

phenyllithium (0.4 mole) cooled to  $-65^{\circ}$  by immersion in a Dry Ice-acetone slurry. The mixture was stirred for two more hours at  $-65^{\circ}$  allowed to warm to room temperature and poured onto a mixture of ice and excess concentrated hydrochloric acid. The layers were separated and the aqueous phase was extracted with several portions of ether. The combined ether extracts were dried over Drierite. The solvent was removed and the residue was distilled first at atmospheric pressure to give 22.5 g. (73%) of trifluoroacetophenone (b.p.  $150-152^{\circ}$ , 2,4-dinitrophenylhydrazone, m.p.  $173.8-174.2^{\circ}$ ) and then at reduced pressure to give 3.1 g. (13%) of benzoic acid (b.p.  $110-113^{\circ}$  at 3 mm., m.p.  $120.4-121.2^{\circ}$  alone and when mixed with an authentic sample).

(B) Addition of Phenyllithium (Two Equivalents) to Trifluoroacetic Acid (One Equivalent) at  $-65^{\circ}$  (Reverse Addition Technique).—Phenyllithium (0.4 mole in 800 ml. of ether) was added over a period of six to eight hours to a rapidly stirred solution of trifluoroacetic acid (22.8 g., 0.2 mole) in 300 ml. of ether and maintained at  $-65^{\circ}$ . The mixture was then treated as described in experiment IA to give 18.3 g. (53%) of trifluoroacetophenone and 3.9 g. (16%) of benzoic acid.

II. Preparation of Diphenylperfluoroalkylcarbinols. The Synthesis of Diphenyltrifluoromethylcarbinol.—Methyl trifluoroacetate (25.6 g., 0.2 mole), dissolved in 50 ml. of ether, was added to rapidly stirred phenyllithium (0.4 mole) at such a rate that the ether refluxed gently throughout the addition. The reaction mixture then was refluxed for one-half hour, quenched and processed as described in experiment IA to give 44.2 g. (88%) of diphenyltrifluoromethylcarbinol, b.p.  $109-110^{\circ}$  at 1.5 mm., m.p.  $74-74.7^{\circ}$ . Similar sized runs with methyl perfluoropropionate and methyl perfluoro-*n*-butyrate gave 52.5 g. (87%) of diphenylperfluoroethylcarbinol and 59.2 g. (84%) of diphenylperfluoro-*n*-propylcarbinol, respectively.

III. Ketones and Carbinols from Methyl Perfluoroalkanoates and Phenyllithium. (A) Addition of Phenyllithium (One Equivalent) to Methyl Trifluoroacetate (One Equivalent) at  $25^{\circ}$  (Reverse Addition Technique).—Phenyllithium (0.2 mole in 800 ml. of ether) was added over a period of six to eight hours to a rapidly stirred solution of methyl trifluoroacetate (25.6 g., 0.2 mole) in 300 ml. of ether maintained at  $25^{\circ}$ . The mixture was then refluxed for one-half hour, quenched and processed as described in experiment IA to give 20.1 g. (58%) of trifluoroacetophenone, b.p.  $150-152^{\circ}$ , and 2.6 g. (10%) of diphenyltrifluoromethylcarbinol, b.p.  $111-113^{\circ}$  at 2 mm., m.p.  $74.0-74.5^{\circ}$ .

(B) Addition of Methyl Perfluoropropionate (One Equivalent) to Phenyllithium (One Equivalent) at  $-40^{\circ}$  (Standard Addition Technique).—Methyl perfluoropropionate (35.6 g., 0.2 mole), dissolved in 50 ml. of ether, was added over a one-half hour period to rapidly stirred phenyllithium (0.2 mole) cooled to  $-40^{\circ}$  by a Dry Ice-ethanol slurry. The reaction mixture was then allowed to warm to room temperature, refluxed for one-half hour and processed as described in experiment IA to give 6.8 g. (15%) of phenyl perfluoroethyl ketone (b.p.  $159-161^{\circ}$ , 2,4-dinitrophenylhydrazone, m.p.  $111.8-112.4^{\circ}$ ) and 13.4 g. (44%) of diphenylperfluoroethylcarbinol (b.p.  $140-143^{\circ}$  at 11 mm., m.p.  $84.0-84.5^{\circ}$ ).

IV. Preparation of 2-Picolyl Perfluoroalkyl Ketones. Synthesis of 2-Picolyl Trifluoromethyl Ketone.—2-Picolyl-lithium<sup>4,5</sup> (0.4 mole in 800 ml. of ether) was added over a period of eight hours to a solution of methyl trifluoroacetate (25.6 g., 0.2 mole) in 300 ml. of ether maintained at  $25^{\circ}$ . The reaction mixture was refluxed for one-half hour and then quenched by pouring onto a mixture of ice and concentrated hydrochloric acid. The aqueous phase was made strongly basic by means of 20% sodium hydroxide solution, extracted several times with ether and the combined extracts dried over sodium sulfate. After removing the solvent and recovered 2-picoline, the residue solidified. In this way there was obtained 33.8 g. (89%) of 2-picolyl trifluoromethyl ketone (m.p.  $113-113.4^{\circ}$  (from 60-70° petroleum ether). *Anal.* Calcd. for  $C_8H_5NOF_3$ : N, 7.41. Found: N, 7.61). The ketone gave a copper salt, m.p.  $219.5-220^{\circ}$  (from 95% ethanol) when treated with aqueous copper(II) acetate solution.

From similar sized runs involving methyl perfluoropropionate and methyl perfluoro-*n*-butyrate the following ketones were obtained: 2-picolyl perfluoroethyl ketone (39.4 g., 83%, m.p.  $98-98.8^{\circ}$  (from 60-70° petroleum ether). *Anal.*

Calcd. for  $C_9H_5NOF_3$ : N, 5.86. Found: N, 5.81; copper salt, m.p.  $180.2-180.6^{\circ}$  (from 95% ethanol) and 2-picolyl perfluoro-*n*-propyl ketone (49.9 g., 87%, m.p.  $92-92.4^{\circ}$  (from 60-70° petroleum ether). *Anal.* Calcd. for  $C_{10}H_5NOF_3$ : N, 4.84. Found: N, 4.87; copper salt, m.p.  $151-152^{\circ}$  (from 95% ethanol)).

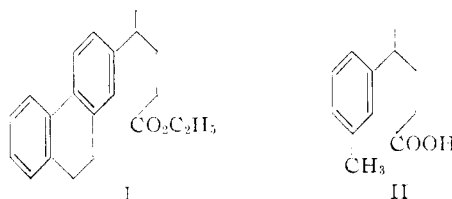
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## The Friedel-Crafts Condensation between $\gamma$ -Valerolactone and Toluene

BY DONALD D. PHILLIPS

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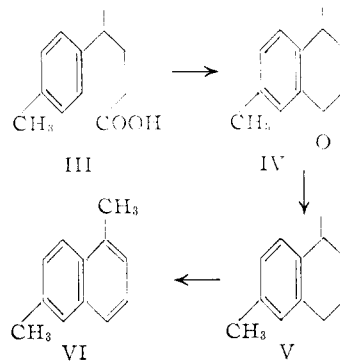
We recently<sup>1</sup> reported a convenient preparation of ester I by the Friedel-Crafts condensation of  $\gamma$ -valerolactone and 9,10-dihydrophenanthrene. That the alkylation had occurred *para* to the biphenyl-type link was established by an independent synthesis of I. We have read with some interest the report<sup>2</sup> that a similar condensation between  $\gamma$ -valerolactone and toluene gave exclusively the *meta* isomer,  $\gamma$ -(*m*-tolyl)-valeric acid (II). In view of the



fact that we wish to use this reaction between  $\gamma$ -valerolactone and various aromatics for the synthesis of picenes of unambiguous structure, we felt it necessary to check the reaction with toluene and establish unequivocally the orientation in the product.

In our hands the condensation invariably resulted in the formation of the expected *para* isomer,  $\gamma$ -(*p*-tolyl)-valeric acid (III), and none of the reported<sup>2</sup> *meta* product could be obtained. At higher temperatures the yield of III was only slightly affected and the addition of excess aluminum chloride resulted merely in the formation of substantial amounts of the cyclized product IV.

The orientation in III was established by oxidation to terephthalic acid (isolated as the dimethyl ester) and by its conversion through the corresponding tetralone (IV) and tetralin (V) to 1,6-dimethylnaphthalene (VI). The infrared absorption spectrum of VI was identical to that of an authentic



(1) D. D. Phillips and E. J. McWhorter, *THIS JOURNAL*, **76**, 4948 (1954).

(2) N. Chaudhuri, *Science and Culture*, **18**, 442 (1953).

sample and the picrates and 2,4,7-trinitrofluorenone complexes on admixture gave no depression in melting point.

### Experimental<sup>3</sup>

**$\gamma$ -(*p*-Tolyl)-valeric Acid (III).**—To 120 ml. of toluene and 40 g. (0.4 mole) of  $\gamma$ -valerolactone was added with stirring over ten minutes 52.3 g. (0.4 mole) of aluminum chloride. The temperature rose from 25 to 75° as a pea-green complex formed. The mixture was stirred at 90° for one hour, decomposed in the usual fashion and distilled to give 50.1 g. (65%) of the acid as a clear, colorless oil, b.p. 133–134° (0.8 mm.),  $n_D^{25}$  1.5138.

*Anal.* Calcd. for  $C_{12}H_{16}O_2$ : C, 74.97; H, 8.39. Found: C, 74.84; H, 8.26.

The yield of acid was 60% when the reaction temperature was maintained at 25°. When the amount of aluminum chloride was increased to two equivalents, about 20% of the tetralone (IV) was obtained as a forerun, b.p. 106–108° (0.8 mm.) and the yield of acid dropped a corresponding amount (to ca. 45%).

Oxidation of the acid in aqueous permanganate followed by esterification of the product gave a 76% yield of dimethyl terephthalate, m.p. 137–138°, identical in all respects with an authentic sample, m.p. 137.5–138.5°.

**4,7-Dimethyl-1-tetralone (IV).**—A mixture of 19.0 g. (0.1 mole) of  $\gamma$ -(*p*-tolyl)-valeric acid and 200 g. of polyphosphoric acid<sup>4</sup> was heated to 100° with stirring for two hours. The olive-green complex was allowed to stand overnight, poured into cold water and extracted with ether. The ether extracts were then shaken with carbonate solution, dried and distilled to give 15.7 g. (91%) of the ketone as a clear colorless liquid, b.p. 106.5–108° (0.8 mm.),  $n_D^{25}$  1.5567;  $d_4^{20}$  1.049.

*Anal.* Calcd. for  $C_{12}H_{14}O$ : C, 82.74; H, 8.10. Found: C, 83.09; H, 8.03.

The semicarbazone crystallized as colorless needles from ethanol, m.p. 193–195°; lit.<sup>6</sup> m.p. 194–195°.

**1,6-Dimethyl-1,2,3,4-tetrahydronaphthalene (V).**—A solution of 14.7 g. (0.084 mole) of tetralone (IV) in 50 ml. of diethylene glycol containing 10 ml. of 85% hydrazine hydrate was heated under reflux for 2.5 hours. To the pale yellow solution was added 11 g. of 85% potassium hydroxide and the mixture was heated without condenser to 190° where it was held for four hours. The usual workup gave on distillation 9.2 g. (68%) of the tetralin, b.p. 108.5–110° (11 mm.),  $n_D^{25}$  1.5320,  $d_4^{20}$  0.946.

*Anal.* Calcd. for  $C_{12}H_{16}$ : C, 89.92; H, 10.08. Found: C, 90.25; H, 9.96.

**1,6-Dimethylnaphthalene (VI).**—A mixture of 3.15 g. (0.02 mole) of tetralin (V) and 0.5 g. of 10% palladium-charcoal catalyst was heated under reflux (250–270°) for three hours. The crude product was taken up in ethanol, filtered and added to a saturated solution of picric acid from which there precipitated 4.8 g. (63%) of an orange picrate, m.p. 111–114°. When crystallized from a saturated solution of picric acid, the picrate formed orange needles, m.p. 113–134°, undepressed on admixture with an authentic sample, m.p. 113–134°.<sup>7</sup>

By chromatography of the picrate on alumina, a pure sample of 1,6-dimethylnaphthalene (b.p. 253–254°,  $n_D^{25}$  1.6055) was obtained and its infrared absorption spectrum was superimposable on that of an authentic specimen. This material was used to prepare the 2,4,7-trinitrofluorenone complex, orange needles from acetic acid, m.p. 138–140°.

(3) Melting points are corrected; boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer model 21 spectrophotometer. Distillations were carried out with a 30-cm. Podbielniak type column with partial reflux head.<sup>4</sup> Analyses are by Geller Labs., Hackensack, N. J.

(4) J. Cason and H. Rapoport, "Laboratory Experiments in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

(5) H. R. Snyder and F. X. Werber, *THIS JOURNAL*, **72**, 2965 (1950).

(6) H. Rupe and F. Schütz, *Helv. Chim. Acta*, **9**, 992 (1926).

(7) The recorded m.p. for the picrate of 1,6-dimethylnaphthalene is 114° (F. B. Kipping and F. Wild, *J. Chem. Soc.*, 1239 (1940)), whereas the picrate of 1,7-dimethylnaphthalene is reported as lemon-yellow needles, m.p. 123–124° (G. Darzens and A. Heinz, *Compt. rend.*, **184**, 33 (1927)).

*Anal.* Calcd. for  $C_{25}H_{17}N_3O_7$ : C, 63.70; H, 3.64; N, 8.91. Found: C, 63.90; H, 3.82; N, 8.81.

The authentic trinitrofluorenone complex was also prepared, orange needles from acetic acid, m.p. 139–140°; mixed m.p. 138–140°.

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## The Preparation and Proof of Structure of 1,4-Bis-*O*-*p*-nitrobenzoylerythritol<sup>1</sup>

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In studies on a new procedure for the correlation of the structure of glycosides<sup>2</sup> it was shown that *D'*- and *L'*-methoxydiethylene glycol, obtained from methyl  $\alpha$ - and from methyl  $\beta$ -*D*-(and *L*)-pentopyranosides, gave upon hydrolysis ethylene glycol and glycolic aldehyde.<sup>3</sup> The former was characterized readily but the identification of the glycolic aldehyde as such in small quantities presented difficulty since the usual aldehyde reagents, the aromatic hydrazines, do not distinguish glycolic aldehyde from glyoxal. Both give bis-hydrazones of glyoxal.<sup>4,5</sup>

To avoid ambiguity the bis-*O*-*p*-nitrobenzoate of *D'*- and *L'*-methoxydiethylene glycol was hydrolyzed so that the glycolic aldehyde would appear as a mono-*O*-*p*-nitrobenzoate, since the *O*-benzoate of glycolic aldehyde<sup>6</sup> had been shown previously to react normally to give a 2,4-dinitrophenylhydrazone<sup>7</sup> and it was anticipated that the *p*-nitrobenzoate would behave similarly. This, proving to be the case, necessitated the synthesis of an authentic specimen of the 2,4-dinitrophenylhydrazone of *O*-*p*-nitrobenzoylglycolic aldehyde.

When erythritol was esterified with two molecular proportions of *p*-nitrobenzoyl chloride the principal product was a bis-*p*-nitrobenzoate. Of the possible structures for such a diester only the 1,4- and 1,2-diester can react with lead tetraacetate. The 1,4-diester I should consume one mole of lead tetraacetate to yield two moles of glycolic aldehyde *O*-*p*-nitrobenzoate; in the case of the 1,2-diester II,<sup>8</sup> one mole of lead tetraacetate would be consumed with the formation of one mole of glyceraldehyde bis-*O*-*p*-nitrobenzoate and one mole of formaldehyde.

The bis-*p*-nitrobenzoate which had been prepared consumed one mole of lead tetraacetate without the formation of formaldehyde. Hence its structure must be represented by I. The *O*-*p*-nitro-

(1) From a thesis submitted to the graduate faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve, 1951. Paper No. 3107, Scientific Journal Series, Minnesota Agricultural Experiment Station.

(2) M. Abdel-Akher, J. E. Cadotte, Bertha A. Lewis, R. Montgomery, F. Smith, and J. W. Van Cleve, *Nature*, **171**, 474 (1953).

(3) F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **77**, 3091 (1955).

(4) A. Wohl and C. Neuberger, *Ber.*, **33**, 3095 (1900).

(5) E. Fisher and K. Landsteiner, *ibid.*, **25**, 2549 (1892).

(6) L. Palfray, H. Halasz and S. Rovira, *Comp. rend.*, **210**, 765 (1940).

(7) H. Ohle and G. A. Melkonian, *Ber.*, **74**, 291 (1941).

(8) There are two theoretically possible 1,2-diester, only one of which (II) is shown, which should be optically active thus forming an enantiomorphic pair.