

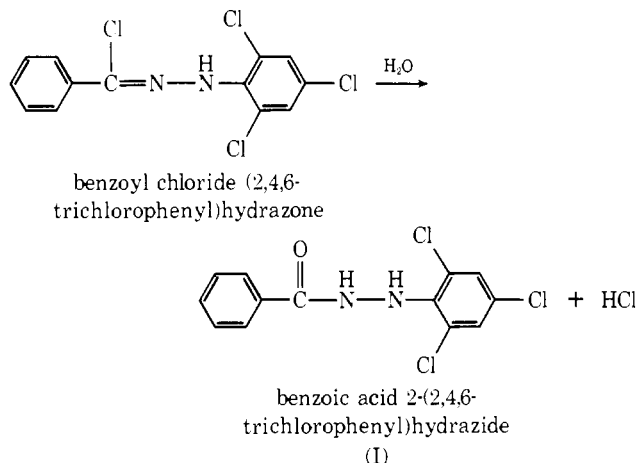
Photolysis of Benzoic Acid 2-(2,4,6-Trichlorophenyl)hydrazide

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The photolysis of benzoic acid 2-(2,4,6-trichlorophenyl)hydrazide was studied in the solid state as a thin film on 170–230 mesh glass beads under a 3000-Å light source without and with a filter that absorbed radiation below 2900 Å. Both ¹⁴C-labeled and unlabeled material was used. Under the experimental conditions the photolytic half-lives were 12 and 16 hr, respectively. Eight photolysis products were identified by TLC, GLC, and GLC-MS by comparison to known standards. The major photolysis products were benzoic acid 2-

(2,4-dichlorophenyl)hydrazide and 2,4,6-trichlorobenzophenone. Others were 2,4,6-trichlorobenzanilide, 2,4-dichlorobenzanilide, 2,6-dichlorobenzanilide, 2,4-dichlorobenzophenone, 1,2-dibenzoyl-1-(2,4,6-trichlorophenyl)hydrazine, and 1,2-dibenzoyl-1-(2,4-dichlorophenyl)hydrazine. Benzene unextractable radioactivity accumulated on the beads to 13% after 36 hr of irradiation. There was 11% unaccountables at this time, probably due to volatile products.

Benzoic acid 2-(2,4,6-trichlorophenyl)hydrazide (I) is the principal hydrolysis product of benzoyl chloride (2,4,6-trichlorophenyl)hydrazone, a compound that has shown good miticidal activity for citrus and other crops (Kaugars et al., 1973). Residues of I were found on citrus leaves that were sprayed with wettable formulations of the hydrazone (Staten, 1972). The photolysis of the hydrazone was reported (Friedman et al., 1974); three non-oxygen-containing compounds and six oxygen-containing photoproducts were identified. Even though I was identified as one of the photoproducts of the hydrazone, it was only a minor one. Two reasons prompted a study of the photolysis of I. Firstly, since it was detected as a residue on the citrus leaves sprayed with the hydrazone, it was desirable to know the photolytic fate of I. Secondly, it was necessary to show if the oxygen-containing photoproducts of the hydrazone were the same as the photoproducts of I.



Since the photolysis of benzoyl chloride (2,4,6-trichlorophenyl)hydrazone (Friedman et al., 1974) was more extensive in the solid state as a thin film on 170–230 mesh glass beads than in hexane solution, the photolysis of I was also carried out in a similar manner. A light source with a maximum energy output at 3000 Å was used. In order to simulate sunlight conditions, the experiment was also performed using a filter which cuts out radiation below 2900 Å (30% transmission at 3000 Å, 6–7% transmission at 2900 Å).

EXPERIMENTAL SECTION

Special equipment used included: Rayonet RPR module with RUL 3000-Å fluorescent uv lamp (Southern New En-

gland Ultraviolet Co., Middletown, Conn.); gas chromatograph with H₂ flame ionization detector (MicroTek MT 220, Tracor, Inc., Austin, Tex.); gas chromatograph-mass spectrometer (LKB 9000, LKB Producter AB Stockholm, Bromma, Sweden); liquid scintillation spectrophotometer (Packard Model 3375); glass beads, regular 170–230 mesh (Applied Science Laboratories, Ann Arbor, Mich.); Corning no. 7740, 5 × 8 in., uv filter (Corning Glass Works, Corning, N.Y.).

Coating of Glass Beads. The glass beads were consecutively washed with hot concentrated HCl, hot concentrated HNO₃, water (until the washings were neutral), acetone, chloroform, and anhydrous ethanol. Beads were dried at 140°C and stored in a desiccator.

A solution of I was prepared in dry benzene to contain 100 mg/5 ml. Three grams of the dry glass beads was transferred into a dry 15-ml medium porosity sintered glass funnel. The benzene solution of I was poured into the funnel, mixed with a glass rod, and allowed to stand for 2–3 min under dry N₂. The solution was then filtered quickly under positive nitrogen pressure. The beads were transferred to a dry petri dish and dried in a vacuum oven at 75°C.

The ¹⁴C-labeled I (uniform label on the trichlorophenyl ring) was incorporated by the same technique using 1 mg of labeled I (2.1 × 10⁷ dpm/mg) and 99 mg of cold material dissolved in 5 ml of benzene.

Exposure of the Coated Beads to Uv Light. One gram or less of the coated beads was spread uniformly onto a 4 × 8 in. section of a clean glass plate which had a 1/8-in. glass ridge along the sides. The beads were exposed with and without the Corning no. 7740 filter to the uv lamp held horizontally exactly 3.5 in. from the glass plate for fixed intervals up to 48 hr. The lamp was a 1-in. tube, bent into a U configuration. The width of the two arms was about 4 in., the same width as the glass plate; therefore, the beads were uniformly exposed to the light. The whole assembly was enclosed in a box for safety reasons. The temperature at the surface of the beads was 34°C.

Gas-Liquid Chromatography. The following procedure was used to determine the rate of photolysis of I. Three-tenths of a gram of the beads was accurately weighed into a 1-ml glass stoppered tube. Exactly 250 μl of a 1.02 mg/ml benzene solution of *n*-pentacosane (internal standard for GLC) was added and mixed thoroughly to effect dissolution. The solution was analyzed by gas-liquid chromatography.

The GLC conditions were: instrument, MicroTek MT 220; detector, H₂ flame ionization; columns, 1% OV-1, 1% QF-1, or 3% QF-1 on Gas-Chrom Q, 100–120, 3 mm i.d. glass, 18-in. U columns; temperatures, inlet 220°C, detector 240°C, column, see Figure 4 and Table I; gas flow, He 40, H₂ 40, and air 400 ml/min.

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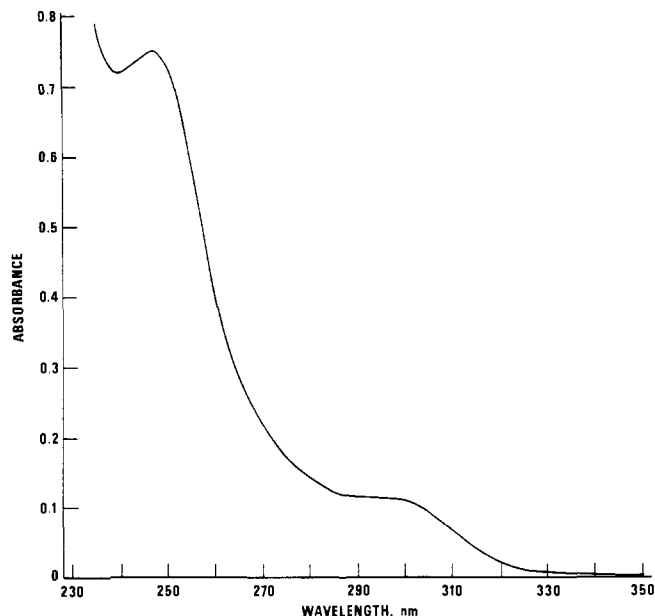


Figure 1. Ultraviolet absorption spectrum of compound I.

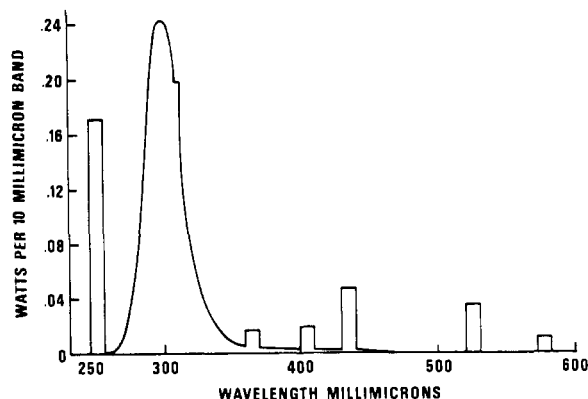


Figure 2. Energy spectrum of the Rayonet RUL 3000-Å lamp.

Thin-Layer Chromatography. One gram of the beads was transferred to a dry 2-ml sintered glass funnel and extracted using four 2-ml portions of warm benzene and filtered into a 15-ml tube under N_2 pressure. The solution was evaporated under a stream of N_2 while the tube was immersed in warm water (45–50°C). The residue was transferred to a 1-ml tube and reconstituted in 0.5 ml of benzene.

Precoated commercial silica gel GF₂₅₄ plates (Analtech Inc., Newark, Del.), 8 × 8 in. scored into 2 × 8 in. sections, 0.25 mm thick, were used. The solvent systems used were: solvent 1, acetic acid–ethyl acetate–hexane (1:20:80); solvent 2, acetic acid–benzene–hexane (3:30:70); solvent 3, ethyl acetate–chloroform (2:98).

Solvent system 1 was very versatile in separating the majority of the photolysis products. Solvent systems 2 and 3 were used to separate unresolved components that were eluted from the first TLC plate. The TLC zones were located using short-wave uv light. If the component of interest was to be used for any subsequent analysis (GLC, TLC, GLC–MS), the zones were scraped and eluted with benzene. When the zone of interest was used for scintillation counting, the scrapings were added directly to the counting vials.

Liquid Scintillation Counting. The liquid scintillation counting was performed in a Packard Model 3375 scintilla-

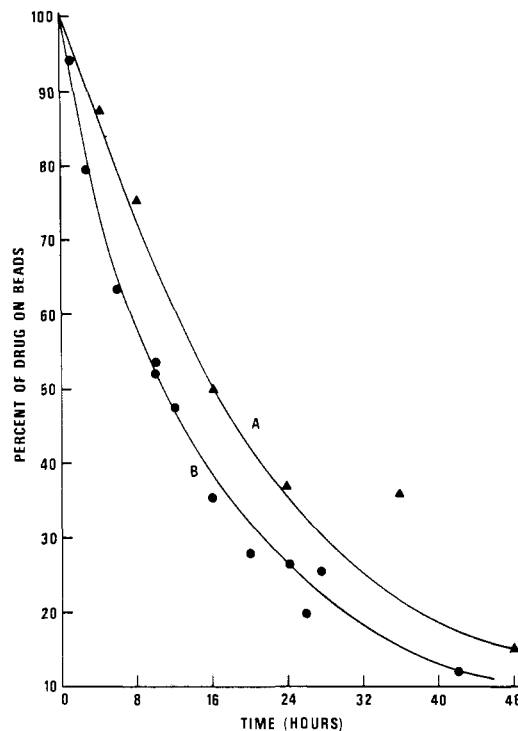


Figure 3. Decline curves for the photodecomposition of I: (curve A) with the no. 7740 Corning filter; (curve B) without the filter.

tion spectrophotometer using Diotol fluor solution. Efficiency correction was made by internal standardization using [¹⁴C]toluene. The data were used to quantitate the radioactivity distribution on the TLC plate.

GLC–Mass Spectrometry. The mass spectra of I and its photolysis products were obtained on an LKB 9000 GLC–mass spectrometer with an electron impact source and a total ion current detector. A 1% OV-1, 3-mm i.d., 2-ft glass column was used. The column temperature varied according to the sample. The ionizing current was 60 μ A and the ionizing voltage was 70 eV. The identity of the photoproducts was made by comparison of R_f values on TLC plates, retention times on the GLC, and confirmed from the mass spectra of authentic reference compounds.

Synthesis of Standards. Compounds I, II, III, IV, V, VI, and IX were prepared by literature methods: I, Johnstone et al. (1971); II, Jaeger (1907); III, Boeseken (1908); IV and IX, Schwartz and Skaptason (1966); V, Grammaticakis (1949); VI, Chattaway and Pearce (1915).

Compounds VII and VIII were prepared by the reaction of benzoyl chloride 2,4,6-(trichlorophenyl)hydrazone or benzoyl chloride 2,4-(dichlorophenyl)hydrazone (Kaugars et al., 1973) with sodium benzoate analogous to the reaction described by Butler and Scott (1970). Compound VII, mp 151.5–152.5°C, and compound VIII, mp 142.5–144°C, both had satisfactory elemental analyses.

RESULTS AND DISCUSSION

Figure 1 shows the uv spectrum of I in ethanol. Figure 2 shows the energy spectrum of the Rayonet RUL 3000-Å lamp. With the use of the filter, only radiation above 2900 Å was transmitted. Since I absorbs poorly in this region, the compound was not expected to be very susceptible to photolysis, but this assumption proved to be wrong.

The coating technique described in the Experimental Section gave beads with a uniform amount of I on the beads. There was always some variation from one batch to another. GLC analysis of the beads used in this study had 1.10 mg of I per g of beads. The surface area of the glass beads was 1.63×10^3 cm²/g as determined by the BET

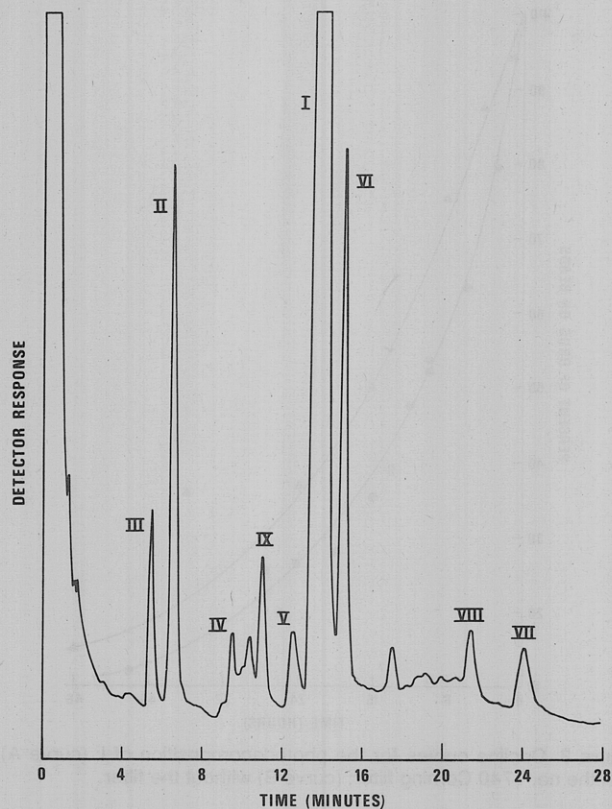


Figure 4. Gas-liquid chromatogram of a benzene extract of I after 24 hr photolysis; 3% QF-1 on Gas-Chrom Q, 100-120, 3 mm i.d. glass column, 18-in. packing length; temperature programmed from 125 to 225°C at 5°C per min.

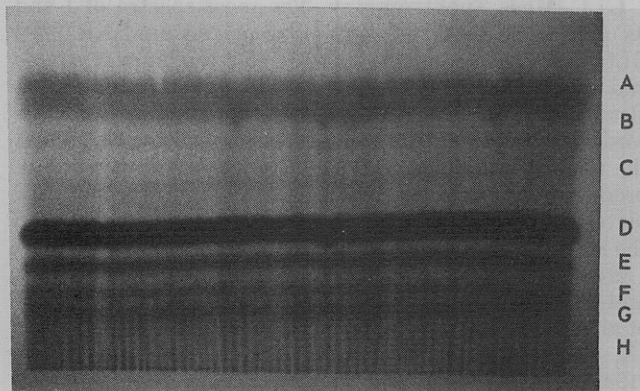


Figure 5. Thin-layer chromatogram of photolyzed I; silica gel GF₂₅₄, 250 μ ; acetic acid-ethyl acetate-hexane (1:20:80). Zones A through H represent major bands and undefined areas. See Table I for the products identified in each band.

method (Brunauer et al., 1938). From a Dreiding model, the area of the molecule was estimated to be 70 Å. From these figures it could be shown that a coating of 1 mg of I per g of the beads is equivalent to about 8 molecular layers.

Figure 3 is a decline curve for the photodecomposition of I with and without the 7740 filter; the first half-lives were 16 and 12 hr, respectively.

Figure 4 shows a temperature-programmed gas-liquid chromatogram of a benzene extract of the beads exposed to 24 hr of uv light (2 g of beads extracted and reconstituted in 0.1 ml of benzene) using the 3% QF-1, 18-in. column. It shows the complexity of the photolysis.

Identification of Photolysis Products. Ten 1-g batches of the beads were exposed to the RUL 3000-Å lamp for 36

Table I. Gas-Liquid Chromatographic Results on the Different TLC Fractions of the 24-hr Photolysis Extract

TLC zone (top to bottom)	1% OV-1, 3 mm i.d., 18 in.		Compd identified by GLC-MS
	Col. temp, °C	T_r , min	
A	125	6	III
	125	8 ^{1/5}	II
B ^a	145	5 ^{3/4}	IV
C ^b	160	6 ^{1/5} + 3 ^{1/2}	V + IX
D ^c	160	7 ^{3/4}	I
E ^d	160	9	VI
F	210	4 ^{4/5}	VII
G	225	3	Unknown (minor)
H	225		

^a There were a few additional small peaks. ^b One additional peak was present. ^c One additional small peak having the same molecular ion as I. ^d One additional small peak having same molecular ion as VI. The retention time (t_r) did not agree with any of the five known isomers.

hr. These were extracted with warm benzene combined and concentrated to 2 ml. The extract was spotted on five 8 × 8 in. TLC plates and developed in solvent system 1. The chromatogram viewed under short-wave uv light is shown in Figure 5. The major bands and the undefined areas were separated into eight zones, A through H. The adsorbent in each zone was scraped from each plate. The corresponding zones were combined and eluted first with benzene and then with ethyl acetate. Each eluate was evaporated to dryness, transferred to 1-ml vials, and finally reconstituted in 100 μ l of benzene. These extracts were subjected to GLC on the OV-1 column and subsequently to GLC-MS on an OV-1 column. GLC analysis showed that most of the fractions were composed of more than one compound.

Table I correlates TLC fractions with retention times on the OV-1 column and the compounds that were identified using the GLC-mass spectrometer. The identification was by comparison to the spectra of known compounds.

Figure 6 shows a thin-layer chromatogram of the photolysate extract alongside the identified photolysis products using TLC solvent system 1. The structures of the identified compounds are shown in Figure 7.

Quantitation of Photolysis Products by Radioisotope Techniques. One-gram quantities of the glass beads coated with ¹⁴C-labeled I were exposed to uv light with the filter as described earlier for up to 36 hr. At intervals, three 20-mg samples were weighed into the counting vials to determine the total radioactivity on the beads. The rest of the beads were extracted as before. The cover filter and the base plate were washed with benzene. The combined extracts were evaporated and reconstituted in exactly 500 μ l of benzene. The extracted beads were saved for counting to determine the amount of unextracted radioactivity. An aliquot of the extract was counted to determine radioactivity of benzene extractables. The data are shown in Table II. The results show a progressive decrease in radioactivity in benzene extractables and increases in both unextracted and unaccounted for materials. After 36 hr the figures were 76.1, 13.2, and 10.7%, respectively. The unaccounted radioactivity may be due to volatiles and to loss on the reaction plate.

For quantitation of the photolysis products a 200- μ l aliquot was spotted on the TLC plate along with identified photolysis products. The plate was developed in TLC solvent 1. The plates were scored into zones according to the pattern in Figure 5 and Table I and scraped.

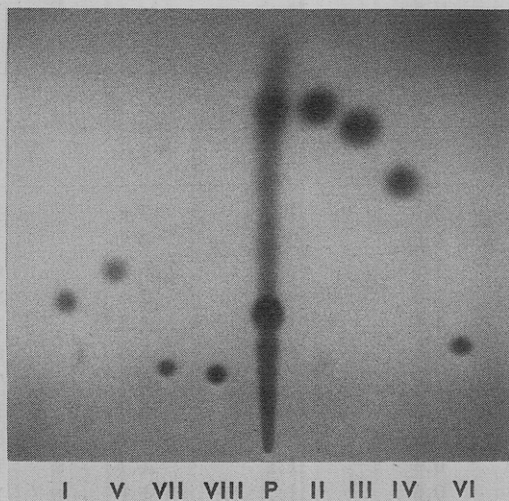


Figure 6. Thin-layer chromatogram of a benzene extract of photolyzed I (spot P) alongside identified photolysis products (see Figure 7); TLC system same as in Figure 5.

Table II. Percent Account of Radioactivity

	0 hr	4 hr	8 hr	16 hr	24 hr	36 hr
Unextractable residue on the beads	3.0	5.1	7.7	9.6	10.4	13.2
Benzene extractables	97.0	91.1	89.7	83.2	81.8	76.1
Unaccounted	0.0	3.8	2.6	7.2	7.8	10.7

Only one other minor GLC peak was detected in this zone. Obviously the higher radioactivity in this zone was due to nonvolatile materials. The benzene unextractable residue on the glass beads progressively increased with time. There also appeared to be a consistent increase in the concentration of the unaccountable radioactivity. It is believed this is due to volatile products and to loss on the reaction plate. The use of the 7740 filter reduced the rate of photolysis, but the photolysis products were the same with and without the filter.

In general, the oxygen-containing products observed from the photolysis of I were the same as those observed from the photolysis of the corresponding acid chloride hydrazide. Although compounds IV, VI, and IX were not detected in the earlier study, they probably were present but went undetected because of their low levels and interferences from other compounds.

Three major reactions were observed: (1) reductive loss of chlorine; (2) loss of either one or two nitrogens; (3) benzoylation. Photochemical reductive dechlorination of aromatic chloro compounds has been reported (Crosby, 1966; Crosby and Leitis, 1969).

Until recently there had been little precedent concerning the photolysis of hydrazides. Stoessel (1964) has reported on the photolysis of aqueous solutions of maleic hydrazide in the presence and absence of oxygen. Several acidic products were identified. Davidson and Lewis (1973) reported that N-N cleavage is the major reaction pathway in the photolysis of hydrazides. Watterson and Shamma (1975) reported that, in addition to N-N cleavage, carbonyl carbon-nitrogen cleavage also occurs. Both these types of cleavage were observed in the photolysis of I.

Hydrazides have been reported to transacylate thermally (Smith, 1966, p 177) and a photochemical equivalent of this reaction can produce VII. A second possible precursor for the additional benzoyl group in VII could be the benzoylazo compound X. Azobenzenes have been shown to be produced by photolysis of hydrazobenzenes (Shizuka et al., 1970) and the benzoylazo compound X, if produced photo-

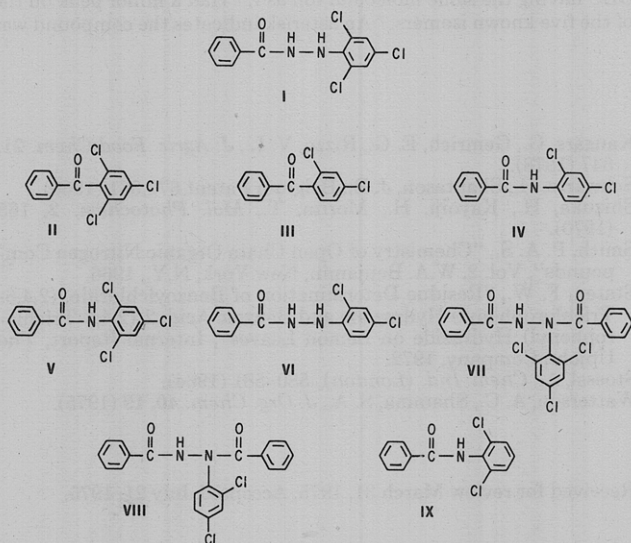
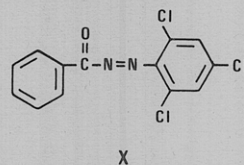


Figure 7. Structures of identified photolysis products of I.

Fractions A and F were eluted with benzene and concentrated. Fraction A was rechromatographed using TLC solvent 2. Fraction F was rechromatographed using solvent system 3. The zones representing the different compounds were scraped from all the plates and transferred into individual liquid scintillation vials and counted.

The data presented in Table III showed the progressive increase in concentration of all the photolysis products. The major photolysis products quantitated by scintillation counting were compounds II and VI representing 6.5 and 8.4% of the radioactivity. The GLC findings (Figure 4) were in agreement with this. Zone B containing IV and zone C containing V and IX accounted for 6.9 and 7.0% of the radioactivity, respectively. The GLC peaks for these compounds were relatively small. As pointed out in the footnote to Table III, there were other GLC peaks in these two zones which might partially account for the discrepancy. Zone A-3 containing compound III accounted for 3.2% of the radioactivity which was corroborated by gas-liquid chromatography. The most serious inconsistency was in the radioactivity (51%) in zone D containing I and the amount shown in the decline curve in Figure 3 by GLC (20-25%).



chemically, could serve as the source of the additional benzoyl group. Acylazo compounds are known to be efficient acylating agents (Smith, 1966, p 185). This benzoylazo compound X could also lose nitrogen to give the observed benzophenones. The observed benzanilides could arise through a photochemical cleavage of the nitrogen-nitrogen bond of VII followed by photochemical dechlorination to form the dichloro derivatives.

ACKNOWLEDGMENT

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Table III. Percent Composition of Photolysis Products Based on Scintillation Counting of Benzene Extractables after TLC Separation

TLC fraction ^a (top to bottom)	Compd identified ^f	% radioactivity at hr					
		0	4	8	16	24	36
Above zone A	*	0.4	0.6	1.0	1.0	2.1	1.8
Zone A-1	*		0.4	0.6	0.5	0.7	1.6
A-2	II	0.3	1.7	1.9	4.1	5.2	6.5
A-3	III	0.2	1.0	0.8	2.1	2.4	3.2
A-4	*	0.3	0.9	1.1	1.3	2.5	1.5
Zone B ^b	IV	1.8	2.4	3.1	6.1	5.3	6.9
Zone C ^c	V + IX	1.0	2.7	4.9	5.2	7.9	7.0
Zone D ^d	I	94.9	83.6	76.9	63.5	54.8	51.1
Zone E ^e	VI	0.4	3.9	5.9	8.6	8.4	8.4
Zone F-1	*	0.1	0.5	0.4	1.1	1.7	1.6
F-2	VII	0.1	0.4	0.5	1.0	1.1	1.2
F-3	VIII	0.1	0.2	0.3	0.8	0.8	1.0
F-4	*		0.1	0.2	0.3	0.5	0.7
Zone G	*	0.2	1.0	1.8	2.6	3.6	3.6
Zone H	*	0.1	0.7	0.6	1.8	2.9	4.1

^a The solvent system for the first TLC was acetic acid-ethyl acetate-*n*-hexane (1:20:80). Zone A was rechromatographed in acetic acid-benzene-hexane (3:30:70) and zone F was rechromatographed in ethyl acetate-chloroform (2:98). ^b There were several minor GLC peaks in this zone. ^c Showed one additional peak. ^d Showed a minor peak on the GLC having the same molecular ion as I. ^e Had a minor peak on the GLC having the same molecular ion as VI. The *t*_R did not agree with any of the five known isomers. ^f An asterisk indicates the compound was not identified.

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