

Attempted preparation of 1,3-diphenoxy-2-propene. A suspension of 19.9 g. (0.05 mole) I and 4.2 g. (0.05 mole) sodium bicarbonate in 75 ml. dimethyl sulfoxide was stirred vigorously and warmed slowly, so that it reached 90° in 63 min. and 100° in 140 min. Carbon dioxide evolution was fairly brisk beginning at the former temperature. After 4 hr. at 100° the reaction mixture was poured onto ice. The gummy solid was broken up, washed thoroughly with water and dried *in vacuo*, wt. 17.3 g. Recrystallization from 2-propanol yielded unchanged I, melting point and mixture m.p. 121–122°.

Oxidation of I by dimethyl sulfoxide. The reaction mixture was prepared as in the experiment above and heated more strongly so that it remained in the range 138–150° for 2 hr. It was then poured onto ice. The precipitated tar was dissolved in benzene and the solution washed several times with water, dried over sodium sulfate and filtered. Evaporation of the benzene at room temperature left 11.6 g. of a brown semisolid residue. Trituration with 2-propanol at room temperature followed by filtration removed 1.2 g. of solid which, after purification, was found to be identical with II. After removal of the propanol from the filtrate, the residual liquid was distilled, b.p. 158–163°/0.30–0.36 mm. Trituration of the distillate with Skellysolve F induced crystallization. The solid after two recrystallizations from 50% 2-propanol melted at 57° (reported² 59–60°). The infrared spectrum showed strong absorption at 5.90 μ .

The 2,4-dinitrophenylhydrazone after recrystallization from ethanol containing a little ethyl acetate melted at 128° (reported² 125–126°).

Anal. Calcd. for C₂₁H₁₇N₄O₆: N, 13.30. Found: N, 13.96.

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Crystalline Racemic Bornyl Acetate

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Although optically pure bornyl acetate has long been known to be a low melting solid with a tendency to supercool, nothing is known about the melting behavior of mixtures of the two optical antipodes. A search of the literature uncovered only a statement by Haller¹ that racemic bornyl acetate did not crystallize, even at -17°. Having samples of pure *d*-bornyl acetate and *l*-bornyl acetate available, the melting point behavior of mixtures of the two was investigated.

When a mixture of equal parts of the dextro and laevo isomers was stored in a freezing chest for a week, crystallization occurred to give a solid mass which had a melting point of 7.0°. With this assurance, a series of mixtures was prepared and the melting points taken: % levo isomer (m.p.); 100%, m.p. 27°; 75%, 18.5°; 62.5%, m.p. 12°; 50%, m.p. 7°; 37.5%, m.p. 12°; 25%, m.p. 17.5°; 0% (i.e. 100% dextro isomer), m.p. 26.5°.

A plot of these melting point data gives a symmetrical fusion curve with a single eutectic point

(1) M. A. Haller, *Comp. rend.*, **109**, 29 (1889).

demonstrating² the formation of a simple conglomerate or racemic mixture. This behavior is to be contrasted with the much more common occurrence of a racemic compound, or, rarely, a solid solution.

EXPERIMENTAL³

The *d*-bornyl acetate, $[\alpha] + 41.2^\circ$, used in this study had a melting point of 26.5° (lit.¹ $[\alpha] + 44.38^\circ$; m.p. 24°). The *l*-bornyl acetate, $[\alpha] - 42.0^\circ$, had a melting point of 27.0° (lit.¹ $[\alpha] - 44.45^\circ$; m.p. 24°). Each sample, and mixture, was originally crystallized by storage in a freezing chest (-10°) for periods up to one week. Thereafter recourse was had to seeding when necessary.

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(2) A. Findlay (ed. Campbell and Smith), *The Phase Rule and Its Applications*, 9th Ed., Dover, New York, 1951, p. 190.

(3) All melting points are uncorrected and rotations (D line) are determined on the supercooled liquid at ambient temperatures. The temperature at which the last crystal disappeared was recorded as the melting point.

Interpretation of Some Reactions on Complex Ionic Bonds^{1a}

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The mechanism of olefin polymerization with Ziegler catalysts has been considered to occur on complex ions, such as $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ from $\text{TiCl}_3/\text{AlR}_3$, with the direct participation of the cation metal and anion metal.^{1b} The initiating step of the polymerization is the activation of the monomer on a cation of a transition element. The second step is the migration of the activated monomer to the anion metal (aluminum for instance, or titanium) which occurs at the moment when the propagation starter (R^- , H^-) neutralizes the cationic transition state of the monomer. The migration can be compared with the addition of a metal alkyl to a Lewis type metal alkyl with the formation of more stable complex ions. The polymerization mechanism of ethylene on $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ complex is formulated below.

