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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF CARBOXYLIC DITHIOCARBAMIC ANHYDRIDES AND RELATED COMPOUNDS[1]

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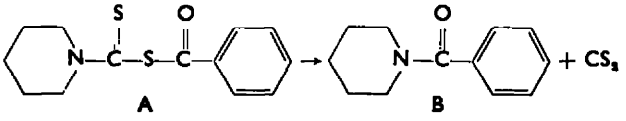
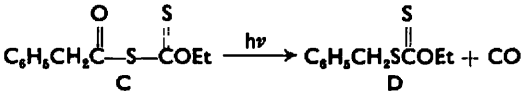
Abstract—The thermal decomposition of benzoic-piperidine dithiocarbamic anhydride A gives the amide, benzoyl piperidide B, and CS_2. Photolysis of A under nitrogen gives amide B (74%), benzoic acid (9%), and the unusual benzoyl cyclopentamethylene thiocarbamyl disulfide G (34%). Photolysis of A in the presence of oxygen yields about 6% of the cyclopentamethylene thiuram disulfide E and 33% of benzoic acid. The most reasonable pathway for this photolysis involves formation of the radicals $C_6H_5\overset{\overset{O}{\|}}{C}\cdot$ and $C_6H_{10}N\overset{\overset{S}{\|}}{C}S$. Compound G is photolyzed slowly to the amide B. Thermal decomposition of G in refluxing cyclohexane yields amide B and cyclopentamethylene thiuram hexasulfide H as the only isolable products. Thermal decomposition of G can initiate free-radical copolymerization.

IN AN earlier paper,[2] it was shown that mixed carboxylicdithiocarbamic anhydrides, such as A, decompose thermally to give the amide B, and carbon disulfide. Similarly,



the acyl xanthate C has been found to decompose thermally to give the corresponding ester and carbon disulfide.[3] Photolysis of C in refluxing benzene gave the xanthate D, with decarbonylation of the acyl group and no carbon disulfide expulsion.[3]



In the present work, the thermal decomposition of A in boiling cyclohexane yielded 89% of the amide B, and 67·5% of theory of carbon disulfide was trapped as the xanthate. A rate run at 80·5° in cyclohexane, in which the disappearance of the mixed anhydride A was followed spectrophotometrically, gave good first order kinetics, with $k_1 = 2{\cdot}85 \times 10^{-5}$ sec^{-1}. Decomposition of A in ethanol was very much faster, having occurred before reflux temperature was attained, and yielded 95·5% of the amide; the more rapid rate in the more polar solvent ethanol, indicates that the transition state for the A → B transformation involves a considerable degree of charge formation and ionic character.

[1] We are indebted to Grant NSF-G11240 from the National Science Foundation for support of this work. A preliminary abstract appeared in *Science* **144**, 568 (1964).
[2] D. S. Tarbell and R. P. F. Scharrer, *J. Org. Chem.* **27**, 1972 (1962).
[3] D. H. R. Barton, M. V. George and M. Tomoeda, *J. Chem. Soc.* 1967 (1962).

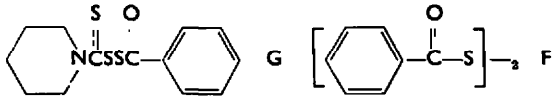
Photolytic decomposition

Results from the photolyses of solutions of the mixed anhydride A in the concentration range 0·01 to 0·03 M in cyclohexane or benzene with two light sources, one emitting light principally of wavelength 2537 Å, the other of wavelength >3000 Å, are summarized in Table 1. The reaction at >3000 Å resulted in less tar and less secondary decomposition of products. As indicated, the products obtained were the amide B, benzoic acid, the thiuram disulfide E and the new unsymmetrical benzoyl cyclopentamethylene thiocarbamyl disulfide G. The following facts were also established experimentally:

1. No thermal decomposition of A occurs under the photolytic conditions employed.
2. Compounds B and G do not hydrolyze to benzoic acid under the workup conditions.
3. No benzene or benzaldehyde is produced in the photolysis of A in cyclohexane.
4. Only negligible amounts of carbon disulfide are produced in the photolysis of A in either cyclohexane or benzene.
5. Carbon disulfide in a concentration of ca. 10^{-2} M is stable to the photolysis conditions.
6. Perbenzoic acid in benzene solution is stable to the photolysis conditions, but when added to a solution of A in benzene and photolyzed, gives rise to an increased yield of benzoic acid.

Item 3 was demonstrated by UV analysis of the recovered solvent, item 4 by the UV and vapor phase chromatographic [v.p.c.] analyses of the recovered solvents, and item 5 by the photolysis of solutions [0·016 M and higher] of carbon disulfide in cyclohexane.

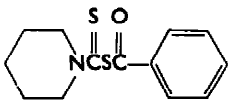
Compound G, a major product isolated from the photolysis, was assigned the structure below, benzoyl cyclopentamethylene thiocarbamyl disulfide, m.p. 108–115° (dec). The disulfide analysis agreed with the empirical formula $C_{13}H_{15}NOS_3$. The IR spectrum of G in KBr was strikingly similar to that of A, with a shift of the carbonyl



frequency from 1680 cm^{-1} to 1697 cm^{-1} and a displacement of the sharp singlet at 680 cm^{-1} by a symmetrical doublet centered at 675 cm^{-1}, constituting the only significant differences. The IR spectrum also resembled quite closely that of an equimolar mixture of cyclopentamethylene thiuram disulfide E and dibenzoyl disulfide F in KBr, but the peaks shown by compound G were much sharper. The contributions of both fragments C_6H_5COS— and $[CH_2]_5NCSS$—, can readily be seen from a comparison of the spectrum of G with those of pure E and F in KBr.[4]

The UV absorption data for compounds E, F and G in cyclohexane are summarized in Table 2. Compound G, in contrast to the mixed anhydride A, showed no absorption in the visible region.

[4] The unsymmetrical disulfide G appears to be of a new type; examples are not listed by E. E. Reid, *Organic Chemistry of Bivalent Sulfur* Vol. 4. Chemical Publishing Co., 1962, and we have not found any elsewhere.

TABLE 1. PHOTOLYSIS OF  (A)

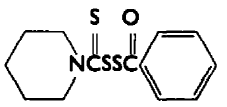
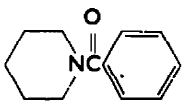
Solvent	Conditions temp,	Wavelength	Photolysis time, hr	Starting material	Yields, % [G] 	[E] 	Benzoic Acid	[B] 
cyclo-hexane	in air, 10°	2537 Å	48·7	none	27	none	23	27
benzene	in air, 16°	2537	120	none	31	2·3	28	22
benzene	in air 22°	>3000	24	none	45	none	21	38
benzene	under N_2 22°	>3000	24	32·3	34	none	9	74
benzene	under O_2, 22°	>3000	24	none	45	6	33	13
benzene	under O_2, 22°	>3000	10	28·1	20	6	24	8

TABLE 2. ULTRAVIOLET ABSORPTION DATA FOR DISULFIDES E, F AND G

Compound	λ_{max} [mμ]	ε_{max}	λ[mμ]	ε
$[[CH_2]_5NC(=S)—S]_2$ [E]	219	2.32×10^4	240–275 (plateau)	1.42×10^4
$[C_6H_5COS]_2$ [F]	240	2.88×10^4	262 (shoulder)	1.84×10^4
$[CH_2]_5NC(=S)—S—COC_6H_5$ [G]	243	2.19×10^4	273 (shoulder)	1.28×10^4

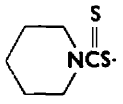
The NMR spectrum of the unsymmetrical disulfide G showed signals at 8·25 τ [singlet], 5·87 τ [triplet], and 1·93, 2·47 τ [complex] with the relative areas 6:4:5. These signals were assigned, respectively, to the six piperidine-ring protons non-adjacent to nitrogen, the four piperidine-ring protons adjacent to nitrogen, and the five aromatic protons.

Photolysis of compound G in benzene at 2537 Å showed some decomposition to the amide B. Photolysis of G in benzene at >3000 Å showed far less extensive decomposition to B. From the thermal decomposition of G without solvent, only amide B and sulfur were isolated.

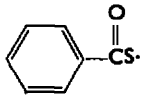
The symmetric disulfides, E and F, were shown to be photolytically stable at >3000 Å. In addition, photolysis of an equimolar mixture of E and F at >3000 Å gave only unchanged starting material. Attempts to synthesize the unsymmetrical disulfide G by oxidation of an equimolar mixture of the piperidine salt of piperidinedithiocarbamic acid and potassium thiobenzoate, C_6H_5COSK, and by acid catalyzed exchange between the thiobenzoate and the thiuram disulfide E were unsuccessful. Only the symmetrical products were obtained.

A scheme for the photolytic decomposition of A is proposed in Chart 1.

That the initial homolysis should proceed as in Eq. (1) is in accord with the above-mentioned photolysis of the acyl xanthates.[3] Furthermore, since G can arise only from an attack of



on A, an attack of

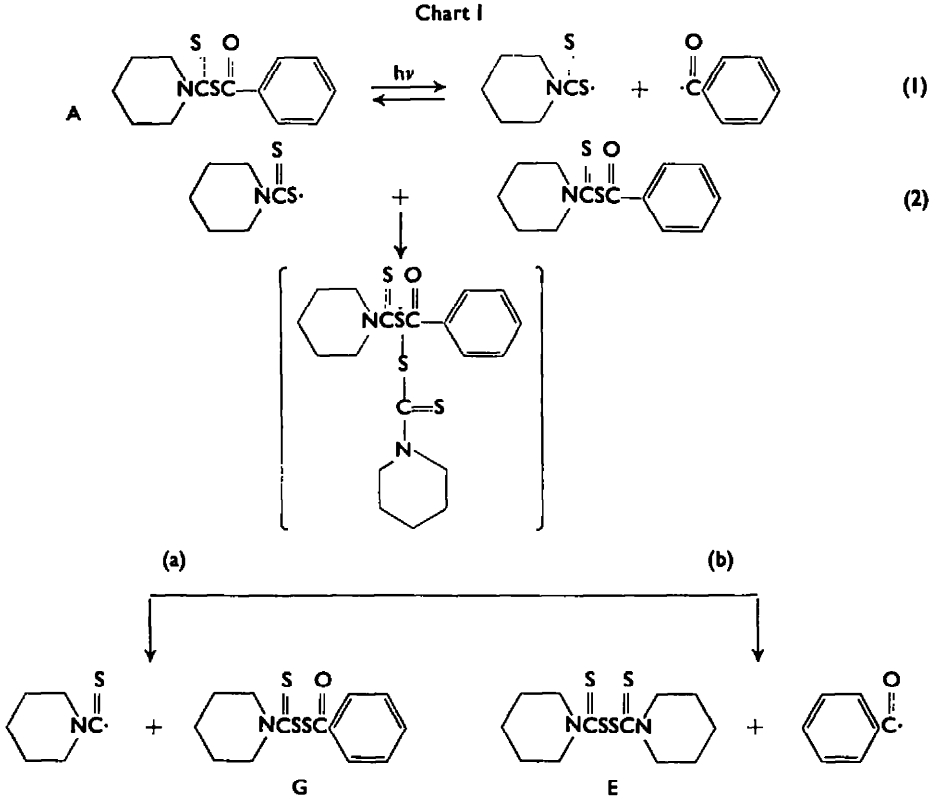


on A, or a combination of these two radicals, the appearance of E in the products, as well as the failure to find dibenzoyl disulfide F in the products, tends to exclude the last two possibilities. Indeed, there is no need to invoke the appearance of the thiobenzoate radical $C_6H_5COS\cdot$ in any phase of the reaction. The intermediate[5] pictured in Eq. (2) may cleave by either path (a) or (b), and the high product ratio of

[5] R. J. Gritter and D. J. Carey, *J. Org. Chem.* **29**, 1160 (1964), present some evidence for this type of intermediate in the interaction of *t*-butoxy radicals with diphenyl sulfide.

G/E suggests that the activation energy for (b) is higher than for (a). The production of benzoic acid from benzoyl radicals in the presence of oxygen has been observed[6,7] but surprisingly little is known about the process; it obviously requires oxygen and a source of abstractable hydrogen. The higher yield of benzoic acid in the presence of oxygen is to be expected, and the α-hydrogens of the piperidine ring of the starting material or of an intermediate species may serve as the hydrogen source. No benzaldehyde could be isolated in the present work and there was no benzil detected, which was formed by benzoyl radicals in another system.[7]

Chart I



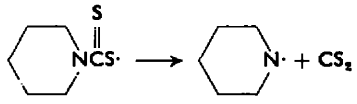
The addition of perbenzoic acid to the photolysis solution resulted in a proportionate increase in the yield of benzoic acid, and effected no other changes in the products of the reaction. Since perbenzoic acid alone in benzene solution was shown to be stable to the photolysis conditions, it constitutes a possible precursor of benzoic acid in the photolysis of pure A.

The benzoyl radicals may react with starting material, with piperidyl radicals or with some precursor of the latter, to form the amide B. The fact that the two modes of disappearance of benzoyl radicals, i.e. formation of benzoic acid and formation of amide, were in competition was illustrated by the photolyses under nitrogen and under oxygen. In the former case, less oxygen was available for benzoic acid formation, and

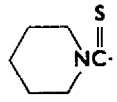
[6] H. Wieland, H. vom Hove and K. Börner, *Liebigs Ann.* **446**, 31 (1926).
[7] L. Horner and W. Naumann, *Liebigs Ann.* **587**, 93 (1954).

only 9% of benzoic acid was isolated, but 74% of amide was obtained. In the presence of oxygen, 33% of benzoic acid was obtained, and only 13% of amide.[8]

The following process is apparently of negligible importance, because there was no more than 2% of carbon disulfide in the solution after photolysis, and blank runs showed that carbon disulfide was not decomposed photochemically under these conditions.

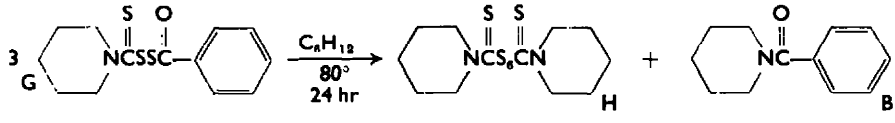


Perhaps the radical species



produced in path (a), might give rise to piperidyl radicals, since the fate of this fragment is not obvious from the observed products. The $(CH_2)_5N—\overset{\overset{S}{\|}}{C}\cdot$ radical could break down to yield a thiocarbene, in addition to the piperidyl radical; the possibility of trapping the thiocarbene structure, in a reaction mixture of this complexity, was considered slight. The thiocarbene and the piperidyl radical may be precursors of the intractable tar which is a major product of the reaction. That Eq. (1) may be an equilibrium process is suggested by the fact that the rate of disappearance of A in the photolysis under nitrogen was retarded considerably, as evidenced by 32% recovery of starting material after 24 hr. Photolysis of a solution of equal concentration in air was complete within 24 hr. Correspondingly, in the photolysis under oxygen, the rate of disappearance of A was accelerated, with a 28% recovery of starting material after only 10 hr irradiation. In the absence of oxygen to scavenge benzoyl radicals, then, portions of the two radical species formed in Eq. (1) may recombine to regenerate starting material.

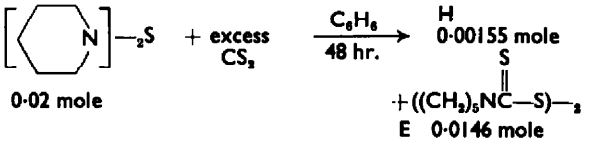
Thermal decomposition of benzoyl cyclopentamethylene thiocarbamyl disulfide (G). Solutions of the unsymmetrical disulfide G (ca. 6×10^{-4} mole) in 25–50 ml cyclohexane yielded, after refluxing for 24 hr, two products: the amide B and the hexasulfide H. Examination of the UV spectrum of the recovered solvent showed the presence of carbon disulfide in only negligible concentration and showed no benzene absorption. The yields of products suggest the following stoichiometry:



The structure of the hexasulfide was apparent from its elementary analysis, its IR spectrum, which was very similar to that of the thiuram disulfide E, and from the fact that it was identical with the material prepared by the action of carbon disulfide on

[8] Benzoyl radicals, generated by photolysis of benzoyl iodide in benzene, give a 12% yield of benzophenone (N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor and L. Tokes, *Chem. & Ind.* 1720 (1962).

piperidine monosulfide.[9] The yields in the latter reaction are indicated below:



The possibility that, in the formation of the hexasulfide H from the unsymmetrical disulfide G, the thiuram disulfide E was an intermediate, is rendered unlikely by the observation that E was recovered unchanged after 40 hr reflux in cyclohexane in the presence of more than 25 mole per cent of free sulfur. However, a 21 hr reflux of a 1:4 molar mixture of E and sulfur in cyclohexane yielded a polysulfide with low carbon–hydrogen content whose UV spectrum in cyclohexane was very similar to that of sulfur.

It was further demonstrated that brief treatment of a 1:4 molar mixture of E and sulfur with boiling carbon disulfide produced H. This transformation may have preparative significance, since it provides a quick, convenient route to the thiuram hexasulfide from easily available starting materials.

The formation of the hexasulfide appears to be favored over that of other possible polysulfides, perhaps due to the low solubility of the hexasulfide.[10]

The ability of G to initiate free radical polymerization at a temperature of 77° was indicated from the production of a 1:1 copolymer of methyl methacrylate and styrene from an equimolar mixture of the monomers in the presence of a catalytic amount of G.[11] It was shown to be a less effective initiator than the thiuram disulfide E and dibenzoyl peroxide, however; the relative weights of copolymer produced by equivalent molar amounts of the three catalysts G, E, dibenzoyl peroxide were 1:2·2:5·6.

From these observations, and by analogy to the thermal behavior of tetrasubstituted thiuram disulfides, which are known to give rise to radicals at moderate temperatures,[12] the decomposition of G in refluxing cyclohexane appears to have free radical character.[13] Indeed, 2-cyanopropyl radicals have been found to attack elemental sulfur in refluxing benzene.[14]

Many reactions of elemental sulfur are known to be ionic in nature, involving attack of nucleophiles ("thiophiles") on sulfur.[15]

Rate studies of the decomposition of G in refluxing cyclohexane solutions ($2{\cdot}7 \times 10^{-5} - 5 \times 10^{-5}$ molar) were carried out by following the buildup of peaks in the UV spectra of aliquots due to the appearance of the polysulfide products. The speed of

[9] E. S. Blake, *J. Amer. Chem. Soc.* **65**, 1267 (1943).

[10] Preferential formation of the hexasulfide H from E and elemental S in refluxing solvents at 110–120° is documented by M. V. Gorelik, L. P. Ignat'eva and L. V. Sakhashchik, *Zh. Priklad. Khim.* **36**, 1624 (1963), in contrast to L. A. Brook, U.S. Patent 2,794,021, *Chem. Abstr.* **51**, 15602 (1957).

[11] Cf. C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *J. Amer. Chem. Soc.* **72**, 48 (1950).

[12] R. J. Kern, *J. Amer. Chem. Soc.* **77**, 1382 (1955); R. E. Davis and C. Perrin, *Ibid.* **82**, 1590 (1960).

[13] The homolytic nature of this S addition reaction to produce the hexasulfide H is reinforced by our present unpublished work on the pyrrolidine analog of A. Photolysis of this new anhydride gives rise to the corresponding pyrrolidine thiuram hexasulfide directly.

[14] D. I. Relyea, P. O. Tawney and A. R. Williams, *J. Org. Chem.* **27**, 1078 (1962).

[15] P. D. Bartlett, A. K. Colter, R. E. Davis and W. R. Roderick, *J. Amer. Chem. Soc.* **83**, 109 (1961) and earlier papers; O. Foss, in N. Kharasch, Editor; *Organic Sulfur Compounds* Vol. I; p. 90 ff. Pergamon Press (1961).

absorption buildup varied rather erratically with the concentration of G as evidenced by plots of absorbancy vs. time. The effects of added reagents upon the speed of decomposition were then investigated, and the following additives showed no accelerating effect: triethylamine, carbon disulfide, dibenzoyl peroxide, and sulfur. Indeed, raising the concentration of free sulfur to $1{\cdot}49 \times 10^{-5}$ molar showed a retarding effect. In contrast, while solutions of pure thiuram disulfide E, of comparable concentration in cyclohexane, were shown to be stable to the reflux conditions, the addition of free sulfur exhibited a dramatic accelerating effect. This may be taken as further evidence against the appearance of E as an intermediate in the decomposition of G in refluxing cyclohexane.

EXPERIMENTAL[16]

Materials. Benzoyl chloride [Baker "Analyzed" Reagent] and piperidine [Eastman Organic Chemicals] were redistilled before use. Cyclohexane [Eastman Spectro Grade], benzene [Mallinckrodt], and all other solvents [Mallinckrodt] were used without further purification.

Benzoic-piperidine dithiocarbamic anhydride [A] was prepared by the method of Tarbell and Scharrer[2] in 60% yield, m.p. 102.5–103.5° [dec], lit. m.p. 100–102°. The IR spectrum in KBr was characterized by the following peaks [cm^{-1}]: 3100–3000w, 2940, 2850, 1680s, 758, 680s. The uv and visible spectra in cyclohexane showed the following absorptions: λ_{max} 239 mμ, ϵ_{max} $2{\cdot}24 \times 10^4$; λ292 mμ, $\varepsilon 1{\cdot}44 \times 10^4$; λ400 mμ, ε256. These figures represent a correction of those previously published.[2]

Benzoyl piperidide [B] was prepared via the Schotten-Baumann rection in 83% yield and was purified by passage through an alumina column in 62% yield. The IR spectrum, run as a film, showed characteristic peaks at 3100–3000, 2940, 2850, 1630, 780, 725, 700 cm^{-1}. The uv spectrum in cyclohexane exhibited λ_{max} 240mμ (shoulder), ϵ_{max} 4.53×10^3. Cooling the oil in acetone-dry ice gave a white solid, m.p. 50–50·5°, lit.[17] m.p. 48°.

Cyclopentamethylene thiuram disulfide (E) was prepared by oxidation of the piperidine salt of piperidine dithiocarbamic acid in anhydrous methanol with I_2 in the same solvent. The product was recrystallized from CS_2–hexane, m.p. 130–131°; lit. m.p.[8] 129–130. The IR spectrum in KBr showed the following major peaks (cm^{-1}): 2990, 2920, 2911 (shoulder), 2860, 1480s, 1430s, 1280w, 1242s, 1220, 1137w, 1106, 1004, 960.

Dibenzoyl disulfide (F)[18] was recrystallized from CS_2–hexane, m.p. 133–134°; the reported[18] value is 129–130°. The IR spectrum in KBr exhibited the following major peaks (cm^{-1}): 3030w, 1705s, 1690s, 1600, 1584, 1450s, 1205s, 1177s, 882s, 730, 685s (doublet), 650, 638.

Attempted preparation of benzoyl pentamethylene thiocarbamyl disulfide (G)

A. A solution of 5.81 g potassium thiobenzoate[18] and the piperidine salt of piperidine dithiocarbamic acid in 70 ml absolute ethanol was cooled to 10–15° and a solution of 10·8 g I_2 in 45 ml absolute ethanol was added dropwise to the stirred reaction mixture. A white precipitate began to form immediately. The color of I_2 persisted in the reaction mixture after slightly more than half of the I_2 solution had been added. The precipitate was collected and washed with 10 ml 95% ethanol and weighed 1·587 g, m.p. 105–131°. Recrystallization from CS_2–hexane gave 0·4254 g pale yellow

[16] All m.p. 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 1 alumina. IR spectra were taken on the Perkin-Elmer Model 421, uv and visible spectra on the Cary Model 11, and vapor phase chromatographic [v.p.c.] analyses were done on the Aerograph A-90-P using a 15′ QF-1 column. Microanalyses are by Antonio G. Revilla of this laboratory and by Micro-Tech Laboratories. The NMR spectrum was taken by Dr. L. D. Colebrook of this laboratory, in CS_2 solution, using a Varian HR-4300 spectrometer. In many instances, thermal decompositions and photolyses were repeated several times under the same conditions, with similar results. Only one representative example of each experiment is described here.

[17] C. Schotten, *Ber. Dtsch. Chem. Ges.* **21**, 2235 (1888).

[18] *Org. Syntheses* **28**, 16 (1948).

crystals, m.p. 124–125·5°, whose IR spectrum in KBr was identical to that of E. A mixed m.p. with E showed no depression.

B. To a stirred suspension of 0·32 g [10^{-3} mole] E at 26° was added dropwise 0·458 g [$2·6 \times 10^{-3}$ mole] piperidine dithiocarbamate salt in 3 ml absolute ethanol. To this was added 3 ml 20% H_2SO_4 dropwise. A new precipitate began to separate as soon as the acid addition was begun. The mixture was stirred overnight and 0·238 g ($8·69 \times 10^{-4}$ mole, 66·8%) white crystals was collected, m.p. 120–125°, whose IR spectrum in KBr was identical to that of dibenzoyl disulfide.

Decomposition of A *in cyclohexane with carbon disulfide collection and product isolation.* A solution of 0·3735 g ($1·408 \times 10^{-3}$ mole) A in 225 ml cyclohexane was refluxed for 40·5 hr at 80·5° [oil bath temp 82°] in a 250 ml round-bottom flask, equipped with a reflux condenser and a N_2 bubbler. The N_2 was passed into 45 ml of a solution of 95% ethanol saturated with KOH. Upon termination of the decomposition, the ethanolic xanthate solution was treated with 1*N* acetic acid, until acid to phenolphthalein but still basic to litmus, and consumed 24·40 ml of 0·0388*N* I_2 solution [0·947 meq], the persistence of I_2 color being taken as endpoint.[19] This corresponds to 67·5% CS_2 trapped during the decomposition. The cyclohexane was evaporated leaving 0·2364 g ($1·28 \times 10^{-3}$ mole; 89%) yellow oil. The IR spectrum was superimposable upon that of B, and when seeded with authentic B, the oil crystallized, m.p. 48·5–50°. The slightly yellow crystals were dissolved in benzene and chromatographed on alumina with benzene–ether eluents, yielding 0·1073 g ($5·77 \times 10^{-4}$ mole; 40·3%) colorless oil, which when seeded, formed transparent crystals of B, m.p. 50·5–52°, mixed m.p. 50·5–52°.

Rate study of decomposition of A *in cyclohexane.* Two hundred forty ml of a $6·44 \times 10^{-3}$ M solution of A in cyclohexane was refluxed at 80·5° in a 250 ml roundbottom flask, shielded from light, and equipped with a drying tube and magnetic stirrer. Five ml aliquots were removed at 1–2 hr intervals through a no-air stopper 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 $k_1 = 2·85 \times 10^{-5}$ sec^{-1}, $t_{1/2} = 2·4 \times 10^4$ sec

Time interval [hr]	0	1·67	3·77	5·77	6·97	9·47	12·37
Absorbancy at λ400 mμ	1·65	1·31	1·00	0·75	0·65	0·47	0·32
Concentration (moles/l. $\times 10^3$)	6·44	5·12	3·91	2·95	2·44	1·83	1·25

Photolysis of A *in cyclohexane at* 2537 Å. A solution of 0·7654 g ($2·88 \times 10^{-3}$ mole) A in 170 ml cyclohexane was placed in a 175 ml cylindical quartz cell with parallel optical faces, path-length 10 cm. This was cooled to 10° in a circulated-water bath with quartz windows. A low-press. Hanovia S 2537 lamp in a helical conformation was used. The distance from the photolysis cell to the lamp was 6 cm. The solution was photolyzed continuously for 48·7 hr, until the yellow color of A had disappeared. The solvent was evaporated *in vacuo* at room temp and recovered for further analysis, until the reaction mixture was reduced to a volume of 17 ml. After several hr, 0·1629 g white crystals had separated, m.p. 100–113°. Concentration of mother liquors yielded an additional 0·0185 g white crystals. The combined 0·1814 g of crystals was recrystallized from 3 ml CS_2–hexane, yielding 0·116 g ($3·90 \times 10^{-4}$ mole; 27%, based on two moles of starting material yielding one mole of product) pale straw-colored crystals, m.p. 112·5–120·5° (dec). An analytical sample had m.p. 108–115° (dec). This compound was assigned the formula $[CH_3]_5NCSSCC_6H_5$ [G]. The IR spectrum in KBr showed the following major peaks [cm^{-1}]: 3053, 2970, 2940, 2915, 2840, 1697s, 1480s, 1435s [doublet], 1280, 1252, 1240s, 1220, 1197s, 1170, 990, 950, 875s, 760, 675s [doublet], 627. (Found: C, 52·71; H, 5·09; S, 32·32. Calc. for $C_{13}H_{15}NOS_2$: C, 52·52; H, 5·09; S, 32·30%).

Evaporation of the solvent from the reaction mixture after the removal of G left 0·592 g yellow oil. This was dissolved in 15 ml ether and extracted twice with 5 ml portions of 10% Na_2CO_3 aq. The aqueous layer was withdrawn and acidified with 12% HCl aq, yielding a white precipitate. The suspension was saturated with NaCl and extracted with 15 ml ether. The ether solution was washed with 5 ml sat. NaCl aq and dried over anhydrous $MgSO_4$. Evaporation of the ether yielded 0·0826 g. ($6·66 \times 10^{-4}$; 23%) white solid, m.p. 120·5–121°, mixed m.p. with benzoic acid 121–121·5°. The IR spectrum in KBr was identical to that of benzoic acid. The ether layer from the original extraction was washed with 5 ml 5% HCl aq followed by 5 ml sat. NaCl aq and was then dried. Evaporation of

[19] Procedure of M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed.* 4, 98 (1932).

the ether yielded 0·344 g yellow-orange oil. This was chromatographed on 20 g alumina, using benzene–ether–methanol as eluents, yielding 0·043 g S and 0·0755 g ($3·99 \times 10^{-4}$ mole; 28%), based on two moles of starting material yielding one mole of product of colorless oil whose IR spectrum was superimposable upon that of the amide B, and which crystallized when seeded, m.p. 50–52°. In a separate experiment, an authentic sample of B was shown to be completely stable to the basic workup used here.

V.p.c. analysis of the recovered cyclohexane showed only one very small peak in addition to that of cyclohexane. This was identified as CS_2 by co-injection and was shown by comparison with standard solutions to be present in a maximum yield of 1·4%, based on starting material. The uv spectrum of the recovered cyclohexane showed no benzene or benzaldehyde absorption.

Photolysis of A *in benzene at* 2537 Å *with control sample.* Two solutions of 1·205 g ($4·73 \times 10^{-3}$ mole) A in 170 ml benzene (total moles $9·46 \times 10^{-3}$) were photolyzed in the same manner as described in the previous experiment, at a water bath temp of 16°, for 120 hr each. The solutions were combined and worked up in the same manner as before, yielding 0·544 g crude G, which was recrystallized from 5 ml CS_2–4 ml hexane, yielding 0·392 g ($1·32 \times 10^{-3}$ mole; 31·2%) G, m.p. 111–113°. An extraction procedure, identical to that in the previous experiment, yielded 0·299 g ($2·38 \times 10^{-3}$ mole; 28%) benzoic acid, m.p. 116°, mixed m.p. 116–118°. Chromatography of the 1·053 g yellow oil left after benzoic acid removal, upon elution with benzene, yielded 0·0756 g yellow oil which solidified, m.p. 107–112°. Recrystallization from CS_2–hexane yielded 0·0346 g ($1·08 \times 10^{-4}$ mole; 2·3%) white crystals, m.p. 131·5–133°, mixed m.p. with the thiuram disulfide E 123°, whose IR spectrum in KBr and uv spectrum in cyclohexane were identical to those of E. Further elution with benzene–ether mixtures afforded 0·1793 g ($9·46 \times 10^{-4}$ mole; 22%) B, which solidified when seeded, m.p. 49–50°, mixed m.p. 50–50·5°. A third solution of the same concentration was placed in the water bath during the entire photolysis, but was shielded from all light. Evaporation of solvent yielded pure A quantitatively, m.p. 98–99°, IR spectrum in KBr identical to that of starting material.

Photolysis of A *in benzene under nitrogen at* >3000 Å. A solution of 1·4422 g ($5·44 \times 10^{-3}$ mole) A in 170 ml benzene was photolyzed as before at >3000 Å for 24 hr at 22°. The solution was purged with dry N_2 through a capillary for 30 min prior to photolysis and during the entire photolysis. It was necessary that the single inlet to the quartz cell be open to the atmosphere, and it was therefore not possible to exclude O_2 entirely. When photolysis was terminated, the solution was still intensely yellow. The solvent was evaporated, leaving 1·4993 g of solid, yellow residue. This was dissolved in 5 ml benzene–3 ml hexane and placed in the refrigerator overnight. Yellow crystals had separated (0·4603 g; 32%), m.p. 94–96°, mixed m.p. with starting material A 97–99°, whose IR spectrum in KBr was superimposable upon that of A. The oily residue was worked up as before, yielding 0·246 g crude G, which was recrystallized to give 0·1893 g ($6·37 \times 10^{-4}$ mole; 34%, based on reacted starting material), m.p. 108–115°. Basic extraction afforded 0·0416 g ($3·41 \times 10^{-4}$ mole; 9%) of benzoic acid, m.p. 106–113°, mixed m.p. 118–119·5°. Chromatography of the 0·4759 g of oily residue yielded 0·2604 g ($1·378 \times 10^{-3}$ mole; 74%) of amide B, which when seeded gave crystals with m.p. 49–50°. None of the thiuram disulfide was found.

Photolysis of A *in benzene under oxygen at* >3000 Å. A solution of 1·4490 g ($5·46 \times 10^{-3}$ mole) A in 170 ml benzene was photolyzed as before at >3000 Å for 24 hr at 22°. The solution was purged with O_2 for 1 hr, prior to, and during photolysis. When photolysis was terminated, the solution was colorless. The solvent was evaporated, leaving 1·506 g oily residue, which was worked up as before, yielding 0·6055 g crude G. This was recrystallized to give 0·362 g ($1·217 \times 10^{-3}$ mole; 45%) G, m.p. 110–112°. Basic extraction afforded 0·2195 g ($1·80 \times 10^{-3}$ mole; 33%) benzoic acid, m.p. 118–120°, mixed m.p. 120–121°. Chromatography of the 0·425 g oily residue gave 0·0541 g ($1·69 \times 10^{-4}$ mole; 6·2%) E, m.p. 130–131°, mixed m.p. 128–130°, and 0·0691 g ($3·65 \times 10^{-4}$ mole; 13%) of B, m.p. 45–49°, mixed m.p. 47–50°.

In a separate experiment under identical conditions, photolysis was interrupted at the end of 10 hr, and the reaction mixture was worked up as before to give 28% starting material, 20% G, 24% benzoic acid, 5·8% E, and 7·6% B (yields based on reacted starting material). The yields of products other than A are not representative, since contamination with starting material made isolation of pure products very difficult, resulting in considerable losses, particularly of compound G.

Photolysis of G *in benzene at* >3000 Å. A solution of 0·0955 g ($3·21 \times 10^{-4}$ mole) G in 50 ml benzene was photolyzed as before for 24 hr, with the medium pressure lamp and Pyrex shield, at a water bath temp of 21°. Evaporation of solvent yielded colorless crystals of G which after thorough

washing with ethanol, weighed 0·0658 g (69%). A small amount of oily residue remained, whose IR spectrum showed mainly absorption due to amide B, contaminated by starting material.

Thermal decomposition of G. The unsymmetrical disulfide G (0·0995 g) was heated at 150° for 15 min. The flask was then cooled to 120° and maintained at this temp for 5·5 hr. The brown, tarry residue solidified on cooling and weighed 0·0727 g. Chromatography of a benzene solution of the residue yielded 0·0068 g ($2·12 \times 10^{-4}$ g-atoms) S and 0·0583 g ($3·12 \times 10^{-4}$ mole; 93%) colorless oil, whose IR spectrum and uv spectrum in cyclohexane were identical to those of B.

Photolysis of the thiuram disulfide E *in benzene at* >3000 Å. A solution of 0·1141 g ($3·56 \times 10^{-4}$ mole) E in 50 ml benzene was photolyzed for 24 hr under the conditions previously described, at >3000 Å, and a water bath temp of 21°. Evaporation of solvent yielded 0·1131 g of pale straw-colored crystals whose IR spectrum in KBr was identical to that of starting material.

Photolysis of dibenzoyl disulfide F *in benzene at* >3000 Å. A solution of 0·1726 g ($5·50 \times 10^{-4}$ mole) F in 50 ml benzene was photolyzed for 24 hr as above, at >3000 Å and a water bath temp of 21°. Evaporation of solvent yielded 0·1747 g of ivory crystals whose IR spectrum in KBr was identical to that of starting material.

Photolysis of an equimolar mixture of the thiuram disulfide E *and dibenzoyl disulfide* F *in benzene for* 16 *hr at* 22° *and* >3000 Å. Only the 2 starting materials could be isolated, and the IR spectrum of crude photolysis product was identical with that of an unphotolyzed mixture.

Photolysis of carbon disulfide in cyclohexane at >3000 Å. One hundred seventy ml of a 1·636 M solution of CS_2 in cyclohexane was photolyzed for 39·7 hr as previously described, at >3000 Å and temp of 11°. A 50 ml control sample was shielded from light and placed in the same cooling bath during photolysis. Both solutions were then diluted to 0·01 ($1·632 \times 10^{-2}$ M), and the uv spectra of these samples were taken. The curves were superimposable, with λ_{max} 317·5mμ, ε88·9; λ313 mμ, ε84·2.

The photolysis was repeated, using a photolysis solution and control of $1·636 \times 10^{-2}$ M concentration and irradiating for 53·5 hr. Again, the uv spectra of the photolyzed sample and control were superimposable, and these were identical with those of the diluted samples from the first experiment.

Photolysis of peroxybenzoic acid in benzene at >3000 Å. A benzene solution containing 0·4815 g of freshly prepared peroxybenzoic acid[20] in 170 ml benzene was photolyzed for 19 hr at >3000 Å and temp of 21°. Evaporation of the benzene solvent at room temp under aspirator pressure left 0·4924 g yellow oil whose IR spectrum was identical to that of the starting material. When placed in the refrigerator, the yellow oil crystallized. The oil was then disolved in 25 ml absolute ether and was extracted with 10 ml 10% Na_2CO_3 aq. The aqueous layer turned cloudy upon acidification with 5% HCl aq. This was extracted with 25 ml absolute ether and the extract dried. Evaporation of the ether left 0·3331 g of yellow oil whose IR spectrum was very similar to that of starting material and which solidified upon cooling.

Photolysis of a mixture of A *and peroxybenzoic acid in benzene at* >3000 Å. A solution of 1·3573 g ($5·12 \times 10^{-3}$ mole) A and 0·480 g ($3·48 \times 10^{-3}$ mole) peroxybenzoic acid in 170 ml benzene was photolyzed as before at >3000 Å for 21·75 hr at 22°. At the termination of the photolysis, the solution was pale yellow. The solvent was evaporated, leaving a yellow semi-solid residue. Basic extraction with 10% Na_2CO_3 aq yielded 0·4935 g ($4·03 \times 10^{-3}$ mole) benzoic acid, m.p. 110–112°, mixed m.p. 121–122°. The IR spectrum in KBr was superimposable upon that of an authentic sample of benzoic acid. The remaining neutral, yellow oil (1·098 g) was treated with a mixture of benzene–hexane, which caused the separation of 0·539 g crude G. This was recrystallized to give 0·4075 g ($1·37 \times 10^{-3}$ mole; 54%) G, m.p. 96–103°. Chromatography of the 0·233 g of orange, oily residue afforded 0·1165 g ($6·16 \times 10^{-4}$ mole; 24%) amide B, whose IR spectrum was superimposable upon that of the pure material and which crystallized when seeded.

Synthesis of piperidyl thiuram hexasulfide (H) *from piperidyl monosulfide and carbon disulfide.*[9] A solution of 4·006 g (0·02 mole) piperidyl monosulfide,[21] m.p. 74·5–75·5°, and 4·0 g (0·052 mole) CS_2 in 20 ml benzene was stirred for 48 hr at room temp. The pale yellow crystals which had separated within 1–2 hr before the termination of the stirring period were filtered and washed with 5 ml benzene, yielding 0·2918 g white crystals, m.p. 127–128°. A second crop of pale yellow crystals (0·4747 g) separated from the mother liquor overnight. The combined 0·7663 g of crystals was recrystallized

[20] *Org. Syntheses* Coll. Vol. I, p. 431.

[21] A. Michaelis, *Ber. Dtsch. Chem. Ges.* **28**, 1012 [1895].

from 45 ml chloroform 25 ml absolute ethanol, yielding 0·6966 g (0·00155 mole) H, m.p. 135–136° (dec), lit. m.p. 137–138°.[8] The IR spectrum in KBr was characterized by the following peaks [cm^{-1}]: 2936m, 2850m, 1480s, 1457m [shoulder], 1438s, 1350–1360w [doublet], 1280m, 1249s, 1226s, 1160w, 1135m, 1105m, 1070w, 1007m, 964m, 946w [shoulder], 892m, 850m, 789w. The uv spectrum in cyclohexane exhibited a broad maximum at λ220 mμ, $\varepsilon 3{\cdot}18 \times 10^4$; a gentle maximum at λ250 mμ, $\varepsilon 2{\cdot}45 \times 10^4$; and a shoulder at λ280 mμ, $\varepsilon 1{\cdot}97 \times 10^4$. After 3 days, an additional 5·0575 g pale yellow crystals (more brightly colored than H) had separated. This was recrystallized from chloroform–ethanol to give 4·6645 g (0·0146 mole) pale yellow needles of cyclopentamethylene thiuram disulfide E, m.p. 128–129° (dec), mixed m.p. 128–129°. The uv spectrum in cyclohexane was superimposable upon that of E. Longer standing of the intial mother liquors yielded an additional 0·2673 g (0·00083 mole E. This was not purified further. Final evaporation of mother liquors gave 0·308 g oily, yellow solid, which crystallized completely upon standing for 2 days. This was recrystallized from 5 ml chloroform–4 ml absolute ethanol to give 0·0944 g yellow crystals whose uv spectrum in cyclohexane appeared to be a composite of that of E and free S.

Thermal decomposition of G *in refluxing cyclohexane.* (1). A suspension of 0·2116 g ($7{\cdot}11 \times 10^{-4}$ mole) G in 50 ml cyclohexane was refluxed, the initially colorless suspension became pale yellow by the time reflux temp was reached, within 3 hr all the solid disappeared, and the solution became distinctly yellow in color. After a 4 hr reflux period, the heat was removed, and a white solid separated upon cooling. Two mg of this was removed, and its IR spectrum in KBr was taken, which appeared very similar to that of the starting material G. The reflux was continued for a total period of 24·5 hr. The solvent was evaporated, leaving 0·2324 g yellow oil, which began to solidfy. This was dissolved in 5 ml CS_2 at room temp and 3 ml 95% ethanol was added. Overnight, 0·1218 g white crystals separated, m.p. 117–117·5° (dec). The IR spectrum in KBr was identical to that of H, prepared as above. This was recrystallized from 5 ml CS_2–3 ml 95% ethanol, yielding 0·0921 g ($2{\cdot}05 \times 10^{-4}$ mole) very pale yellow crystals whose IR spectrum in KBr and uv spectrum in cyclohexane were superimposable upon those of H. (Found: C, 31·96, H, 4·55; N, 6·06; S, 56·55. Calc. for $C_{12}H_{20}N_2S_6$: C, 32·11; H, 4·49; N, 6·24; S, 57·15%).

Evaporation of the initial CS_2 ethanol mother liquor after the removal of the hexasulfide H yielded 0·0726 g ($3{\cdot}84 \times 10^{-4}$ mole) yellow oil whose IR spectrum was identical to that of benzoyl piperidide (B). When seeded with pure B, the oil crystallized, m.p. 48–49°, mixed m.p. 48–49·5°. The uv spectrum of the recovered cyclohexane solvent showed CS_2 present in only negligible concentration, as determined from a single peak at 210 mμ (2). A suspension of 0·1826 g ($6{\cdot}14 \times 10^{-4}$ mole) G in 25 ml cyclohexane was refluxed as above for 23 hr. Similar workup afforded 0·1072 g pale yellow crystals, which was recrystallized from CS_2–ethanol to give 0·0905 g ($2{\cdot}02 \times 10^{-4}$ mole) H, m.p. 116–117·5° (dec). The IR spectrum in KBr was very similar to that of authentic H, and the uv spectrum in cyclohexane was identical to that of H, exhibiting the following absorption: λ_{max} 220mμ, ε_{max} $3{\cdot}15 \times 10^4$; λ250 mμ, $\varepsilon 2{\cdot}48 \times 10$; λ280 mμ, $\varepsilon 2{\cdot}07 \times 10^4$. The uv spectrum of the recovered solvent, compared with a series of solutions of graduated concentrations of CS_2 in cyclohexane, showed CS_2 in a concentration less than $8{\cdot}32 \times 10^{-7}$ M. A yield of 0·0479 g ($2{\cdot}48 \times 10^{-4}$ mole) crystalline B was obtained.

Treatment of a 1:4 *molar mixture of the thiuram disulfide* E *and sulfur with boiling carbon disulfide.* A mixture of 0·150 g ($4{\cdot}68 \times 10^{-4}$ mole) E and 0·0602 g ($1{\cdot}88 \times 10^{-3}$ g atoms) S in 2 ml CS_2 was boiled for 5 min. The solution was filtered from portions of insoluble, pale yellow, crystalline residue, and to the filtrate was added 2 ml absolute ethanol, causing fine, short, ivory-colored needles to separate, m.p. 135–136° (dec), mixed m.p. with E 111–112°, mixed m.p. with H 136–137°. The IR spectrum in KBr and the uv spectrum in cyclohexane were identical to those of H. (Found: C, 32·13; H, 4·62. Calc. for $C_{12}H_{20}N_2S_6$: C, 32·11; H, 4·49%).

Reflux of a mixture of E *and sulfur in cyclohexane.* A suspension of 0·2379 g ($7{\cdot}42 \times 10^{-4}$ mole) E and 0·0062 ($1{\cdot}94 \times 10^{-4}$ g-atoms) S in 50 ml cyclohexane was refluxed for 40·3 hr. When reflux temp was attained, all the solid had gone into solution. The solvent was evaporated, leaving an ivory-colored crystalline residue. This was recrystallized from 4 ml CS_2–2 ml absolute ethanol, yielding 0·2036 g ivory-colored crystals, m.p. 114·5–122·5° (dec), whose uv spectrum in cyclohexane was identical to that of E. Recrystallization from 3 ml CS_2–3 ml absolute ethanol gave 0·1523 g ($4{\cdot}75 \times 10^{-4}$ mole) ivory-colored crystals, m.p. 127·5–129° (dec), mixed m.p. with E 126–128°, whose uv spectrum in cyclohexane was superimposable upon that of E. The uv spectrum of the recovered solvent showed the presence of CS_2 in a concentration less than $2{\cdot}5 \times 10^{-5}$ M.

Copolymerization of styrene and methyl methacrylate at 77° in presence of the thiuram disulfide E, *the unsymmetrical disulfide* G *and dibenzoyl peroxide.*[22] Both monomers used in this experiment were freshly distilled. To four 25 ml flasks, containing 5·207 g (0·05 mole) styrene (Eastman) and 5·005 g (0·05 mole) methyl methacrylate (Matheson, Coleman, and Bell) and equipped with reflux condensers, were added the following initiators: flask 1, nothing; flask 2, 2·42 mg (10^{-5} mole) dibenzoyl peroxide (Lucidol); flask 3, 3·20 mg (10^{-5} mole) E; flask 4, 2·97 mg (10^{-5} mole) G. All 4 flasks were placed in an oil bath preheated to 77° and maintained at this temp throughout the reaction period of 3·5 hr. At the end of this time, the contents of each flask were poured, with constant stirring, into separate beakers, each containing 100 ml absolute methanol. Each white, solid mass of polymer was filtered, washed with 15 ml absolute methanol, dried in a vacuum desiccator for 24 hr, and weighed. The polymers were recrystallized from 7–15 ml benzene–25–35 ml absolute methanol. The following Table summarizes the data and results:

Sample no.	Initiator	Initial wgt. of polymer	%Conversion[a]	C%	H%	Mole % styrene in polymer
1	none	0·0825 g	0·807	76·19	7·78	50·2
2	dibenzoyl peroxide	0·8943 g	8·75	78·52	8·31	57·4
3	E	0·3515 g	3·44	75·40	8·10	47·8
4	G	0·1569 g	1·54	76·18	7·87	50·2

[a] Based on ratio of product wt to combined wts of monomers. Polystyrene requires 92·26% C: polymethylmethacrylate requires 59·98% C.

Rate studies of the decomposition of dilute solutions of G *in refluxing cyclohexane.* Each of the following decompositions of G was carried out in the same fashion, in the presence of various additives. Only one representative run is described, following which is a summary of the results of the entire study.

One hundred ml of a $2·75 \times 10^{-4}$ M solution of G in cyclohexane was placed in a 250 ml, 3-neck flask, equipped with a reflux condenser, magnetic stirrer, $CaCl_2$ tube, and no-air stopper. The solution was heated to reflux in an oil bath maintained at 88°, and 5 ml samples were withdrawn at timed intervals. The uv spectra of all samples were taken, and they exhibited the gradual buildup of an intense shoulder at 226 mμ, where initially there had been a gentle minimum. Also, two less intense bands gradually arose at 255 mμ and 276 mμ (shoulder). The absorbancies of each of the three bands, as listed below, were plotted vs. time (hr) and each plot gave a good straight line.

Sample No.	Time interval (hr)	$A_{226m\mu}$	$A_{255m\mu}$	$A_{276m\mu}$
1	0	0·46	0·35	0·30
2	1	0·76	0·42	0·36
3	2·1	0·85	0·46	0·39
4	3·2	0·98	0·50	0·42
5	4·6	1·16	0·55	0·45
6	6·1	1·33	0·59	0·49
7	7·6	1·54	0·66	0·60

Subsequent decompositions of G with an added reagent in the concentrations listed below were carried out and similar plots made of the three new absorption bands, as just described. The slopes of these lines were compared to those of the corresponding lines from an identical decomposition of the same concentration of pure G. The differences in slopes were consistent in direction for each analogous pair of lines and indicated the effect of the additive on the rate of the decomposition.

[22] W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.* **84**, 1561 [1962].

Concentration of G	Additive (concentration)	Effect on Decomp
$3{\cdot}53 \times 10^{-5}$ M	sulfur ($1{\cdot}87 \times 10^{-6}$ M)[a]	none
$3{\cdot}53 \times 10^{-5}$ M	sulfur ($9{\cdot}35 \times 10^{-6}$ M)[a]	none
$3{\cdot}53 \times 10^{-5}$ M	$(C_2H_5)_3N$ ($3{\cdot}52 \times 10^{-5}$ M)	none
$3{\cdot}53 \times 10^{-5}$ M	Bz_2O_2 ($3{\cdot}16 \times 10^{-7}$ M)	none
$2{\cdot}75 \times 10^{-5}$ M	sulfur ($1{\cdot}49 \times 10^{-5}$ M)[a]	retarding
$2{\cdot}75 \times 10^{-6}$ M	CS_2 ($1{\cdot}66 \times 10^{-6}$ M)	none
$5{\cdot}04 \times 10^{-5}$ M	Bz_2O_2 ($5{\cdot}00 \times 10^{-6}$ M)	none

[a] Molar concentration of S based on monatomic units.

In a reflux of a $3{\cdot}92 \times 10^{-5}$ M solution of pure E under the conditions described above for G, the uv spectrum showed no significant change throughout the 8·75 hr reflux period. However, in the presence of $1{\cdot}87 \times 10^{-5}$ M S, a sample of the same solution of E exhibited changes in the uv spectra of withdrawn samples, similar to those changes observed for the decomposition of G.

The presence of $5{\cdot}61 \times 10^{-5}$ M S in a similar decomposition of a $2{\cdot}32 \times 10^{-5}$ M solution of H showed no acceleratory influence.