repeated recrystallizations from 90% methanol and pentane; m.p., 95–96°.

Anal. Calcd. for $C_{29}H_{62}N_4O$: C, 72.16; H, 12.95; N, 11.61. Found: C, 72.01; H, 12.88; N, 11.68.

This compound was identical with 1,1,5,5-tetraheptylcarbohydrazide which was synthesized as described below.

The major component of the reaction remained in the mother liquors. After several recrystallizations from petroleum ether (b.p. 60–68°), it melted at 70–72° and did not depress the melting point of I. The infrared spectra of the two materials were identical.

1,1,5,5-Tetraheptylcarbohydrazide.—A solution of 1.14 g. (0.005 mole) of 1,1-diheptylhydrazine in 6 ml. of pyridine was cooled and shaken while 0.25 g. (0.0025 mole) of liquid phosgene was added. After a few minutes, 10 ml. of water was added to the reaction mixture; then it was concentrated under reduced pressure. The residue was made alkaline and the precipitate was removed by filtration. After recrystallization from aqueous methanol it melted at 94–95° and was shown to be identical with the compound isolated in the preceding experiment.

Hydrogenation of a Mixture of *n*-Heptaldehyde and 1-Heptyl-2-carbomethoxyhydrazine.—A mixture of 2.85 g. (0.025 mole) of *n*-heptaldehyde, 4.7 g. (0.025 mole) of 1-heptyl-2-carbomethoxyhyrazine, 17 ml. of methanol, and 0.15 g. of prereduced platinum oxide catalyst was shaken for about 12 hr. with hydrogen at an initial pressure of 50 p.s.i. After removal of the catalyst and solvent, 7 g. of a solid residue was obtained. Recrystallization of this material from petroleum ether (b.p. 60–68°) afforded 4.5 g. (63%) of I which melted at 70–72°. There was obtained 2.5 g. of material from the mother liquors which remained oily at room temperature and was not investigated.

The Application of the Henkel Process to *o*-Phenylbenzoic and *o*-Toluic Acids

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As an extension of our investigation[1] on the mechanism of the Henkel process,[2,3] by which potassium benzoate or dipotassium phthalate is converted into dipotassium terephthalate, the reaction was applied to potassium *o*-phenylbenzoate and potassium *o*-toluate under similar conditions.

Although the reaction with potassium *o*-toluate gave a considerable amount of toluene, it is of interest to note that 2-methylterephthalic acid was also isolated from the reaction mixture. It is probably formed in the same way as the disproportionation of potassium benzoate.

Potassium *o*-phenylbenzoate gave appreciable amounts of both *m*- and *p*-phenylbenzoate together with diphenyl. A small amount of 4,4′-diphenyldicarboxylic acid was also found in this reaction.

Experimental

The Reaction of Potassium *o*-Toluate.—A mixture of finely powdered potassium *o*-toluate (3 g.) and cadmium carbonate (0.24 g.) in a test tube having a rubber stopper fitted with a constricted glass tube was heated for 1.5 hr. at 410° in a metal bath. While heating continuous evolution of toluene was observed. The toluene was collected by cooling and confirmed as 2,4-dinitrotoluene, m.p. and mixture m.p. 69.7°.[4] The solid product was dissolved in boiling water. Colloidal black material was removed by filtration with the aid of zinc sulfate,[1a] the filtrate being acidified with hydrochloric acid and then extracted with ether. On evaporation of ether there was obtained white solid. The petroleum ether-soluble portion of this material consisted of pure starting material, while the insoluble portion (0.13 g.) was shown to be 2-methylterephthalic acid by converting it into the dimethyl ester, m.p. and mixture m.p. 75.5°, lit.,[5] m.p. 76°.

Reactions carried out in ampoules showed similar results. Better yields were obtained using cadmium iodide instead of cadmium carbonate or in the presence of a small amount of water.

Reaction of Potassium *o*-Phenylbenzoate.—*o*-Phenylbenzoic acid was prepared by heating fluorenone with potassium hydroxide, its m.p. being 114°.[6] A mixture of dry potassium *o*-phenylbenzoate (5 g.) and cadmium iodide (1.5 g.) in a sealed tube was heated in an autoclave at 410° for 2 hr. The product was dissolved in 100 ml. of water and extracted with ether. On evaporation the extract gave 2.26 g. of diphenyl, m.p. and mixture m.p. 70°.[7]

The aqueous layer was acidified and then extracted with ether. After evaporation of the ether the residue was separated into two portions, a benzene-soluble one (1.35 g.) and a benzene-insoluble one (200 mg.). The soluble portion was dissolved in concentrated sulfuric acid, poured into water, made alkaline, and then extracted with ether. This process was effective to remove the unchanged *ortho* isomer as fluorenone (620 mg.). From this alkaline solution there was obtained 410 mg. of white crystalline material, which gave, on recrystallization from dry methanol, 50 mg. of *p*-phenylbenzoic acid, m.p. 225°, lit,.[8] m.p. 224°, and mixture m.p. with an authentic material which was prepared by the Gomberg reaction of diazotized *p*-toluidine and benzene followed by potassium permanganate oxidation, 225°. From the mother liquor of the recrystallization, there was obtained 35 mg. of *m*-phenylbenzoic acid by repeated recrystallizations using aqueous methanol as solvent, its m.p. being 160°, lit.,[9] m.p. 160°. The mixture m.p. was 160°, the authentic sample was prepared *via* the same way as the *p*-isomer. The benzene-insoluble portion gave, after conversion into its dimethyl ester and repeated recrystallizations from aqueous methanol, 4,4′-dicarbomethoxydiphenyl (less than 1 mg.), m.p. 224°, lit.,[10] m.p. 225°, and mixture m.p. with an authentic material prepared from diazotized *p*-aminobenzoic acid, 224°.

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(1) (a) Y. Ogata, M. Tsuchida, and A. Muramoto, *J. Am. Chem. Soc.*, **79**, 6005 (1957); (b) Y. Ogata, M. Hojo, and M. Morikawa, *J. Org. Chem.*, **25**, 2082 (1960).

(2) B. Raecke, *et al.*, to Henkel & Cie, G. m. b. H., German Patents 936,036, December (1955); 945,627 (1956); and additional patents; B. Raecke, *Angew. Chem.*, **70**, 1 (1958).

(3) Y. Ogata, *Chem. Chem. Ind.* (Japan), **11**, 148 (1958).

(4) W. H. Gibson, R. Duckham, and R. Fairbairn, *J. Chem. Soc.* **121**, 270 (1922).

(5) W. H. Bentley and W. H. Perkin, *ibid.*, **71**, 157 (1897).

(6) C. Graebe and A. S. Rateanu, *Ann.*, **279**, 257 (1894).

(7) K. v. Auwers and A. Frühling, *ibid.*, **422**, 192 (1921).

(8) G. Ciamician and P. Silber, *Ber.*, **28**, 1549 (1895).

(9) L. Olgiati, *ibid.*, **27**, 3385 (1894).

(10) A. E. Tschitschibabin, *ibid.*, **40**, 1810 (1907).