Photo-decarbonylation of β-Styryl Isocyanates (1)

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β-Styryl isocyanate (**1**, R = H) and its β-methyl- (**1**, R = CH_3) and β-phenyl- (**1**, R = C_6H_5) derivatives underwent both extensive polymerization and the loss of the elements of carbon monoxide upon irradiation at 254 nm in cyclohexane. The formation of 2,5-diphenylpyrazine (**3**) and indole **4**, (R = H) from **1**, (R = H) and 2,3-dimethyl-5,6-diphenylpyrazine (**6**) and 2-methylindole (**4**, R = CH_3) from **1**, (R = CH_3) provided diagnostic evidence for styryl nitrene (**2a**) intermediates. The formation of both phenylacetonitrile (**5**, R = H) and α-phenylpropionitrile (**5**, R = CH_3) was assigned to an initial rearrangement of the residue, $C_8H_6(R)\ddot{N}$: (**2**), into a ketenimine concerted with the elimination of carbon monoxide from **1**. Isomerization then produced a nitrile. β-(β-phenyl)styryl isocyanate (**1**, R = C_6H_5) gave no product requiring the intermediacy of a nitrene and/or an azirine. The formation of 2,3,4,5-tetraphenylpyrrole (**8**) was assigned to a dimerization of the isocyanate concerted with or following the elimination of the elements of carbon monoxide and isocyanic acid, and the formation of 3-phenylisocarbostyril (**9**) was assigned to a ring-closure of the isocyanate in an excited triplet state. Each isocyanate gave stilbene and trace amounts of oxidative fragmentation into benzaldehyde and benzonitrile. Solvent participation produced benzylcyclohexane and bicyclohexyl. Two unidentified solids, $C_{17}H_{14}N_2O$ and $C_{12}H_{14}N_2O$, were obtained from **1**, (R = CH_3).

A preliminary report (1b,2) described photoelimination of nitrogen from β-styryl azide and carbon monoxide from β-styryl isocyanate. Both led to the formation of phenylacetonitrile, presumably by similar mechanisms. Continued investigations with the isocyanates (**1**, R = H, CH_3, C_6H_5), readily available by the Curtius reaction from the corresponding cinnamoyl azides (3), revealed that elimination occurred both without and concerted with rearrangement of the residue **2** (1b,4).

Results.

Although extensive polymerization (5) occurred, irradiating styryl isocyanates (**1**, R = H, CH_3, C_6H_5) in cyclohexane at 254 nm; also brought about the elimination of the elements of carbon monoxide (unisolated). The elimination residue **2** (R = H) afforded the formation of 2,5-diphenylpyrazine (**3**), indole (**4**, R = H) and phenylacetonitrile (**5**, R = H). The corresponding products - 2,3-dimethyl-5,6-diphenylpyrazine (**6**), 2-methylindole (**4**, R = CH_3) and α-phenylpropionitrile (**5**, R = CH_3) - were derived from the residue **2** (R = CH_3). In contrast, irradiation of the styryl isocyanate (**1**, R = C_6H_5) did not give tetraphenylpyrazine (**7**), 2-phenylindole and diphenylacetonitrile; however, 2,3,4,5-tetraphenylpyrrole (**8**) and 3-phenylisocarbostyril (**9**) were obtained.

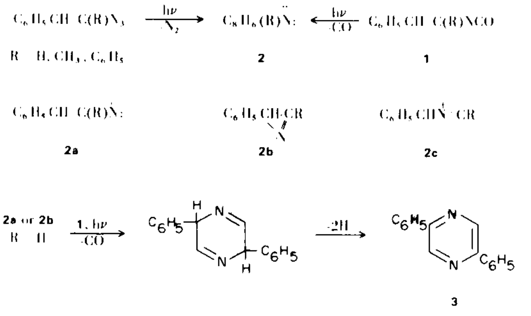
Additional products from the isocyanate (**1**, R = CH_3) included the dimer of *N*-methylphenylketenimine (**10**, R = CH_3), two unidentified solids, $C_{17}H_{14}N_2O$ and $C_{12}H_{14}N_2O$ and methyl phenylacetate, formed by adding methanol to product mixtures containing the ketenimine (**10**).

During irradiation of each isocyanate (**1**) oxidative fragmentation gave benzaldehyde (**11**) and benzonitrile (**12**) and solvent participation gave benzylcyclohexane (**13**) and bicyclohexyl (**14**). (By a dark reaction, exposure to air gave trace amounts of benzaldehyde from **1** (R = CH_3) (6)). Stilbene was also produced by the irradiation of each isocyanate. A separate experiment established the formation of benzonitrile (**12**) in trace amount by irradiating 2,3-diphenylazirine (**2b**, R = C_6H_5) in cyclohexane at 254 nm (7).

The precursor, a cinnamoyl azide ($C_6H_5CH{=}C(R)CON_3$), was substituted for the corresponding isocyanate (1) without introducing a significant change in the product mixture from irradiation.

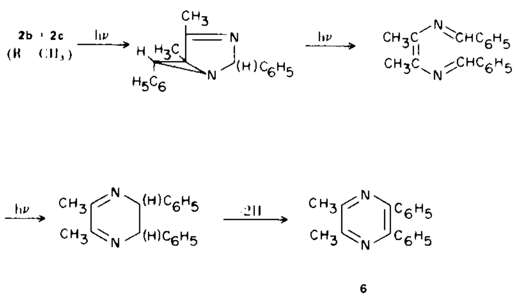
Discussion.

An elimination of carbon monoxide from **1** without rearrangement of the residue **2** would leave a vinyl nitrene (**2a**) and/or an azirine (**2b**) (8). The intermediate **2** could combine with itself, its precursor or with solvent, or it could rearrange or fragment. Since photodimerization of 2-phenyl-2*H*-azirine (**2b**, R = H) into (a) diazabicyclohexene(s) (9) and subsequent transformation into 4,5-diphenylpyrimidine and 2,3-diphenylpyrazine were not detected, it was concluded that the formation of 2,5-diphenylpyrazine (**3**) did not proceed from a diazabicyclohexene by isomerization and aromatization. Instead the formation of pyrazine (**3**) was attributed to an interaction between the intermediate, as either the nitrene (**2a**) or azirine (**2b**) but not as the nitrile ylide (**2c**), and its precursor, a vinyl isocyanate (10); however, an explanation based on a hypothetical dimerization of the isocyanate (**1**, R = H) concerted with or followed by an elimination of two molecules of carbon monoxide and subsequent aromatization has not been excluded (11).

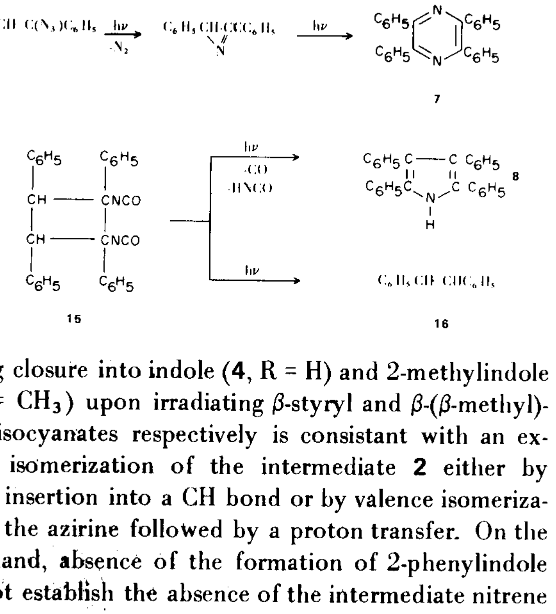


For the transformation **1** (R = CH_3) → **6**, initial self combinations of either **1** or **2** as well as interaction between the two are conceivable. Although none of these would require a rearrangement of the carbon-nitrogen skeleton, each would require a head-to-head attack rather than a head-to-tail combination. The latter leads to the formation of **3** from **1** and also accounts for the phototransformation of vinyl azides into certain pyrazines (12). A search for 2,5-diphenyl-3,6-dimethylpyrazine (corresponding to 2,5-diphenylpyrazine **3** from **1** (R = H)) and 2,6-diphenyl-3,5-dimethylpyrazine was unsuccessful. By separate experiment, it was established that under comparable conditions, 2,5-diphenyl-3,6-dimethylpyrazine did not isomerize into **6**.

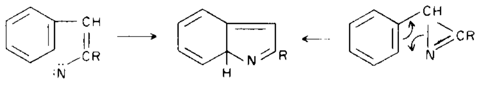
Assuming a sufficient concentration of **2** and a photodimerization of aryl azirines reported to have generality (9b), it is proposed that a combination of **2b** and **2c** (R = CH_3) gave a 2*H*-1,3-diazabicyclohexene which was subsequently transformed into **6** by consecutive valence isomerizations (9d) and aromatization. The simultaneous, and expected, formation of 2,4-diphenyl-5,6-dimethylpyrimidine (9b) was not detected. Previously unknown, 2,3-dimethyl-5,6-diphenylpyrazine (6) was established by its independent synthesis from benzil and 2,3-diaminobutane.



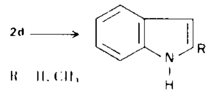
From the irradiation of both α-azido-trans-stilbene (13) and 2,3-diphenylazirine (**2b**, R = C_6H_5) (9d) in cyclohexane, tetraphenylpyrazine (**7**) was obtained in yields of 40 percent with no other product reported (7), *vide ante.* In contrast, the irradiation of β-(β-phenyl)-styryl isocyanate (**1**, R = C_6H_5) gave none of the expected pyrazine (**7**) (as well as none of the isomeric tetraphenylpyrimidine); instead, tetraphenylpyrrole (**8**) was formed. Assuming that the intermediacy of either **2a** or **2b** (R = C_6H_5) would have given at least a detectable amount of tetraphenylpyrazine (**7**), it follows that a dimerization of the isocyanate (**1**, R = C_6H_5) either before or simultaneously with an elimination of carbon monoxide was required (14). Three- four- (15a), five- (15b) and six-membered ring intermediate could lead to the pyrrole (**8**). Although the precursor for **8** was not established, fragmentation of the dimer as a cyclobutane derivative would also offer an explanation for the formation of stilbene (**16**). The formation of **16** from the other styryl isocyanates (**1**, R = H, CH_3) would also be accounted for by a cycloreversion of similar dimers.



Ring closure into indole (**4**, R = H) and 2-methylindole (**4**, R = CH_3) upon irradiating β-styryl and β-(β-methyl)-styryl isocyanates respectively is consistant with an expected isomerization of the intermediate **2** either by nitrene insertion into a CH bond or by valence isomerization of the azirine followed by a proton transfer. On the other hand, absence of the formation of 2-phenylindole does not establish the absence of the intermediate nitrene and/or azirine (**2a**,**b**, R = C_6H_5) since an indole was not reported as a product from the irradiation of β-(β-phenyl)-styryl azide (13) and was not produced in a chromatographically detectable amount from the irradiation of 2,3-diphenylazirine (**2b**, R = C_6H_5) in cyclohexane, methanol or methylene chloride (7). Ring-closure from the isocyanate (**1**) was not excluded but was considered improbable in the absence of a known insertion into a CH bond by either an isocyano or azido nitrogen.



2a **2d** **2b**



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The formation of pyrazines and indoles was considered to be strong diagnostic evidence for the intermediacy of **2** (R = H, CH_3). In addition, an instability of 2-phenyl-2*H*-azirine (**2b**, R = H) and other 2*H*-azirines particularly toward oxygen (8) and polymerization (16) was observed. Oxidative (trace amounts of oxygen are assumed) fragmentation of **2b** (R = H, CH_3) accounted for the formation of benzaldehyde (**11**) and benzonitrile (**12**). Only the intermediacy of an azirine offered a straightforward explanation for the formation of the latter product from isocyanates (**1**, R = H, CH_3) (7). Apparently the production of stilbene from each of the isocyanates (**1**, R = H, CH_3, C_6H_5) by irradiation required fragmentation and combination steps, but not necessarily in that order.

Solvent participation was revealed in the formation of benzylcyclohexane (**13**) and bicyclohexyl (**14**) and may be accounted for by the appropriate combination of benzyl and cyclohexyl radicals. Generation of the radicals, in turn, by the abstraction of hydrogen by phenyl carbene as a triplet (a tentative assignment (17)) would depend on the proposed photoproduction of the carbene by a fragmentation of the azirine (**2b**). It is in agreement with a similar cleavage of 2,3-diphenyl-2*H*-azirine into phenylcarbene and benzonitrile (7).

$$\mathbf{2b} \xrightarrow[h\nu]{O_2} \underset{\mathbf{11}}{C_6H_5CHO} + \underset{\mathbf{12}}{C_6H_5CN}$$

$$\mathbf{2b} \xrightarrow[-HCN]{h\nu} C_6H_5\ddot{C}H \xrightarrow{C_6H_{12}} C_6H_5CH_2\cdot + \cdot C_6H_{11} \longrightarrow$$

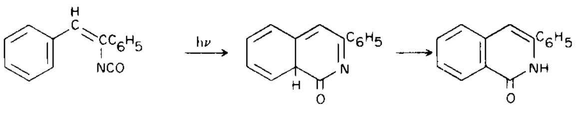
$$\underset{\mathbf{13}}{C_6H_5CH_2C_6H_{11}} + \underset{\mathbf{14}}{(C_6H_{11})_2}$$

In view of the several investigations demonstrating that 2*H*-azirines do not photoisomerize into either nitriles or ketenimines (7,9,13,18), the formation of phenylketenimine (**10**, R = H) and phenylacetonitrile (**5**, R = H) by irradiating the isocyanate (**1**, R = H) and the formation of *N*-methylphenylketenimine (**10**, R = CH_3) and α-phenylpropionitrile (**5**, R = CH_3) by irradiating the isocyanate (**1**, R = CH_3) have been assigned to a rearrangement of **2** concerted with the elimination of carbon monoxide from **1**. Initial migration of R from carbon to nitrogen would lead to the formation of phenylketenimine (**10**, R = H) which was detected but not isolated, and to the formation of *N*-methylphenylketenimine (**10**, R = CH_3) isolated as a dimer with unknown structure (19). Treatment of the product mixture with methanol and hydrochloric acid transformed **10** (R = CH_3) into methyl phenylacetate. Tautomerization of **10** (R = H) accounts for phenylacetonitrile (**5**, R = H) and a similar photomigration of methyl from nitrogen to carbon (20) accounts for α-phenylpropionitrile (**5**, R = CH_3). The formation of **5** by direct proton transfer or methyl migration, whichever is appropriate, from carbon to carbon appears unlikely since irradiation of 4-phenyl-5-deutero-1,2,3-triazole gave (**5**, R = H) but did not produce **5** (R = D) (7).

$$\mathbf{1} \xrightarrow[-CO]{h\nu} \underset{\mathbf{10}}{C_6H_5CH{=}C{=}NR} \xrightarrow{h\nu} \underset{\mathbf{5}}{C_6H_5CH(R)CN}$$

R = H, CH_3

Photoisomerization of **1a** and **1b** was not observed but photocyclization of **1** (R = C_6H_5) led to the formation of 3-phenylisocarbostyril (**9**) in 2.4 percent yield by irradiating **1** (R = C_6H_5) in cyclohexane at 254 nm, 15.0 percent yield by irradiating in cyclohexane at 300 nm and 29.8 percent yield by irradiating in benzene at 254 nm. An increase in ring-closure on changing the solvent from cyclohexane to benzene, E_T 85 kcal, while irradiating at 254 nm is consistent with a triplet excited state for **1** (R = C_6H_5) as an intermediate (21,22). A small increase in the cyclization by irradiating in cyclohexane at 300 nm rather than 254 nm has not been explained.



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EXPERIMENTAL

Instrument data were obtained from a Beckman IR-10 and/or a Perkin-Elmer Model 521 infrared spectrometer, a Varian A-60A nmr spectrometer, a Perkin-Elmer Model 270 mass spectrometer except where noted, and a Perkin-Elmer Model 202 ultraviolet spectrometer except where noted. Irradiation experiments were carried out in a Rayonet Photochemical Reactor. Melting points were determined with a Thomas-Hoover capillary apparatus. Both mp and bp are uncorrected. Elemental analyses were obtained from Microtech Laboratories, Inc., Skokie, Illinois. Gas chromatograph analyses were obtained from a Varian 1800 gas chromatograph equipped with a flame detector and a column of either 5% polyphenyl ether (6 ring) on 80-100 mesh AW DMCS Chrom G, 6′ x 0.25″ (Column A), or 15% Carbowax 20M on 80-100 mesh Chrom W, 6′ x 0.12″ (Column B), or 10% GE XE-60 on AW DMCS Chrom W, 6′ x 0.12″ (Column C).

The preparation of styryl isocyanates (**1**, R = H, CH_3, C_6H_5) was previously described (3).

Irradiation of β-Styryl Isocyanates (**1**, R = H).

Spectrograde cyclohexane was refluxed over lithium aluminum hydride, distilled into an irradiation quartz tube fitted with a bubbler inlet tube through a rubber septum and a gas outlet from a side arm at the top. The system was purged with a slow stream of nitrogen for about 100 hours. Following purging for shorter periods, irradiation developed cloudiness and an opaque film on the wall of the tube after about 10 hours. With a hypodermic needle, the isocyanate was added through the septum to the irradiation tube to give a solution containing approximately 3 mg. of **1** per ml. After irradiation at 254 nm for 26 hours, the solvent from a 100 ml. aliquot was removed *in vacuo*, the residue was dissolved in a minimum amount of methylene chloride, the solution was transferred to a 5 ml. volumetric flask, 5 μl. of bromobenzene was added and methylene chloride was added to fill the flask. For gc analysis the product mixture was applied to column A, *vide ante*, under a column head pressure of 30 psi and temperature programming to give 4 minutes at 80°, 2 minutes at 20°/minute, 2 minutes at 120°, 4 minutes at 20°/minute and 18 minutes at 200°. Each product was identified by comparing rt from columns A and B and mass spectral fragmentation patterns for samples from column B with rt and ms data similarly obtained for authentic samples. Rt assignments in minutes and product yields (ranges in percent for five or more runs) from column A were obtained for bromobenzene (internal standard) 4.3, benzaldehyde 7.4 (0.28 to 1.29), benzonitrile 8.1 (0.03 to 0.14), bicyclohexyl 11.8 (trace), phenylacetonitrile 12.8 (0.78 to 4.31), benzylcyclohexane 15.1 (trace), indole 16.3 (0.19 to 1.16), stilbene 25.9 (trace) (23) and unreacted isocyanate 15.4. The product 2,5-diphenylpyrazine was isolated in 4.02 percent yield by elution with 800 ml. of hexane-benzene (1:2) from the product mixture on a column of silica gel 2 x 20 cm (30-70 mesh) after 700 ml. of the same solvent had removed benzaldehyde, benzonitrile, indole, *cis*-stilbene and phenylacetonitrile. By comparing mass spectra and ir absorption with authentic data and by mixture m.p. 193-194° (24) the sample was identical with an independently prepared sample.

Comparable results were obtained when cinnamoyl azide ($C_6H_5CH{=}CHCON_3$ (3)) was irradiated in place of β-styryl isocyanate.

Irradiation of β-(β-Methyl)styryl Isocyanate (**1**, R = CH_3).

After similar preparation and irradiation at 254 nm for 28 hours, the cyclohexane solution showed ir absorption at 2260 (NCO), 2038 (C=C=N) and 1740-1650 (broad, C=O) cm^{-1}. The solvent was removed *in vacuo*, the residue was triturated with a minimum amount of carbon tetrachloride, and the mixture was filtered to remove a solid. The solution was transferred to a 10 ml. volumetric flask, 10 μl. of bromobenzene was added and carbon tetrachloride was added to fill the flask. For gc analysis the mixture was applied to column A under a column head pressure of 24 psi and temperature programming to give a 2 minutes at 80°, 2 minutes at 20°/minute, 8 minutes at 120°, 2 minutes at 30°/minute, 4 minutes at 180°, 2 minutes at 12°/minute, 8 minutes at 204°. The chromatographic separation gave compounds identified by rt on columns A and C, and mass spectral fragmentation patterns for samples from column C, through comparison with data similarly obtained for authentic samples. Rt assignments for column A and product yields (ranges in percent for five or more runs) were obtained for cyclohexanol 3.4 minutes (trace), bromobenzene 4.4 minutes (internal standard), benzaldehyde 7.2 minutes (0.14 to 0.44), benzonitrile 8.1 minutes (0.05 to 0.26), bicyclohexyl 13.8 minutes (trace), benzyl methyl ketone 14.4 minutes (0.2 to 4.0), α-methylphenylacetonitrile 16.2 minutes (0.53 to 1.29), benzylcyclohexane 19.9 minutes (0.67 to 1.30), 2-methylindole 24.7 minutes (0.09 to 0.82), and *cis*-stilbene 25.9 minutes (trace), along with unreacted starting material 18 minutes.

The portion of the product mixture soluble in carbon tetrachloride was treated for 7 hours at room temperature with 5 ml. of 0.4 *M* methanolic sodium methoxide. The solution was decanted from the precipitated solid mixed with 5 ml. of methanol and 2 ml. of 1.5 *M* hydrochloric acid, and kept at room temperature for 7 hours. After concentration, the residue was slurried in chloroform, filtered and extracted with water, dried (magnesium sulfate), and concentrated under reduced pressure. By gc analysis the residue (2.5 to 3.5 g.) contained increased amounts of benzaldehyde and benzyl methyl ketone along with methyl benzoate. Though benzonitrile and methyl benzoate were difficult to separate by columns, the gc peak gave a parent ion m/e 103 (benzonitrile) before hydrolysis, and a parent ion m/e 136 (methyl benzoate) after hydrolysis. Methyl phenylacetate, rt 15.4 minutes from column A, from the hydrolysis of the ketenimine (**10**), was also present (1 to 2 percent).

The combined fractions of the insoluble solid, 50 mg., 2.53%, m.p. 191-193°, contained the dimer of the ketenimine (**10**) and were recrystallized from ethyl acetate; ir (chloroform): 3070, 3010, 2930, 1650, 1580, and 1115 cm^{-1} (19) and nmr (deuteriochloroform) δ 2.41 (s, 3.0), 7.2-7.7 (m, 4.20), 7.7-8.2 (m, 2.10), and 8.39 (s, 1.06). The mass spectrum showed a parent ion at m/e 262.

Anal. Calcd. for $C_{18}H_{18}N_2$: N, 10.68; m.w. 262.4. Found: N, 10.19.

The liquid residue obtained from chloroform was chromatographically separated from a 2 x 30 cm column containing 50 g. of 30-70 mesh silica gel. Elution of the column with hexane (500 ml.) and a 3:1 hexane-benzene mixture (500 ml.) gave a liquid residue. It was combined with subsequent fractions and analyzed by gc on a 5′ x 1/8″ Carbowax 20M on Chromosorb W column; column temperature 141°; detector 252°; injector 228°; carrier gas (He) 36 ml./minute. A substance with rt 8.9 minutes was identified as benzylcyclohexane by ir (chloroform): 3080, 3010, 2940, 2870, 1615, and 1460 cm^{-1}, and identical comparison of gc retention time and mass spectral fragmentation pattern (parent ion m/e 174) with corresponding values for an authentic sample. Elution with 3:2 hexane-benzene (500 ml.) gave a liquid residue (125 mg.) in which benzaldehyde (rt 3.8 minutes, major component) with methyl benzoate and α-methylphenylacetonitrile (rt 5.2 and 13.2 minutes, respectively) were present; ir (3495 cm^{-1}) indicated the presence of a small quantity of 2-methylindole (**4**, R = CH_3). Silica gel sheets (Eastman Chromogram Sheets, K301R2) were streaked with the mixture and developed with 3:2 hexane-benzene. A band with an Rf comparable to that for authentic 2-methylindole was removed and slurried in chloroform; after concentration, the residue was spotted on slides along with authentic **4** (R = CH_3) and developed by the hexane-benzene mixture. The unknown and authentic 2-methylindole gave identical tlc R_f values and the same green fluorescence under short wavelength uv light. Further elution of the column with 3:2 hexane-benzene (500 ml.) yielded a liquid residue (41 mg.) in which α-methylphenylacetonitrile (**5**, R = CH_3), was the major component along with some benzaldehyde and traces of methyl phenylacetate and with benzyl methyl ketone (produced by hydrolysis of **1** (R = CH_3) in yields ranging from 0.2 to 4.0%. Methyl phenylacetate was eluted in the next fraction with 3:2 hexane-benzene (250 ml.) along with some benzaldehyde. Elution with 1:1 hexane-benzene (750 ml.) gave a liquid which partially solidified. The liquid was identified by its gc retention time as benzyl methyl ketone. Filtration and washing the precipitate with a few drops of cold hexane yielded a yellow solid 50 mg., 2.55%, m.p. 141-142.5°; ir (chloroform) 3050, 2970, 2920, 2860 (aromatic and aliphatic C-H) in addition to sharp, medium to strong peaks at 1615, 1562, 1535, 1478, 1442, 1390, 1342, and 1305 cm^{-1}; nmr (deuteriochloroform) δ 2.40 (s, 3.00), 7.28-7.60 (m, 6.2), 7.75-8.25 (m, 4.14) and 8.59 (s, 1.03); m/e 262. The structure of this compound has not been determined.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.37; N, 10.68; m.w. 262.3. Found: C, 77.72; H, 5.47; N, 10.54.

The next fraction, eluted with 1:2 hexane-benzene (250 ml.), and 1:3 (500 ml.) yielded a liquid residue which later solidified. The solid, 65 mg., 3.35%, recrystallized from hexane; m.p. 97-98°; ir (carbon tetrachloride) 3080, 3055, 3030, 2990, 2940, 2917 in addition to intense sharp peaks at 1445, 1400, 1230, 1165, 965, and 690 cm^{-1}; nmr (carbon tetrachloride) δ 2.53 (s, 3.00) and 7.1-7.6 (m, 5.35); m/e 260. The compound was identified as 2,3-dimethyl-5,6-diphenylpyrazine (**6**) by comparing tlc behavior, ir, nmr, and mass spectra with corresponding data obtained from authentic material, prepared from benzil and 2,3-diaminobutane.

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76; m.w. 260. Found: C, 83.04; H, 5.96; N, 10.74.

Subsequent elution with benzene (500 ml.) and benzene-acetone mixtures (19:1) (150 ml.) 2:1 (350 ml.) gave an orange viscous liquid believed to be polymeric material 1.04 g., 43.5%. The material appeared to be unchanged by heating in acid or base. Further elution with benzene-acetone 1:1 (400 ml.), and 2.3 (100 ml.) yielded 260 mg., 17.2% of a pale yellow solid. Recrystallization from ethanol gave colorless crystals, m.p. 191-193° dec.; ir (chloroform) 3434 (NH) and 1716 cm^{-1} (CO, broad); nmr (DMSO-d_6) δ 1.03 (s), 1.93 (s), 3.30 (broad absorption) and 7.0-7.8 (m); m/e 202.

Anal. Calcd. for $C_{12}H_{14}N_2O$: C, 71.25; H, 6.97; N, 13.85; m.w. 202.2. Found: C, 71.48; H, 7.05; N, 13.80.

This compound has not been identified. Upon hydrolysis in dilute sodium hydroxide it gave a 78% yield of benzyl methyl ketone. Stripping the column with methanol yielded a brown viscous liquid, 0.23 g., 9.65%.

Irradiation of β-(β-Phenyl)styryl Isocyanate (**1**, R = C_6H_5).

A solution of 3.75 g. (15.1 mmoles) of α-phenylcinnamoyl azide ($C_6H_5CH{=}C(C_6H_5)CON_3$) (**3**) in 50 ml. of cyclohexane was refluxed for 7 hours, as nitrogen was eliminated and the isocyanate (**1**, R = C_6H_5) was formed. (Disappearance of azide and production of isocyanate was followed by ir). The solution was diluted to a volume of *ca.* 400 ml. with anhydrous cyclohexane, deoxygenated with a slow stream of nitrogen for 40-48 hours (after which time the volume had decreased to 350 ml.), irradiated at 254 nm for 15 hours, filtered to remove 3-phenylisocarbostryil, (**9**) and concentrated under reduced pressure. The residue was treated with a small amount of carbon tetrachloride, filtered and concentrated to give **9**, 90 mg. (combined fractions) 2.4% (3.1% based on starting material reacted).

The residue was hydrolyzed in 8 ml. of acetone and 1 ml. of 1.5 *N* hydrochloric acid for 20 hours at room temperature. Removal of the acetone, dissolution in chloroform, extraction with water, drying (magnesium sulfate) and removal of the chloroform gave a mixture which was chromatographed on a 2 x 30 cm silica gel column (30-70 mesh). Fraction 1, eluted with 3:2 benzene-hexane (500 ml.) contained a white solid **8**, 115 mg., 4.4%; ir (chloroform) 3490 cm^{-1} (NH); nmr shows only aromatic protons. The compound was identified as 2,3,4,5-tetraphenylpyrrole on the basis of mass spectral (25) analysis, m/e 371, m.p. 214-215° (26), and nitrogen analysis.

Anal. Calcd. for $C_{28}H_{21}N$: N, 3.77. Found: N, 4.01.

Fraction 2, eluted with 1:1 (250 ml.) and 3:2 (250 ml.) of benzene-hexane yielded 430 mg., 14.7% of deoxybenzoin (produced by hydrolysis of **1** (R = C_6H_5). Subsequent elution with 1:1 benzene-acetone and pure methanol yielded what appeared to be polymeric material, 2.20 g., 67% by weight, which was not further characterized.

A product mixture was obtained for gc analysis by the following procedure. Dried cyclohexane (300 ml.) was deoxygenated with a slow stream of nitrogen (20 ml./minute) for 80 hours in a quartz photolysis tube. α-Phenylcinnamoyl azide ($C_6H_5CH{=}C(C_6H_5)$-CON_3) 20 (10 g., 4.02 mmoles) was added and the tube was heated in boiling water for 5 hours. The solution was cooled to room temperature under positive nitrogen pressure and irradiated at 254 nm for 19 hours. After evaporation of the solvent, the residue was dissolved in methylene chloride, quantitatively transferred to a 10 ml. volumetric flask and mixed with 10 μl. bromobenzene as an internal standard.

The product mixture was subjected to qualitative and quantitative analysis by gas chromatography on column B with a column head pressure of 22 psi and temperature programmed as follows: 6 minutes at 90°, 12 minutes at 12°/minute and 24 minutes at 234°. The following compounds were detected in trace amounts and identified by the identical comparison of their retention times with those of authentic samples: bromobenzene (internal standard), 3 minutes, bicyclohexyl, 5.2 minutes, benzaldehyde, 6.6 minutes, benzonitrile, 9.1 minutes, benzylcyclohexane, 11.9 minutes, *cis*-stilbene, 16.4 minutes, *trans*-stilbene, 20.2 minutes (23). Diphenylacetonitrile (23 minutes) could not be detected in the reaction mixture. Authentic 2-phenylindole was not eluted under these conditions.

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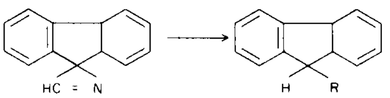

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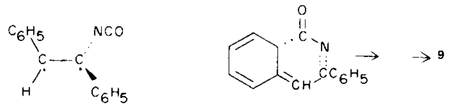

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