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The Reaction of 3,5-Diphenyl-1,2-dithiolium Perchlorate with Active Methylenes

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Synopsis. 3,5-Diphenyl-1,2-dithiolium perchlorate (**1**) was synthesized in a new, convenient way, and the reaction of **1** with several active methylene compounds was studied. The compounds possessing no less than one ester group gave novel products, 3-substituted 4,6-diphenyl-2*H*-thiopyran-2-ones, while those possessing a carbamoyl group gave 3-substituted 2-hydroxy-4,6-diphenylpyridines or 3-cyano-1,4,6-triphenyl-2-pyridone. Malononitrile, however, gave 1-mercapto-1,3-diphenyl-4,4-dicyanobutadiene (**10**). On treatment with methyl iodide or *p*-chlorobenzyl chloride, **10** gave 1-methylthio- or 1-(*p*-chlorobenzylthio)-1,3-diphenyl-4,4-dicyanobutadiene, and also led to bis(1,3-diphenyl-4,4-dicyanobutadienyl) disulfide on treatment with hydrogen peroxide.

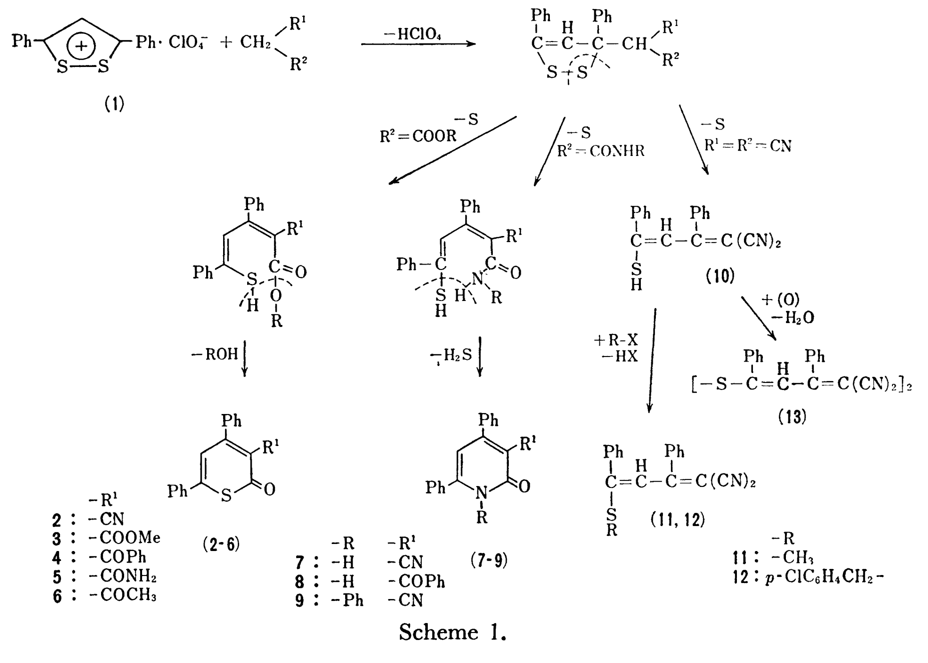
The reaction of 3-alkylthio-1,2-dithiolium salts or 1,2-dithiol-3-thiones with active methylenes gives 1,2-dithiol-3-ylidene derivatives with the liberation of methanethiol or hydrogen sulfide.[1] However, it is difficult to suppose that 3,5-diaryl- or 3,5-dialkyl-1,2-dithiolium salts give 1,2-dithiol-3-ylidenes by the same reaction course. There is thus an interest in the study of the behavior of these salts toward active methylenes. In this investigation, the reaction of 3,5-diphenyl-1,2-dithiolium perchlorate (**1**) with several active methylenes was checked, and some new information was obtained.

Results and Discussion

The synthesis of **1** has already been done by two methods.[2,3] In this study, another new method was applied: hydrogen sulfide was passed into a dibenzoylmethane–iron bromide(III) mixture in chlorobenzene, and simultaneously bromine was added drop by drop.

Methyl cyanoacetate, dimethyl malonate, ethyl benzoylacetate, ethyl carbamoylacetate, and methyl acetoacetate were refluxed with **1** in methanol to give novel products, **2**—**6** respectively, in good yields. According to their mass spectra, the molecular weights were measured and found to be 289, 322, 368, 307, and 306 respectively. The IR spectra of **2**—**6** resembled each other. The absorption assigned to an ester group was absent in the spectra of **2**, **4**—**6**; this fact suggested that an ester group of these reagents participated in these reactions. On treatment with *p*-toluenesulfonic acid, **4** easily gave 2,4,6-triphenylpyrylium salt, while releasing carbonyl sulfide. These spectral results, the chemical evidence, and their analytical data confirm that **2**—**6** are 3-cyano, 3-methoxycarbonyl, 3-benzoyl, 3-carbamoyl, and 3-acetyl-4,6-diphenyl-2*H*-thiopyran-2-one. The reaction courses seem to be shown in Scheme 1. This recyclization process resembles the reaction of 1,3-diphenyl-2-propyn-1-one with dimethyl malonate, which affords 3-methoxycarbonyl-4,6-diphenyl-2-pyrone.[4]

Cyanoacetamide, benzoylacetamide, or cyanoacetanilide was treated with **1** to give **7**, **8**, or **9** in a good yield. **7** and **8** were identified by direct comparison with the authentic samples and found to be 2-hydroxy-3-cyano- and 2-hydroxy-3-benzoyl-4,6-diphenylpyridines respectively.[5,6] With regard to **9**, its molecular weight was measured as 348. The IR spectrum and the



Scheme 1.

TABLE 1. DATA FOR **2**—**6**, **9**—**13**

Compd	Solv. for recryst.	Mp (°C)	Yield (%)	Formula	Found (Calcd) %				
					C	H	N	S	Cl
2	EtOH	178.0	94	$C_{18}H_{11}NOS$	74.60 (74.71	3.84 3.84	4.79 4.84	11.08 11.08)	
3	EtOH	195.0	61	$C_{19}H_{14}O_3S$	70.81 (70.79	4.35 4.38		9.93 9.94)	
4	MeCN	156.7	65	$C_{24}H_{16}O_2S$	78.29 (78.21	4.39 4.38)			
5	AcOH	270.3	48	$C_{18}H_{13}NO_2S$	70.26 (70.34	4.35 4.26	4.54 4.56	10.56 10.43)	
6	EtOH	179.2	60	$C_{19}H_{14}O_2S$	74.99 (75.11	4.81 4.85)			
9	MeCN	232.6	63	$C_{24}H_{16}N_2O$	82.74 (82.74	4.65 4.63	8.02 8.04)		
10	MeCN	225.3	95	$C_{18}H_{12}N_2S$	74.79 (74.97	4.25 4.20	9.79 9.71	11.12 11.12)	
11	EtOH	159.0	69	$C_{19}H_{14}N_2S$	75.38 (75.47	4.69 4.67	9.29 9.26	10.66 10.60)	
12	EtOH	180.4	61	$C_{25}H_{17}N_2SCl$	72.78 (72.72	4.11 4.15	6.86 6.78	7.48 7.76	8.58 8.58)
13	MeCN	254.1	96	$C_{36}H_{22}N_4S_2$	75.40 (75.23	3.80 3.86	9.68 9.75	11.17 11.16)	

TABLE 2. THE IR AND MASS SPECTRA FOR **2**—**6**, **9**—**13**

Compd	IR spectra (cm^{-1})	Mass spectra (*m/e*)
2	2210(CN), 1633, 1555, 1496, 1487, 1444	289(M), 261(M−CO), 191($C_{15}H_{11}$), 121 (C_6H_5CS), 77(C_6H_5)
3	1727(CO), 1605, 1562, 1509, 1489, 1440	322(M), 294(M−CO), 263(M−$COOCH_3$), 234(263−CO, H), 191, 121, 77
4	1673(CO), 1605, 1556, 1505, 1486, 1439	368(M), 340(M−CO), 263(M−C_6H_5CO), 234, 191, 121, 105(C_6H_5CO), 77
5	3440(NH), 1664(CO), 1603, 1552, 1501, 1486, 1441	307(M), 279(M−CO), 263(M−$CONH_2$), 234, 191, 121, 77
6	1720(CO), 1606, 1563, 1505, 1494, 1446	306(M), 278(M−CO), 263(M−CH_3CO), 234, 121, 77
9	2210(CN), 1650, 1566, 1514, 1486, 1441, 1365, 1201	348(M), 347(M−1), 320(M−CO), 180, 140, 77
10	2160(CN), 1581, 1554, 1528, 1470, 1230, 1207, 1188	288(M), 255(M−SH), 228(255−HCN), 140, 77
11	2216, 1572, 1523, 1492, 1406, 1368, 1261, 1077	302(M), 301(M−1), 255(M−SCH_3), 151 (M/2), 102(C_6H_5CCH), 77
12	2208, 1570, 1524, 1490, 1409, 1367, 1089	414(M+2), 412(M), 411(M−1), 344, 255 (M−$SCH_2C_6H_4Cl$), 125($ClC_6H_4CH_2$)
13	2200, 1570, 1523, 1489, 1409, 1366	576(M+2), 575(M+1), 574(M), 288 (M/2+1), 287(M/2), 255, 140, 77

analytical data confirmed that **9** is 3-cyano-1,4,6-triphenyl-2-pyridone. The reaction course seems to be similar to the course by which thiopyran-2-ones are given; however, hydrogen sulfide is eliminated during the recyclization process.

Malononitrile gave only a thiol, **10**, on treatment with **1**. **10** remained unchanged on treatment because the cyano group of **10** may have no ability of cyclization. The reaction of **10** with methyl iodide or *p*-chlorobenzyl chloride afforded an alkylthiobutadiene, **11** or **12**, with the liberation of a hydrogen halide. **10** was easily oxidized by hydrogen peroxide to give a disulfide, **13**. The structures of **10**—**13** were identified by means of their IR and mass spectra and analytical data. The reaction of **1** with other active methylenes, such as dibenzoylmethane, nitromethane, 1,3-indandione, and benzoylacetonitrile, was also attempted, but it is failed to give any stable products.

Hence, it is proved that the reaction of 3,5-diphenyl-1,2-dithiolium perchlorate, **1**, with active methylenes proceeds as shown in Scheme 1.

Experimental

*Preparation of 3,5-Diphenyl-1,2-dithiolium Perchlorate (**1**).* Into a solution of dibenzoylmethane (23 g) and iron bromide(III) (45 g) in chlorobenzene (175 ml), hydrogen sulfide was passed; simultaneously bromine (20 g) was stirred in, drop by drop, over a 30-min period. After that, the reaction temperature was gradually elevated to 110 °C, and maintained at that point for 2 h; the introduction of hydrogen sulfide was stopped. After having been refluxed for another hour, the reaction mixture was allowed to stand in a refrigerator overnight. The resulting precipitate was filtered, dried *in vacuo*, washed with water, and dissolved again in hot ethanol. The solution was filtered to remove any insoluble substances, poured into an ethanol solution of sodium perchlorate, and allowed to stand overnight. This gave 22 g (61.9 %) of yellow needles of **1** (mp 260.4 °C).

*Reaction of **1** with Active Methylenes.* Into a mixture of an active methylene (2.4 mmol) and 0.72 g (2 mmol) of **1** in 3 ml of methanol, we stirred 2.5 mol dm^{-3} MeONa–MeOH (2 ml) at room temperature; after a while, the mixture was refluxed for 1 h and poured into dilute hydrochloric acid. The resulting precipitate was filtered and purified by recrystallization from an appropriate solvent. The data of **2**—**6**, **9**, and **10**, are summarized in Table 1, while their IR and mass spectra are shown in Table 2. When the procedure described above has used, cyanoacetamide or benzoylacetamide gave 2-hydroxy-3-cyano-4,6-diphenylpyridine (**7**) or 2-hydroxy-3-benzoyl-4,6-diphenylpyridine (**8**) in a 68.2 or 64.2 % yield respectively. Their IR spectra could be completely superimposed on those of authentic samples.

*Conversion of **4** to 2,4,6-Triphenylpyrylium Tetrafluoroborate.* A mixture of **4** (0.50 g) and *p*-toluenesulfonic acid (5.00 g) was heated at 140 °C for 2 h, and then poured into 50 ml of 1 mol dm^{-3} tetrafluoroboric acid. The resulting precipitate was collected by filtration to give 2,4,6-triphenylpyrylium tetrafluoroborate almost quantitatively; its IR spectrum completely agreed with that of the authentic sample.[7]

*1-Methylthio- or 1-(*p*-Chlorobenzylthio)-1,3-diphenyl-4,4-dicyanobutadiene (**11** or **12**).* Into a mixture of malononitrile (0.16 g), 0.72 g (2 mmol) of **1**, and 3 mmol of methyl iodide or *p*-chlorobenzyl chloride in 3 ml of methanol we stirred 2.5 mol dm^{-3} MeONa–MeOH (2 ml) at room temperature. The reaction mixture was allowed to stand overnight and then poured into dilute hydrochloric acid. The resulting precipitate was filtered and purified by recrystallization to give **11** or **12**. These results are also shown in Tables 1 and 2.

*Bis(1,3-diphenyl-4,4-dicyanobutadienyl) Disulfide (**13**).* Into a solution of **10** (0.58 g) in DMF (5 ml), an aqueous solution of 30 % hydrogen peroxide (1 ml) was stirred drop by drop. The reaction mixture was kept at 50 °C for 2 h and then poured into water. The resulting precipitate was filtered and purified by recrystallization to give **13**. These data are also shown in Tables 1 and 2.

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