The Kinetics and Mechanism of the Reaction of 2-Thenoyl Chloride with Anilines in Benzene

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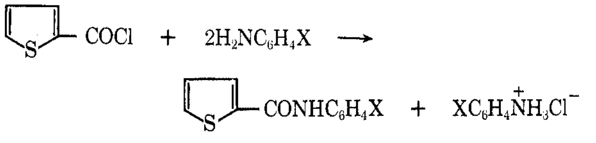
The rate of the reaction of 2-thenoyl chloride with various substituted anilines has been measured in benzene at four temperatures. The reaction is second order overall and pseudo first order with respect to each reactant. The rate constants are increased by electron-donating substituents, while they are decreased by electron-withdrawing groups. The activation parameters and the slopes of the Hammett (−3.45) and Bronsted (1.14) plots are similar to those of the reaction of benzoyl chloride with anilines. The results show that the reaction mechanism of 2-thenoyl chloride with anilines is the same as for reaction of benzoyl chloride; 2-thenoyl chloride, however, reacts more slowly than predicted from the pK_a of 2-thenoic acid. The Tommila equation points out that the carbonyl carbon atom of 2-thenoyl chloride is less positively charged, and therefore less reactive toward aniline, than that of benzoyl chloride.

In several reactions thiophene derivatives do not behave according to the Hammett relation.[1] In fact the esters of 2-thenoic acid, in contrast to those of 3-thenoic acid, saponified at a rate considerably slower than otherwise expected from the pK_a of 2-thenoic acid.[2] At first this seemed to be due to a steric effect of the adjacent sulfur atom,[2] but later, when the same effect was found in the esters of 2-furoic acid, it was ascribed to a stereospecific acid strengthening factor that causes these acids to be stronger.[3,4] Recently the heteroatom was treated as an ortho substituent and it was attempted to correlate the data of the saponification rates of 2-thenoates and 2-furoates by means of the Taft–Ingold relation.[5]

In connection with our present studies on thiophene derivatives,[6–8] in this paper we report a study of the reaction between 2-thenoyl chloride and meta- and para-substituted anilines in benzene solution in order to investigate whether 2-thenoyl chloride reacts as expected from the pK_a of 2-thenoic acid. Whereas the kinetics of benzoylation of anilines have been extensively studied,[9–20] no studies of the reaction between 2-thenoyl chloride and anilines are reported.

The reaction between 2-thenoyl chloride and meta- and para-substituted anilines in benzene takes place quantitatively according to eq 1.


(1)

X = H, m-CH_3, p-CH_3, m-CH_3O, p-CH_3O, m-Cl, p-Cl

The reaction was followed kinetically by filtering the completely insoluble aniline hydrochloride, dissolving this in water, and estimating the chloride by Volhard's method (see Experimental Section).

We found that the reaction of 2-thenoyl chloride with anilines follows second-order kinetics, first order with respect to each reactant. The mechanism was the same as for benzoylation of aniline, but 2-thenoyl chloride reacts at a rate considerably slower than that expected from the pK_a of 2-thenoic acid. The Tommila equation showed that the carbonyl carbon atom of 2-thenoyl chloride is less positively charged than that of benzoyl chloride.

Results and Discussion

The observed reaction rates of 2-thenoyl chloride with large excess of aniline in benzene at 25°, listed in Table I, show that the reaction is pseudo first order.

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF 2-THENOYL CHLORIDE WITH ANILINE IN BENZENE AT 25°

Run no.	Initial concn of 2-thenoyl chloride, mol/l.	$k_1 \times 10^3$, sec^{-1}
1	0.01	1.47
2	0.005	1.51
3	0.0025	1.48

The rate constants at 25° using constant molar ratios of the reactants (1:2) indicate that the reaction is second order overall (Table II). The results of Table

TABLE II
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-THENOYL CHLORIDE WITH ANILINE IN BENZENE AT 25° AT DIFFERENT DILUTIONS

Run no.	Initial concn of 2-thenoyl chloride, mol/l.	$k_2 \times 10^2$, l. mol^{-1} sec^{-1}
1	0.01	2.56
2	0.005	2.52
3	0.0025	2.49

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(19) G. V. Semenyuk, N. M. Oleinik, and L. M. Litvinenko, *Reakts. Sposobnost Org. Soedin.*, **4**, 760 (1967); *Chem. Abstr.*, **70**, 2931 (1969); *Zh. Obshch. Khim.*, **38**, 2009 (1968); *Chem. Abstr.*, **70**, 19475 (1969).

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TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-THENOYL CHLORIDE WITH META- AND PARA-SUBSTITUTED ANILINES IN BENZENE

No.	Registry no.	Substituent	pK_a[a]	$k_2 \times 10^2$, l. mol^{-1} sec^{-1} 10°	15°	17.5°	25°	30°	35°	45°
1	62-53-3	H	4.58		1.63		2.52		4.02	6.04
2	108-44-1	m-CH_3	4.69				3.60	4.34	5.64	8.14
3	106-49-0	p-CH_3	5.12	5.23		7.56	10.1		15.5	
4	536-90-3	m-CH_3O	4.20				1.91	2.56	2.93	5.08
5	104-94-9	p-CH_3O	5.29	26.1	29.4	35.0	44.8			
6	108-42-9	m-Cl	3.34				0.162	0.193	0.270	0.441
7	106-47-8	p-Cl	3.98		0.351		0.633		0.964	1.62

[a] Reference 26.

II also show that the velocity constants do not change appreciably with the dilution. The kinetic of the reaction of 2-thenoyl chloride with anilines in benzene is thus as expected from eq 1 with the rate law (eq 2).

$$\text{rate} = k[C_4H_3SCOCl]\,[H_2NC_6H_4X] \qquad (2)$$

The reaction between 2-thenoyl chloride and anilines takes place quantitatively according to eq 1; no other products were observed. Products of the reaction were isolated as described in the Experimental Section. Numerous experiments showed that the precipitation of aniline hydrochloride was instantaneous and quantitative. In fact, when equal volumes of a 0.01 M benzene solution of 2-thenoyl chloride were mixed with a 0.02 M solution of aniline in benzene and maintained at the kinetic temperature until completion, the completely insoluble aniline hydrochloride was formed. The precipitate was at once filtered off, washed with benzene, and dissolved in water and the chloride was titrated with 0.01 N silver nitrate by the Volhard method. The end point of the reaction was the theoretical. The amount of 2-thiophenecarboxanilide, isolated from the filtrate as described, was in all cases $\geq 95\%$ of that expected from the formation of 1 mol of anilide per 1 mol of acid chloride consumed in agreement with eq 1.

The substituent effect on the rate constants, reported in Table III, shows that the reaction rate depends on the electron density on the nitrogen atom of aniline: electron-donating substituents in aniline increase the rate, while electron-withdrawing groups decrease the rate.

A comparison of these results with those of reaction of benzoyl chloride with anilines[10,13,20] shows that 2-thenoyl chloride reacts more slowly than benzoyl chloride, although 2-thenoic acid (pK_a = 3.49) is stronger than benzoic acid (pK_a = 4.20).[1]

The activation energies and log A values were calculated from the rate constants at different temperatures by the method of least squares, the plots of log k against $1/T$ being linear in all cases (Figure 1).

The entropies of activation, ΔS^*, were computed for 25° by the formula[21] of eq 3.

$$\Delta S^* = 4.576\,(\log A - \log T) - 49.21 \text{ (cal/mol °K)} \qquad (3)$$

It can be noted that the values of the activation parameters, listed in Table IV, are similar to those of the reaction of benzoylation of aniline.[10,13,20] The values of the activation energies show a regular variation with substituents in aniline: electron-donating substituents decrease E_A while electron-withdrawing groups increase E_A. The large negative entropies of activation are as expected by bimolecular reactions with a highly polar transition state.[22]

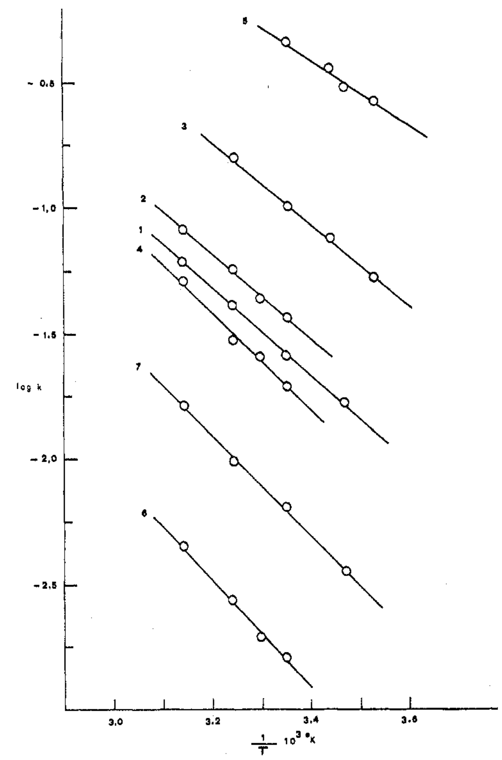

Figure 1.—The Arrhenius activation energy plots. The numbers on the curves refer to the series numbers in Table III.

TABLE IV

ACTIVATION PARAMETERS FOR THE REACTION RATES IN TABLE III

Substituent	E_A, kcal mol^{-1}	ΔS^* at 25°, cal mol^{-1} $°K^{-1}$	log A
H	7.94	−41.1	4.25
m-CH_3	7.79	−41.0	4.27
p-CH_3	7.47	−39.9	4.49
m-CH_3O	8.97	−38.2	4.88
p-CH_3O	6.20	−41.2	4.21
m-Cl	9.70	−40.8	4.31
p-Cl	9.08	−40.1	4.46

The plot of log k at 25° against Hammett's σ constants[23] is linear with a slope of −3.45 (Figure 2). The sensitivity of the rates to substituents in the aniline

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(21) M. Simonetta, "Chimica Fisica," Manfredi, Ed., Milano, 1966, p 278.

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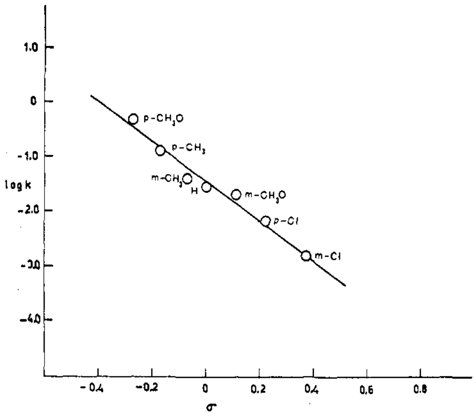

Figure 2.—Hammett plot for the reaction of 2-thenoyl chloride with substituted anilines in benzene at 25°.

(ρ −3.45) is comparable with that found for the reaction of benzoylation of aniline.[24,25]

The plot of the rate constants at 25° for the reaction of 2-thenoyl chloride with the various anilines in benzene solution against the pK_a at 25° in water[26] of the corresponding protonated aniline is linear as shown by the Bronsted plot in Figure 3. The sensitivity of the reaction rates to the basicity of the nucleophile, as measured by the slope of the Bronsted plot (β 1.14) is comparable with that found for the reaction of benzoyl chloride with anilines (0.97), calculated from the experimental data of Stubbs and Hinshelwood.[13]

The sign of the Bronsted slope is as expected for a nucleophilic substitution. We cannot discuss here the value of the Bronsted coefficient, usually related to the extent of bond formation in the transition state, since it was calculated with the reaction rates measured in benzene and the pK_a values measured in water. As is well known, this is a limit to the interpretation of Bronsted coefficients.[23]

To provide some insights into the unusual rate behavior of the 2-thenoyl chloride reaction, we have made use of a simplified Tommila equation relating reaction rate ratios to local charges and bond lengths (eq 4),[20]

$$\ln \frac{k_s}{k_u} = -\frac{e_C\delta e_X}{RTr_1} - \frac{\Delta W}{RT} \qquad (4)$$

where k_s = the rate constant of the substituted compound, k_u = the rate constant of the unsubstituted compound, e_C = the effective electric charge of the carbon atom in the reaction centre, δe_X = the increment, positive or negative, caused to the charge by the substituent introduced in the attacking reagent X, r_1 = the distance X–C in the transition state, and $\Delta W/RT$ = the nonelectrostatic part of ln (k_s/k_u) in the reaction

$$\mathrm{X} + \mathrm{C}\overset{r_0}{\text{—}}\mathrm{Y} \longrightarrow \mathrm{X}\overset{r_1}{\text{—}}\mathrm{C}\overset{r_2}{\text{—}}\mathrm{Y} \longrightarrow \text{products}$$

where C is the center of the reaction, usually a carbon atom, X is the attacking agent, and Y is the leaving group.

The nitrogen atom in the aniline, owing to its lone electron pair, is electrically negative, while the carbon atom of the acid chloride, owing to the influences of the oxygen atom and the chlorine atom, is positively charged.

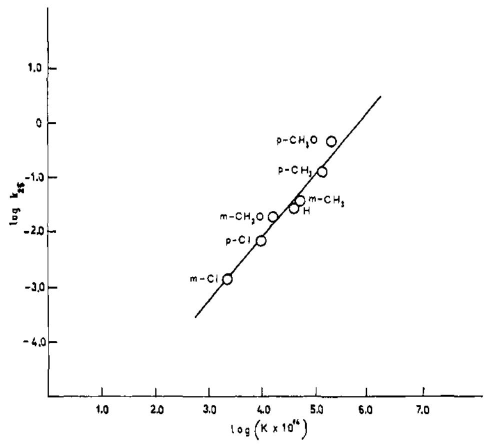

Figure 3.—Plot of log k_{25}° for the reaction of 2-thenoyl chloride with substituted anilines in benzene against the logarithm of their dissociation constants in water at 25° (Bronsted plot).

When the substituents in aniline are electron withdrawing the lone electron pair on the nitrogen atom is bound more tightly. Thus δe_X is positive, and, as e_C also is positive, the product $e_C\delta e_X$ is positive, and, if the term $-e_C\delta e_X/RTr_1$ is greater than the term $\Delta W/RT$, log (k_s/k_u) should be negative. The more the substituent attracts electrons, the greater is δe_X and the more negative log (k_s/k_u).

On the contrary, when the substituents in aniline are electron donating, δe_X is negative, the product $e_C\delta e_X$ is, therefore, negative, and log (k_s/k_u) is positive. The more the substituent repels electrons, the more negative is δe_X and the greater log (k_s/k_u). This is in accordance with the experimental results listed in Table V, where the log (k_s/k_u) values at 25° for the benzoyl chloride reaction are also reported.

TABLE V

VALUES OF LOG (k_s/k_u) AT 25° FOR THE REACTION OF 2-THENOYL CHLORIDE OR BENZOYL CHLORIDE WITH META- AND PARA-SUBSTITUTED ANILINES IN BENZENE

Substituent	2-Thenoyl chloride[a] reaction	Benzoyl chloride reaction
p-Cl	−0,62580	−0,66144[b] −0,67800[c] −0,69252[d]
m-Cl	−1,23061	−1,23441[c]
p-CH$_3$	0,58506	0,63662[b] 0,62578[c]
m-CH$_3$	0,13051	0,26597[c]
p-CH$_3$O	1,23624	
m-CH$_3$O	−0,12548	

[a] The rate constant values used were calculated from the Arrhenius equation. [b] Reference 10. [c] Reference 13. [d] Reference 20.

The results show that, when the substituents in aniline are electron withdrawing, the log (k_s/k_u) values for the 2-thenoyl chloride reaction are less negative than those for the benzoyl chloride reaction. When the substituents in the amine are electron donating the log (k_s/k_u) values for reaction of 2-thenoyl chloride are less positive than those of the benzoylation reaction. Since the anilines in the reaction with 2-thenoyl chloride

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[24] Jaffé[25] reports a ρ value of −2.78, calculated from experimental data of other authors.[10,13] Other authors recently have found a value of −3.37.[19]

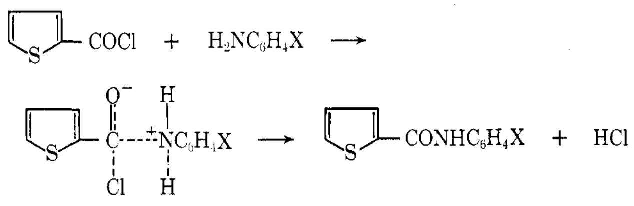
[25] H. H. Jaffé, Chem. Rev., 53, 191 (1953).

[26] G. M. Badger, "The Structures and Reactions of the Aromatic Compounds," Cambridge, 1954, p 196.

or benzoyl chloride are the same, the electric charge in the nitrogen atom of the $-NH_2$ group has the same value. This implies a change of the electric charge in the carbonyl carbon atom of 2-thenoyl chloride: the carbonyl carbon atom of 2-thenoyl chloride is less positively charged than that of benzoyl chloride.

The results, then, lead us to postulate that the reaction of 2-thenoyl chloride and anilines in benzene is similar to the benzoyl chloride reaction involving the attack of the lone pair of the electrons of the amino group to the carbonyl carbon atom (Scheme I).

SCHEME I



The slower reaction rate of 2-thenoyl chloride, in comparison with that of benzoyl chloride, can be ascribed to the resonance between the thiophene ring and the carbonyl group that makes it more stabilized, and therefore less reactive towards aniline, than the carbonyl group of benzoyl chloride.

Experimental Section

Materials.—2-Thenoyl chloride (a Fluka commercial product) was fractionated to constant boiling point.

The various aniline derivatives were purified to constant melting point or boiling point by recrystallisation or fractionation.

The solvent used was benzene (R. P. Carlo Erba), and no special purification was undertaken, since numerous experiments showed that elaborate purification was unnecessary.

Kinetic Procedure.—The reaction was followed kinetically using the method described for benzoylation of aniline.[9,10] Into each of several glass-stoppered bottles were introduced, by means of volumetric pipets, equal volumes (50 ml) of standard solutions of 2-thenoyl chloride and of appropriate aniline derivative in benzene.

All the reagents were mixed at the temperature of the experiment. The bottles were immediately stoppered, shaken, and placed into a constant-temperature bath (±0.01°). At suitable intervals, the bottles were removed from the constant-temperature bath and the aniline hydrochloride formed was filtered and washed with solvent. The precipitate was transferred to a beaker and dissolved in water, to which were added the washings from the filter and the original bottle, and the chloride was titrated with 0.01 N silver nitrate by the Volhard method.

The pseudo-first-order rate constants with a large excess of aniline over 2-thenoyl chloride and the second-order rate constants with constant molar ratios (2:1) of the reactants were calculated. The concentration ranges of 2-thenoyl chloride used for the pseudo-first order rate measurements varied from 0.01 to 0.0025 M.

The pseudo-first-order rate constants were calculated from the usual equation

$$k_1 = \frac{1}{t}\, 2.303 \log \frac{a}{a - x}$$

where t is the time in seconds, a is the initial concentration of the acid chloride in moles/liter, x is the concentration of product in moles/liter at time t, and k_1 is the velocity constant in seconds^{-1}.

Since, according to eq 1, two molecules of aniline are removed for each molecule of 2-thenoyl chloride, the second-order rate constants are derived from the formula $dx/dt = k_2(a - x)/(2a - 2x)$, hence

$$k_2 = \frac{1}{2 \times 60t}\left(\frac{1}{100 - X} - \frac{1}{100}\right)\frac{100}{a}$$

where t is the time in minutes, X is the percentage change, k_2 is the velocity constant (liters/mole seconds), and a is the initial concentration of the acid chloride in moles/liter. For the second-order rate measurements the initial concentrations of the reactants after mixing were thus 2-thenoyl chloride 0.005 M, aniline 0.01 M. For some compounds for which the reactions were too fast to be measured accurately at this concentration (p-toluidine and p-anisidine, compounds 3 and 5 in Table III), the initial concentrations were 0.005 M aniline and 0.0025 M 2-thenoyl chloride.

Typical pseudo-first-order and second-order kinetic runs are shown in Tables VI and VII.

TABLE VI

PSEUDO-FIRST-ORDER KINETIC RUN FOR THE REACTION OF 2-THENOYL CHLORIDE WITH ANILINE IN BENZENE AT 25°[a]

Elapsed time, min	0.01 N $AgNO_3$, ml	log $(a/a - x)$
0	0	0
2	10.35	0.1006
4	15.7	0.1637
6	21.0	0.2369
8	25.9	0.3164
10	30.25	0.4036
12	33.4	0.4792
14	36.2	0.5593

[a] The data refer to the second kinetic run in Table I.

TABLE VII

SECOND-ORDER KINETIC RUN FOR THE REACTION OF 2-THENOYL CHLORIDE WITH ANILINE IN BENZENE AT 25°[a]

Time, min	Reaction %	$k_2 \times 10^2$, l. mol^{-1} sec^{-1}
20	23.1	2.50
30	31.4	2.54
40	37.8	2.53
50	43.0	2.51
60	47.4	2.50
70	51.2	2.50
80	54.6	2.51
120	64.6	2.53
150	69.6	2.54
240	78.5	2.54
		Mean 2.52

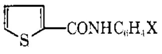
[a] The data refer to the second kinetic run in Table II.

All rates were run in duplicate to the least 80% completion with less than 3% deviation between the two rate constants in all cases. At temperatures other than 15 or 25°, rate coefficients were corrected for thermal expansion or contration of the solvent. All rate constants were calculated by a least squares computer program with an Olivetti Programma 101.

Product Analysis.—Standard solutions of the appropriate aniline and 2-thenoyl chloride in benzene were mixed in a glass-

TABLE VIII

PHYSICAL CONSTANTS OF 2-THIOPHENECARBOXANILIDES[a]

No.		Mp, °C	Ref
1	X = H	140	27
2	m-CH_3	107	28
3	p-CH_3	169	28
4	m-CH_3O	140–141	6
5	p-CH_3O	140	29
6	m-Cl	138	28
7	p-Cl	161	28

[a] All the compounds were crystallized from aqueous ethanol.

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(27) G. M. Badger, R. T. Howard, and A. Simons, *J. Chem. Soc.*, 2849 (1952).

(28) Buu-Hoy and Nguyen-Hoan, *Recl. Trav. Chim. Pays-Bas*, **68**, 5 (1949).

(29) C. Tsuchiya, *Nippon Kagaku Zasshi*, **82**, 1395 (1961).

stoppered bottle and maintained at the kinetic temperature until completion. After concentration of the benzenic solution to small volume, the corresponding 2-thiophenecarboxanilide precipitated was filtered, washed free from aniline hydrochloride with water, dried, and recrystallized from suitable solvent. In all cases the amount of 2-thiophenecarboxanilide was $\geq 95\%$ of that expected from the formation of 1 mol of anilide per 1 mol of acid chloride consumed. The mixture melting points with authentic samples of 2-thiophenecarboxanilides revealed no depression. Physical constants of 2-thiophenecarboxanilides are listed in Table VIII.

Registry No.—2-Thenoyl chloride, 5271-67-0.

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The Synthesis of Aldehydes from Dihydro-1,3-oxazines

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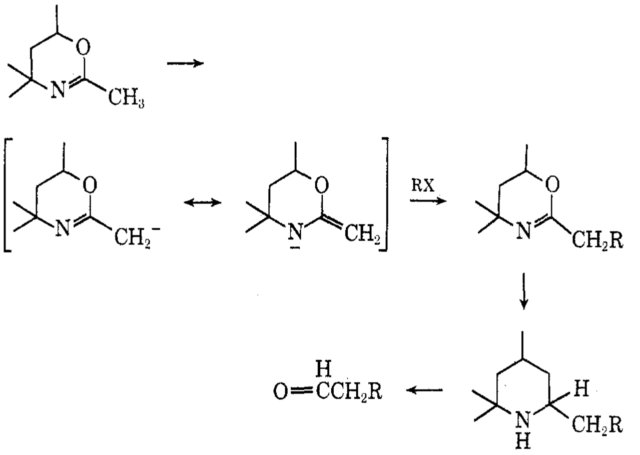
The use of readily available dihydro-1,3-oxazines (DHO) as precursors to substituted acetaldehydes, α,β-unsaturated aldehydes, cycloalkanecarboxaldehydes, and a variety of functionalized aldehydes is reported. The method is useful for both a two-carbon homologation of electrophiles to aldehydes as well as a three-carbon homologation of nucleophiles (RMgX, malonates, enamines). The scope and limitations of this synthesis are discussed.

In 1969, a series of brief reports[2-4] appeared which outlined a technique for the preparation of aldehydes based upon the dihydro-1,3-oxazine (DHO) ring system, and this is depicted in Scheme I. It is now desirable to describe in detail the studies which led to the successful implementation of this process. The anticipated approach required that (a) a readily available dihydro-1,3-oxazine be utilized as starting material, (b) a stable carbanion be generated by the use of some suitable base, (c) reaction of the carbanion with carbon electrophiles lead only to C-alkylation, since N-alkylation would result in an undesirable side product, (d) a mild and efficient reduction be employed to reduce the C=N link in the sensitive oxazine ring, and (e) hydrolytic cleavage conditions be utilized to generate the aldehydic product from the tetrahydro-1,3-oxazine (THO).

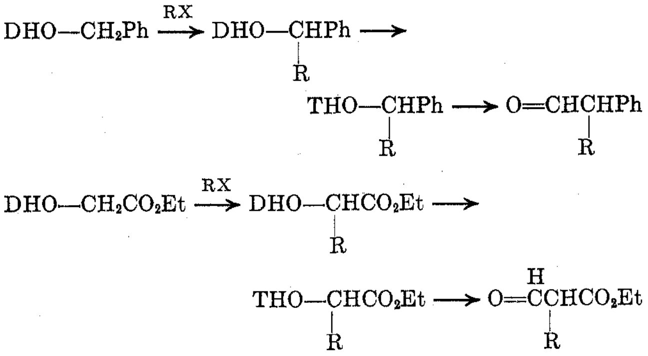
SCHEME I



The scheme would, in effect, be a two-carbon homologation of electrophiles to aldehydes and may be considered as the *aldehyde equivalent* to the malonic ester synthesis. A similar concept has been reported by Stork[5] utilizing metalated enamines which were alkylated by alkyl halides and hydrolyzed to produce the elaborated aldehyde, whereas a one-carbon homologation of electrophiles was described by Corey and Seebach[6] employing the versatile lithiodithiane system.

Oxazine systems which possessed 2 substituents other than methyl were also viewed as candidates for this sequence and are shown in Scheme II. Thus, the use of the 2-benzyl or the 2-carboethoxymethyl oxazines could serve as precursors to α-phenyl and α-carboethoxy aldehydes, respectively. Furthermore, the 2-vinyl-dihydro-1,3-oxazine was examined (Scheme III) to determine if it was suitable as a three-carbon homolog for organometallics. Recently, there have been reports from Walborsky[7] and this laboratory[8] which allow a

SCHEME II



$$\mathrm{DHO{-}CH_2Ph} \xrightarrow{\mathrm{RX}} \mathrm{DHO{-}\underset{R}{C}HPh} \longrightarrow \mathrm{THO{-}\underset{R}{C}HPh} \longrightarrow \mathrm{O{=}CH\underset{R}{C}HPh}$$

$$\mathrm{DHO{-}CH_2CO_2Et} \xrightarrow{\mathrm{RX}} \mathrm{DHO{-}\underset{R}{C}HCO_2Et} \longrightarrow \mathrm{THO{-}\underset{R}{C}HCO_2Et} \longrightarrow \mathrm{O{=}\overset{H}{C}\underset{R}{C}HCO_2Et}$$

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