Fusion of ester XII with ammonium formate[9] in a nitrogen atmosphere, and then dealkylation by hydrochloric acid in acetic acid gave (±)-amide I, as orange needles from dimethylformamide (dec. *ca.* 250°; $\lambda_{\max}^{\text{MeOH(H}^+)}$ 433, 385, 330, 270 mμ, log ϵ 4.39, 4.19, 3.93, 4.44; $\lambda_{\max}^{\text{KBr}}$ 2.95, 6.33, 7.03, 8.06, 9.32 μ).

Natural 6-demethylchlorotetracycline was converted by known methods[2a] 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.[10] Since the location of the 6-methyl group has been proven by degradation,[1,11] the present synthesis furnishes compelling support for the accepted framework of the tetracycline molecule.

[9] We are grateful to S. Kushner for valuable suggestions, including the use of this reagent.

[10] We are indebted to W. Fulmor and associates for the spectroscopic data, A. C. Dornbush and staff for microbiological assays, R. D. Mills for chromatographic work and L. Brancone and his staff for the microanalytical data cited herein.

[11] (a) J. S. Webb, R. W. Broschard, D. B. Cosulich, W. J. Stein and C. F. Wolf, THIS JOURNAL, **79**, 4563 (1957); (b) J. H. Boothe, A. Green, J. P. Petisi, R. G. Wilkinson and C. W. Waller, *ibid.*, **79**, 4564 (1957).

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CRYSTALLIZATION OF B_2O_3 AT HIGH PRESSURES[1]

Sir:

Solid B_2O_3 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_3BO_3, microcrystals have been prepared.[2,3] Kracek, Morey and Merwin[3] were only able to prepare crystals having maximum dimensions of 0.05 mm. from experiments lasting eight months. Consequently, the only structural study[2] was based on powder diffraction data. In view of the possibility of incomplete dehydration which, for instance, had led to earlier erroneous conclusions,[4] 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_2O_3 by high pressure treatment of the powdered glass.

Pure B_2O_3 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 40,000 atmospheres. At pressures below about 20,000 atmospheres and 400°, the ordinary hexagonal crystals[2,3] were obtained (density = 2.46 g./cm.[3]). At higher pressures, a denser crystalline modification was found which has a density of 2.95 g./cm.[3] 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_2O_3 is reported to be 450 ± 2°.[3] Structural and related studies of single crystals of the two forms are now in progress.

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[1] This research was supported in part by the U. S. Air Force under Contract No. AF33(616)-5699, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

[2] S. V. Berger, *Acta Chem. Scand.*, **7**, 611 (1953).

[3] F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, **35A**, 14 (1938).

[4] S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, **18**, 55 (1935).

CRYSTALLINE POLY-(ALKYL ACRYLATES)

Sir:

Both free-radical[1,2] and anionic[1,3] 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.[4] More recently, the preparation of crystalline poly-(*t*-butyl acrylate) was described by Miller and Rauhut.[5] 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, $\overline{M}v$ 1.3 × 10^6. 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-

[1] T. G. Fox, *et al.*, THIS JOURNAL, **80**, 1768 (1958).

[2] T. G. Fox, *et al.*, *J. Polymer Sci.*, **31**, 173 (1958).

[3] R. G. J. Miller, *et al.*, *Chem. and Ind.*, 1323 (1958).

[4] J. D. Stroupe and R. E. Hughes, THIS JOURNAL, **80**, 2341 (1958).

[5] M. L. Miller and C. E. Rauhut, *ibid.*, **80**, 4115 (1958).

lithium compounds or, preferably, by organomagnesium compounds. The addition of 228 g. of degassed monomer to 0.04 mole of phenylmagnesium bromide in 744 ml. of anhydrous toluene maintained at −65°, and then after eighteen hours precipitation of the reaction mixture in petroleum ether, produces a 91% conversion to polymer, $\overline{M}v$ 205,000. This polymer crystallizes readily and is difficult to obtain in the amorphous state. Dilatometric measurements indicate a glass transition of −11° and a crystal melting point of 162°. Powder diffraction patterns exhibit strong scattering from spacings at 8.4 (vs); 5.15 (s); 4.85 (s); and 4.20 (s) Å. Figure 1 illustrates the diffraction characteristics of crystalline type II fibers. Fiber data also have been obtained for type I poly-(isopropyl acrylate); preliminary crystal structure analyses[6] suggest the syndiotactic arrangement for type I and the isotactic for type II.

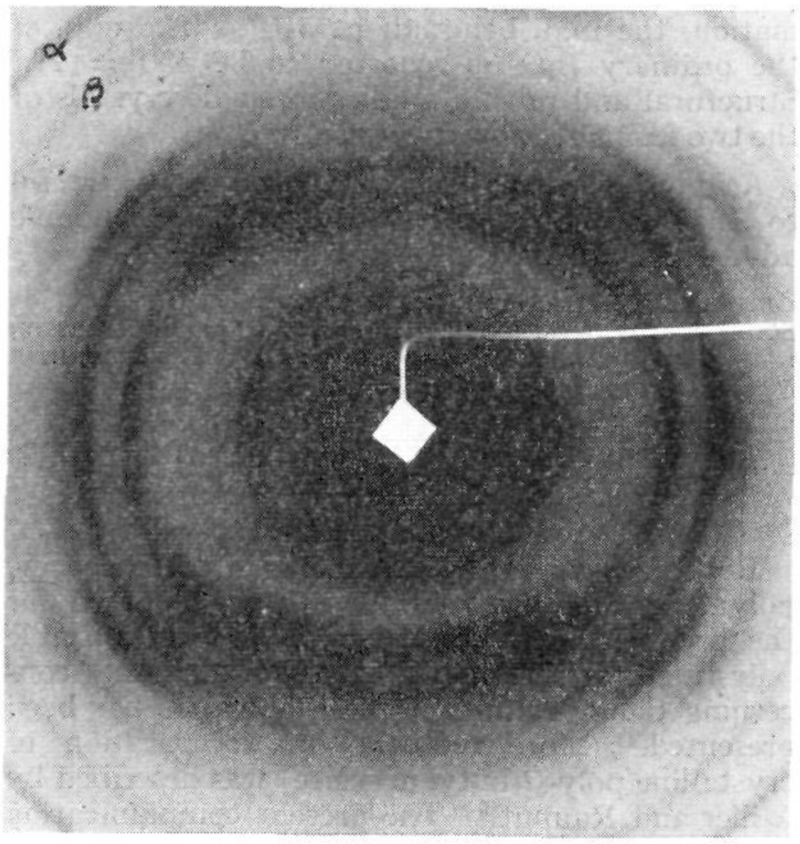

Fig. 1.—X-Ray fiber diffraction pattern of crystalline type II PiPA; stretch orientation vertical; Ni filtered Cu radiation; flat plate camera. Exposure geometry calibrated by superposed, unfiltered 2.81 Å. NaCl data.

By similar methods, two different crystallizable forms (I and II) of poly-(cyclohexyl acrylate) have been prepared. Polymers of *sec*-butyl and *tert*-butyl acrylates resulting from Grignard initiated polymerizations crystallize readily. The X-ray and infrared characteristics of crystalline poly-(*t*-butyl acrylate) prepared by the Grignard technique agree closely with those described[5] for polymer prepared with a lithium dispersion. However, the Grignard polymers remain crystalline at temperatures well above the 72° transition temperature reported earlier.[7]

Polymers of isopropyl, *sec*-butyl, and *tert*-butyl acrylates prepared by the Grignard method undergo rapid, spontaneous crystallization accompanied by marked changes in the infrared spectra. In contrast, polymers of cyclohexyl and isobornyl acrylates prepared by the same method usually require treatment with borderline solvents. Polymers of methyl, ethyl, and the higher *n*-alkyl acrylates prepared by the same techniques do not appear to be crystalline. These observations suggest the significance of branching at the α-carbon atom of the alkyl group in determining either the stereospecificity of the polymerizations or the crystallizability of the products. Study of the mechanism of this effect is in progress.

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[6] Paper in preparation

[7] No first-order transition is observed dilatometrically below 120°; decomposition of the sample at higher temperatures prevented accurate determination of the melting point.

DIPHENYLMETHYLENE, $(C_6H_5)_2C$, A DIRADICAL SPECIES

Sir:

The chemical properties of carbenes (CH_2,[1] CBr_2,[2] CCl_2,[3] $CHCOOC_2H_5$,[1,4] $CHCOR$[5]) which lead to assignment of a non-radical singlet structure are: (a) stereospecific *cis* addition to *cis*- and *trans*-2-butene, (b) reactivity characteristic of electrophilic reagents, (c) failure to correlate reactivity in addition to olefins with that anticipated for radical reagents, and (d) low reaction probability for $CH_2 + O_2$.[6]

The assignment of a non-radical singlet structure was predicted on the unsupported assumption that a triplet methylene would have the properties of a radical reagent.

It is now apparent that diphenylmethylene (obtained by photolysis of diphenyldiazomethane) does indeed have the properties anticipated for a diradical species, thus providing strong support for the singlet states assigned to previously studied carbenes and a triplet state for diphenylmethylene.

We wish to report that diphenylmethylene reacts[7] with *cis*- and *trans*-2-butene to produce cyclopropanes (product ratios from *cis*-2-butene 1:15 and from *trans*-2-butene 1:2.3) and olefins by nonstereospecific reaction paths. Diphenylmethylene also reacts with 1,3-butadiene and 1,1-diphenylethylene > 100 times more rapidly than with isobutylene, 1-hexene, or cyclohexene, a radical re-

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[1] P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

[2] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[3] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[4] P. S. Skell and R. M. Etter, *Chem. and Ind.*, 624 (1958).

[5] P. S. Skell, A. Y. Garner and R. C. Woodworth, "Bivalent Carbon Reaction Intermediates, Carbenes," Abst. page 174 (presented at 16th Intern. Congr. Chem., Organic Section, Paris, France, 1957).

[6] A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954); R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **78**, 4831 (1956); R. A. Holroyd and F. E. Blacet, *ibid.*, **79**, 4830 (1957); H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

[7] Photolyses in the presence of olefins produce cyclopropanes and olefins. Pure products were separated by conventional methods. Competitions were carried out similarly, using a mixture of olefins, analyses being performed by chromatography to eliminate uncertainties about product identities. In the experiments with the *cis*- and *trans*-2-butenes the recovered olefins were not isomerized.