

*Anal.* Calcd. for  $C_{19}H_{18}N_6O_4$ : N, 18.57. Found: N, 18.35.

**2-Picolyl 2-Furyl Ketone.**—From 0.40 mole of ethyl 2-furancarboxylate and the 2-picolyl lithium prepared from 0.40 g. atom of lithium, 0.21 mole of bromobenzene and 0.40 mole of 2-picoline, there was obtained 10.3 g. (27.4% yield, 42% based on ester not recovered) of product, b.p. 141–143° (1 mm.). Two recrystallizations from petroleum ether (b.p. 30–60°, Skellysolve F) gave yellow needles, m.p. 49–51°, stable at room temperature. With two moles of 2-picoline per mole of ester the yield was 23%.

*Anal.* Calcd. for  $C_{11}H_8NO_2$ : N, 7.48. Found: N, 7.70.

The picrate<sup>8</sup> melted at 149–150° after recrystallization from alcohol and slowly darkened on exposure to light.

*Anal.* Calcd. for  $C_{17}H_{12}N_4O_4$ : N, 13.45. Found: N, 13.59.

The 2,4-dinitrophenylhydrazone, m.p. 166–167.5°, was prepared with acetic acid as a catalyst in 68% yield. Two crystallizations from 95% alcohol gave the purified hydrazone, m.p. 170–172°.

*Anal.* Calcd. for  $C_{17}H_{12}N_6O_8$ : N, 19.07. Found: N, 19.44.

When 2-picolyl 2-furyl ketone was treated with 2,4-dinitrophenylhydrazine in the presence of hydrochloric acid,<sup>9</sup> a product decomposing at 248–252° resulted. This seemed to be a mixture of the hydrazone and furyldinitropyridylindole since warming the hydrazone with a little dilute hydrochloric acid converted it to the high-melting material.

**2-Picolyl 2-Thienyl Ketone.**—When 0.40 mole of ethyl 2-thiophenecarboxylate was heated under reflux with 0.20 mole of picolyl lithium, prepared from 0.40 g. atom of lithium, 0.20 mole of bromobenzene and 0.40 mole of 2-picoline, the yield of 2-picolyl 2-thienyl ketone was 10.6 g. (26% yield, 43% based on ester not recovered), of yellow sirup, b.p. 167–172° (1 mm.). Recrystallization at 5° from petroleum ether (b.p. 30–60°, Skellysolve F) gave pale yellow needles, m.p. 28.5–29.5°.

*Anal.* Calcd. for  $C_{11}H_8NOS$ : N, 6.89. Found: N, 6.92.

The picrate<sup>8</sup> was obtained as yellow needles, m.p. 154–155°, after recrystallization from alcohol.

*Anal.* Calcd. for  $C_{17}H_{12}N_4O_8S$ : N, 12.96. Found: N, 13.00.

The 2,4-dinitrophenylhydrazone<sup>9</sup> was obtained as dark red needles, m.p. 194.5–195.5° (43% yield), after recrystallization from alcohol.

*Anal.* Calcd. for  $C_{17}H_{12}N_6O_8S$ : N, 18.27. Found: N, 18.25.

**Wolff-Kishner Reduction.**—The Huang-Minlon<sup>10</sup> modification of this reduction was used. Solutions of 0.02 mole of the 2-picolyl ketones, 0.06 mole of sodium hydroxide and 3 ml. of 85% hydrazine hydrate in 50 ml. of diethylene glycol were employed. The reduction products were purified by distillation from sodium metal through the helix packed column. All were colorless liquids when first obtained, but at room conditions they rapidly changed to dark brown sirups.

1-Phenyl-2-(2-pyridyl)-ethane was obtained in 83% yield, b.p. 110–112° (1 mm.),  $n_D^{25}$  1.5197. Preparation of the picrate<sup>8</sup> gave yellow crystals, m.p. 135–135.5°. Recrystallization from alcohol gave the *monopicrate*, m.p. 128–129°, mixed m.p. with the picrate of the product obtained by a different method,<sup>11</sup> m.p. 128–129°.

*Anal.* Calcd. for  $C_{19}H_{18}N_4O_7$ : N, 13.59. Found: N, 13.67.

1-(2-Furyl)-2-(2-pyridyl)-ethane was prepared in 64% yield, b.p. 100–101° (1 mm.) or 113–117° (8 mm.),  $n_D^{25}$  1.5132. The initial precipitate obtained in preparation of the picrate was recrystallized from alcohol to give the *monopicrate*, yellow needles, m.p. 112–113.5°.

*Anal.* Calcd. for  $C_{17}H_{14}N_4O_8$ : N, 13.93. Found: N, 14.03.

1-(2-Thienyl)-2-(2-pyridyl)-ethane was obtained in 40% yield, b.p. 115–119° (1 mm.),  $n_D^{25}$  1.5428. The precipitate from the reaction of hydrocarbon with a saturated alcoholic solution of picric acid was the *dipicrate*, yellow needles, m.p. 130.5–132°.

*Anal.* Calcd. for  $C_{23}H_{17}N_7O_{14}S$ : N, 15.15. Found: N, 15.04.

Recrystallization from alcohol gave the *monopicrate*, m.p. 99.5–100°.

*Anal.* Calcd. for  $C_{17}H_{14}N_4O_7S$ : N, 13.29. Found: N, 13.35.

(10) Huang-Minlon, *THIS JOURNAL*, **68**, 2487 (1946).

(11) Ziegler and Zeiser, *Ann.*, **485**, 192 (1931).

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## The Friedel-Crafts Reaction with Disubstituted Ethylene Oxides. II. $\alpha$ -Methylstyrene Oxide

BY WILLARD T. SOMERVILLE<sup>1</sup> AND PAUL E. SPOERRI

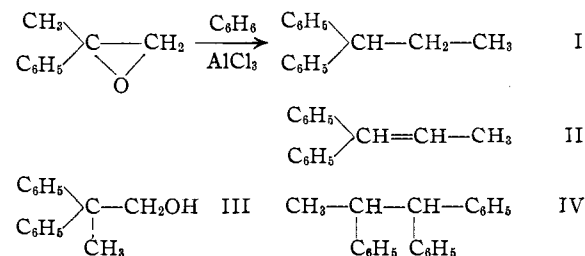
The Friedel-Crafts reaction of  $\alpha$ -methylstyrene oxide in benzene has been found to give the expected alcohol 2,2-diphenylpropanol-1 together with 1,1,2-triphenylpropane, 1,1-diphenylpropene and 1,1-diphenylpropane. The exclusive formation of the rearranged product 1,1,2-triphenylpropane as a product of the secondary condensation is contrasted with the secondary products obtained from the Friedel-Crafts reaction with isobutylene oxide. The above three hydrocarbons are formed as the result of a rearrangement and a mechanism is proposed for this rearrangement.

Previous work on 2,3-butylene oxide and isobutylene oxide<sup>2</sup> has been extended to include  $\alpha$ -methylstyrene oxide, in order to determine whether the same type of rearrangements occurred.

$\alpha$ -Methylstyrene oxide was treated with a twenty molar excess of benzene in the presence of two moles of anhydrous aluminum chloride at 5–10°. Under these conditions the reaction proceeded with the formation of 1,1-diphenylpropane (I), 1,1-diphenyl-1-propene (II), 2,2-diphenyl-1-propanol (III) and 1,1,2-triphenylpropane (IV).

(1) Taken in part from a dissertation presented by Willard T. Somerville to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(2) Somerville and Spoerri, *THIS JOURNAL*, **72**, 2185 (1950).



The unsaturated hydrocarbon, II, obtained melted at 48° and was at first believed to be the low melting (*cis* ?) form of  $\alpha$ -methylstilbene, since this substance has been reported as a dehydration product of 2,2-diphenyl-1-propanol by other

workers.<sup>3</sup> Since it could not be isomerized to the higher melting *trans* (?) (84°) form<sup>4</sup> the structure was investigated by oxidation with dichromate and sulfuric acid. The structure was shown to be 1,1-diphenyl-1-propene (II) by the formation of acetic acid and of benzophenone. This was further confirmed by a mixed melting point with a synthetic sample.

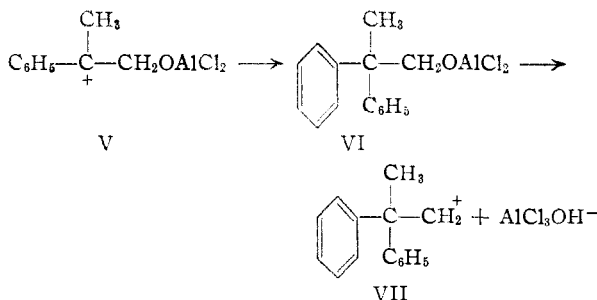
Although the corresponding saturated hydrocarbon (I) could not be obtained entirely free from the propene II, it had physical constants in agreement with the literature values.<sup>5,6</sup> The alcoholic portion of the distillate was a very viscous liquid. It was identified as 2,2-diphenyl-1-propanol (III) by the preparation of the known phenylurethan.<sup>3</sup> This alcohol is the phenyl analog of the neophyl alcohol obtained from isobutylene oxide.<sup>2</sup>

A comparison with the products obtained from isobutylene oxide suggested that a mixture of 1,2,2- and 1,1,2-triphenylpropanes might be the expected products of the secondary condensation of  $\alpha$ -methylstyrene oxide. However, the rearranged product 1,1,2-triphenylpropane was the sole product obtained. It formed white crystals melting at 73°,<sup>7</sup> the only triphenylpropane with this melting point.

This product is analogous to the 2,3-diphenylbutane obtained from isobutylene oxide (ref. 2).

### Discussion of Results

The formation of all three hydrocarbon products from  $\alpha$ -methylstyrene oxide and benzene in the presence of aluminum chloride involves a change in the carbon skeleton. Probably, the first step in the reaction involves the opening of the weakened carbon-oxygen bond<sup>8</sup> of the oxide-aluminum chloride complex to form a carbonium ion, which because of the resonance stabilization involving the benzene ring probably exists predominantly as the tertiary carbonium ion V. The aluminum chloride salt of the alcohol VI forms a carbonium ion VII under the influence of hydrogen chloride, always present in the reaction mixture.



It is believed that carbonium ion VII undergoes a series of Whitmore 1,2-shifts forming carbonium ion X.

In the first 1,2-shift, one of the phenyl groups

(3) Favorski, *J. Russ. Phys.-Chem. Soc.*, **50**, 78 (1920); Ramart and Amagat, *Ann. chim.*, [10] **8**, 316 (1927).

(4) Ellingboe and Fuson, *THIS JOURNAL*, **55**, 2960 (1933).

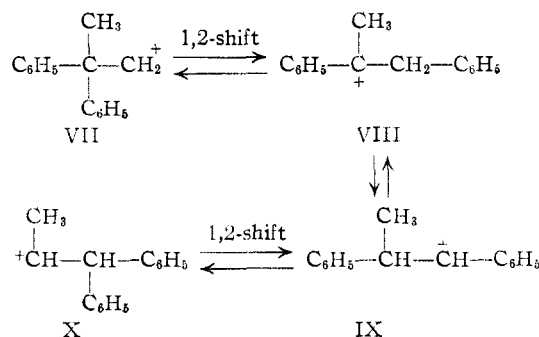
(5) Klages and Hellmann, *Ber.*, **37**, 1450 (1904).

(6) Sabatier and Murat, *Compt. rend.*, **155**, 387 (1912).

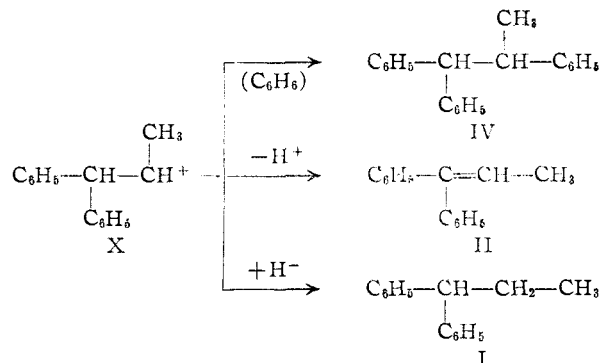
(7) Schlenk and Bergmann, *Ann.*, **463**, 46 (1928); Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937).

(8) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 303.

migrates forming carbonium ion VIII. The tautomeric ion IX may be postulated as being formed from VIII by a hydride shift. This is followed by a second 1,2-shift of a phenyl group to complete the rearrangement. This carbonium ion X may



then react with benzene to form 1,1,2-triphenylpropane (IV), may lose a proton to form 1,1-diphenyl-1-propene (II) or may be reduced or undergo a hydride ion transfer<sup>9</sup> to produce 1,1-diphenylpropane (I). The formation of "hydro-



genation" products during Friedel-Crafts reactions has been commented upon by Egloff and Nightingale.<sup>10</sup> It is entirely possible that 1,2,2-triphenylpropane may be very easily rearranged by aluminum chloride to the 1,1,2-isomer just as  $\alpha$ , $\alpha$ -dimethyldibenzyl is rearranged to 2,3-diphenylbutane.<sup>2</sup> This rearrangement would also involve a preliminary scission of the molecule.

### Experimental<sup>11</sup>

**$\alpha$ -Methylstyrene Oxide.**— $\alpha$ -Methylstyrene chlorohydrin was prepared by the method of Emerson<sup>12</sup> as given for styrene chlorohydrin. The crude, undistilled chlorohydrin (1686 g.) obtained from 1260 g. of methylstyrene was saponified by refluxing for 2 hours with a solution of 675 g. of potassium hydroxide in 2.4 l. of water. The oily layer was washed neutral without acidification and vacuum distilled. The physical constants of the oxide were: b.p. 48° (2 mm.);  $n_D^{20}$  1.5212 and  $d_4^{20}$  1.0220. The yield was 64.2% based on the  $\alpha$ -methylstyrene.

**Friedel-Crafts Condensation of  $\alpha$ -Methylstyrene Oxide.**—The condensation was carried out using twenty moles of benzene and two moles of aluminum chloride per mole of oxide according to the procedure previously described.<sup>1</sup> The crude product obtained from 933 g. (6.74 moles) of oxide after removal of the benzene, was refluxed with an

(9) Bartlett, Condon and Schneider, *THIS JOURNAL*, **66**, 1531 (1944).

(10) Egloff, *et al.*, *Chem. Revs.*, **20**, 360 (1937); Nightingale, *ibid.*, **25**, 329 (1939).

(11) The microanalyses were done by the Clark Microanalytical Laboratories, Urbana, Illinois.

(12) Emerson, *et al.*, *THIS JOURNAL*, **67**, 516 (1945).

equal volume of aqueous 10% sodium hydroxide solution for 4 hours, to remove any remaining acid. It was then washed and vacuum distilled at 2 mm. of pressure over a 10 cm. packed column. The distillate, which was collected in 26 fractions, seemed to consist of three principal sections.

Section 1	b.p. 113-132°	348 g.
Section 2	b.p. 137-159°	102 g.
Section 3	b.p. 159-177	357 g.
Residue		574 g.

**Isolation of 1,1-Diphenyl-1-propene.**—Section one was redistilled through an 18" modified Widmer column. In this manner 225 g. of colorless liquid b.p. 109-111° (2 mm.) was obtained. The index of refraction was not constant but varied from  $n_D^{20}$  1.5720 to 1.5858. It was then refrigerated and a crystalline material separated. This was removed by low temperature filtration (113 g.) and recrystallized from hot alcohol. The melting point of 48° did not change on further recrystallization. A mixed m.p. with 1,1-phenyl-1-propene of m.p. 48-49° was 48-48.5°. It decolorized a solution of bromine. The yield of purified product was 68 g. (5.2% of theory).

*Anal.* Calcd. for  $C_{15}H_{14}$ : C, 92.74; H, 7.26. Found: C, 92.74; H, 7.37.

As a further identification, ca. 0.5 g. was oxidized by boiling with a solution of potassium dichromate in water and sulfuric acid. The vapors had a faint odor of acetic acid and reddened blue litmus paper. Glacial acetic acid was then added to improve the solubility, and on further boiling oxidation took place rapidly. The mixture was cooled and extracted several times with benzene. The combined extracts were washed with water and then sodium carbonate solution.

The benzene solution was then dried and evaporated. The oily residue which had the characteristic odor of benzophenone was added to an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine hydrochloride. In a few minutes, a red-orange precipitate of hydrazone was observed. This was filtered, pressed dry and recrystallized from glacial acetic acid. It then melted sharply at 239° (cor.). The 2,4-

dinitrophenylhydrazone of benzophenone has this same melting point.<sup>13</sup>

**Isolation of 1,1-Diphenylpropene.**—The liquid portion from the cold filtration of the 1,1-diphenyl-1-propene was carefully redistilled through a 12-inch column to give 50 g. of a colorless liquid, b.p. 105° (1.6 mm.),  $n_D^{20}$  1.5655;  $d_{20}^{20}$  0.9846. It had a bromine number of 6.1, equivalent to 6.6% of diphenylpropene. The physical constants of 1,1-diphenylpropane have been reported as  $n_D^{15}$  1.5657<sup>8</sup> and  $d_{20}^{15}$  0.9881.<sup>8</sup>

**Isolation of 2,2-Diphenyl-1-propanol.**—The second section was also carefully refractionated to obtain 55 g. (3.85% of theory) of 2,2-diphenyl-1-propanol, a very viscous liquid having the following properties: b.p. 143-145° (1.8 mm.),  $n_D^{20}$  1.5924.

*Anal.* Calcd. for  $C_{15}H_{16}O$ : C, 84.87; H, 7.59. Found: C, 85.80; H, 7.78.

This alcohol readily gave a phenylurethan which after recrystallization had a m.p. of 148-148.2°. The reported m.p. of this derivative is 148-149°.<sup>3</sup>

*Anal.* Calcd. for  $C_{22}H_{21}O_2N$ : C, 79.23; H, 6.40. Found: C, 79.77; H, 6.32.

**Isolation of 1,1,2-Triphenylpropane.**—Upon redistilling the third section through a 12" modified Widmer column, a very viscous pale yellow liquid was obtained with the physical constants: b.p. 172° (2 mm.);  $n_D^{20}$  1.5980. On long standing a small crystal was observed in one fraction. Upon seeding the other fractions with this seed, a pale yellow crystalline solid was obtained. This solid after recrystallization from alcohol had a m.p. of 73° which was not altered by further recrystallization (yield 252 g., 13.7%).

The melting point has been reported as 73-75°<sup>6</sup> and 76-77°.<sup>7</sup>

*Anal.* Calcd. for  $C_{21}H_{20}$ : C, 92.60; H, 7.40. Found: C, 92.63; H, 7.50.

(13) Shriner and Fuson, "Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

BROOKLYN, N. Y.

RECEIVED JUNE 10, 1950

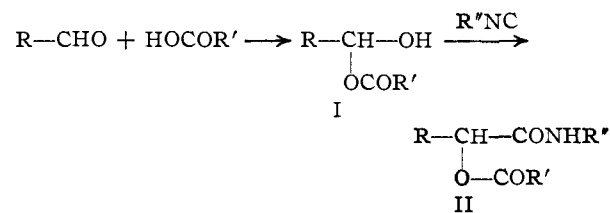
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Passerini Reaction. III. Stereochemistry and Mechanism<sup>1,2</sup>

BY ROBERT H. BAKER AND DAVID STANONIS

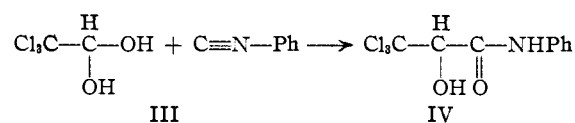
Certain aldehydes and unsymmetrical ketones produce with *l*-menthoxyacetic acid and phenyl isocyanide the diastereomeric *l*-menthoxyacetoxyanilides. Methods of separation of these are described. The kinetics of a typical Passerini reaction has been found to be third order, first order in each of the reactants. A mechanism is postulated which shows the reaction to be related to the second order Beckmann rearrangement.

Passerini<sup>3</sup> proposed that the mechanism of formation of  $\alpha$ -acyloxyanilides (II) from phenylisocyanide, an aldehyde and an acid involved two steps. First, the acid was supposed to attack aldehyde to form I and then this reacted with isocyanide to form II.



Evidence cited to support this scheme was the fact that chloroaldehyde or ketone hydrates would

react without acid to produce the hydroxyanilide, IV,<sup>4</sup> and that certain optically active acids in



ketone solutions showed anomalous rotations.<sup>5</sup> The weakness in the argument lies in the lack of a reasonable explanation of how such intermediates as I or III could react with isocyanide to yield II or IV. We have previously pointed out that the anomalous rotation is not compelling evidence of the formation of intermediates of type I,<sup>6</sup> and we point out later in this paper an alternate interpretation of the aldehyde hydrate reaction.

Earlier<sup>6</sup> we have sought to make use of the Passerini reaction in the production of optically

(1) This investigation was supported by a grant from the Abbott Fund of Northwestern University.

(2) Presented at the Philadelphia Meeting of the American Chemical Society, April, 1950.

(3) M. Passerini, *Gazz. chim. ital.*, **51**, 126 (1921).

(4) M. Passerini, *ibid.*, **52**, 432 (1922).

(5) M. Passerini, *ibid.*, **55**, 726 (1925).

(6) R. H. Baker and L. E. Linn, *THIS JOURNAL*, **70**, 3721 (1948).