears to be desirable for optimum yields. Low temperature in the 0–5C range minimizes the formation of ester, when ethanol is used as solvent, and minimizes the hydrolysis to fatty acid with the water in the 85% hydrazine hydrate when ether alone is used as solvent. The reaction of the acid chloride with water in the solvent, or with ethanol when this is used, is decreased as the chain length of the acid chloride is increased. The yields of monohydrazides increase as the homologous series of fatty acids is ascended, partly as a

TABLE V

Fatty Acid *Sym*-Dihydrazides from Saturated Fatty Acid Chlorides

$$2RCOCl + NH_2NH_3OH + 2NaOH \longrightarrow RCONHNHCOR + 2NaCl + 3H_2O$$

Formula	R Group	Optimum yield, %	Melting point, C	Analysis Carbon Theo.	Carbon Found	Hydrogen Theo.	Hydrogen Found	Nitrogen Theo.	Nitrogen Found
$C_{16}H_{32}N_2O_2$	C_7H_{15}	73.1	158.5–159	67.56	68.00	11.34	11.37	9.85	9.77
$C_{20}H_{40}N_2O_2$	C_9H_{19}	79.0	154 –155	70.53	70.44	11.84	11.86	8.23	8.31
$C_{24}H_{48}N_2O_2$	$C_{11}H_{23}$	81.9	149 –150[a]	72.67	72.62	12.20	12.18	7.06	7.05
$C_{32}H_{64}N_2O_2$	$C_{15}H_{31}$	89.2	150 –151.5	74.28	74.63	12.48	12.35	6.19	6.21
$C_{32}H_{64}N_2O_2$	$C_{15}H_{31}$	93.0	144 –145[b]	75.53	75.29	12.68	12.66	5.50	5.33
$C_{36}H_{72}N_2O_2$	$C_{17}H_{35}$	95.0	139.5–140.5	76.53	76.41	12.85	12.59	4.96	4.89

[a] Reference (3); reported mp 149C.
[b] Reference (2); reported mp 147C.

consequence of decreasing solubility of monohydrazides in the organic solvents.

The yield of monohydrazide falls sharply with the octanoic derivative (only 7.1%) when the ether/ethanol solvent combination is used. The initially formed monohydrazide is apparently sufficiently soluble in the ethanol component to be largely reacylated to the *sym*-dihydrazide. An improved yield of octanoic monohydrazide (31.5%) is obtained when ether alone is used as the solvent since the monohydrazide is precipitated before reacylation can occur. When pyridine is employed as solvent throughout the series, the reaction medium is completely homogeneous and little yield of monohydrazide results. Intermediate monohydrazide is largely reacylated to *sym*-dihydrazide. With the C–8 homolog no monohydrazide is obtained. Although good yields of monohydrazides are obtained for the lauric and higher homologs when the ether/ethanol mixed solvent is employed, the use of ether alone improved the yield of the desired monohydrazide.

The advantages of acid chloride acylation over conventional syntheses of monohydrazides, such as hydrazinolysis of methyl esters, is that the reaction is irreversible and is capable of being carried out rapidly at low temperatures. For unsaturated monohydrazides this may be the only satisfactory synthesis. Note the formation of stearic monohydrazide by the reduction of ethyl oleate, when refluxed with excess 43% hydrazine hydrate in ethanol (9), although it was at one time assumed that oleic monohydrazide could only be prepared when the ethyl ester is permitted to stand for long periods of time in a mixture of hydrazine and liquid ammonia (16), the oleic derivative could probably be readily prepared if all reagents were degassed and the reaction was carried out in an inert atmosphere. Hydrazine will reduce only in the presence of oxygen.

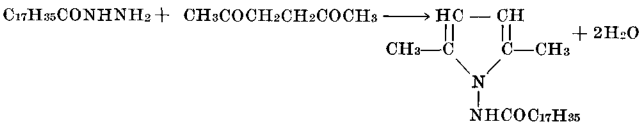
For the preparation of *sym*-dihydrazides the heterogeneous Schotten-Baumann technique is satisfactory. In this reaction the aqueous sodium hydroxide neutralizes the evolved hydrogen chloride and prevents the formation of monohydrazide hydrochloride or hydrazine hydrochloride. The monohydrazide, which forms rapidly, is considerably more soluble in the acid chloride phase of the heterogeneous reaction medium than in water and, although a weaker base than hydrazine hydrate, is reacylated in the oil phase. When used in excess, hydrazine hydrate is thus relatively unreactive because it is concentrated in the aqueous phase. Low temperature of reaction minimizes formation of sodium soap from the acid chloride. The optimum reaction conditions for *sym*-dihydrazide formation throughout the series are vigorous agitation at 0–5C and the use of 2:1 moles acid chloride to hydrazine hydrate.

Physical Properties of Monohydrazides and sym-Dihydrazides

The pure monohydrazides of the saturated fatty acids are all pearly plate-like crystalline solids which melt sharply at 72C (octanoic) to 44C (stearic) higher than the melting points of the acids from which they are derived. These compounds are considerably more insoluble in practically all solvents than their monohydrazide counterparts. Benzene appears to be one of the few good recrystallization solvents. The infrared absorption spectra for the dihydrazides in a light mineral oil indicates three characteristic absorption maxima: 926, 1598, and 3220 cm^{-1} (in the -NH region) whereas decanoic monohydrazide exhibited absorption at 1174, 1627, 3190, and 3290 cm^{-1}. The infrared absorption of several aromatic and aralkyl monohydrazides in chloroform solution has been reported by Jensen (8). Bands at 1670, 1620, and 1500 cm^{-1} were noted. The melting point of the unsymmetrical dihydrazide, N-myristoyl, N′-lauroylhydrazide, is lower than that of the symmetrical dihydrazide corresponding to either component acyl group.

Chemical Properties of Monohydrazides

Although a number of mixed aromatic-aliphatic dihydrazides and unsymmetrical aliphatic dihydrazides [such as N-acetyl, N′-palmitoyl hydrazine (2)] have been prepared, few mixed dihydrazides containing two long-chain acyl groups have been reported. The acylation of myristic monohydrazide with lauroyl chloride in the presence of pyridine gives N-myristoyl, N′-lauroylhydrazine. The formation of substituted pyrroles by the condensation of monohydrazides with 1,4-diketones, as previously demonstrated for isonicotinic monohydrazide and acetonylacetone by Yale and coworkers (18), was extended to the reaction of stearic monohydrazide and acetonylacetone:



Although fatty acid monohydrazides contain an "amide-hydrogen" atom, the possible condensation with 1,4-diketones like acetonylacetone to yield isomeric six-membered ring pyridazine derivatives (1) is remote. The basic nature of the amino group of the monohydrazides is demonstrated by the quaternization of a 92% stearic dimethylhydrazide to dimethylbenzylstearoylhydrazimium chloride and to trimethylstearoylhydrazimium chloride:

$$\mathrm{RCONHN(CH_3)_2 + CH_3Cl \longrightarrow RCONH\overset{\oplus}{N}(CH_3)_3\,\overset{\ominus}{Cl}}$$

$$\mathrm{RCONHN(CH_3)_2 + C_6H_5CH_2Cl \longrightarrow RCONH\overset{\oplus}{N}(CH_3)_2CH_2C_6H_5\,\overset{\ominus}{Cl}}$$

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