

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF CARBOXYLIC DITHIOCARBAMIC ANHYDRIDES AND RELATED COMPOUNDS—III¹

E. H. HOFFMEISTER and D. S. TARBELL
Department of Chemistry, University of Rochester
Rochester, New York 14627

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Abstract—Photolysis of benzoic dimethylamine dithiocarbamic anhydride (XXII) in benzene solution yields benzoic acid, sulfur, benzoyl dimethylamine thiocarbamyl disulfide (XXIII) tetramethyl thiuram disulfide (XX) and N,N-dimethylbenzamide (XXI). Under the same conditions, photolysis of benzoic methylamine dithiocarbamic anhydride (XV) gives benzoic acid, sulfur, benzoyl methylamine thiocarbamyl disulfide (XVII) dibenzoyl disulfide (XVIII) and N-methyl benzamide (XVI). Possible differences in the mechanisms of the two photochemical reactions are discussed. The monomethylamino compound (XV) in solution can decompose thermally by two pathways, the type of decomposition being determined by the solvent. Compound XV can yield the amide XVI and carbon disulfide by one pathway; thiobenzoic acid and presumably methyl isothiocyanate are formed by the second pathway. The dimethylamino compound (XXII) decomposes thermally by only one pathway to yield the amide XXI and carbon disulfide. Kinetic measurements on the decomposition of XV and XXII to the corresponding amide and carbon disulfide were carried out by following the change in the NMR spectrum.

DISCUSSION

IN PREVIOUS work,^{2,3} the photochemical and thermal decomposition of mixed carboxylic dithiocarbamic anhydrides from certain cyclic secondary amines was studied. It seemed desirable to explore and compare these features of the chemistry of the corresponding anhydrides from acyclic amines; methylamine benzoic dithiocarbamic anhydride (XV) and dimethylamine benzoic dithiocarbamic anhydride (XXII) were therefore prepared and studied. In contrast to the synthesis of the three cyclic-amine anhydrides previously studied,^{2,3} an aqueous-tetrahydrofuran solvent system was found most suitable for preparing anhydrides XV and XXII. An attempted synthesis of anhydride XXII in chloroform solution, similar to the techniques used for the preparation of the cyclic-amine anhydrides studied previously, gave a yellow liquid product, which was a mixture of the anhydride and the amide. The physical data for anhydrides XV and XXII are summarized in Table 1.

Photolytic decomposition. The photolyses of solutions of XXII (0.013–0.016 molar) in benzene at $>3000 \text{ \AA}$ and $11\text{--}13^\circ$ for 20–23 hr were shown to be entirely analogous to the photolysis of piperidine benzoic dithiocarbamic anhydride.² The products isolated from irradiation of two samples of XXII are listed in Table 2. The low yield

¹ We are indebted to Grant NSF-G11240 from the National Science Foundation for support of this work.

² E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron* **21**, 35 (1965).

³ E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron* **21**, 2857 (1965).

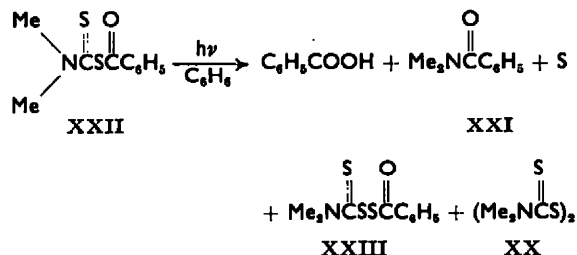


TABLE I. PHYSICAL DATA FOR ANHYDRIDES XV AND XXII

Anhydride:	$\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{NCSCC}_6\text{H}_5 \\ \diagup \\ \text{H} \end{array}$ XV			$\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{NCSCC}_6\text{H}_5 \\ \diagup \\ \text{Me} \end{array}$ XXII		
	$\lambda(\text{m}\mu)$	ϵ		$\lambda(\text{m}\mu)$	ϵ	
M.p. (dec):	90-90.5°			59-59.5°		
C=O $\nu(\text{cm}^{-1})$:	1656			1682		
UV and visible spectra in cyclohexane:	250 (shoulder)	1.22×10^4		240 (max)	2.39×10^4	
	264 (max)	1.38×10^4		280-290 (plateau)	1.64×10^4	
	302 (shoulder)	5.45×10^3		400	248	
	370 (shoulder)	342				
NMR spectrum:	$\tau(\text{ppm})^a$	mult.	rel. area	$\tau(\text{ppm})^b$	mult.	rel. area
	-0.9 (broad)	1	1	2.1-2.7	compl.	5
	2.0-2.7	compl.	5	6.54	1	6
	6.63 (center)	2	3			

NMR spectra recorded in ^a CDCl₃ and ^b CS₂TABLE 2. PHOTOLYSIS OF $\text{Me}_2\text{NCSCC}_6\text{H}_5$, XXII

Temp (°C)	Conc of XXII (mole/l.)	Time (hr)	Yields, %				
			Benzoic acid	Sulfur	$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Me}_2\text{NCSSCC}_6\text{H}_5 \\ \text{XXIII} \end{array}$	$\begin{array}{c} \text{S} \\ \parallel \\ \text{(Me}_2\text{NCS)}_2 \\ \text{XX} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{Me}_2\text{NCC}_6\text{H}_5 \\ \text{XXI} \end{array}$
11	0.013	23.3	38	25	29	none	5
13	0.016	19.6	44	6	19	3	indeterminable

of the amide XXI in the photolysis at 11° suggested that significant amounts of this rather water-soluble product might have been lost in the reaction workup, which involved a basic extraction. To assess this possibility, the photolysis, tabulated next, at 13° was carried out on an equimolar mixture of anhydride XXII and amide XXI; 77% of the amide was recovered, disregarding the small amount of this which probably arose from the photolysis of XXII. From this experiment, which, unlike the first

experiment, involved the workup of a double batch of photolysis product to minimize losses, 3% of tetramethyl-thiuram disulfide (XX) was isolated, which was identified by comparison with an authentic sample. A control experiment showed this symmetric disulfide (XX) to be stable to the photolysis conditions. Compound XXIII was

assigned the structure $\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{NCSSCC}_6\text{H}_5 \\ \diagup \\ \text{Me} \end{array}$, benzoyl dimethylamine thiocarbamyl disulfide,

and is the second representative of this new type of unsymmetric disulfide which we have found. This was identified by elemental analysis and from the data summarized in Table 3. In particular, the IR spectrum in KBr bears a strong resemblance to that of the piperidine analog, described previously,² and also to its parent anhydride

TABLE 3. PHYSICAL DATA FOR UNSYMMETRIC DISULFIDES XVII AND XXIII

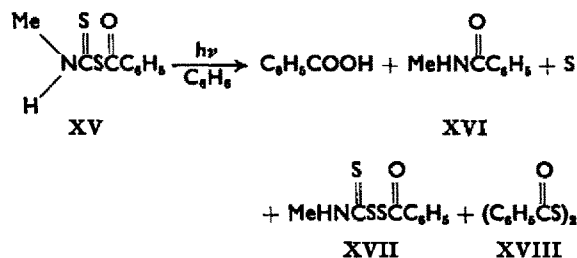
Disulfide:	$\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{NCSSCC}_6\text{H}_5 \\ \diagup \\ \text{H} \end{array}$ XVII		$\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{NCSSCC}_6\text{H}_5 \\ \diagup \\ \text{Me} \end{array}$ XXIII			
	M.p. (dec):	83.5–84.5°	M.p. (dec):	112.5–117.5°		
C=O ν (cm ⁻¹):	1687	C=O ν (cm ⁻¹):	1700			
	λ (m μ)	ϵ	λ (m μ)	ϵ		
UV spectrum	252 (max)	3.23×10^4	242 (max)	2.30×10^4		
in cyclohexane:	280 (shoulder)	7.97×10^8	270 (shoulder)	1.23×10^4		
	τ (ppm) ^a	mult.	rel. area	τ (ppm) ^b	mult.	rel. area
NMR	1.9–2.8	compl.	2	2.05	compl.	2
spectrum:	6.80	2	1	2.50	compl.	3
	(center)			6.48	1	6

NMR spectra recorded in ^a CDCl₃ and ^b CS₂.

(XXII). Likewise, the shape and position of the UV bands are nearly identical to those of the piperidine analog.² The photolysis mixtures were searched carefully for dibenzoyl disulfide, but none was found. This observation, combined with the discovery of the thiuram disulfide (XX) in the products, supports a photolytic scheme for the decomposition of XXII analogous to that proposed for the piperidine analog.²

The photolysis of a 0.014 molar solution of anhydride XV in benzene at >3000 Å and 16° for 48 hr provided an interesting variation to the established mode of decomposition,² as shown in Chart I. As shown below, no thiuram disulfide product

appeared,⁴ but was supplanted by a 4% yield of dibenzoyl disulfide (XVIII). The products from this and from a lengthier photolysis at 20° are summarized in Table 4. A shielded control sample accompanying the latter run showed no change. The third



$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ \text{MeHNCSSCC}_6\text{H}_5 \end{array}$
 TABLE 4. PHOTOLYSIS OF MeHNCSSCC₆H₅ (XV)

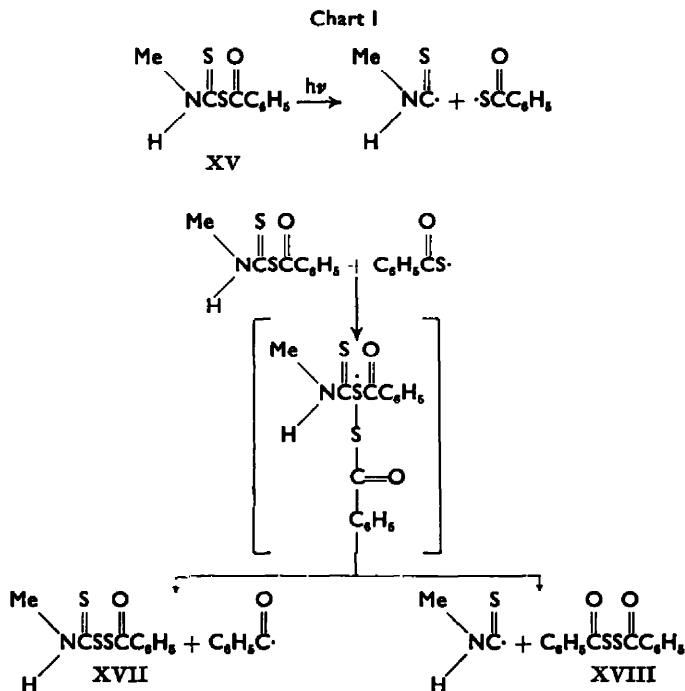
Temp (°C)	Conc. of XV (mole/l.)	Time (hr)	Benzoic acid	Sulfur	Yields, %		
					$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ \text{MeHNCSSCC}_6\text{H}_5 \\ \text{XVII} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ (\text{C}_6\text{H}_5\text{CS})_2 \\ \text{XVIII} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{MeHNCC}_6\text{H}_5 \\ \text{XVI} \end{array}$
16	0.014	48.0	39	13	57	4	18
20	0.046	82.3	39	39	none	2	43

example of the new, unsymmetric disulfide type, $\begin{array}{c} \text{Me} \quad \text{S} \quad \text{O} \\ \diagdown \quad \parallel \quad \parallel \\ \text{N} \text{CSSCC}_6\text{H}_5 \\ \diagup \\ \text{H} \end{array}$ (XVII) benzoyl

methylamine thiocarbonyl disulfide, constituted a major product of the reaction. Its structure was assigned from elemental analysis and the data summarized in Table 3, and, again, the similarity of its IR spectrum in KBr to that of its anhydride precursor is notable. The absence of XVII from the 82-hr photolysis mixture, as well as the increased yield of amide XVI and elemental sulfur suggest that prolonged photolysis under these conditions tended to decompose XVII into these more stable products. This contrasts the photochemical stability of XVII in the absence of complicating photolysis intermediates and side products, since XVII was recovered unchanged from a 45-hr photolysis of a 0.005 molar solution in benzene at >3000 Å and 14°. Thermal decomposition of a 0.013 molar solution of XVII in refluxing cyclohexane for 22.5 hr gave 66% of dibenzoyl disulfide, 21% of amide XVI and 32% of sulfur. The same sample of unsymmetric disulfide was unaffected by refluxing in cyclohexane for only 2.5 hr, however.

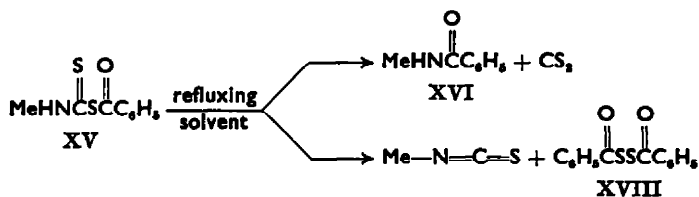
The isolation of dibenzoyl disulfide from the photolysis of the anhydride XV can be explained by the reaction sequence shown in Chart I. Unlike the behavior of all the anhydrides from disubstituted amines, the initial homolysis produces a thiocarbonyl radical and a thiobenzoate radical. It is this latter species which then attacks

⁴ Sym-dialkylated members of the thiuram disulfide group are much less stable than the tetra-alkylated members, cf. von Braun and K. Weissbach, *Ber. Dtsch. Chem. Ges.* 63, 2836 (1930).



starting material to produce the intermediate sulfonium radical. As before, fragmentation of this intermediate to the unsymmetric disulfide (XVII) takes preference over the alternative cleavage to give the symmetric disulfide (XVIII). Benzoic acid and the amide XVI are evidently formed in the same manner as mentioned previously.²

Thermal decomposition. The monomethyl anhydride (XV) in refluxing solution decomposed by two competing pathways, shown below, to give the amide, carbon disulfide, dibenzoyl disulfide, and presumably methyl isothiocyanate which vaporized or was destroyed under the reaction conditions. Which pathway predominated



depended upon the solvent used, and the yields of XVI and XVIII isolated from refluxes of 0.75 to 4.6 hr in various solvents are shown in Table 5.⁵ The final entry involved merely heating a sample of XV at 40° in a benzene-water mixture. That solvents of increasing polarity favor amide formation is the obvious trend. If the decomposition runs which yielded dibenzoyl disulfide (XVIII) were worked up immediately, a pungent yellow oil whose IR spectrum was superimposable upon that

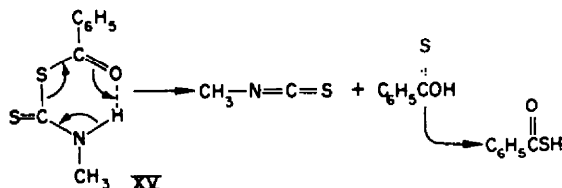
⁵ J. von Braun, *Ber. Dtsch. Chem. Ges.* 36, 3520 (1903), reported that Et-NHCSSCOC₆H₅ yielded N-ethylbenzamide and CS₂ in boiling EtOH.

TABLE 5. DECOMPOSITION OF ANHYDRIDE XV IN VARIOUS SOLVENTS

Solvent (dec temp)	Percent	Percent
	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{NHCC}_6\text{H}_5 \end{array}$, XVI	$\begin{array}{c} \text{O} \\ \\ (\text{C}_6\text{H}_5\text{CS})_2 \end{array}$, XVIII
Cyclohexane (81.4°)	0	50
n-Heptane (98°)	0	51
Benzene (80°)	9	50
Ethanol (abs.) (78°)	51	14
Benzene:water (80 ml:6 ml) (40°)	89	0

of thiobenzoic acid was isolated. After standing in the air for several hr, this was totally converted to XVIII.

It is tempting to postulate that the mode of decomposition of XV to form thiobenzoic acid and methyl isothiocyanate involves an internally hydrogen-bonded, 6-membered transition state, as shown, with immediate isomerization of the thione acid to the thiol structure which is the reactive species in chemical transformations.⁶



Indeed, indications of internal hydrogen bonding in XV are exhibited in the IR and NMR spectra. The N—H stretching band in the infrared spectrum appears as a very broad doublet at the low frequencies of 3210 and 3170 cm^{-1} , and the carbonyl stretching frequency occurs at 1656 cm^{-1} , which is 24–26 cm^{-1} lower than the value for all of the other anhydrides in this study. The NMR spectrum reveals the amino proton at the low field value -0.9τ , which similarly suggests intramolecular hydrogen bonding.^{7–9} For the amide (XVI) and the unsymmetric disulfide (XVII) which have no opportunity for internal 6-membered ring formation, the N—H stretch appears as a reasonably sharp singlet in the IR spectra at 3330 and 3310 cm^{-1} , respectively. Also, for both compounds, the amino proton is buried under the aromatic proton signals at 2.0–2.8 τ in the NMR spectra.

⁴ D. Plant, D. S. Tarbell and C. Whiteman, *J. Amer. Chem. Soc.* **77**, 1572 (1955).

⁷ Cf. the very similar chemical shifts of the amino proton in the 6-membered chelate rings of certain α,β -unsaturated β -keto methylamines and N-methyl-2-carbamoyl-dimadone in CCl_4 , CHCl_3 , or CDCl_3 , in G. Dudek and R. H. Holm, *J. Amer. Chem. Soc.* **84**, 2691 (1962); G. Dudek and G. P. Volpp, *Ibid.* **85**, 2697 (1963); G. Dudek and E. P. Dudek, *Ibid.* **86**, 4283 (1964); G. Dudek, *J. Org. Chem.* **30**, 50, 548 (1965).

⁸ N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, *NMR Spectra Catalog* Vol. II; spectrum 652. Varian Associates, National Press, U.S.A. (1963).

⁹ Cf. amino-proton chemical shift in 2,6-bismethylaminohepta-2,5-dien-4-one in J. D. Edwards, J. E. Page and M. Pianka, *J. Chem. Soc.* 5200 (1964).

Decomposition of XV at 91° without solvent, followed by sublimation of the product, gave the pure amide in 98% yield.

The absorption spectrum of XV made it convenient to follow its decomposition to the amide spectrophotometrically. However, its moderate speed of decomposition at 60–70° in carbon tetrachloride was amenable to rate measurements in the heated sample chamber of the Varian A-60 nmr spectrometer. Three rate runs at 60, 65 and 70° were performed entirely in the NMR instrument, using continuously spun samples and tracing their spectra at 1–2 hr intervals. With progressing time, a doublet, centered at 7.03 τ , appeared and continued to grow, concomitant with the gradual diminution of the doublet intensity at 6.63 τ . From the ratios of the peak areas, the concentrations of the anhydride remaining were calculated. Formation of the amide whose methyl signal occurs at 7.03 τ was the only reaction detected during the decomposition period. For each run, a plot of $-\log c$ vs. time gave a good straight line, and the rates were reproducible within 2%. Data for a typical 7-hr run at 60° are given below, from which $k_1 = 8.51 \times 10^{-6} \text{ sec}^{-1}$ was obtained. The first order rate constants and half-times for decomposition are presented in Table 6.

time interval (hr)	3.91	5.00	6.17	7.33
rel. area XV/XVI Me peaks	8.63	6.74	5.10	4.31

A plot of $\log k_1$ vs. $1/t$ for the three determinations gave the straight line shown in Fig. 1, with $\Delta H_a = 21.5 \text{ kcal. mole}^{-1}$. The calculated entropy of activation at 65°, $\Delta S_{65^\circ} = -16.0 \text{ eu}$, suggests a highly ordered transition state for amide formation.¹⁰

TABLE 6. FIRST ORDER RATE CONSTANTS FOR DECOMPOSITIONS OF ANHYDRIDES XV AND XXII IN CARBON TETRACHLORIDE AND CYCLOHEXANE AT VARIOUS TEMPERATURES

Solvent	Temp (°C)	$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ \text{MeNHCSCC}_4\text{H}_9 \text{ XV} \end{array}$		
		Spectral method	k_1 (sec ⁻¹)	$t_{1/2}$ (sec)
CCl ₄	60	NMR	8.51×10^{-6}	8.14×10^4
CCl ₄	65	NMR	1.33×10^{-5}	5.20×10^4
CCl ₄	70	NMR	2.16×10^{-5}	3.21×10^4
		$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Me}_2\text{NCSCC}_4\text{H}_9 \text{ XXII} \end{array}$		
CCl ₄	70	NMR	7.46×10^{-6}	9.30×10^4
CCl ₄	76.7	visible	3.09×10^{-5}	2.24×10^4
C ₆ H ₁₁	81.4	visible	8.80×10^{-5}	7.88×10^3

Like its piperidine, pyrrolidine and morpholine analogs, the dimethylamine anhydride (XXII) forms the amide quantitatively. Its rate of disappearance in solution, however, was significantly slower than that of XV, so that an NMR run at 70° in carbon tetrachloride was the only one feasible by this method. The procedure compared the integrated intensities of the diminishing anhydride methyl singlet at 6.51 τ

¹⁰ Cf. D. S. Tarbell and R. P. F. Scharrer, *J. Org. Chem.* **27**, 1972 (1962).

and of the new amide methyl singlet arising at 7.04τ . Data for a typical 5-hr run at 70° are given below, from which $k_1 = 7.46 \times 10^{-6} \text{ sec}^{-1}$ was obtained. At tempera-

Time interval (hr)	2.00	3.17	3.73	4.61	5.33
Rel. area XXII/XXI Me peaks	18.7	10.9	9.2	7.6	6.1

tures below 70° , the variation in peak heights was not great enough for reliable measurements. Since this anhydride absorbs at $400 \text{ m}\mu$, its rate of disappearance followed spectrophotometrically in refluxing solvents was also possible. Refluxes in both carbon tetrachloride at 76.7° and cyclohexane at 81.4° exhibited convenient rates for accurate measurements. Good first order rate plots were obtained for the decompositions at all three temperatures and are listed with the corresponding half-times in Table 6.

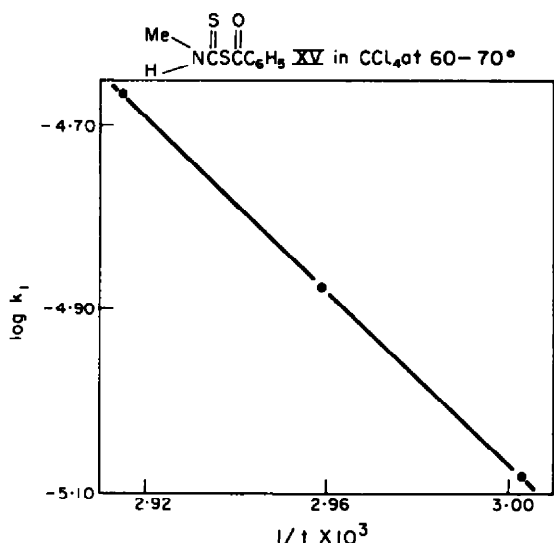


FIG. 1. Plot of $\log k_1$ vs. $1/T$ for anhydride XV.

EXPERIMENTAL^{11,12}

Methylamine benzoic dithiocarbamic anhydride (XV). To a solution of 0.703 g benzoyl chloride in 5 ml redistilled tetrahydrofuran at 0° was added 0.691 g methylamine dithiocarbamate (XIV)¹⁰ with swirling. Water (5 ml) was added dropwise, and a white solid immediately precipitated. This was filtered and dried (0.882 g). The crude anhydride was recrystallized from 5 ml benzene-5 ml pet. ether to give 0.713 g (68%) XV, m.p. $90-90.5^\circ$ (dec), lit. m.p. $90-91^\circ$.¹⁰ The IR spectrum in KBr was characterized by the following peaks (cm^{-1}): 3210, 3170, 3050 w, 3000 w, 2960 w, 2925 w, 1656 s, 1600, 1585, 1540 s, 1467, 1440 (shoulder), 1350 (broad), 1320 w, 1310 w, 1210 s, 1185, 1155, 1100, 1040, 1000, 930, 900 s, 770, 710 (shoulder), 690 (center of doublet) s, 645, 615 w. The UV spectrum in cyclohexane exhibited the following absorptions: λ 250 $\text{m}\mu$ (shoulder), ϵ_{250} 1.22×10^4 ; λ_{max} 264 $\text{m}\mu$, ϵ_{max} 1.38×10^4 ; λ 302 $\text{m}\mu$ (shoulder), ϵ_{302} 5.45×10^3 ; λ 370 $\text{m}\mu$ (shoulder), ϵ_{370} 342. The NMR spectrum in CDCl_3 showed the following signals: -0.9τ (broad), $2.0-2.73\tau$ (complex), 6.63τ (center of doublet) with the relative areas 1:5:3.

¹¹ See *Materials* and footnotes 9 in Ref. 3. All NMR spectra were taken on a Varian A-60 spectrometer using a TMS internal standard.

¹² We are grateful to Dr. L. D. Colebrook of this laboratory for his guidance in the NMR kinetic measurements.

¹³ K. Bodendorf, *J. Prakt. Chem.* (2) 126, 233 (1930).

N-methylbenzamide (XVI) was prepared from benzoyl chloride and aqueous methylamine and melted at 80–80.5°.¹⁴ The IR spectrum in KBr was characterized by the following peaks (cm⁻¹): 3330, 3090 w, 3060 w, 3040 w, 3010 w, 2940 w, 2800 w, 1645 s, 1610, 1585 s, 1550 s, 1500, 1450 w, 1414, 1355 (shoulder) w, 1336, 1314 s, 1167, 1077 w, 1038, 995 (center of quadruplet) w, 939, 830, 809, (720, 710, 700, triplet) s, 670, 645. The UV spectrum in cyclohexane showed the following absorptions: λ_{\max} 222 m μ , ϵ_{\max} 1.08 $\times 10^4$; λ 267 m μ (shoulder), ϵ_{267} 640; λ 275 m μ (shoulder), ϵ_{275} 430. The NMR spectrum in CDCl₃ gave signals at 2.12–2.76 τ (complex) and 7.03 τ (centre of doublet).

Photolysis of XV at >3000 Å with control sample. A 1.680 g sample of XV was dissolved in 170 ml benzene and a 10 ml aliquot removed and shielded from all light. The remaining 160 ml was photolyzed, accompanied by the control sample, as previously described at >3000 Å and 20° for a total of 82.3 hr. Interruption of the photolysis after 16.5 hr yielded 0.094 g (96%) unchanged starting material from the control sample, m.p. 90–95°, and, after recrystallization, a 79% recovery of starting anhydride from the photolysis solution. This recovered starting material, accompanied by the shielded control sample, was photolyzed an additional 65.8 hr. Evaporation of the solvent from the control afforded 0.082 g (91% recovery) unchanged XV, m.p. 89–89.5°. The yellow photolysis mixture yielded, after solvent evaporation, 1.206 g brown–orange paste. This was treated with 7 ml petroleum ether, leaving 0.926 g pale brown solid. The latter was dissolved in 2 ml anhydrous ether, filtered, and 1 ml pet. ether added, which caused the separation of 0.015 g (2%) transparent rhomboids, whose IR spectrum in KBr and UV spectrum in cyclohexane were superimposable upon those of dibenzoyl disulfide,³ m.p. 132–133°, mixed m.p. 133–134°. The pet. ether filtrate was evaporated, leaving 0.137 g benzoic acid. Evaporation of the ether–pet. ether filtrate left a brown, semi-solid residue, which was then treated with 4 ml water–1 ml MeOH–2 ml acetone. This caused the precipitation of 0.074 g (39%) elemental S, m.p. 112–113°, which showed no absorption in the IR and whose UV spectrum in cyclohexane was identical to that of S. Solvent removal left 0.641 g brown oil, which was dissolved in 15 ml ether and extracted with base, as previously described.³ This gave 0.146 g benzoic acid, for a total yield of 0.283 g (39%) benzoic acid, m.p. 115–116°, mixed m.p. 118–119.5°. The neutral layer from the extraction afforded 0.287 g crude amide XVI. This was recrystallized from 5 ml anhydrous ether–1.5 ml pet. ether, to give 0.222 g (43%, based on 2 moles of starting material giving 1 mole amide) XVI, m.p. 79.5–80.5°, mixed m.p. 79.0–80.5°.

Photolysis of XV at >3000 Å and 16° for 48 hr. Four 0.500 g portions of XV dissolved in 170 ml benzene were photolysed separately at 16° and >3000 Å for 48 hr each, as previously described. The solvent was evaporated under red. press. at room temp and the residues combined to give 2.827 g yellow–orange paste. This was dissolved in 50 ml ether and extracted with base, yielding 0.445 g (39%) benzoic acid, m.p. 119–120°, mixed m.p. 121–122°. Evaporation of the ether from the neutral layer left 1.327 g yellow–brown paste. This was recrystallized from 14 ml anhydrous ether–7 ml pet. ether, affording 0.063 g dibenzoyl disulfide. Further crystallization from 4 ml anhydrous ether–2 ml pet. ether gave 0.057 g (4%) dibenzoyl disulfide, m.p. 129–130°, mixed m.p. 131–132°. The original ether–pet. ether mother liquor yielded 0.727 g additional tan-colored needles. This was recrystallized from 10 ml anhydrous ether–5 ml pet. ether, giving 0.649 g (57%, based on 2 moles of starting material giving 1 mole of product) straw-colored, transparent needles, m.p. 83.5–84.5° (dec).



This compound was assigned the formula CH₅NHCSSCC₆H₅ (XVII). The IR spectrum in KBr showed the following peaks (cm⁻¹): 3310 m, 3060 w, 2960 w, 2930 w, 2190 (broad)w, 2110 (broad)w, 1687 s, 1600 w, 1585 w, 1523 (broad)s, 1455 s, 1420 w, 1360 s, 1319 w, 1210 s, 1182 m, 1160 w, 1096 w, 1039 s, 1000 w, (928 s, 885 s, doublet), 770 s, 680 s, 640 (center of doublet)m. The UV spectrum is given in Table 3. The NMR spectrum in CDCl₃ showed signals at 1.9–2.8 τ (complex) and 6.80 τ (center of doublet) with the relative areas 2:1. (Found: C, 44.55; H, 3.70; N, 5.94. Calc. for C₆H₅NOS₂: C, 44.42; H, 3.73; N, 5.75%.)

From the original mother liquor remaining after the removal of XVII, an additional 0.047 g crystals were recovered, which yielded, after crystallization from ether–CHCl₃–pet. ether, 0.038 g (13%, based on 1 mole of starting material giving 1 g-atom S) elemental S, m.p. 114.5–115.5°, mixed m.p. 114.5–116°. Evaporation of the final mother liquor afforded 0.238 g brown solid. This was

¹⁴ P. van Romburgh, *Rec. Trav. Chim.* 4, 388 (1885).

recrystallized from 2 ml anhydrous ether-1 ml pet. ether, giving 0.114 g (18%) XVII, m.p. 74-75°, mixed m.p. 74-75°.

Reflux of XVII in cyclohexane. A 0.280 g sample of XVII in 80 ml cyclohexane was recovered unchanged (94% yield, identified by m.p. and the IR spectrum in KBr) after refluxing 2.5 hr.

A 0.160 g sample of the unsymmetric disulfide (XVII) in 50 ml cyclohexane was refluxed for 22.5 hr. Evaporation of the solvent left 0.110 g pale yellow oil which quickly solidified. The odor of H₂S was apparent. The IR spectrum in KBr of the solid residue showed contributions from both XVIII and XVI. This mixture was treated with 5 ml ether and 5 ml pet. ether, which caused the separation of 0.059 g (66%) XVIII, m.p. 119-121°, mixed m.p. 124.5-126°. The IR spectrum in KBr was identical to that of authentic dibenzoyl disulfide. Subsequently, 0.007 g (32%) S precipitated from the filtrate, m.p. 110.5-111°, mixed m.p. 109.5-110.5°. To the mother liquor was added 1 ml pet. ether, and 0.019 g (21%) XVI separated, m.p. 80-84°, mixed m.p. 77-78°, whose IR spectrum in KBr matched that of an authentic sample.

In the following series of thermal decompositions of XV, the products, XVIII and the amide XVI were identified, in each case, by m.p. and mixed m.p. with an authentic sample and by their IR spectra in KBr.

Reflux of XV in cyclohexane for 4.0 hr. A 0.248 g sample of XV in 75 ml cyclohexane was refluxed for 4.0 hr in an oil bath, preheated to 89°. A 45 ml aliquot of the solution was allowed to stand at room temp overnight. The solvent was then removed under red. press., leaving 0.100 g transparent crystals. This was recrystallized from 6 ml anhydrous ether-4 ml pet. ether to give 0.048 g (50%) XVIII, mixed m.p. 129.5-131.5°.

Reflux of XV in cyclohexane for 4.6 hr with isolation of thiobenzoic acid. A 0.230 g sample of XV in 75 ml cyclohexane was refluxed for 4.6 hr. Evaporation of the solvent gave 0.130 g yellow oil, whose IR spectrum was identical to that of authentic thiobenzoic acid (94.3%, Evans Chemetics, Inc.). The oil crystallized completely within several hr. The resulting solid was recrystallized from 3 ml anhydrous ether, giving 0.053 g (36%) XVIII, mixed m.p. 126.5-127.5°.

Reflux of XV in n-heptane. A 0.230 g sample of XV in 75 ml n-heptane (Spectro Grade, Matheson, Coleman and Bell) was refluxed at 98° for 2 hr. Removal of solvent gave 0.076 g (51%) XVIII, mixed m.p. 125-126°.

Reflux of XV in benzene. XV (0.240 g) in 75 ml benzene was refluxed for 4 hr. The solvent was evaporated, leaving 0.141 g white crystals. Their IR spectrum in KBr showed major contributions from XVIII, contaminated by the amide XVI. This was recrystallized from anhydrous ether-pet. ether to yield 0.078 g (50%) XVIII, mixed m.p. 129-130°. Concentration of the mother liquors afforded 0.014 g (9%) XVI, mixed m.p. 77-78°.

Reflux of XV in absolute ethanol. XV (0.243 g) in 75 ml EtOH (predistilled from Mg turnings) was refluxed for 2.5 hr at 78°. Evaporation of the solvent left 0.168 g yellow oil, whose IR spectrum showed absorption due primarily to XVI, contaminated by thiobenzoic acid. The oil solidified and was recrystallized from anhydrous ether-pet. ether to give 0.080 g (51%) XVI, mixed m.p. 78.5-79.5°, followed by 0.022 g (14%) XVIII, mixed m.p. 132.5-134°.

Decomposition of XV in a benzene-water mixture. A solution of 30.8 g XV in a mixture of 80 ml benzene-6 ml water was heated to 40° on the steam bath for 45 min. The solvent was allowed to evaporate at room temp, during which time transparent crystals separated. These were recrystallized from CS₂-pet. ether, yielding 17.6 g (89%) XVI, mixed m.p. 79-79.5°.

Decomposition of XV without solvent. A 0.208 g sample of XV was heated to 91° in a sublimation apparatus. The solid melted to a yellow liquid, which then bubbled and became brown. This was then sublimed at 102° for 2.5 hr, yielding 0.128 g (98%) XVI, mixed m.p. 78.5-79.5°.

Thermal decomposition of the anhydride XV in carbon tetrachloride at 60°, carried out and followed in the NMR. A 0.3 ml sample of a 0.357 molar solution of XV in CCl₄ in a stoppered sample tube was heated to 60° in the Varian A-60 NMR sample chamber. The sample was spun continuously at 30 r/s and the spectra taken with integration at 1-2 hr intervals, using a sweep width of 250 c/s. The concentration of XV remaining was determined from each spectrum, and a plot of -log c vs. time gave a good straight line with $k_1 = 8.51 \times 10^{-8} \text{ sec}^{-1}$, $t_{1/2} = 8.14 \times 10^4 \text{ sec}$.

The above experiment was repeated, and a plot of -log c vs. time gave a good straight line with $k_1 = 8.35 \times 10^{-8} \text{ sec}^{-1}$, $t_{1/2} = 8.30 \times 10^4 \text{ sec}$.

Dimethylamine dithiocarbamate XIX, from CS₂ and aqueous dimethylamine,¹⁵ m.p. 123-124° (dec),

¹⁵ A. Hutin, *Mon. Sci.* 7, 193 (1917); *Chem. Abstr.* 12, 103 (1918).

was oxidized to XX, m.p. 153.5–154.5°, with iodine.¹⁶ The IR spectrum in KBr was characterized by the following peaks (cm^{-1}): 2930 w, 1500 s, 1405 w, 1380 s, 1240 s, 1150 m, 1040 w, 975 s, 850 s. The UV spectrum in cyclohexane exhibited λ_{max} 213 $\text{m}\mu$, ϵ_{max} 2.58×10^4 ; λ 280 $\text{m}\mu$ (shoulder), ϵ_{280} 1.30×10^4 . The NMR spectrum in CS_2 showed a single spike at 6.48 τ .

N,N-Dimethylbenzamide was prepared from benzoyl chloride and aqueous dimethylamine; it was obtained crystalline by cooling in a dry-ice bath, m.p. 44.5–45.5°.^{5,17} The UV spectrum in cyclohexane showed λ_{max} 240 $\text{m}\mu$ (shoulder), ϵ_{max} 3.31×10^4 . The NMR spectrum in CS_2 displayed signals at 7.07 τ (singlet) and 2.73 τ (broad, singlet) with the relative areas 6:5.

Benzoic dimethylamine dithiocarbamic anhydride XXII. To a solution of 1.406 g benzoyl chloride in 10 ml redistilled tetrahydrofuran at 0° was added gradually 1.607 g XIX with rapid stirring. About 0.5 ml water was added to bring XIX into solution, and the reaction mixture was stirred an additional 5 min. This was then diluted with 50 ml water, which caused a yellow oil to settle to the bottom. Most of the water–tetrahydrofuran was decanted, the residue was extracted with 15 ml ether, and the ether layer was dried. Evaporation of the ether left 0.740 g yellow crystals mixed with yellow oil. This was recrystallized from 5 ml anhydrous ether–1 ml pet. ether, affording 0.492 g (22%) bright yellow rhomboids, m.p. 59–59.5° (dec).¹⁸ The IR spectrum in KBr was characterized by the following peaks (cm^{-1}): 3050 w, 2940 w, 1682 s, 1600 w, 1578 w, 1537 (broad) s, 1404 m, 1389 s, 1320 w, 1240 m, 1209 s, 1179 m, 1150 m, 1075 m, 1049 w, 990 m, 892 s, 773 m, 687 s, 643 m, 617 w. The UV and visible spectra in cyclohexane exhibited the following absorption: λ_{max} 240 $\text{m}\mu$, ϵ_{max} 2.39×10^4 ; λ 280–290 $\text{m}\mu$ (plateau), ϵ_{280} 1.64×10^4 ; λ 400 $\text{m}\mu$, ϵ_{400} 248. The NMR spectrum in CS_2 showed signals at 6.54 τ (singlet) and 2.1–2.7 τ (complex) with the relative areas 6:5.

Thermal decomposition of XXII in carbon tetrachloride at 70°, carried out and followed in the NMR. A 0.3 ml. sample of a 0.650 molar solution of XXII in CCl_4 in a stoppered sample tube was heated to 70° in the Varian A-60 NMR sample chamber. The sample was spun continuously at 30 r/s and the spectra taken at 1–2 hr intervals, using a sweep width of 250 c/s. The concentration of XXII from each spectrum was calculated, and a plot of $-\log c$ vs. time gave a good straight line with $k_1 = 7.46 \times 10^{-4} \text{ sec}^{-1}$, $t_{1/2} = 9.30 \times 10^4 \text{ sec}$.

Rate study of decomposition of XXII in refluxing carbon tetrachloride (76.7°) from the visible spectrum. A 3.94×10^{-3} molar solution of XXII (100 ml) in carbon CCl_4 was refluxed at 76.7° (oil bath temp 83°) in a 250 ml roundbottom flask, equipped with reflux condenser and magnetic stirrer. Aliquots (5 ml) were withdrawn at timed intervals and their visible spectra scanned at 400 $\text{m}\mu$ on the Cary. A plot of $-\log c$ vs. time gave a good straight line with $k_1 = 3.09 \times 10^{-5} \text{ sec}^{-1}$, $t_{1/2} = 2.24 \times 10^4 \text{ sec}$.

Photolysis of XXII at >3000 Å and 11° for 23.3 hr. A 0.500 g sample of XXII dissolved in 170 ml benzene was photolysed at >3000 Å and 11° for 23.3 hr, as previously described. The solvent was evaporated from the clear solution at red. press. and room temp, leaving 0.417 g colorless oil. Basic extraction afforded 0.100 g (38%) benzoic acid, m.p. 120–120.5°. The neutral layer was washed with 10 ml water, dried and treated with 5 ml pet. ether, which caused the separation of 0.137 g white crystals. These were recrystallized from 2 ml CS_2 –1 ml CHCl_3 –0.5 ml pet. ether to give 0.079 g (29%, based on 2 moles starting material giving 1 mole product) ivory-colored rhomboids, m.p. 112.5–117.5°

$$\begin{array}{c} \text{S} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{dec}). \end{array}$$

This compound was assigned the structure $(\text{CH}_3)_2\text{NCSSCC}_6\text{H}_5$, XXIII. The IR spectrum in KBr showed the following peaks (cm^{-1}): 3060 w, 2930 w, 1700 s, 1600 w, 1588 w, 1510 (broad) s, 1455 s, 1417 w, 1385 s, 1316 w, 1310 w, 1245 s, 1206 s, 1175 s, 1150 m, 1130 w, 1100 w, 1070 w, 1050 w, 1000 m, 978 s, 885 s, 850 m, 770 s, 680 s, 645 s, 613 w. The UV spectrum in cyclohexane was characterized by the following absorptions: λ_{max} 242 $\text{m}\mu$, ϵ_{max} 2.30×10^4 ; λ 270 $\text{m}\mu$ (shoulder), ϵ_{270} 1.23×10^4 . The NMR spectrum in CS_2 showed signals at 2.05 τ (complex), 2.50 τ (complex), and 6.48 τ (singlet) with the relative areas 2:3:6. (Found: C, 46.65; H, 4.49. Calc. for $\text{C}_{10}\text{H}_{11}\text{NOS}_2$: C, 46.60; H, 4.30%.)

The filtrate remaining after the separation of XXIII was evaporated, leaving 0.185 g yellow oil. This was dissolved in 2 ml benzene and chromatographed on 10 g alumina with benzene–anhydrous ether as eluents, giving 0.018 g (26%, based on 1 mole starting material giving 1 g-atom S) elemental S,

¹⁶ J. v. Braun, *Ber. Dtsch. Chem. Ges.* 35, 820 (1902); E. S. Blake, *J. Amer. Chem. Soc.* 65, 1267 (1943).

¹⁷ F. Hallmann, *Ber Dtsch. Chem. Ges.* 9, 846 (1876).

¹⁸ The same m.p. is reported by v. Braun.⁵

m.p. 112–112.5°, mixed m.p. 113–114.5°, and 0.008 g (5%, based on 2 moles of starting material giving 1 mole of amide) XXI, m.p. after seeding 43.5–44.5°, mixed m.p. 44.5–45.5°.

Photolysis of an equimolar mixture of XXI and XXII at >3000 Å and 13° for 19.6 hr. Two portions of equimolar mixtures of 2.78×10^{-2} mole each of XXII and XXI, dissolved in 170 ml benzene, were photolyzed as before at >3000 Å and 13° for 19.6 hr. The solvent was evaporated and the residues combined to give 1.883 g yellow oil. This was dissolved in ether and extracted with base, as in the previous experiment, to yield 0.294 g (44%) benzoic acid, m.p. 116–117°. The neutral layer was washed with water, dried, and allowed to stand. Within 1 hr a crop of ivory-colored crystals had separated from the ether solution. These were collected, washed well with abs. EtOH, dried, yielding 0.020 g (3%, based on 2 moles starting material giving 1 mole product) XX, m.p. 139–139.5° (dec). The IR spectrum in KBr and the UV spectrum in cyclohexane were superimposable upon those of authentic XX. Further separation from the mother liquor gave 0.156 g white crystals. Recrystallization from 3 ml CHCl₃–0.5 ml anhydrous ether–0.5 ml pet. ether afforded 0.135 g (19%) XXIII. A final portion of yellow crystals separated from the 0.626 g residual oil. These were recrystallized from CHCl₃ to yield 0.010 g (6%) S, m.p. 112.5°, mixed m.p. 113–113.5°. The remaining 0.552 g yellow–orange oil was chromatographed on alumina to give 0.318 g (maximum recovery 77%, disregarding that a small percentage of this amide may have been formed from the photolysis of XXII) XXI, m.p. after seeding 43.5–44°, mixed m.p. 44.5–45°.