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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF CARBOXYLIC DITHIOCARBAMIC ANHYDRIDES AND RELATED COMPOUNDS—II[1,2]

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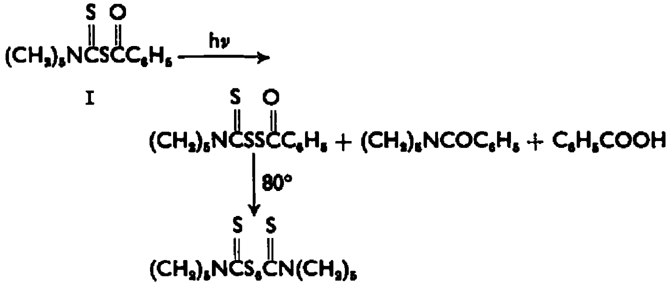
Abstract—Photolysis of a benzene solution of benzoic–pyrrolidine dithiocarbamic anhydride (II) yields benzoic acid, N-benzoylpyrrolidine (III) and pyrrolidyl thiuram hexasulphide (V). Similar photolysis of benzoic-morpholine dithiocarbamic anhydride (VII) gives benzoic acid, N-benzoylmorpholine (VIII) and morpholyl thiuram (13-S) polysulphide (X). A mechanism involving stepwise sulphur displacements on a growing thiocarbamyl polysulphide radical is proposed. Thermal decompositions of the anhydrides II and VII in refluxing solvents afford the corresponding amides, III and VIII, and carbon disulphide. Long chain morpholyl thiuram polysulphides can be generated both thermally and photochemically.

IT WAS shown earlier that the photolysis of benzoic-piperidine dithiocarbamic anhydride (I) yielded the unusual benzoyl piperidine-thiocarbamyl disulphide, as well as benzoic acid and N-benzoylpiperidine. The disulphide was converted to the thiuram hexasulphide by heat, in a reaction which appeared to proceed by free radical intermediates.



$$(CH_2)_5N\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{h\nu}$$

I

$$(CH_2)_5N\overset{S}{\overset{\|}{C}}SS\overset{O}{\overset{\|}{C}}C_6H_5 + (CH_2)_5NCOC_6H_5 + C_6H_5COOH$$

$$\Big\downarrow 80^\circ$$

$$(CH_2)_5N\overset{S}{\overset{\|}{C}}S_6\overset{S}{\overset{\|}{C}}N(CH_2)_5$$

Compound I was found to rearrange thermally in a first order process to the amide, N-benzoylpiperidine, and CS_2.

The present paper and the following one present a study of four analogs of the benzoic dithiocarbamic anhydride (I) which differ significantly from I in their photochemical and thermal reactions. The physical properties of the pyrrolidine (II) and the morpholine (VII) compounds are given in Table 1.

Anhydride II, a bright yellow oil, resisted all efforts at crystallization and, therefore, could not be obtained in a condition suitably pure for rate studies of its thermal decomposition in refluxing cyclohexane. The IR spectrum indicated that the principal impurity in II was a small amount of the corresponding amide, N-benzoylpyrrolidine (III), and because the amide III is stable photochemically, the photolysis of II could be studied profitably.

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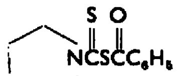
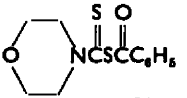
[1] We are indebted to Grant NSF-G11240 from the National Science Foundation for support of this work.

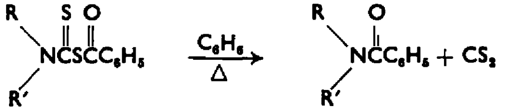
[2] Part I, E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron* **21**, 35 (1965).

TABLE 1. PHYSICAL DATA FOR ANHYDRIDES II AND VII

Anhydride	m.p. (dec)	C = O ν (cm^{-1})	Ultra-violet and visible spectra in cyclohexane	
			λ (mμ)	ε
 II	—	1680	238 (max) 283 400	2·39 × 10^4 1·54 × 10^4 223
 VII	122·5–123°	1680	240 (max) 292 412	1·97 × 10^4 1·32 × 10^4 199

The physical properties for anhydride II were determined from the freshly prepared yellow oil. Anhydride VII was a yellow, crystalline solid, whose synthesis from morpholyl dithiocarbamate (VI) and benzoyl chloride was made difficult because of its decomposition to the amide, N-benzoylmorpholine (VIII), resulting in low yields of ~28%.

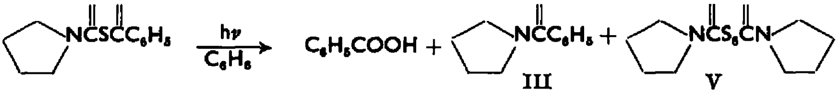
Thermal decomposition. Thermal decomposition of the pyrrolidine anhydride (II) in refluxing benzene gave the amide (III) in 97% yield in accord with the scheme previously suggested.[3] Similarly, thermal decomposition of the morpholine compound (VII) in warm benzene, catalysed by ethanol, which was shown to have a marked acceleratory effect on the decomposition of the piperidine analog of this anhydride,[2] gave the amide (VIII) in 87% yield.



R, R′ = $(CH_2)_4$ or $O(CH_2CH_2)_2$

A rate study of the decomposition of VII in refluxing cyclohexane (81·4°), in which the disappearance of VII was followed spectrophotometrically, gave good first order kinetics with $k_1 = 1{\cdot}7 \times 10^{-5}$ sec^{-1} and $t_{1/2} = 4{\cdot}1 \times 10^4$ sec.[4]

Photolytic decomposition. The photolysis of solutions of II (0·032 and 0·045 molar) in benzene at >3000 Å and 10–14° for ~63 hr, as previously described,[2] gave the following products with their respective yields: benzoic acid (25–31%), amide III (10–17%), and pyrrolidyl thiuram hexasulphide (V; 32–59%), m.p. analytical sample 134·5–135°. The hexasulphide (V[5]) was identified by elemental analysis, and by IR



and UV spectra. The IR spectrum in KBr is strikingly similar to that of pyrrolidyl thiuram disulphide (IV) which was synthesized for comparison. No trace of an

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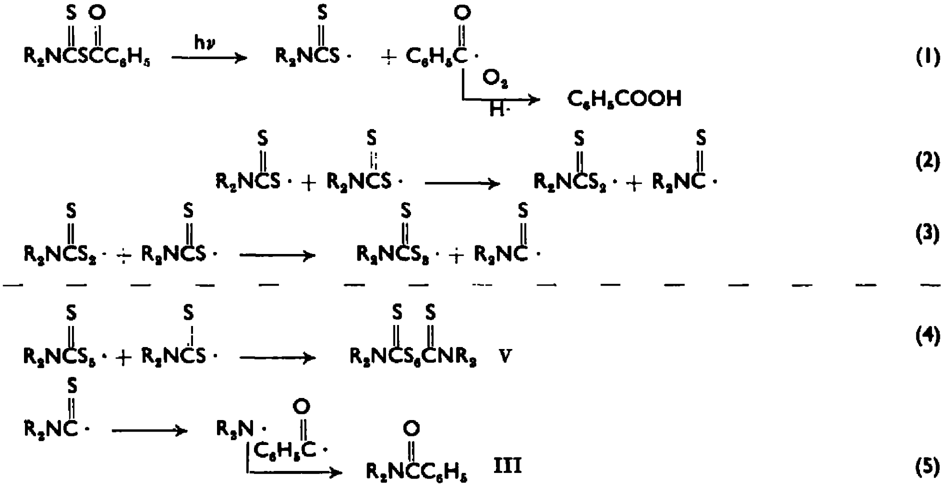
[3] D. S. Tarbell and R. P. F. Scharrer, *J. Org. Chem.* 27, 1972 (1962).

[4] Cf. the half-time of 2·4 × 10^4 sec for the piperidine analog I of VII in Ref. 2 under similar conditions.

[5] This hexasulphide does not appear to have been described before.

unsymmetric disulphide, analogous to that isolated[2] from the photolysis of the piperidine anhydride (see above) was found. The pyrrolidine hexasulphide (V) is presumably the result of a free radical process; this strengthens the argument that the piperidine hexasulphide[2] is formed by a free radical thermal process.

The following reaction scheme represents a possible route to the observed products.[6,7] The increased yield of V, obtained from the more concentrated photolysis



$$R_2N\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{h\nu} R_2N\overset{S}{\overset{\|}{C}}S\cdot + C_6H_5\overset{O}{\overset{\|}{C}}\cdot \qquad (1)$$

$$C_6H_5\overset{O}{\overset{\|}{C}}\cdot \xrightarrow[H\cdot]{O_2} C_6H_5COOH$$

$$R_2N\overset{S}{\overset{\|}{C}}S\cdot + R_2N\overset{S}{\overset{\|}{C}}S\cdot \longrightarrow R_2N\overset{S}{\overset{\|}{C}}S_2\cdot + R_2N\overset{S}{\overset{\|}{C}}\cdot \qquad (2)$$

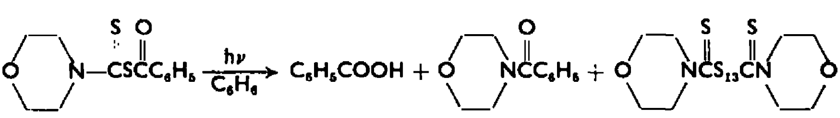
$$R_2N\overset{S}{\overset{\|}{C}}S_2\cdot + R_2N\overset{S}{\overset{\|}{C}}S\cdot \longrightarrow R_2N\overset{S}{\overset{\|}{C}}S_3\cdot + R_2N\overset{S}{\overset{\|}{C}}\cdot \qquad (3)$$

$$R_2N\overset{S}{\overset{\|}{C}}S_5\cdot + R_2N\overset{S}{\overset{\|}{C}}S\cdot \longrightarrow R_2N\overset{S}{\overset{\|}{C}}S_6\overset{S}{\overset{\|}{C}}NR_2 \quad \text{V} \qquad (4)$$

$$R_2N\overset{S}{\overset{\|}{C}}\cdot \longrightarrow R_2N\cdot \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}\cdot} R_2N\overset{O}{\overset{\|}{C}}C_6H_5 \quad \text{III} \qquad (5)$$

solution, suggests, for this run, a higher frequency of collision of thiocarbamyl polysulphide and dithiocarbamyl radicals, necessary for sulphur displacement on the growing polysulphide chain.

Differences in concentration of photolysis solutions of the morpholine anhydride (VII) reflect pronounced changes in the nature of the sulphur-containing product. A 40-hr photolysis of a 0·030 molar solution of VII in benzene at >3000 Å and 16° gave the following products in the yields indicated: benzoic acid (18%), amide VIII (56%) and the thiuram polysulphide, $C_{10}H_{16}N_2O_2S_{15}$, morpholyl thiuram (13-S) polysulphide (X; 37%), m.p. 111–112·5° (dec). Polysulphide X was identified by



VIII X

sulphur analysis, UV and IR spectra. Morpholyl thiuram disulphide (IX) was prepared and characterized, m.p. 144·5–145·5° (dec), and its IR spectrum in KBr compared to that of polysulphide X. Changes in the low frequency region, similar to those noted for the pyrrolidine and piperidine thiuram hexasulphides,[2] were evident

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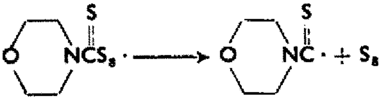
[6] Thiuram polysulphide radicals have been postulated previously, and have been invoked as retarders in polymerization studies; see, e.g., T. Ferington and A. V. Tobolsky, *J. Amer. Chem. Soc.* **80**, 3215 (1958).

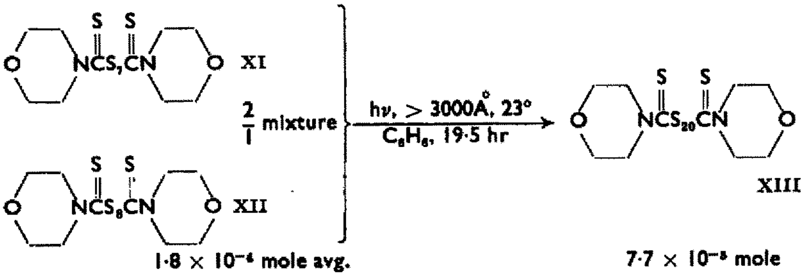
[7] Combination of any of the sulphide radical species in Eqs (3) and (4) to give a thiuram polysulphide with a shorter sulphur chain than V is possible; such products were not isolated, and hence, if formed, must have reacted further, by stages such as the following:

$$R_2NCS(S)_4SCNR_2 + R_2NCSS\cdot \longrightarrow R_2NCSS_6\cdot + 2R_2NCS\cdot$$

for the morpholine compound with the polysulphide chain. In contrast, photolysis of a 0·019 molar solution of VII in benzene for 24·2 hr at 22° yielded 24% of benzoic acid, 44% of amide VIII and 23% of elemental sulphur. No thiuram polysulphide was isolated. The postulated reaction scheme is similar to that outlined for anhydride II, except that a longer sequence of sulphur displacements ensues, before the final combination step to give X. For the more dilute run, perhaps a cleavage step similar to that below, producing free sulphur, occurs before successful encounters can be made between dithiocarbamyl radical and the growing polysulphide chain.[8] The tendency for the morpholine photolytic system to generate longer chain polysulphides than the pyrrolidine or piperidine systems is explicable in terms of the comparative solubilities of the analogous thiuram polysulphides. The pyrrolidine and piperidine thiuram disulphides are much less soluble than morpholine thiuram disulphide (IX) in chloroform or carbon disulphide, which are the most suitable solvents for these systems. Further, the thiuram hexasulphides of pyrrolidine and piperidine are nearly insoluble in hydrocarbon solvents and thus precipitate very readily from solutions in which they are formed. Perhaps, only after the formation of a more extended sulphur chain, does the morpholine polysulphide linkage approach these solubility limits.



The facility of formation of morpholine thiuram polysulphide products was illustrated by the rapid uptake of sulphur atoms by disulphide (IX) in boiling carbon disulphide to form a mixture of the thiuram heptasulphide (XI) and octasulphide (XII). Moreover, the photolysis of this resulting mixture of XI and XII in benzene for 19·5 hr led to the isolation of a thiuram polysulphide, $C_{10}H_{16}N_2O_2S_{22}$ XIII, containing a chain of twenty sulphur atoms. The conversion of the mixture of XI and XII to XIII was quantitative with respect to sulphur atoms, probably accompanied by photolytic destruction of the excess morpholyl fragments. The three new morpholyl polysulphides were also identified by sulphur analyses and spectral data. The m.ps of XIII and of the mixture of XI and XII were all very close to that of rhombic sulphur.



Disulphides IV and IX were shown to be completely stable to the irradiation conditions and, thus, were apparently not photochemical intermediates in the reactions studied.

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[8] Cf. the reaction series in R. E. Davis and C. Perrin, *J. Amer. Chem. Soc.* 82, 1590 (1960).

EXPERIMENTAL[*]

Materials. Benzoyl chloride (Baker "Analyzed" Reagent) was redistilled before use. Cyclohexane (Eastman Spectro Grade), benzene (Mallinckrodt), and all other solvents (Mallinckrodt) were used without further purification.

Pyrrolidyl dithiocarbamate was prepared from redistilled pyrrolidine and CS_2 and recrystallized from 95% EtOH in 65% yield, m.p. 152–153° (dec).

Benzoic-pyrrolidine dithiocarbamic anhydride (II). To a solution of 2·184 g pyrrolidyl dithiocarbamate in 10 ml $CHCl_3$ in an ice–MeOH bath was added dropwise 1·405 g benzoyl chloride, with rapid stirring. The solution immediately became bright yellow. The solvent was evaporated under red. press. at room temp, leaving a yellow, semi-crystalline paste. This was treated with 10 ml anhydrous ether, and the amine hydrochloride filtered off. The solvent was removed under red. press. at room temp, leaving 2·126 g (85%) yellow oil, which failed to crystallize upon standing or upon treatment with several solvent combinations. The IR spectrum of the yellow oil was characterized by the following peaks (cm^{-1}): 3080, 3060, 3030 w (triplet), 2980, 2950, 2920, 2880, 1680 s, 1630 w, 1600 w, 1570, 1470 (broad), 1445 s, 1330, 1250, 1205, 1177, 1151, 1100, 1087 w, 1048 w, 1010, 956, 890 s, 865 (shoulder), 820 w, 772, 682 s, 643. The UV and visible spectra in cyclohexane showed the following absorptions: λ_{max} 238 mμ, ε_{max} $2{\cdot}39 \times 10^4$; λ 283 mμ, ε_{283} $1{\cdot}52 \times 10^4$; λ 400 mμ, ε_{400} 223.

In a separate experiment, 2·5 g of the yellow liquid anhydride (II) was seeded with a tiny crystal of N-benzoylpyrrolidine (III). Pale yellow crystals gradually separated, and crystallization was aided by placing the flask on the rotary evaporator for several minutes, during which time considerable bubbling occurred in the yellow oil. The pale yellow crystals were filtered, washed with 3 ml pet. ether, and dried, and weighed 1·469 g. Two recrystallizations from 2 ml anhydrous ether–1 ml pet. ether yielded 0·837 g (49%) transparent rhombohedra, m.p. 53–54°, whose IR spectrum in KBr was identical to that of III, prepared below. (Found: C, 75·68; H, 7·54. Calc. for $C_{11}H_{13}NO$: C, 75·40; H, 7·48%.)

N-*Benzoylpyrrolidine* was prepared from benzoyl chloride, pyrrolidine and NaOH aq; it was purified by chromatography on alumina, and the colourless oil obtained crystallized in a dry-ice–acetone bath, m.p. 52·5–53°. The UV spectrum in cyclohexane showed λ_{max} 240 mμ (shoulder), ε_{max} $1{\cdot}20 \times 10^4$.

Pyrrolidyl thiuram disulphide (IV). To a solution of 2·184 g I in 25 ml 95% EtOH was added dropwise a solution of 1·27 g I_2 in 30 ml 95% EtOH with rapid stirring. The I_2 consumption was quantitative, and the white, crystalline product weighed 1·384 g (95%), m.p. 139·5–141° (dec). Recrystallization from 7 ml CS_2–6 ml abs EtOH yielded 1·328 g (91%) translucent rhomboids, m.p. 143–144° (dec). The IR spectrum in KBr was characterized by the following peaks (cm^{-1}): 2980, 2965, 2880, 1460 s, 1440 vs (broad), 1343, 1327, 1292 vw, 1251, 1214, 1174, 1150 s, 1037, 1008, 996, 953 s, 914 w, 852, 810 w, 680 w. The UV spectrum in cyclohexane showed λ230 mμ, ε_{230} $2{\cdot}02 \times 10^4$; λ285 mμ (shoulder); ε_{285} $1{\cdot}24 \times 10^4$. (Found: C, 41·19; H, 5·67. Calc. for $C_{10}H_{16}N_2S_4$: C, 41·06; H, 5·51%.)

Although this thiuram disulphide is mentioned repeatedly in the literature as a fungicide, there does not seem to be an adequate characterization of it.

Thermal decomposition of anhydride II *in refluxing benzene.* A solution of 1·114 g II in 75 ml benzene was refluxed at 80° (oil bath temp 86°) for 55 hr with thorough agitation. At the end of 19- and 38-hr intervals the reflux was interrupted, the solvent removed, and the IR spectrum taken of the residual, yellow oil. This was then redissolved in 75 ml benzene and the reflux continued for a total period of 55 hr. The IR spectra showed a gradual diminution of the carbonyl band at 1680 cm^{-1} and the growth of a new band at 1630 cm^{-1}. The spectrum of the final 0·880 g yellow oil exhibited broader less distinct peaks than those of the preceding samples, with the 1680 cm^{-1} band having nearly disappeared. This oil was chromatographed on 20 g alumina to give 0·753 g (97%) III, m.p. 52·5–53° mixed m.p. 52·5–53°.

Photolysis of II *at* >3000 Å *with control sample.* A 1·444 g sample of II dissolved in 175 ml benzene, accompanied by a 0·425 g control sample in 50 ml benzene and shielded from all light, was photolysed as previously described at >3000 Å and a bath temp of 10° for 62·8 hr. The solvent was

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[*] All m.ps were taken, with correction, in a well circulated oil bath with a temp rise of 2°/min. All chromatograms were performed on Woelm activity grade I alumina. IR spectra were taken on the Perkin–Elmer model 421 and UV and visible spectra on the Cary Model 11. Micro-analyses are by Antonio G. Revilla of this laboratory and by Micro-Tech laboratories.

evaporated from the control, leaving 0·412 g yellow oil, whose IR spectrum was very similar to that of starting material, with some broadening of the corresponding peaks. Evaporation of solvent from the photolysis mixture afforded 1·169 g yellow oil, whose IR spectrum showed a broad band at 1740–1680 cm^{-1}, new peaks at 1600 cm^{-1}, 718 cm^{-1} and a doublet at 680 cm^{-1}. This photolysis residue was treated with 6 ml anhydrous ether–0·5 ml $CHCl_3$ and cooled in a dry-ice–MeOH bath, which caused the separation of 0·214 g yellow solid. Further treatment of the filtrate with anhydrous ether–pet. ether gave an additional 0·016 g white crystals. The combined 0·230 g of solid was recrystallized from 4 ml $CHCl_3$–4 ml CS_2–4 ml EtOH, yielding 0·128 g (32% based on 6 moles of starting material giving 1 mole product) ivory crystals, m.p. 134·5–135° (dec), whose elemental analysis corresponded to $C_{10}H_{16}N_2S_8$, pyrrolidyl thiuram hexasulphide (V). The IR spectrum in KBr was very similar to that of IV, and exhibited the following bands (cm^{-1}): 2975, 2950, 2870, 1470 s, 1340, 1330 (doublet), 1255, 1220 w, 1180 w, 1152 s, 1040 w, 1000, 952 s, 918 w, 854 w, 680 w. The ultraviolet spectrum in cyclohexane showed λ_{max} 250 mμ, ε_{max} $2{\cdot}20 \times 10^4$; λ280 mμ, ε_{280} $1{\cdot}54 \times 10^4$. (Found: C, 28·61; H, 3·89; N, 6·77; S, 60·75. Calc. for $C_{10}H_{16}N_2S_8$: C, 28·54; H, 3·83; N, 6·66; S, 60·97%.)

Evaporation of solvent from the filtrate of the photolysis mixture, after the removal of V, left 0·756 g yellow oil. The IR spectrum was quite indistinct, but was characterized by aromatic and aliphatic C—H stretching, broad absorption in the 3200–2300 cm^{-1} region, and carbonyl bands at 1715 cm^{-1} and 1630 cm^{-1} only. The yellow oil was dissolved in 10 ml anhydrous ether and extracted with 10 ml 10% Na_2CO_3 aq. The aqueous layer was acidified, giving a white precipitate, which was extracted with anhydrous ether, and the ether layer dried. Evaporation of the ether yielded 0·220 g (31%) benzoic acid, m.p. 113–114°, mixed m.p. 116–117°. The original ether layer afforded, after seeding, 0·199 g crude amide III. This was recrystallized from 3 ml anhydrous ether–2 ml pet. ether to give 0·167 g (17%) of III, m.p. 49·5–51°, mixed m.p. 49·5–51°.

A similar basic workup of the control sample yielded no benzoic acid, and the IR spectrum of the recovered neutral, yellow oil was identical to that of the original control sample.

The photolysis experiment was repeated with 1·978 g II in 170 ml benzene at 14° for a 64-hr irradiation period. Similar workup of the 1·976 g photolysis residue gave 0·224 g (59%) V, m.p. 133–134·5° (dec), mixed m.p. with the analytical sample 136–136·5° (dec), 0·241 g (25%) benzoic acid, m.p. 117·5–119°, mixed m.p. 120·5–121·5°, and, after chromatography of the crude amide III on alumina, 0·151 g (10%) pure III, m.p. 51·5–52·5°, mixed m.p. 52·5–54°.

Morpholyl dithiocarbamate VI was prepared from redistilled morpholine and CS_2 and recrystallized from water–MeOH as ivory needles in 75% yield, sublimation pt. 180–182°.

Decomposition of anhydride VII *in warm benzene, catalysed by ethanol to give amide* VIII. A solution of 1·24 g VII in 6 ml benzene was heated gently on the steam bath for 5 min, and 4 ml 95% EtOH was added dropwise with swirling. The flask was removed from the heat, and within 3 min the solution became colourless. Solvent evaporation left 0·881 g colourless oil which crystallized when seeded with VIII. Recrystallization from 10 ml ether–4 ml pet. ether gave 0·775 g (87%) pure N-benzoylmorpholine, m.p. 74–75°. The UV spectrum in cyclohexane showed λ_{max} 240 μ (shoulder), ε_{max} $4{\cdot}69 \times 10^3$. (Found: C, 69·05; H, 6·90. Calc. for $C_{11}H_{13}NO_2$: C, 69·09; H, 6·85%.)

Benzoic-morpholine dithiocarbamic anhydride VII. To a suspension of 1·26 g powdered VI in 10 ml $CHCl_3$, cooled in an ice–MeOH bath, was added dropwise 0·703 g benzoyl chloride with rapid stirring. The solvent was then removed at room temp, leaving a bright yellow paste. This was treated with 20 ml anhydrous ether, causing portions of the yellow, crystalline anhydride to separate along with the insoluble amine hydrochloride. The solid was then filtered and treated with 12 ml benzene. The yellow anhydride dissolved and was filtered from the amine hydrochloride. The benzene was evaporated from the filtrate at room temp, leaving bright yellow crystals. These were washed with 1·5 ml ice-cold 95% EtOH and dried. The original ether filtrate (bright yellow) was evaporated leaving a mixture of colourless, transparent crystals and bright yellow crystals. These were treated with 3 ml ice-cold 95% EtOH, which dissolved the transparent crystals and left the yellow crystals. These were filtered and combined with the first portion of yellow crystals for a total crude yield of 0·396 g (30%) anhydride VII. This was recrystallized from 4 ml benzene–3 ml pet. ether, giving 0·375 g (28%) VII, m.p. 122·5–123° (dec), with crystalline structure change at 121·5–122·5°. The IR spectrum in KBr was characterized by the following peaks (cm^{-1}): 3060, 2970, 2920, 2860, 1680 s, 1595 w, 1486 s, 1440, 1390, 1308, 1270 s, 1208 s, 1175, 1110, 1030, 987, 890 s, 870, 775, 700, 683 s, 640. The UV and visible spectra in cyclohexane showed the following absorptions: λ_{max} 240 mμ, ε_{max} $1{\cdot}97 \times 10^4$; λ292 mμ, ε_{292} $1{\cdot}32 \times 10^4$; λ412 mμ, ε_{412} 199.

The EtOH filtrates were combined and evaporated, leaving 0·779 g crystalline N-benzoylmorpholine (VIII). Recrystallization from 10 ml anhydrous ether–2 ml pet. ether afforded 0·524 g (55%) VIII, m.p. 71·5–73°, mixed m.p. with analytical sample of VIII 73–74°.

Morpholyl thiuram disulphide IX. To a suspension of 2·503 g powdered VI in 70 ml 95% EtOH was added dropwise a solution of 1·27 g I_2 in 30 ml 95% EtOH with rapid stirring. The initial, white solid in suspension was gradually replaced by a pale tan solid during the addition. The I_2 uptake was quantitative. The pale tan crystals were filtered, washed with 50 ml water, dried and weighed 1·106 g. This was recrystallized from 45 ml CS_2–5 ml $CHCl_3$–15 ml 95% EtOH, yielding 0·874 g (54%) transparent, tan plates, m.p. 144·5–145·5° (dec). The IR spectrum in KBr was characterized by the following peaks (cm^{-1}) 2970, 2920, 2860, 1476 s, 1420 s, 1360 w, 1300, 1265 s, 1230 s, 1210, 1176, 1112 s, 1060, 1030 s, 976 s, 910 w, 866 w, 855, 806–793 w (doublet), 642–630 w. The UV spectrum in cyclohexane showed λ 221 mμ, ε_{221} $2\cdot06 \times 10^{4}$; λ 240–290 mμ (plateau), ε_{250} $1\cdot53 \times 10^{4}$. (Found: C, 37·25; H, 5·04. Calc. for $C_{10}H_{16}N_2O_2S_4$: C, 37·01; H, 4·97%.)

Rate study of decomposition of VII *in refluxing cyclohexane.* $5\cdot93 \times 10^{-3}$ molar solution of VII (125 ml) in cyclohexane was refluxed at 81·4° (oil bath temp 89°) in a 250 ml round-bottom flask, equipped with a drying tube and magnetic stirrer. Five ml aliquots were withdrawn at timed intervals and their visible spectra scanned on the Cary. From the following data, a plot of log c vs. time gave a good straight line with $k_1 = 1\cdot7 \times 10^{-5}$ sec^{-1}, $t_{1/2} = 4\cdot1 \times 10^{4}$ sec.

Time interval (hr)	0·0	1·1	2·2	3·7	5·1	6·5	7·7	8·8
Absorbancy at λ 412 mμ	1·18	1·05	0·99	0·93	0·83	0·76	0·70	0·66
Conc. (moles/l. $\times 10^{3}$)	5·93	5·27	4·97	4·65	4·14	3·79	3·49	3·31

Photolysis of VII *in benzene at* >3000 Å. A solution of 1·084 g VII in 170 ml benzene (bright yellow in colour) was photolysed as previously described at >3000 Å and a bath temp of 16° for 39·6 hr. The solvent was evaporated from the colourless photolysis solution leaving 1·450 g viscous, pale yellow oil. Treatment with 5 ml anhydrous ether–0·6 ml pet. ether caused the separation of 0·027 g tan-coloured solid. This was filtered, and the solvent was evaporated from the filtrate, leaving 1·147 g yellow oil. Basic extraction of this residue yielded 0·089 g (18%) benzoic acid, m.p. 115–116°, mixed m.p. 115·5–116°. The neutral layer was washed with 10 ml water and the ether was evaporated, giving a brown oil. Treatment with 2 ml $CHCl_3$–10 ml MeOH caused the separation of 0·080 g small, needle-like crystals. These were filtered and combined with the 0·027 g initial solid and recrystallized from 3 ml $CHCl_3$–2 ml 95% EtOH to yield 0·079 g (37%, based on 13 moles starting material giving 1 mole product) pale yellow needles, whose sulphur analysis corresponded to $C_{10}H_{16}N_2O_2S_{15}$, morpholyl thiuram (13-S) polysulphide X, m.p. 111–112·5° (dec). The IR spectrum in KBr resembled that of thiuram disulphide IX, with noticeable changes in the low frequency region,[10] and was characterized by the following peaks (cm^{-1}): 2980 w, 2900 w, 2860 w, 1467, 1436, 1424 s, 1390 w, 1358 w, 1300, 1271 s, 1233, 1215 s (doublet), 1115 s, 1060, 1035, 985 s, 907 w, 863, 809 w, 640 w. The UV spectrum in cyclohexane showed the following absorptions: λ 263 mμ, ε_{263} $1\cdot52 \times 10^{4}$; λ 280 mμ, ε_{280} $1\cdot46 \times 10^{4}$. (Found: S, 70·83. Calc. for $C_{10}H_{16}N_2O_2S_{15}$: S, 71·02%.)

Upon standing, 0·473 g colourless crystals of VIII separated from the $CHCl_3$–MeOH filtrate, after the removal of X. Recrystallization from 7 ml anhydrous ether–4 ml pet. ether afforded 0·433 g (56%) VIII, m.p. 72·5–73·5°, mixed m.p. 74·75°.

Photolysis of VII *in benzene at* >3000 Å *with control sample.* A 0·755 g sample of VII was dissolved in 170 ml benzene and a 7 ml aliquot was removed and shielded from all light. The remaining 163 ml VII was photolysed, accompanied by the control sample, as previously described at >3000 Å and 22° for 24·2 hr. Solvent evaporation from the yellow control sample left 0·046 g yellow oil, which crystallized; the crystals, after washing with 1·5 ml 95% EtOH, melted at 123–124·5° (dec), with a crystalline structure change at 121–122°. The IR spectrum in KBr was identical to that of the starting

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[10] The IR spectrum in KBr of a mechanical mixture of approximately equal amounts by weight of IX and free sulphur is identical to that of pure IX, suggesting that substance X is indeed a long sulphur-chain thiuram polysulphide rather than a mixture of the disulphide and free sulphur. Further evidence that X represents a true compound rather than a 1:13 molar mixture of sulphur and thiuram disulphide IX is offered from the observation that sulphur and IX, in this molar ratio, crystallize independently from a $CHCl_3$–EtOH solution. The crystals of each component are easily distinguishable and separable, and the mixture m.ps of each with an authentic sample show no depression.

material. The solvent was evaporated from the colourless photolysis solution, leaving 0·887 g yellow oil, which, upon basic extraction, yielded 0·089 g (24%) benzoic acid, m.p. 115–116°, mixed m.p. 117·5–119°. Treatment of the 0·634 g oily residue with $CHCl_3$–EtOH gave 0·083 g yellow–brown solid, which was recrystallized from 1 ml CS_2–2 ml $CHCl_3$–6 ml EtOH to yield 0·023 g (23%, based on 1 mole of starting material giving 1 g-atom S) free S, m.p. 110·5–113°, mixed m.p. 110·5–112°, which gave no IR absorption from a concentrated KBr pellet. The final photolysis residue crystallized, affording, after recrystallization from 2 ml anhydrous ether–2 ml pet. ether, 0·265 g (44%) VIII, m.p. 74–75°, mixed m.p. 73·5–74·5°.

Treatment of a 1:11 *molar mixture of thiuram disulphide* IX *and sulphur with boiling carbon disulphide.* A solution of 0·1623 g IX and 0·1764 g recrystallized S in 5 ml CS_2 was boiled for 3 min on the steam bath. The solution was then filtered and 0·5 ml 95% EtOH was added, causing 0·195 g pale yellow crystals to separate. These were recrystallized from 3·5 ml $CHCl_3$–2 ml EtOH, affording 0·182 g pale yellow prisms, m.p. 114–115° (dec), whose S analysis suggested an approximately 2:1 molar mixture of $C_{10}H_{16}N_2O_2S_9$, morpholyl thiuram heptasulphide XI, and $C_{10}H_{16}N_2O_2S_{10}$, morpholyl thiuram octasulphide XII. The IR spectrum in KBr resembled that of IX with distinct changes in the low frequency region, and was characterized by the following peaks (cm^{-1}): 2965 w, 2915 w, 2855 w, 1470 s, 1422 s, 1357 w, 1300, 1267 s, 1230 s, 1210 (shoulder), 1176 w, 1111 s, 1060, 1030 s, 979 s, 906 w, 856 w, 800 w, 630 w. The UV spectrum in cyclohexane (based on an avg. mol. wt. of 493·6 g) showed λ 263 mμ, ε_{263} 8·53 × 10^3; λ 280 mμ, ε_{280} 7·74 × 10^3. (Found: S, 61·01. Calc. for $C_{10}H_{16}N_2O_2S_{10}$: S, 62·06. Calc. for $C_{10}H_{16}N_2O_2S_9$: S, 59·52%.)

Photolysis of the above 2:1 *molar of* XI *and* XII *in benzene at* >3000 Å. A 0·087 g sample of the above mixture of polysulphides was dissolved in 170 ml benzene and photolysed as previously described at >3000 Å and 23° for 19·5 hr. The photolysis solution was filtered and the solvent evaporated, leaving 0·100 g of yellow–brown solid. This was recrystallized from 2 ml $CHCl_3$–1·5 ml 95% EtOH, affording 0·069 g straw-coloured crystals, m.p. 111–112° (dec), whose S analysis indicated morpholyl thiuram (20-S) polysulphide XIII. The IR spectrum in KBr resembled closely that of the starting material and of the thiuram polysulphide X. (Found: S, 78·16. Calc. for $C_{10}H_{16}N_2O_2S_{22}$: S, 78·24%.)