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FLAVONOIDS, 39.[+] THE REACTION OF 3-MESYLOXYFLAVANONES WITH O- AND S-NUCLEOPHILES, SYNTHESIS OF 3-THIOCYANATO- AND 3-ACETYLTHIO-FLAVANONES

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Abstract - The action of either cyanate or acetate ions on trans-3-mesyloxyflavanones 1 led to the formation of flavones 2 and aurones while the reaction with the respective S-nucleophiles (thiocyanate and thioacetate ions) resulted in cis- and trans-3-thiocyanato- and 3-acetylthioflavanones (6 and 11). The participation of the concurrent nucleophilic substitution, β-elimination and elimination with ring-contraction is dependent on the "hard-soft" character of the nucleophile and the increase of the "soft" character favours the displacement.

In the preceding papers we have reported[1,2] on the reaction of 3-alkyl- and -arylsulphonyloxyflavanones with various N-nucleophiles. The nucleophilic substitution allows the preparation of novel 3-substituted-flavanones hardly available by other routes.

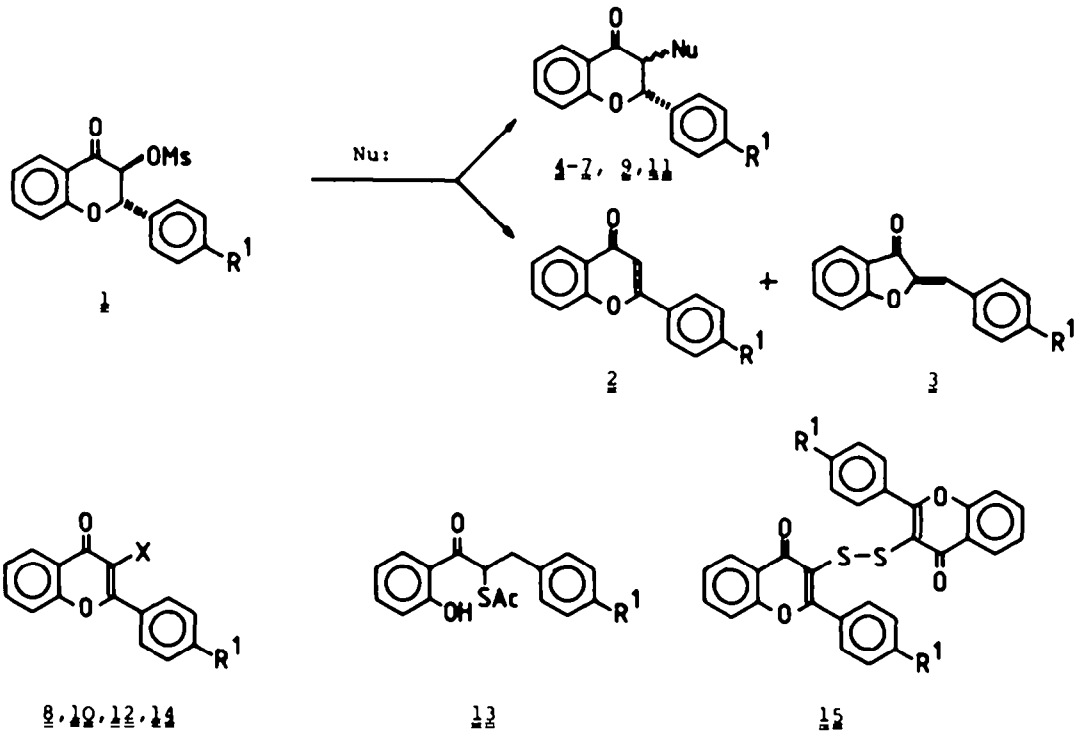
The reaction of trans-3-mesyloxy-4'-R^1-flavanones (1a,b) with NaOAc, KOAc or KOCN in various solvents in the presence or absence of phase-transfer catalysts resulted in a mixture of 4'-R^1-flavones (2a,b) and 4'-R^1-aurones (3a,b).

Table 1. Conditions and product ratios of the reaction of 1 with acetate and cyanate ions

Starting material	Reagent/ /solvent/temp.	Catalyst[+]	Reaction time /h/	Unchanged 1	Yield (%) 2	3
1a	NaOAc/DMSO/25°	-	144	-	80.1	10.9
	KOAc/PhH/Δ	C(25)	43	13.1	46.5	30.4
	KOAc/MeCN/Δ	C(5)	36	14.2	76.0	1.5
	KOCN/DMSO/25°	-	72	-	66.6	17.5
	KOCN/Me_2CO/Δ	-	60	24.7	55.7	11.3
	KOCN/PhH/Δ	C(25)	21	-	31.3	48.0
1b	NaOAc/DMSO/25°	-	150	-	66.6	30.1
	KOAc/PhH/Δ	C(25)	24	-	53.8	32.5
	KOAc/MeCN/	C(25)	24	-	85.0	7.1
	KOAc/PhH/	A(5)	70	6.7	55.8	21.1
	KOCN/DMSO/25°	-	72	-	47.2	52.5
	KOCN/PhH/Δ	C(25)	14	-	25.3	53.1

[+]C: 18-Crown-6 A: Adogen 464

[+]Part 38. see ref. 14.



1

4-7, 9, 11

2

3

8, 10, 12, 14

13

15

	a	b	c	d	e
R^1	H	OMe	i-Pr	Cl	NO_2

	4	5	6	7	9	11
Nu	OAc	OCN	SCN	NCS	N_3	SAc

	8	10	12	14
X	NH_2	SCN	SAc	SH

The formation of substitution products (4 or 5) could not be observed similarly to the reaction with primary and tertiary amines[2].

By treatment of flavanones 1a-e with KSCN in acetone the hitherto unknown 3-thiocyanato-4'-R^1-flavanones (6a-e) were obtained as a cca. 3:2 mixture of the trans- and cis-isomers. The displacement process was accompanied by the formation of flavones 2a-e but neither aurones 3 nor 3-isothiocyanato-flavanones (7) could be detected. The increase of Hammett σ value of the R^1 favoured the formation of 2 and eclipsed the production of 6. With the exception of 1e, a small amount of starting material could be also detected which did not disappear by prolonging the reaction time, in accord with the earlier observation[3] showing the reaction between ω-haloacetophenones and $SCN^{\ominus}$ ion to be an equilibrium process which affords ω-thiocyanatoacetophenones but no isothiocyanates.

The preparation of 7 was attempted by the thermal rearrangement[4,5] of 6. By heating of trans-6a or cis-6b in abs. xylene for 12-18 hrs no 7 could be observed but C_3-epimerization proceeded instead, resulting in mixtures of trans--cis-6 of nearly similar ratio than that detected in the case of transformation 1 ⟶ 6. The epimerization proceeds also in acetone at room temperature and rate is

accelerated by magnitudes upon the addition of KSCN. The trans ⇌ cis isomerization, resulting in equilibrium mixture, can be explained by a mechanism involving a dissociation leading to ion-pair and an "internal return" process[5]. This may be completed by a nucleophilic substitution because of the "leaving-group" character of the thiocyanate ion[3,6,7]. This proposed mechanism is also supported by the fact that the treatment of trans-6 with NaN_3 afforded 3-aminoflavone (8). The formation of 8 can be explained by the competitive substitution reaction of the azide ion, the initially produced 3-azidoflavanone (9) transformed into 8 in a secondary reaction[1].

By dehydrogenation of trans-6 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) 3-thiocyanatoflavone (10) was synthesized.

The reaction of trans-1a,b,d,e, with KSAc resulted in the cis- and trans-3-acetylthio-4'-R^1-flavanones (11a,b,d,e), and as by-products 3-acetylthio-4'-R^1-flavones (12a,b,d), 1-(2-hydroxyphenyl)-3-(4-R^1-phenyl)-2-acetylthio-1-propanones [2'-hydroxy-α-acetylthiodihydro-chalcones] (13a,b) and bis [2-(4'-R^1-phenyl)-3-chromonyl] disulfides (15a,d) have been isolated and identified (Table 2).

Table 2. Conditions and product ratios of the reaction of 1 with thioacetate ion

Starting material	Conditions*	Isolated products (%)					
		11 (trans/cis+)	2	12	13	15	Unchanged 1
1a	A;45h	74.0 (56:44)	<1.0	3.0	4.2	-	-
	B;26h	58.0 (60:40)	1.9	15.2	5.3	1.9	-
	C;4.5h	91.0 (58:42)	1.0	1.0	1.1	traces	2.0
	D;25 min	78.3 (62:38)	1.1	2.0	5.1	traces	4.3
1b	A;100h	72.0 (71:29)	2.5	a	a	a	5.4
	C;6.5h	86.2 (69:31)	traces	traces	1.4	-	2.3
	D;12 min	74.0 (68:32)	1.1	1.7	a	-	8.5
1d	D;12 min	57.0 (60:40)	5.0	4.9	a	2.9	4.4
	C;4h	81.3 (59:41)	traces	1.3	a	1.5	4.1
1e	C;2h	84.1 (57:43)	2.6	a	a	a	2.1

a: not isolated; +Determined from the ^{1}H-NMR spectrum of the eluted mixture of isomers; *A - abs. EtOH/25°C; B - abs. Me_2CO/25°C; C - abs. MeCN/18-crown-6/N_2/25°C, D - abs. MeCN/18-crown-6/N_2/reflux

Compounds 12, 13 and 15 are produced by various secondary transformations (base-induced disproportionation, deacetylation and oxidation, respectively) of flavanones 11. An evidence for disproportionation was obtained by treatment of 11a and 11b with KOAc (under N_2 atmosphere) resulting in the mixture of 12a-13a and 12b-13b, respectively. A similar base-induced disproportionation has been postulated also for 3-hydroxyflavanones[8,9]. By deacetylation of 12a with NaOMe in MeOH 3-mercaptoflavone (14a) was prepared. Compound 14a was found to be readily oxidized into the corresponding disulfide 15a even on t.l.c. separation.

According to our earlier[1,2] and present results it can be established that the participation of the possible reaction paths in the reaction of mesylates 1 with nucleophiles depends primarily on the "hard-soft" character of the nucleophiles. With "soft" and "borderline" agents (i.e. $SCN^{\ominus}$, $SAc^{\ominus}$, $N_3^{\ominus}$,

secondary amines) nucleophilic substitution takes place and the increase of the "soft" character is associated with a higher share of the substitution. The high reactivity of some α-keto-mesylate toward S-nucleophiles have already been reported[10]. In the reaction of 1 with "hard" agents (primary amines, $OAc^{\ominus}$, $OCN^{\ominus}$) elimination with ring contration (resulting in 3) takes place besides β-elimination (leading to 2). The decisive role of the "hard-soft" character is demonstrated by the different reaction of the $OCN^{\ominus}$ and $SCN^{\ominus}$ ions possessing nearly equal nucleophilicity[11] but different "hard-soft" character.

EXPERIMENTAL SECTION

Mp.s are uncorrected, IR spectra were recorded with a Perkin-Elmer 283 instrument in KBr discs unless otherwise stated. ^{1}H-NMR spectra were obtained on JEOL MH-100 (100 MHz) and Bruker WP 200 SY (200 MHz) spectrometers in $CDCl_3$ solutions (internal standard TMS, δ=0 ppm). Mass spectra were recorded with a VG-7035 GC-MS system (EI, 70 eV, 150°C). Kieselgel 40 or Kieselgel Woelm (Akt.I.) were used for column Chromatography, eluent: petroleum ether-ethyl acetate (4:1) unless otherwise specified.

All the isolated flavones (2a-g) and aurones (3a,b) were identified on the basis of mp.[9,12-17,21], mixed mp., t.l.c. examination (Kieselgel 60 F_{254}; toluene-ethyl acetate (4:1)) and IR spectra.

4'-R^1-flavones (2a,b) and 4'-R^1-aurones (3a,b)

a/ A soln of 1a,b[1] (3 mmol) and anh. KOAc or freshly prepared KOCN (6 mmol) in abs. DMSO (15-20 ml) was allowed to stay at room temp. When the reaction completed (see Table 1) the reaction mixture was poured into water, the ppt was separated by column chromatography.

b/ A soln of 1a (3.1 mmol) and KOCN (6.2 mmol) in abs. Me_2CO (30 ml) was refluxed for 60 hrs, the inorganic salts were filtered off and the filtrate was concentrated. Abs. Et_2O was added to the residue, the precipitated KOCN was filtered off, and the evaporated filtrate was fractionated by column chromatography.

c/ A soln of 1a,b (1 mmol) and KOAc (1 mmol) in abs. MeCN or benzene (12 ml) was refluxed in the presence of 18-crown-6 (Table 1). The concentrated reaction mixture was fractionated by column chromatography.

d/ A mixture of KOAc (1 mmol) in water (8 ml) and of 1b (1 mmol), Adogen 464 (0.05 mmol) in benzene (12 ml) was stirred under reflux for 70 hrs. After dilution with water the mixture was extracted with ether (3x20 ml), the dried ($MgSO_4$) and evaporated extract was fractionated by column chromatography.

3-Thiocyanato-4'-R^1-flavanones (6a-g)

a/ A mixture of 1a-g[1] (6 mmol), KSCN (13 mmol) and abs. Me_2CO (35 ml) was refluxed for 28 hrs and worked up as described for the reaction with KOCN, method b/. Pure isomers of 6 could be occasionally separated by fractional crystallization of the eluted trans-cis-mixture from hexane-ethyl acetate (6-10:1). Some of mp.'s are non-characteristic due to thermal isomerization (the samples were pure isomers according to ^{1}H-NMR).

The reaction of 1a afforded 85.8 % of 6a, 11.1 % of 2a and 3.2 % of unreacted 1a.

trans-6a, m.p. 125-126°C. ^{1}H-NMR 5.46 (d,H-2), 4.54 (d,H-3), (J_{23} = 11.5 Hz); IR 2150 (SCN), 1690 (C=O), 982 (DHP$^+$). Found: S, 11.52; N, 4.73. $C_{16}H_{11}NO_2S$ requires: S, 11.37; N, 4.98.

cis-6a. ^{1}H-NMR 5.84 (d,H-2), 4.29 (d,H-3), (J_{23} = 2.7 Hz).

The reaction of 1b 74.3 % of 6b, 8.3 % of 2b and 12.7 % of unreacted 1b.

trans-6b, m.p. 110-116°C. ^{1}H-NMR 5.43 (d,H-2), 4.44 (d,H-3) (J_{23} = 11.3 Hz), 3.87 (s,OMe); IR 2154 (SCN), 1696 (C=O), 1248 (C-O-C), 980 (DHP). Found: S, 9.81; N, 4.36. $C_{17}H_{13}NO_3S$ requires: S, 10.30; N, 4.50.

cis-6b, m.p. 100-120°C. ^{1}H-NMR 5.78 (d,H-2), 4.22 (d,H-3) (J_{23} = 2.6 Hz), 3.87 (s,OMe); IR 2152 (SCN), 1685 (C=O), 1251 (C-O-C), 956 (DHP). Found: S, 10.25; N, 4.41. $C_{17}H_{13}NO_3S$ requires: S, 10.30; N, 4.50.

The reaction of 1c afforded 89.4 % of 6c, 7.8 % of 2c and 2.5 % of unreacted 1c.

trans-6c, m.p. 93-96°C. ^{1}H-NMR 5.59 (d,H-2), 4.57 (d,H-3) (J_{23} = 11.3 Hz), 2.98 (m,$CHMe_2$), 1.30 (d,$CHMe_2$); IR 2158 (SCN), 1693 (C=O), 1385, 1365 (CH_3), 982 (DHP). Found: S, 9.78; N, 4.27. $C_{19}H_{17}NO_2S$ requires: S, 9.91; N, 4.33.

cis-6c, m.p. 90-102°C, ^{1}H-NMR 5.82 (d,H-2), 4.23 (d,H-3) (J_{23} = 2.8 Hz), 2.98 (m,$CHMe_2$), 1.30 (d,$CHMe_2$); IR 2158 (SCN), 1687 (C=O), 1385, 1370sh (CH_3), 957 (DHP). Found: S, 10.11; N, 4.39. $C_{19}H_{17}NO_2S$ requires: S, 9.91; N, 4.33.

The reaction of 1d afforded 79.6 % of 6d, 11.6 % of 2d and 5.5 % of unreacted 1d.

trans-6d, m.p. 123-129°C. ^{1}H-NMR 5.49 (d,H-2), 4.43 (d,H-3) (J_{23} = 11.6 Hz); IR 2158 (SCN), 1701 (C=O), 1087 (Ar-Cl), 984 (DHP). Found: S, 10.11; N, 4.79. $C_{16}H_{10}ClNO_2S$ requires: S, 10.15; N, 4.44.

+DHP: "breathing" vibration of dihydropyranone skeleton

cis-6d, m.p. 135-155°C. ^{1}H-NMR 5.83 (d,H-2), 4.23 (d,H-3) (J_{23} = 2.7 Hz); IR 2162 (SCN), 1680 (C=O), 1090 (Ar-Cl), 995, 947 (DHP). Found: S, 10.10; N, 4.54. $C_{16}H_{10}ClNO_2S$ requires: S, 10.15; N, 4.44.

The reaction of 1e afforded 32.5 % of 6e and 45.6 % of 2e.

trans-6e. ^{1}H-NMR ($CDCl_3$-DMSO-d_6) 5.74 (d,H-2), 4.99 (d,H-3) (J_{23} = 11.5 Hz).

cis-6e. ^{1}H-NMR ($CDCl_3$-DMSO-d_6) 6.20 (d,H-2), 4.61 (d,H-3) (J_{23} = 2.6 Hz). For the mixture of isomers found: S, 9.97; N, 8.49. $C_{16}H_{10}N_2O_4S$ requires: S, 9.83; N, 8.58.

b/ A mixture of 1a (3.1 mmol), KSCN (6.5 mmol), 18-crown-6 (0.8 mmol) and abs. MeCN (30 ml) was refluxed for 10 hrs and worked up as described in method a/ to obtain 136 mg (13.6 %) of unreacted 1a, 678 mg (76.7 %) of 6a and 68 mg (5.7 %) of 2a.

3-Thiocyanatoflavone (10)

A soln of trans-6a (0.68 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.6 mmol) in abs. dioxane (15 ml) was refluxed for 16 hrs. After cooling the precipitated 2,3-dichloro-5,6-dicyano-hydroquinone was filtered off and the concentrated filtrate was fractionated by column chromatography to obtain 131 mg (68.9 %) 10, m.p. 150-152°C (EtOH). IR (CCl_4) 2161 (SCN), 1665 (C=O), 1352, 1329 (flavone skeleton). Found: N, 4.89; S, 11.55. $C_{16}H_9NO_2S$ requires: N, 5.01; S, 11.48.

3-Aminoflavone (8)

A mixture of trans-6a (0.36 mmol), NaN_3 (1.5 mmol) and Me_2CO (10 ml) was refluxed for 8 hrs and diluted with water. The precipitated crude 8 (77.3 %, m.p. 124-133°C) was crystallized from petroleum ether - ethyl acetate (5:1) to yield 36 mg (42.2 %) 8, m.p. 136-137°C, lit.[18] 137-138°C.

3-Acetylthio-4'-R1-flavanones (11a,b, d,e)

a/ A soln of 1 (3 mmol) and KSAc (6 mmol) in abs. EtOH or abs. Me_2CO (30 ml) was stirred at room temp. When the reaction was complete the inorganic salts were filtered off, the filtrate was poured into water and extracted with CH_2Cl_2. The dried extract was concentrated and the sirupy residue was separated by column chromatography using benzene as eluent.

b/ A soln of 1 (3 mmol), KSAc (6 mmol) and 18-crown-6 (0.75 mmol) in abs. MeCN (30 ml) was stirred under N_2 atmosphere at room or reflux temp and then worked up as described in method a/.

Details of reaction conditions and the product ratios are given in Table 2. The isomeric mixtures of 11 were subjected to fractional crystallization from abs. EtOH.

trans-11a, m.p. 115-118°C. ^{1}H-NMR 5.51 (d,H-2), 4.80 (d,H-3) (J_{23} = 11.4 Hz), 2.14 (s,SAc); IR 1696 (C=O), 1689 (SAc), 1113, 964 (C-S-C), 983 (DHP). Found: C, 68.33; H, 4.93; S, 11.53. $C_{17}H_{14}O_3S$ requires: C, 68.43; H, 4.73; S, 10.75.

cis-11a. ^{1}H-NMR 5.82 (d,H-2), 4.83 (H-3) (J_{23} = 2.7 Hz), 2.06 (s,SAc).

trans-11b, m.p. 136-138.5°C. ^{1}H-NMR 5.45 (d,H-2), 4.81 (d,H-3) (J_{23} = 11.7 Hz), 3.84 (s,OMe), 2.30 (s,SAc); IR 1712 (C=O), 1693 (SAc), 1112, 961 (C-S-C), 1023 (C-O-C), 975 (DHP). Found: C, 65.56; H, 4.93; S, 9.92. $C_{18}H_{16}O_4S$ requires: C, 65.84; H, 4.92; S, 9.76.

cis-11b. ^{1}H-NMR 5.78 (d,H-2), 4.83 (d, H-3) (J_{23} = 2.9 Hz), 3.84 (s,OMe), 2.24 (s,SAc).

trans-11d, m.p. 113-116°C. ^{1}H-NMR 5.47 (d,H-2), 4.76 (d,H-3) (J_{23} = 11.6 Hz), 2.27 (s,SAc); IR 1703, 1698 (C=O), 1681 (SAc), 1108, 1102, 960 (C-S-C), 1085 (Ar-Cl). Found: Cl, 10.71; S, 9.73. $C_{17}H_{13}ClO_3S$ requires: Cl, 10.65; S, 9.63.

cis-11d, m.p. 158-160°C. ^{1}H-NMR 5.79 (d,H-2), 4.79 (d,H-3) (J_{23} = 2.9 Hz), 2.22 (s,SAc); IR 1712 (C=O), 1693 (SAc), 1122, 1112 (C-S-C). Found: Cl, 10.78; S, 9.60. $C_{17}H_{13}ClO_3S$ requires: Cl, 10.65; S, 9.63.

trans-11e. ^{1}H-NMR 5.60 (d,H-2), 4.78 (d,H-3) (J_{23} = 11.5 Hz), 2.28 (s,SAc).

cis-11e, m.p. 168-170°C. ^{1}H-NMR 5.95 (d,H-2), 4.85 (d,H-3) (J_{23} = 2.2 Hz), 2.22 (s,SAc); IR 1709 (C=O), 1683 (SAc), 1518, 1348 (NO_2), 1109 (C-S-C).

12a, m.p. 134-135.5°C (EtOH-petroleum ether). IR 1698 (SAc), 1650 (C=O), 1358, 1332 (flavone skeleton), 1108, 951, 946 (C-S-C); MS 296 (M^+, <1 %), 254 (100), 253 (99), 252 (2.5), 209 (4), 197 (11), 181 (6), 165 (9), 152 (10) 134 (15.5), 121 (10), 120 (4), 105 (6), 92 (16), 77 (97).

12b, m.p. 142-143.5°C (EtOH-petroleum ether). IR 2841 (OMe), 1698 (SAc), 1640 (C=O), 1355, 1336 (flavone skeleton), 1127, 951 (C-S-C); MS 326 (M^+, 1) 284 (98), 283 (100), 268 (6), 253 (2.5), 252 (12), 164 (6), 149 (5), 148 (6), 121 (5), 120 (6), 92 (4).

12d, m.p. 104-105°C (EtOH-petroleum ether). IR 1704 (SAc), 1649 (C=O), 1353, 1333 (flavone skeleton), 1107, 957 (C-S-C), 1090 (Ar-Cl); MS 330 (M^+, <1), 288 (94), 287 (100), 253 (29), 252 (8), 224 (6), 195 (3), 168 (6), 132 (9), 123 (10.5), 121 (3.5), 120 (3.5), 92 (9).

13a, yellow syrup. ^{1}H-NMR 11.95 (deuterable s,OH), 5.49 (ABX,H-2), 3.45, 3.05 (ABX,H-3) (J_{AB} = 14.3 Hz, J_{AX} = 8.3 Hz, J_{BX} = 6.8 Hz), 2.31 (s,SAc); IR (nujol) 1701 (SAc), 1641 (chelated C=O), 1129, 949 (C-S-C); MS 300 (M^+, 1), 258 (2.5), 225 (59), 224 (28), 223 (12), 207 (2), 163 (5), 147 (9), 121 (100), 120 (8), 104 (7), 93 (11).

13b, yellow syrup. ^{1}H-NMR 12.04 (deuterable s,OH), 5.45 (ABX,H-2), 3.39, 2.98 (ABX, H-3) (J_{AB} = 13.95 Hz, J_{AX} = 8.5 Hz, J_{BX} = 6.8 Hz), 3.74 (s,OMe), 2.31 (s,SAc); IR (neat) 2834 (OMe), 1698 (SAc), 1634 (chelated C=O), 1128, 950 (C-S-C); MS 330 (M^+, 1), 255 (73), 254 (32.5), 253 (16.5), 237 (4), 161 (3.5), 147 (3), 134 (20), 121 (100), 108 (7.5), 93 (8).

15a, m.p. 260-261°C (EtOH). IR 1646 (C=O), 1350, 1333 (flavone skeleton); MS 506 (M^+, 15), 442 (1), 253 (100), 252 (25), 224 (7), 197 (4), 195 (3), 89 (12).

15d, m.p. 276-277°C (EtOH-petroleum ether). IR 1650 (C=O), 1350, 1331 (flavone skeleton), 1090 (Ar-Cl); MS 574 (M^{+}, <1), 510 (<1), 287 (95), 286 (100), 258 (15), 253 (15), 252 (6), 224 (5), 195 (16), 158 (17), 157 (18), 131 (21), 105 (10), 103 (20).

Disproportionation of 11a,b

A soln of trans-11a (1 mmol) and anh. KOAc (1.5 mmol) in abs. MeCN (15 ml) was refluxed under N_2 for 75 min, poured into water and extracted with CH_2Cl_2. The concentrated extract was subjected to column chromatography (eluent: PhH) to yield 68 mg (22.6%) 13a and 94 mg (26.9%) 12a.

Analogous treatment of trans-11b (1.5 mmol) yielded 80 mg (15.9%) 13b and 132 mg (26.6%) 12b.

3-Mercaptoflavone (14a)

A mixture of 12a (0.77 mmol) and NaOMe (1.2 mmol) in abs. MeOH (10 ml) was stirred in N_2 atmosphere at room temp for 2 hrs. Removing the solvent the residue was treated with abs. PhH (3 ml). The ppt was filtered off and recrystallized from petroleum ether-ethyl acetate (3:2) to obtain 140 mg (71.2%) 14a, m.p. 160° (dec). ^{1}H-NMR 8.08 (dd,H-5), 1.70 (deuterable s,SH); IR 1635, 1619sh (C=O), 1358 (flavone skeleton); MS 254 (M^{+}, 59), 253 (59), 252 (25), 222 (35), 120 (14), 78 (40), 77 (35), 70 (48), 61 (91), 57 (100), 56 (81).

bis(2-Phenyl-3-chromonyl)disulfide (15a)

A soln of 12a (0.5 mmol) and NaOMe (0.9 mmol) in abs. MeOH (10 ml) was stirred under N_2 at room temp for 2 hrs, poured into water and extracted with CH_2Cl_2. Chromatography of the dried and evaporated extract on Kieselgel 60 $F_{254+366}$ (Merck) plate afforded 39 mg (30.6 %) 15a.

REFERENCES

[1] T.Patonay, M.Rákosi, G.Litkei and R.Bognár, Liebigs Ann. Chem., 161 (1979)

[2] T.Patonay, G.Litkei and R. Bognár, Acta Chim. Acad. Sci. Hung., 108, 135 (1981)

[3] T.Thorstenson and J.Songstad, Acta Chem. Scand., 32A, 133 (1978)

[4] M.Böqemann, S.Petersen, O.-E.Schultz and H. Söll, Methoden der Organischen Chemie (Ed. by E. Müller), Band IX, 867, Houben-Weyl, Berlin (1955)

[5] A.Iliceto, A.Fava, U.Mazzucato and O.Rossetto, J. Am. Chem. Soc., 83, 2729 (1961)

[6] K.Maartman-Moe, K.A.Sanderud and J. Songstad, Acta Chem. Scand., 36B, 211 (1982)

[7] S.Oae, N.Yamada, K.Fujimori and O. Kikuchi, Bull. Chem. Soc. Jpn., 56, 248 (1983)

[8] a/ K.G.Marathe, K.R.Chandorkar and S.D.Limaye, Rasayanam 2, 48 (1952); Chem. Abs., 47, 6942d (1953)

b/ S.D.Limaye, Rasayanam 2, 58 (1955); Chem. Abs., 50, 1133Id (1956)

[9] J.E.Gowan, P.M.Hayden and T.S.Wheeler, J. Chem. Soc., 862 (1955)

[10] S.S.Simons, M.Pons and D.F.Johnson, J. Org. Chem., 45, 3084 (1980)

[11] T.Austad, L.B.Engemyr and J.Songstad, Acta Chem. Scand., 25, 3535 (1971)

[12] Atlas of Spectral Data and Physical Constants for Organic Compounds (Ed. J.G.Grasselli, W.M.Ritchey), 2nd Ed., Vol.3., 320, CRC, Cleveland (1975)

[13] D.M.Fitzgerald, J.F.O'Sullivan, E.M. Philbin and T.S.Wheeler, J. Chem. Soc., 860 (1955)

[14] T.Patonay, R.Bognar and G.Litkei, Tetrahedron, 40, 2555 (1984)

[15] W.Baker, J.B.Harborne and W.D.Ollis, J. Chem. Soc., 1294 (1952)

[16] L.Reichel and G.Hemmel, Ann., 625, 184 (1959)

[17] P.Friedlaender and G.Neudörfer, Ber. Dtsch. Chem. Ges., 30, 1077 (1897)

[18] C.O'Brien, E.M.Philbin, S.Ushioda and T.S.Wheeler, Tetrahedron, 19, 373 (1963)