

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.⁸ Further elution gave small amounts of tetracyano-*p*-hydroquinone (*ca.* 1 mg.) which exhibited blue-green fluorescence in solution, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 408 m μ .

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 NaNO₂ 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: $\lambda_{\text{max}}^{\text{KBr}}$ 4.45, 7.12, 7.23, 8.00, 8.15, 8.33, and 12.83 μ ; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 354 m μ (ϵ 5630), 399 (3980), 269 (10,620), 260 (11,610), 253 (13,350), 240 (46,900), and 232 (71,200).

Anal. Calcd. for C₁₀Cl₂N₄: 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: $\lambda_{\text{max}}^{\text{KBr}}$ 2.85, 2.97, 3.07, 4.47, 6.06, 6.35, 6.90, 7.79, and 12.00 μ ; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 432 m μ (ϵ 7720), 275 (9300), 260 (28,200), and 222 (39,300).

Anal. Calcd. for C₁₀H₂ClN₄: 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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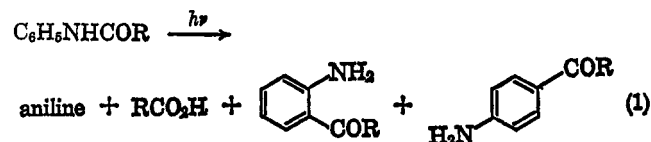
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Carbonyl compounds, when irradiated with ultraviolet light, have given rise to many interesting reactions. In a number of instances, a bond which is immediately attached to the carbonyl group cleaves. This is known where the other substituents attached to this bond are alkyl,³ phenoxy,⁴ and vinyl ether⁵ groups. The photochemical reactions of the phenoxy carbonyl 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 AlCl₃ 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 in-



teresting 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.

TABLE I
ANILIDE IRRADIATION PRODUCTS AND YIELDS, %

Compd.	<i>ortho</i> isomer	<i>para</i> 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.

Kobsa⁸ has proposed a mechanism for the photo Fries reaction involving homolysis of the starting material into a free-radical pair, held together in a

(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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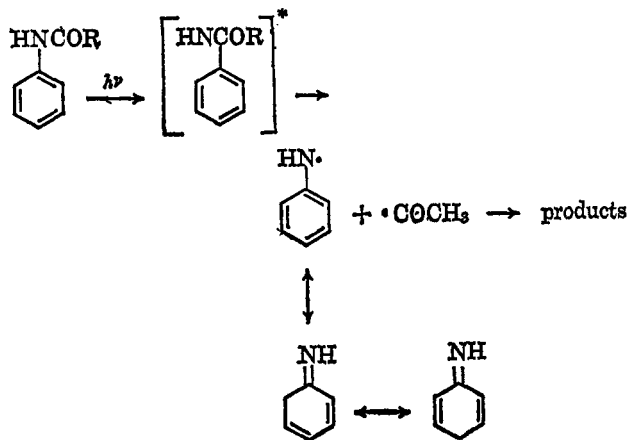
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solvent cage, with subsequent rearrangement. An analogous mechanism would seem plausible for our reaction. This suggests an intramolecular mechanism for the rearrangement.



Preliminary experiments have shown that the mechanism is probably more complex. Irradiation of an alcoholic solution of acetanilide containing *o*-toluidine⁹ produced mainly *o*-aminoacetophenone and *p*-aminoacetophenone together with some 2-amino-3-methylacetophenone and 4-amino-3-methylacetophenone which were detected by gas-liquid chromatography. Similarly, photolysis of *o*-acetotoluidide in the presence of aniline gave mainly 2-amino-3-methylacetophenone and 4-amino-3-methylacetophenone together with some *o*-aminoacetophenone and *p*-aminoacetophenone.

It is noteworthy that benzoic acid could be isolated from the anhydrous benzanilide reaction mixture. In none of the other cases could the acids be isolated or detected in the reaction mixtures. This suggests the possibility of a different mechanism operating in this reaction.

The detailed mechanism of the reaction is being further investigated.

Experimental¹⁰

Reagents.—The anilides were recrystallized until no further improvement in melting point was observed and dried *in vacuo* before use.

Irradiation of Acetanilide. Method A.—Acetanilide (10.00 g.) was dissolved in 500 ml. of anhydrous ethanol. The solution was placed in a cylindrical vessel and irradiated with an immersion-type, 550-w. Hanovia high-pressure mercury arc lamp for 3 days. Nitrogen was bubbled through the solution during the irradiation. The solvent was removed by careful distillation on a steam bath using a Vigreux column. The residue was extracted with ether which left 3.75 g. of crystalline substance

(9) *o*-Acetotoluidide rearranges under ultraviolet irradiation to 2-amino-3-methylacetophenone, 4-amino-3-methylacetophenone, and *o*-toluidine (unpublished results from the Daniel Sieff Laboratory).

(10) Reaction series A has been performed at the University of North Dakota and series B at the Daniel Sieff Institute. Melting points are uncorrected. All organic solutions were dried with anhydrous magnesium sulfate or sodium sulfate before removal of solvent. Gas-liquid chromatography (g.l.c.) was carried out with (A) Beckman GC-2 with di-*n*-decylphthalate on firebrick and an Aerograph Autoprep A-700 with SE 30 on Chromosorb P, and (B) a "Fye" Argon instrument on a 10% Apiezon M-alite column at 145°. Thin layer chromatography was performed on Kieselgel G (Darmstadt); mixtures of acetone-petroleum ether (b.p. 60–70°) were compared with authentic samples by means of their melting points, mixture melting points, infrared spectra, and thin layer chromatography. Liquids were characterized by their retention times in g.l.c. Yields are based on converted anilides (series A) and on anilides employed (series B).

which was essentially starting material. The 10% HCl extract of the above ether solution was neutralized and extracted with ether. After removal of ether, a dark brown liquid was obtained which, on steam distillation followed by extraction of the steam volatile part with ether, gave 1.06 g. of a red-orange liquid. Vapor phase chromatography of this liquid exhibited two components corresponding in retention time to *o*-aminoacetophenone and aniline. The amounts of these two were determined by quantitative vapor phase chromatography to be 0.80 g. (13%) and 0.25 g. (6%), respectively. *o*-Aminoacetophenone was separated from aniline by vacuum distillation and the oxime was made. It had m.p. 107–108° (lit.¹¹ m.p. 109°).

The nonsteam volatile portion was extracted with ether and 1.0 g. of a brownish yellow solid remained on evaporation of the ether. Recrystallization first from benzene-petroleum ether and then from benzene gave 0.75 g. (12%) of pale yellow crystals of *p*-aminoacetophenone that melted at 105–106° (lit.¹² m.p. 105–106°).

Method B.—A solution of acetanilide (3 g.) in anhydrous ethanol (100 ml.) was irradiated¹³ (using a quartz immersion tube) for 8 hr. (no further change in the ultraviolet or infrared spectra of the mixture was observed upon longer irradiation). The solvent was removed under reduced pressure (no aniline was present in the distillate). The residue was steam distilled, the distillate was saturated with sodium chloride and extracted with ether, and the ether solution was washed with 10% hydrochloric acid. The basic fraction (980 mg.) was shown by g.l.c. to consist of 600 mg. (20% yield) of *o*-aminoacetophenone and 380 mg. (18%) of aniline. *o*-Aminoacetophenone was separated from aniline by vacuum distillation and the benzoyl derivatives were prepared. They showed m.p. 99–101° and 164–166° for the *o*-aminoacetophenone and the aniline derivatives, respectively (lit.^{14,5} m.p. 98 and 167°).

The steam nonvolatile fraction contained a heavy, gummy residue which was removed by hot filtration. The filtrate was treated with sodium chloride and ether extracted. The basic material (750 mg., m.p. 95–100°) was isolated in the usual manner. Crystallization from acetone-petroleum ether gave a pure sample of *p*-aminoacetophenone, m.p. 108–110°.

Parallel experiments yielded 15–18% aniline, 17–20% *o*-aminoacetophenone, and 21–25% *p*-aminoacetophenone.

Unreacted acetanilide could be recovered from the reaction mixtures.

Irradiation of Propionanilide. Method A.—Propionanilide (10.00 g.) in 500 ml. of anhydrous ethanol in the apparatus described above was irradiated for 3 days. After irradiation the solution was subjected to the same work-up as above. One gram of starting material was recovered. A steam-volatile product (1.55 g.) was obtained. The amounts of *o*-aminopropiophenone and aniline were found by vapor phase chromatography to be 1.16 g. (13%) and 0.39 g. (7%), respectively. *o*-Aminopropiophenone was separated from aniline by dissolving the mixture in a minimum amount of ethanol and adding water dropwise to turbidity. A solid then separated. It was crystallized from petroleum ether and sublimed under vacuum to give a colorless crystalline product, m.p. 45–46° (lit.¹⁵ m.p. 46–47°). An oxime was made and it had a m.p. of 88–89° (lit.¹⁵ m.p. 88–89°). The crystalline, steam nonvolatile product obtained was filtered and crystallized from 95% ethanol twice to give 0.85 g. (9%) of *p*-aminopropiophenone, m.p. 139–140° (lit.¹⁶ m.p. 140°).

Method B.—Propionanilide (3 g.) in anhydrous ethanol (100 ml.) was irradiated for 18 hr. The usual work-up led to 1.01 g. of steam-volatile basic product. Part of the product (400 mg.) precipitated upon addition of sodium chloride to the distillate. Crystallization from petroleum ether gave pure *o*-aminopropiophenone, m.p. 47–49°. Ether extraction of the distillate followed by the usual work-up gave a basic oil which was shown (g.l.c.) to consist of *o*-aminopropiophenone (250 mg.) and aniline (350 mg., 17%).

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The steam nonvolatile basic residue (750 mg., m.p. 125–132°) was crystallized from acetone–petroleum ether to give pure *p*-aminopropiophenone, m.p. 140–142°.

Yields of 19, 18–20, and 20–23% of aniline, *o*-aminopropiophenone, and *p*-aminopropiophenone, respectively, were obtained in a series of identical experiments.

Irradiation of Butyranilide. Method B.—Butyranilide (3 g.) in anhydrous ethanol (100 ml.) was irradiated for 18 hr. The usual work-up led to a steam-volatile basic fraction (930 mg.) which was shown by g.l.c. to consist of *o*-aminobutyrophenone (510 mg., 17%) and aniline (420 mg., 20%). *o*-Aminobutyrophenone was separated from aniline by vacuum distillation; it was crystallized from petroleum ether (refrigerator) and showed m.p. 46–48° (lit.¹⁷ m.p. 45°).

p-Aminobutyrophenone (700 mg., m.p. 81–87°) was isolated from the steam nonvolatile residue. After crystallization from acetone–petroleum ether it exhibited m.p. 95–97° (lit.¹⁸ m.p. 94–95°). Unreacted butyranilide could be isolated from the reaction mixtures.

Irradiation of Benzanilide. Method A.—Benzanilide (10.00 g.) dissolved in 500 ml. of anhydrous ethanol in the apparatus already described was irradiated for 3 days. After irradiation the alcohol was evaporated on a steam bath. The residue was extracted with ether and the undissolved solid was filtered. This contained 6.75 g. of starting material. The ether solution was extracted twice with 10% HCl and the aqueous part was neutralized with 10% sodium hydroxide and extracted with ether. V.p.c. of this solution indicated a trace of aniline. Evaporation of the ether solution after washing and drying over anhydrous magnesium sulfate gave a solid, which on crystallization twice from benzene–petroleum ether using decolorizing charcoal gave 0.38 g. (12%) of white crystalline needles of *p*-aminobenzophenone, m.p. 123–124° (lit.¹⁹ m.p. 123–124°).

The original ether solution was then extracted with 10% sodium bicarbonate solution. The aqueous portion produced 0.55 g. (27%) of a white solid after acidification followed by extraction with ether. This solid was found to be identical with an authentic sample of benzoic acid.

The residual ether solution was concentrated and chromatographed over neutral alumina. With petroleum ether (b.p. 60–70°) in earlier fractions 0.15 g. (6%) of a liquid is obtained. It had an identical retention time with that of an authentic sample of ethyl benzoate. Further chromatography, using petroleum ether, gave a yellow solid, which upon crystallization followed by vacuum sublimation and a final crystallization gave 0.45 g. (14%) of bright yellow crystals of *o*-aminobenzophenone, m.p. 105–106° (lit.²⁰ m.p. 105–106°).

Carbon Monoxide and Hydrogen Determination.—Butyranilide (10.5 g.) was dissolved in 700 ml. of dry, distilled ethanol. The solution was degassed by bubbling nitrogen through the solution in the irradiation vessel. The solution was sealed with a space at the top of the containing vessel filled with nitrogen and irradiated with a Hanovia 550-w. lamp for 24 hr. The accumulated gases over the reaction mixture were displaced into a deflated polyethylene bag. This gas was subjected to vapor phase chromatography on a Molecular Sieve 13-A column in a Burrell Kromo-Tog Model K-3 apparatus. Peaks were present on the chromatogram which corresponded to standard samples of CO and H₂. As a further check for CO, the sample gases were passed through a CO-indicating tube (no. 47134)²¹ and the color change which occurred indicated the presence of CO.

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Fragmentation of 1,10-Decalindiol Monotosylates¹

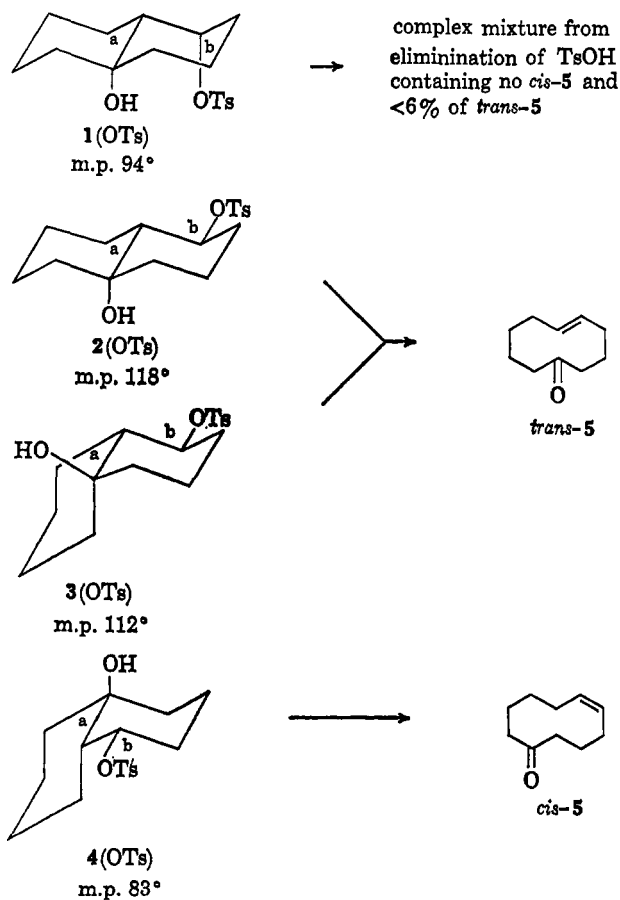
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Fragmentations of cyclic 1,3-diol monosulfonates have been shown to be of interest in the syntheses of several cyclononones² and cyclodecenones.³ We now briefly report additional results in the 1,10-decalindiol → 5-cyclodecenone series which emphasize the synthetic value of the method when antiperiplanar⁴ bonds can be broken in the fragmentation.

The four 1,10-decalindiol monotosylates 1–4(OTs) were subjected to the action of potassium *t*-butoxide⁵ in *t*-butyl alcohol for 1 hr. at 40°. Monotosylates 2- and 3(OTs) were individually converted in high yield



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