

Fusion of ester XII with ammonium formate<sup>9</sup> in a nitrogen atmosphere, and then dealkylation by hydrochloric acid in acetic acid gave ( $\pm$ )-amide I, as orange needles from dimethylformamide (dec. ca. 250°;  $\lambda_{\text{max}}^{\text{M}^{\text{OH}(\text{H}^+)}}$  433, 385, 330, 270 m $\mu$ , log  $\epsilon$  4.39, 4.19, 3.93, 4.44;  $\lambda_{\text{max}}^{\text{KBr}}$  2.95, 6.33, 7.03, 8.06, 9.32  $\mu$ ).

Natural 6-demethylchlorotetracycline was converted by known methods<sup>2a</sup> to dextrorotatory I (found: C, 59.15; H, 3.89; N, 3.87). Comparison with the synthetic amide by means of the characteristic infrared and ultraviolet spectra, bioassays and chromatographic behavior unambiguously demonstrated the chemical identity of the two samples.<sup>10</sup> Since the location of the 6-methyl group has been proven by degradation,<sup>1,11</sup> the present synthesis furnishes compelling support for the accepted framework of the tetracycline molecule.

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#### CRYSTALLIZATION OF B<sub>2</sub>O<sub>3</sub> AT HIGH PRESSURES<sup>1</sup>

Sir:

Solid B<sub>2</sub>O<sub>3</sub> is commonly encountered as a glass, the preparation of the crystalline oxide being extremely difficult. By the conventional method of careful stepwise dehydration of H<sub>3</sub>BO<sub>3</sub>, microcrystals have been prepared.<sup>2,3</sup> Kracek, Morey and Merwin<sup>3</sup> were only able to prepare crystals having maximum dimensions of 0.05 mm. from experiments lasting eight months. Consequently, the only structural study<sup>2</sup> was based on powder diffraction data. In view of the possibility of incomplete dehydration which, for instance, had led to earlier erroneous conclusions,<sup>4</sup> attempts have been made to prepare by other methods single crystals for structural studies. This note describes the preparation of relatively large crystals of B<sub>2</sub>O<sub>3</sub> by high pressure treatment of the powdered glass.

Pure B<sub>2</sub>O<sub>3</sub> glass of >99% purity was obtained from the Pacific Coast Borax Company. No heavy metals were detected by spectroscopic analysis. Samples were contained in platinum or graphite capsules and subjected to pressures of 15,000 to 70,000 atmospheres at 300 to 600°. Rapid conversion to microcrystals was achieved in short periods. Thus, for example, at 600°, devitrification was complete after two minutes at

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40,000 atmospheres. At pressures below about 20,000 atmospheres and 400°, the ordinary hexagonal crystals<sup>2,3</sup> were obtained (density = 2.46 g./cm.<sup>3</sup>). At higher pressures, a denser crystalline modification was found which has a density of 2.95 g./cm.<sup>3</sup> by sink-float method. The refractive indices and the X-ray powder diffraction data of the two forms are also widely different. Under optimum conditions, single crystals of both forms having dimensions up to 0.2 mm. have now been prepared. The dense crystals are only slowly attacked by water and dilute hydrofluoric acid. Preliminary experiments by high temperature X-ray diffraction showed that these may be heated slowly to above 500° with no observable transformation, the m.p. being about 510°. The m.p. of the ordinary B<sub>2</sub>O<sub>3</sub> is reported to be 450  $\pm$  2°.<sup>3</sup> Structural and related studies of single crystals of the two forms are now in progress.

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#### CRYSTALLINE POLY-(ALKYL ACRYLATES)

Sir:

Both free-radical<sup>1,2</sup> and anionic<sup>1,3</sup> stereospecific polymerization methods have been reported for the preparation of several types of crystallizable poly-(methyl methacrylate), and evidence concerning the structures of these polymers has been presented.<sup>4</sup> More recently, the preparation of crystalline poly-(*t*-butyl acrylate) was described by Miller and Rauhut.<sup>5</sup> The present communication reports the application of these stereospecific polymerization methods to a series of alkyl acrylates.

Poly-(isopropyl acrylate) has been synthesized in two different forms which crystallize in different, non-polymorphic structures possessing distinctly different infrared spectra. Unlike polymers of methyl methacrylate prepared by the same methods these polymers do not crystallize in a third structure on mixing. Type I poly-(isopropyl acrylate) is prepared at low temperature (< -70°) by photosensitized or cobalt-60 initiated free-radical polymerization in bulk or in toluene. For example, 30 g. of the monomer containing 0.12 g. of benzoin, degassed under vacuum and irradiated for 1.25 hours at -100° with a 60-watt ultraviolet source, yields 7.2 g. of polymer,  $\bar{M}_v$  1.3  $\times$  10<sup>6</sup>. Crystallization may be effected readily by annealing or by solvent swelling techniques. X-Ray diffraction patterns of the crystalline material show strong scattering from spacings at 7.4 (vs); 4.35 (ms); and 4.25 (s) Å.

Poly-(isopropyl acrylate) of type II is prepared by anionic polymerization initiated by organo-

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