extinction coefficients at the maxima are seen to be 6190 and 4900, respectively. A much greater decrease in intensity is noted in the absorption maxima of *n*-butyl N-nitro-N-*n*-butylcarbamate and ethyl N-nitro-N-*t*-butylcarbamate which fall in the same position but the extinction coefficients at the maxima are seen to be 6710 and 2690, respectively. Although at present there is no theoretical treatment which will satisfactorily explain intensities, it is interesting to note that the intensity decrease is noted in the spectra of the only two compounds which could inhibit attainment of coplanarity in the N-nitro group and thus decrease the extent of its resonance.

The only dinitrodicarbamate which was measured, N,N′-dinitro-N,N′-dicarbethoxy-1,6-diaminohexane, exhibited an extinction coefficient of almost twice that of the mono nitro compounds, was expected since the ratio of N-nitro groups at any given concentration would be two to one.

All spectrophotometric measurements were made with 0.0001 *M* solutions in specially purified ethyl alcohol,[4] in 1-cm. quartz cells in a Beckman quartz spectrophotometer, model DU. The results are summarized in Table I.

(4) A. Castille and V. Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

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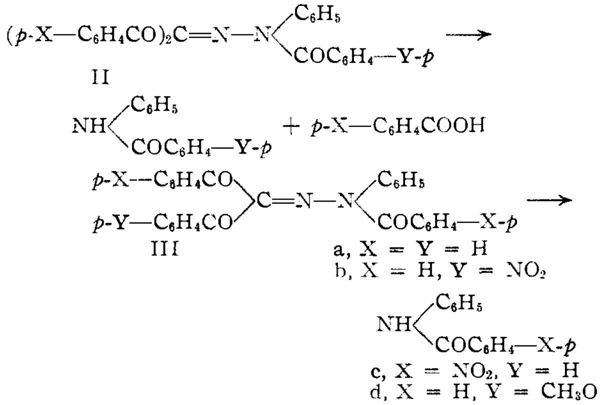
## The N,N-Cleavage of Benzoylphenylhydrazones by Bases[1]

BY DAVID Y. CURTIN[2] AND CHARLOTTE SANANES RUSSELL

During the course of the work described in the preceding paper[3] an attempt was made to separate a mixture of the two hydrazones, IId and IIId, by chromatography on alumina. It was found, however, that when the hydrazones were adsorbed on the column from benzene and eluted with benzene containing 10% ethanol the only products obtained were benzanilide and anisanilide in estimated yields of 52 and 33%.



$$(p\text{-X—}C_6H_4CO)_2C{=}N{—}N\begin{matrix}C_6H_5\\ COC_6H_4\text{—Y-}p\end{matrix} \longrightarrow NH\begin{matrix}C_6H_5\\ COC_6H_4\text{—Y-}p\end{matrix} + p\text{-X—}C_6H_4COOH$$

II

$$\begin{matrix}p\text{-X—}C_6H_4CO\\ p\text{-Y—}C_6H_4CO\end{matrix}C{=}N{—}N\begin{matrix}C_6H_5\\ COC_6H_4\text{—X-}p\end{matrix} \longrightarrow NH\begin{matrix}C_6H_5\\ COC_6H_4\text{—X-}p\end{matrix}$$

III

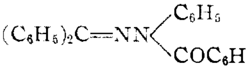
a, X = Y = H
b, X = H, Y = $NO_2$
c, X = $NO_2$, Y = H
d, X = H, Y = $CH_3O$

Further investigation showed that diphenyltriketone benzoylphenylhydrazone (IIa) gave a 60% yield of benzanilide. Not only was this reaction of interest in its own right but it provided a means of establishing the structures of the nitro-substituted diphenyltriketone benzoylphenylhydrazones (IIIb, IIc and IIIc) obtained in the previous paper[2] since their method of formation gave no basis for distinguishing between the isomeric formulas, II and III.

The structure of the hydrazone which had been designated as *p*-nitrophenyl phenyltriketone (IIIb) was established by its conversion to benzanilide in 75% yield by chromatography on alumina. Similarly the structure of *p*-nitrophenyl phenyltriketone *p*-nitrobenzoylhydrazone (IIIc) was assigned on the basis of its cleavage to *p*-nitrobenzanilide in 64% yield.

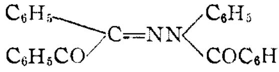
It has been found, moreover, that the N,N-cleavage can be effected with dilute boiling sodium hydroxide solution. IIIb, when treated with boiling 0.5% sodium hydroxide solution, gave benzanilide in 60% yield together with a mixture of benzoic and *p*-nitrobenzoic acid. Although IIIc had reacted smoothly on alumina, treatment with sodium hydroxide failed to convert it to isolable products. Bis-*p*-nitrophenyl triketone benzoylphenylhydrazone (IIc) reacted readily with dilute sodium hydroxide to give a 74% yield of benzanilide and 70% of *p*-nitrobenzoic acid.

In an attempt to extend this reaction, benzophenone *p*-nitrobenzoylphenylhydrazone (IV) was prepared and its behavior toward base studied. Twelve hours of refluxing with 5% sodium carbonate did not alter IV. Absorption of IV on alumina and elution with benzene–ethanol yielded 26% of benzophenone phenylhydrazone and 74% recovered IV. Dilute hydrochloric acid converted IV to benzophenone and *α*-*p*-nitrobenzoylphenylhydrazine.



$$(C_6H_5)_2C{=}NN\begin{matrix}C_6H_5\\ COC_6H_4NO_2\end{matrix}$$

IV

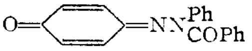


$$\begin{matrix}C_6H_5\\ C_6H_5CO\end{matrix}C{=}NN\begin{matrix}C_6H_5\\ COC_6H_5\end{matrix}$$

V

Benzoin benzoylphenylhydrazone (V) was also examined. V could be recovered unchanged after chromatography on alumina but when allowed to stand adsorbed on the column for nine days and then eluted, a 67% yield of benzil phenylhydrazone was the only neutral product isolated. V was unchanged by refluxing 1% sodium hydroxide. More concentrated (12%) sodium hydroxide gave a small amount of benzoic acid but no other identifiable product.

An N,N-cleavage of acylphenylhydrazones appears to have been observed previously in only one case. Auwers and Eisenlohr[4] found *p*-quinone benzoylphenylhydrazone (VI) to be converted on treatment with 1% aqueous sodium hydroxide to benzanilide (in yields up to 75%), together with *p*-aminophenol (small amounts), benzoic acid, *p*-hydroxyazobenzene and ammonia.



VI

Mechanisms for the cleavage of II may be formulated with initial attack of hydroxyl ion at either carbon or nitrogen. Attempts to distinguish

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(1) Abstracted from a thesis presented by Mrs. C. S. Russell in partial fulfillment of the requirements for the Ph.D. Degree at Columbia University.

(2) Department of Chemistry, University of Illinois, Urbana, Ill.

(3) D. Y. Curtin and C. S. Russell, THIS JOURNAL, **73**, 5160 (1951).

(4) K. Auwers and F. Eisenlohr, *Ann.*, **369**, 209 (1909).

between these two possibilities have thus far been unsuccessful.

### Experimental[5]

**N,N-Cleavage of Diphenyltriketone Benzoylphenylhydrazone (IIa), *p*-Nitrophenyl Phenyltriketone (IIIb) and *p*-Nitrophenyl Phenyltriketone *p*-Nitrobenzoylphenylhydrazone (IIIc) on Alumina.**—The hydrazone (0.0001–0.0002 mole) was adsorbed on a column of adsorption alumina[6] (10–12 inch long and 0.75–1.25 inch in diameter) from a dry benzene (50–75 cc.) solution. Dry benzene did not effect elution and there was no evidence of reaction until the column was eluted with dry benzene containing from 1 to 10% ethanol. When the mixed solvent was added a warm yellow band which was formed moved down the column. IIa and IIIb each gave benzanilide (59%, m.p. 159–162°, and 75%, m.p. 157–160°, respectively) as shown by m.p. and mixed m.p. with an authentic sample, m.p. 161–162°. Further elution with other solvents gave only a small amount of oily product which could not be induced to crystallize. IIIc gave a 64% yield of *p*-nitrobenzanilide, m.p. 214–215°. The mixed m.p. with an authentic sample, m.p. 216.5–217.5°, was not depressed.

**N,N-Cleavage of *p*-Nitrophenyl Phenyltriketone Benzoylphenylhydrazone (IIIb) and Bis-*p*-nitrophenyl Triketone Benzoylphenylhydrazone (IIc) with Dilute Sodium Hydroxide.**—A suspension of 0.1 g. of IIIb or IIc in 15 ml. of 0.5% sodium hydroxide and 10 cc. of water was refluxed for 2.5 hours. The anilide was collected by filtration of the cold solution. From IIIb was obtained a 61% yield of benzanilide, m.p. 159–161°. IIc gave a 74% yield of benzanilide, m.p. 156.5–159.5°. Acidification of the filtrate gave, from IIIb, a mixture of *p*-nitrobenzoic acid and benzoic acid in 95 and 65% yields. From the filtrate from IIc was obtained a 70% yield of *p*-nitrobenzoic acid as shown by m.p. and mixed m.p.

**Benzophenone *p*-Nitrobenzoylphenylhydrazone (IV).**—To a solution of 13 g. (0.048 mole) of benzophenone phenylhydrazone and 30 ml. of dry pyridine cooled in an ice-bath was added 11.2 g. (0.0597 mole) of *p*-nitrobenzoyl chloride in 150 cc. of dry ether over a period of 20 minutes. The mixture was allowed to stand at room temperature for 24 hours and then refluxed for seven hours. Distillation of the filtrate left an oil which crystallized on standing in a refrigerator. The yield of crude benzophenone *p*-nitrobenzoylphenylhydrazone, m.p. 139–146°, was 75%. After repeated recrystallization from ether–ethanol the compound melted at 151.5–152.5°.

*Anal.* Calcd. for $C_{26}H_{19}N_3O_3$: C, 74.1; H, 4.5; N, 10.0. Found: C, 73.7; H, 4.6; N, 10.0.

An attempt to prepare this compound by adding *p*-nitrobenzoyl chloride (13 g.) to benzophenone phenylhydrazone (15 g.) in 100 cc. of pyridine and allowing the mixture to stand at room temperature overnight gave only 3.5 g. of *p*-nitrobenzoic anhydride and 10 g. of recovered phenylhydrazone.

IV could be hydrolyzed to α-*p*-nitrobenzoylphenylhydrazine, m.p. 191–192° dec., lit.[7] m.p. 195–196°, in 43% yield (57% on the basis of unrecovered starting material) by treatment for 2.5 hours with refluxing 6 *N* hydrochloric acid.

Treatment of 0.10 g. of IV with 5 cc. of refluxing 5% sodium carbonate solution for 12 hours leads only to recovery of 95% of the starting material.

When IV was eluted from an alumina column with benzene a 26% yield (96% based on unrecovered starting material) of benzophenone phenylhydrazone, m.p. 133.5–135.5°, was obtained. A mixed m.p. showed no depression.

**Benzil Benzoylphenylhydrazone[8] (V).**—V could be recovered unchanged from an alumina column by elution with benzene in 95% yield. When 0.5 g. of V was allowed to stand for nine days, however, in benzene (75 cc.) containing three drops of 95% ethanol in contact with alumina, a 67% yield of benzil phenylhydrazone, m.p. 131–135.5°, was obtained.

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[5] All melting points are corrected. Analyses were carried out by Dr. Francine Schwarzkopf, Elmhurst, New York.

[6] Eimer and Amend Adsorption Alumina, 80–200 mesh, activated by heating at 300°.

[7] G. Lockemann, *Ber.*, **43**, 2223 (1910).

[8] K. Auwers and A. Bennecke, *Ann.*, **378**, 243 (1910).

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## A New Preparation of 2-Amino-4-phenylpyrimidine[1,2]

By W. K. Detweiler and E. D. Amstutz

Several investigators[3–5] have reported the preparation of 2-amino-4-phenylpyrimidine by ring closure methods which involved the use of guanidine salts. We have now found that this compound is also formed by the reaction of phenyllithium with 2-aminopyrimidine in refluxing toluene.

Although it is possible that this substituted pyrimidine was formed by a 1,2-addition of phenyllithium[6] to the nitrogen-to-carbon double bond of the pyrimidine ring, there does not appear to be any evidence to exclude a 1,4-addition to the conjugated system of the iminodihydro form of 2-aminopyrimidine.

### Experimental

**2-Amino-4-phenylpyrimidine.**—2-Aminopyrimidine (9.51 g., 0.1 mole) in 500 ml. of hot dry toluene was added over a half-hour period to phenyllithium[7] (prepared from 31.4 g. of bromobenzene and 2.78 g. of lithium metal) in 140 ml. of anhydrous ether. The ether was allowed to distil from the reaction mixture during this addition; when the bath temperature reached 115°, the condenser was set for reflux and the residual mixture was refluxed with stirring for 7 hours. While cooling the reaction mixture in an ice-bath, a few ml. of water and 300 ml. of a 1:1 mixture of concentrated hydrochloric acid and water were cautiously added with stirring. The acidic extract was separated from the toluene and adjusted to a *p*H 9 by cautiously adding 48% sodium hydroxide to the cooled solution. The precipitated tan solid was filtered, washed with cold water and dried; yield 6.9 g., m.p. 146–157°. Recrystallization from 95% ethanol after treatment with decolorizing charcoal gave 3.4 g. (20%) of cream-colored needles, m.p. 162–164°. Two additional recrystallizations from ethanol gave nearly colorless needles, m.p. 164.4–165.1°. The last trace of color was removed by vacuum sublimation at 9 mm. pressure; the melting point was not significantly altered. *Anal.* Calcd. for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.11; H, 5.37; N, 24.47.

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[1] Abstracted, in part, from a thesis presented by W. K. Detwiler to the Graduate Faculty of Lehigh University of partial fulfillment of the requirements for the Ph.D. degree, June, 1941.

[2] The authors wish to thank the Wm. S. Merrell Company for the financial support of this research.

[3] E. Benary, *Ber.*, **63B**, 2601 (1930).

[4] J. M. Sprague, L. W. Kissinger and R. W. Lincoln, This Journal, **63**, 3028 (1941).

[5] K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946).

[6] For the 1,2-addition of phenyllithium to pyridine see J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 517.

[7] The phenyllithium used in this reaction was prepared according to the instructions given in "Organic Syntheses."[6]

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## Preparation of Some Heterocyclic Biurets[1,2]

By W. K. Detweiler and E. D. Amstutz

The Davis–Blanchard[3] method of synthesizing ω-substituted biurets from nitrobiuret has been

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[1] Abstracted, in part, from a thesis presented by W. K. Detweiler to the Graduate Faculty of Lehigh University in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

[2] The authors wish to thank the Wm. S. Merrell Company for the financial support of this research and for helpful discussions in connection with this work.

[3] T. L. Davis and K. C. Blanchard, This Journal, **51**, 1803 (1929).