

[CONTRIBUTION NO. 317 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

## $\omega$ -(*p*-Amino-*N*-ethylanilino)-alkanoic Acids as Photographic Developers

BY MAYNARD S. RAASCH

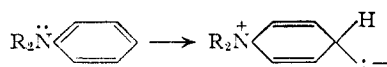
RECEIVED DECEMBER 8, 1952

A series of photographic developers of the formula  $p\text{-H}_2\text{NC}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)_n(\text{CH}_2)_n\text{COOH}$ , where  $n$  is 3, 4, 5, 7 and 10, has been synthesized and tested. Activity as developers increases as  $n$  increases from 3 through 5 but then drops off.

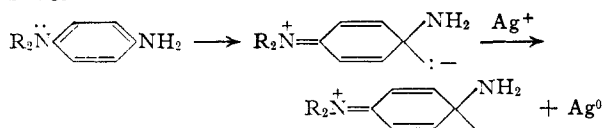
### Introduction

In correlating structure with activity of photographic developers of the *N,N*-disubstituted *p*-phenylenediamine type, a concept that has proved of some usefulness relates the activity with the basicity of the molecule, or of the amines of which the developer is a *p*-amino or *p*-aminophenyl derivative. Thus, *p*-aminodiethylaniline is a more energetic developer than *p*-aminodimethylaniline; the basic dissociation constants of diethylamine and dimethylamine are  $12.6 \times 10^{-4}$  and  $7.4 \times 10^{-4}$ , respectively. However, the concept must be used with caution, as a multiplicity of factors influence the activity of the developer molecule,<sup>1</sup> and activity does not always correlate with small differences in reported values of basic dissociation constants. As illustrated by the experiments of this article, the principle can be applied in a restricted range of a homologous series where an electron-attracting group is terminally attached to an alkylene group connected with the nitrogen atom. The electron-attracting group, by normal inductive effect, makes the unshared pair of electrons on the nitrogen atom less available for coordination with a proton and decreases the basicity of the nitrogen atom. Likewise, this effect apparently makes the electrons less available for release to an oxidizing agent such as the silver ion encountered in photographic development.

A related correlation has been published<sup>2</sup> for the reaction of aromatic amines with diazonium salts. The degree of freedom of the electrons of the nitrogen atom and their ability to shift into a quinonoid structure is compared to the ability of the nitrogen



atom to coordinate a proton, *i.e.*, its basicity. The quinonoid structure is believed to favor coupling on the theory that coupling takes place by attack of the positive diazonium ion at the negative para position. A similar mechanism can be postulated for ease of donation of an electron by a phenylenediamine developer to a silver ion to form a semi-quinone ion, the first oxidation stage, and free silver



(1) Cf. R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum and A. Weissberger, *THIS JOURNAL*, **73**, 3100 (1951).

(2) S. I. Burmistrov, *J. Gen. Chem. (USSR)*, **18**, 1361 (1948).

The basicity correlation implies that if an acid group is to be attached to the nitrogen atom, the group must be separated from the nitrogen atom by a number of carbon atoms in order not to diminish the basicity of the nitrogen atom and the developer activity. For example, in the series  $\text{H}_2\text{N}(\text{CH}_2)_n\text{SO}_3\text{H}$ , basicity does not reach a near asymptotic value until  $n$  is 6.<sup>3</sup> That is, the inductive effect of the sulfonic acid group apparently extends through at least six carbon atoms. This conclusion on the necessary distant placement of the solubilizing group in a *p*-phenylenediamine type of developer has also been given in German wartime disclosures.<sup>4a,b</sup>

### Results and Discussion

The present work describes the preparation of developers of the structure  $p\text{-H}_2\text{NC}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)_n(\text{CH}_2)_n\text{COOH}$ , where  $n$  is 3, 4, 5, 7 and 10, and the results obtained in a simple photographic test wherein the compounds were allowed to act during a fixed time in a conventional developing procedure on two types of film given a time-scale exposure. The films used were du Pont Release Positive Type 225 black and white film and a monolayer photographic film containing a polyvinyl acetal of *m*-benzoylacetylbenzaldehyde,<sup>5</sup> which serves the dual function of silver halide binder and yellow color former. Measurement was made of the log relative exposure required to produce a density of 0.2, an arbitrary figure near the lower end of the H and D curve, and the gamma. The results are presented in Table I with values for *p*-aminodiethylaniline as a comparison.

TABLE I

DEVELOPER ACTIVITY OF  $p\text{-H}_2\text{NC}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)_n(\text{CH}_2)_n\text{CONa}$

$n$	Type 225		Yellow monolayer	
	Log rel. exp. density = 0.2	$\gamma$	Log rel. exp. density = 0.2	$\gamma$
3	0.24	0.5	0.45	1.5
4	.09	.8	.27	1.4
5	0	.8	.12	1.1
7	.09	.7	.15	1.2
10	.39	.7	.39	1.2
<sup>a</sup>	0	1.0	0	1.5

<sup>a</sup> *p*-Aminodiethylaniline control.

On Type 225 film similar gammas (0.7 to 0.8) were obtained except for the poorest member ( $n = 3$ ) while the exposure required to give a density of 0.2 decreased, as anticipated, as  $n$  increased from

(3) P. Rumpf, *Bull. soc. chim.*, [5] **5**, 871 (1938).

(4) (a) PB 44740, I. G. Farbenindustrie A. G., German patent application 77099, application date March 3, 1944; (b) PB 74177, I. G. Farbenindustrie, A. G., "Reports on Photochemistry," FIAT Microfilm Reel D 6, pp. 01152-01153.

(5) D. M. McQueen, U. S. Patent 2,464,597 (March 15, 1949); D. M. McQueen, U. S. Patent 2,513,190 (June 27, 1950).

3 to 5. However, rather unexpectedly, required exposure increased when  $n$  was 7 and a further increase was encountered when  $n$  was 10. The applicability of the developers to a yellow color-forming polyvinyl acetal film, which is not rendered soluble in water by coupling with these solubilized compounds, is also shown. Here the already involved process of development is further complicated by a dye-forming reaction, but the relative exposure data approximately parallel those for Type 225 film, though the gammas obtained varied somewhat more (1.1 to 1.5). The relative exposure data are plotted in Fig. 1. A physical factor is believed to be responsible for the drop in activity when  $n$  is 7 and 10. It is suggested that diffusibility of the developer into the film has been lessened, perhaps because of increased micelle size or concentration as well as greater molecular size. As judged by the pinacyanole dye test, all of these developer solutions have a micellar structure. The effect of a long chain in decreasing the diffusibility of a developer has been noted in 2-dodecylhydroquinone.<sup>6</sup>

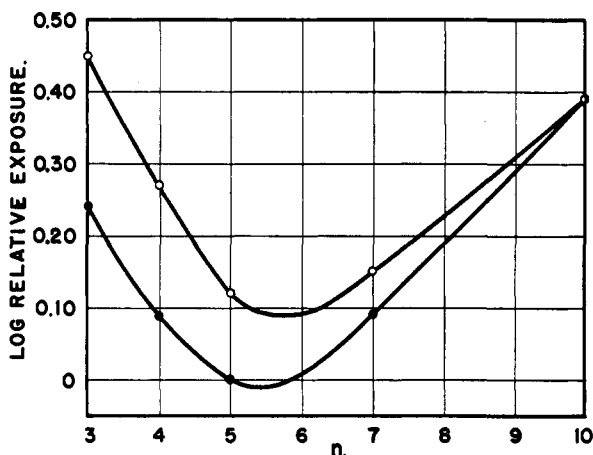


Fig. 1.—Comparison of log relative exposures to obtain density of 0.2 with  $p$ - $H_2NC_6H_4N(C_2H_5)(CH_2)_nCOOH$ ,  $n = 3, 4, 5, 7, 10$ ; ●, on du Pont type 225 film; ○, on yellow color-forming monolayer.

Solubilized color developers such as those of this series are of practical use in developing films containing polyvinyl acetal color formers of the type referred to, whereas with migratory color formers such as 1-phenyl-3-methyl-5-pyrazolone a soluble dye is formed and bleeds from the film during processing.<sup>8b</sup> In alkaline developer solutions, salts are formed and the low lipid solubility makes them less apt to cause skin irritation than *p*-aminodiethylaniline. This has been borne out by tests on guinea pigs with sodium  $\epsilon$ -(*p*-amino-*N*-ethylanilino)-caproate.

A spectral curve, measured on color developed film, of the azomethine dye obtained from  $\gamma$ -(*p*-amino-*N*-ethylanilino)-butyric acid and the polyvinyl acetal of *m*-benzoylacetamidobenzaldehyde is given in Fig. 2. The curves for the dyes obtained with the four higher members of this series of developers are similar to Fig. 2 except that the ab-

(6) C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1945, p. 364.

sorption maximum shifts from 447 to 440  $m\mu$  in proceeding through the series. This hypsochromic shift may have physical causes due to the surface-active properties of the developers. A reversible color shift caused by the action of cationic dispersing agents on azomethine dyes in film has been recorded.<sup>7</sup>

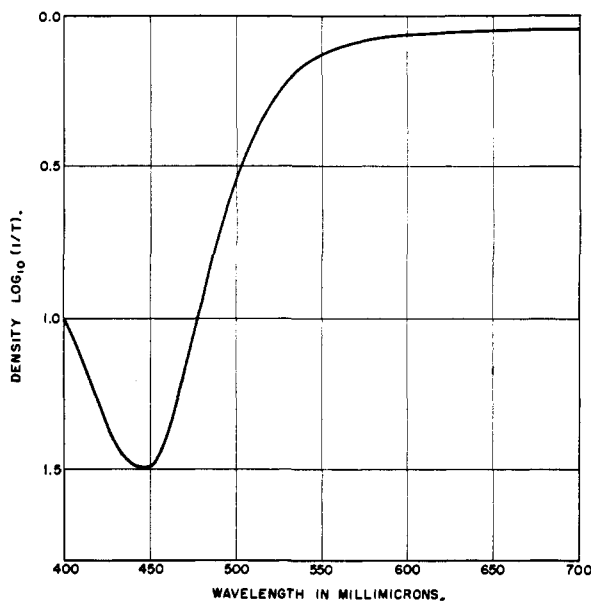
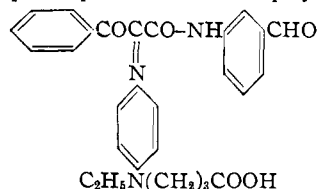
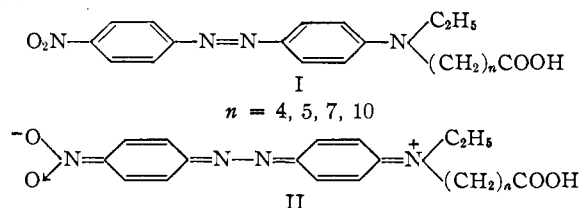


Fig. 2.—Absorption spectrum of film of polyvinyl acetal of



In the synthesis of these developers, the azo dyes represented by formula I were prepared as intermediates. With the thought that a quinonoid structure such as II might have a greater contribution in the higher members of the series and shift the wave length of maximum absorption, spectral curves of the dyes in dioxane were measured. However, the curve for each was the same (Fig. 3), and each had a molecular extinction coefficient of 8600.



### Experimental<sup>8</sup>

The general procedure for preparing the developers involved heating ethylaniline with 0.5 mole of  $\omega$ -halogen al-

(7) V. W. Blanchard, U. S. Patent 2,551,091 (May 1, 1951).

(8) The following compounds related to those of the present series have been described: (a) *p*-amino-*N*-methylanilinoacetic acid,<sup>4b</sup> (b)  $\beta$ -(*p*-amino-*N*-methylanilino)-propionic acid (P. W. Vittum, A. Weissberger and L. S. Wilder, U. S. Patent 2,435,616 (Feb. 10, 1948)), and (c) *p*-amino-*N*-methylanilinoacetamide and ethyl *p*-amino-*N*-methyl-*m*-toluidinoacetate (J. B. Dickey and J. G. McNally, U. S. Patent 2,374,337 (April 24, 1945)).

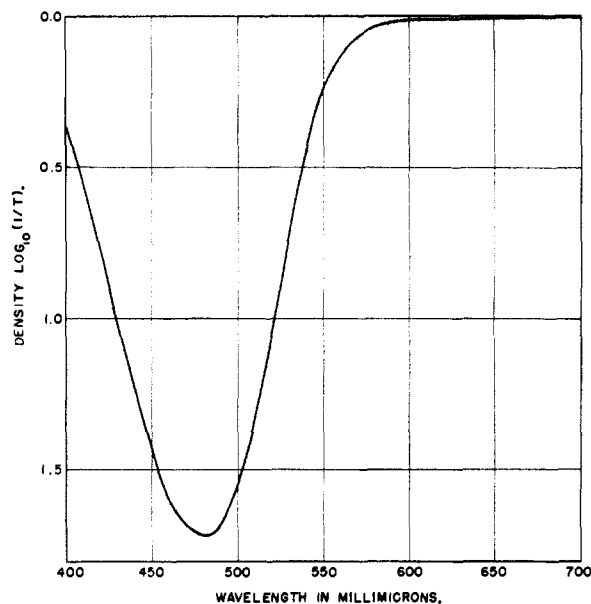
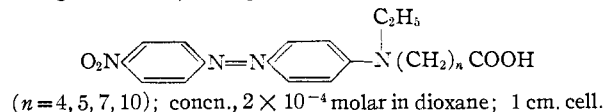


Fig. 3.—Absorption spectrum of



kanoic acid ester, hydrolyzing the ester, steam distilling from alkaline solution to remove excess ethylaniline, coupling with a diazonium compound, and reducing the azo dye. The rather soapy, difficultly recrystallizable  $\omega$ -(*N*-ethyl-anilino)-alkanoic acids were not isolated.

**Sodium  $\gamma$ -(*N*-Ethylanilino)-butyrate.**—Methyl  $\gamma$ -iodobutyrate<sup>9</sup> (49 g., 0.215 mole) and ethylaniline (52 g., 0.43 mole) were heated on a steam-bath for 16 hours. The product was washed with a solution of 20 g. (0.25 mole) of sodium bicarbonate, followed by water, to remove iodide ions. The washed product was refluxed for 1 hour with 9 g. (0.22 mole) of sodium hydroxide in 75 ml. of water and then steam distilled to remove ethylaniline. The solution of sodium  $\gamma$ -(*N*-ethyl-anilino)-butyrate so obtained was used directly for azo coupling.

**Sodium  $\gamma$ -(*N*-Ethyl-*p*-phenylazoanilino)-butyrate.**—To the solution prepared above was added 25 ml. of acetic acid. After cooling to 5°, a diazonium solution prepared from 20 g. (0.215 mole) of aniline was added followed by 45 g. of sodium acetate in 75 ml. of water. After the mixture had stood in ice for 4 hours, the gummy dye was collected and converted to its crystalline sodium salt by treatment with 20% sodium carbonate solution. The sodium salt crystallized from water or from sodium chloride solution in well-formed orange crystals. These crystals evidently were hydrated. When filtered off and allowed to stand, they coalesced, as if part were dissolving in the water of hydration. When dried at 105°, the anhydrous salt, m.p. 185–188°, was obtained. The yield was 48 g. or 67%, based on methyl  $\gamma$ -iodobutyrate.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_3\text{Na}$ : N, 12.6. Found: N, 12.7, 12.7.

**$\gamma$ -(*p*-Amino-*N*-ethyl-anilino)-butyric Acid.**—Thirty grams of the above azo dye, 150 ml. of water and 2 g. of palladium-on-charcoal catalyst were charged into a shaker bomb and hydrogenated at 70° and 1500–2000 lb./sq. in. for 2 hours. The filtered product was extracted with benzene to remove aniline, an equivalent quantity (7.2 ml.) of hydrochloric acid was added, and the solution was evaporated to dryness under reduced pressure. The amino acid was extracted from the sodium chloride with absolute ethanol and crystallized twice from ethanol-benzene; m.p. 101–103°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2$ : N, 12.6. Found: N, 12.4, 12.1.

(9) L. Henry, *Compt. rend.*, **102**, 369 (1886).

**$\delta$ -(*N*-Ethylanilino)-valeric Acid.**—Ethylaniline (121 g., 1 mole) and  $\delta$ -chlorovaleronitrile<sup>10</sup> (59 g., 0.5 mole) were heated at 100° for 15 hours and 1 hour at 135°. The product was refluxed with 200 ml. of concd. hydrochloric acid for 3 hours. This solution was evaporated to dryness under reduced pressure and the residue was dissolved in 800 ml. of water and made alkaline with sodium hydroxide. The liberated ethylaniline was separated. The last traces were removed by steam distillation. Upon adjustment of the pH of the solution to 6.2, 55 g. (50% yield) of  $\delta$ -(*N*-ethyl-anilino)-valeric acid separated as an oil.

**$\delta$ -[*N*-Ethyl-*p*-(*p*-nitrophenylazo)-anilino]-valeric Acid.**—The 55 g. of  $\delta$ -(*N*-ethyl-anilino)-valeric acid was dissolved in 300 ml. of water and 30 ml. of acetic acid. *p*-Nitroaniline (33 g., 0.24 mole) was diazotized<sup>11</sup> and added to this solution followed by 80 g. of sodium acetate. After the mixture had stood at 10–20° for 0.5 hour, the dark red dye (31 g., 32% yield) was filtered off and recrystallized from dioxane to give 24 g. melting at 192–193°.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_4$ : N, 15.1. Found: N, 15.0, 14.8.

**$\delta$ -(*p*-Amino-*N*-ethyl-anilino)-valeric Acid.**—Thirty-four grams of the above azo dye, 200 ml. of dioxane and 2 g. of palladium-on-charcoal catalyst were charged into a shaker bomb and hydrogenated at 25–55° and 800–1500 lb./sq. in. for 30 min. The product was filtered, evaporated to dryness under reduced pressure, and the residue was extracted with 800 ml. of hot benzene to remove *p*-phenylenediamine. The residue (18 g., 83% yield) was recrystallized from ethanol-benzene to yield a product melting at 105–110°.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 66.1; H, 8.54; N, 11.9. Found: C, 65.8, 65.9; H, 8.60, 8.43; N, 11.4, 11.4.

**Sodium  $\epsilon$ -(*N*-Ethylanilino)-caproate.**—Using the procedure described for sodium  $\gamma$ -(*N*-ethyl-anilino)-butyrate, a solution of sodium  $\epsilon$ -(*N*-ethyl-anilino)-caproate was prepared starting with ethylaniline and ethyl  $\epsilon$ -bromocaproate.<sup>12</sup>

**$\epsilon$ -[*N*-Ethyl-*p*-(*p*-nitrophenylazo)-anilino]-caproic Acid.**—The sodium  $\epsilon$ -(*N*-ethyl-anilino)-caproate was coupled with diazotized *p*-nitroaniline and the resultant red dye was crystallized from ethanol; 96% yield, based on ethyl  $\epsilon$ -bromocaproate, m.p. 136–137°.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_4$ : N, 14.6. Found: N, 14.3, 14.3.

**Sodium  $\epsilon$ -(*p*-Amino-*N*-ethyl-anilino)-caproate.**—Eighty-five grams of the above azo dye, 150 ml. of dioxane and 2 g. of palladium-on-charcoal catalyst were charged into a shaker tube and hydrogenated at 50–70° and 1000–2000 lb./sq. in. for 2 hours. The product was filtered and evaporated under reduced pressure. The residue was dissolved in an equivalent of sodium hydroxide solution and again evaporated to dryness under reduced pressure. The residue was extracted with hot benzene to remove *p*-phenylenediamine. The sodium  $\epsilon$ -(*p*-amino-*N*-ethyl-anilino)-caproate left behind was purified by dissolving in methanol, treating with charcoal, and reprecipitating by the slow addition of ether.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2\text{Na}$ : N, 10.4. Found: N, 10.4, 10.5.

**Sodium  $\eta$ -(*N*-Ethylanilino)-caprylate.**—This was prepared starting with ethylaniline and ethyl  $\eta$ -bromocaprylate.<sup>13</sup>

**$\eta$ -[*N*-Ethyl-*p*-(*p*-nitrophenylazo)-anilino]-caprylic Acid.**—The sodium  $\eta$ -(*N*-ethyl-anilino)-caprylate was coupled with diazotized *p*-nitroaniline. The red azo dye formed in 83% yield, based on ethyl  $\eta$ -bromocaprylate, and melted at 130° after two recrystallizations from ethanol (83% return).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{25}\text{N}_4\text{O}_4$ : N, 13.6. Found: N, 13.5, 13.4.

**Sodium  $\eta$ -(*p*-Amino-*N*-ethyl-anilino)-caprylate.**—The above azo dye was reduced and the developer was isolated as described for the corresponding caproate.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_2\text{Na}$ : N, 9.33. Found: N, 8.58, 8.45.

The low analysis is attributed mainly to the presence of inorganic impurities. Developer solutions were made up on the basis of nitrogen content.

(10) Electrochemicals Department, E. I. du Pont de Nemours & Co.

(11) L. F. Fieser and H. T. Thompson, *THIS JOURNAL*, **61**, 376 (1939).

(12) G. B. Brown and C. W. H. Partridge, *ibid.*, **66**, 839 (1944).

(13) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75B**, 291 (1942); C. F. H. Allen and C. V. Wilson, *Org. Syntheses*, **26**, 52 (1946).

**Sodium 11-(N-Ethylanilino)-hendecanoate.**—11-Bromohendecanoic acid for this preparation was made as follows: One hundred eighty-four grams (1 mole) of 10-hendecenoic (undecylenic) acid, b.p. 166–168° (10 mm.), was placed in a flask fitted with a stirrer and gas inlet and outlet tubes, and the solution was maintained at 35°. To it was added 0.75 g. of  $\alpha, \alpha'$ -azobis-( $\alpha, \gamma$ -dimethyl- $\gamma$ -methoxyvaleronitrile),<sup>14</sup> a free radical catalyst with a half-life of 7.7 hours at 35°. Hydrogen bromide was passed in during 1.5 hours until an excess was present. The solution was then evaporated. The crude acid melted at 36–44°. It was recrystallized twice from 500 ml. of petroleum ether (b.p. 30–75°) by cooling the solution to –20° before filtering, and then melted at 49–50°. The yield was 168 g. or 64%.<sup>15</sup>

11-Bromohendecanoic acid (70 g., 0.26 mole) and ethylaniline (109 g., 0.9 mole) were heated on a steam-bath for 12 hours. To the mixture was added 22 g. of sodium hydroxide in 50 ml. of water and the liberated ethylaniline was removed by steam distillation. The solution was evaporated to dryness.

**11-[N-Ethyl-*p*-(*p*-nitrophenylazo)-anilino]-hendecanoic Acid.**—The above dry salt was dissolved in 800 ml. of glacial acetic acid. *p*-Nitroaniline (38.4 g., 0.28 mole) was diazotized and added to the acetic acid solution. After addition of 80 g. of sodium acetate the mixture was allowed to stand for 0.5 hour. The red dye was filtered off, washed with 50% acetic acid and then with water. The yield was 104 g. or 87%, based on 11-bromohendecanoic acid. The compound was recrystallized from methanol in 81% return to give red plates melting at 130–131°.

(14) J. A. Robertson, U. S. Patent 2,586,995 (Feb. 26, 1952).

(15) Cf. J. C. Smith, *Chemistry & Industry*, 461 (1938).

*Anal.* Calcd. for  $C_{26}H_{34}N_4O_4$ : N, 12.3. Found: N, 12.2, 12.2.

**11-(*p*-Amino-N-ethylanilino)-hendecanoic Acid Sulfate.**—Reduction of the dye was carried out as described for the corresponding valerate. The solution of the reduction mixture was filtered, evaporated to dryness, and extracted with 250 ml. of hot water to remove *p*-phenylenediamine. The water-insoluble amino acid was converted to its sulfate in ethanol and recrystallized from ethanol; m.p. 147–149°, yield 90%.

*Anal.* Calcd. for  $C_{19}H_{22}N_2O_2 \cdot H_2SO_4$ : N, 6.65. Found: N, 6.55, 6.56.

**Exposure and Development.**—Films were given a time-scale exposure by means of a sector wheel. They were then developed for 10 min. at 20° in a solution containing, per liter, 0.0125 mole of developer, 10 g. of sodium sulfite, 25 g. of sodium carbonate and 2 g. of potassium bromide. Following development, the films were washed, fixed and bleached by conventional means. Spectral curves were obtained on a GE recording spectrophotometer and yellow densities were read at the wave length of maximum absorption.

**Acknowledgments.**—The author wishes to thank Dr. J. P. Weiss and Mr. V. W. Blanchard of the du Pont Photo Products Department for carrying out the photographic tests, and Dr. F. C. McGrew for helpful discussions.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

## 2,2-Diphenyl-3,3-dimethylethylenimine and Related Compounds

BY HENRY M. KISSMAN,<sup>1</sup> D. S. TARBELL AND JOHN WILLIAMS

RECEIVED JANUARY 17, 1953

The preparation of 2,2-diphenyl-3,3-dimethylethylenimine (I) by the action of phenylmagnesium bromide or phenyllithium on isobutyrophenone oxime is described. The identity of I is established through an alternate synthesis by ring closure from 1-chloro-1,1-diphenyl-2-amino-2-methylpropane (VII) and through acid-catalyzed cleavage to 1,1-diphenyl-2-amino-2-methylpropanol (III).

The present study of the synthesis and properties of 2,2-diphenyl-3,3-dimethylethylenimine (I) was undertaken in connection with the problem of the resolvability of the trivalent nitrogen atom in the ethylenimine ring.<sup>2</sup> It was also hoped that this completely substituted ethylenimine would be more stable than the ones previously studied.<sup>2</sup> The best method of preparation was found to be the action of phenylmagnesium bromide or phenyllithium at elevated temperatures on isobutyrophenone oxime.<sup>3</sup> When a mixture of the two stereoisomers of isobutyrophenone oxime<sup>4</sup> was allowed to react with excess phenylmagnesium bromide in refluxing toluene there was isolated from the reaction

(1) Beunit Mills Fellow, 1949–1950.

(2) Previous papers in this series: (a) H. M. Kissman and D. S. Tarbell, *THIS JOURNAL*, **74**, 4317 (1952); (b) D. S. Tarbell and D. K. Fukushima, *ibid.*, **68**, 2499 (1946); (c) T. L. Cairns, *ibid.*, **63**, 871 (1941).

(3) This procedure was discovered by (a) J. Hoch, *Compt. rend.*, **198**, 1865 (1934), and has been extended to the preparation of a number of aryl-substituted ethylenimines by Campbell; (b) K. N. Campbell, B. K. Campbell, J. F. McKenna and E. P. Chaput, *J. Org. Chem.*, **8**, 103 (1943); (c) K. N. Campbell, B. K. Campbell, L. G. Hess and I. J. Schaffner, *ibid.*, **9**, 184 (1944).

(4) H. M. Kissman and J. Williams, *THIS JOURNAL*, **72**, 5323 (1950).

mixture a small amount of aniline<sup>5</sup> and a high-boiling oil; this solidified to form colorless plate-like crystals which softened at 60° and melted at 185°. The hydrochloride of this compound could be recrystallized to a constant m.p. of 227–228°, and it had the composition required for the hydrochloride of I.

The action of phenyllithium on isobutyrophenone oxime in boiling toluene gave a mixture of basic products, which could be separated by chromatography and distillation into aniline and a yellow oil. The oil had the same boiling point as the product from the phenylmagnesium bromide reaction but it could not be made to solidify. It had the elementary composition required for the ethylenimine I. An analysis and neutral equivalent determination on the hydrochloride confirmed this result but the salt melted at a somewhat lower temperature than the hydrochloride of the product obtained in the first reaction. The phenylurea derivative II of the products of both reactions had the same m.p.'s and

(5) J. Hoch (*Compt. rend.*, **203**, 799 (1936)) explains the formation of aniline in the reaction of propiophenone oxime and phenylmagnesium bromide by assuming a rearrangement of the oxime to the corresponding anilide. Aniline would be formed in a reaction of this amide with more of the Grignard reagent.