treated with oxalic acid in ether to give 11.4 g. of an oxalate melting at 110–111.3°. This compound was identified as 1-ethyl-1-methylhydrazine oxalate by a mixed melting point with an authentic sample.

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The Schmidt Reaction between 1,1,3-Triphenylpropyne-2-ol-1 and Hydrogen Azide[1]

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In connection with other work, now discontinued, the Schmidt reaction between 1,1,3-triphenylpropyne-2-ol-1 (I) and hydrogen azide has been investigated. The product, identified as the anilide (III) of *β*-phenylcinnamic acid by an independent synthesis from *β*-phenylcinnamoyl chloride and aniline, is also obtained from *β*-phenylbenzalacetophenone (II) and hydrogen azide in the presence of sulfuric acid. The Meyer-Shuster rearrangement of I to II, a preparative method for II, apparently occurs in the transformation of I to III. Migration of a phenyl group rather than a diphenylvinyl group from carbon to nitrogen also occurs, in agreement with an earlier observation that migration of a vinyl group in a Schmidt reaction was not found.[3]

$$\underset{\text{I}}{(C_6H_5)_2C(OH)C\equiv CC_6H_5} \xrightarrow{H_2SO_4} \underset{\text{II}}{(C_6H_5)_2C{=}CHCOC_6H_5}$$

$$\text{I or II} \xrightarrow[HN_3]{H_2SO_4} \underset{\text{III}}{(C_6H_5)_2C{=}CHCONHC_6H_5}$$

EXPERIMENTAL[4]

Preparation of the anilide (III) *from* I. To a suspension of 1.5 g. (0.023 mole) of sodium azide in 10 ml. of chloroform cooled in an ice bath, 3.0 ml. (0.055 mole) of concd. sulfuric acid was added slowly. A solution of 3.30 g. (0.0116 mole) of 1,1,3-triphenylpropyne-2-ol-1 (I)[5] in 15 ml. of chloroform was added during 45 min. at room temperature. After stirring for an additional 45 min., the mixture was poured on 100 g. of ice, and extracted with ether. Evaporation of solvents gave an oil which was dissolved in benzene and applied to a column of alumina (Alcoa grade F-20). Elution with benzene gave yellow-green, red, and light yellow bands. The first two were removed from the column with benzene and the third with acetone. On evaporation of solvents, tars were obtained from the first two but the third gave a colorless solid, m.p. 139–140°, 0.53 g. (15%), after two recrystallizations from a mixture of benzene and ligroin, identified as the anilide (III) of *β*-phenylcinnamic acid.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.19; H, 5.71; N, 4.67. Found: C, 84.87; H, 5.45; N, 4.63.

Preparation of the anilide (III) *from* II. To 3.5 g. (0.0124 mole) of *β*-phenylbenzalacetophenone (II), m.p. 91–92°,[6] in 30 ml. of chloroform and 1 ml. (0.018 mole) of concd. sulfuric acid a solution of hydrogen azide (excess) in 37 ml. of chloroform was added dropwise over a period of 30 min. as the temperature was kept below 35°. Stirring was continued for 1 hr., the mixture was washed with water, and the organic layer evaporated on a waterbath. Recrystallization of the residue from a mixture of benzene and ligroin gave 1.45 g. (40%) of product, m.p. 137–138°.

Oxidation of III in acetone by potassium permanganate gave benzophenone, m.p. 48° (86%) and acid alcoholysis gave impure ethyl *β*-phenylcinnamate, b.p. 280°, $n_{\mathrm{D}}^{25.5}$ 1.6010[7] and aniline, isolated as its hydrochloride, m.p. and mixture m.p. 197.5–199° (88%).

Hydrogenation of the anilide (III). A solution of 0.21 g. (0.007 mole) of III in 25 ml. of ethanol which contained 15 mg. of platinum oxide was treated with hydrogen at room temperature and normal pressure for 20 hr. After filtration and evaporation of the solvent 0.19 g. (91%) of a white solid, m.p. 180–181° was obtained. One recrystallization from aqueous ethanol gave the anilide of *β*,*β*-diphenylpropionic acid, 0.16 g. m.p. 181–182°.[8]

Anal. Calcd. for $C_{21}H_{19}NO$: C, 83.68; H, 6.35; N, 4.65; O, 5.38. Found: C, 83.09; H, 6.29; N, 4.67; O, 5.53.

Preparation of the anilide (III). After the vigorous reaction brought about by adding 4.5 g. (0.02 mole) of *β*-phenylcinnamic acid[7] to 14.7 g. (0.12 mole) of thionyl chloride had subsided the mixture was refluxed for 30 min., and excess thionyl chloride was removed by distillation. Ten milliliters of benzene followed by a solution of 5 ml. (0.09 mole) of aniline in 45 ml. of benzene was added to the residue. After a few minutes at room temperature the mixture was washed with ligroin to precipitate the anilide of *β*-phenylcinnamic acid which was removed by filtration, washed with ligroin, and recrystallized from a mixture of benzene and ligroin as a colorless solid, 4.0 g. (67%), m.p. and mixture m.p. with III prepared from I or II, 133.5–134.0°.

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(3) L. H. Briggs, G. G. De Ath, and S. R. Ellis, *J. Chem. Soc.*, 61, (1942).

(4) Semimicro analyses by Alfred Bernhardt, Max Planck Institut Mülheim (Ruhr), Germany. Melting points are uncorrected.

(5) C. Moureu, C. Dufraise, and C. Mackall, *Bull. soc. chim. France*, 393 (1923).

(6) K. H. Meyer and K. Schuster, *Ber.*, 55, 819 (1922).

(7) R. Heilman and R. Glenat, *Bull. soc. chim. France*, 1586 (1955) report b.p. 157–158° (3 mm.) n_{D}^{23} 1.5950.

(8) J. F. Eijkman, *Chem. Weekblad* 5, 655 (1909).

Reaction of Thiophosgene with Azide Ion[1]

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In consideration of additional methods for the preparation of 5-substituted amino-1,2,3,4-thia-

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(1) The authors gratefully acknowledge the support of these studies by the Air Force Office of Scientific Research.

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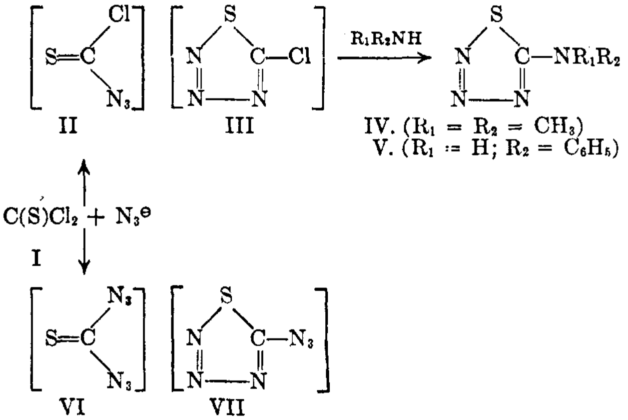
triazoles,[3] (IV, etc.), the nucleophilic displacement of a chlorine atom from thiophosgene (I) by azide ion to form 5-chlorothiatriazole (III) appeared to offer a direct route to this ring system. The electron-withdrawing property of the thiatriazole ring indicated that the 5-chloro substituent itself would be easily detached by nucleophilic displacement by amines to give the desired products. These expectations were realized. However, the intermediate 5-chlorothiatriazole (III), a low-melting oily-solid (when preserved at 0°), proved to be too treacherous to handle, several preparations giving violent detonations of an unpredictable nature.[4] *Great caution should be exercised in handling any reaction proportion of thiophosgene and azide ion.* That the initial condensation product has the structure III was demonstrated by its conversion to 5-substituted amino-1,2,3,4-thiatriazoles of known structure[5] (IV and V).

III, *i.e.*, 5-chlorothiatriazole. The product proved to be too unstable for analysis. Another difficult problem involves the removal of traces of unchanged thiophosgene (detected by the infrared spectra of III). Due to the sensitivity of the material to detonation and its general instability it was not considered expedient to solve this problem but rather to use the material as such for further reaction. However, in an attempt to consume all of the thiophosgene, an experiment involving two moles of sodium azide to one mole of thiophosgene was attempted. While the reagents were successfully mixed, the precipitated material, while suspended in water at −5°, detonated violently completely pulverizing the reaction flask, stirrer, and dropping funnel. It is assumed that the diazide of thiocarbonic acid (VI) or 5-azidothiatriazole (VII) is the sensitive material responsible for the detonation.



The reaction of 1*M* proportions of thiophosgene with sodium azide in water as a solvent at −5° precipitates a 94% yield of an oily yellow solid. The substance fumed in the atmosphere giving off hydrogen chloride; accordingly, it was preserved over phosphorus pentoxide at 0°. The infrared absorption of this immediate precipitate (in chloroform solution) gave a medium to weak intensity band at 2140 cm.$^{-1}$ indicating the presence of the azido group. This would indicate that the product was the acyclic chloroazido-thiocarbonate, II, however, it was subsequently discovered that the infrared azido absorption was due to traces of azide ion either suspended or dissolved in the oily product. The azide frequency was removed by water-washing the chloroform solution of the initial precipitate or by careful low-temperature washing of the precipitate. Under these conditions the asymmetric azide band disappears. Hence, it is concluded that the structure of the product is

EXPERIMENTAL[6]

5-Chloro-1,2,3,4-thiatriazole (III). In a 500-ml. flask equipped with a condenser, stirrer, and a dropping funnel there were placed 2 g. (0.031 mole) of sodium azide and 100 ml. of distilled water. The flask was cooled to −5° by means of an ice-salt bath. While maintaining constant stirring, 3.6 g. (0.031 mole) of thiophosgene was added over a 30-min. period. A yellow solid precipitated almost immediately. To ensure completion of the reaction, stirring was continued for an additional 2 hr. The precipitate was then immediately filtered by suction on a pre-cooled Buchner funnel. An inverted funnel fed from a nitrogen cylinder kept air from the material. The product was then carefully washed with 500 ml. of ice-cold water and the yellow oily solid placed in a desiccator over phosphorus pentoxide and stored at 0°. The product weighed 3.5 g. (94%). Successful runs were made using two and three times the quantities of reagents employed above.

5-Dimethylamino-1,2,3,4-thiatriazole (IV). Reaction of 1.2 g. (0.01 mole) of III with excess of dimethylamine in aqueous solution, with stirring at −5° for 2 hr. and allowed to stand for 12 hr., gave a yellow solid. This was washed with cold water and dried over calcium chloride in a vacuum desiccator. Recrystallization from petroleum ether (b.p. 35°–80°) gave 0.6 g. (50%) of colorless needles (m.p. 49–51°), identified as IV by mixture melting point with an authentic specimen.[5]

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[3] E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959).

[4] Detonations occurred both during the preparation of III and in its subsequent reaction with amines.

[5] E. Lieber, C. N. Pilai, and R. D. Hites, *Can. J. Chem.*, **35**, 832 (1957).

[6] The thiophosgene was obtained from the Rapter Laboratories, Chicago, Ill.

5-Anilino-1,2,3,4-thiatriazole (V). Following the above procedure, the reaction mixture of similar quantities of III with aniline (in ethanol) gave a crude yellow precipitate after 16 hr. Recrystallization from dry ethanol gave 0.7 g. (40%), m.p. 136°, of colorless rod-shaped crystals identified as V by mixture melting point with an authentic specimen.

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Syntheses of Some 1-(2-Phenylethyl)benzimidazoles

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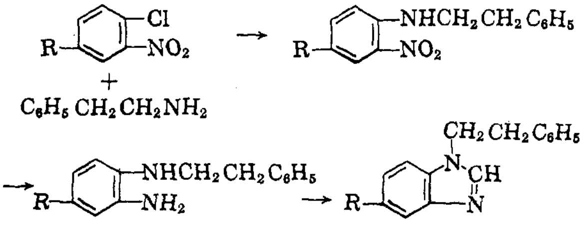
The preparation of several 1-(2-phenylethyl)-benzimidazoles, whose adrenergic properties are being evaluated, and their intermediate nitroanilines and *o*-phenylenediamines are described in this note. The diamines were isolated only in those cases where they were new compounds.



R = H, Cl, $COOC_2H_5$, COOH, $CONH_2$, $CONHNH_2$

EXPERIMENTAL

All melting points were determined in an apparatus described by Wagner and Meyer[1] using silicone oil and internal electrical heating. The values are uncorrected. Some of the compounds reported did not have sharp melting points even though they were obtained analytically pure. In these cases they were recrystallized to a constant melting point range before analysis.

Preparation of o-nitrophenylethylaminobenzenes. The general method is illustrated with the preparation of 2-nitrophenylethylaminobenzene.

N-(2-Phenylethyl)-2-nitroaniline (I). 1-Chloro-2-nitrobenzene (78.8 g., 0.5 mole) was dissolved in 100 ml. of xylene and 121.2 g. (1 mole) of β-phenylethylamine was added. The solution was refluxed for 6 hr., cooled to room temperature, and the β-phenylethylamine hydrochloride removed by filtration. The solid was washed with xylene. The filtrate plus the washings were distilled *in vacuo* to give an oil that was solidified by treating with petroleum ether (b.p. 30–60°). The product was recrystallized from 95% ethyl alcohol and obtained as orange crystals, yield 54%, m.p. 71.5–72.5°.

Anal. Calcd. for $C_{14}H_{14}N_2O_4$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.35; H, 6.09; N, 11.42.

N-(2-Phenylethyl)-2-nitro-4-chloroaniline (II). Compound II was prepared from 1,4-dichloro-2-nitrobenzene and β-phenylethylamine. The product was recrystallized several times from 95% ethyl alcohol, yield 50%, m.p. 89–92° (orange crystals).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: C, 60.76; H, 4.73; Cl, 12.81; N, 10.13. Found: C, 61.00; H, 4.56; Cl, 12.73; N, 10.13. Found: C, 61.00; H, 4.46; Cl, 12.73; N, 10.18.

N-(2-Phenylethyl)-2-nitro-4-carbethoxyaniline (III). This compound was prepared from ethyl 3-nitro-4-chlorobenzoate by the procedure used for compound I. The product was recrystallized repeatedly from 95% ethyl alcohol, yield 69%, m.p. 100–105° (orange crystals).

Anal. Calcd. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 65.12; H, 5.78; N, 8.93.

N-(2-Phenylethyl)-o-phenylenediamine (IV). *N*-(2-Phenylethyl)-2-nitroaniline (24.2 g., 0.1 mole) was hydrogenated over 0.3 g. of platinum oxide. After removing the catalyst, 17 ml. of concd. hydrochloric acid was added to the filtrate. The dark solution was concentrated *in vacuo* to give an oil which solidified on standing under dry ether overnight. The dihydrochloride was washed with ether and dried, yield 57%. The product was sufficiently pure for subsequent reactions.

The free base was obtained by dissolving the dihydrochloride in water and neutralizing the solution with ammonium hydroxide. The oil, which formed, solidified on standing overnight. After drying, the product was recrystallized from petroleum ether (b.p. 30–60°) m.p. 53–55°.

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.20. Found: C, 79.11; H, 7.56; N, 13.37.

N-(2-Phenylethyl)-2-amino-4-chloroaniline (V). To an intimate mixture of 27.6 g. (0.1 mole) of compound II and 59.7 g. of stannous chloride, 95 ml. of concd. hydrochloric acid was gradually added. After the reaction had subsided, the mixture was heated on a steam bath for 15 min. On cooling, a gel formed. An equal volume of ethanol was added and a vacuum distillation was carried out. This process was repeated until the precipitate became crystalline. It was then treated with 50% sodium hydroxide in the cold. The resulting oil was extracted with diethyl ether and the extract dried over anhydrous potassium carbonate. The ether was removed under reduced pressure in an atmosphere of nitrogen. The residual oil was dissolved in petroleum ether (b.p. 30–60°), treated with decolorizing carbon and the solution allowed to stand overnight. The solid product so obtained was recrystallized from petroleum ether (b.p. 30–60°), yield 65%, m.p. 48–50°.

Anal. Calcd. for $C_{14}H_{15}ClN_2$: C, 68.14; H, 6.13; Cl, 14.37; N, 11.36. Found: C, 68.08; H, 6.20; Cl, 14.17; N, 11.46.

1-(2-Phenylethyl)benzimidazole (VI). *N*-(2-Phenylethyl)-*o*-phenylenediamine (14.3 g., 0.05 mole) was dissolved in 150 ml. of 98% formic acid and the solution refluxed for 3 hr. The solution was concentrated to about 25 ml. *in vacuo* and neutralized with ammonium hydroxide. The product was removed, washed with water and dried. It was recrystallized from a mixture of diethyl ether and petroleum ether (b.p. 30–60°) with the aid of decolorizing carbon, yield 78%, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.61. Found: C, 80.90; H, 6.21; N, 12.61.

1-(2-Phenylethyl)-5-chlorobenzimidazole (VII). Compound VII was prepared from *N*-(2-phenylethyl)-2-amino-4-chloroaniline by the method used for compound VI. Neutralization with ammonium hydroxide gave an oil which was dissolved in diethyl ether and dried over anhydrous potassium carbonate. A solid was obtained when the ether was removed. Otherwise the procedure was the same as the one used for VI. The yield was 75%, m.p. 74°.

Anal. Calcd. for $C_{15}H_{13}ClN_2$: C, 70.17; H, 5.10; Cl, 13.81; N, 10.91. Found: C, 70.34; H, 5.21; Cl, 13.75; N, 10.96.

1-(2-Phenylethyl)-5-carbethoxybenzimidazole (VIII). *N*-(2-Phenylethyl)-2-nitro-5-carbethoxyaniline (15.7 g., 0.05 mole) in 100 ml. of ethanol was hydrogenated over 0.3 g. of platinum oxide. After removing the catalyst, dry hydrogen chloride was passed into the filtrate. The precipitated hydrochloride was washed with dry ether. Fifteen grams of the hydrochloride was refluxed in 100 ml. of 98% formic acid for 5 hr. The solution was concentrated *in vacuo* to about 25

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[1] E. C. Wagner and J. Meyer, *Ind. Eng. Chem., Anal. Ed.*, 10, 584 (1938).