The solvent was removed under reduced pressure to give a residue which was treated with water to give 0.2 g of a product which melted at 219° on recrystallization from 2-propanol and was identical with **1b** described above by mixture melting point, spectral comparison, and tlc behavior.

N-Thioformyl derivative **4e** was obtained in 71% yield by refluxing **4b** with thiophosgene in toluene: mp 236° on recrystallization from methylene chloride-ether; ir 3250, 1660, and 1610 cm⁻¹.

Anal. Calcd for $C_{18}H_{16}ClN_5OS$: C, 56.03; H, 4.18; N, 18.15. Found: C, 56.21; H, 4.36; N, 17.86.

N-Morpholinothioformyl derivative **4f** was obtained in 56% yield from **4e** and morpholine, mp 166° on recrystallization from methylene chloride-ether.

Anal. Calcd for $C_{22}H_{24}N_6O_2S$: C, 60.54; H, 5.54; N, 19.26. Found: C, 60.76; H, 5.52; N, 19.22.

2-Methylamino-3-(*N*-carbethoxy-*N*-methyl)aminoformimidoyl-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**4g**).—To a suspension of **4a** (2.31 g, 0.01 mol) in dioxane (80 ml) containing pyridine (0.8 g) was added ethyl chloroformate (1.08 g, 0.01 mol) and the mixture was heated with stirring under reflux for 4 hr. The precipitate obtained on cooling was filtered and recrystallized from methylene chloride to give 1.8 g of **4g**: mp 190°; ir 3510, 1680, and 1660 cm⁻¹; uv λ max 260 mμ (log ε 4.48).

Anal. Calcd for $C_{14}H_{17}N_5O_3$: C, 55.43; H, 5.65; N, 23.09. Found: C, 55.16; H, 6.17; N, 22.91.

6-Oxo-3*H*,6*H*-1,2-dihydropyrimido[4,5-*e*]-1,4-diazepine (**6**).—Ethylenediamine (3.6 g, 0.06 mol) was added to a stirred suspension of **1a** (4.16 g, 0.02 mol) in dioxane (50 ml) and heated under reflux for 4 hr. The precipitate obtained on cooling was filtered and washed with water and ethanol. On recrystallization from chloroform-dioxane 2.9 g (78%) of product was obtained: mp 310°; ir 1680, 1610, and 1460 cm⁻¹; uv⁶ λ max 217 and 265 mμ; nmr (CF_3COOH) δ 4.25 (s, broad, 4 H, $NHCH_2$ and $=NCH_2$), 7.3-7.7 (m, 3 H, C-9, C-10, and C-11 protons), 8.32 (m, 1 H, CH=N), 9.03 (d, 1 H, C-8 proton).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 25.97. Found: C, 61.49; H, 4.75; N, 25.77.

(6) Only qualitative assay could be performed owing to the high degree of insolubility of the compound in solvents.

## Syntheses and Cis–Trans Isomerization of Light-Sensitive Benzenediazo Sulfides

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Although until recently benzenediazoalkyl sulfides were considered highly decomposable,[1] Van Zwet and Kooyman succeeded in preparing benzenediazo-*tert*-butyl sulfide and its 2,4,6-trimethyl derivative and in determining the cis–trans isomerization and other phys-

(1) R. Pütter in "Methoden der Organischen Chemie," Houben-Weyl, Georg Thieme Verlag, Stuttgart, 1965, p 567, band 10/3.

ical properties.[2] We were unable to prepare other derivatives by the same method but found a more general synthesis which is presented in the Experimental Section. In this way a number of new derivatives were synthesized and studied, especially in view of their applicability in photographic physical development systems, a subject extensively discussed elsewhere.[3] For photographic applications the very slow thermal cis-to-trans isomerization and the stability of the cis isomer are important properties which were also helpful in studying the synthesis. The reaction was found to depend on the equilibrium between diazonium ion **1** and benzene-*cis*-diazo sulfide **2**. The substituents X
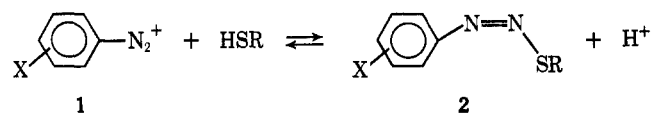
appear to determine the quantity of cis isomer **2** formed when the reactants **1** and thiol are brought together. The solution of the reactants showed, *e.g.*, when X was $3,5-Cl_2-4-N(CH_3)_2$, immediately the absorption spectrum of the cis isomer **2** which must mean according to empirical determinations that there was at most 4% diazonium left. A dilute solution of H_2SO_4 had to be added to move the equilibrium to the left which produced the diazonium spectrum. On the other hand, when, *e.g.*, X was $2,5-(OCH_3)_2-4-(4'-tolylmercapto)$, a compound photographically uninteresting and therefore not extensively studied, the diazonium spectrum was observed which changed to the cis spectrum if NaOH solution was added to move the equilibrium to the right. Generally, when the NaOH solution was added too rapidly, the diazonium salt decomposed with the formation of nitrogen. Optimum yields of pure cis isomers were obtained when the NaOH solution was slowly added to give a final pH of 6.

The final step in the synthesis is the thermal isomerization of the cis isomers to obtain the photographically applied trans isomers. We found that the thermal isomerization in benzene, the solvent chosen by Van Zwet and Kooyman,[2] even in yellow safe-light was accompanied by decomposition. Much purer products were obtained by heating in isooctane at 90° for 2 hr.

The data in Table I were calculated from 5 to 12

TABLE I

THERMAL CIS-TO-TRANS ISOMERIZATION RATE CONSTANTS k IN ETHANOL AT 60° FOR BENZENEDIAZO SULFIDES ($C_6H_5N_2SR$) WITH SUBSTITUENTS X ATTACHED TO THE BENZENE RING[a]

X	R	10^4k, sec⁻¹	Log f	A, kcal/mol
4-NO₂	*tert*-Butyl	0.52 ± 0.01	12.4 ± 0.7	25.3 ± 1.0
2-Cl-4-NO₂	*tert*-Butyl	0.83 ± 0.01	11.7 ± 0.7	24.0 ± 1.1
4-CN	*tert*-Butyl	0.48 ± 0.01	18.3 ± 0.9	28.8 ± 1.3
4-Cl	*tert*-Butyl	0.39 ± 0.04	11.2 ± 1.0	23.8 ± 1.6
4-NO₂	*tert*-Octyl	1.40 ± 0.01	12.2 ± 0.4	24.4 ± 0.6
4-NO₂	$C(C_6H_5)_3$	35 ± 2	11.7 ± 0.3	21.5 ± 0.5

[a] Frequency factors f and activation energies A.

points by the method of least squares. The deviations are standard deviations. The correlation coefficients were all better than 0.99. Frequency factors f

(2) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **86**, 993 (1967).

(3) H. Jonker, C. J. Dippel, H. J. Houtman, C. J. G. F. Janssen, and L. K. H. van Beek, *Photogr. Sci. Eng.*, **13**, 1 (1969).

TABLE II

TRANS AND CIS ISOMERS OF SUBSTITUTED BENZENEDIAZO SULFIDES, C6H5N2SR[a]

R	X	Isomer	Uv, nm (ε)	Nmr chemical-shift values					
				C(CH3)3	C(C6H5)3	C6H4	C6H3	C6H2	Other
C(CH3)3	4-NO2	Trans	351 (20,000)	1.66		7.61, 8.27			
		Cis	356 (17,000)	1.61		7.10, 8.33			
C(CH3)3	2-Cl-4-NO2	Trans		1.67			7.31, 8.08, 8.32		
		Cis		1.64					
C(CH3)3	4-Cl	Trans	332 (17,700)	1.62		7.34, 7.40			
C(CH3)3	4-Cl-2-CH3	Trans	334 (13,500)	1.65			7.13		2.52 (CH3)
		Cis		1.60			7.13		2.05 (CH3)
C(CH3)3	4-CN	Trans	338 (19,000)	1.65		7.62			
		Cis		1.61		7.08, 7.75			
C(CH3)3	3,5-Cl2-4-N(CH3)2	Trans	348 (12,700)	1.63				7.39	2.91 (N(CH3)2)
		Cis		1.61				7.03	2.93 (N(CH3)2)
tert-Octyl	4-NO2	Trans	355 (19,800)						
Adamantyl	4-NO2	Trans	345 (19,200)						
C(C6H5)3	4-NO2	Trans	356 (19,900)		7.25[b]	7.09, 7.20, 8.04, 8.18[b]			
		Cis			7.22[b]	6.98, 7.13, 8.16, 8.31[b]			
C(C6H5)3	4-Cl	Trans	338 (18,800)						
C(C6H5)3	3-Cl-4-N(CH3)2	Trans	368 (20,500)						

[a] X = substituents on the benzene ring.   [b] Data reported by Van Zwet and Kooyman.[2]

TABLE III

SUBSTITUTED BENZENEDIAZO SULFIDES, C6H5N2SR[a]

R	X	Registry no. Cis	Registry no. Trans	Mp, °C	Calcd, % C	H	N	S	Cl	Found, % C	H	N	S	Cl
C(CH3)3	4-NO2	29577-81-9	29577-82-0	60-62	50.20	5.47	17.56	13.40		50.3	5.2	17.7	13.4	
C(CH3)3	2-Cl-4-NO2	29577-83-1	29577-84-2	76.5-77	43.89	4.42	15.53	11.71	12.95	43.9	4.4	15.5	11.8	13.2
C(CH3)3	4-Cl		29577-85-3	47-49	52.51	5.73	12.25	14.02	15.50	52.4	5.7	12.9	14.1	15.4
C(CH3)3	4-Cl-2-CH3	29577-86-4	29577-87-5	40-42	54.42	6.23	11.54	13.21	14.60	53.1	6.3	11.6	13.4	14.9
C(CH3)3	4-CN	29577-88-6	29577-89-7	104-106	60.25	5.97	19.16	14.62		59.9	5.8	19.5	14.8	
C(CH3)3	3,5-Cl2-4-N(CH3)2		29577-90-0	47-49	47.06	5.59	13.72	10.47	23.15	46.8	5.8	13.9	9.8	23.5
tert-Octyl	4-NO2		29577-91-1	62-64	56.92	7.17	14.22	10.85		56.3	6.9	13.7	11.1	
n-Adamantyl	4-NO2		29577-92-2	148-150										
C(C6H5)3	4-NO2		29577-93-3	143-145 dec[b]	70.58	4.51	9.88	7.52		70.1	4.5	10.0	7.6	
C(C6H5)3	4-Cl		27843-80-7	125-126 dec	72.36	4.61	6.75	7.73	8.54	72.3	4.9	6.8	7.7	8.55
C(C6H5)3	3-Cl-4-N(CH3)2		29577-95-5	135 dec	70.81	5.28	9.17	6.99	7.74	70.3	5.2	9.25	7.1	7.8

[a] X = substituents on the benzene ring.   [b] Van Zwet and Kooyman[2] found 145° dec

and activation energies were derived from $k = f$ $\exp(-A/RT)$ between 20 and 70°. Substituents on the benzene ring had little influence on the rate of cis-to-trans isomerization, unless obviously ortho to the diazo group, *e.g.*, when X was 2-Cl-4-NO$_2$. The isomerization rates increased when bulkier groups R were attached to the sulfur atom, but the activation energies decreased as expected.

Van Zwet and Kooyman[2] gave two possible mechanisms for the thermal cis-to-trans isomerization, namely *via* rotation about the N–N bond or *via* ionization and recombination. For azobenzene derivatives, Talaty and Fargo[4] proposed a third mechanism with a linear transition state in which one or both nitrogen atoms undergo a change in hybridization to the sp state. The arguments for this third mechanism were the low activation energies of 21–24 kcal/mol in combination with the absence of large solvent effects. Since the benzenediazo sulfides of Table I have activation energies of 21–28 kcal/mol and generally small solvent effects,[2] the same mechanism of thermal cis-to-trans isomerization *via* a linear transition state seems to hold.

The effect of substituents X on the absorption spectra (Table II) also suggests a resemblance to azobenzenes. Both classes of compounds have the main absorption peaks of the 4-NO$_2$ derivatives considerably shifted to the visible with respect to the unsubstituted compounds. This has been attributed to polar resonance structures,[5] but the solvent effects are not entirely consistent with that interpretation. The main absorption peak of 4-nitro-benzenediazo-*tert*-butyl sulfide was found at 351 nm in ethanol but at 388 nm in benzene. Similar effects were reported in ref 2.

Experimental Section

The purity of the cis and trans benzenediazo sulfides was tested by silica gel thin layer chromatography with cyclohexane eluent and by nmr and ir. The nmr spectra were recorded in our analytical department by Mr. H. M. van den Bogaert on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Analyses were performed by the TNO Organic Chemistry Institute at Utrecht. In the synthetic work assistance was given by Mr. Th. C. J. M. Hegge. The absorption spectra were recorded with a Unicam SP800 spectrophotometer, the triphenylmethyl sulfides in ethyl acetate, the others in 98% ethanol. Isomerization rate constants were determined by photoisomerizing the ethanolic solutions of the trans isomers at 405 nm and spectrophotometrically following the thermal reverse isomerization from the resultant cis isomer to the trans form. The stoppered cells were placed in a constant temperature housing. Since both isomers are light-sensitive, the experiments were carried out in yellow safe-light to prevent photoisomerization.

Anilines and Diazonium Tetrafluoroborates.—Most of the anilines were commercial products. Two of them, 3-Cl-4-N(CH$_3$)$_2$-aniline and 3,5-Cl$_2$-4-N(CH$_3$)$_2$-aniline, were prepared by known methods[6,7] which were improved in that the N(CH$_3$)$_2$ group was introduced by passing gaseous HN(CH$_3$)$_2$ into the solution of the bromobenzene derivative in dimethylformamide.[8] The diazonium boron tetrafluorides were prepared as reported earlier.[8]

Benzenediazo Sulfides.—The benzenediazoalkyl sulfides were obtained as follows. The alkylthiol (0.1 mol) was added to a solution of 0.1 mol of diazonium·BF$_4$ in 250 ml of acetone cooled to 0°. The pH was adjusted with the help of pH paper to a value

of between 5 and 6 adding dropwise about 160 ml of 2.5% aqueous NaOH in about 1 hr.

If the cis isomer did not crystallize it was extracted with benzene. The extract was dried (Na$_2$SO$_4$) and the solvent removed at reduced pressure at 20°. The residual product was dissolved in 250 ml of isooctane. If the cis isomer did crystallize, it was directly dissolved in isooctane. The solution was kept at 90° for 2 hr to achieve the cis-to-trans isomerization. The solvent was removed at reduced pressure. The crude products were recrystallized from ethanol, yields 50–80% (Table III).

The benzenediazotriphenylmethyl sulfides were prepared by the method given in ref 2 (p 1004).

Base-Catalyzed Reaction of Methyl α-Cyano-β-(2-thienyl)acrylate

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In extension of our previous studies on base-catalyzed ring opening–closure reaction of α-cyano-β-furylacrylic esters, which led to the formation of γ-(4-alkoxycarbonyl-5-aminofuryl)acroleins,[2] we wish to report the one-step synthesis of rather complex thiophenes. When methyl α-cyano-β-(2-thienyl)acrylate (1) was allowed to stand overnight in morpholine or in piperidine at room temperature, a colored product resulted in 56 and 69% yields, respectively. The product obtained was assigned as the structure of methyl 2-cyano-5-(4-methoxycarbonyl-5-amino-2-thienyl)-2,4-pentadienoate (2), on the basis of ir, nmr, and mass spectral data.
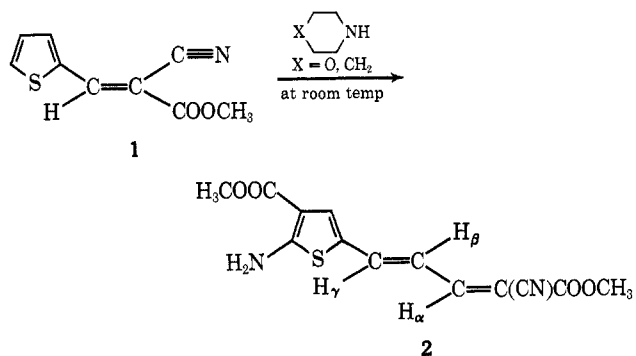
On the other hand, when methyl cyanoacetate (4) and thiophene-2-carboxaldehyde were mixed in morpholine or in piperidine directly, the same product 2 was also obtained in the range of 29–51% yields even when a 1:1 molar proportion of the reactants was used. The yields, in these reactions, were improved slightly by the use an excess of 4, thus giving 32–71% 2. It is impossible to isolate the expected cyanoacrylate 1 in any case. Furthermore, aminals[3–5] are commonly produced by the reaction of a secondary amine with an aldehyde;

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