3,5-DIARYL-1,2,4-DITHIAZOLIUM SALTS AS SYNTHONS FOR OPEN-CHAINED AND HETEROCYCLIC COMPOUNDS

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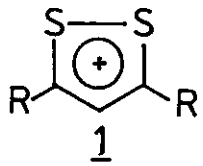
Abstract - The preparation and application of 3,5-diaryl-1,2,4-dithiazolium salts in the synthesis of various open-chained and heterocyclic compounds is summarized.

INTRODUCTION

Heterocyclic compounds can serve as useful synthons in synthetic organic chemistry especially if they are readily available and sufficiently reactive. Pyrylium salts[1,2] and 1,2-dithiolium salts 1[3] are such types of heterocycles and their synthetic potential is well documented.



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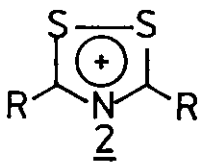

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In contrast, the chemistry of the aza-analogues of 1, the 1,2,4-dithiazolium salts 2, has scarely been explored. The first reported representatives of this class of compounds are the 3,5-diamino-1,2,4-dithiazolium salts obtained by the oxidation of dithiobiurets[4,5]. 1,2,4-Dithiazolium salts 2 possessing only one leaving group, such as substituted mercapto[6,7] or amino[8,9] group were described subsequently. These salts react with nucleophiles often by substitution reactions. Only recently 3,5-diaryl-1,2,4-dithiazolium salts have become available. We would like to give a review on the synthetic application of these 3,5-diaryl-1,2,4-dithiazolium salts, which exclusively undergo ring opening or ring transformation reactions when treated with nucleophilic reagents.

SYNTHESIS OF 3,5-DIARYL-1,2,4-DITHIAZOLIUM SALTS

3,5-Diaryl-1,2,4-dithiazolium salts 4 (see Table 1) are most conveniently accessible by the oxidation of arylthioamides 3 in an acidic medium[10-15], the

Table 1: Symmetrically Substituted 3,5-Diaryl-1,2,4-dithiazolium Salts 4

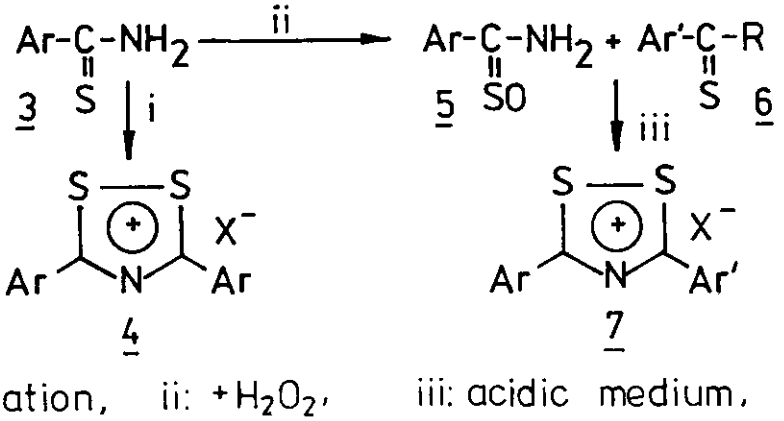
entry	Ar	X	yield (%)	mp (°C)[a]	ref.
4a	C_6H_5	ClO_4	92	264	16
			72	266-267(N/E)	11
4b	C_6H_5	I_3	89	177-179(N/E)	11
			60	177	12
4c	4-CH_3-C_6H_4	ClO_4	64	225-227(N/E)	11
4d	4-CH_3-C_6H_4	I_3	98	221-222(N/E)	11
4e	4-CH_3O-C_6H_4	ClO_4	90	261	12
4f	4-CH_3O-C_6H_4	I_3	81	215	12
			72	212-213(N/E)	11
4g	4-CH_3O-C_6H_4	BF_4	49	245	16
4h	4-CH_3O-C_6H_4	$FeBr_4$	46	200	12
4i	4-Cl-C_6H_4	ClO_4	86	238(N/E)	19
4j	4-Cl-C_6H_4	I_3	85	204-206(N/A)	19
4k	4-$(CH_3)_2N$-C_6H_4	ClO_4	66	285	12
			51	279-281(N/A)	11
4l	4-$(CH_3)_2N$-C_6H_4	I_3	47	285-286(N/A)	11
4m	4-$(CH_3)_2N$-C_6H_4	$FeCl_4$	98	233	12
4n	3,4-$(CH_3O)_2$-C_6H_3	ClO_4	91	275-276(N/A)	11
4o	2-HO-C_6H_4	Br	90[b]	360[c]	15
4p	2-$C_{10}H_7$	I_3	95	251	12

a) decomposition; recrystallised from:
N: nitromethane, E: ether, A: acetic acid

b) yield of the corresponding deprotonated compound 9

c) mp of the corresponding perchlorate

thioamides may be generated from the corresponding nitriles and H_2S directly in the reaction mixture[10,12]. Various oxidising reagents , such as H_2O_2, halogens or even air can be used. The oxidation proceeds via intermediate thioamide-S-oxides 5[11]. If isolated, these thioamide-S-oxides, or the corresponding N-substituted compounds, can be reacted with thioamides 6 (R = N-unsubstituted or substituted amino) other than 3[11,16-18], or with dithioesters 6 (R = SR)[16-18], in an acidic medium without an additional oxidising reagent and gives rise to 1,2,4-dithiazolium salts 7 (see Table 2) bearing different aryl substituents in position 3 and 5. Furthermore, 3,5-diaryl-1,2,4-dithiazolium salts 4 are also formed in oxidation reactions of N',N'-disubstituted N-thioaroyl-amidines[11,13]. Though various anions X^- such as ClO_4^-, Br^-, I_3^-, BF_4^- or $FeCl_4^-$ can be found in the products 4 or 7 the 1,2,4-dithiazolium salts are usually isolated as stable perchlorates ($X^- = ClO_4^-$) or as triiodides ($X^- = I_3^-$) if iodine is used as the oxidising reagent. In these cases the 3,5-diaryl-1,2,4-dithiazolium salts are easy to isolate and can be stored in closed containers at room temperature.



i: oxidation, ii: $+H_2O_2$, iii: acidic medium.

HYDROLYSIS OF 3,5-DIARYL-1,2,4-DITHIAZOLIUM SALTS

The hydrolysis of the 3,5-diaryl-1,2,4-dithiazolium salts 4 takes place with ease when they are heated briefly in an aqueous-solvent mixture or in water itself, preferably in the presence of a base. N-Acylthioamides 8 (see Table 3) are formed in high yields[20]. Alternative known routes to these thioamide derivatives 8 are the hydrolysis of N-thioacylamides[21], the acylation of thioamides [22-24], and the reaction of Grignard reagents with aroylisothiocyanates[25]. A more hydrolysis resistant 1,2,4-dithiazolium salt is the 3,5-bis-orthohy-

Table 2: Unsymmetrically Substituted 3,5-Diaryl-1,2,4-dithiazolium Perchlorates 7 ($X^- = ClO_4^-$)

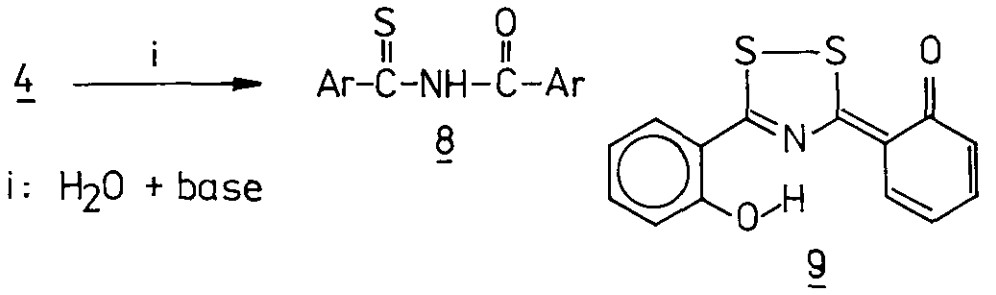
entry	Ar	Ar'	yield (%)	mp (°C)	ref.
7a	C_6H_5	4-CH_3-C_6H_4	62	214	14
7b	C_6H_5	4-CH_3O-C_6H_4	41	219-221	11
			55	208	14
7c	C_6H_5	4-HO-C_6H_4	51	185	14
7d	C_6H_5	4-Cl-C_6H_4	73	195	14
7e	C_6H_5	4-$(CH_3)_2N$-C_6H_4	86	197	14
7f	C_6H_5	2-thienyl	69	208	14
7g	C_6H_5	2-furyl	58	200	14
7h	4-CH_3-C_6H_4	2-C_7H_{10}	34	217	14

Table 3: N-Thioacylamides 8[20]

entry	Ar	yield (%)	mp (°C)	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)	ir (in KBr) (cm^{-1}) C=O	NH
8a	C_6H_5	62	108-109	249(4.31),277(4.04), 319s(3.78),478(2.27)	1705	3250
8b[a)]	p-CH_3-C_6H_4	95	184	256(4.44),328s(3.70), 476(2.35)	1680	3215
8c	p-CH_3O-C_6H_4	76	126-127	256s(4.14),283(4.24), 304(4.19),352(3.84), 467(2.78)	1690	3220
8d	p-Cl-C_6H_4	88	210-212	269s(4.19),295(4.31), 327s(4.06),483(2.51)	1685	3210

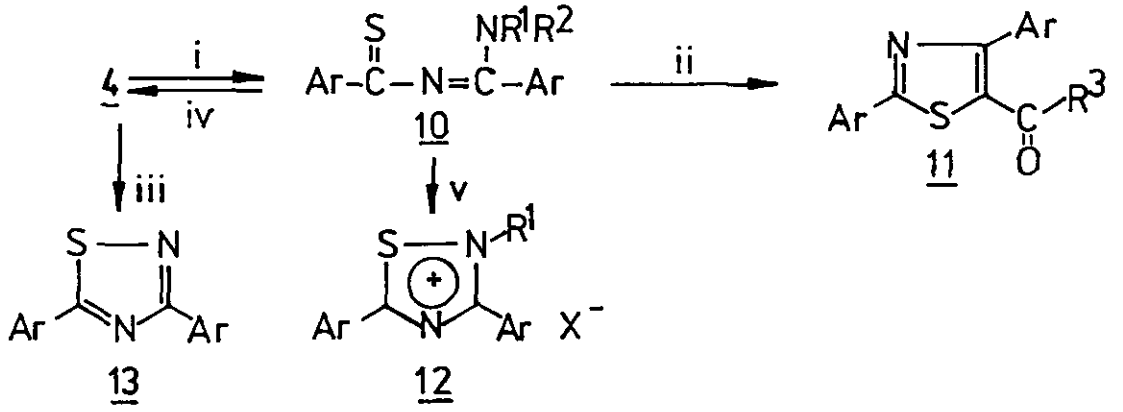
a) ^{1}H-nmr (DMSO-d_6), δ: 2.31(s,3H); 2.37(s,3H); 7.19(d,2H,J=6Hz); 7.34(d,2H,J=6Hz); 7.60(d,2H,6Hz); 7.88(d,2H,J=6Hz); 12.33(s,1H)

droxyphenyl derivative which donates only one proton when treated with water and is isomerized into a compound with an ortho-quinomethide structure 9.[15]



REACTION WITH AMINES AND HYDRAZINES

3,5-Diaryl-1,2,4-dithiazolium salts 4 possessing anions other than I^-_3 react with primary or secondary aliphatic or aromatic amines by the substitution of one S-atom to give N-thioacylamidines 10 (see Table 4)[26] after brief heating of the reactants in a polar solvent. These sulfur containing compounds are also formed if an excess of amine is used. They can further be transformed into thiazoles 11 (see Table 5)[19] by reaction with α-halomethylketones. The oxidation of the N-thioacylamidines 10 under acidic conditions leads to different products depending on the nature of the substituents R^1 and R^2. If one of the substituents is a hydrogen atom 1,2,4-thiadiazolium salts 12 (see Table 5)[27] are obtained. In contrast, the starting 3,5-diaryl-1,2,4-dithiazolium salts 4 appear if N',N'-disubstituted N-thioacylamidines 10 (R^1, $R^2 \neq H$) are oxidised[19]. The reaction of 3,5-diaryl-1,2,4-dithiazolium salts 4 with ammonia does not yield open chained products 10 but gives instead recyclized 3,5-diaryl-1,2,4-thiadiazoles 13



i: + HNR^1R^2, ii: + Hal-CH_2-CO-R^3, iii + NH_3, - H_2S,
iv: + HX, oxidation (R^1,$R^2 \neq H$), v: + HX, oxidation (R^2=H),

Table 4: N-Thioacylamidines 10 [26]

entry	Ar	R^1	R^2	yield (%)	mp (°C)[a]	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)
10a	C_6H_5	$(CH_2)_2O(CH_2)_2$		76	129-131(E)	235(4.22),287(4.18), 356(3.85),481(2.21)
10b	C_6H_5	H	$n\text{-}C_3H_7$	74	148-149(E)	292(4.10),362(3.89), 480(3.18)
10c	C_6H_5	H	C_6H_{11}	54	129 -130(L)	292(4.17),362(3.90), 480(2.18)
10d	C_6H_5	H	$C_6H_5CH_2$	62	123-124(L)	290(4.21),359(3.87), 482(2.18)
10e	$4\text{-}CH_3\text{-}C_6H_4$ [b]	C_2H_5	C_2H_5	73	134-136(E)	235(4.26),295(4.21), 356(3.85),461(2.26)
10f	$4\text{-}CH_3\text{-}C_6H_4$ [c]	H	$n\text{-}C_3H_7$	71	144-145(E)	236(4.18),305(4.21), 476(2.21)
10g	$4\text{-}CH_3\text{-}C_6H_4$	H	$n\text{-}C_4H_9$	56	106-108(L)	301(4.22),360(3.91), 475(2.25)
10h	$4\text{-}CH_3\text{-}C_6H_4$	H	$C_6H_5CH_2$	73	125-126(E)	306(4.27),338s(4.04), 480(2.24)
10i	$4\text{-}CH_3\text{-}C_6H_4$	H	C_6H_5	61	164-165(A)	297s(4.21),321(4.31), 355s(4.15),498s(2.56)
10j	$4\text{-}CH_3\text{-}C_6H_4$	H	$4\text{-}Cl\text{-}C_6H_4$	64	176-177(A)	238(4.33),292(4.35), 360(3.90),466s(2.32)
10k	$4\text{-}CH_3O\text{-}C_6H_4$	H	$4\text{-}CH_3O\text{-}C_6H_4$	86	131-132(E)	309s(4.13),366(4.31), 481(2.84)

a) recrystallized from:
E: ethanol, L: ligroin, A: acetonitrile

b) ^{1}H-nmr (DMSO-d_6), δ: 1.11(m,6H); 2.23(s,6H);3.38(m,4H); 7.03(d,2H,J=8Hz); 7.11(s,4H); 7.91(d,2H,J=8Hz)

c) ^{1}H-nmr (DMSO-d_6), δ: 0.81(t,3H,J=8Hz); 1.40(m,2H,J=8Hz); 2.20(s,6H); 3.25(m,2H); 7.05(d,2H,J=8Hz); 7.13(d,2H,J=8Hz); 7.38(d,2H,J=8Hz); 8.00(d,2H,J=8Hz)

Table 5: 2,4-Diarylthiazolyl Ketone 11, 3,5-Diaryl-1,2,4-thiadiazolium Perchlorates 12 ($X^- = ClO_4^-$) and 3,5-Diaryl-1,2,4-thiadiazoles 13

entry	Ar	R^1 or R^3	yield	mp (°C)[a]	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)	ref.
11	$4\text{-}CH_3O\text{-}C_6H_4$	C_6H_5[b]	81	149-150(L)		19
12a	C_6H_5	$n\text{-}C_3H_7$	67	127-129(N/E)	284s(4.01),312(4.34), (455)[c]	27
12b	C_6H_5	$C_6H_5\text{-}CH_2$	69	178(N/E)	249s(4.01),312(3.34), (459)[c]	27
12c	$4\text{-}CH_3\text{-}C_6H_4$	$C_6H_5\text{-}CH_2$	32	228(A)	253s(4.03),335(4.49), (450)[c]	27
13a	C_6H_5	-	**76**[d] **75**[e]	89-90(L/W)	258(4.52),293s(3.85),	**11** **12**
13b	$4\text{-}CH_3O\text{-}C_6H_4$	-	**63**[d] **83**[e]	138-139(L)	288(4.57),321s(4.01)	**11** **12**
13c	$4\text{-}(CH_3)_2N\text{-}C_6H_4$	-	**78**[e]	223	348(4.63)[f]	**12**

a) recrystallized from:
L: ethanol, N: nitromethane, E: ether, W: water, A: acetic acid

b) NR^1R^2 = morpholino in the reactand 10, Hal = Br

c) CT-complex with tetrabutyl ammonium iodide

d) X^- in 4 = ClO_4^- e) X^- in 4 = I_3^- f) in ethanol

(see Table 5)[11,12,14] which have been frequently observed in oxidation reaction of thioamides (see Lit. 11 and references cited there). A mechanism for this ring transformation accompanied by the elimination of H_2S was suggested[11].

Surprisingly, the interaction of 3,5-diaryl-1,2,4-dithiazolium triiodides 4 ($X^- = I^-_3$) with an excess of primary amines does not give N-thioacylamidines 10 but N-imidoylamidines salts 14 (see table 6)[28] or the corresponding deprotonated compounds 15 as far as a further base is added to the reaction mixture. The same products 14 are obtained if 3,5-diaryl-1,2,4-dithiazolium perchlorates 4 ($X^- = ClO_4^-$) or N'-monosubstituted N-thioacylamidines 10 ($R^2 = H$) are reacted with primary amines in the presence of an oxidising reagent.

Table 6: N-Imidoylamidines 15 and Corresponding Hydroiodides 14 ($X^- = I^-$)[28]

entry	Ar	R^1	yield (%)	mP (°C)[a] 15	14
a	C_6H_5	$C_6H_5CH_2$	94	176-177(B)	232-234(A)
b	C_6H_5	$(CH_3)_2CH$	39	136-138(L)[b]	264-265(A)[c]
c	C_6H_5	C_6H_{11}	85	135-136(L)	269-271(A)
d	p-CH_3O-C_6H_4	C_6H_{11}	62	oil	289-290(A)
e	p-Cl-C_6H_4	$(CH_3)_2CH$	76	136-137(L)[d]	309-310(A)

a) recrystallized from:
B: n-butanol, A: acetic acid, L: ligroin

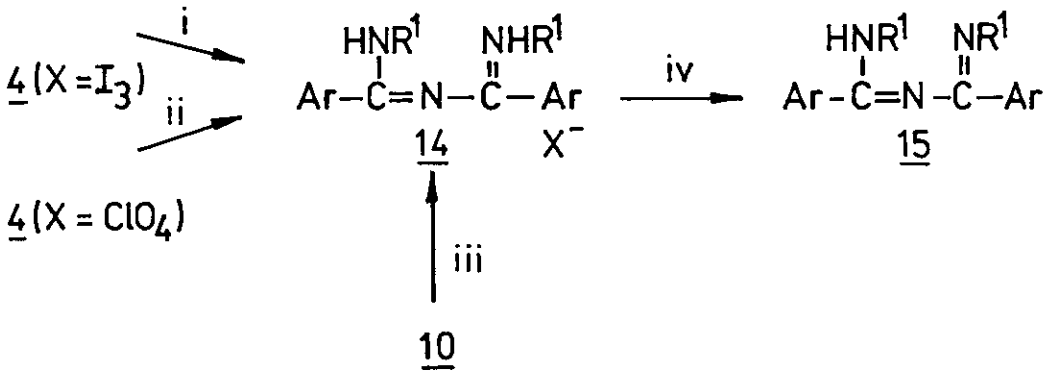
b) uv $\lambda_{max}^{CH_3CN}$ (lg ϵ): 225s(4.17),274s(3.80)

c) uv $\lambda_{max}^{CH_3CN}$ (lg ϵ): 247(4.45),287(4.17),763(2.80)

d) ^{1}H-nmr ($CDCl_3$), δ: 0.98(s,3H); 1.06(s,3H); 4.00(broad); 7.04(d,4H,J=9Hz); 7.23(d,4H,J=9Hz)

Hence the formation of the N-amidoylamidinium salts 14 can be assumed to proceed via intermediate N'-monosubstituted N-thiacylamidines 10 (R^2 = H) which are then oxidised to corresponding 1,2,4-thiadiazolium salts followed by ring cleavage and substitution of the remaining sulfur atom by the amine.

The access to N-imidoylamidines 15 based on 1,2,4-dithiazolium salts 4 is a useful alternative to already known syntheses that usually give different substitution patterns[29,30] or only boron complexes[31] of these compounds.



i: + R^1NH_2, ii: + R^1NH_2 + I_2, iii: + 2 R^1NH_2 + I_2,
iv: + base, - H^+

The substitution of both the sulfur atoms in the 3,5-diaryl-1,2,4-dithiazolium salts 4 by amino groups without any oxidation step takes place when 4 are ring transformed by means of bifunctional amino compounds. The interaction of the 4 with hydrazines, for example, gives rise to the formation of 3,5-diaryl-1,2,4-triazoles 16 (see Table 7)[12,14,32].

Intermediates such as ring opened monosubstitution products 10 (R^2 = H, R^1 =NHR) were not observed. Acylhydrazines loose the acyl group in the course of the reaction with the 4 and N-unsubstituted triazoles 16 (R = H) are obtained[14,16,33]. The 3,5-diaryl-1,2,4-thiadiazolium salts 4 react with N,N'-dimethylhydrazine, hydroxylamine, or benzamidine in a manner similar to their reaction with mono or unsubstituted hydrazines, namely as C_3-synthon. In these ways triazolium salts 17[14], 1,2,4-oxadiazoles 18 (see Table 8)[12,14] and 1,3,5-triazines 19 (see Table 8)[14,16] can easily be synthesized from 4.

Table 7: 3,5-Diaryl-1,2,4-triazoles 16

entry	Ar	R	yield[a]	mp (°C)[b]	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)	ref.
16a	C_6H_5	H	77[c] 92[f]	191(E)[d]	255(4.30)[e]	12 16
16b	C_6H_5	C_6H_5	42	100-102(E/W)	247(4.41),281s(4.00), 286(3.85)	32
16c	4-CH_3-C_6H_4	C_6H_5	46	116-118(E)	252(4.56)	32
16d	4-CH_3-C_6H_4	4-NO_2-C_6H_4	61	189-190(P)	260(4.53),322(4.01)	32
16e	4-CH_3O-C_6H_4	H	93[c]	216(A)	264(4.43)[i]	12
16f	4-CH_3O-C_6H_4	C_6H_5	96	143-145(E)	265(4.61)	32
16g	4-CH_3O-C_6H_4[g]	4-NO_2-C_6H_4	98	221(A)	266(4.57),344(3.92)	32
16h	4-CH_3O-C_6H_4[h]	4-NO_2-C_6H_4	56	182-183(A)	264(4.51),344(3.88)	32
16i	4-$(CH_3)_2N$-C_6H_4	H	80[c]	274(DMF)	309(4.69)[i]	12
16j	2-HO-C_6H_4	H	72	323-326 (subl.)		33

a) $X^- = ClO_4^-$ in the reactand 4, otherwise indicated

b) recyclized from:
E: ethanol, W: water, P: n-propanol, A: acetonitrile

c) $X^- = I_3^-$

d) m.p. of the corresponding hydroperchlorate: 285-287 °C [32]

e) in ethanol; corresponding hydroperchlorate in dichloromethane: 256(4.26) [32]

f) benzoylhydrazine was used instead of hydrazine

g) ^{1}H-nmr (DMSO-d_6), δ: 3.77(s,3H); 3.79(s,3H); 6.85(d,2H,J=7Hz); 6.90(d,2H,J=7Hz); 7.49(d,2H,J=7Hz); 7.73(d,3H,J=7Hz); 8.05(d,2H,J=7Hz); 8.36(d,2H,J=7Hz)

h) only one substituent, the other one represents C_6H_5

i) in ethanol

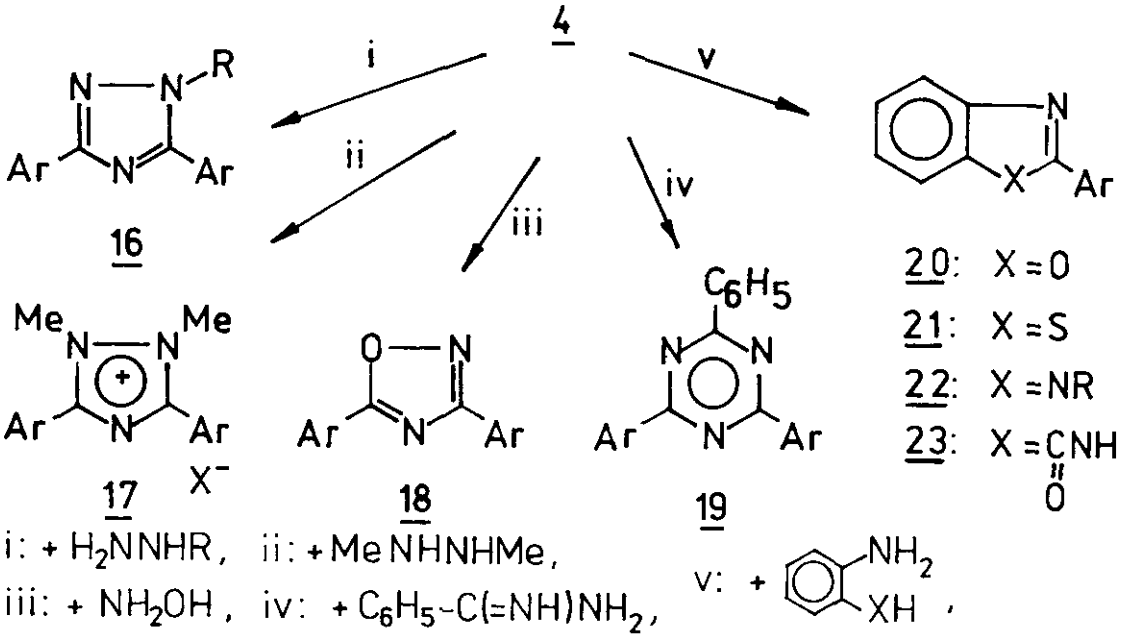
Table 8: 3,5-Diaryl-1,2,4-oxadiazoles 18, 2,4,6-Triaryl-1,3,5-triazines 19, Benzazoles 20 - 22, and Benzopyrimidines 23

entry	Ar	X	yield	mp (°C)[a]	uv λ^{E}_{max} (log ε)	ref.
18a	C_6H_5	-	81[b]	108(M)	244(4.51)	12
18b	4-CH_3O-C_6H_4	-	82[b]	127(E)	273(4.58)	12
18c	4-$(CH_3)_2N$-C_6H_4	-	80[b]	231(D)	333(4.72)	12
19	C_6H_5	-	73[c]	234		16
20	C_6H_5	-	74[c]	102		16
21	C_6H_5	S	68	114		16
22	C_6H_5	NH	86[c]	293		16
23	C_6H_5	CONH	79	240		16

a) recrystallized from:
M: methanol, E: ethanol, D: DMF

b) X^- in 4 = I_3^-

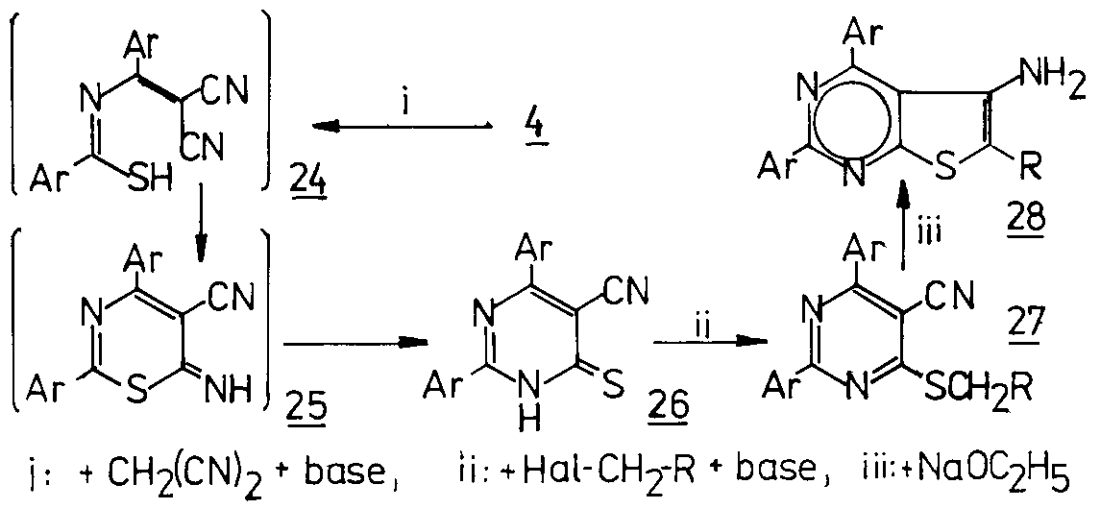
c) X^- in 4 = ClO_4^-



In contrast to these ring transformations, only one of the carbon atoms of the 1,2,4-dithiazolium salts 4 is incorporated into the resulting heterocyclic product when compounds of type 4 react with anilines possessing a nucleophilic substituent in 2-position, such as OH, SH, NH_2 or $CONH_2$. By the attack of both nucleophilic sites of the corresponding anilines at the same ring carbon atom of the 1,2,4-dithiazolium salts 4 and cleavage of both the C-S and the C-N bonds, corresponding benzazoles 20 - 22 (X = O,S,NH) (see Table 8)[14,16] or benzopyrimidines 23 (X = CONH) (see Table 8)[14,16] are formed.

REACTION WITH ACTIVE METHYLENE COMPOUNDS

When malodinitrile, a C-nucleophile, is reacted with 3,5-diaryl-1,2,4-dithiazolium salts 4 in the presence of a base such as triethylamine, high yields of 4,6-diaryl-2(1H)-pyrimidinthiones 26 (see Table 9) are obtained[34]. The reaction probably proceeds via intermediate substitution products 24 which undergo nitrile cyclization. The resulting 2-iminothiazines 25 are then transformed into the final products 26 by Dimroth-rearrangement. Other malonic acid derivatives, such as ethyl cyanoacetate or cyanoacetamide, react similarly[39]. For reactions of compound 9 with benzyl cyanides see ref. 40.



Further reaction of the 2(1H)-pyrimidinthiones 26 with acceptor substituted methylhalides in the presence of triethylamine yields S-alkylation products 27 which can be cyclized by means of sodium ethoxide to the corresponding 2,4-diaryl-5-aminothieno[2,3-d]pyrimidines 28 (see Table 9)[35].

Table 9: 2(1H)-Pyrimidinthiones 26, 4-Alkylmercapto-pyrimidines 27, and 2,4-Diaryl-5-aminothieno[2,3-d]pyrimidones 28

entry	Ar	R	yield	mp (°C)	ir (in KBr)	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)	ref.
26a	C_6H_5	-	74	249-250 (CH_3COOH)	CN:2230	256s(4.11),288(4.42), 410(3.41)	34
26b[a]	4-CH_3-C_6H_4	-	82	243-245 (CH_3COOH)	CN:2230	265(4.05),310(4.49) 410(3.42)	34
26c	4-CH_3O-C_6H_4	-	89	263-265 (CH_3COOH)	CN:2230	277s(4.09),327(4.64), 406(3.66)	34
26d	4-Cl-C_6H_4	-	57	265-266 (CH_3COOH)	CN:2220	265s(4.19),311(4.12), 418(3.62)	19
27a	C_6H_5	4-Br-C_6H_4CO	67[b]	195-196 (ethanol)	CN:2225 CO:1700	278,321s[c]	19
27b	4-CH_3-C_6H_4	C_6H_5CO	73[b]	185-186 (ethanol)	CN:2210 CO:1720	225(4.22),249(4.29), 324(4.08)	19
27c	4-CH_3O-C_6H_4	CH_3CO	84[d]	165-166 (ethanol)	CN:2215 CO:1740	263s(4.05), 291s(4.35), 318(4.56)	19
28a	C_6H_5	4-Br-C_6H_4CO	71[b][e] 86[f]	230-231 (CH_3CN)	NH:3300 3480	266(4.31),310(4.51), 424(4.08)	35
28b	C_6H_5	CH_3CO	83[d][e]	237-239 (CH_3CN)	NH:3310 CO:1640	270(4.22),308(4.13) 410(3.66)	35
28c	4-Cl-C_6H_4	4-Br-C_6H_4CO	83[b][e]	290-292 (dioxane)	NH:3300 3490 CO:1670	270(4.22),308(4.13), 410(3.66)	19

a) ^{1}H-nmr(DMSO-d_6), δ: 2.30(s,6H); 7.24(d,4H,J=8Hz); 7.81(d,2H,J=8Hz); 7.99(d,2H,J=8Hz); 6.33(s); 6.98(s); 7.63(s)

b) Hal = Br

c) qualitative

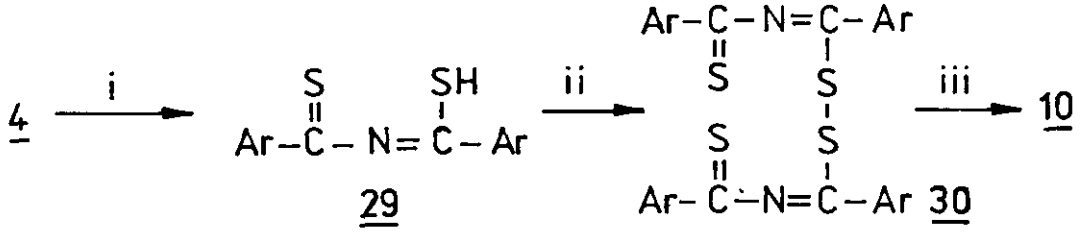
d) Hal = Cl

e) starting from corresponding 26

f) starting from corresponding 27

REACTION OF 3,5-DIARYL-1,2,4-DITHIAZOLIUM SALTS WITH THIOLS-REDUCTION

As the results of the reaction of 3,5-diaryl-1,2,4-dithiazolium salts 4 with thioles such as ethyl mercaptane, 2-mercaptoacetates or hydrosulfide no substitution products could be obtained but the hitherto unknown N-thioacylthioamides 29 (see Table 10) were obtained[36]. Hence a reductive S-S-ring cleavage of the 4 has occurred. These dithiocarbonyl compounds 29 appear as a red oil which is sensitive to oxidation. In all cases except compound 29a the oxidation took place in air before the oil had become crystalline and only corresponding disulfides 30, which exhibit a yellow colour[36] could be isolated. The primary reduction products 29 can be trapped, however, by their complex formation with heavy metal ions such as Ni^{2+} or Co^{2+} [19]. The disulfides 30 form the starting 3,5-diaryl-1,2,4-dithiazolium salts 4 again when treated with an acid. The interaction of the 30 with arylamines gives rise to the formation of corresponding N-thioacylamidines 10 [19].



i: + RSH, ii: oxidation, iii: + H_2NR^1,

CONCLUSIONS

3,5-Diaryl-1,2,4-dithiazolium salts 4 are readily available by the oxidation of arylthioamides in an acidic medium and possess a high synthetic potential. Their reactions with nucleophiles can be classified into four types:

1. S-S bond ring cleavage by reduction (formation of 29 or 30) - action as S-C-N-C-S-synthon
2. Substitution of one sulfur atom to give ring opened (i.e. 8, 10) or recyclized products (i.e. 13 or 26) - action as S-C-N-C-synthon
3. Substitution of both sulfur atoms leading to open-chained (14 or 15) or recyclized products (i.e. 16, 17, 18 or 19) - action as C-N-C-synthon
4. Twofold nucleophilic substitution at the same ring carbon atom accompa-

Table 10: N-Thioacylthioamide 29a and Disulfides 30[36]

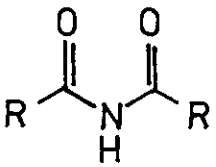
entry	Ar	yield[a)]	mp (°C)	uv $\lambda_{max}^{CH_2Cl_2}$ (log ε)
29a	4-CH_3O-C_6H_4	78(T)	142-143 (ethanol)	284(4.25),339s(3.37),464(2.52), 513(2.21)
30a	C_6H_5[b)]	41(T) 37(M)	136-138 (CH_3CN)	
30b	4-CH_3-C_6H_4	67(T)	153-155 (CH_3NO_2)	276(4.18),382(2.91)
30c	4-CH_3O-C_6H_4	78(T)	138-140 (CH_3CN)	274(4.19),289(4.22),427(4.42)

a) reducing reagent: T: ethyl thioglykolate, M: ethyl mercaptane

b) Ni^{2+}-chelate of the corresponding 30a: $C_{28}H_{20}N_2S_4Ni$, mp 233-234 (dec.) (DMF): $\lambda_{max}^{CH_2Cl_2}$ (log ε): 248(4.35),326(4.45),364(4.51),492(3.99)

nied by C-S and C-N-bond cleavage (formation of compounds 20 - 22) - action as C-synthon.

Following these reaction patterns a variety of N and often S-containing open chained or heterocyclic products can be synthesized possessing hitherto unknown substitution patterns in most cases. The corresponding experimental procedures are simple and usually afford high yields in short reaction times. It can be seen that the 3,5-diaryl-1,2,4-dithiazolium salts reveal a much higher synthetic potential than simple diacylamines 31, which can be considered as parent compounds of the 4, and hence can be compared with other activated derivative of diacylamines such as N-acyl amide chlorides 32[37] or the aza-analogous 3-chloro-propene iminium salts 33[38].



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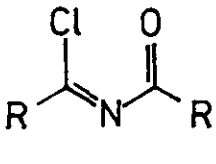

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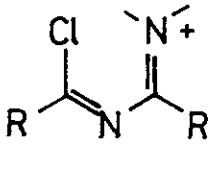

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