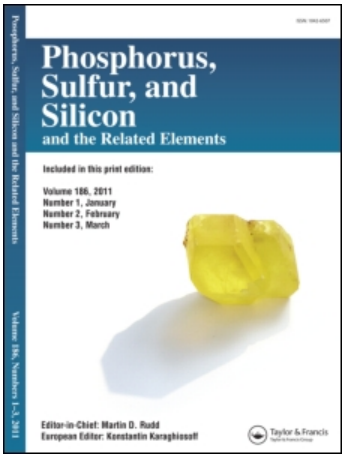

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ALKYLATIOIM, ACYLATION, AND ARYLATION PRODUCTS OF 1-CYANO-ISOTHIOCHROMANE

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ALKYLATION, ACYLATION, AND ARYLATION PRODUCTS OF 1-CYANO-ISOTHIOCHROMANE[1]

by

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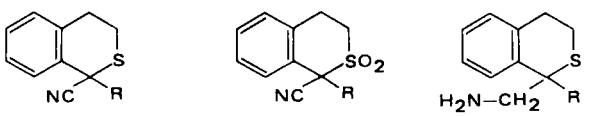
ABSTRACT

1-Cyano-isothiochromane (**1a**) can be alkylated in position 1, using the carbanion that is formed from sodium amide, sodium hydride, or *n*-butyllithium. With methyl iodide or ethyl iodide **1c** and **1d** are formed; with α-halogenated ether or thioether, **1e** and **1f**; with propargyl bromide, **1h**; with bromo acetophenone, **1i**; and with ethyl chloroacetate, **1k**. Similarly, acylation with benzoyl chloride leads to **1l**, and with 2,4-dinitrofluorobenzene to **1m**. The alkylation products of **1a** can be oxidized with peracids to the sulfones **2** and with $LiAlH_4$ reduced to 1-aminomethyl-isothiochroman (**3**). Acid hydrolysis of **1** gave isothiochromane-1-carboxylic acids, **4**, whereas when **1** is treated with hydrogen peroxide in alkaline medium the S-dioxide and the S-oxide acid amides, **5** and **6** respectively, are formed.

The reaction of 1-cyano-isothiochromane (**1a**) with alkyl halides in the presence of sodium amide had hitherto led to alkylation in position 1[2,3] only with allylbromide, benzylchloride or β-dialkylamino ethyl chlorides. The reason for the earlier observation, that with other alkyl halides or acyl halides apparently no substitution had taken place was probably the fact that all three components were heated simultaneously under reflux. In our hands the reaction was found to take place with such simple alkyl halides as methyl iodide and ethyl iodide (leading to **1c** and **1d**, respectively), as well as more reactive compounds such as α-haloether or thioether (to yield **1e** and **1f**, respectively). This was accomplished by preparing the carbanion from **1a** in benzene/sodium amide solution, removing with dry nitrogen the ammonia formed, and finally adding the alkyl halide. The yields could be improved as we prepared the carbanion from dimethylformamide/sodium hydride solution, a method, which among others, has been applicable to the alkylation of Reissert compounds[4] and of 1-cyano-homoisochromane[5].



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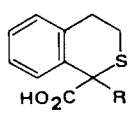

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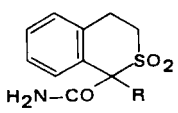

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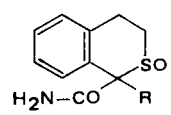
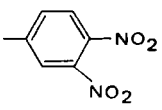


6

a: R = H; **b**: R = D; **c**: R = CH_3; **d**: R = C_2H_5; **e**: R = CH_3OCH_2; **f**: R = CH_3SCH_2; **g**: R = CH_3–SO_2–CH_2; **h**: R = HC≡C–CH_2; **i**: R = C_6H_5–CO–CH_2; **k**: R = H_5C_2O–CO–CH_2; **l**: R = C_6H_5–CO;

m: R = 

The nmr spectra of the reaction products prove most useful for their identification. With isothiochromane (CCl_4 solvent) one finds a multiplet at ~τ 3.0 for the phenyl protons, a singlet at τ 6.45 for the two C-1 protons and a multiplet of the A_2B_2 type at τ 7.3 for the C-3 and C-4 protons. Of interest is a comparison of these values with those previously obtained from the spectrum of isochromane[6]; here the bands of the C-1 and C-3 protons have been shifted by 1 ppm each downfield through the influence of the electronegative oxygen, so that aside from the multiplet for the phenyl protons at τ 3.0 and the singlet for the C-1 protons at τ 5.36, two triplets for the C-3 and C-4 protons at τ 6.17 and τ 7.30, respectively, are observed. 1-Cyano-isothiochromane (**1a**, CCl_4) shows a spectrum made up of three groups of signals, a multiplet for the aromatic protons at τ 2.8, a singlet at τ 5.40 for the C-1 proton easily exchangeable with deuterium and whose τ value as a result of the cyano groups is shifted considerably to lower value, a multiplet for the C-3 and C-4 protons in the range between τ 6.6 to 7.3. 1-Methyl-1-cyano-isochromane (**1c**, $CDCl_3$) is characterized by τ 2.7 (multiplet) for the aromatic protons, τ 6.5–7.50 for the C-3 and C-4 protons and by τ 7.97

(singlet) for the methyl group. In the spectrum of 1-methoxymethyl-1-cyano-isothiochromane (**1e**, CCl_4) one finds, alongside with the two multiplets in **1a**, a singlet by τ 6.60 for the methyl protons, and an AB signal (centred at τ 6.24, J_{AB} 10 Hz, δ_{AB} 13.5 Hz) for the diastereotopic methylene protons. 1-methyl-mercapto-methyl-1-cyano-isothiochromane (**1f**, CCl_4) gives an analogous spectrum, in which the signal of the methyl protons (τ 7.87) and the AB-quartet of the methylene protons (midpoint τ 6.79, J_{AB} 14 Hz, δ_{AB} 7.8 Hz) are shifted to higher fields as a result of the smaller electronegativity of sulfur.

The carbanion prepared from sodium hydride in dimethylformamide reacted further on treatment with alkyl halides. Propargyl bromide, for example, gives **1h**, which was also obtained in better yield, when using the lithium salt obtained through reaction of **1a** and *n*-butyl-lithium in ether-dioxane mixture.

The ir spectrum (KBr) of **1h** is characterized by the sharp CH valence vibration band at 3300 cm^{-1}, the nitrile band by 2232 cm^{-1} and the weak C≡C absorption band around 2119 cm^{-1}. In the nmr spectrum, one finds the signal for the acetylene proton through coupling with the methylene protons of the propargyl group as a triplet (J = 3 Hz) centred τ 7.87.

Bromoacetophenone gives the crystalline phenacyl compound **1i**, on reaction with the carbanion of 1-cyano-isothiochromane.

The ir spectrum (KBr) of **1i** shows along with the nitrile band (2242 cm^{-1}) the C=O valence vibration in the same position as acetophenone (1680 cm^{-1}). The nmr spectrum ($CDCl_3$) shows the diastereotopic methylene protons again as an AB signal (midpoint τ 5.18, J_{AB} 10 Hz, δ_{AB} 22.0 Hz). The multiplet for the C-3 and C-4 protons lies between τ 6.5–7.8. The signals of the 2 ortho-protons of the benzoyl moiety form a multiplet at τ 2.0, the remaining seven aromatic protons fall together in a further multiplet between τ 2.2–3.2.

From ethylchloroacetate and the lithium derivative of **1a** one obtains the liquid substitution product **1k**, which was purified through repeated distillation in high vacuum.

Besides the nitrile band at 2232 cm^{-1} the ir spectrum (film) of **1k** shows the C=O valence vibrational band at 1739 cm^{-1}. The nmr spectrum (CCl_4) allows for the clear recognition of the ethyl group signals at τ 8.74 (triplet) and τ 5.83 (quartet), whereas the methylene proton signal is overshadowed by the C-3 and C-4 proton multiplet.

Reaction of the carbanion of 1-cyano-isothiochromane (**1a**) with benzoylchloride gives the crystalline benzoyl compound *11* which shows the nitrile ir (KBr) absorption band at 2217 cm^{-1} and a –C=O valence vibrational band at 1745 cm^{-1}. Finally, as an example of an aryl halide we also reacted 2,4-dinitrofluorobenzene with 1-cyano-isothiochromane and sodium hydride in DMF. In an exothermic reaction, a violet-colored mixture is formed which, after addition of ice and acidification gives yellow crystals, **1m**. The ir spectrum (KBr) showed two symmetric and asymmetric valence vibrations for the nitro group at 1357 resp. 1548 cm^{-1} as well as the nitrile absorption at 2232 cm^{-1}.

The alkylation products of 1-cyano-isothiochromane are suitable for manifold further reactions. Thus are obtained—through oxidation with phthalomonoperacid[7] or hydrogen perioxide/glacial acetic acid—the crystalline sulfones **2c**, **2d**, **2e** and from **1f** the corresponding disulfone **2g**. The ir spectra of sulfones shows an absorption band at 2247 cm^{-1} for the nitrile group, as well as the asymmetric (1300–1430 cm^{-1}) and the symmetric (1135–1160 cm^{-1}) bands for the SO_2-valence vibrations. Reduction of the nitrile group with $LiAlH_4$ gives the 1-amino methyl derivatives **3e**, **3d**, **3e**, and **3f**, which are easily isolated as the hydrochloride and characterized through their ir (KBr) spectra. The NH_3^+ group of these is recognized by the valence vibration at 2899–2924 cm^{-1}, and the asymmetric and symmetric deformation vibrations at 1575–1600 cm^{-1} and 1313–1500 cm^{-1}, respectively. Hydrolysis of the nitrile group by heating of **1c** and **1d** with a mixture of glacial acetic acid and concentrated hydrochloric acid or 48% hydrobromic acid solution gives the crystalline 1-methyl-isothiochromane-1-carbonic acid and 1-ethyl-isothiochromane-1-carbonic acid (**4c**, **4d**), respectively. Considerable difficulty is, however, encountered in the acid hydrolysis of 1-cyano-isothiochromanes having bulky substituents in position 1 and in the hydrolysis of the methoxymethyl derivative **1e** and the propargyl derivative **1h**. In all the cases investigated the partial hydrolysis of the nitrile group with hydrogen peroxide in alkaline solution went quite smoothly to produce amides, such as **5c**, **5d**, **5e**, and **5h**, whereby in all cases the sulfur atom of the heterocyclic system was oxidized to the sulfone stage. In the presence of 1*M* hydrogen peroxide, the sulfoxide, such as **6c**, was obtained. This result is in agreement with the observation that sulfides, with hydrogen peroxide in slightly alkaline solution are first oxidized to the sulfoxide and then to the sulfone.[8]

The spectra (KBr) of the acid amides show two bands in the region of the NH-valence vibration, a sharp band at 3448–3484 cm^{-1} and a fairly broad band at 3195–3226 cm^{-1}, further the amide (I and II) band, both falling at 1680–1700 cm^{-1}. Between 1111–1163 cm^{-1} and 1290–1323 cm^{-1} one recognizes the frequently split bands for the symmetric and asymmetric SO_2-valence vibration.

Experimental Section

Alkylation or Acylation of 1-Cyano-isothiochromane (1a)

Method A

Under stirring and elimination of water vapor 6.5 ml of a 30% sodium amide in benzene is added to 30 mmoles of **1a** in 70 ml absolute benzene. Within a short time, there is a violent generation of NH_3, with a slight warming and a red-brown mass precipitates. On heating for 90 min with stirring, slight refluxing and passage through dry N_2 for the removal of the ammonia formed. Finally, one slowly adds, at room temperature, 40–50 millimoles of freshly prepared alkylating agent (dissolved in 20 ml benzene) and keeps the suspension gently boiling for 3–5 hours. On cooling the undissolved, is filtered off, washed with water and finally washed (depending on the reaction of the wash water) with 0.5 *N* HCl and 5% NaOH and then washed once again with water and then dried with sodium sulfate. After concentrating the solution, the residue obtained is distilled or also directly recrystallized.

Method B

With stirring, elimination of damp, and with ice cooling, one adds to a solution of 20 millimoles of **1a** in 80 ml of absolute dimethyl formamide, 1.0 g of a 50% suspension of sodium hydride in paraffin oil. In this case it is recommended to first remove the paraffin oil by repeated washing with petroleum ether. The mixture is yellowish green in color with a strong hydrogen gas generation. After 10 min one adds slowly 30 millimoles of freshly prepared alkylating agent, whereby the coloration disappears. Stirring is continued for 2 hr at room temperature; the mixture is poured into 20 ml ice water and the extraction carried out with ether. After drying over calcium chloride, the solution is concentrated under vacuum, and the residue is distilled or recrystallized directly.

The substitution products prepared by the two methods are shown in Table I.

1-Deutero-1-cyano-isothiochromane (1b)

Under elimination of water vapor and the passage of dry N_2 gas, was quickly added by −15° 10 ml of a 20% solution of *n*-butyllithium in hexane to a 5.2 g solution of **1a** in a mixture of 85 ml absolute dioxane and 40 ml absolute ether and stirred for 30 min in the cooling bath. To the yellow suspension so formed 6.0 ml of deuterium oxide is added within 10 min and then for 10 hr at room temperature. It is filtered, the filtrate shaken with 4 ml D_2O, dried, concentrated, and the residue distilled in high vacuum.

Melting point 69–70°.

Yield: 4.8 g (91%) **1b**, which according to the nmr spectrum has a deuterium incorporation of 95%.

Anal. Calc. for $C_{10}H_8DNS$: C, 68.18; H and D, 5.72; N, 7.95; S, 18.20.
Found: C, 67.97; H and D, 5.76, N, 7.90, S, 17.84.

1-[Propin-(2')-yl]-1-cyano-isothiochromane (1h)

The preparation of the carbanion is carried out as described under **1b**. Finally, 4.8 g propargylbromine in 30 ml absolute ether is added and stirred further for 10 hr at room temperature. After processing and drying, it was distilled in high vacuum. After the unreacted **1a**, 5.0 g (78%) of **1h** goes over at 10^{-2} torr air bath, 145–155°C as a colorless oil, which hardens on rubbing with ethanol.

Melting point: 50–51° (from ethanol).

Anal. Calc. for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57; S, 15.03.
Found: C, 73.19; H, 5.09; N, 6.49; S, 14.92.

Ethyl (1-cyano-isothiochromane-1)acetate (1k)

The preparation is analogous to **1h**, starting with ethyl chloroacetate. The yield obtained was 2.4 g (30%) at 10^{-2} torr (air bath) and going over at 150–155° as a viscous oil, N_D^{20} 1.5593.

Anal. Calc. for $C_{14}H_{15}NO_2S$: C, 64.35; H, 5.78; N, 5.36; S, 12.27.
Found: C, 64.39; H, 5.91; N, 5.32; S, 12.39.

1-Cyano-1-[2', 4'-dinitrophenyl]-isothiochromane (1m)

Under stirring and exclusion of water vapor a solution of 3.5 g **1a** and 3.8 g 2,4-dinitrofluorobenzene in 40 ml absolute dimethylformamide was reacted with 1.0 g 50% sodium hydride suspension in paraffin oil. The mixture generates hydrogen vigorously, warms, and attains a violet color. It was stirred for 2 hr, then poured into 200 ml ice water; dilute hydrochloric acid was added until disappearance of the color. Extraction was achieved with methylene chloride and drying with calcium chloride. The residue was concentrated in vacuum and hardened with carbon tetrachloride. The resulting light yellow crystals of melting point 180–181° are recrystallized from methylene chloride/methanol.

Yield: 2.5 g (37%).

Anal. Calc. for $C_{16}H_{11}N_3O_4S$: C, 56.30; H, 3.25; N, 12.30; S, 9.40.
Found: C, 55.82; H, 3.25; N, 12.00; S, 9.39.

1-Methyl-1-cyano-isothiochromane-2,2-dioxide (2c)

Hydrogenperoxide (3.0 g 30%) was added to 1.9 g of **1c** in 30 ml of glacial acetic acid and warmed on a waterbath for 2 hr. After concentrating in vacuum the residue solidified by rubbing with ethanol. Melting point 75–77° (from ethanol).

Yield: 1.9 g (86%).

Anal. Calc. for $C_{11}H_{11}NO_2S$: C, 59.70; H, 5.01; N, 6.33; S, 14.49.
Found: C, 59.63; H, 5.00; N, 5.87; S, 14.98.

The sulfones **2d** and **2e** shown in Table I were prepared similarly.

1-Methylsulfomethyl-1-cyano-isothiochromane-2,2-dioxide (2g)

A mixture of 0.5 g **1f** in 20 ml absolute ether at −5° and 4.7 g phthalomonoperacid[7] in 200 ml ether was prepared and left standing at room temperature for 4 days. After shaking

TABLE I

Physical Properties and Analytical Data

Compound	Mp. °C (recryst. from)	Bp,°C/Torr n_D^{20}	Yield %	Empirical formula	Calcd. % / Found % C	H	N	S
1-Methyl-1-cyano-isothiochromane	53° (ethanol)		A: 78 B: 90	$C_{11}H_{11}NS$	69.80 69.86	5.86 6.01	7.40 7.10	16.94 16.76
1-Ethyl-1-cyano-isothiochromane		115–120°/0.02 1.5760	A: 71 B: 87	$C_{12}H_{13}NS$	70.89 70.94	6.44 6.58	6.89 6.94	15.78 16.08
1-Methoxymethyl-1-cyano-isothiochromane		120–130°/0.01 1.5780	A: 77 B: 85	$C_{12}H_{13}NOS$	65·72 65.75	5.97 6.01	6.39 6.32	14.62 15.15
1-Methylmercaptomethyl-1-cyano-isothiochromane		130–140°/0.01 1.6102	A: 52 B: 80	$C_{12}H_{13}NS_2$	61.23 61.30	5.57 5.68	5.95 6.19	27.25 27.35
1-Phenacyl-1-cyano-isothiochromane	183–185° (ethanol/chloroform)		B: 29	$C_{18}H_{15}NOS$	73.69 73.56	5.15 4.97	4.77 4.58	10.93 10.93
1-Benzoyl-1-cyano-isothiochromane	145–146° (ethanol)		B: 98	$C_{17}H_{13}NOS$	73.09 73.02	4.69 4.67	5.01 5.28	11.47 12.01
1-Ethyl-1-cyano-isothiochromane-2,2-dioxide	107–109° (ethanol)		58	$C_{12}H_{13}NO_2S$	61.25 61.34	5.57 5.33	5.95 5.99	13.63 13.37
1-Methoxymethyl-1-cyano-isothiochromane-2,2-dioxide	89–90° (ethanol)		85	$C_{12}H_{13}NO_3S$	57.35 57.58	5.22 5.35	5.58 5.39	12.76 13.02
1-Methyl-1-aminomethyl-isothiochromane-hydrochloride	209–211° (ethanol/ether)		74	$C_{11}H_{16}NS]Cl$	57.50 57.24	7.02 7.49	6.10 6.19	13.96[a] 14.00
1-Aminomethyl-1-ethyl-isothiochromane-hydrochloride	204–206° (ethanol/ether)		53	$C_{12}H_{18}NS]Cl$	59.11 58.73	7.45 7.87	5.75 5.74	13.15[b] 13.17
1-Aminomethyl-1-methylmercaptomethyl-isothiochromane-hydrochloride	171–173° (ethanol/ether)		58	$C_{12}H_{18}NS_2]Cl$	52.25 52.06	6.58 6.56	5.08 5.08	23.24[c] 23.22
1-Methyl-1-carbamoyl-isothiochromane-2,2-dioxide	191–193° (ethanol)		75	$C_{11}H_{13}NO_3S$	55.21 55.29	5.48 5.59	5.86 5.62	13.41 12.88
1-Ethyl-1-carbamoyl-isothiochromane-2,2-dioxide	151–153° (ethanol)		79	$C_{12}H_{15}NO_3S$	56.90 56.78	5.97 6.03	5.53 5.49	12.65 12.22
1-Methoxymethyl-1-carbamoyl-isothiochromane-2,2-dioxide	167–169° (ethanol/petroleum/ether)		41	$C_{12}H_{15}NO_4S$	53.52 53.85	5.61 5.82	5.20 5.29	11.91 11.90
1-[Propin-(2')-yl]-1-carbamoyl-isothiochromane-2,2-dioxide	188–190° (ethanol/petroleum ether)		82	$C_{13}H_{13}NO_3S$	59.30 59.42	4.97 4.99	5.32 5.35	12.18 12.48

[a]Calcd. for Cl 15.42, found 15.79; [b]Calcd. for Cl 14.54, found 14.31; [c]calcd. for Cl 12.85, found 13.29.

with sodium bicarbonate solution, the ether solution was dried and then concentrated in a vacuum; mp, 148–150° (from methylene chloride/ethanol).

Yield: 0.4 g (67%).

Anal. Calc. for $C_{12}H_{13}NO_4S_2$: C, 48.15; H, 4.38; N, 4.68; S, 21.42.
Found: C, 48.14; H, 4.47; N, 4.72; S, 21.80.

1-Aminoethyl-1-methoxymethyl-isothiochromane (3e)

To a suspension of 0.5 g lithium aluminum hydride in 20 ml absolute ether one added (with stirring and exclusion of water vapor) 2.2 g of 1e in 30 ml ether so slowly that the mixture just slightly boiled. It was left at reflux and boiling for another 40 min and after cooling with ice water, it was hydrolyzed through the addition of 4 ml water; separated with the help of a grit and washed with ether. The entire ethereal phase, after drying with potassium carbonate was concentrated to about 10 ml. By passage of hydrogen chloride gas the hydrochloride of 3e was precipitated and recrystallized from ethanol/ether mixture. The free amine was obtained by the dissolution of the hydrochloride in water, addition of sodium hydroxide and extraction with ether. Colorless oil which distills over at 10^{-2} torr, 104–108° air bath, N_D^{22} 1.5852; nmr (CCl_4): Ar,

τ 2.7 m, 4H; O–CH_2, τ 6.42, s, 2H; CH_3 τ 6.68, s, 3H; N–CH_2, τ 7.00, 2H, AB; C-3 and C-4, τ 6.78–7.35, m, 4H; NH_2, τ 8.87, s, 2H.

Yield: 1.0 g (45%)

Anal. Calc. for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67; N, 6.27; S, 14.36.
Found: C, 64.36; H, 7.73; N, 6.23; S, 14.67.

The hydrochlorides **3c**, **3d**, and **3f**, shown in Table I were prepared similarly.

1-Methyl-1-carboxy-isothiochromane (4c)

3.8 g of **1c** in 40 ml of glacial acetic acid after addition of 50 ml of hydrochloric acid (38%) were heated under reflux for 10 hr. After concentrating the resulting solution in vacuum, the residue was treated with potassium carbonate solution, then washed through shaking with ether, then finally acidified with dilute hydrochloric acid. Colorless needles of melting point 188–190° (from dilute ethanol). Nmr (CCl_4): OH, τ –0.9, s, 1H; Ar, τ 2.8, m, 4H; C-3 and C-4, τ 6.9, m, 4H; CH_3, τ 8.23, s, 3H.

Yield: 3.0 g (72%).

Anal. Calc. for $C_{11}H_{12}O_2S$: C, 63.42; H, 5.81; S, 15.40.
Found: C, 63.15; H, 6.02; S, 15.15.

21 g of **4c** in 30 ml abs. tetrahydrofuran were treated with excess of ether solution of diazomethane. After 24 hr it was concentrated and the residue distilled at 10^{-1} torr (air bath) and 90–95°. The methyl ester of **4c** in a colorless oil, n_D^{25} 1.5678. Nmr (CCl_4): Ar, τ 2.8, m, 4H; OCH_3, τ 6.42, s, 3H; C-3 and C-4 τ 6.6–7.6, m, 4H; CH_3, τ 8.25, s, 3H.

Yield: 1.9 g (86%)

Anal. Calc. for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42.
Found: C, 65.12; H, 6.51; S, 14.52.

1-Ethyl-1-carboxy-isothiochromane (4d)

This was prepared similar to **4c** by heating 2.8 g of **1d** in 30 ml glacial acetic acid with 25 ml hydrobromic acid solution (48%). Colorless crystals of melting point 135–136° (from ethanol/water).

Yield: 1.6 g (52%).

Anal. Calc. for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42.
Found: C, 64.51; H, 6.56; S, 14.84.

Through reaction with diazomethane one obtained the methyl ester of **4d**. Colorless crystals of melting point 53–54° (from methanol).

Yield: 96%.

Anal. Calc. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57.
Found: C, 66.23; H, 6.59; S, 13.56.

1-Methyl-1-carbamoyl-isothiochromane-oxide (6c)

Compound **1c** (0.95 g) in 30 ml ethanol was treated with 0.6 g hydrogen peroxide (30%) through addition of 6*N* sodium hydroxide brought to about pH 8 (indicator paper) and with stirring left for 4 hr at temperature of 50–60°. On cooling, it was neutralized with 6*N* sulfuric acid and evaporated in vacuum. The residue was extracted with methylene chloride, and one obtained colorless crystals of melting point 156–158° (from ethanol/petroleum ether). Ir (KBr): NH_2 3205, 3448 cm^{-1}; C=O, 1686 cm^{-1}; SO, 1035 cm^{-1}.

Yield: 0.5 g (45%).

Anal. Calc. for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27; S, 14.36.
Found: C, 59.00; H, 5.98; N, 6.23; S, 14.59.

In like manner the sulfone **5c** was obtained by the addition of 1.6 g hydrogen peroxide (30%); this procedure also applies to the sulfones **5d**, **5e**, and **5h** (see Table I).

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