Chemistry of α,β-Unsaturated Thione Dimers. 1. Preparation of α,β-Unsaturated Thione Dimers and Thermolysis of These Dimers in the Presence of Acrylonitrile or Acrylamide

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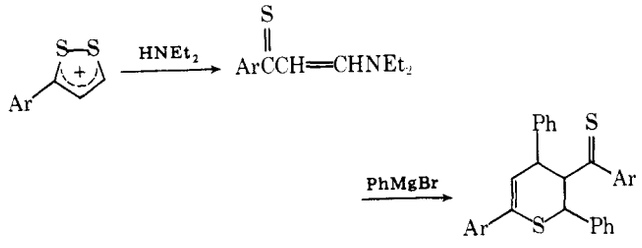
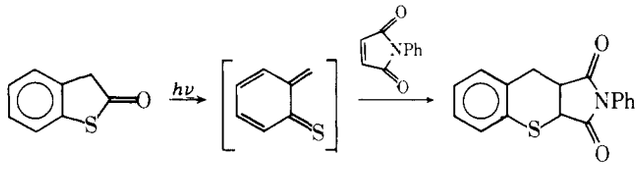
Thiochalcone, 4'-methoxythiochalcone, 2-benzylidene-1-thiotetralone, 2-(*p*-methoxybenzylidene)-1-thiotetralone, and 2-(*p*-chlorobenzylidene)-1-thiotetralone dimers have been prepared by the reaction of corresponding α,β-unsaturated ketones with P_4S_{10}. When these dimers were heated in the presence of acrylonitrile or acrylamide, monomeric unsaturated thiones generated by the decomposition of the dimers reacted with the acrylic compounds to give some cycloadducts of the Diels–Alder type, such as 3,4-dihydro-2*H*-thiopyran or 5,6-dihydrobenzo[*h*]thiochroman derivatives.

α,β-Unsaturated thiones are little known because of their instability in the monomeric form[1] and tendency to undergo [4 + 2] cycloaddition in which the thione itself may serve as a dienophile or a diene.

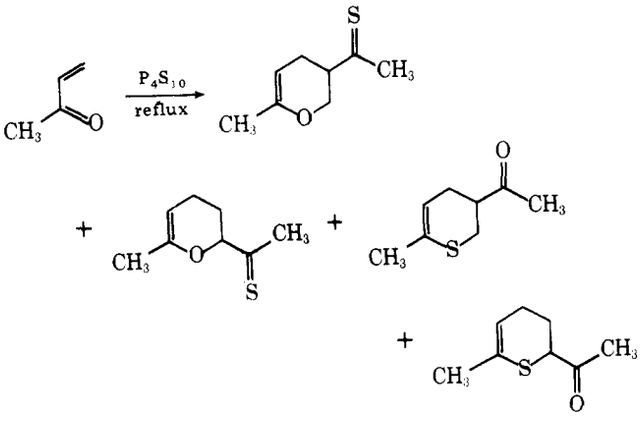
For example, Quiniou et al.[2] reported that treatment of vinylogous thioamide with phenylmagnesium bromide gave 3-methoxythiobenzoyl-6-methoxyphenyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran, via a thiochalcone intermediate.



The photoreaction of the thiolactone in the presence of *N*-phenylmaleimide afforded good chemical evidence for the intermediacy of the ortho-quinoid thioketone.[3]



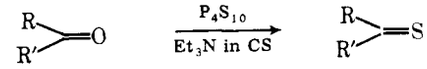
Recently, Lipkowitz et al.[4] reported that treatment of methyl vinyl ketone with P_4S_{10} in pyridine gave four isomeric products. This work also provided some suggestions for the cycloaddition of α,β-unsaturated thiones.



In this paper we wish to describe the satisfactory preparation of α,β-unsaturated thione dimers and the thermolysis of these dimers in the presence of acrylonitrile or acrylamide.

Preparation of α,β-Unsaturated Thione Dimers

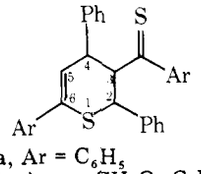
Tetraphosphorus decasulfide (P_4S_{10}) is well known as a reagent for the thionation of nonenolisable ketones. The reactions are usually carried out by refluxing the ketone dissolved in toluene or xylene with suspended P_4S_{10}.[5] Under the same conditions, however, thionation of α,β-unsaturated ketones was unsuccessful. We have investigated other procedures for the preparation of ordinary thiones (**2**), and found that treatment of ketones (**1**) with P_4S_{10} takes place with ease in carbon disulfide solution in the presence of triethylamine.



1a, R = R' = C_6H_5
b, R = CH_3; R' = C_6H_5

2a, R = R' = C_6H_5
b, R = CH_3; R' = C_6H_5

Under these conditions, the reaction of chalcone or 4'-methoxychalcone with P_4S_{10} proceeded readily to give the corresponding thione dimer in moderate yield. The results are shown in Table I. The NMR spectrum of 4'-methoxythiochalcone dimer **3b** was identical with that reported by Quiniou et al.[2] and thiochalcone dimer **3a** gave a similar NMR spectrum.



3a, Ar = C_6H_5
b, Ar = *p*-CH_3O-C_6H_4

Similarly, 2-arylidene-1-thiotetralone dimers (**4**) were obtained by the reaction of 2-arylidene-1-tetralone with P_4S_{10}. The structures of **4** are supported by analytical and spectral data. The elemental analyses of mass spectra were in agreement with the proposed structures **4** or **5**. The NMR spectra showed sharp one-proton singlets at δ 3.6 and 5.6 ppm; these were assigned to the C-4 and the C-2 protons in the 3,4-dihydro-2*H*-thiopyran ring, respectively, so the structure **5** can be excluded. However these spectral data do not enable the stereochemistry of **4** to be deduced.

It would be probable that the formation of these dimers (**9**) proceed via an α,β-unsaturated thione intermediate (**7**), from which **9** is formed via path A or path B as illustrated in Scheme I, and the structure of **9** suggests that the cycloaddition re-

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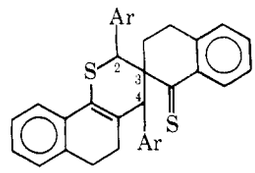
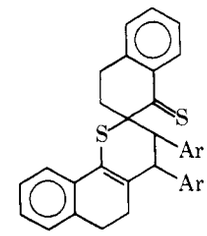
Table I. Preparation of Thiones

product	registry no.	reaction conditions: temp °C	reaction conditions: time	yield, %[a]
thioacetophenone	16696-68-7	10–15	1 h	27
thiobenzophenone	1450-31-3	reflux	1 h	76
3a	67254-57-3	20–25	1 day	38
3b	67314-93-6	20–25	1 day	50
4a	67254-58-4	20–25	1 week	45
4b	67254-59-5	20–25	1 week	50
4c	67254-60-8	20–25	1 week	62

[a] Based on the ketone.



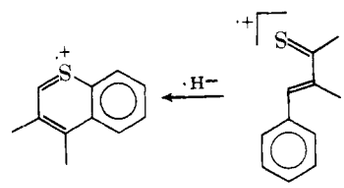
4a, Ar = C_6H_5
b, Ar = p-CH_3O-C_6H_4
c, Ar = p-Cl-C_6H_4



5a, Ar = C_6H_5
b, Ar = p-CH_3O-C_6H_4
c, Ar = p-Cl-C_6H_4

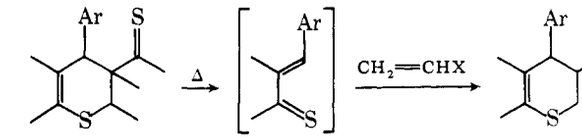
action of **7** shows the opposite regioselectivity to that of α,β-unsaturated ketones.[4,6]

The mass spectra of **3** and **4** showed evidence for the retro-Diels–Alder reaction: intense ions for α,β-unsaturated thiones, and the characteristic peak recognized by the assumption that the α,β-unsaturated thione ion loses a hydrogen to give the stable thiopyrrylium ion.



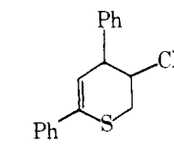
The Thermolysis of α,β-Unsaturated Thione Dimers in the Presence of Acrylonitrile or Acrylamide

In the preparation of α,β-unsaturated thione dimers, we observed that the yield of the dimer decreased and the formation of polymeric substances increased with raising reaction temperature. This suggested the dissociation of the dimers into unstable thione monomers upon heating so trapping of the monomers by the thermolysis of the dimer in the presence of acrylonitrile or acrylamide has been examined.

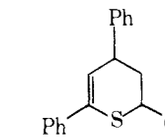


X = CN, $CONH_2$

The thermolysis of **3a** in the presence of acrylonitrile gave the cycloadduct **10a** in 44% yield. The IR spectrum of the product showed a sharp band at 2250 cm^{-1}, attributable to the nitrile group and the elemental analysis and mass spectra are in agreement with the proposed structure, **10a** or **11a.** The

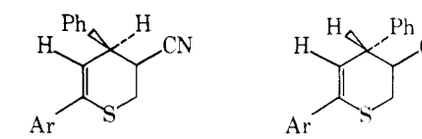


10a



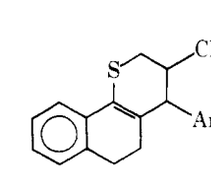
11a

NMR spectrum showed signals at δ 3.0–3.5 (m, 3 H), 3.9 (t, 1 H), 6.1 (d, 1 H), and 7.2–7.8 (m, 10 H). The doublet at δ 6.1 (J = 4.8 Hz) is assigned to the olefinic proton while the triplet at δ 3.9 is attributed to the benzylic proton by spin decoupling. Therefore the isomeric structure **11a** can be excluded.[7] In addition to providing the molecular weight, the mass spectra showed evidence for the retro-Diels–Alder reaction: an intense ion at 224 for thiochalcone was observed. The NMR spectrum of 2-cyano-6-methoxyphenyl-4-phenyl-3,4-dihydro-2*H*-thiopyran (**10b**) showed signals at δ 5.9 (d, 0.5 H, J = 4.0 Hz) and 6.0 (d, 0.5 H, J = 4.8 Hz). These signals suggest that the product is a mixture of the two epimers **10b.**

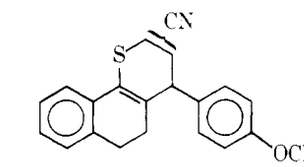


10b, Ar = p-CH_3O-C_6H_4

Similarly, the reaction of **4** and acrylonitrile gave the cycloadducts **12.** The analytical and spectral data of **12a** and **12c** were in agreement with the proposed structure, but the position of the nitrile group was not determined in **12b.**



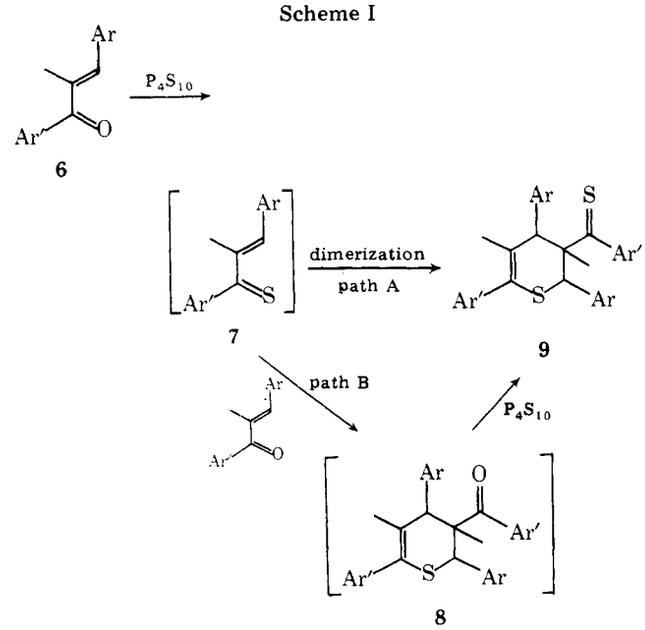
12a, 12c

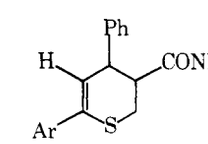


12b

3a reacted with acrylamide in dry benzene to give the adduct **13a** in 40% yield. The IR spectrum showed bands at 3400 (NH_2), 3200 (NH_2), and 1660 cm^{-1} (C=O). The molecular ion (m/e 277) and thiochalcone fragment (m/e 224) were observed in the mass spectra. In the NMR spectrum, the doublet at δ 6.2 (J = 7.0 Hz) is assigned to the olefinic proton while the

Scheme I





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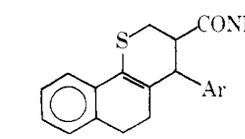

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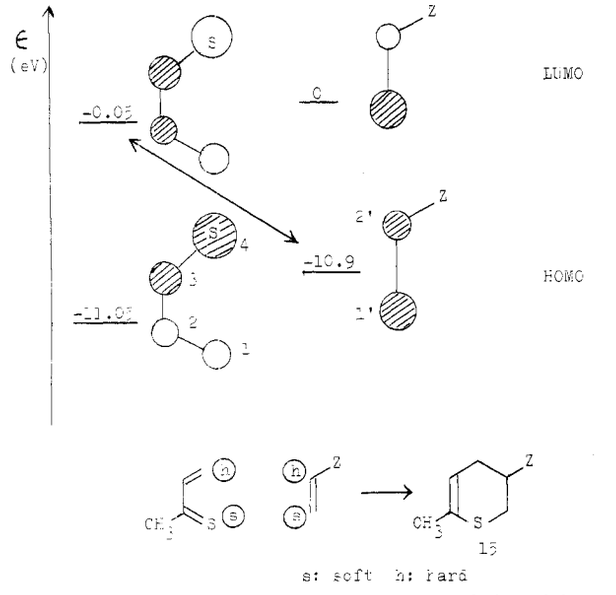

Figure 1. Estimated π frontier orbital energies for methyl vinyl thione and olefins (Z = CN, CHO). (Solid arrow indicates the dominant interaction).

Table II. Reaction of α,β-Unsaturated Thiones with Acrylonitrile and Acrylamide

product	registry no.	reaction time, min	yield, %
	Acrylonitrile		
10a	67254-61-9	30	44
10b		60	74
12a	67254-62-0	120	53
12b	67254-47-1	15	53
12c	67254-63-1	60	59
	Acrylamide		
13a	67254-64-2	30	40
13b	67254-65-3	60	48
14a	67254-66-4	60	71
14b	67254-67-5	20	49
14c	67254-68-6	70	71

double doublet at δ 4.16 is attributed to the benzylic proton by spin decoupling. The reaction of **3b–4c** with acrylamide afforded the corresponding adducts (**13b, 14a, 14b,** and **14c**). The results are presented in Table II.

Experimental Section

All melting and boiling points are uncorrected. Column chromatography was performed on a 100–200 mesh Florisil column by eluting with ligroin–benzene (1:1). ^{1}H-NMR spectra were recorded at 60 MHz on a JEOL JNM-PMX 60 spectrometer using Me_4Si as internal standard. IR spectra were obtained on an Hitachi Model 260-10 infrared spectrometer. Mass spectral data were obtained with an Hitachi double focusing mass spectrometer RMU-7M. Commercial acetophenone and benzophenone were used without further purification. All α,β-unsaturated ketones were prepared by the Aldol condensation of the corresponding ketone with aldehyde.[8] Acrylonitrile and acrylamide were obtained commercially. Acrylonitrile was dried over molecular sieves 3A and was carefully fractionated at atomospheric pressure. Acrylamide was recrystallized from benzene.

Thioacetophenone. To a stirred suspension of acetophenone (9.6 g) and P_4S_{10} powder (7.1 g) in dry carbon disulfide (30 mL) was added dropwise triethylamine (6 mL) at 10–15 °C. The mixture was stirred at room temperature for 1 h and filtered and the filtrate was evaporated. The deep-purple residue was distilled to give thioacetophenone (**3 g**): bp 55 °C (0.3 mm) [lit.[5] bp 78–82 °C (1 mm)].

Thiobenzophenone. A suspension of benzophenone (18.2 g), P_4S_{10} powder (6.7 g), and triethylamine (10 mL) was gently refluxed for 1 h under nitrogen atmosphere. After the reaction was over, the mixture was filtered and the filtrate was evaporated. The deep-blue residue was distilled to give thiobenzophenone (**15 g**): bp 127–131 °C (0.04–0.06 mm) [lit.[5] bp 129–133 °C (0.06 mm)].

A Typical Procedure for the Preparation of α,β-Unsaturated Thione Dimers. A suspension of chalcone (0.01 mol), P_4S_{10} powder (1 g), and triethylamine (1 mL) in dry carbon disulfide (20 mL) was allowed to stand at 20–25 °C under nitrogen atomosphere for 1 day. The reaction mixture was filtered and the filtrate was evaporated. The residue was chromatographed on Florisil gel (25 g) using ligroin–benzene (1:1) as the eluent. The solvent was evaporated and the residue was recrystallized from benzene–ethanol giving thiochalcone dimer (**3a**) as blue crystals: mp 134–135 °C; MS (70 eV) *m/e* 224 (12), 223 (100); NMR (CCl_4) δ 3.96 (dd, 1 H, *J* = 3.5 and 6.6 Hz), 4.95 (d, 1 H, *J* = 11.5 Hz), 5.18 (dd, 1 H, *J* = 3.5 and 11.5 Hz), 6.23 (d, 1 H, *J* = 6.6 Hz), and 6.9–7.8 (m, 20 H). Anal. Calcd for $C_{30}H_{24}S_2$: C, 80.32; H, 5.39; S, 14.29. Found: C, 80.12; H, 5.51; S, 14.20.

4′-Methoxythiochalcone dimer 3b: mp 145–148 °C (lit.[2] mp 151–152 °C); NMR ($CDCl_3$) δ 3.76 (s, 3 H), 3.82 (s, 3 H), 4.06 (dd, 1 H, *J* = 3.6 and 6.6 Hz), 5.06 (d, 1 H, *J* = 11 Hz), 5.38 (dd, 1 H, *J* = 3.6 and 11 Hz), 6.28 (d, 1 H, *J* = 6.6 Hz), and 6.8–7.8 (m, 18 H). Anal. Calcd for $C_{32}H_{28}O_2S_2$: C, 75.55; H, 5.54; S, 12.60. Found: C, 75.64; H, 5.71; S, 12.66. The NMR spectrum is identical with that reported by Quiniou et al.[2].

2-Benzylidene-1-thiotetralone dimer 4a: mp 171–172 °C; MS (70 eV) *m/e* 250 (39), 249 (100); NMR (CCl_4) δ 2.0–3.1 (m, 8 H), 3.6 (s, 1 H), 5.6 (s, 1 H), and 6.9–7.5 (m, 18 H). Anal. Calcd for $C_{34}H_{28}S_2$: C, 81.56; H, 5.63; S, 12.81. Found: C, 81.91; H, 5.78; S, 12.94.

2-(*p*-Methoxybenzylidene)-1-thiotetralone dimer 4b: mp 135–136 °C; MS (15 eV) *m/e* 560 (M^+, 6), 280 (47), 279 (88); NMR ($CDCl_3$) δ 2.0–3.1 (m, 8 H), 3.6 (s, 1 H), 3.7 (s, 3 H), 3.8 (s, 3 H), 5.6 (s, 1 H), and 6.6–7.3 (m, 16 H). Anal. Calcd for $C_{36}H_{32}O_2S_2$: C, 77.11; H, 5.75; S, 11.43. Found: C, 77.42; H, 5.87; S, 11.15.

2-(*p*-Chlorobenzylidene)-1-thiotetralone dimer 4c: mp 173–174 °C: MS (15 eV) *m/e* 569 (M^+, 1), 285 (54), 284 (94), 283 (100), 250 (20), 249 (93); NMR ($CDCl_3$) δ 1.78–2.38 (m, 2 H), 2.62–3.17 (m, 6 H), 3.65 (s, 1 H), 5.60 (s, 1 H), and 6.85–8.27 (m, 16 H). Anal. Calcd for $C_{34}H_{26}S_2Cl_2$: C, 71.69; H, 4.60; S, 11.26. Found: C, 71.49; H, 4.48; S, 11.30.

A Typical Procedure for the Thermolysis of α,β-Unsaturated Thione Dimers with Acrylonitrile. A suspension of thiochalcone dimer (0.448 g, 1 mmol) in acrylonitrile (8 mL) was gently refluxed for 0.5 h under nitrogen atomosphere. The excess acrylonitrile was removed and recrystallization of the residue from 30 mL of ligroin gave 3-cyano-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran (**10a**) (0.245 g) as colorless needles: mp 131–132 °C; MS (70 eV) *m/e* 277 (M^+, 11), 224 (58), 223 (100); IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 3.0–3.5 (m, 3 H), 3.9 (t, 1 H, *J* = 5.0 and 4.8 Hz), 6.1 (d, 1 H, *J* = 4.8 Hz), and 7.2–7.8 (m, 10 H). Anal. Calcd for $C_{18}H_{15}NS$: C, 77.97; H, 5.45; S, 11.55. Found: C, 77.65; H, 5.31; S, 11.46.

3-Cyano-6-(*p*-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-thiopyran (10b): mp 95–98 °C (recrystallized from ligroin); MS (70 eV) *m/e* 307 (M^+, 19), 254 (61), 253 (100); IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 3.0–3.5 (m, 3 H), 3.8 (s, 3 H), 3.8–4.0 (m, 1 H), 5.9 (d, 0.5 H, *J* = 4.0 Hz), 6.0 (d, 0.5 H, *J* = 4.8 Hz), and 6.8–7.5 (m, 9 H). Anal. Calcd for $C_{19}H_{17}NOS$: C, 74.27; H, 5.54; S, 10.43. Found: C, 74.51; H, 5.66; S, 10.22.

3-Cyano-4-phenyl-5,6-dihydrobenzo[*h*]thiochroman (12a): mp 223–225 °C (recrystallized from benzene–ligroin); MS (70 eV) *m/e* 303 (M^+, 28), 250 (39), 249 (100); IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 2.0–3.6 (m, 7 H), 3.8 (d, 1 H, *J* = 3.5 Hz), and 7.0–7.6 (m, 9 H). Anal. Calcd for $C_{20}H_{17}NS$: C, 79.17; H, 5.65; S, 10.57. Found: C, 79.12; H, 5.77; S, 10.70.

2(or 3)-Cyano-4-(*p*-methoxyphenyl)-5,6-dihydrobenzo[*h*]-thiochroman (12b): mp 126–128 °C (recrystallized from ligroin); MS (70 eV) *m/e* 333 (M^+, 54), 280 (69), 279 (100); IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 2.0–2.3 (m, 2 H), 2.56–3.3 (m, 5 H), 3.6–3.86 (4 H), and 6.8–7.56 (m, 8 H). Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; S, 9.61. Found: C, 75.75; H, 5.65; S, 9.74.

3-Cyano-4-(*p*-chlorophenyl)-5,6-dihydrobenzo[*h*]thiochroman (12c): mp 130–132 °C (recrystallized from ligroin); MS (70 eV) *m/e* 337 (M^+, 50), 284 (50), 283 (86), 249 (100); IR (KBr) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 2.0–3.5 (m, 7 H), 3.7 (d, 1 H, *J* = 4.0 Hz), and 7.0–7.6 (m, 8 H). Anal. Calcd for $C_{20}H_{16}ClNS$: C, 71.11; H, 4.74; S, 9.49. Found: C, 71.23; H, 4.80; S, 9.40.

A Typical Procedure for the Thermolysis of α,β-Unsaturated Thione Dimers with Acrylamide. A solution of thiochalcone dimer (0.448 g, 1 mmol) and acrylamide (0.142 g, 2 mmol) in dry benzene (8 mL) was gently refluxed for 0.5 h under nitrogen atomosphere. The benzene was removed and recrystallization of the residue from ethanol

gave 3-carbamoyl-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran (**13a**) (0.236 g) as colorless crystals: mp 223–224 °C; MS (70 eV) *m/e* 295 (M^+, 22), 224 (59), 223 (100); IR (KBr) 1660 cm^{-1} (C=O); NMR (Me_2SO) δ 4.16 (dd, 1 H, *J* = 7 and 4 Hz), 6.2 (d, 1 H, *J* = 7 Hz), 6.9 (br band, 2 H), and 7.0–7.6 (m, 10 H). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; S, 10.85. Found: C, 73.21; H, 5.86; S, 10.88.

3-Carbamoyl-6-(*p*-methoxyphenyl)-4-phenyl-3,4-dihydro- (14a): mp 174–176 °C (recrystallized from benzene); MS (70 eV) *m/e* 321 (M^+, 52), 250 (44), 249 (100); IR (KBr) 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.7–2.26 (m, 2 H), 2.56–3.2 (m, 5 H), 3.9 (d, 1 H, *J* = 6 Hz), 5.6 (br band, 2 H), and 6.9–7.6 (m, 9 H). Anal. Calcd for $C_{20}H_{19}NOS$: C, 74.73; H, 5.96; S, 9.97. Found: C, 74.98; H, 6.04; S, 9.95.

3-Carbamoyl-4-(*p*-methoxyphenyl)-5,6-dihydrobenzo[*h*]-thiochroman (14b): mp 175–176 °C (recrystallized from benzene); MS (70 eV) *m/e* 351 (M^+, 79), 280 (42), 279 (64); IR (KBr) 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.9–3.1 (m, 7 H), 3.7 (s, 3 H), 3.9 (d, 1 H, *J* = 6 Hz), 5.5 (br band, 2 H), and 6.7–7.5 (m, 8 H). Anal. Calcd for $C_{21}H_{21}NO_2S$: C, 71.79; H, 5.98; S, 9.12. Found: C, 71.74; H, 5.96; S, 9.00.

3-Carbamoyl-4-(*p*-chlorophenyl)-5,6-dihydrobenzo[*h*]thiochroman (14c): mp 138–140 °C (recrystallized from benzene); MS (70 eV) *m/e* 355 (M^+, 28), 284 (17), 283 (29), 249 (36); IR (KBr) 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.9–3.1 (m, 7 H), 3.9 (d, 1 H, *J* = 3 Hz), 5.8 (br band, 2 H), and 7.0–7.5 (m, 8 H). Anal. Calcd for $C_{20}H_{18}ClNOS$: C, 67.51; H, 5.06; S, 9.01. Found: C, 67.52; H, 5.11; S, 8.97.

Registry No.—**10b** isomer 1, 67254-69-7; **10b** isomer 2, 67254-70-0; acrylonitrile, 107-13-1; acrylamide, 79-06-1; acetophenone 98-86-2; tetraphosphorus decasulfide, 12066-62-5; chalcone, 94-41-7; 4′-methoxychalcone, 959-33-1; 2-benzylidene-1-tetralone, 6261-32-1; 2-(*p*-methoxybenzylidene)-1-tetralone, 49629-37-0; 2-(*p*-chlorobenzylidene)-1-tetralone, 49545-70-2.

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(7) We can account for the regioselectivity in these cycloadditions by frontier molecular orbital theory. A simple qualitative frontier orbital treatment of the reaction between methyl vinyl thione,[4] selected as a model for α,β-unsaturated thiones, and olefins,[7a] (C=CZ, Z = CN, CHO) is represented in Figure 1, and application of the "hard and soft" concept allows us to predict that the first bond would link the softest centers,[7b] i.e., atom 4 with 1′ to give **15**. (a) K. N. Houk, *J. Am. Chem. Soc.*, **95**, 4092 (1973). (b) G. Desimoni and G. Tacconi, *Chem. Rev.*, **75**, 651 (1975).
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Synthesis and Reactions of Some *N*-Acylated and *N*-Sulfonylated *N,N′*-Dialkylureas

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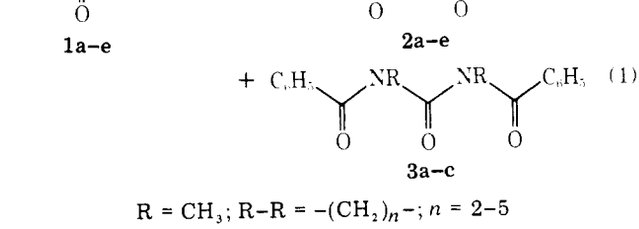
N,N′-Dialkylureas (**1**) are *N*-mono or *N,N′*-diacylated on treatment with various acyl chlorides: benzoyl chloride/base leads to *N*-benzoyl- and/or *N,N′*-dibenzoylureas (**2** and **3**). Similarly, cyclic *N*-mono- and *N,N′*-bisarenesulfonyl) ureas (**4** and **5**) are formed on reacting arenesulfonyl chlorides with imidazolidin-2-one and perhydropyrimidin-2-one. *N*-Benzoyl-*N′*-oxamoylureas (**12**) are obtained on successive treatment of **2** with oxalyl chloride and arylamine. Several *N*-benzoyl-*N′*-oxamoylureas undergo facile skeletal rearrangement on heating in methanol, yielding 1-aryl-3-(ω-benzamidoalkyl)imidazolidine-2,4,5-triones (**13**).

N,N′-Disubstituted ureas react with acylating agents on either the nitrogen or the carbonyl oxygen with formation of *N*- or *O*-acylated products. Evidence has been presented that many *N*-acylations of amides involve an initial attack on the more nucleophilic carbonyl oxygen; the thereby formed *O*-acylated intermediates rapidly rearrange to the thermodynamically more stable *N*-acylated products.[1] Detailed reports describing the synthetically important reactions of substituted ureas with phosgene and thionyl and phosphoryl chloride have been published.[2] Recently, we reported the *N*-benzoylation of cyclic *N,N′*-dialkylureas which lead to products of potential interest as masked isocyanates.[3] In conjunction with this work we investigated the feasibility of acylating and sulfonylating certain linear and cyclic *N,N′*-dialkylureas on both nitrogen atoms[4] and studied subsequent reactions of some of the obtained products. Treatment of *N,N′*-dimethylurea (**1a**) with molar amounts of benzoyl chloride in methylene chloride solution, using triethyl amine as an HCl scavenger, produces *N,N′*-dimethyl-*N*-benzoylurea (**2a**) in 81% yield and small amounts of *N,N′*-dimethyl-*N,N′*-dibenzoylurea (**3a**) (excess benzoyl chloride produces **3a** exclusively). Cyclic five- and six-membered ring ureas, such as imidazolidin-2-one (**1b**) and hexahydropyrimidin-2-one (**1c**), give mixtures of *N*-mono and



(1)

R = CH_3; R–R = $-(CH_2)_n-$; *n* = 2–5

N,N′-dibenzoylated products **2b,c** and **3b,c** under identical conditions while seven- and eight-membered ring ureas, i.e., perhydro-1,3-diazepin-2-one (**1d**) and perhydro-1,3-diazocin-2-one (**1e**), again produce *N*-monobenzoylated products exclusively.[3] Yields and melting points of all new compounds are presented in Table I.

The reaction of *N,N′*-dialkylureas with arenesulfonyl chlorides proceeds by O attack and subsequent elimination of sulfonic acid to give carbodiimides.[5,6] Treatment of the acyclic urea **1a** with benzenesulfonyl chloride and triethylamine in chloroform solution does indeed give *N,N′*-di-

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