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°, $n_D^{25.5}$ 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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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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