2,2′,4,4′-Tetrabromo-N-methyldiphenylamine (IIa).—N-Methyldiphenylamine[13] (50 g., 0.273 mole) was dissolved in a mixture of carbon tetrachloride and chloroform (50:50 v./v., 1100 ml.) and a solution of N-bromosuccinimide (200 g., 1.125 moles) was added slowly at room temperature in 20 hr. The mixture was water washed and dried over magnesium sulfate, and the solvent was removed. The yield was 126 g. of solid, m.p. 143–146°. Recrystallization from hot Skellysolve C afforded an 83% yield of pure 2,2′,4,4′-tetrabromo-N-methyldiphenylamine (IIa), m.p. 142–144°, $\lambda_{\max}^{CHCl_3}$ 291 mμ (ε 14,500).

Anal. Calcd. for $C_{13}H_9Br_4N$: C, 31.3; H, 1.82; Br, 64.2. Found: C, 31.6; H, 1.66; Br, 64.3.

2,8-Dibromo-5-methyl-10,10-diphenyl-5,10-dihydrophenazasiline (IVa).—To an ether (300 ml.) solution of 2,2′,4,4′-tetrabromo-N-methyldiphenylamine (37.4 g., 0.075 mole) was added an ether solution of *n*-butyllithium (175 ml., 0.12 mole). After addition of dichlorodiphenylsilane (18.9 g.) in ether (90 ml.), the reaction was found to be complete in 22 hr. at −5 to 0°. The solution was washed with water and the organic layer was dried over anhydrous sodium sulfate. Solid 2,8-dibromo-5-methyl-10-diphenyl-5,10-dihydrophenazasiline recovered on removal of the solvent weighed 30.6 g., m.p. 170–198°. The product recrystallized from *n*-butyl alcohol, m.p. 200–202°, $\lambda_{\max}^{CHCl_3}$ 221 mμ (ε 33,200).

Anal. Calcd. for $C_{15}H_{19}Br_2NSi$: Br, 30.7. Found: Br, 30.7.

2,8-Dibromo-5-ethyl-10,10-dimethyl-5,10-dihydrophenazasiline (XI).—To a slurry of 2,2′4,4′-tetrabromo-N-ethyldiphenylamine (II, 25.6 g., 0.5 mole) in 175 ml. of dry ether at −5 to 0° was added ethereal *n*-butyllithium (6.4 g., 0.10 mole). To the resulting dilithio intermediate (III) was added dimethyldichlorosilane (6.4 g., 0.05 mole) at 0–5°. After 20 hr. the reaction mixture was water washed and dried over anhydrous sodium sulfate, and the ether was distilled, leaving 19.0 g. of crude solid product. Recrystallization from isopropyl alcohol yielded pure 2,8-dibromo-5-ethyl-10,10-dimethyl-5,10-dihydrophenazasiline (XI), m.p. 132.5–134°, $\lambda_{\max}^{CHCl_3}$ 295 mμ (ε 20,500).

Anal. Calcd. for $C_{15}H_{17}Br_2NSi$: Br, 38.9. Found: Br, 38.9.

2,8-Dibromo-5,10,10-trimethyl-5,10-dihydrophenazasiline (XIa).—The same procedure as for the 5-ethyl derivative XI was followed to produce the above product, m.p. 148–149°.

Anal. Calcd. for $C_{14}H_{15}Br_2NSi$: C, 45.4; H, 3.81; Br, 40.02. Found: C, 45.25; H, 3.96; Br, 40.03.

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (V).—Hydrogenation of 2,8-dibromo-5-ethyl-10,10-diphenylphanazasiline (535 mg., 0.001 mole) in benzene (3 ml.) with 5% palladium on charcoal (250 mg.) and sodium acetate (500 mg.) was carried out at 25° for 4 hr. at 35- to 40-p.s.i.g. pressure. The charge was filtered, water washed, and dried with anhydrous sodium sulfate. The crude product upon removal of benzene weighed 377 mg., m.p. 115–125°, and was bromine free. Recrystallization of 353 mg. of crude product from ethanol yielded pure 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (310 mg., 88% yield), m.p. 122–125°. Mixtures with authentic 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline showed no depression of the melting point.

5-Methyl-10,10-diphenyl-5,10-dihydrophenazasiline (Va).—A solution of 2,8-dibromo-5-methyl-10,10-diphenylphenazasiline (1.3 g., 0.0025 mole) in a mixture of benzene (10 ml.) and ethanol (10 ml.) was hydrogenated with potassium acetate (0.612 g., 0.0063 mole) and 5% palladium on charcoal (0.1 g.) under 40-p.s.i.g. pressure for 72 hr. Work-up similar to Va yielded a crude product weighing 1.08 g. Recrystallization from ethyl acetate and then Skellysolve B afforded pure 5-methyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 186–188°. This agrees with the compound reported by Gilman.[1,2]

2,8-Dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazastanine (VIII).—In the usual manner, 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (25.6 g., 0.05 mole) in diethyl ether (150 ml.) was first treated with ethereal *n*-butyllithium (159 ml., 0.10 mole) at 0°. After Color Test II[14] was negative, indicating complete reaction of *n*-butyllithium, a solution of diphenyltin dichloride (18.9 g., 0.055 mole) in diethyl ether (50 ml.) was added. After overnight reaction at 25°, the reaction mixture was water washed and dried with anhydrous sodium sulfate, and the crude solid obtained after removal of solvent was purified by chromatography on alumina, 39.3% yield, m.p. 177–178°.

Anal. Calcd. for $C_{26}H_{21}Br_2NSn$: C, 50.0; H, 3.38; Br, 25.5. Found: C, 50.5; H, 3.40; Br, 25.1.

2,8-Dimethyl-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (X).—To a suspension of 42.8 g. (0.08 moles) of the dibromosiline IV in 350 ml. of ether at 10° was added a total of 0.21 mole of ethereal *n*-butyllithium. A clear solution was first obtained, and then a precipitate separated. After 2 hr. the interconversion reaction was complete and 35.2 g. (0.25 mole) of methyl iodide in ether was added. The mixture was stirred for 16 hr. to complete the reaction. After hydrolysis and neutralization with acid, the solid product was extracted with benzene, and the solution was evaporated to give 32 g. of crude crystals, m.p. 147–156°. After chromatography on alumina and recrystallization from hexane, 16.1 g. (50%) of X was obtained, m.p. 162.5–163°, $\lambda_{\max}^{CHCl_3}$ 223 mμ (ε 36,600).

Anal. Calcd. for $C_{28}H_{27}NSi$: C, 83.94; H, 6.68. Found: C, 83.76; H, 6.43.

5-Ethyl-10-,10-diphenyl-5,10-dihydrophenazasiline (V).—A suspension of 2,8-dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV, 10.7 g., 0.02 mole) in dry diethyl ether (150 ml.) was slowly treated with ethereal *n*-butyllithium (57.3 ml., 0.055 mole) at 0°. After 1.5 hr. at 10–15° tests indicated complete interconversion of lithium for bromine. The suspension was poured on 400 g. of ice and water and neutralized with dilute sulfuric acid, and the ether layer was washed with water. Crude product obtained by distillation of solvent was bromine free. After five recrystallizations from isopropyl alcohol, 2.0 g. of product, m.p. 120.5–122°, was obtained. Mixture with an authentic sample of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline showed no depression of the melting point.

2,2′,8,8′-Tetrabromo-5,5′-diethyl-10,10′-spirobi(5,10-dihydrophenazasiline) (VI).—To a suspension of 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (115.2 g., 0.0025 mole) in diethyl ether (675 ml.) was slowly added 0.45 mole of ethereal *n*-butyllithium at −5 to 0° during 50 min.; this was held for 1.25 hr. A solution of silicon tetrachloride (19.6 g., 0.1152 mole) in diethyl ether (90 ml.) was then added at −30° in 0.5 hr. The reaction mixture was held at 25° for 19 hr. and then mixed with water. The white solid was filtered, washed with water, dried, and upon recrystallization from diethyl ether yielded pure VI, 62.0 g. (75.1% yield), m.p. 275–276.5°, $\lambda_{\max}^{CHCl_3}$ 321 mμ (ε 21,300).

Anal. Calcd. for $C_{28}H_{22}Br_4NSi$: C, 45.8; H, 3.02. Found: C, 45.5; H, 3.46.

5,5′-Diethyl-10,10′-spirobi(5,10-dihydrophenazasiline) (VII).—Debromination of 2,2′,8,8′-tetrabromo-10,10′-diethylspirobiphenylphenazasiline (7.34 g., 0.01 mole) in benzene (100 ml.) was accomplished, using a solution of potassium acetate (2.9 g., 0.06 mole in 60 ml. of ethanol), 5 g. of 5% palladium on charcoal, and 40-p.s.i.g. pressure at 60°, in 1.75 hr. After removal of catalyst, water wash, and solvent distillation, bromine-free crude product was obtained, weighing 4.0 g. Ethyl acetate recrystallization yielded 3.4 g. (81%) of 5,5′-diethyl-10,10′-spirobi(5,10-dihydrophenazasiline), m.p. 214–216°, $\lambda_{\max}^{CHCl_3}$ 223 mμ (ε 55,120). This agrees with the compound obtained by Gilman and Zeuch,[3] m.p. 215.5–217°.

Acknowledgment.—Analytical results were obtained by Mr. R. N. Boos and Miss L. E. May. The ultraviolet spectra were run by Mr. A. Kalowsky. Special thanks are due Dr. F. M. Meigs for his organizational support.

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(13) C. S. Gibson and D. C. Vining, *J. Chem. Soc.*, **123**, 831 (1923).

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Tetracyano-*p*-phenylenediamine

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Contribution No. 1087 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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In the course of studies aimed at the synthesis of hexacyanobutadiene[1] from 1,1,2,2-tetracyanoethane[2]

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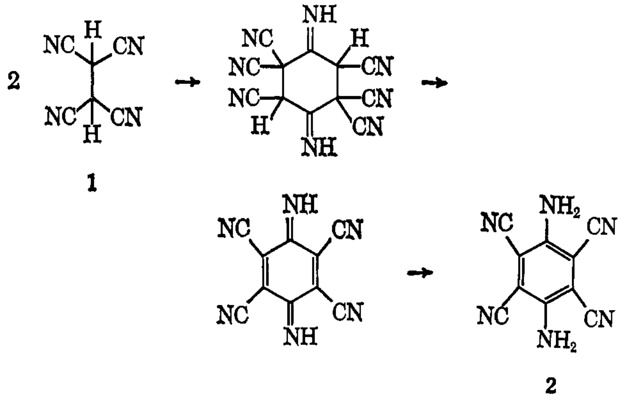
(1) O. W. Webster, *J. Am. Chem. Soc.*, **86**, 2898 (1964).

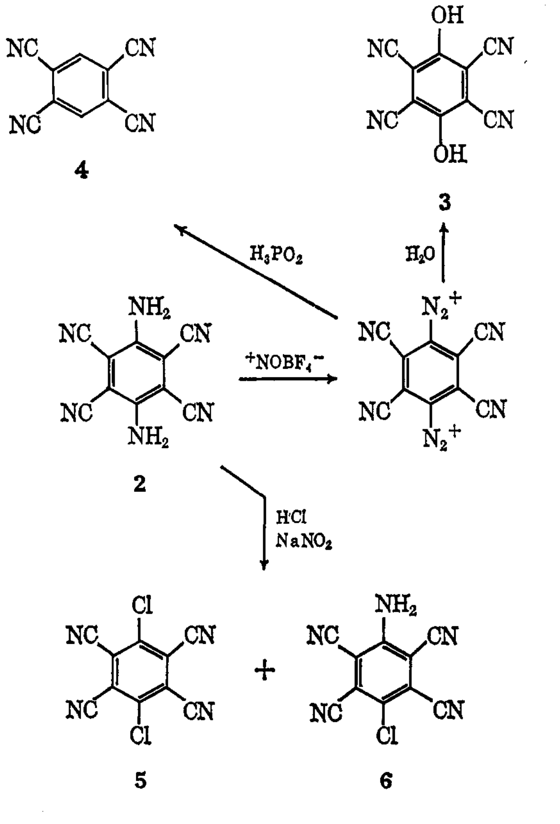
(2) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

(1), it was found that the previously unknown tetracyano-*p*-phenylenediamine (2) was formed in 3.7% yield when the tetracyanoethane 1 was heated in dry acetic acid with potassium acetate. Other products found in the reaction included potassium tetracyanoethylene ion radical,[3] potassium tricyanoethenolate,[4] potassium pentacyanopropenide,[4] hydrogen cyanide, and potassium 1,1,2,3,4,5,5-heptacyanopentadienide.[1] With acetone as solvent, potassium heptacyanopentadienide was produced in 35% yield, but no tetracyano-*p*-phenylenediamine could be detected. Tetracyanoethane under more basic conditions gives hexacyanobutenediide.[1]

We believe the diamine is formed by a double Thorpe condensation of tetracyanoethane, followed by elimination of two molecules of hydrogen cyanide to give an intermediate imine that is reduced to the *p*-phenylenediamine 2 by tetracyanoethane.



Tetracyano-*p*-phenylenediamine is a bright orange-red fluorescent solid ($\lambda_{max}^{CH_3CN}$ 498 mμ) that decomposes at about 275°. The compound is very sensitive to nucleophilic reagents, and this may account for the low yield in the synthesis reaction.



The diamine was treated with nitrosyl fluoroborate, and the resulting tetrazonium salt was converted to tetracyano-*p*-hydroquinone[5] (3) in 35% yield and to tetracyanobenzene[6] (4) in 65% yield.

A mixture of 1,4-dichloro-2,3,5,6-tetracyanobenzene (5) and 1-amino-4-chloro-2,3,5,6-tetracyanobenzene (6) resulted from reaction of the diamine 2, hydrochloric acid, and sodium nitrite.

Experimental

Tetracyano-*p*-phenylenediamine (2).—To a solution of 80 g. of freshly fused potassium acetate in 650 ml. of glacial acetic acid and 80 ml. of acetic anhydride cooled in ice was added, in about 10-g. portions, over 30 min., 130 g. (1.0 mole) of tetracyanoethane with stirring under nitrogen. The temperature rose spontaneously to about 15° while the solution became dark. Stirring was continued at ice-bath temperatures for 1 hr. and at room temperature for 24 hr. The dark mixture was taken to dryness on a rotary evaporator, 500 ml. of distilled water was added, and the mixture was stirred rapidly until no further solution took place. Celite filter aid was added, and the mixture was filtered. The filter cake was dried *in vacuo* and suspended in 250 ml. of acetonitrile, and the slurry was chromatographed over 2 lb. of Woelm acidic alumina. Continued elution with acetonitrile and concentration of the washings provided 3.72 g. (3.7%) of tetracyano-*p*-phenylenediamine as deep red microcrystals, dec. pt. *ca.* 275°. The ultraviolet and visible spectrum had $\lambda_{max}^{CH_3CN}$ 498 mμ (ε 6930), 288 (7570), and 263 (18,000). The infrared spectrum was indicative of a highly symmetrical structure and had bands at 3400, 3300, 2200, 1630, and 1280 cm.$^{-1}$. A sample for analysis was recrystallized from acetonitrile.

Anal. Calcd. for $C_{10}H_4N_6$: C, 57.7; H, 1.94; N, 40.3; mol. wt., 208. Found: C, 58.2; H, 2.35; N, 40.2; mol. wt. (freezing point depression in DMSO), 211.

1,1,2,3,4,5,5-Heptacyano-1,3-pentadienide.—Tetracyanoethane (5.0 g.) was added in one portion to a mixture of 6.0 g. of anhydrous potassium acetate in 100 ml. of reagent grade acetone under nitrogen. While stirring for 16 hr., a dark red solid was deposited. The mixture was diluted with ether, and the precipitate was collected on a filter. A cold water wash removed excess potassium acetate and pentacyanopropenide. The remaining red potassium salt was recrystallized from water to give potassium heptacyanopentadienide (1.3 g., 35% yield), identified by its visible spectrum.[1]

Tetracyano-*p*-hydroquinone (3).—To a cold suspension of tetracyano-*p*-phenylenediamine (0.75 g.) in 50 ml. of dry nitromethane was added 1.0 g. of nitrosyl fluoroborate (Ozark-Mahoning Corp., Tulsa, Okla.) in one portion. Urea (0.2 g.) was added as a solid to destroy excess nitrosating agent. Water (2 ml.) was added, and the mixture was warmed on a steam bath for 3 hr. The mixture was cooled, the aqueous layer was separated, and the organic layer was dried and then evaporated to dryness. The residue was taken up in ethyl acetate and chromatographed over Woelm neutral alumina. The bright yellow band was eluted with ethyl acetate and evaporated to dryness, and the product was recrystallized from chloroform–acetone, yielding 0.33 g. of yellow microcrystals: dec. pt. >275°; λ_{max}^{EtOAc} 408 mμ (ϵ_{max} 7000), 254 (25,200), and 216 (37,000); infrared bands at 3600, 3560, 3330, 2250, 1640, 1560, 1290, and 912 cm.$^{-1}$. In solution, the hydroquinone was yellow with a bluish green fluorescence, while the anion in methanolic potassium carbonate solvent was orange-red with a yellow fluorescence.

Anal. Calcd. for $C_{10}H_2N_4O_2$: C, 57.2; H, 0.96; N, 26.7. Found: C, 56.9; H, 1.12; N, 26.6.

1,2,4,5-Tetracyanobenzene (4).—To a cold suspension of 350 mg. of tetracyano-*p*-phenylenediamine in 25 ml. of dry nitromethane was added 420 mg. of solid nitrosyl fluoroborate in one portion. After stirring 30 min., the orange-red diamine had completely dissolved leaving a yellow-tan solution. Three

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[3] O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

[4] W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *ibid.*, **80**, 2795 (1958).

[5] K. Wallenfels and G. Bachmann, *Angew. Chem.*, **73**, 142 (1961).

[6] D. D. MacRitchie and E. A. Lawton, *J. Org. Chem.*, **24**, 359 (1959).

milliliters of 50% aqueous hypophosphorous acid was added in one portion, and the mixture was stirred overnight at 25°. The mixture was diluted with a saturated salt solution, and the organic layer was separated and dried. The solvent was removed *in vacuo*, the residue was taken up in ethyl acetate, and chromatographed on neutral alumina (Woelm). Elution with ethyl acetate gave a yellow solution which, when evaporated to dryness and recrystallized from ethanol, yielded pyromellitonitrile (0.16 g., 56%), m.p. 260–263° (sealed tube), identical in all respects with an authentic sample prepared by dehydration of pyromellitic tetramide.[6] Further elution gave small amounts of tetracyano-*p*-hydroquinone (*ca.* 1 mg.) which exhibited blue-green fluorescence in solution, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 408 mμ.

1,4-Dichloro-2,3,5,6-tetracyanobenzene (5) **and 1-Amino-4-chloro-2,3,5,6-tetracyanobenzene** (6).—To a stirred suspension of 0.95 g. (4.56 mmoles) of 1,4-diaminotetracyanobenzene in 100 ml. of acetonitrile and 10 ml. of 6 *N* hydrochloric acid was slowly added (0.5 hr.) a solution of 3.0 g. (43.5 mmoles) of $NaNO_2$ in 10 ml. of water. The reaction mixture was then heated at 50° for 0.5 hr. On dilution with 1 l. of water, 0.87 g. of a mixture of 1,4-dichlorotetracyanobenzene and 1-amino-4-chlorotetracyanobenzene precipitated. The two substances were separated by chromatography on Woelm alumina (acid, activity grade I) using ethylene chloride–ethyl acetate. The white dichloro compound (0.53 g., 47% yield) was eluted first followed by yellow aminochlorotetracyanobenzene (0.10 g., 10% yield). An analytical sample of 1,4-dichlorotetracyanobenzene, dec. 329°, was prepared by recrystallization from ethylene chloride: $\lambda_{\max}^{\mathrm{KBr}}$ 4.45, 7.12, 7.23, 8.00, 8.15, 8.33, and 12.83 μ; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 354 mμ (ε 5630), 399 (3980), 269 (10,620), 260 (11,610), 253 (13,350), 240 (46,900), and 232 (71,200).

Anal. Calcd. for $C_{10}Cl_2N_4$: C, 48.7; Cl, 28.7; N, 22.7. Found: C, 48.9; Cl, 28.4; N, 22.7.

An analytical sample of 1-amino-4-chlorotetracyanobenzene was prepared by recrystallization from ethylene chloride. It decomposed at 330° (sealed tube) without melting: $\lambda_{\max}^{\mathrm{KBr}}$ 2.85, 2.97, 3.07, 4.47, 6.06, 6.35, 6.90, 7.79, and 12.00 μ; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 432 mμ (ε 7720), 275 (9300), 260 (28,200), and 222 (39,300).

Anal. Calcd. for $C_{10}H_2ClN_5$: C, 52.7; H, 0.88; N, 30.9. Found: C, 52.9; H, 1.05; N, 30.0.

The Photoanilide Rearrangement

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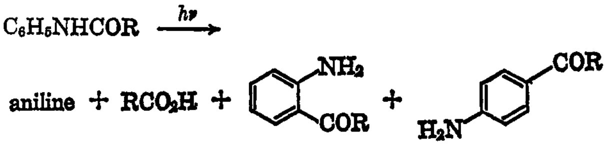
Carbonyl compounds, when irradiated with ultraviolet light, have given rise to many interesting reactions. In a number of instances, a bond which is immediately attached to the carbonyl group cleaves. This is known where the other substituents attached to this bond are alkyl,[3] phenoxy,[4] and vinyl ether[5] groups. The photochemical reactions of the phenoxycarbonyl compounds, *i.e.*, phenyl esters, yield products of rearrangement similar to the Fries reaction. Hence this rearrangement is now termed the photo Fries reaction.

We became interested in applying this cleavage to still another carbonyl derivative, the anilides. In contrast to the Fries reaction on phenyl esters, the rearrangement of the structurally analogous anilides by Lewis acids is not well known.[6] Acetanilide and propionanilide are known to rearrange to *p*-aminoacetophenone and *p*-aminopropiophenone, respectively, with $AlCl_3$ as a catalyst. The *ortho* isomer was believed to be present in the reaction of acetanilide. In a similar manner, benzanilide provided only the *p*-amino ketone.

We now wish to report the photochemistry of acetanilide, propionanilide, butyranilide, and benzanilide.[7] The irradiations were completed using absolute ethyl alcohol as the solvent in a quartz vessel under 1 atm. of nitrogen. The results are summarized in the general reaction 1 and compiled in Table I. It is interesting to note that a 3-day irradiation time (with a Hanovia 550-w. lamp) had an adverse effect on the yields based on recovered starting material. Caution had to be exercised in the isolation of *o*-aminobenzophenone because it was only slowly soluble in 10% HCl and, as a consequence, could be missed in the reaction mixture if little care were exercised.



(1)

TABLE I

ANILIDE IRRADIATION PRODUCTS AND YIELDS, %

Compd.	*ortho* isomer	*para* isomer	Aniline	Acid
Acetanilide	14[a]	12[a]	6[a]	...
	20[b]	25[b]	18[b]	...
Propionanilide	13[a]	10[a]	7[a]	...
	22[b]	25[b]	17[b]	...
Butyranilide	17[b]	23[b]	20[b]	...
Benzanilide	14[a]	12[a]	Trace[a]	27[a]

[a] Results at the University of North Dakota with a 550-w. high-pressure Hanovia mercury arc lamp and 3-day irradiation periods. [b] Results at the Daniel Sieff Research Institute with Hanau Q 81 high-pressure mercury vapor lamps and 8–18 hr. irradiation periods.

Some experiments were carried out to help elucidate the mechanism of this reaction. Carbon monoxide and hydrogen were detected in the gases from the butyranilide reaction mixture. This indicates that the reaction probably follows a pathway involving a butyryl radical.[8] No acetaldehyde could be detected in the exhaust gases from the reaction of acetanilide in ethanol indicating that the acetyl radical, when formed, preferentially loses carbon monoxide rather than abstracting a hydrogen atom.

Both *o*-aminoacetophenone and *p*-aminoacetophenone were stable under the reaction conditions (when irradiated with Hanau Q 81 lamps), therefore neither is an intermediate in the formation of the other.

Kobsa[8] has proposed a mechanism for the photo Fries reaction involving homolysis of the starting material into a free-radical pair, held together in a

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(1) Daniel Sieff Research Institute.

(2) Taken in part from the Ph.D. Dissertation of D. V. Rao, University of North Dakota, 1965. This investigation was supported in part by a Public Health Service Research Grant GM No. 01012-13 from the National Institute of General Medical Sciences, U. S. Public Health Service, and a Faculty Research Grant from the University of North Dakota.

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(7) D. Elad, *Tetrahedron Letters*, No. **14**, 873 (1963); V. I. Stenberg and D. V. Rao, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963; Abstracts of Papers, p. 90Q.

(8) *Cf.* H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).